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AND COMMUNICATION



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Advancing High-Energy and High-Power Lithium-Ion Batteries: Ageing and Dynamic Performance

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InoBat, a Slovakia-based battery technology company, advances lithium-ion batteries through vertically integrated R&D capabilities, spanning coin-cell development to pilot-scale production of large format cells. Building on the successful development of high-energy chemistry featuring high-nickel NMC9055 cathodes and high-silicon graphite anodes, validated from coin cells to 33 Ah cells with energy densities exceeding 330 Wh/kg, InoBat provides a unique platform for advanced battery research. Leveraging this infrastructure, the joint project with the Slovak university of technology investigates fundamental ageing mechanisms governing the performance, reliability, and dynamic behavior of next-generation high-energy and high-power lithium-ion batteries. The project focuses on Ni-rich cathodes combined with graphite and graphite SiOx composite anodes under diverse conditions, including temperature variations, dynamic cycling, storage, and radiation exposure. Advanced electrochemical and multi-analytical characterization, including in-situ/in-operando analysis, enables the development of comprehensive degradation models for durable battery technologies.

Lithium-ion batteries (LIBs) are key enablers of decarbonization in transportation and renewable energy storage due to their high energy density and versatile applications. However, their production is energy and material intensive, creating the need for improved battery lifetime, higher performance, and reduced environmental impact. Current research therefore focuses on increasing energy density, extending operational lifetime, improving safety, and reducing material consumption [1][2].

Battery ageing remains one of the major challenges limiting LIB performance and reliability. Degradation originates from complex electrochemical and chemical interactions between electrodes, electrolyte, and inactive components, including solid electrolyte interphase (SEI) evolution, lithium plating, electrolyte decomposition, structural changes of active materials, and loss of active lithium [3]. These mechanisms are strongly influenced by operating conditions such as temperature, charge/discharge rate, and state of charge [4].

Relevance, Quality and Innovativeness of this Research

High-Ni layered oxide cathodes, such as NMC811 and NMC9055, combined with graphite–silicon-based anodes, represent promising pathways toward next-generation high-energy batteries due to their increased specific capacity. However, the degradation

mechanisms of these advanced chemistries are still not fully understood, particularly for high-Ni cathodes and silicon-containing anodes [5]. Moreover, most ageing studies have been performed under conventional laboratory conditions, while battery behaviour under radiation exposure remains insufficiently explored despite its importance for aerospace and extreme-environment applications [6].

This research addresses these challenges by combining advanced electrochemical ageing studies with ion beam analysis (IBA) to investigate degradation mechanisms in high-performance LIBs. Battery cells based on NMC811/NMC9055 cathodes and graphite-SiOx anodes evaluated under different cycling conditions, temperatures, storage environments, and radiation exposure. A dedicated in-situ and in-operando characterization platform will be developed to monitor the distribution and migration of light elements during battery operation.

The expected outcomes will support the development of safer, longer-lasting, and higher-energy-density batteries and strengthen European expertise in sustainable energy storage technologies [7].

Experimental Approach and Key Findings

This work presents a comprehensive investigation of ageing mechanisms in high-energy lithium-ion batteries by integrating advanced cell development at InoBat with multi-scale characterization capabilities at the Slovak University of Technology (STU). Four battery chemistries, including NMC811/graphite, NMC811/SiOx–graphite, NMC9055/graphite, and NMC9055/SiOx–graphite, were prepared as coin cells under controlled glovebox conditions to ensure reproducible and contamination-free assembly.



Figure 1. Coin cell assembly activities and students training at Inobat.

The evolution of degradation mechanisms was evaluated through a combination of electrochemical, structural, morphological, and chemical analyses. Electrochemical performance degradation was assessed using galvanostatic cycling enabling correlation between capacity loss and interfacial processes. Structural and morphological changes associated with ageing were investigated using XRD, SEM/EDS revealing the evolution of electrode materials, surface degradation, and formation of ageing-related products.

The results demonstrate the influence of cathode nickel content and silicon incorporation in the anode on degradation behavior, highlighting the complex relationship between high-energy chemistry and long-term stability. The analysis revealed key ageing-related processes, including interfacial degradation, lithium redistribution, structural changes of active materials, and electrolyte decomposition.

These findings contribute to the rational design of safer, longer-lasting, and higher-energy-density battery systems for sustainable mobility and advanced energy-storage applications.

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Recovery of Graphite from NMC Black Mass via Hydrometallurgical Leaching

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Hydrometallurgical recycling of spent Lithium Nickel Manganese Cobalt Oxide (NMC) batteries primarily focuses on extracting high-value transition metals (Li, Ni, Mn, Co), often leaving behind spent graphite as an underutilized solid residue. Recovering battery-grade graphite from this residue is critical for establishing a circular battery supply chain in Europe. However, hydrometallurgical purification faces major hurdles due to persistent inorganic contaminants. This study addresses the recovery and purification of anode graphite extracted from NMC black mass. While standard mineral acid leaching successfully dissolves transition metals, aluminum species originating from current collector foils or cathode ceramic coatings form chemically inert, highly stable Al_2O_3 phases that resist typical hydrometallurgical leaching routes.

Introduction

Recycling of spent lithium-ion batteries (LIBs) is gaining critical importance to secure the supply chain of Critical Raw Materials and support a closed-loop circular economy. Black mass derived from shredded end-of-life cells—comprising a complex mixture of spent graphite anodes, nickel-manganese-cobalt (NMC) cathode residues, and current collector fragments—represents a primary resource for hydrometallurgical recovery [1][2]. While hydrometallurgical leaching and separation effectively extract high-value transition metals, recovering high-purity battery-grade graphite requires thorough purification [3]. Restoring spent graphite's structural integrity and removing non-carbonaceous contaminants are essential steps to successfully reintroduce recycled active materials back into battery manufacturing, thereby significantly mitigating the environmental footprint of primary material mining [1][2].

The initial and most critical phase in reconditioning graphite from NMC black mass involves the meticulous removal of structural and chemical impurities. During cycling, the graphite matrix accumulates degradation products, including the solid electrolyte interphase (SEI) layer, fluorinated polymer binders (e.g., PVDF), and residual lithium salts (LiPF_6) [3][4]. Furthermore, mechanical shredding and chemical leaching during hydrometallurgical processing frequently leave behind metallic impurities—such as structural copper/aluminium particles or insoluble oxides (e.g., spherical Al_2O_3 inclusions and residual secondary cathode agglomerates). Achieving the required purity demands targeted purification approaches, most commonly combining acid/alkali chemical leaching, thermal calcination, and physical separation methods. [1][2][3][4].

Experiment

Industrial NMC black mass containing spent graphite, NMC cathode active material, binder residues (PVDF), and current collector fragments was processed via hydrometallurgical leaching. To extract the transition metals (Ni, Mn, Co, Li), the black mass was treated with sulfuric acid (H_2SO_4) in the presence of hydrogen peroxide (H_2O_2) as a reducing agent at elevated temperatures (80 °C).

Following acid leaching, the mixture was filtered to separate the leach solution containing dissolved metal sulfates from the solid graphite residue. The collected graphite residue was washed thoroughly with deionized water and dried at 50 °C.

The hydrometallurgically treated graphite particles were evaluated using Scanning Electron Microscopy (SEM). Energy-Dispersive X-ray Spectroscopy (EDS) was conducted to map elemental distributions, quantify residual impurities (particularly Al, O, Cu, and residual transition metals), and monitor the effectiveness of the leaching steps.

Figure 1-A reveals strong compositional contrast between the darker graphite-rich matrix and bright agglomerates corresponding to heavier metallic impurities and cathode residues. The higher-magnification image (Figure 2-B) confirms a highly mixed microstructure, where planar, flake-like anode graphite particles are intermixed with distinct spherical secondary cathode agglomerates.

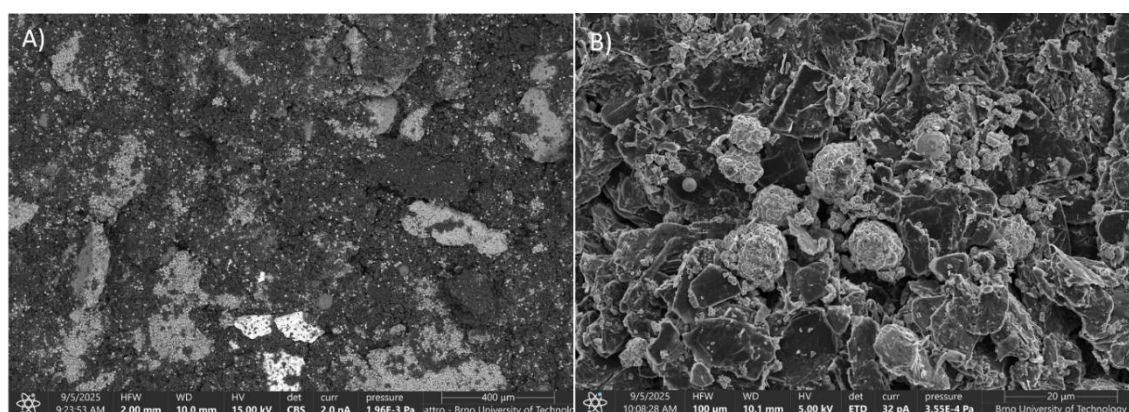


Figure 1. SEM images of received black mass A) Scale 400 μm B) Scale 20 μm

Figure 2-A demonstrates the flake-like morphology of the recovered graphite matrix, within which a distinct, smooth spherical particle (~35–40 μm in diameter) is embedded. The corresponding EDS elemental profile (Figure 2-B) confirms this inclusion as an inorganic alumina (Al_2O_3) impurity or a surface-oxidized aluminium particle, evidenced by the co-existence of Al (2.5 wt.%) and O (10 wt.%), likely originating from structural cell components or ceramic separator coatings. Furthermore, the detection of fluorine (3.5 wt.% F) indicates residual PVDF binder.

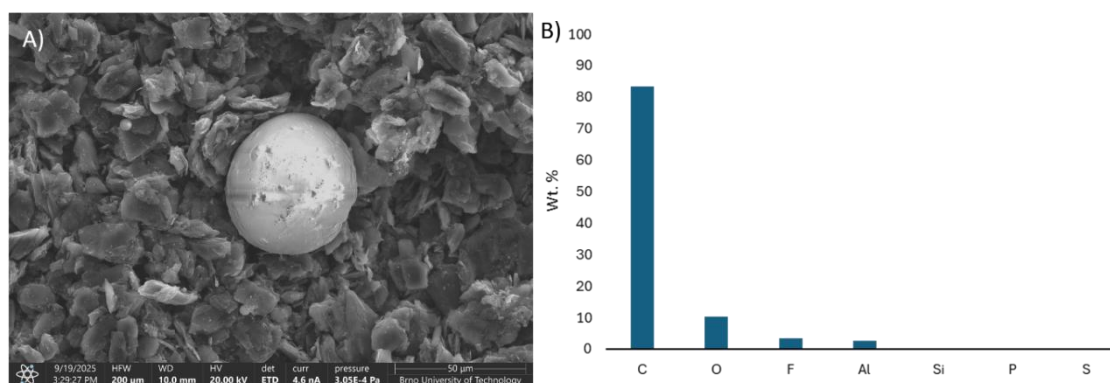


Figure 2. A) SEM image of graphite after leaching in H_2SO_4 B) EDS of graphite

Standard acidic hydrometallurgical leaching successfully removed the majority of NMC transition metals (Ni, Mn, Co). However, elemental analysis (EDS) of the dried solid residue revealed a persistent, high-concentration presence of aluminum and oxygen, confirming the accumulation of insoluble Al_2O_3 particles mixed within the graphite flakes.

Conclusion

Recovering graphite from NMC black mass via hydrometallurgy is a promising route for sustainable battery recycling, but persistent Al_2O_3 contamination remains a critical obstacle. While standard acidic leaching successfully removes transition metals (Ni, Mn, Co, Li), aluminum oxides originating from foils and separator coatings remain embedded in the graphite matrix. Complete purification requires the implementation of secondary treating to selectively remove alumina and restore battery-grade performance.

Acknowledgments

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Towards an In-Depth Understanding of the Interfacial Reactions of Lithium-Metal Electrodes

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Li-metal electrodes are considered the next great leap forward towards achieving higher energy density batteries. However, their high reactivity with essentially all liquid and solid electrolytes remains a formidable challenge – concerning both the cycle life of the cell and its safety owing to the commonly inhomogeneous, potentially dendritic lithium deposition upon continuous stripping and plating.

Herein, our most recent efforts to deepen our understanding of the reactions and processes occurring at the lithium|electrolyte interface using liquid and/or solid electrolyte systems will be presented. Additionally, the lecture will cover our recent insights into the reactions occurring at the interface between lithium metal and the current collector – an interface that is commonly overlooked, but not less important, especially with regard to the rapidly increasing interest in “zero-excess” lithium-metal batteries, offering even greater energy densities.

Engineering Silicon-Graphite Anodes for High-Energy Lithium-Ion Batteries

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Lithium-ion batteries store energy through reversible lithium intercalation into electrode materials, where the theoretical capacity is determined by the maximum amount of lithium that can be accommodated in the host structure. Graphite, the commercial anode standard, is limited by its intercalation mechanism to 372 mAh g⁻¹, motivating the search for higher-capacity alternatives. Silicon offers a higher theoretical capacity, but its >300 % volume expansion during cycling causes mechanical failure and unstable solid electrolyte interface formation. This study explores metal organic framework (MOF) MIL-101(Fe) as a functional additive in silicon/graphite composite anodes to mitigate these issues. The MIL-101(Fe) enhances ion transport, buffers silicon expansion, and promotes a more stable SEI. Incorporation of MIL-101(Fe) leads to higher reversible capacity and improved cycling stability compared with MIL-free electrodes, demonstrating the promise of MOF-engineered Si/Gr composites for next-generation high-energy lithium-ion batteries.

Introduction

Lithium-ion (Li-ion) batteries are the leading electrochemical energy storage systems for electric vehicles (EVs) and portable electronics due to their high efficiency, long cycle life, and relatively high energy density. The growing demand for EVs and portable devices has intensified the need for next-generation Li-ion batteries with improved power and energy densities. However, the relatively low theoretical capacity of graphite anodes (372 mAh g⁻¹) limits further enhancement of battery performance [1]. Silicon has emerged as one of the most promising alternative anode materials because of its exceptionally high theoretical gravimetric capacity (3579 mAh g⁻¹ for Li₁₅Si₄), which is nearly ten times higher than that of graphite [2]. In addition, silicon possesses a low electrochemical potential (~0.5 V), high natural abundance, and environmentally benign nature, making it attractive for the development of safe and cost-effective high-energy-density batteries [3].

Despite these advantages, the practical implementation of silicon anodes remains challenging due to the severe volume expansion (>300 %) that occurs during lithiation/delithiation. These large volume changes result in mechanical degradation, particle pulverization, unstable solid electrolyte interphase (SEI) formation, continuous

electrolyte consumption, and loss of electrical contact with the current collector, ultimately leading to rapid capacity fading [4]. To address these limitations, silicon is frequently combined with carbon-based materials that improve electronic conductivity and buffer the mechanical stress during cycling [5].

Recently, metal-organic frameworks (MOFs) have attracted considerable attention as functional materials for silicon-based anodes because of their high porosity, tunable structure, and large surface area. In silicon/graphite (Si/Gr) composite anodes, MOFs can facilitate ion and electron transport, accommodate silicon volume expansion, and promote the formation of a more stable solid electrolyte interface (SEI) layer. These effects contribute to improved cycling stability and electrochemical performance. In this work, MIL-101(Fe) was incorporated into Si/Gr composite anodes to investigate its influence on electrode stability and electrochemical behaviour. The incorporation of MIL-101(Fe) enhanced the reversible capacity and cycling stability of the electrode material, demonstrating the potential of MOF-assisted engineering strategies for advanced silicon-based Li-ion battery anodes.

Experimental

MIL-101(Fe) was synthesised according to modified solvothermal procedures reported in the literature [6]. For synthesizing MIL-101(Fe), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10.6 g, 39.2 mmol) and terephthalic acid (H_2BDC , 3.296 g, 19.84 mmol) were dissolved in 240 mL of DMF to form a clear solution. This mixture was sealed and heated at 110 °C for 12 h. After cooling, the resulting orange solid was collected by filtration and purified via 48 h Soxhlet extraction in methanol to remove excess linker and trapped guest molecules. The cleaned product was then dried for 24 h, yielding 2.92 g of MIL-101(Fe). To prepare MIL-101-derived carbon, MIL-101(Fe) was heated in a tubular furnace under flowing nitrogen at 800 °C, using a heating rate of 2 °C min⁻¹, and held at that temperature for 2 h.

The anodes were prepared using Si/Gr and carbonised MIL-101(Fe) as a matrix for Si. The electrodes used in this study were composed of 20 wt% Si (50 nm; Nanoamorphous materials), 50 wt% graphite, 10 wt% carbonised MIL-101(Fe), 10 wt% Super C65, and 10 wt% carboxymethyl cellulose (CMC). The benchmark was prepared with 20 wt% Si, 60 wt% graphite, and the remaining components were kept the same. The electrode slurry was mixed with water and ethanol (10:1) using a shear mixer for 15 min at 12,000 rpm. The prepared slurry was coated on a Cu current collector using an automatic doctor blade machine. The electrode sheets were dried under vacuum at 80 °C for 24 h, and electrodes with a diameter of 12 mm were punched out. The mass loading of active material was controlled at ~1.5 mg cm⁻². A glass fibre (GF/A; Whatman) separator with a diameter of 18 mm was soaked with electrolyte in a composition of 0.8 M LiPF_6 + 0.2 M LiFSI in EC and EMC (3:7) + 10 % FEC (E-Lyte). Li metal with a diameter of 15.6 mm was used as a reference electrode, and coin cells CR2032 were assembled.

Results and Discussion

The half cells were first preconditioned for one cycle at 0.05 C, followed by cycling at 0.5 C for 400 cycles (see Figure 1). The initial capacity at 0.5 C was ~1080 mAh g⁻¹ for Si/MIL, while for Si it was ~820 mAh g⁻¹, respectively. After 400 cycles, the capacity decreased to 630 mAh g⁻¹ and 559 mAh g⁻¹ for Si/MIL and Si electrodes, respectively.

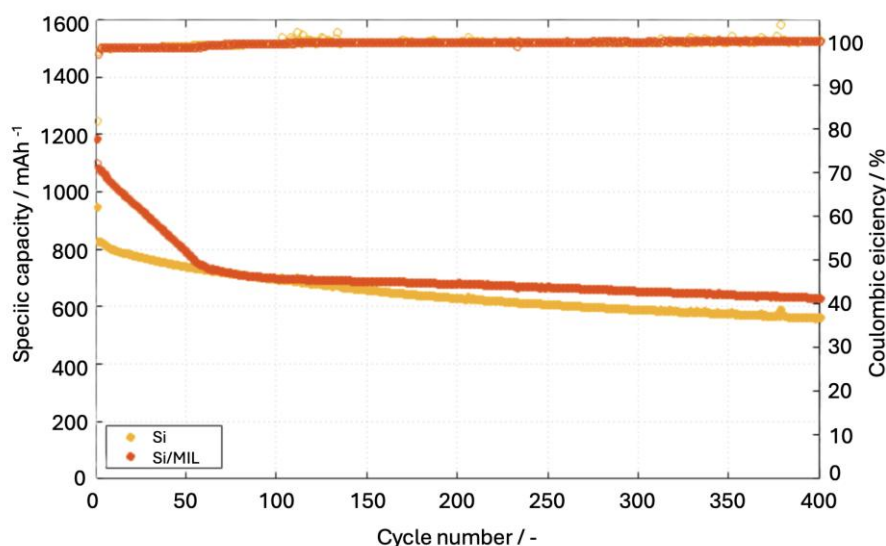


Figure 1. Long-term cycling performance at 0.5 C of the Si and Si/MIL electrodes.

Conclusions

Li-ion battery performance is strongly governed by the stability of the anode during repeated lithiation and delithiation. The electrochemical data show that MIL-101(Fe) incorporation leads to a more robust and stable Si-based anode. Across long-term cycling, the Si/MIL electrode consistently delivers higher capacities and slower degradation than pure silicon, indicating that the MOF additive improves structural integrity.

Acknowledgments

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Realistic and Accelerated Battery Testing Based on Real-World Profiles

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Lithium-ion batteries are operated under dynamic conditions that are not fully represented by conventional laboratory tests. This work presents a modular workflow for generating realistic cell-level test profiles from long-term operational data. The method combines representative-window selection, optional shortening of long resting periods, and model-based conversion of system-level power into a cell-level current profile.

Introduction

Lithium-ion batteries are used in applications with highly dynamic operating conditions such as electric vehicles, ancillary services, and energy trading, where battery lifetime is strongly influenced by the applied load profile, state-of-charge variation, and resting periods. Representative laboratory testing is therefore essential for evaluating battery behaviour under conditions similar to real operation.

Motivation and State of the Art

Battery lifetime is still frequently evaluated using simplified constant-current or constant-power cycles. Although these tests are reproducible and simple, studies have shown that static and dynamic profiles can produce different degradation rates and mechanisms. This means that the results from these conventional tests may not fully reflect real battery operation (1), (2).

More realistic test profiles have been developed mainly for electric vehicles, using either standard driving cycles or measured operational data (3), (4). Similar approaches have also been applied in specialized areas such as satellite battery testing (5). However, these methods are usually designed for a specific application or remain focused on system level profiles.

Research Gap and Contribution

A general workflow for converting long-term operational data into a shorter cell-level laboratory profile remains less established. This work proposes a modular tool combining representative-window selection, shortening of long resting periods, and model-based conversion of the resulting power profile into a cell-level current or power profile. The method enables realistic and time-efficient battery testing for different applications.

Methodology

The proposed workflow transforms long-term system operational data into a shorter duration cell-level battery test profile. As shown in Figure 1, the input consists of a measured power profile and, optionally, the corresponding state-of-charge profile. The data are divided into windows with fixed set length, and each window is described using

selected operating metrics. The window that best represents the typical behaviour of the full dataset is then selected.

Long resting periods within the selected interval are shortened to reduce the required laboratory test duration. Finally, the filtered power profile is scaled to the cell level and converted into a current profile using a battery cell model. During this step, the simulated cell current and state of charge are checked against the defined operating limits.

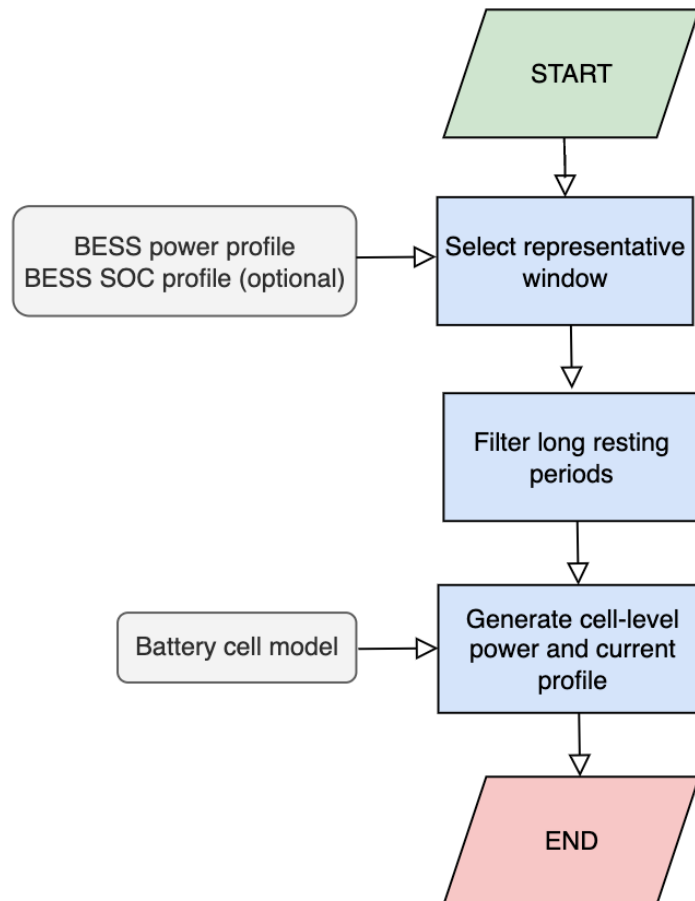


Figure 1. Simplified workflow for generating a representative cell-level battery test profile from operational data.

Demonstration and Results

The proposed workflow was demonstrated using one year of measured power and SOC data from a household BESS coupled with a residential PV system. The original dataset obtained from (6) was divided into one-week windows, and the most representative week was selected according to the chosen operational metrics.

The original 168-hour profile was reduced to 91 hours by shortening long resting periods. The reduced power profile was subsequently converted to the cell level using the battery model. The resulting current profile remained within the defined current and SOC limits, and the simulated SOC followed the measured SOC trajectory with an RMSE of 3.48 %. The selected BESS power profile and the corresponding generated cell-current profile are shown in Figure 2.

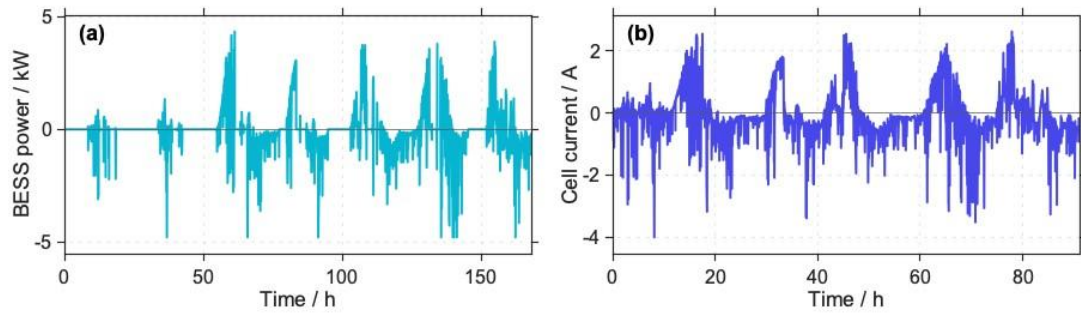


Figure 2. Representative one-week power profile selected from a household BESS coupled with a residential PV system (a) and the corresponding generated cell-level current profile (b).

Conclusion

This work presents a modular workflow for converting long-term field data into a representative current or power profile suitable for laboratory battery testing. The method combines selection of representative window, possible shortening of long resting periods, and conversion of the BESS power profile into a cell-current profile based on battery cell model. The demonstration using residential PV-coupled BESS data showed that the approach can generate a realistic, shortened laboratory profile from measured operation. Future work will focus on experimental validation and possible development of the profile-reduction methods such as microcycle reduction.

Acknowledgments

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Effect of Calcination Profile on the Structure, Morphology and Electrochemical Performance of Spray-Dried LiFePO₄ Cathode Materials

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Lithium iron phosphate (LiFePO₄) cathode material was synthesized by spray drying using a ferric acetylacetonate-based precursor solution. The synthesized powders were calcined at different temperatures (600–800 °C) under a nitrogen atmosphere to investigate the influence of thermal treatment on the structure and electrochemical properties of the material. SEM analysis revealed spherical particles with diameters below 2 μm, while EDS confirmed the expected Fe:P stoichiometry. Thermogravimetric analysis identified two major decomposition stages, with DTG minima at approximately 220 °C and 350 °C, providing insight into the thermal decomposition behavior of the precursor. X-ray diffraction confirmed the formation of the olivine LiFePO₄ phase after thermal treatment. The synthesized materials were further characterized by electrochemically to evaluate the influence of calcination conditions on their performance.

Introduction

Lithium iron phosphate (LiFePO₄, LFP) remains one of the most attractive cathode materials for lithium-ion batteries thanks to its excellent thermal stability, long cycle life, intrinsic safety, and relatively low cost. Despite these advantages, its practical rate capability is limited by low electronic conductivity and moderate lithium-ion diffusivity. Consequently, electrochemical performance strongly depends on particle size, morphology, crystallinity, carbon coating quality, and electrode architecture. [1][2]

Spray drying has emerged as a highly efficient and industrially scalable synthesis method capable of producing homogeneous precursor particles with controlled composition and narrow particle-size distribution. Previous studies demonstrated that spray-dried LFP powders exhibit predominantly spherical submicron morphology with good compositional homogeneity and high potential for industrial scale-up. [3][4][5]

However, preliminary electrochemical measurements revealed considerable polarization and increased internal resistance, suggesting the limiting factors associated with decomposition kinetics during calcination and subsequent electrode microstructure [5].

The present work therefore focuses on identifying these kinetic limitations and proposing practical strategies for improving electrochemical performance through optimization of the calcination profile, reinforcement of the in-situ carbon network, and improved electrode compaction.

Experimental

LiFePO₄ precursor solution based on ferric acetylacetonate, lithium dihydrogen phosphate and citric acid was prepared and processed by spray drying. The obtained powders were calcined at different temperatures (600 - 800 °C) under a nitrogen atmosphere. Morphology and elemental composition were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), thermal decomposition by thermogravimetric analysis (TGA/DTG), and phase composition by X-ray diffraction (XRD). Cathodes were prepared using the synthesized active material, conductive carbon, and PVDF binder in a weight ratio of 80:10:10 with N-methyl-2-pyrrolidone (NMP) as the solvent. The slurry was coated onto an aluminum current collector using an automatic film applicator with a wet thickness 200 µm, dried at 60 °C for 24 h, punched into 18 mm electrodes, compacted at 30 kN, and finally vacuum-dried at 110 °C for 24 h. Electrochemical performance was evaluated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCPL), and electrochemical impedance spectroscopy (EIS).

Results and discussion

As shown in Figure 1, the spray-dried LFP powders had a spherical morphology. The particle diameter ranged from 0.2 µm to 1.1 µm. The analysis confirmed the uniform distribution of elements in the synthesized powders. The detailed elemental composition is summarized in Table 1. EDS elemental mapping confirmed the homogeneous distribution of the constituent elements throughout the particles. The measured Fe:P atomic ratio was close to 1:1, confirmed the expected stoichiometry.

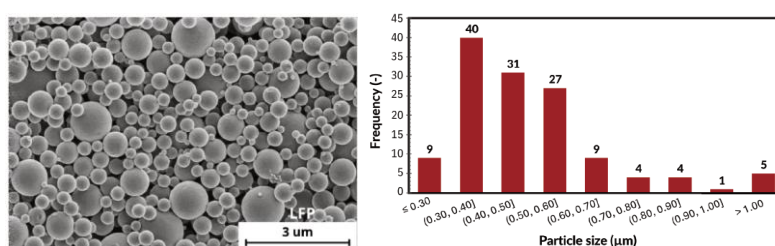


Figure 1. SEM picture of synthesized powder (left) and LFP particle size distribution (right)

TABLE I. EDS analysis of synthesized powder of LFP

Element	Atomic Ratio (%)	Atomic Ratio Error (%)
C	23.2	0.1
O	64.2	0.3
P	6.2	0.0
Fe	6.4	0.0

TGA and DTG revealed a major mass loss between approximately 180 and 250 °C, corresponding to the decomposition of organic precursor components. Mass stabilization was reached above 500 °C with a total mass loss of ~50 % (Figure 2). The XRD analysis confirmed the presence of a single olivine LiFePO₄ phase without detectable secondary impurities, indicating complete phase formation after spray drying and thermal treatment.

Galvanostatic charge–discharge measurements (Figure 2) revealed an initial discharge capacity of 118 mAh g⁻¹ at 0.1 C. Although the electrochemical activity of the prepared LiFePO₄ was confirmed, the relatively low specific capacity indicates that further optimization of the synthesis and thermal treatment is required.

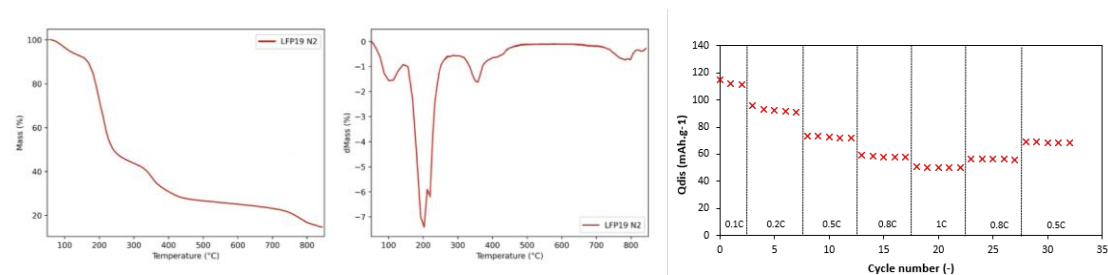


Figure 2. TGA and DTG analysis of LFP (left, middle), galvanostatic charge-discharge measurements (right)

Conclusion

Spray drying proved to be a suitable laboratory-scale route for the preparation of homogeneous LiFePO₄ precursor powders. The obtained results indicate that electrochemical performance is influenced not only by phase purity but also by the thermal decomposition pathway during calcination and the resulting carbon network. TGA/DTG analysis identified two critical decomposition regions around 200 °C and 350 °C, providing guidance for the optimization of the calcination profile.

Based on these findings, the present work is focused on investigating the influence of different calcination profiles and sucrose addition as a secondary carbon source on the structural, morphological, and electrochemical properties of spray-dried LiFePO₄ cathode materials.

Acknowledgments

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Effect of Temperature on Degradation and Cycle Life of Lithium-Ion Batteries

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Lithium-ion batteries are widely applied in electric vehicles and stationary energy storage systems; however, their performance and lifetime are strongly influenced by operating temperature. This study investigates the effects of ambient temperature (-10°C, 24°C, and 50°C) on the electrochemical behaviour and aging of commercial 18650 Li-ion cells through long-term cycling and electrochemical impedance spectroscopy. The results reveal progressive capacity fade and increasing internal resistance with cycle number, with degradation strongly dependent on temperature. Cells cycled at 24°C exhibited the highest capacity retention and the lowest resistance growth, whereas operation at 50°C led to accelerated aging, rapid capacity loss, and premature cell failure. Low-temperature cycling was also associated with a reduction in battery performance. EIS analysis confirmed significant changes in impedance characteristics associated with aging. The findings highlight the critical role of temperature control and provide guidance for the optimization of battery thermal management systems.

Introduction

Lithium-ion (Li-ion) batteries are widely used in electric vehicles, portable electronic devices, and stationary energy storage systems due to their high energy density, long cycle life, and excellent electrochemical performance. However, their durability is strongly affected by operating conditions, particularly ambient temperature, which significantly influences electrochemical reactions and aging mechanisms. Understanding the relationship between temperature and battery degradation is essential for improving battery lifetime and optimizing thermal management strategies. Therefore, this study investigates the effect of operating temperature on the discharge capacity, internal resistance, and long-term cycling performance of commercial 18650 Li-ion cells.

Results and discussion

Five commercial 18650 Li-ion cells were initially characterized by measuring their discharge capacity and charge/discharge voltage profiles. The cells exhibited highly

repeatable electrochemical performance, with an initial discharge capacity of approximately 2.74 Ah and stable charge–discharge characteristics following the conventional constant current–constant voltage (CC–CV) charging protocol. Long-term cycling tests were subsequently conducted at three ambient temperatures (-10°C , 24°C , and 50°C). The results demonstrated a gradual decrease in discharge capacity and a simultaneous increase in internal resistance with increasing cycle number. The degradation rate was strongly temperature dependent. Cells cycled at 24°C showed the highest capacity retention and the slowest increase in internal resistance throughout 2500 cycles. In contrast, cells operated at 50°C experienced accelerated aging, characterized by rapid capacity fade, a significant increase in internal resistance, and premature failure of some samples before reaching 1000 cycles. At -10°C , capacity degradation was also observed, although the increase in internal resistance was less pronounced. This behaviour is attributed to reduced lithium-ion diffusion, increased polarization, and possible lithium plating during charging, whereas degradation at elevated temperature is primarily associated with accelerated solid electrolyte interphase (SEI) growth, electrolyte decomposition, and irreversible loss of active lithium.

Analysis of the EIS spectra indicates that the cell typically exhibits the lowest overall impedance at intermediate SOC levels (approximately 40–70%), where charge-transfer processes and lithium-ion transport are the most efficient. In contrast, at extreme states of charge (close to 0% and 100% SOC), an increase in impedance is observed due to slower electrochemical reaction kinetics and enhanced diffusion limitations.

Elevated temperature accelerates the aging processes occurring within the cell, including the growth of the solid electrolyte interphase (SEI), electrolyte degradation, and the gradual loss of the electrochemically active surface area of the electrodes. As a result, the charge-transfer resistance increases, lithium-ion diffusion becomes less efficient, and the overall polarization of the cell is enhanced. The obtained results indicate that long-term cycling at $+50^{\circ}\text{C}$ has a more detrimental effect on the electrochemical performance of the cell than cycling at -10°C , although noticeable degradation of the impedance characteristics is also observed under low-temperature conditions.

Conclusion

The experimental results confirm that operating temperature has a decisive influence on the electrochemical performance and lifetime of commercial Li-ion cells. Elevated temperatures significantly accelerate degradation processes, while low temperatures reduce electrochemical efficiency and promote lithium plating, both leading to capacity loss and increased internal resistance. Among the investigated conditions, room temperature (24°C) provided the most favourable balance between capacity retention and resistance growth, ensuring the longest cycle life. The observed correlation between discharge capacity and internal resistance highlights the importance of effective thermal management for extending battery service life. These findings provide valuable guidance for the design and optimization of battery thermal management systems (BTMS) in electric vehicles and stationary energy storage applications.

Acknowledgments

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Methodological Approach to EIS Measurement and Interpretation in Li-ion Batteries

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Electrochemical impedance spectroscopy is a powerful non-destructive tool for Li-ion battery diagnostics, but the measured response strongly depends on experimental conditions. This paper presents a concise methodological framework for reliable and reproducible EIS measurement and interpretation. The proposed approach focuses on controlling the battery state, minimizing measurement artifacts, and validating the acquired data before electrochemical interpretation. Its consistent application and reporting can improve the reliability and comparability of battery impedance studies.

Introduction

Lithium-ion batteries are a key energy-storage technology used in electric mobility, stationary storage systems, and portable electronics due to their high energy and power density. During operation, however, their capacity, internal resistance, efficiency, and thermal behavior gradually change because of aging, cycling, temperature, and operating conditions. These changes can reduce performance, accelerate degradation, and increase safety risks. Reliable battery diagnostics are therefore necessary not only to estimate the state of charge (SOC) and state of health (SOH), but also to evaluate power capability, detect abnormal behavior, and determine whether a battery remains suitable for its intended application. The behavior of a battery cell is commonly characterized by its open-circuit voltage (OCV), available capacity, and impedance. Among these parameters, impedance is particularly sensitive to SOC, temperature, and aging state, making it valuable for battery characterization across the relevant operating range (1). Therefore, a comprehensive understanding of cell behavior across the entire operating range is essential for efficient design and management of battery systems.

Electrochemical impedance spectroscopy (EIS) is particularly attractive for battery diagnostics. During an EIS measurement, a small sinusoidal voltage or current perturbation is applied to the battery at a defined operating point, and the corresponding response is measured over a range of frequencies. The resulting complex impedance describes the magnitude and phase relationship between the excitation and response signals. Since electrochemical and transport processes have different characteristic time constants, EIS can help identify contributions associated with electrical connections and current collectors, electrolyte resistance, interfacial films, charge-transfer reactions, and mass transport within the electrodes (2). However, published impedance spectra are not always accompanied by sufficient information about operating conditions, measurement settings, and data quality. Since the measured response is strongly affected by SOC, temperature, operating history, and test setup, incomplete reporting can considerably limit the reproducibility and interpretation of the results. This paper therefore summarizes a concise methodological framework for EIS measurement and

interpretation, emphasizing controlled operating conditions, transparent reporting, and systematic data validation.

Methodological approach to EIS measurement

Reliable EIS measurements require consistent control of cell state, instrumentation, excitation parameters, and data validation. The following steps are intended to minimize uncontrolled variations that could otherwise be misinterpreted as changes in battery condition.

Pre-measurement cell stabilization

Before EIS measurement, the cell should be brought to a defined quasi-stationary state. The tested cell should have completed the prescribed conditioning cycles, and its measured capacity should be determined under defined conditions for consistent SOC adjustment. The required SOC should then be established using the same charging or discharging procedure, followed by temperature stabilization and relaxation until predefined voltage and temperature stability criteria are met. The direction and rate of the preceding load should remain consistent between comparable measurements.

Measurement setup and cell connection

The measurement setup should be selected with respect to the expected impedance magnitude and frequency range of the tested cell. Since Li-ion batteries generally exhibit low impedance, parasitic resistance and inductance introduced by cables, contacts, and fixtures may significantly distort the measured spectrum, particularly at high frequencies. The suitability of the potentiostat should be verified using the manufacturer's accuracy specifications and, when available, its EIS accuracy contour plot. The expected impedance should remain within the region corresponding to acceptable magnitude and phase errors over the selected frequency range (3). The instrument calibration status and any applied fixture compensation should also be documented.

A four-wire (Kelvin) connection should be used whenever possible, with separate current-carrying and voltage-sensing leads connected as close as possible to the cell terminals. The contacts should be mechanically stable and reproducible, while the cables should be kept short and arranged consistently to minimize parasitic inductance, electromagnetic interference, and unintended coupling. Cable routing, fixture geometry, and contact positions should remain unchanged between comparable measurements and should be documented together with the instrument configuration.

Measurement parameters

Impedance can be measured under potentiostatic (PEIS) or galvanostatic (GEIS) control. In PEIS, a sinusoidal voltage perturbation is imposed, and the current response is measured, whereas in GEIS a sinusoidal current is imposed and the resulting voltage response is recorded. For a linear and stationary system, both modes should provide equivalent impedance spectra. PEIS is suitable when the potential around a defined operating point must be controlled and the resulting current remains within the instrument limits. For low-impedance Li-ion cells, however, even a small voltage perturbation may generate a relatively large AC current and challenge the regulation of the potentiostat. GEIS is therefore often preferred because the excitation current can be controlled directly. Furthermore, it allows measurements to be performed under a non-

zero DC current during charging or discharging (3). In both operating modes, the perturbation amplitude should be large enough to ensure an adequate signal-to-noise ratio while remaining sufficiently small to preserve linear system behavior. At minimum, the control mode, DC bias, perturbation amplitude, frequency range, number of points per decade, integration or averaging settings, sweep direction, and number of repeated measurements should be reported.

Conventional EIS typically employs a single-sine sweep, in which individual frequencies are measured sequentially. Alternatively, multisine excitation applies several sinusoidal components simultaneously and can significantly reduce the acquisition time (5). This is advantageous when changes in the cell state during measurement should be minimized. Dynamic EIS can also be used to monitor impedance while the battery operating point changes, for example during charging or discharging. These approaches provide faster or time-resolved impedance information but require careful selection of the excitation amplitude and assessment of non-stationarity and nonlinear distortion. The selected excitation type, DC bias, frequency range, and acquisition settings should therefore be clearly reported.

Data validation and interpretation

Before interpretation, the measured impedance data should be assessed for repeatability and consistency. Repeated measurements performed under unchanged conditions should produce comparable spectra. Nyquist and Bode plots should be inspected for excessive noise, outliers, discontinuities, and high-frequency artifacts caused by the measurement setup. Visual smoothness alone does not confirm data validity. For conventional EIS, Kramers-Kronig relations can be used to assess whether the spectrum is consistent with the assumptions of a causal, linear, and stationary response. Dynamic EIS requires dedicated assessment of the time-varying operating point and nonlinear distortion. Only sufficiently consistent data should be used for further interpretation and model fitting (2).

In general, the high-frequency response is associated mainly with inductive contributions from the measurement setup and the ohmic resistance of the cell. The intermediate-frequency region contains contributions from interfacial films and charge-transfer processes, while the low-frequency response is dominated by mass transport and diffusion. However, these frequency regions are not universal and individual processes may overlap depending on cell chemistry, SOC, temperature, and aging state. Equivalent-circuit models should therefore be selected according to both the measured spectrum and the expected electrochemical processes. A low fitting error alone does not guarantee a physically meaningful or unique interpretation. Residuals, parameter uncertainty, repeatability, and the physical plausibility of fitted values should also be considered (6).

Conclusions

Reliable EIS diagnostics require consistent control of cell state, measurement setup, excitation parameters, and data validation. Pre-measurement stabilization, four-wire connection, operation within the accuracy limits of the instrument, and complete reporting of acquisition settings are essential. The acquired spectra should be assessed for repeatability and consistency before electrochemical interpretation or equivalent-circuit fitting. Applying this workflow reduces the risk of confusing experimental artifacts with genuine changes in battery behavior and improves comparability between studies.

Acknowledgments

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Processing of Correlative SPM-SEM NMC Cross-Section Measurements

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Correlative scanning-probe and electron microscopy has become a powerful route to the local structural, chemical, and electronic properties that govern lithium-ion battery degradation [1]. Integrating an atomic force microscope within a scanning electron microscope (AFM-in-SEM) on the LiteScope platform allows secondary-electron imaging (SEM), tapping-mode topography (AFM), conductive AFM (CAFM), and energy-dispersive X-ray spectroscopy (EDS) to be acquired on the exact same cross-section under identical vacuum conditions [2,3]. The scientific value of such multimodal datasets, however, is realised only through a systematic data-processing pipeline: the raw channels must be co-registered, segmented into individual particles, reduced to quantitative per-particle descriptors, and subjected to a statistically sound correlation analysis. This contribution focuses on that pipeline.

The workflow is demonstrated on broad-ion-beam-polished cross-sections of NMC111 composite cathodes in three states of health - pristine, post-formation, and after 50 galvanostatic cycles. Each region of interest is interrogated by all four channels, yielding co-located maps of morphology, elemental composition, and local resistance across a statistically representative secondary-particle population.

Processing proceeds in four stages. (i) Artefact mitigation and resistance calculation: trace and retrace CAFM currents are combined by a per-pixel maximum to suppress transient contact-loss artefacts, and an apparent local resistance is obtained via Ohm's law at the 10 V operating bias. (ii) Multimodal co-registration: using the high-resolution AFM topography as the spatial reference, the SEM, CAFM, and EDS layers are point-registered and resampled onto a common pixel grid to form a single multi-channel image. (iii) Particle segmentation: the high-contrast SEM channel is thresholded and refined by hole-filling and a watershed transform, and the resulting binary mask is propagated, unchanged, across every channel so that all descriptors of a given particle derive from the same pixels. (iv) Per-particle descriptor extraction: a custom Python routine computes geometric (equivalent diameter, distance to the current collector), elemental (relative Ni, Mn, Co, O), and electrical descriptors for each particle, the latter as the median resistance over the whole particle and over concentric core (inner 20 %) and edge (outer 10 %) zones.

The reduced descriptors are then characterised statistically. Distributional testing (Shapiro–Wilk) separates two families — log-normal resistance descriptors and non-normal geometric and elemental descriptors — dictating log-space treatment of resistance and non-parametric summaries elsewhere. Pairwise associations are quantified by the Pearson coefficient, tested via the Student t-statistic, and bracketed by 95 % confidence intervals from the Fisher z-transformation. Applied consistently

across the three states of health, this analysis links particle geometry, composition, and local resistance and reveals how these relationships evolve with cycling.

The framework converts qualitative correlative imaging into reproducible, statistically grounded, per-particle diagnostics, and scales naturally to additional channels (KPFM, SIMS, BSE) and larger particle populations as the dataset grows.

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Impact of Modifications on Thermal Stability of Lithium-Ion Battery Separators

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The thermal stability and surface properties of three lithium-ion battery separators were investigated: Celgard 2500, an uncoated separator, and a separator coated with a High Purity Nano Al₂O₃ (HPA) layer. Samples were exposed to temperatures between 25°C and 150°C to evaluate temperature-induced changes in morphology, chemical structure, and wettability. Thermal deformation became significant above 100°C, with clear differences in the response of individual materials. FTIR analysis confirmed that all separators were based on polyolefin materials and showed no evidence of chemical degradation within the investigated temperature range. Contact angle measurements performed with LP30, LP57, and LP57-2 electrolytes demonstrated that the HPA-coated separator exhibited the best wettability at room temperature. However, the effect became less pronounced as the temperature increased. The results indicate that separator performance and safety-related properties are strongly temperature dependent and should be evaluated under conditions relevant to battery operation and thermal abuse scenarios.

Introduction

Lithium-ion battery separators play a critical role in ensuring safe battery operation by preventing direct electrical contact between the electrodes while allowing ionic transport. Elevated temperatures may induce separator shrinkage, deformation, and changes in surface properties, increasing the risk of internal short circuits [1]. Ceramic-coated separators have been developed to improve thermal stability and electrolyte wettability [2]; however, their behavior under thermal stress remains an important research topic. The aim of this work was to evaluate the influence of temperature on the morphology, chemical structure, and wettability of three relevant separator materials.

Experimental

Three separator materials were investigated: Celgard 2500 (A), an uncoated separator (B), and an HPA-coated separator (C).

The HPA for this work was manufactured by Cadoux Limited of Cottesloe, Australia. The coating of HPA on ultra-high-molecular weight (UHMW) polyethylene (PE) separator (C) was performed by mist aerosol spraying technique, which resulted in application of a solvent-based dispersion of finely-sized HPA powder, followed by

drying to evaporate the carrier liquid. The objective of HPA coating was on one hand to allow unrestricted lithium transport across the membrane with minimal added resistance, and on another hand to improve high temperature stability and safety of the battery cell employing the coated separator. Media milling was used to prepare dispersions of HPA in a compatible solvent system. The dispersion formulation consisted of 21wt.% of alumina powder deagglomerated to $D_{50}=1.05\ \mu\text{m}$, 3wt.% organic thermoplastic binder and 24wt.% non-volatile solids. Preparation of dispersion was followed by reduction with solvent to enable the air brush spray, which applied the alumina ceramic coating onto the UHMW PE separator followed by air drying. This work employed fast evaporating air dry solvents based on ethyl alcohol. Dry separator substrates were evaluated for Dry Film Thickness (DFT), coating uniformity and added specific weight.

Samples were prepared as discs with a diameter of 20 mm and exposed to temperatures of 25°C, 60°C, 90°C, 120°C, and 150°C for 2 h in a laboratory drying oven.

The chemical structure of the separators before and after thermal exposure was analyzed using ATR-FTIR spectroscopy. Wettability measurements were performed using three electrolytes: LP30 (1 M LiPF_6 in EC:DMC 1:1), LP57 (1 M LiPF_6 in EC:EMC 3:7), and LP57-2 (LP57 + 2 wt.% VC). Contact angles were determined at various temperatures to evaluate temperature-induced changes in the separator surface properties.

Results and Discussion

No significant morphological changes were observed for any separator between 25°C and 90°C. However, at 120°C clear differences in thermal response became evident. Celgard 2500 exhibited noticeable deformation, whereas the uncoated separator largely retained its original geometry. The HPA-coated separator showed characteristic curling behavior resulting from asymmetric stress development within the ceramic-coated structure.

At 150°C, all investigated materials underwent severe thermomechanical deformation. Celgard 2500 lost structural rigidity, while both the uncoated and HPA-coated separators experienced a substantial loss of structural continuity.

FTIR spectra confirmed the polyolefin nature of all separators. Characteristic C–H stretching bands ($2950\text{--}2850\ \text{cm}^{-1}$) and methylene deformation bands ($1470\text{--}1450\ \text{cm}^{-1}$) were observed [3][4]. No new absorption bands appeared after thermal treatment, indicating the absence of chemical degradation up to 150°C.

Contact angle measurements demonstrated a strong dependence of wettability on separator type. The HPA-coated separator exhibited the lowest contact angle values and dynamic wetting behavior at room temperature. However, the beneficial effect became less pronounced at elevated temperatures, accompanied by an increase in contact angle and suppression of dynamic droplet spreading.

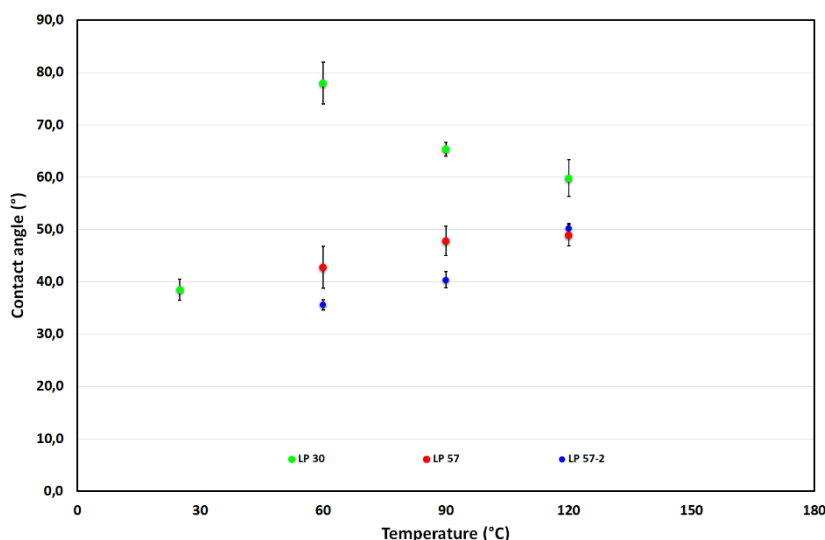


Figure 1. Dependence of the contact angle on temperature for the HPA-coated separator in the presence of LP30, LP57, and LP57-2 electrolytes.

The results indicate that ceramic coatings significantly improve electrolyte affinity under ambient conditions but may lose part of their effectiveness after thermal exposure.

Conclusions

The investigated separators remained chemically stable up to 150°C, as confirmed by FTIR analysis. Nevertheless, significant thermomechanical deformation occurred above approximately 100°C, which may adversely affect battery safety. The HPA coating improved wettability at room temperature but exhibited reduced effectiveness at elevated temperatures. These findings demonstrate that separator performance and safety characteristics are strongly temperature dependent and should be evaluated under realistic thermal conditions.

Acknowledgments

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Giving Battery Metals a Second Life: High-Entropy Transition Metal Oxides for Advanced Li-Ion Battery Applications via Ultrasonic Spray Pyrolysis

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The growing demand for critical raw materials driven by the energy transition and electromobility underscores the need for sustainable battery recycling and resource recovery strategies. Our research focuses on the manufacture of high-entropy transition-metal oxides as advanced anode materials for lithium-ion batteries, utilizing metals recovered from spent battery waste. By integrating circular economy principles with advanced materials engineering, the project converts secondary resources into high-value functional materials. Owing to their compositional complexity, high-entropy oxides offer significant potential for enhanced electrochemical performance and tailored physicochemical properties. This approach promotes the recirculation of critical raw materials, reduces dependence on primary resource extraction, and contributes to the development of a more sustainable and resource-efficient battery value chain.

Introduction

The global energy transition and the rapid expansion of electromobility are accelerating an unprecedented increase in demand for raw materials used in energy storage technologies. Particular importance is attributed to metals employed in lithium-ion batteries, whose availability is becoming one of the key factors determining the future development of advanced energy systems. The growing consumption of natural resources, the limited geographical distribution of mineral deposits, and the increasing vulnerability of global supply chains have transformed the recovery and reuse of metals from spent batteries into not only a technological challenge but also a strategic component of resource sovereignty and economic security [1][2].

In this context, battery scrap is no longer perceived as waste but rather as a valuable secondary resource reservoir that can be reintegrated into manufacturing cycles in accordance with the principles of the circular economy. Such an approach simultaneously mitigates pressure on the natural environment, reduces the carbon footprint associated with primary resource extraction, and enhances overall resource efficiency. Of particular significance is the recovery of critical raw materials, whose importance to the European energy and transportation sectors continues to grow steadily.

Despite their high level of technological maturity, lithium-ion batteries remain the subject of intensive research and development efforts aimed at improving electrochemical performance, operational safety, and the sustainability of their production. Among the most promising research directions is the design of novel electrode materials derived from recycled feedstocks. High-entropy materials have attracted considerable attention due to their unique chemical complexity, which enables the achievement of advantageous electrochemical properties while simultaneously providing greater flexibility in compositional design [3][4].

Our research focuses on the development of innovative anode materials based on high-entropy transition metal oxides synthesized from metals recovered from end-of-life battery waste. This approach integrates advanced materials engineering with circular economy principles, demonstrating the feasibility of giving a second life to valuable elements contained in spent electrochemical cells.

Experimental and Results

Nanostructured high-entropy metal oxides were successfully synthesized by ultrasonic spray pyrolysis of nitrate precursor solutions obtained from the digestion of battery alloys. The process was carried out at 900°C under an argon flow rate ranging from 800 to 1600 ml/min. ICP-OES analysis confirmed that the resulting materials exhibited stoichiometries consistent with the targeted compositions. X-ray diffraction (XRD) measurements revealed the formation of the desired crystalline phases, while SEM-EDX elemental mapping demonstrated a homogeneous distribution of constituent elements throughout the particles. These results confirm the effectiveness of ultrasonic spray pyrolysis as a synthesis route for compositionally complex oxide materials and highlight its potential for the fabrication of advanced energy-storage materials. The resulting materials represent not only a potential alternative to conventional anode materials used in lithium-ion batteries but also a tangible example of sustainable development in practice, achieved through the closure of material loops within the battery value chain and the efficient recirculation of critical raw materials.

Acknowledgments

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Electrochemical Parameters of Lithium Manganese Iron Phosphate with a Graphene-Containing Binder

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This publication is devoted to the study of the electrochemical properties of a cathode based on lithium manganese iron phosphate with a graphene-containing binder. The improvement in the cyclability of the graphene-modified electrodes consists in an increase in the conductivity of the poorly conductive lithium manganese iron phosphate, as confirmed by electrochemical impedance spectroscopy (EIS) data and by the capacity retention data upon prolonged cycling.

Introduction

The relentless pursuit of high-energy-density, safe, and cost-effective energy storage systems has positioned lithium-ion batteries (LIBs) at the forefront of modern technology, powering everything from portable electronics to electric vehicles and grid-scale storage. Among the various cathode materials that define battery performance, olivine-structured phosphates have garnered significant attention due to their excellent thermal and electrochemical stability. While lithium iron phosphate (LiFePO₄) has become a commercial success owing to its safety and long cycle life, its relatively low energy density (~586 Wh kg⁻¹) limits its applicability in next-generation applications that demand higher specific energy.

Lithium manganese iron phosphate (LiM_nxFe_{1-x}PO₄, LMFP) has emerged as a compelling alternative within the olivine family. By incorporating manganese, which offers a higher operating voltage (~4.1 V versus Li⁺/Li) compared to iron, LMFP can achieve an energy density approximately 20% higher than that of LiFePO₄ while maintaining similar cost-effectiveness and safety advantages. However, the practical deployment of LMFP is severely hindered by intrinsic drawbacks: its inherently low electronic conductivity and sluggish lithium-ion diffusion kinetics, which result in poor rate capability and limited electrochemical activity. Furthermore, manganese-rich compositions suffer from the Jahn–Teller distortion of Mn³⁺ ions and subsequent manganese dissolution into the electrolyte, leading to rapid capacity fade and structural degradation during cycling.

To overcome these limitations, various strategies have been explored, including particle size reduction, cationic doping, and carbon coating. Among these, carbon coating has proven particularly effective for enhancing the electronic conductivity of phosphate-based cathodes. In this context, graphene (a two-dimensional carbon allotrope with exceptional electrical conductivity, high specific surface area, and remarkable mechanical flexibility) has emerged as a transformative conductive additive.

Recent studies have demonstrated that incorporating graphene into LMFP composites yields substantial improvements in electrochemical performance, including increased discharge capacity, superior rate capability, and enhanced cycling stability.

In this work, the effect of a graphene-containing binder on the electrochemical properties of lithium manganese iron phosphate, the kinetics of lithium-ion transport, interfacial stability, and overall battery performance is demonstrated. By elucidating the mechanisms underlying the improvement of the electrochemical properties of LMFP when using the graphene-containing binder, this study aims to contribute to the rational design of high-performance and low-cost cathode materials for next-generation lithium-ion batteries.

Experimental Section

$\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ was a commercial material (“Qiqiling Electrochemistry”, Guangzhou, China). Electrochemical tests were performed in sample $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ cells on a Neware potentiostat/galvanostat (Shenzhen, Guangdong, China). The working electrodes consisted of 93 wt.% LMFP, 1.5 wt.% conductive additive (SP), and 5.5 wt.% of the graphene-containing binder. The graphene-containing binder was prepared by mixing the water-soluble binder material NV-1A (Zhejiang Casnovo New Materials Co Ltd.) with a few-layer graphene material. The ratio of the dry residue of the polymer binder to graphene was 4 wt.% and 1.5 wt.%, respectively.

A 150 μm layer of the slurry was put on an aluminum foil with a doctor blade and then dried at 100 – 120 $^{\circ}\text{C}$ 18-21 h under a vacuum. The quantity of $\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ in a dried remainder was $\approx 7.1 \text{ mg}\cdot\text{cm}^{-2}$. Coin-type cells were assembled in 2032 cases with Celgard 2500 separator and an electrolyte containing 1 M LiPF_6 in a mixture of ethylene carbonate and dimethyl carbonate in a 1:1 mass ratio. The reference and counter electrode was the lithium metal. Galvanostatic tests were performed within the voltage range of 2.0–4.3 V at different current rates (0.05 – 1C).

Results and Discussion

Charge/discharge curves for $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ sample cells at 0.05C are given in Fig. 1a. These curves show two pairs of clearly defined plateaus near 3.5 V and 4.1 V, corresponding to the redox potentials of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ pairs, respectively, and the capacity ratio of these plateaus is approximately 7/3, which is consistent with the Mn/Fe ratio in the raw material. The specific capacity of the coin cells with NV-1A binder is 144 mAh/g, which is consistent with the data sheet for the electrode material.

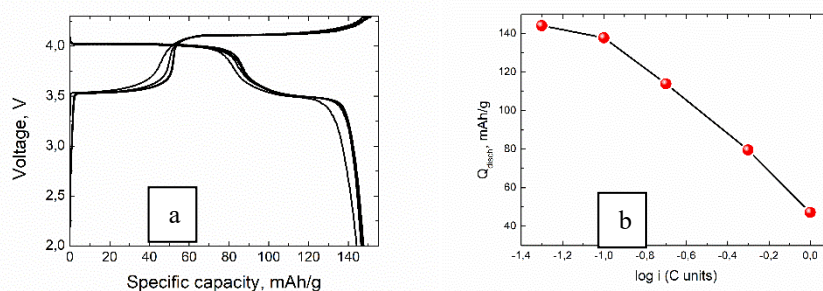


Figure 1. Charge/discharge curves for sample $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ (a) and the dependence of the discharge capacity on the current density for $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ sample (b).

The coulombic efficiency in the first cycle for $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ coin cells is 95% for NV-1A, respectively, and increases to 98% ($\pm 0.1\%$) in the third cycle. An increase in the density of charge/discharge current from 0.05C to 1C leads to a regular decrease in specific capacity from 144 mAh/g at 0.05C to 48 mAh/g at 1C (Fig. 1b).

The capacity retention upon cycling of $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ coin cells using NV-1A binder is shown in Fig. 2. It was shown that at a current rate of 0.2C, the discharge capacity of the coin cells containing the NV-1A binder was 77% on the 11th cycle. After the rate capability tests, this value changed from 75% on the 26th cycle to 63% on the 125th cycle, with a capacity loss of $\sim 0.12\%$ per cycle. In addition, the degradation of the coin cells upon cycling was evaluated by electrochemical impedance spectroscopy (EIS).

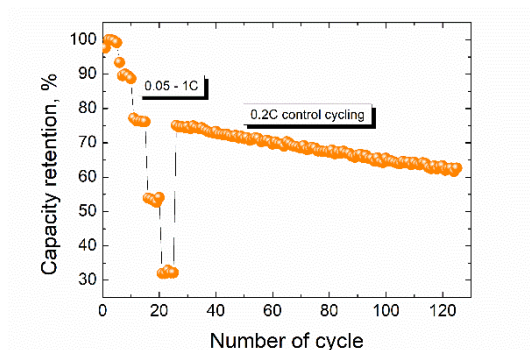


Figure 2. The dependence of the capacity retention on the current density upon cycling, as well as the change in the capacity retention at 0.2C on the cycle number for the $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ sample.

The evolution of the impedance spectra during cycling of $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ coin cells is shown in Fig. 3. During cycling of the cells, an increase in the internal resistance (R_{ct}) was observed. The most pronounced increase in R_{ct} occurs during the initial 15 cycles, where the resistance rises by a factor of 2.4 compared to the freshly assembled sample (98 and 233 Ω , respectively), and only by a factor of 2 upon subsequent cycling (cycles 15–125). The Nyquist diagrams also reveal a notable transformation of the impedance spectra. As the internal resistance increases, the single semicircle in the spectrum, observed in the frequency range from 1×10^5 to 20 Hz and attributed to the charge transfer process across the electrode–electrolyte interface, transforms into two clearly distinguishable semicircles after 125 cycles. The formation of the second semicircle is associated with the formation and densification of a blocking layer on the surface of the cathode material, consisting of products of the interaction between manganese ions and the electrolyte at high potentials, such as MnF_2 , MnCO_3 , etc. The formation and densification of this layer on the cathode material surface are the main contributors to the degradation of the specific capacity upon cycling, as observed in Fig. 2.

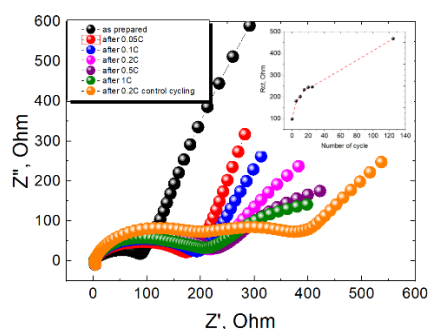


Figure 3. EIS data after different current density cycling, as well as the change in the resistance at 0.2C for the $\text{Li}||\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ sample.

The Effect of Mechanical Compression and Thermal Load on Capacity Decline in Lithium-Ion Cells

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Understanding capacity loss is essential for optimising battery lifespan and reliability. This work evaluates degradation mechanisms of lithium-ion cells, connected with operation temperature. By testing commercial automotive cells under mechanical pressure and different operating temperatures, we find some possibilities how to prolong its lifespan and performance.

Introduction

With the electric vehicle (EV) industry demanding higher energy density and faster charging, mitigating capacity degradation has become a major technological challenge. While stress factors, such as high current loads, are well documented, battery ageing remains a multifaceted degradation process influenced by structural changes in the material and local operating conditions. This study focuses on these mechanical and thermal factors to help optimise thermal management and the design of battery modules.

Cell chemistry

Cathode materials

There are several materials which were used as the cathode in automotive-focused cells. First and most dominant on the European market is NMC, which is an evolution of the first production cathode LCO. There is nickel and manganese to increase capacity and stability. Currently, NMC811 is used in combination with a theoretical capacity of 280 mAh.g⁻¹. Another material, which is based on LCO, is NCA. This material focuses more on performance and sacrifices a little bit of stability in comparison with NMC. The theoretical capacity of NCA8155 is 279 mAh.g⁻¹. The last currently used material in automotive is LFP. This material is highly reliable, safe and cobalt-free. Actual generation of this material achieves the theoretical capacity of 170 mAh.g⁻¹. [1][2]

Anode materials

The most common commercially used anode material is graphite (C). This anode material offers a capacity of 372 mAh.g⁻¹ with low potential vs Li/Li⁺. Another commercially used material is LTO. This material offers high cycle life and best safety with a capacity of 175 mAh.g⁻¹. On the other hand, it has high potential with Li/Li⁺. The most promising anode material with a capacity of 3579 mAh.g⁻¹, the biggest problem with silicon is its volume changes (up to 300%), which leads to particle cracking and capacity loss. Silicon is currently used as a composite C/Si as an additive for capacity increase. [3][4][5]

Degradation processes and thermal effect

Degradation processes

Lithium-ion battery degradation is an irreversible chemical and mechanical process that permanently reduces capacity and performance. In electric vehicles, this aging directly compromises driving range and long-term reliability. Consequently, modern battery research heavily focuses on identifying and mitigating these complex degradation mechanisms, particularly solid electrolyte interphase (SEI) layer growth and electrode cracking (see Figure 1). [6][7]

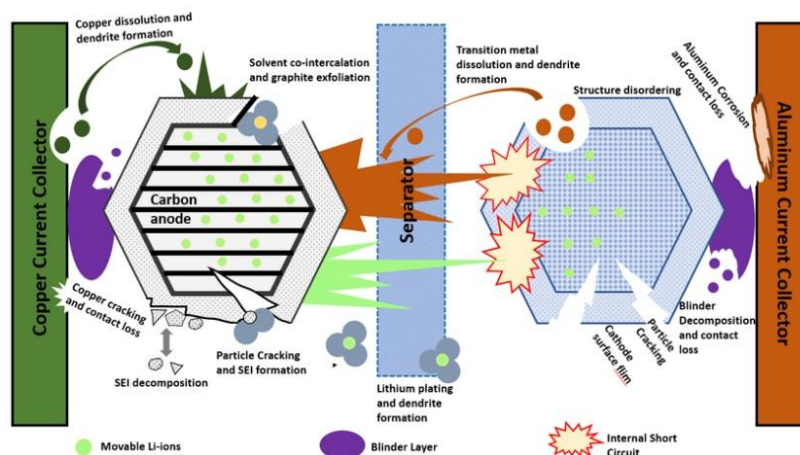


Figure 1. Li-ion battery degradation processes [8]

Thermal effects

Lithium-ion batteries operate optimally between 15°C and 35°C. Operating outside of this window reduces performance, safety, and lifespan. At low temperatures, performance drops due to spiked internal resistance. Extreme cold can even freeze the electrolyte or cause lithium plating on the anode, inducing irreversible capacity loss and possible fire. High temperatures accelerate cyclic and calendar ageing by causing crystallographic shifts in the electrodes, electrolyte decomposition, binder migration, and continuous SEI growth. Without precise thermal management, these exothermic reactions can start thermal runaway, resulting in structural failure or explosion.[9]

Experiment

In this experiment were tested automotive NMC pouch cells with a capacity of 78 Ah. The first part of the experiment was testing if is possible to prolong battery life with external force applied on the housing of the cell. The external force was made by a spring-loaded clamp, and the applied forces were 5, 10, and 20 kg with one uncompressed cell. Tested cells were cycled in the window of 80% DoD with 0.33C. After 600 cycles, the results show minimal difference in clamping force, but the results of the compressed cell were more stable than the uncompressed one.

In the second part, were tested same calls in different operating temperatures (5, 25 and 45°C) with two DoD (70 and 100 %). These cells were cycled at 0.3C for 500 cycles. The result showed that the biggest degradation was achieved on cells at 45 °C with 100% DoD, and this effect can be reduced by reducing the DoD, which can prolong the lifespan of the battery. On the other hand, the effect of 5°C was reversible.

Conclusion

Results show that ambient temperatures significantly influence battery life, with high temperatures accelerating degradation and low temperatures limiting performance. This thermal impact can be minimised by lowering the Depth of Discharge (DoD). Selecting the right lithium-ion chemistry for the application is equally critical. Additionally, testing indicates that appropriately calibrated external pressure stabilises pouch cells during cycling.

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Operando Scanning Electron Microscopy as a Multiscale Tool for Investigating Structural Degradation of Lithium-ion and post-Li-ion Batteries

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Understanding how the internal structure of lithium-ion batteries evolves during operation is central to improving their reliability and lifetime. This contribution motivates operando scanning electron microscopy (SEM) as a characterization approach that images structural and morphological changes as they happen and relates them to the measured electrochemical behavior. Unlike ex-situ or post-mortem methods, it allows a single region of an electrode to be followed continuously throughout cycling, connecting whole-electrode behavior with the response of individual active-material particles. The associated poster presents the workflow and the structural evolution it reveals.

Introduction

Lithium-ion (Li-ion) batteries have become an indispensable part of modern technology, powering devices from smartphones and portable electronics to electric vehicles and grid-scale storage owing to their high energy density and long cycle life. Despite this widespread adoption, their performance, safety, and lifespan remain limited by a range of degradation processes that must be understood and mitigated. Battery degradation is a complex interplay of electrochemical, mechanical, thermal, and chemical mechanisms, including growth of the solid-electrolyte interphase (SEI), lithium plating and dendrite formation, transition-metal dissolution, and mechanical failures such as electrode expansion and active-material particle cracking. Many of these mechanisms are structural in nature and evolve dynamically over a wide range of length scales, directly affecting capacity retention, cycle life, and, in extreme cases, cell safety. [1][2]

Optimizing electrode materials and cell designs to counter these processes, as well as introducing advanced chemistries such as silicon-rich anodes and solid-state systems, relies on detailed characterization of the internal structure. Ex-situ and post-mortem techniques have provided much of the current understanding, but they capture only static snapshots taken after cell disassembly. Sample preparation must typically be carried out in a protective atmosphere because battery materials are sensitive to moisture, oxygen, and nitrogen, and disassembly itself can damage or degrade the

sample. Moreover, once a cell is opened it undergoes intrinsic relaxation, so the features observed may no longer represent the working state. Crucially, ex-situ analysis cannot follow the same region continuously; before-and-after comparisons are therefore made on non-identical areas, and information about how a given feature actually evolved during operation is lost. [1][2]

In-situ and operando techniques overcome these limitations by probing the battery under working conditions. By identifying structural and chemical states at the moment they occur and correlating them directly with the electrochemical response, they provide a far clearer picture of the underlying degradation mechanisms. A variety of probes such as electrons, X-ray, optical, infrared, and ultrasound are now applied in the battery field, each offering a distinct combination of resolution and length scale [3][4].

Among these, SEM occupies a particularly valuable position. It combines high spatial resolution with access to a comparatively large area and volume, spanning from the electrode level to individual particles while still resolving nanometer-scale features. Transmission electron microscopy offers atomic resolution but is restricted to very small, specially prepared volumes, making it best suited to fundamental studies; X-ray, optical, infrared, and ultrasound probes cover larger scales but at substantially lower resolution. Operando SEM therefore bridges these regimes, making it well suited to studying particle- and electrode-level phenomena such as cracking, expansion, delamination, and dendrite formation under practical operating conditions as a knowledge that is relevant to both fundamental research and battery manufacturing [3][4].

Realizing this potential is nonetheless challenging. Conventional carbonate-based electrolytes evaporate under the high vacuum of the SEM chamber, and preparing electrode surfaces smooth enough for high-resolution imaging without introducing artifacts is difficult. Existing operando SEM cell designs each involve trade-offs, sacrificing statistical representativeness, image resolution, or access to buried components such as current collectors and separators. These obstacles can be addressed by combining broad ion beam (BIB) cross-section preparation, inert sample transfer, and non-volatile ionic-liquid electrolytes that remain stable under vacuum and promote robust, predominantly inorganic interphases. Together, these measures ensure that the observed morphological changes can be attributed to intrinsic material behavior rather than to the measurement environment, which is essential if operando SEM is to deliver reliable, mechanistically meaningful insight. [3][4][5]

General Workflow

The considerations above can be met by a single operando SEM workflow that follows the internal structure of a working cell at both the electrode and the particle level. In outline, a smooth electrode cross-section is first prepared by broad ion beam (BIB) polishing, exposing an artifact-free plane suitable for high-resolution imaging. The prepared sample is transferred to the microscope under an inert atmosphere to avoid contamination by air or moisture, and inside the chamber it is connected through

a vacuum feedthrough to an external potentiostat. Electrochemical cycling then proceeds while the same region is imaged continuously, with each frame tied to the corresponding point on the electrochemical curve; semi-automated acquisition and image analysis allow both wide overview and high-magnification views to be captured and quantified over successive cycles. Because the procedure does not depend on a volatile liquid electrolyte, it adapts to different cell formats and chemistries, including solid-state systems whose electrolytes are inherently vacuum-compatible. This contribution focuses on the rationale and the workflow itself; the structural evolution and other phenomena it can reveal are shown on the poster. [5][6][7]

Outlook

The value of operando SEM grows as batteries evolve beyond today's Li-ion designs. Because the workflow is independent of any particular cell format or electrolyte, it transfers readily to chemistries in which mechanical failure is a primary lifetime-limiting factor, most notably high-capacity silicon-anode Li-ion cells and sodium-ion (Na-ion) batteries, whose large volume changes and cracking are far easier to understand when observed directly than when inferred from electrochemistry alone. Together with the solid-state systems discussed above, these represent the central direction of ongoing work.

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Declaration of AI-assisted technologies in the writing process

During the preparation of this paper the authors used Claude Opus 4.8 (Anthropic) in order to enhance text quality, fix grammar errors, and improve readability. After using this tool, the authors reviewed and edited the content as needed and took full responsibility for the content of the published article.

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Microstructural Evolution of Ni-Based Fuel Electrodes in Reversible Solid Oxide Cells

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The long-term performance of reversible solid oxide cells depends strongly on the microstructural stability of Ni-based fuel electrodes. The microstructure is highly impacted during the transition between fuel cell and electrolysis modes. Several commercially available NiO-containing powders were reduced in hydrogen at 800 °C and exposed to repeated water-vapor pulses. Pronounced Ni redistribution, particle coarsening and neck growth occurred in structures with insufficient ceramic support, whereas Ni–yttria-stabilized zirconia composites containing a continuous, well-distributed ceramic scaffold retained a substantially more stable microstructure. Steam exposure alters the H₂/H₂O-controlled population of adsorbed H-, OH- and O-containing species and increases the local oxygen chemical potential, potentially modifying interfacial energies or enabling transient redox-assisted Ni transport. Although the surface chemistry is reversible, the resulting Ni redistribution may persist. The results identify ceramic-phase morphology as a key factor governing Ni connectivity and resistance to degradation under dynamically changing fuel-electrode atmospheres.

Introduction

Reversible solid oxide cells combine fuel-cell (FC) and electrolysis (EC) operation in a single high-temperature device. Each of the operation regimes introduces different requirements on the gas composition in the fuel electrode compartment. While FC regime requires high concentration of hydrogen at the fuel electrode, the EC regime requires high steam concentration. Hence it is inevitable that transition of the operating regime requires also a change in gas composition. However, gas composition may induce morphological changes to the electrode. The Ni–YSZ (cermet composed of Ni and yttria-stabilized zirconia) fuel electrode is particularly sensitive because its performance depends on a fine, interconnected Ni network that provides electronic conductivity and catalytic activity, while YSZ supplies oxide-ion transport and stabilizes the microstructure. Ni coarsening reduces the active Ni surface and the density of Ni–YSZ–gas boundaries and can eventually disrupt electronic or interfacial contact. Steam-rich conditions, redox fluctuations and electrochemical polarization may further accelerate this evolution [1][2].

The overall fuel-electrode reaction, $\text{H}_2\text{O}(\text{g}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + \text{O}^{2-}(\text{YSZ})$, comprises adsorption, dissociation, charge transfer and oxide-ion incorporation at Ni surfaces, YSZ surfaces and their boundary [3]. Even near equilibrium, H₂/H₂O establishes a dynamic population of H*, OH* and O* species; hydroxyl species can also be strongly stabilized on YSZ [4]. A steam-rich atmosphere may therefore alter surface coverage

and interfacial energetics without bulk oxidation of Ni. This work examines how the initial powder-derived structure and the ceramic scaffold affect Ni coarsening and neck development during repeated changes in steam activity. This information is crucial for the development of degradation-resistant fuel electrodes for reversible cell, whose main attribute is the ability to alter between the steam and hydrogen-rich gas feed.

Experiments

Several commercially available NiO and NiO-YSZ powders were selected to provide different initial particle morphologies and packing characteristics. The specimens were reduced in flowing hydrogen at 800 °C to convert NiO to metallic Ni and establish the initial porous microstructure. Afterward, gas composition was altered periodically between 50:50 H₂:N₂ and 10:10:80 H₂:N₂:H₂O. It was necessary to prevent the penetration of ambient oxygen into the experimental environment to prevent direct Ni oxidation.

Microstructure of samples with different numbers of steam-rich atmosphere exposition periods was examined by scanning electron microscope.

Results

Reduction of the different NiO precursors produced distinct metallic networks whose stability depended on the particle arrangement and the scaffold provided by the ceramic phase. Repeated steam pulses caused pronounced Ni coarsening and neck growth in electrodes with insufficient YSZ support. In contrast, a continuous and well-distributed YSZ framework separated Ni domains, limited the available transport length and helped preserve the Ni microstructure. Local Ni-rich regions still coarsened, showing that phase topology and contact distribution are at least as important as the nominal YSZ fraction.

Given the morphological changes that occurred in the absence of O₂, the coarsening was likely due to the presence of surface-adsorbed species and may reflect two coupled effects. Changes in H*, OH* and O* coverage may modify Ni–gas, Ni–YSZ and Ni–Ni interfacial energies and favor transport from highly curved particles towards larger particles or necks. In addition, the higher oxygen chemical potential may form oxidized or hydroxylated Ni species at defect-rich surfaces and interfaces, potentially providing a redox-assisted transport pathway. Restoration of H₂-rich conditions removes oxygen-containing species, but the redistributed Ni remains; the gas-phase cycle can therefore be chemically reversible yet microstructurally irreversible. The stabilizing effect of a well-developed YSZ scaffold supports a major role of geometrical confinement and interfacial pinning, although the present experiments cannot distinguish quantitatively between surface diffusion, volatile-species transport and local redox-assisted transport.

Conclusions

Repeated changes in steam activity at 800 °C can promote irreversible evolution of the metallic Ni network in model fuel electrodes. The severity of this evolution is governed primarily by the initial morphology and by the presence and spatial distribution of the ceramic scaffold. Ni-rich structures with insufficient support undergo substantial particle coarsening and neck growth, whereas a continuous, well-distributed YSZ phase constrains Ni transport and preserves a finer, better-connected microstructure. The effect of steam is plausibly linked to reversible changes in H*, OH* and O*-containing

surface species established by the H₂/H₂O equilibrium, which may modify interfacial energies and enable transient redox-assisted Ni transport. This mechanistic explanation remains a hypothesis rather than a direct identification of the mobile species. The findings emphasize that fuel-electrode optimization for reversible SOCs must address not only catalytic activity and nominal composition, but also ceramic-phase topology and resistance to dynamically induced redistribution of Ni.

Acknowledgement

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Optimization of Tape-Cast YSZ Electrolytes for Reversible Solid Oxide Fuel Cells

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Thin ceramic electrolytes are essential for highly efficient solid oxide cells, but their fabrication becomes more difficult as the sample area increases. This work presents the optimization of tape casting for self-supporting 8 mol.% yttria-stabilized zirconia electrolytes. The development included multiple iterations of organic suspension together with optimization of homogenization, casting, drying, and sintering. The final procedure produced planar, gas-tight plates with dimensions of 5×5 cm and a thickness of approximately 200 μm . To compare the tape-cast electrolytes, uniaxially pressed samples were used as a laboratory reference and commercial YSZ wafers as a benchmark. Scanning electron microscopy showed a microstructure comparable to commercial YSZ wafers. Conductivity was measured between 400 and 800 °C using silver electrodes; and comparable values were obtained for tape-cast, pressed, and commercial samples. The process therefore enabled scale-up from pressed laboratory specimens to larger tape-cast electrolytes while preserving their functional properties and significantly reducing their thickness.

Introduction

Solid oxide cells can operate reversibly as fuel cells or high-temperature electrolyzers and are relevant to efficient electricity generation, hydrogen production, and energy storage [1]. Their ceramic electrolyte must combine high oxide-ion conductivity with gas-tightness, chemical stability, mechanical integrity, and compatibility with the adjoining electrodes [2]. Yttria-stabilized zirconia (YSZ) is widely used as an electrolyte because it combines suitable ionic conductivity with high-temperature stability and thermomechanical compatibility with state-of-the-art catalysts. However, the electrolyte is the main contributor to cell ohmic resistance, and this contribution increases with its thickness. Reducing the thickness is therefore beneficial, provided that gas-tightness and mechanical stability are retained. Producing self-supporting YSZ components becomes particularly challenging for larger areas at thinner scales.

The uniaxial pressing offers a simple and reproducible route to small ceramic specimens, but its scale-up to large areas is limited and the directly achievable thickness is suitable only for laboratory applications. Tape casting is more suitable for larger areas, although it requires coordinated control of suspension composition, homogenization, casting, drying, and thermal treatment [3]. This work aimed to develop a reproducible tape-casting process for YSZ electrolytes of variable dimensions and a thickness below 250 μm , and to compare them with pressed samples and commercial wafers.

Experiments

YSZ-TC powder containing 8 mol.% Y_2O_3 was supplied by Fuel Cell Materials. The suspension contained YSZ, toluene and ethanol as solvents, Tergitol® (Merck) as a surfactant, diethyl phthalate (Merck) as a plasticizer, and polyvinyl butyral (PVB; Kuraray) as a binder. The optimized suspension contained approximately 60 wt.% YSZ.

The liquid components were first mixed with PVB to form the liquid vehicle, after which the YSZ powder was added. No filtration or degassing was applied. The suspension was cast onto glass plates using a doctor blade with a gap height of 1.25 mm. Suspension composition, homogenization, substrate, drying, and thermal treatment were optimized iteratively.

Uniaxially pressed YSZ samples (thickness approx. 1 mm) prepared by an established laboratory procedure [4] were used as the process reference. Commercial YSZ wafers (thickness 150 μm) provided an additional benchmark.

Tape-cast, pressed, and commercial samples were characterized using the same general approach. The microstructure of sintered electrolytes was examined by scanning electron microscopy; and conductivity was measured using electrochemical impedance spectroscopy in a two-electrode assembly with brush deposited silver electrodes between 400 and 800 °C.

Results

Transferring the preparation method from uniaxial pressing to tape casting required optimization of both the suspension and the subsequent process steps. The suspension optimization mainly included the selection of suitable binder and ratio of the organic additives necessary for suspension of desired quality and rheologic properties. Before the suspension casting itself, the experiments showed that homogenization was a critical parameter. The 24 h homogenization on the roller mixer was necessary to obtain a suspension suitable for reproducible casting and handling without the need for degassing or filtering.

The casting of prepared ceramic suspension was done with a doctor-blade gap of 1.25 mm, followed by sample drying. The substrate material and drying conditions had to be optimized together with the suspension to obtain green bodies suitable for subsequent handling and furnace sintering. The best results were achieved while casting onto glass sheets followed by low-temperature drying (-17 °C) in freezing box for 7 days. Such prolonged drying procedure allowed to obtain thin green bodies without any cracks or other layer deformities.

The bending of the electrolyte sheets was the principal difficulty during sintering procedure. Mechanical loading of the green body in the furnace was tested as a means of suppressing deformation, but did not provide a satisfactory solution. To retain the green body planarity slower temperature changes had to be adapted. In addition, the sintering procedure established for uniaxially pressed electrolytes, 1360 °C for 6 h, was insufficient for the tape-cast samples and did not provide the required microstructure, i.e. required level of densification. Increasing the firing temperature to 1550 °C and extending the sintering time to 24 h produced a substantial improvement. The optimized process yielded self-supporting plates with dimensions of 5 × 5 cm and a thickness of approximately 200 μm . SEM observations showed that the sintered tape-cast samples had a microstructure comparable to that of the commercial YSZ wafers. Thus, the

optimized sintering treatment provided not only the required macroscopic shape but also a microstructure corresponding to the commercial reference material.

Conductivity measurements were performed from 400 to 800 °C. The conductivity was calculated from the measured resistance using the electrolyte thickness and electrode area. Although, at lower temperatures (<700 °C), the commercial electrolytes wafers showed slightly higher conductivity. At and above 700 °C, the tape-cast electrolyte exhibited conductivity comparable to both the pressed material and the commercial wafer. Together with the confirmed gas-tightness and the SEM observations, these results show that the change in shaping method and the optimized sintering treatment did not reduce the principal functional properties of the YSZ electrolyte.

Conclusions

This study demonstrates that scale-up cannot be treated solely as a change in shaping technique. Suspension composition, homogenization, drying, and sintering acted as an interconnected sequence. Optimization of suspension and homogenization was required to eliminate unsuitable green bodies, whereas the firing protocol was decisive for planarity, gas-tightness, and the final microstructure.

A reproducible tape-casting procedure was developed for self-supporting 8YSZ electrolytes with dimensions of 5 × 5 cm and a thickness of approximately 200 µm. Sintering at 1550 °C for 24 h produced planar and gas-tight electrolytes with a microstructure comparable to commercial YSZ wafers. The conductivity of tape-cast samples was comparable to that of pressed and commercial samples. The developed procedure therefore provides a successful scale-up route from pressed laboratory electrolytes to larger tape-cast components without loss of their key functional properties.

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Partially Unzipped Carbon Nanotubes with DNA - Hybrid Nanocomposites for Oxygen Electrodes of Alkaline Fuel Cells

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Hybrid nanocomposite consisting of partially unzipped multiwalled carbon nanotubes with deposited deoxyribonucleic acid was synthesized. Composite was studied as an electrode material for the oxygen electrode of a fuel half-cell. Its electrochemical characteristics as an oxygen electrode are close to those of electrodes made of platinum-doped carbon nanotubes.

Introduction

The use of a hybrid nanocomposite of carbon nanotubes (CNTs) with deoxyribonucleic acid (DNA) in the oxygen reduction reaction is a cutting-edge direction in electrocatalysis and bioelectronics, which allows creating efficient, stable and environmentally friendly electrodes without the use of expensive platinum. In such hybrid materials, the carbon framework is responsible for electron transfer, and DNA molecules are highly ordered biological matrices and structure modifiers. Pure CNTs tend to stick together and form bundles due to Van der Waals forces. DNA can effectively interact with nanotubes, separating them from bundles, which was shown by us earlier [1]. Partially unzipped multiwalled carbon nanotubes (PUMWCNTs) combine the high conductivity of the inner intact tube and the large surface area of the outer unzipped graphene layers, and the use of DNA solves the fundamental problems of metal-free electrocatalysis. The aim of this work is to develop and study the physicochemical properties of metal-free biocomposite materials based on PUMWCNTs and DNA for use as functional components of oxygen electrodes of an alkaline fuel half-cell.

Experimental

To form the active layer of the electrode, we used fluorinated PUMWCNTs, which were synthesized and purified by the chemical-electrochemical method presented in [2,3]. Nanotubes subjected to ultrasonic dispersion in an aqueous solution, after which a DNA solution (Sigma-Aldrich, D1626) with a concentration of 4 mg/ml was added to it. The entire system was re-homogenized in an ultrasonic disperser. The obtained material was dried and used to manufacture oxygen electrodes by pressing. The work also investigated the current-voltage characteristics of hybrid nanocomposite obtained by drying an aqueous solution of fluorinated PUMWCNTs, an aqueous solution of DNA and their mixture in the ratio of 20 wt.% PUMWCNTs to 80 wt.% DNA (DNA/PUMWCNTs20).

Results and discussion

At room temperatures for the studied PUMWCNTs, DNA and their

DNA/PUMWCNTs20 hybrid nanocomposite films, the I-V characteristics are linear and symmetrical (Figure 1). At low temperatures, the current-voltage characteristics remain symmetrical, but nonlinearity begins to appear, which is especially noticeable for the DNA/PUMWCNTs20 hybrid nanocomposite. The nonlinear behavior of the I-V characteristics at low temperatures is due to the dependence of the electrical resistance R on the magnitude of the applied electric field. The temperature dependence of the resistance (Figure 2) of the DNA/PUMWCNTs20 hybrid nanocomposite occupies an intermediate position between the temperature dependences for its individual components DNA and PUMWCNTs. At the same time, the temperature dependence of the DNA/PUMWCNTs20 hybrid nanocomposite has a unique shape, which may indicate different charge transfer mechanisms that operate in the composite material and in its individual components at the same temperatures.

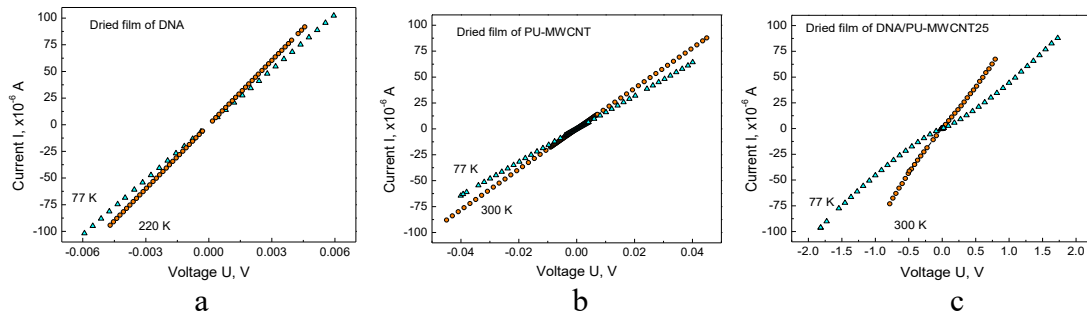


Figure 1. Current-voltage characteristics of DNA (a), PUMWCNTs (b) and hybrid nanocomposite of DNA/PUMWCNTs20 (c) at low and room temperatures.

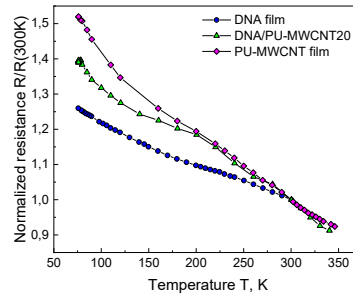


Figure 2. Temperature dependences of the electrical resistance of films DNA, PUMWCNTs and DNA/PUMWCNTs20 hybrid nanocomposite films. The values of resistance are normalized to the value of electrical resistance at a temperature of 300 K.

It should be noted that the content of 20 wt.% PUMWCNTs in the DNA/PUMWCNTs20 hybrid nanocomposite is significant. As a rule, the percolation threshold for composites based on carbon nanotubes and dielectric polymers does not exceed 10%. In our case, even 20 % PUMWCNTs was not enough to form a percolation network of nanotubes. This is evidenced by the high resistivity ρ at room temperatures of the DNA/PUMWCNTs20 hybrid nanocomposite with $\rho \sim 10 \Omega \cdot \text{m}$, which is several orders of magnitude higher than the electrical resistivity for PUMWCNTs with $\rho \sim 4 \cdot 10^{-4} \Omega \cdot \text{m}$, for DNA approximately $\rho \sim 1 \cdot 10^{-3} \Omega \cdot \text{m}$.

It can be assumed that DNA effectively envelops carbon nanotubes and prevents the formation of electrical contacts between them. In this case, the electrical conductivity of the composite should be determined by DNA. It is also possible that a percolation network is formed, but it is thin and therefore has a high total electrical resistance R . In this case, charge transfer should occur sequentially along a chain of carbon nanotubes, between which good electrical contacts are formed.

From the data obtained, it can be concluded that the conductivity of the DNA/PUMWCNTs20 hybrid nanocomposite is higher than the conductivity of pure DNA, and the conductivity mechanisms will be the same as for DNA. Therefore, using the hybrid nanocomposite as a material for the electrode will give much better electrode quality parameters. The electrode will have a significantly larger area of the active working surface, which in its characteristics will be close to the carbon nanotubes. Oxygen electrodes were made from these materials and investigated in a fuel half-cell in an alkaline electrolyte. The studies were carried out on a fuel half-cell, with a zinc electrode used as the anode. The fuel half-cell with gas diffusion electrodes is described in [3]. Figure 3 shows the discharge characteristics of oxygen electrodes fabricated from a hybrid nanocomposite consisting of partially unzipped multi-walled carbon nanotubes with DNA (Figure 3, curve 2). For comparison, the characteristics of an electrode based on the original PUMWCNTs (Figure 3, curve 1) and an electrode based on MWCNTs with deposited platinum (Figure 3, curve 3) are provided. The obtained results demonstrate that materials based on the hybrid composite of PUMWCNTs with DNA are catalytically active for the fabrication of oxygen electrodes. This is confirmed by their comparison with the characteristics of electrodes based on MWCNTs with deposited platinum. Consequently, such materials may be promising candidates as environmentally friendly metal-free electrodes for oxygen electrodes in fuel cells.

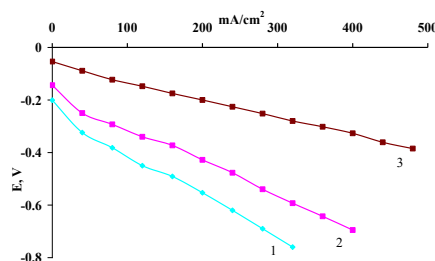


Figure 3. Current-voltage characteristics of oxygen electrodes with an active layer made of different electrode materials: 1 - PUMWCNTs, 2 - PUMWCNTs with deposited DNA; 3 - MWCNTs with deposited 10% Pt.

Conclusions

Developed method for obtaining metal-free hybrid nanocomposite based on fluorine doped PUMWCNTs and DNA has been developed and optimized. It has been shown that the hybrid nanocomposite is a good catalyst for oxygen electrodes of fuel cells.

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Synthesis and Optical Properties of WO₃/Pt Structure Film

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By electrodeposition with interferometric control of the film thickness, a WO₃/Pt structure was formed that is able to change the intensity of its coloration with increasing hydrogen content in the air. Measurement of the film potential depending on the hydrogen content showed that the coloring process is controlled by two competing electrochemical reactions of hydrogen oxidation and oxygen reduction, the equilibrium of which depends on the hydrogen content in the air. A design was developed and a prototype of an optical hydrogen sensor based on nanosized WO₃/Pt films was manufactured with increased (up to 0.01 vol.% H₂ in a mixture with air) sensitivity to hydrogen in the range of low (0 – 10% H₂) concentrations. A significant increase in sensitivity of this optical sensor was achieved by registering the intensity of infrared light after its multiple passage through the WO₃/Pt film.

Hydrogen is an environmentally friendly source of energy – it can be obtained from water, and after combustion it turns back into water [1]. On the other hand, hydrogen is colorless, odorless and in the presence of oxygen it easily ignites with a high flame propagation rate. The combustion range for hydrogen in a mixture with air is 4.0–74.2%, which is much wider than for methane (5.0–15.0%). Due to the small size of the molecule, it can also easily seep through a layer of any material if there are micropores or microcracks in it. Therefore, to ensure the safety and economy of transportation, storage and use of hydrogen, constant monitoring of its content in the composition of the gas mixtures used is necessary, as well as timely notification to personnel about the occurrence of a hydrogen leak and the appearance of its explosive concentration in the room. In this regard, the development of hydrogen sensors, which must be sufficiently sensitive, safe and operate at room temperatures, is an urgent task. Optical hydrogen sensors based on palladium films or films of transition metal oxides such as WO₃ and MoO₃ comply with safety regulations to the greatest extent. Optical sensors based on such films allow for continuous and reliable control of the concentration of this gas in a mixture with air or oxygen. In addition, these sensors allow for visual detection of the appearance of hydrogen in a room, or to monitor its appearance in gas mixtures in closed volumes. Covered with a thin catalytically active layer of platinum or palladium, WO₃ and MoO₃ films acquire a blue color when exposed to molecular hydrogen, the intensity of which is determined by the concentration of hydrogen in the gas mixture. The coloring of oxide films by gases is known as the chemichromic effect, in contrast to the electrochromic effect that occurs on these films when exposed to a cathodic current in an electrochemical cell.

In a hydrogen-air environment, a mixed potential is established on platinum, which corresponds to the equality on its surface of the hydrogen oxidation current, according to the reaction $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$, and the oxygen reduction current, according to the reaction [2].



Equating these currents, we obtain for the stationary potential of the platinum hydrogen-air electrode:

$$E = E^* + [RT/(1-\alpha_0)F] \ln[\text{O}_2] - [RT/(1-\alpha_0)F] \ln[\text{H}_2], \quad [2]$$

where α_0 – transfer coefficient. At room temperature and relatively small, no more than a few percent by volume, hydrogen concentrations in air, equation (2) leads to a linear dependence of E on $\log [\text{H}_2]$ with a slope $0,059/(1-\alpha_0)$, where, as for the ionization of oxygen on platinum in solutions H_2SO_4 , $\alpha_0 \approx 0,5$.

In the presence of ohmic contact between platinum and the WO_3 film, due to the joint diffusion of electrons and protons into the oxide, this stationary potential is also established in the WO_3 film, which corresponds to a certain degree of its coloring. Determination of the potential of the WO_3/Pt film relative to the potential of the silver chloride electrode (SCE) after coloring it with a hydrogen-air mixture with different volumetric hydrogen contents was carried out by bringing the film into liquid contact with this reference electrode through an aqueous electrolyte (0.1N H_2SO_4). Dependence of the potential of the WO_3/Pt film obtained on hydrogen content in the mixture with air is shown in Figure 1.

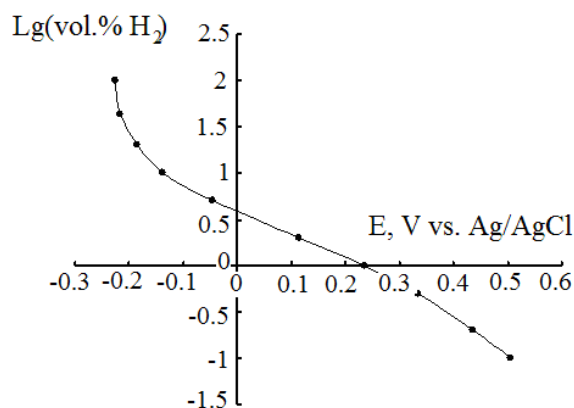


Figure 1. Dependence of the potential of the WO_3/Pt film on the hydrogen content in the mixture with air

Analysis of the data in Figure 1 showed that, as in the case of the electrochromic effect [3], when coloring the WO_3 film with hydrogen using a catalytic platinum layer, an electrochemical equilibrium of hydrogen oxidation in air is established with an increase in its volume content. Accordingly, to measure a low hydrogen content, it is necessary to maximize the optical path length through the WO_3 layer.

We have developed a design and manufactured a laboratory sample of such an optical hydrogen sensor based on WO_3 films with thin layer of platinum as a catalyst for the chemichromic process. Sensitivity of these sensors to hydrogen was increased by repeatedly passing light through a WO_3/Pt film, cathodically deposited over a transparent SnO_2 layer on a glass substrate. Laboratory tests have shown that the dependence of optical transmittance on hydrogen content corresponds to an exponential equation of the form $Y = Y_0 + A_1 \cdot \exp(-X/t_1) + A_2 \cdot \exp(-X/t_2)$. This approach allows us to determine the hydrogen content with an accuracy of 0.1 vol%.

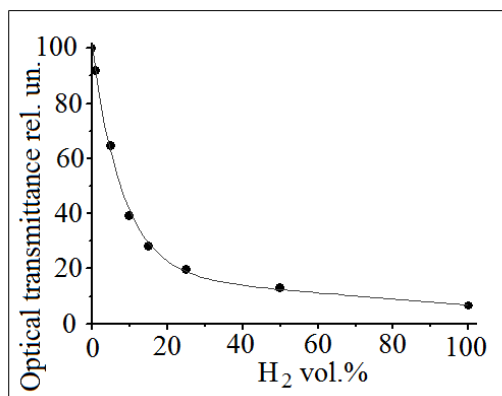


Figure 2. Dependence of optical light transmission film on the hydrogen content in the mixture with air.

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Magnetron Sputtered Thin Film Electrocatalysts for Hydrogen Economy

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Sustainable energy production, conversion, and storage has become one of the most pressing challenges of modern society. Among the various strategies for addressing this challenge, electrochemical technologies play a central role by enabling the efficient conversion of chemical energy into electrical energy and vice versa [1]. In particular, hydrogen has emerged as a promising energy carrier, making its efficient production and utilization a cornerstone of the developing hydrogen economy [1][2]. Water electrolysis, especially when powered by renewable energy sources, represents an environmentally friendly route to hydrogen generation, producing no direct greenhouse gas emissions or harmful pollutants [3].

Introduction

This report presents our recent progress in the development of electrocatalysts based on thin and ultrathin films of transition and noble metals for two key electrochemical applications: the hydrogen evolution reaction (HER) in water electrolyzers and the oxygen reduction reaction (ORR) in fuel cells. The catalysts were fabricated by magnetron sputtering under high-vacuum conditions, a versatile deposition technique that enables precise control over film composition, thickness, and microstructure while ensuring excellent reproducibility. Furthermore, thin-film deposition by magnetron sputtering allows the stabilization of metastable or high-pressure phases that are inaccessible in bulk materials, thereby providing unique opportunities for catalyst design. Our research focuses on establishing clear relationships between the composition, architecture, and microstructure of these thin-film catalysts and their electrochemical performance in energy conversion applications.

Acknowledgments

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In-Situ/Operando Characterizations for Electrochemical Ionic (De)Intercalation into Graphite for Zn-Gr Dual Ion Batteries

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Graphite is a promising cathode material for aqueous zinc-based dual-ion batteries (Zn-DIBs); however, its limited interlayer spacing restricts efficient anion intercalation and results in sluggish electrochemical kinetics. In this work, a synergistic ultrasonic–acid treatment strategy is employed to regulate the graphite structure by expanding interlayer galleries and introducing surface functional groups to enhance reversible anion storage. The tailored graphite (Us.exf.Gr) demonstrates improved electrochemical reversibility, achieving stable cycling over 1000 cycles with a coulombic efficiency above 90%, compared with approximately 70% for ultrasound-treated graphite (Us.Gr). The enhanced performance is attributed to the enlarged interlayer spacing, increased active sites, and improved accessibility of anions, which facilitate faster charge transfer and reversible intercalation/deintercalation processes.

The anion storage mechanism and structural evolution of tailored graphite were systematically investigated using in situ Raman spectroelectrochemistry and operando X-ray diffraction, providing real-time insights into the reversible structural transformations during electrochemical cycling. Electrochemical kinetic analysis further confirms enhanced ion transport and improved reaction dynamics in the modified graphite electrode. This study highlights the effectiveness of combined structural engineering and advanced in situ/operando characterization for understanding anion intercalation mechanisms and provides a pathway for developing durable and high-performance graphite cathodes for sustainable aqueous zinc-based dual-ion batteries.

Temperature Profiles in a Lead-Acid Battery During Charging When Ambient Temperature Changes

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The paper deals with the study of temperature changes inside the battery during charging at different ambient temperatures. For this reason, 2 temperature sensors were placed in the battery and the temperature changes inside the battery during cycling were measured. It was found that, in addition to the charge current, the temperature changes are influenced by the ambient temperature.

Introduction

The thermal behavior of a lead-acid battery during charge and discharge processes is dictated by cell architecture, degradation state, and specific cycling regimes. Accurate modeling or assessment of these temperature variations requires a comprehensive evaluation of all thermal sources. This encompasses the heat released via electrochemical reactions, ohmic and polarization resistances (Joule heating), as well as heat dissipation to the environment.

Furthermore, lead-acid batteries frequently encounter fluctuating environmental temperatures during service. Low ambient temperatures elevate internal resistance, reducing both power and available capacity. Conversely, elevated temperatures lower internal resistance and boost power output, yet they simultaneously accelerate degradation mechanism rates (such as self-discharge, grid corrosion, and water electrolysis during charging). In flooded designs, this accelerates water consumption, potentially exposing electrodes. In valve-regulated (sealed) configurations, elevated temperatures intensify the internal oxygen recombination cycle during charging, introducing the risk of thermal runaway.

In the event of ambient temperature fluctuations, the most rapid thermal transmission occurs through the casing's lateral walls due to their direct contact with the internal elements and electrolyte. The base of the container features greater thickness, whereas the upper lid lacks direct electrolyte contact and the layer of air prevents major temperature changes due to its low thermal conductivity.

Experiment

To investigate the dynamics of temperature changes inside a lead-acid battery during repeated changes in ambient temperature, a maintenance-free 12 V ZAP Plus Calcium 74 Ah battery was used. The battery is assembled from 6 cells connected in series, housed in an ABS plastic container that has a reinforced bottom for load-bearing capacity. The individual cells are separated by plastic partitions.

Two Pt100 temperature sensors were placed in the vertical plane passing through the center of the battery. The 1st sensor was placed between the outer edge of the plate

and the plastic container in the 1st cell (No. 1); the 2nd sensor was placed between the plate and the plastic partition in the 2nd cell closer to the center of the battery (No. 2).

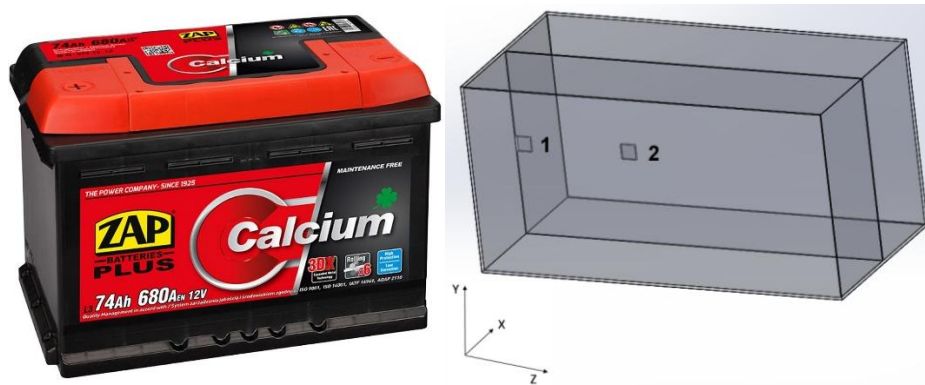


Figure 1. ZAP Plus 74 Ah 12 V lead-acid battery and diagram of the layout of 2 temperature sensors.

In experiment, temperature changes were measured for discharged lead-acid battery during charging at a current of 20 A with a voltage limitation of 14.4 V (2.4 V per cell), terminated at 2 A, followed by standing for 12 hours at an ambient temperature that was changed from the initial 21 °C to -37 °C (Fig. 2).

From the beginning of charging, the temperature of the battery at the point of contact with the side wall (sensor 1) drops from 21 °C to 11.5 °C in 1.2 hours. After reaching the voltage limitation, the temperature drop continues further with a slight break at the time the voltage limitation is reached. The temperature at the point of contact with the side wall continues to decrease exponentially even after the charging current is disconnected at 3 hours, reaching -27 °C after 12 hours.

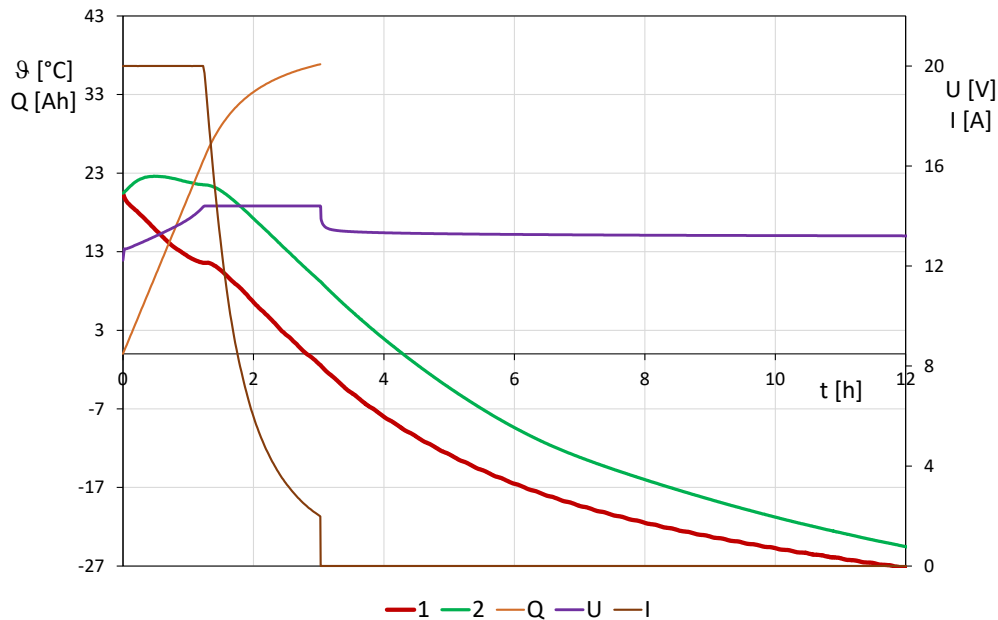


Figure 2. Temperature dependence of 2 measured points in a lead-acid battery during discharge and charge at a temperature of -37 °C.

The temperature inside the battery (sensor 2) rises from 21 °C to 22.5 °C during the first 0.5 hours, after which it gradually begins to fall to 21.5 °C at 1.2 hours. After reaching the voltage limitation, the temperature inside the battery decreases exponentially even after the charging current is disconnected at 3 hours, reaching -24.5 °C after 12 hours.

For the sensor at the point of contact with the side wall, cooling from the ambient environment outweighs the heating from the charging current right from the beginning of the measurement.

For the sensor inside the battery, heating due to charging predominates during the first half hour; cooling begins only when the cooling of the battery from the ambient environment reaches the internal areas. The time at which cooling begins to outweigh heating depends on the thermal conductivity of the electrodes, the electrolyte, and the battery container. During charging, the battery consumed 37 Ah. The shorter charging time, and thus the lower charging capacity in this measurement, is related to the increase in internal and polarization resistance during charging due to the gradual decrease in battery temperature.

Conclusion

From the temperature dependencies inside the battery and at the point of contact with the side wall during the charging of a lead-acid battery after changing the ambient temperature from 21 °C to -37 °C, a significant change in temperatures inside the battery and in the peripheral areas can be seen. Low temperature increases internal and polarization resistance and reduces capacity, and the dynamics of temperature changes in different regions of the battery also play a role here. This dynamic depends on the thermal conductivity of the materials inside the battery.

Acknowledgments

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Importance of Demineralized Water Production Method on Water Electrolysis Durability

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The quality of demineralized water is essential for the efficiency, reliability, and lifetime of water electrolyzers. Water purity requirements differ among technologies, with PEM electrolyzers requiring ultrapure water ($<1 \mu\text{S cm}^{-1}$), while alkaline systems tolerate slightly lower purity ($<10 \mu\text{S cm}^{-1}$). Appropriate water treatment therefore depends on both the electrolyser type and the quality of the available water source. This work investigates the integration of Mechanical Vapor Compression Desalination (MVCD) with final polishing and a zero liquid discharge (ZLD) process to produce ultrapure water from seawater or brackish water. Energy and mass balance simulations, supported by laboratory experiments, demonstrate the technical feasibility and energy demand of the proposed system.

Introduction

Seasonal overproduction of renewable electricity increases the need for technologies capable of long-term energy storage. While batteries are suitable for short-term balancing, water electrolysis (WE) enables large-scale conversion of renewable electricity into hydrogen, which can be stored, transported using existing infrastructure, and utilised for the production of low-carbon chemicals, heating, and transportation.

High-quality demineralised water is essential for reliable hydrogen production by electrolysis[1]. Any failure of the water treatment system may reduce efficiency, interrupt hydrogen production, or even cause irreversible damage to the electrolyser stack.

PEM electrolyzers require ultra-pure water (typically $<1 \mu\text{S cm}^{-1}$) because dissolved contaminants can reduce proton conductivity, poison electrocatalysts, accelerate membrane degradation, and shorten stack lifetime. In contrast, alkaline electrolyzers tolerate slightly lower water quality (typically $<10 \mu\text{S cm}^{-1}$), although excessive impurities still promote scaling, electrolyte contamination, and degradation of electrodes and diaphragms, reducing efficiency and increasing maintenance requirements.

Another important factor affecting water electrolysis systems is the fluctuating power supply associated with renewable energy sources [2]. These fluctuations also influence the demineralisation process, which must be capable of operating reliably despite frequent start-up and shutdown cycles. This imposes new requirements on conventional water treatment technologies. Electrolysis plants typically employ reverse osmosis (RO)-based water treatment systems. Raw water first undergoes pretreatment, including filtration and activated carbon adsorption, followed by reverse osmosis or ion exchange (IX) to remove the majority of dissolved salts and organic contaminants. Final

polishing is then performed using mixed-bed ion exchange resins, electrodeionisation (EDI), or a combination of both technologies to produce ultra-pure water with the required conductivity and total organic carbon (TOC) content. Continuous monitoring of conductivity, resistivity, silica concentration, TOC, and microbial contamination is commonly implemented to ensure compliance with electrolyser manufacturer specifications. However, frequent interruptions in operation may adversely affect these systems by promoting membrane compaction, colloidal scaling, and biofilm formation during stagnant periods, thereby compromising long-term operational stability.

Thermal desalination processes are more energy-intensive than reverse osmosis but are considerably more resistant to the operational issues associated with intermittent operation. For installations requiring high reliability and limited maintenance access, they may therefore represent a more robust solution. A mechanical vapour compression distillation (MVCD) unit requiring no external chemical dosing was designed to provide reliable long-term operation under these conditions.

Another important challenge is the treatment of the high-salinity concentrate generated during the demineralisation process. Increasingly stringent environmental regulations often prohibit its direct discharge into the environment. One of the few viable solutions is the implementation of a zero liquid discharge (ZLD) system, which eliminates liquid waste streams from the electrolysis plant. As with the demineralisation process itself, the ZLD system must also be capable of reliable operation under intermittent operating conditions.

Experimental

MVCD unit

MVCD demineralisation is based on the phase change of water and therefore exhibits high tolerance to variations in source water quality. It is also inherently resistant to biological contamination and fouling. Its principal disadvantage, compared with membrane-based processes such as reverse osmosis (RO), is its higher energy consumption. However, when considered in the context of hydrogen production, where approximately 50 kWh/kg H₂ and the total water demand is approximately 14 kg (compared with the theoretical requirement of 9 kg) [2] the additional energy required for MVCD represents only a small fraction of the overall energy consumption. 1 m³ of demineralised water is sufficient to produce approximately 70 kg of hydrogen, requiring around 3,550 kWh of electrical energy for electrolysis. The production of demineralised water from seawater requires approximately 5 kWh m⁻³ using reverse osmosis (RO)[3] and around 20 kWh m⁻³ using mechanical vapour compression distillation (MVCD). Thus, even for MVCD, the energy required for water treatment represents less than 1% of the total energy consumed for hydrogen production. Consequently, factors such as process robustness, operational reliability, and tolerance to intermittent operation become more important than minimising the energy consumption of the water treatment process.

MVCD alone cannot produce water of sufficient purity for water electrolysis. Therefore, a final polishing step using electrodeionisation (EDI) or mixed-bed ion exchange resins is required to achieve the water quality specified by electrolyser manufacturers.

The system is intended for installation in locations where maintenance and servicing are challenging, such as offshore wind farms, remote desert regions, and other isolated

sites. Operation without the need for an external supply of treatment chemicals is therefore envisaged. Instead, the required chemicals should be generated on-site using electrochemical processes.

When seawater is used as the feed source, the concentrate generated during demineralisation can, subject to local environmental regulations, be discharged back into the sea. In contrast, in inland or environmentally sensitive locations, such as deserts, a zero liquid discharge (ZLD) system becomes essential, as disposal of the concentrate could have an unacceptable environmental impact.

ZLD unit

The ZLD unit offers a significant advantage through the utilisation of waste heat generated by the water electrolyser. This has the potential to substantially reduce the demand for external thermal energy. The main challenge, however, is the fluctuating operation of the electrolyser, which results in an intermittent heat supply. Consequently, the ZLD unit must be capable of adjusting its operating capacity in response to the availability of waste heat while maintaining stable operation.

To simplify handling and transport, the final product of the ZLD process, in addition to distilled water, is a concentrated brine with a solids content of approximately 50 wt%. This concentrated slurry can be readily pumped into storage tanks and transported for subsequent processing, such as the recovery of valuable chemicals or the production of industrial feedstocks.

Conclusion

Water treatment is a crucial part of hydrogen production from renewable energy sources. As demonstrated, the energy requirements of water treatment are not the decisive factor; instead, the primary objective of the designed unit is high operational durability and reliability. MVCD offers high resistance to biological contamination and good tolerance to intermittent operation and process interruptions. The ZLD unit represents an optional part of the system, with the potential to utilise waste heat generated during water electrolysis and further improve the overall process efficiency.

Acknowledgments

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Cyclic Characteristics of Activated Carbon Anode in Hybrid System with LiMn_2O_4 Cathode and Aqueous-Organic Electrolyte

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For such industrial activated carbons (ACs) as Norit, Kuraray, Kausorb and Chinese technical, the formation of a high-capacity electric double layer in supercapacitors with both organic and aqueous electrolytes is well known, but information regarding their use in hybrid systems with aqueous-organic electrolytes is significantly limited. Therefore, the work discusses the electrochemical behavior of some industrial AC samples as anodes in the hybrid system $\text{AC}|\text{Li}_2\text{SO}_4\text{-water-tetraglyme}|\text{LiMn}_2\text{O}_4$.

Introduction

Activated carbon (AC) is considered as an effective anode material in hybrid batteries with aqueous electrolytes and cathodes based on lithium-manganese spinel LiMn_2O_4 . The disadvantages of using AC in hybrid electrochemical systems include its relatively low specific capacity and differences in the kinetics of intercalation/deintercalation and adsorption/desorption reactions. In addition, it is important that the electrolyte composition supports only direct electrochemical processes at both electrodes, ensuring the stability of the specific capacity during cycling. It was previously shown that the addition of tetraglyme (TG) to an aqueous Li_2SO_4 solution promotes the formation of a stable electrode/electrolyte interface on the LiMn_2O_4 surface, which improves the kinetics of lithium intercalation/deintercalation reactions during cycling [1]. However, simultaneously with the positive effect of TG on cathode characteristics, a gradual shift in the AC potential occurs, which leads to a shift in the cell voltage and limits the number of charge/discharge cycles. In aqueous solutions, an electric double layer forms at the surface of AC, which mainly consists of hydrated lithium cations. The addition of TG creates conditions for the emergence of competitive adsorption, which depends on the surface properties of AC and its different affinity for water and TG molecules. Analysis of the cyclic behavior of AC in aqueous-organic electrolytes allows us to establish the role of AC's surface properties in stabilizing the specific characteristics of cells with a LiMn_2O_4 cathode and electrolytes with a competitive cationic solvation shell.

Experimental

The active cathode material used was lithium-manganese spinel LiMn_2O_4 synthesized by the solid-phase method from a mixture of electrolytic manganese dioxide and lithium carbonate [1]. Four industrial samples of activated carbon, namely Norit DLC Supra 30, Kuraray YP-80F, Kausorb-212 and Chinese technical, were used as the active anode material. The anode consisted of 83% activated carbon, 10% carbon black P-267E, and 7% F-4D binder. The anode thickness was 390 μm , and the area was 2 cm^2 . The electrolyte used was a 1 mol/kg solution of Li_2SO_4 (99.5%, Sigma-Aldrich) in a mixture

of double-distilled water and tetraethylene glycol dimethyl ether (TG or tetraglyme, 99%, Sigma-Aldrich), with a volume percentage ratio of 85:15.

Electrochemical studies were carried out in Teflon cells in a two- or three-electrode configuration on a Neware battery testing system (China) and P-30 potentiostat in different testing modes. Cycling current density for the galvanostatic test was 3 C (1 C = 148 mA/g). During galvanostatic cycling, a constant charge capacity of 100 mAh/g was maintained with a floating final charge voltage with a cut-off value of 2.1 V.

Results and Discussion

Analysis of the potentiodynamic characteristics of cells with different ACs, taken before the start of galvanostatic cycling, showed that all AC samples fully provide a two-stage LiMn_2O_4 charge/discharge process, which is confirmed by the presence of two characteristic peaks on the anodic and cathodic branches of the curves. Fig. 1 shows the change in the charge/discharge mid-voltage of the cells and the discharge specific capacity during galvanostatic cycling at 3 C with a fixed charge capacity of 100 mAh/g. During cycling, a gradual increase in the average charge voltage (black curve) and discharge voltage (red curve) is observed.

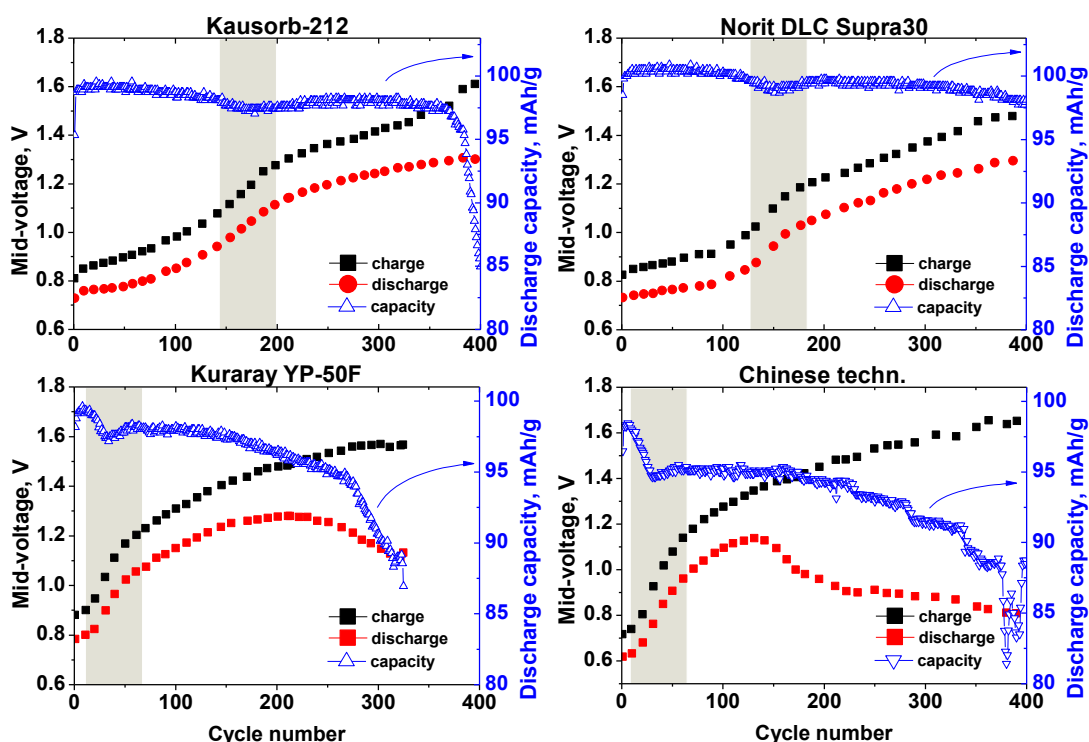


Figure 1. Change in the charge/discharge mid-voltage of the cells and the specific discharge capacity of spinel during cycling.

The presented dependences show different numbers of cycles with stable discharge capacity and changes in their nature depending on the AC brand. The dips in the dependence of specific capacity on cycle number, after which the capacity increases again, coincide with jumps in the average charge/discharge voltage (highlighted in gray) and can be explained by changes in the kinetics and mechanism of charge transfer at the AC anode. In the first cycles, with a relatively stable average charge/discharge voltage, a solid electrolyte interface (SEI) with low resistance is formed (Fig. 2). During cycling, the thickness of this film increases, which leads to blocking of micropores and

mesopores and an increase in the internal resistance (IR) component due to the formation of a passivating layer. As a result, the charge transfer mechanism shifts from pure adsorption/desorption to slowed diffusion through the passivating layer. Further recovery and relative stabilization of the capacity can be associated with two competing processes, namely: partial desolvation, reorientation of molecules in the pores (“activation” of the pores) or electrochemical reformatting of the SEI, due to which new channels for the transport of lithium ions are opened, reducing the IR. The contribution of each of these mechanisms depends on the surface properties of the AC and is determined by the pore architecture, surface cleanliness, and mechanical stability of the framework, and these factors require additional experimental studies.

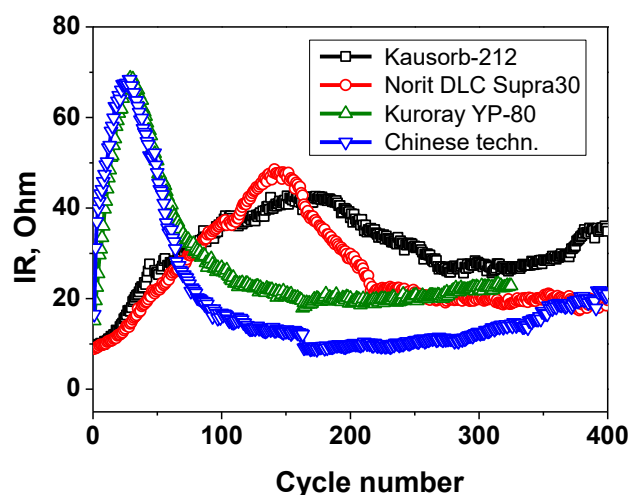


Figure 2. Dependence of internal resistance on cycle number for cells with different AC anodes.

Acknowledgments

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Operando Thermography-Assisted Mapping of Interfacial Current Distribution in Electrochemical Batteries

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Mapping the spatial distribution of interfacial current is important for understanding reaction heterogeneity, local polarization, and uneven electrode utilization in electrochemical batteries. However, conventional electrochemical measurements usually provide only area-averaged current responses and cannot directly resolve local current-density variations across the electrode surface. Here, we propose an operando thermography-assisted strategy [1] to reconstruct the apparent two-dimensional current-density distribution of cathodes in aqueous Zn batteries.

In this work, infrared thermography is combined with chronoamperometry to monitor the transient thermal response of working battery electrodes under constant-voltage polarization. MnO₂/graphite foil and graphite/stainless-steel cathodes paired with Zn anodes are selected as model battery configurations. The heat generation in the electrochemical cell is considered to originate from ohmic heating, electrochemical-reaction-related heat, and polarization-associated thermal contributions. To isolate the electrochemical thermal signal, a no-electrolyte control cell is used to establish the baseline background heating, which is then subtracted from the total thermal response measured in the electrolyte-containing cell. The early-stage temperature-rise rate is employed as the thermal descriptor because it is closely related to local current flow. After background correction, the obtained spatial thermal signal is converted into a relative current-distribution map and further calibrated by the simultaneously recorded chronoamperometric current to generate an absolute current-density map.

This experiment-guided thermographic method provides a direct and visual approach to evaluating non-uniform interfacial current distribution in battery electrodes. By linking operando thermal imaging with electrochemical current response, the proposed strategy bridges macroscopic electrochemical measurements and local interfacial reaction behavior. This approach may provide useful insight into electrode heterogeneity, current localization, and structure-performance relationships in aqueous Zn batteries and other electrochemical energy-storage systems.

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Development and Multiphysics Optimization of Next-Generation Flow Batteries with Hybrid Lithium-Sulfur (Li-S) Integration for Large-Scale Energy Storage

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The global transition toward renewable energy demands scalable, safe, and efficient electrical energy storage systems capable of balancing long-duration capacity with rapid power response. This study presents an integrated development approach for next-generation flow batteries combined with a hybrid Lithium-Sulfur (Li-S) system framework. Industrial-scale single-cell Vanadium Redox Flow Battery (VRFB) hardware was experimentally evaluated to quantify hydraulic pressure losses, non-linear flow distributions, and electrochemical loss mechanisms using polarization curves and Electrochemical Impedance Spectroscopy (EIS). To reduce empirical trial-and-error costs, 2D and 3D COMSOL Multiphysics models were calibrated to optimize flow-field geometry and fluid dynamics under transient operating conditions. Furthermore, a novel versatile stack design and tailor-made membranes are introduced for organic electrolytes. Coupling high-capacity Li-S batteries for fast transient response with flow batteries for continuous energy delivery provides a robust, cost-effective blueprint for future industrial-scale grid energy storage.

Introduction

The global transition toward renewable and clean energy sources represents one of humanity's primary obligations in mitigating climate change and securing a sustainable future. Due to the inherent intermittency of solar and wind energy, reliable electrical energy storage systems are imperative for grid stabilization. Redox flow batteries (RFBs) have emerged as a leading candidate for long-duration stationary energy storage owing to their unique decoupling of energy capacity and power rating, long operational lifespan, intrinsic safety, and non-flammability.

However, modern grid applications increasingly require both long-duration energy discharge and rapid high-power dynamic response. To address these dual requirements, recent architectural strategies explore hybrid battery storage systems, coupling redox flow batteries with high-energy-density chemistries such as Lithium-Sulfur (Li-S) batteries. While RFBs handle continuous bulk energy buffering, Li-S batteries characterized by their high theoretical specific capacity (1675 mAh/g), low material cost, and environmental friendliness provide transient peak-shaving and rapid power delivery [1]. This work presents a dual strategy: optimizing industrial-scale Vanadium RFBs (VRFBs) and novel Organic RFBs (ORFBs), while designing versatile stack hardware and control strategies compatible with hybrid Li-S integration.

Experimental

To evaluate performance under realistic operating conditions, an industrial-scale single-cell stack design was constructed and tested. Hydraulic efficiency is critical in flow battery architectures, as pumping losses directly affect round-trip efficiency, especially when integrated alongside sensitive secondary systems like Li-S battery racks.

Measurements were conducted across a range of electrolyte flow rates to quantify pressure losses and internal velocity distributions. The experimental data revealed a non-linear relationship between flow rate and total pressure drop. This non-linearity is dictated by manifold geometry, channel dimensions, and the compression dynamics of the porous carbon felt electrodes. The resulting hydraulic parameters provide calibrated inputs for multi-physics models and hybrid system power-management algorithms.

Electrochemical characterization of the single-cell stack was conducted to resolve primary voltage loss mechanisms:

- **Polarization (U-I) Curves:** Measurements were recorded to quantify activation polarization, ohmic losses, and mass transport limitations. These parameters are essential for defining power-sharing thresholds in a hybrid Li-S/RFB system.
- **Electrochemical Impedance Spectroscopy (EIS):** EIS spectra were acquired across various states of charge (SoC) and current densities. High-frequency ohmic resistance was found to be governed by membrane conductivity and ionic transport, whereas low-frequency features reflected mass-transport constraints within the porous electrodes.
- **Extended Cycling:** Long-term charge-discharge cycling verified structural durability, capacity retention, and operational stability over extended periods.

Computational Multiphysics Modeling

Because experimental development consumes significant time and financial resources, numerical modeling is critical for accelerating cell scale-up, geometry refinement, and dynamic thermal/flow management in hybrid deployments.

Using COMSOL Multiphysics, two-dimensional (2D) and three-dimensional (3D) finite-element models were constructed. The simulation workflow included:

- **Geometry:** Drafting 2D channel profiles and expanding to full 3D cell domains.
- **Physics Setup:** Coupling Navier-Stokes flow equations with tertiary current distribution and species transport in porous media.
- **Hybrid System Inputs:** Simulating dynamic pressure drops and electrolyte velocity profiles under fluctuating loads representative of hybrid Li-S peak-shaving duty cycles.

The calibrated COMSOL models enable precise identification of velocity stagnation zones, local pressure surges, and non-uniform current distributions, optimizing the stack design prior to commercial manufacturing.

Next-Generation Organic Systems and Li-S Hybridization

To overcome resource limitations associated with inorganic vanadium, novel organic electrolytes were developed while establishing a framework for hybrid storage

integration [2]. Validated chemistries are tested in a newly designed, versatile lab-scale stack compatible with both organic and inorganic electrolytes. Novel organic active species demand cost-effective, custom-synthesized membranes to prevent crossover. Concurrently, power electronics and battery management system (BMS) control algorithms are being developed to interface the RFB stack with a Li-S battery module. In this hybrid topology, the Li-S array absorbs high-frequency power spikes, mitigating dynamic stress on the flow battery pumping system [3].

Conclusions

This study presents a unified, multidisciplinary approach combining empirical hydraulic analysis, electrochemical impedance diagnostics, numerical COMSOL simulations, and hybrid system conceptualization. Experimental validation of an industrial-scale VRFB cell provided key parameters for dynamic modeling, while the introduction of a hybrid Li-S/RFB architecture offers a compelling path toward balancing high energy density with long-duration operational stability. Combining novel versatile stack design with hybrid storage topologies provides a robust blueprint for next-generation grid energy storage.

Acknowledgments

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Electrochemical Intercalation of Na⁺ and K⁺ into Titanium Disulfide from NaSCN and KSCN Melts with Dimethyl Sulfone

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This work investigates the electrochemical intercalation of Na⁺ and K⁺ into a Ti_{1.02}S₂ cathode using NaSCN/KSCN–DMS salt-solvate melts at 155 °C and 190 °C. The cation solvation degree critically affects reaction kinetics, phase formation, and reversibility. In NaSCN–DMS systems, excess solvent shifts potentials negatively by 90 ± 10 mV and halves the intercalation degree (from $x = 0.8$ to 0.45) due to solvent co-intercalation. High salt concentrations suppress this effect by preventing structural modification into electrochemically inactive ternary solvated compounds. Potassium intercalation is irreversible with high overpotential. Transitioning from pure KSCN melt to solvent mixtures drops the intercalation degree from >0.25 to 0.1 and shifts potentials negatively by 200 mV, showing that solvated K⁺ intercalation requires energy absorption. Additionally, carbon additives narrow the cycling range to 0.8 V by catalyzing sulfide formation. Minimized solvent content ensures optimal performance for medium-temperature power sources.

A large number of studies are devoted to the effect of the solvent on electrode processes in fully solvated systems, i.e., in conventional 1-molar solutions. Electrode processes in systems with partially solvated ions, where the mole fractions of the solvent and the salt are nearly identical, have not been fully investigated. At the same time, the study of such systems would allow a clearer identification of solvation effects by realizing a state that is intermediate between a solution and an ionic melt. In practice, this will make it possible to significantly reduce operating temperatures of batteries while retaining the advantages of molten salts. It was shown that a combination of a high-boiling dipolar organic solvent with a low-melting salt could be successful model of a partially solvated system (1-5).

In this work, melts of sodium and potassium thiocyanates with DMS were used to study the electrochemical intercalation of Na⁺ and K⁺ cations into titanium disulfide with the composition Ti_{1.02}S₂. The high temperature at which sulfones can operate, on the one hand, and the low solvation energy of cations, on the other hand, made it possible to use this solvent to study the effect of cation solvation on the electrochemical characteristics of Me_xTiS₂ intercalates as potential cathode materials for secondary medium-temperature power sources. The solvation shell of the cation reduces the reversibility and cycling capability of the M⁺/TiS₂ system (1,2). The electrochemical characteristics of titanium disulfide were studied at 155 °C for the NaSCN–DMS system and at 190 °C for the KSCN–DMS system, as determined by the thermal stability limits.

Two types of melt compositions were used as electrolytes. The first composition (10 mol% NaSCN) belongs to the DMS-rich region, where sodium ions are fully solvated. In the second composition (45 mol% NaSCN), sodium thiocyanate is taken in an excess amount relative to the solvate complex, which melts incongruently at around 99 °C. Thus, both solvated and unsolvated sodium ions coexist in this melt. For the system with KSCN, a pure salt melt can also be used due to its low melting point. During cycling, a carbon black and binder content within 20% catalyzes the formation of sulfides in the melt under cathodic polarization, which narrows the cycling range of titanium disulfide to 0.8 V.

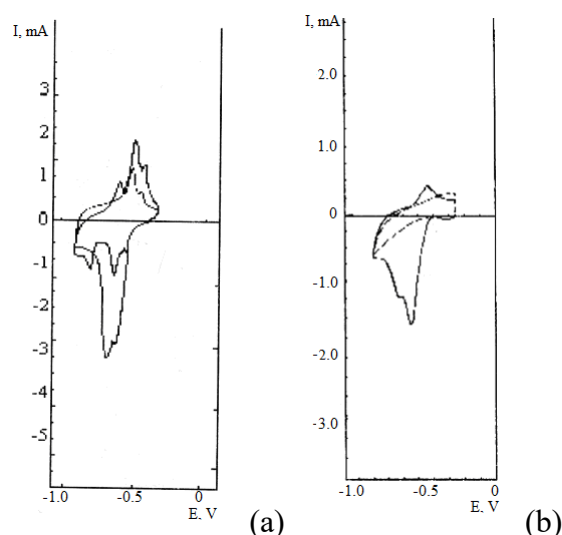


Figure 1 CVA of intercalation Na^+ and K^+ into $\text{Ti}_{1.02}\text{S}_2$ electrode from the melts of the NaSCN–DMS (a) and KSCN–DMS (b) with compositions of 10:90 (mol.%).

The melt composition significantly affects the electrochemical behavior of the cathode (Fig. 1 a). An increase in the solvent content within the NaSCN–DMS system causes: 1) the appearance of new peaks in the cathodic and anodic parts of the curve; 2) a nearly twofold decrease in the degree of Na^+ intercalation, which is $x = 0.45$ and $x = 0.8$ $\text{Na}^+/\text{mol Ti}_{1.02}\text{S}_2$ for melts (10 mol% NaSCN), and (45 mol% NaSCN), respectively; 3) a significant reduction in cathodic and anodic capacity during cycling. (Table I).

TABLE I. Influence of melt composition on the characteristics of the charge-discharge process in the NaSCN–DMS system (at $t = 150\text{ }^\circ\text{C}$ and $V = 0.5\text{ mV/S}$)

NaSCN– DMS composition (mol.%)	Ti _n S ₂	Cycle numb er	Cathodic peak potential	Cathodic peak current	Anodic peak potential	Anodic peak current	Intercalation degree	
			E _{max} , V	I _{max} , mA	E _{max} , V	I _{max} , mA	x _{cath}	x _{an}
45 : 55	Ti _{1.02} S ₂	1	-0.550	4.65	-0.425	2.65	0.83	0.44
		2	-0.475	1.55	-0.425	3.00	0.43	0.42
10 : 90	Ti _{1.02} S ₂	1	-0.625	2.45	-0.500	1.67	0.48	0.30
		2	-0.540	1.75	-0.600	0.96	0.25	0.20

Furthermore, the equilibrium and peak potentials shift to the negative region by $90 \pm 10\text{ mV}$, indicating that intercalation occurs with greater difficulty in the solvent-excess electrolyte. The system shows limited reversibility, with a 55% initial coulombic efficiency and 50–60% capacity retention in subsequent cycles. This degradation stems from structural modification into a ternary solvated compound, where trapped solvated

Na⁺ ions become electrochemically inactive, making insertion more reversible at lower solvent concentrations (3,4).

According to Fig. 1 b and Table II, electrochemical analysis of Ti_{1.02}S₂ cathodes in KSCN–DMS melts indicates that K⁺ cation intercalation into the layered lattice proceeds irreversibly with pronounced overpotential, while the presence of two cathodic peaks demonstrates a multi-stage insertion mechanism (5).

TABLE II. Influence of melt composition on the characteristics of the charge-discharge process in the KSCN–DMS system for Ti_{1.02}S₂ (at t = 190 °C and V = 0.5 mV/S)

KSCN– DMS composition (mol.%)	E at x=0.02,V	Cathodic peak potential E _{max} , V	Cathodic peak current I _{max} ,mA	Intercalation degree at I _{max} at E = -0.8V	
100 : 0	-0.310	-0.415	2.93	0.23	0.5
		-0.500	1.38	0.41	
70 :30	-0.500	-0.560	1.50	0.11	0.25
		-0.650	1.03	0.18	
10 : 90	-0.525	-0.600	1.45	0.10	0.25
		-0.675	1.05	0.17	

The introduction of the solvent significantly degrades the intercalation characteristics, shifting the peak potentials toward the negative region and reducing the maximum intercalation degree by more than half (from >0.25 to 0.1 K⁺ per mole), whereas at elevated temperatures, titanium disulfide functions as a highly reversible electrode in sodium salt melts, providing a high degree of intercalation up to 0.8 Na⁺ per mole of Ti_{1.02} S₂.

Thus, the intercalation of a solvated potassium ion proceeds with energy absorption and primarily reduces ion mobility, whereas for the sodium ion, solvation triggers the formation of new phases.

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Optimization of Electrolyte-to-Sulfur Ratio and Separator Selection for Enhanced Electrochemical Performance of Lithium–Sulfur Batteries

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Lithium–sulfur (Li–S) batteries are promising post-lithium-ion systems because of their high theoretical specific capacity (1675 mAh g⁻¹) and theoretical energy density approaching 2600 Wh kg⁻¹ (1–3). Practical implementation is limited by polysulfide dissolution, shuttle effect and the large electrolyte demand. This work investigates the influence of the electrolyte-to-sulfur (E/S) ratio and separator selection on electrochemical performance. Sulfur cathodes containing 60 wt.% sulfur were tested with GF/A and Celgard® 2325 separators using E/S ratios between 5 and 55 $\mu\text{L mg}^{-1}$. The optimum performance was achieved for the GF/A separator at an E/S ratio of 40 $\mu\text{L mg}^{-1}$, delivering 1062.1 mAh g⁻¹ at 0.2 C with 92.5% capacity retention after 35 cycles. Lower electrolyte contents resulted in incomplete sulfur utilization, whereas excessive electrolyte promoted polysulfide dissolution.

Introduction

Lithium–sulfur (Li–S) batteries have attracted considerable attention as one of the most promising post-lithium-ion energy storage technologies owing to their theoretical specific capacity of 1675 mAh g⁻¹ and theoretical energy density approaching 2600 Wh kg⁻¹ [1–3]. In addition to the high energy density, sulfur is abundant, inexpensive and environmentally benign, making Li–S batteries attractive for large-scale energy storage and electric mobility [3][4]. Despite these advantages, their practical application remains limited by several challenges, including the dissolution of lithium polysulfides into the electrolyte, the shuttle effect, sluggish redox kinetics and the large electrolyte volume required for stable cycling [3–6]. The electrolyte-to-sulfur (E/S) ratio has a significant influence on the practical energy density of Li–S cells. Excess electrolyte promotes polysulfide dissolution and decreases the gravimetric energy density, whereas insufficient electrolyte results in incomplete electrode wetting, limited ionic transport and poor sulfur utilization [4–6]. Besides electrolyte quantity, separator properties strongly influence polysulfide migration, electrolyte retention and electrochemical stability. Therefore, simultaneous optimization of electrolyte amount and separator architecture is essential for the development of practical high-energy Li–S batteries. This work investigates the combined influence of the E/S ratio and separator type on the electrochemical performance of Li–S batteries. Two separator materials with significantly different structural properties were investigated: GF/A glass microfiber, characterized by high electrolyte uptake, and the thin polyolefin Celgard® 2325 separator, representing a lean-electrolyte configuration.

Experimental

Sulfur composite cathodes were prepared by slurry casting using sulfur (60 wt.%), Super P conductive carbon (30 wt.%) and polyvinylidene fluoride (PVDF) binder (10 wt.%) dispersed in N-methyl-2-pyrrolidone (NMP). The slurry was coated onto carbon-coated aluminium foil using a 200 μm doctor blade and subsequently dried at 60 $^{\circ}\text{C}$ for 24 h, and subsequently vacuum-dried for 12 h. Circular electrodes with a diameter of 18 mm and an active material loading of approximately 1.92 mg cm^{-2} were assembled into EL-Cell[®] test cells using lithium metal as the counter and reference electrode.

The electrolyte consisted of dioxolane/dimethyl ether (DOL/DME) (2:1, v/v) containing 0.7 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.25 M lithium nitrate (LiNO_3). Two separator materials were investigated: GF/A glass microfiber and Celgard[®] 2325 polypropylene/polyethylene membrane. E/S ratios ranging from 5 to 55 $\mu\text{L mg}^{-1}$ were evaluated.

Electrochemical characterization included cyclic voltammetry between 1.8 and 3.0 V at a scan rate of 0.1 mV s^{-1} . The first two galvanostatic charge–discharge cycles were performed between 1.6 and 2.8 V at 0.1 C, while the subsequent cycles were conducted between 1.8 and 2.8 V at current rates ranging from 0.1 C to 2 C.

Results and Discussion

Representative rate capability profiles obtained for the GF/A separator and the Celgard[®] 2325 separator are presented in Figure 1.

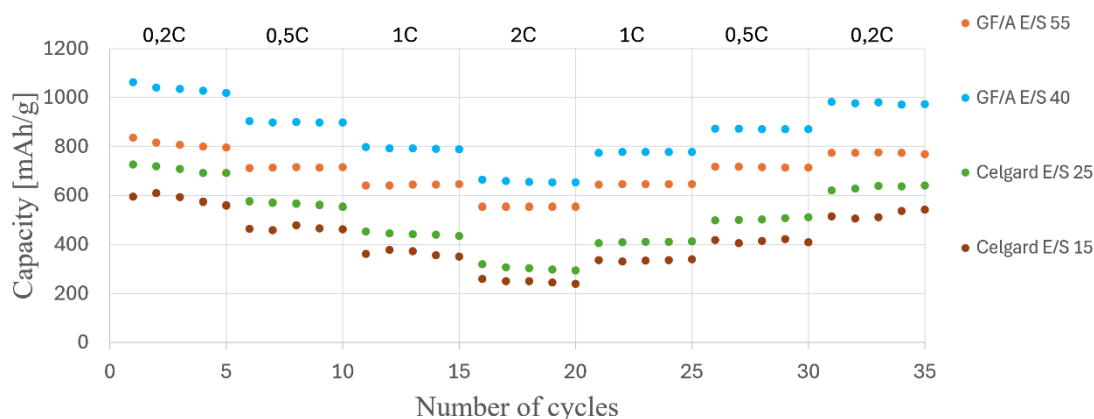


Figure 1. Comparison of the rate capability of Li–S cells assembled with GF/A and Celgard[®] 2325 separators at different E/S ratios (E/S).

The GF/A separator with $\text{E/S} = 40 \mu\text{L mg}^{-1}$ (Figure 1.) exhibited the highest electrochemical performance, delivering an initial discharge capacity of 1062.1 mAh.g^{-1} at 0.2 C. At the highest current rate 2 C, the capacity remained approximately 650 mAh g^{-1} , corresponding to about 61% of the initial value. After returning to 0.2 C, the capacity recovered to approximately 975 mAh g^{-1} , indicating good reversibility and efficient sulfur utilization.

In contrast, the Celgard[®] 2325 with $\text{E/S} = 25 \mu\text{L mg}^{-1}$ separator delivered a lower initial discharge capacity of approximately 725.6 mAh g^{-1} at 0.2 C. At 2 C, the capacity

decreased to approximately 295 mAh g⁻¹ (about 41% of the initial value), before recovering to approximately 635 mAh g⁻¹ after returning to 0.2 C.

Nevertheless, its lower electrolyte uptake enabled operation with a reduced electrolyte volume, decreasing the inactive electrolyte content and increasing the potential cell-level energy density. These results demonstrate that separator selection should balance electrochemical performance with practical cell design, where lean-electrolyte operation is essential for the development of high-energy Li-S batteries.

Conclusions

The electrochemical performance of Li-S batteries is strongly influenced by both the E/S ratio and separator architecture. Among the investigated systems, the GF/A separator with an E/S ratio of 40 $\mu\text{L mg}^{-1}$ provided the highest reversible capacity and the best cycling stability. Although the Celgard[®] 2325 separator enabled operation with lower electrolyte volumes, its lower electrolyte retention limited sulfur utilization and reversible capacity. These findings demonstrate that simultaneous optimization of separator properties and electrolyte quantity represents an effective strategy for improving the practical energy density and long-term cycling stability of Li-S batteries, providing useful guidance for the design of next-generation high-energy rechargeable batteries.

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Toward Vanadium-Free Redox Flow Batteries: The Potential of Organic Electrolytes

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The growing demand for efficient large-scale energy storage has increased interest in the development of organic electroactive materials for redox flow batteries (RFBs). Organic compounds offer several advantages, including structural tunability, potential low-cost production, and reduced environmental impact compared to traditional inorganic systems. Their electrochemical behavior can vary significantly depending on molecular structure and operating conditions, influencing parameters such as reversibility, stability, solubility, and ion transport. Experimental studies in this work indicate that appropriately designed organic electrolytes can provide favorable electrochemical performance and suitable transport properties for practical battery applications. The diversity of available organic materials enables the design of tailored systems for different electrolyte environments and operational requirements, highlighting their strong potential for future sustainable energy storage technologies.

Introduction

The increasing penetration of intermittent renewable energy sources such as solar and wind power has intensified the demand for efficient and scalable energy storage technologies. Among the available systems, redox flow batteries (RFBs) represent a promising solution for large-scale stationary energy storage due to their independent scaling of power and energy, long cycle life, and enhanced operational safety. However, conventional vanadium redox flow batteries still suffer from high material costs and limited sustainability associated with vanadium resources (1). Recent research has increasingly focused on organic redox-active molecules as alternatives to vanadium systems. Compounds such as quinones, alloxazines, viologen and nitroxyl radicals offer high solubility, tunable redox potentials, and good chemical stability, enabling laboratory-scale performances comparable to conventional vanadium RFBs (2). Among the investigated organic electrolytes, viologen derivatives have attracted significant attention due to their highly reversible redox behavior, favorable reduction potentials, high aqueous solubility, and good electrochemical stability in neutral aqueous systems. Viologen-based electrolytes are also considered promising negolytes owing to their reversible one-electron transfer mechanism, tunable electrochemical properties, and facile molecular functionalization. It has been shown that the introduction of hydroxyl, sulfonate, or quaternary ammonium functional groups can effectively suppress radical dimerization, improve cycling stability, and enhance the overall electrochemical performance of aqueous organic redox flow batteries [3][4].

Anthraquinone-based electrolytes also represent highly promising candidates for aqueous organic redox flow batteries because of their low crossover, reversible redox behavior, and the possibility of exchanging two electrons per molecule. Their electrochemical performance strongly depends on the nature and position of solubilizing functional groups, which influence electrolyte solubility, redox potential, and long-term stability [5][6]. Recent advances demonstrated that properly functionalized anthraquinone derivatives can achieve high electrolyte concentrations together with remarkably low-capacity fade rates, indicating strong potential for practical large-scale stationary energy storage applications [5][7].

Experimental

Electrochemical measurements were carried out using cyclic voltammetry in a conventional three-electrode setup consisting of a glassy carbon working electrode, platinum auxiliary electrode, and Ag/AgCl reference electrode. Prior to measurements, the working electrode was polished and electrochemically activated to ensure reproducible results. Solutions containing 10 mM of the investigated organic compounds were prepared in 1 M NH_4Cl supporting electrolyte. Before each experiment, the solutions were deaerated with argon to eliminate dissolved oxygen. Cyclic voltammograms were initially recorded over a wide potential range from -1.2 V to $+1.0$ V vs. Ag/AgCl at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$. Subsequently, measurements were performed at scan rates ranging from 5 to $500 \text{ mV}\cdot\text{s}^{-1}$ to investigate electron-transfer kinetics and transport properties. Diffusion coefficients were determined using the Randles–Ševčík equation based on the dependence of peak current on the square root of the scan rate. Cyclic voltammetry was selected because it provides rapid information about redox potentials, reversibility, electrochemical stability, and mass-transport characteristics of electroactive systems.

The cyclic voltammetry measurements revealed distinct electrochemical behavior for the two investigated compounds. He_2VBr_2 displayed sharp and highly reversible redox peaks typical for viologen systems, while DPivOHQ underwent a broader two-electron quinone/hydroquinone transformation. The peak-to-peak separation (ΔE_p) was significantly lower for He_2VBr_2 (68 mV) than for DPivOHQ (100.6 mV), indicating faster electron-transfer kinetics and higher reversibility of the viologen derivative. In both systems, the peak currents increased linearly with the square root of the scan rate, confirming diffusion-controlled electrochemical processes.

The calculated diffusion coefficients for He_2VBr_2 were $1.02 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ for oxidation and $1.30 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ for reduction, which agrees well with values reported for other viologen derivatives in aqueous electrolytes. This demonstrates that the substitution on the viologen structure does not negatively affect mass transport. For DPivOHQ, the diffusion coefficients were $5.89 \times 10^{-7} \text{ cm}^2\cdot\text{s}^{-1}$ for oxidation and $3.60 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ for reduction. The observed asymmetry suggests partial kinetic limitations associated with the two-electron process. Nevertheless, the obtained values remain within the expected range for anthraquinone-based systems.

Overall, the results demonstrate the complementary behavior of both molecular classes. He_2VBr_2 is more suitable for neutral and mildly acidic electrolytes due to its rapid and reversible kinetics, whereas DPivOHQ offers the advantage of higher charge-storage capacity through a two-electron process and remains more favorable for acidic or alkaline conditions.

Conclusion

This study compared the electrochemical properties of anthraquinone- and viologen-based organic electrolytes for redox flow battery applications. The viologen derivative He₂VBr₂ exhibited highly reversible redox behavior, fast electron-transfer kinetics, and diffusion coefficients consistent with literature data, making it a promising candidate for neutral aqueous electrolytes. In contrast, the anthraquinone derivative DPivOHQ provided a two-electron redox mechanism advantageous for increased charge-storage capacity but showed somewhat slower kinetics under neutral conditions. The results confirm that the suitability of anthraquinone and viologen systems strongly depends on the intended operating environment.

Acknowledgments

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Diffusion Behavior of Sodium Ions in TiO₂ and MnO₂ Electrodes at the Electrode/Electrolyte Interface with a Non-Aqueous Electrolyte

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X-ray powder diffraction analysis, scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), the Brunauer-Emmett-Teller (BET) method, electrochemical impedance spectroscopy (EIS), and galvanostatic cycling were used to investigate the influence of phase composition and morphology on the apparent diffusion coefficients of Na⁺ in sodium-ion batteries with TiO₂ and MnO₂ anodes. EIS revealed that sodium intercalation into metal oxides (MO) is a multi-step process in which sodium ions first migrate through a surface film formed on the electrode, followed by insertion into the electrode accompanied by charge transfer and diffusion through the electrode bulk. These processes were observed in all samples. All oxide samples exhibited similar apparent Na⁺ diffusion coefficients in the range of $1.3\text{--}2.6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and open-circuit potential (OCP) values between 2.15 and 2.70 V. Galvanostatic cycling of the batteries revealed a significant loss of coulombic efficiency during the first cycle, with the capacity loss increasing to 93% for TiO₂ and 86% for MnO₂ electrodes after 15 cycles, respectively, due to the formation of a passivation.

The practical application of sodium-ion batteries is limited by the slow kinetics of relatively large sodium ions in electrode intercalation compounds and the high probability of forming a thick passivation layer on the electrode surface through interactions with electrolyte anions. Metal oxides (MO), such as TiO₂ and Mn_xO_y, have been identified as promising candidates for sodium-ion intercalation. They can be prepared using various facile synthesis methods, including hydrothermal, solid-state, sol-gel, polymer-pyrolysis, and combustion processes (1). Although these materials offer several synthetic advantages compared with other systems, their poor rate capability in sodium-ion batteries limits their practical application. The main reason for the low rate performance is the sluggish kinetics of large Na⁺ ions within the host matrix. One approach to overcoming this limitation is to shorten the diffusion path for sodium insertion/extraction by modifying the diffusion coefficients of Na⁺ through changes in the composition, structure, and morphology of the metal oxides. In the present work, the diffusion behavior of sodium ions in TiO₂ and Mn_xO_y materials was studied using cyclic voltammetry and electrochemical impedance spectroscopy in a non-aqueous hybrid electrolyte. The diffusion coefficients of sodium in Na-ion cells were compared for two oxides with different structural and textural properties, and the reasons for the loss of capacity during cycling are discussed.

Active electrode materials based on titanium and manganese oxides were modified using a molten-route process in a citric acid medium to tune phase composition and surface characteristics (2). X-ray diffraction, scanning electron microscopy coupled

with energy-dispersive spectroscopy, and nitrogen sorption isotherms were used to evaluate the structural and textural properties of the obtained materials. Electrochemical measurements of Na-ion cells containing titanium- and manganese-oxide-based anodes were performed using an Autolab PGSTAT301N electrochemical workstation (Metrohm Autolab) in CR2016 coin cells with sodium metal as the counter electrode. A 1 M solution of NaClO₄ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and fluoroethylene carbonate (FEC) in a volume ratio of 4:5:1 was used as the electrolyte. Celgard 2400 polypropylene film was used as the separator. Galvanostatic cycling was carried out using a Neware Battery Testing System (China) in the voltage range of 0.01-3.0 V at a current density of 0.1 C. The current densities were calculated based on the theoretical 1 C values of 335 and 1018 mA g⁻¹ for TiO₂ and Mn₂O₃, respectively.

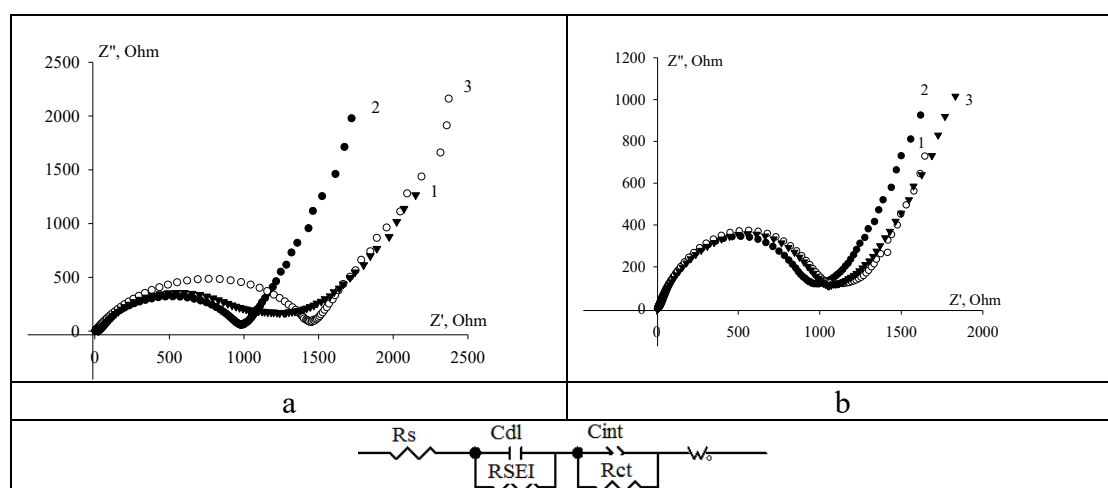


Figure 1. EIS and equivalent circuit of the Na-cells before cycling: a- initial titanium oxides [1] and modified by citric acid with the ratio 1:1 [2] and 1:2 [3]; b- the initial manganese oxides [1] and modified by citric acid with the ratio 1:1 [2] and 1:2 [3]

The Nyquist plots of MO electrodes in a non-aqueous electrolyte exhibit two depressed semicircles in the high- and medium-frequency regions, corresponding to Na⁺ migration through the SEI layer (R_{SEI}) and the charge-transfer resistance (R_{ct}), respectively. A steep line appears in the low-frequency region, indicating the onset of finite-length diffusion. C_{dl} corresponds to the capacitance of the SEI layer, while C_{int} represents the pseudocapacitance associated with adsorption phenomena occurring at the SEI film on the MO electrode surface. According to the equivalent circuit, sodium intercalation into MO is a multi-step process in which sodium ions first migrate through the surface film formed on the electrode, followed by insertion into the electrode, charge transfer, and diffusion through the electrode bulk. These processes were observed in all samples. All oxide samples exhibited apparent Na⁺ diffusion coefficients approximately two orders of magnitude higher than those reported for spinel materials [1]. Based on these results, the reduction in charge-transfer resistance achieved through surface modification had only a slight effect on the Na⁺ diffusion rate and open-circuit potential (OCP) (Table I). Galvanostatic cycling revealed a significant loss of coulombic efficiency during the first cycle, with the capacity loss increasing to 93% for TiO₂ and 86% for MnO₂ electrodes after 15 cycles (Table II). This indicates the absence of an efficient desolvation process at the electrode/electrolyte interface due to the adsorption of electrolyte components on the SEI layer, which may hinder sodium-ion mobility. Therefore, Na-ion solvation may promote the formation of new phases, such as a thick insoluble passivation layer containing electrolyte decomposition products, particularly in the presence of a high oxygen content on the oxide surface [3].

TABLE I. Porosity, ionic resistance, OCP, surface oxygen amount, and apparent diffusion coefficients of Na⁺ in Na-ion elements

Sample	Micro-pore fraction, %	R _{ion} , Ohm	OCP, V	D ^{app} _{Na+} 10 ⁻¹⁰ cm ² s ⁻¹	Me _x O _y
TiO ₂ initial	2.7	1238±0.5	2.68±0.5	1,36	TiO ₂
TiO ₂ CA 1	11.3	933±0.5	2.47±0.5	2,53	TiO _{5,9}
TiO ₂ CA 2	10.5	1467±0.5	2.70±0.5	1,43	TiO _{6,5}
Mn ₂ O ₃ initial	15.3	1008±0.5	2.22±0.5	2,36	MnO _{2,4}
Mn ₂ O ₃ CA 1	14.5	1061±0.5	2.15±0.5	2,02	MnO _{5,9}
Mn ₂ O ₃ CA 2	10.4	1105±0.5	2.23±0.5	1,96	MnO _{6,7}

TABLE II Galvanostatic cycling results Na-ion elements with non-aqueous electrolyte

Sample	Specific capacity of 1 st cycle, mAh/g		Coulombic efficiency of 1 st cycle, %	Specific capacity of 15 th cycle, mAh/g		Discharge capacity loss after 15 cycles, %
	Discharge	Charge		Discharge	Charge	
TiO ₂ Initial	174.7	32.7	18.7	21.2	20.3	87.9
TiO ₂ CA 1-2	189.2	41	21.7	11.4	11.2	94
TiO ₂ CA 1-3	159.1	33.9	21.3	13.4	12.8	91.6
Mn ₂ O ₃ Initial	73.3	19.1	25.9	12.8	12	82.5
Mn ₂ O ₃ CA 1-1	84.7	21.6	25.5	14.4	13.2	83
Mn ₂ O ₃ CA 1-2	60.6	14.4	23.8	8.8	8.1	85.5

Acknowledgments

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Walnut Shell-Derived Hard Carbon as an Anode Material for Na-ion Batteries

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This study presents the preparation and characterization of hard carbon derived from lignocellulosic walnut shell biomass for application in sodium-ion batteries. This precursor was selected due to its wide availability, dense structure, and high carbon content, providing ideal conditions for achieving optimal morphology. Initially, the shells underwent mechanical grinding in a ball mill, followed by acid leaching to eliminate impurities. After pH neutralization, the material was subjected to high-temperature carbonization under an inert nitrogen atmosphere. Following a final milling step, negative electrodes were fabricated using a water-soluble carboxymethylcellulose binder. Structural analysis via X-ray diffraction confirmed the successful formation of a disordered carbon framework featuring expanded interlayer spacing. Finally, electrochemical characterization through cyclic voltammetry and cycling tests validated the reversible sodiation and de-sodiation processes, demonstrating the material's viability as an anode.

Introduction

Driven by the escalating need for sustainable energy storage solutions, sodium-ion batteries (Na-ion) are gaining attention as a viable alternative to conventional lithium-ion batteries (Li-ion). This shift is primarily motivated by the abundant supply and cost-effectiveness of the requisite raw materials. Nevertheless, engineering optimal anode materials that allow for the efficient and reversible insertion of sodium ions continues to be a critical challenge. Because of its characteristic disordered structure, hard carbon has emerged as a highly promising candidate. An additional key benefit is that this carbonaceous material can be sustainably derived from renewable precursors, including various forms of biomass [1].

Experimental

This study focuses on the preparation and characterization of hard carbon derived from walnut shells, a lignocellulosic biomass selected for its wide availability, naturally dense structure, and high carbon content, which together provide ideal conditions for achieving optimal anode morphology [2].

First, four whole walnuts (total weight 42.5 g) were cracked open and disassembled, yielding 26 g (61 wt.%) of shells and inner husks and 16.5 g of the nuts themselves (39 wt.%). The shells and inner husks were then coarsely ground and subjected to a comprehensive pretreatment process involving hot-demineralised water leaching to remove dust and impurities, degreasing by rinsing in ethanol at 60 °C, and acid leaching

in 1M HCl to remove mineral impurities. The purified, pH-neutral precursor was then dried in a controlled atmosphere at 60 °C for 24 hours before undergoing a three-stage carbonization process: initial treatment in air at 180 °C for 3 hours, followed by heating in a nitrogen atmosphere at 500 °C for 2 hours, and final high-temperature carbonization at 1000 °C for 2 hours.

The resulting hard carbon was ground in a planetary ball mill Fritsch Pulverisette 7 using zirconia components and processed into an aqueous suspension containing 85 wt.% of active material, 10 wt.% of conductive additive SuperP, and 5 wt.% of carboxymethylcellulose (CMC) binder. This suspension was applied using a blade coater in a wet-film thickness of 200 μm onto a carbon-coated aluminium foil, resulting in an average active material loading of 2.97 $\text{mg}\cdot\text{cm}^{-2}$. Electrochemical performance was evaluated in EL-CELL[®] ECC-Std half-cells using 1M NaPF₆ electrolyte in an EC:PC ratio of 1:1 (v/v), a Whatman GF/C separator and a metallic sodium disc as a counter electrode. Measurements were performed on a 16-channel BioLogic VMP-3e potentiostat using cyclic voltammetry (CV) at scan rates of 5, 1, 0.5, and 0.1 $\text{mV}\cdot\text{s}^{-1}$, followed by formation cycles of 0.1C (capacity calculated from the theoretical capacity of 300 $\text{mAh}\cdot\text{g}^{-1}$) and symmetric rate capability testing up to a load of 2C (RC) using the real capacity obtained from the formation cycles.

Results and Discussion

The electrochemical performance and sodium storage behavior of the walnut shell-derived hard carbon are summarized in Figure 1.

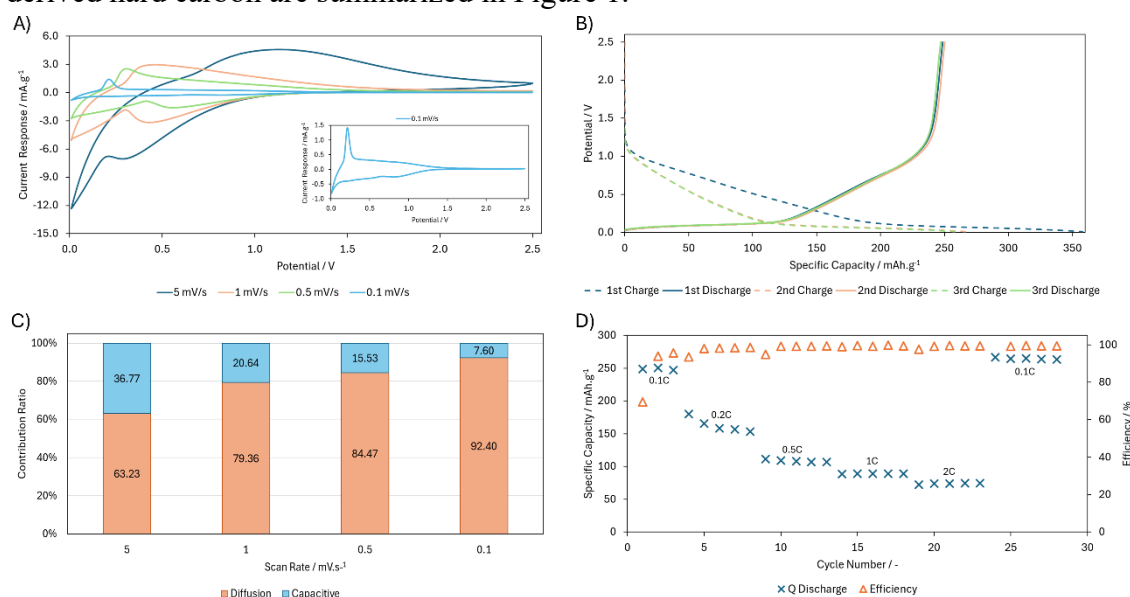


Figure 1. Electrochemical evaluation of the prepared hard carbon half-cells: A) Cyclic voltammograms at various scan rates with a detailed view at 0.1 $\text{mV}\cdot\text{s}^{-1}$; B) Galvanostatic charge-discharge curves from the formation cycles at 0.1C; C) Bar chart illustrating the normalized capacitive and diffusion-controlled capacity contributions at different scan rates; and D) Rate capability performance at various current densities up to 2C.

The CV curves measured at four different scan rates, with a detailed view at 0.1 $\text{mV}\cdot\text{s}^{-1}$ (Figure 1A), reveal a sharp anodic peak at approximately 0.2 V. The sharpness and low-potential position of this peak indicate highly reversible and thermodynamically well-defined sodium extraction, which is typically associated with the extraction of sodium clusters from the closed pores of the hard carbon [3]. The

galvanostatic charge-discharge profiles from the formation cycles at 0.1C (Figure 1B) exhibit an initial irreversible capacity loss, resulting in a solid initial Coulombic efficiency (ICE) of 84 %. The voltage profiles are distinctly divided into a high-voltage sloping region and a low-voltage plateau. Notably, the low-voltage plateau region contributes $\sim 125 \text{ mAh} \cdot \text{g}^{-1}$ to the total reversible capacity of $\sim 250 \text{ mAh} \cdot \text{g}^{-1}$. This means that $\sim 50 \%$ of the capacity originates from the low-potential plateau, which is highly desirable for maximizing the energy density in full-cell practical applications [4]. To further elucidate the storage kinetics, the capacitive and diffusion-controlled contributions were derived from the CV measurements. As illustrated in the corresponding bar chart (Figure 1C), the diffusion-controlled charge storage fraction clearly increases as the scan rate decreases, reflecting the time-dependent nature of deep sodium insertion into the carbon matrix [5]. Finally, the rate capability test (Figure 1D) demonstrates the material's response to increasing current loads up to 2C. Although the specific capacity naturally decreases at higher rates, maintaining approximately $75 \text{ mAh} \cdot \text{g}^{-1}$ at 2C, the electrode exhibits excellent structural stability and reversibility, evidenced by the immediate and full recovery of the initial capacity upon returning the current load to 0.1C.

Conclusion

The synthesis of hard carbon from walnut shells provides a highly efficient and sustainable anode material for Na-ion batteries. Electrochemical characterization using cyclic voltammetry demonstrated clear and reversible sodium insertion and desorption processes. The practical applicability of the material was verified by cycling tests, which revealed a specific capacity of approximately $250 \text{ mAh} \cdot \text{g}^{-1}$ along with a high initial Coulombic efficiency of 84%. Overall, this approach, which involves converting agricultural waste into a high-quality carbon precursor, effectively minimizes the environmental impact of SIB production while maintaining highly competitive energy storage capabilities.

Acknowledgments

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Synergistic Effects of Imidazolium Ionic Liquids and Palladium Nanoparticles on the Durability of Ni–MH Battery Negative Electrode

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Several systems of nickel-metal hydride negative electrodes in alkaline electrolytes with or without ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide) additive were studied with the goal of obtaining their electrochemical characteristics. Two types of electrode materials were studied – unaltered AB5-type alloys and the same alloys modified with palladium nanoparticles. The electrode materials underwent a series of electrochemical experiments in the environment of pure 6 M potassium hydroxide, as well as potassium hydroxide electrolyte with addition of ionic liquid. The electrodes' morphology, microstructure and the atomic composition were examined before and after the electrochemical testing in each electrolyte. It was established that the addition of ionic liquid in concentration as low as 0.01 wt% lowered the AB5 alloy corrosion current density. Long-term capacity tests revealed that the presence of an ionic liquid in the electrolyte acts synergistically with palladium nanoparticles, thereby increasing the overall and average capacity of the studied systems.

Introduction

The nickel-metal hydride secondary electrochemical cells are one of the most commercially used energy storage systems, alongside lithium-ion and lead-acid batteries. Compared to these two systems, they possess certain advantages, like lower toxicity and higher stability. They do, however, exhibit some drawbacks, which limit their applicability. One of those drawbacks is the corrosion of negative electrode material (hydrogen-absorbing AB5-type alloy), caused by the presence of highly alkaline electrolyte [1]. The corrosion process, which occurs both during standard cycling of the battery, as well as during its storage at open circuit conditions, impacts such traits as long-term cycling stability, longevity and capacity of the system [1]. Limiting the corrosion processes occurring in the cell could lead to such improvements as longer lifespan and better capacity retention.

Results and discussion

In order to inhibit the corrosion process in studied energy storage systems, imidazolium-based ionic liquids (ILs) were added to the alkaline electrolyte (0.01 wt%).

ILs act as a mixed-type corrosion inhibitors, adsorbing on the surface of the negative electrode material and blocking the anodic and cathodic reactive sites [2]. The electrochemical testing has confirmed a positive impact of studied compounds on corrosion parameters of hydrogen-absorbing alloy. The mechanism of corrosion inhibition provided by ionic liquids leads however to certain drawback, like lower capacity, which is caused by blocking of active sites on the material's surface [3]. The AB5-type alloy also requires activation in KOH electrolyte environment, which is circumvented by addition of palladium nanoparticles. In this case Pd acts as a catalyst material and improves the kinetic characteristics of hydrogen adsorption and absorption into the AB5-type absorbing alloy, rendering the activation obsolete [4]. Moreover, long-term capacity tests, performed in every single cycle during long-term polarization, revealed that the presence of an ionic liquid in the electrolyte acts synergistically with palladium nanoparticles, thereby increasing the overall and average capacity of the studied systems by enhancing the kinetics of hydrogen absorption and mitigating corrosion of the AB5 alloy (Figure 1).

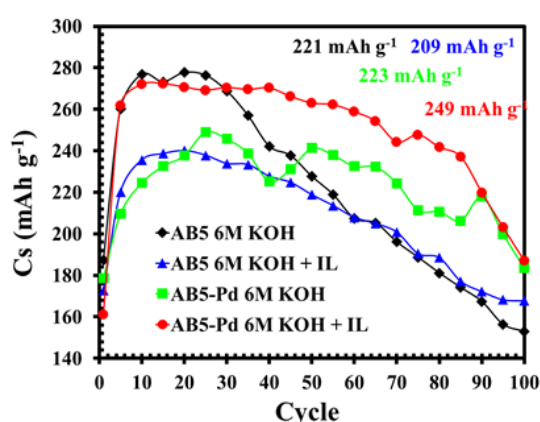


Figure 1. Specific capacity C_s values recorded during long-term capacity studies of unmodified and Pd-modified AB5-type electrodes in various electrolytes.

Acknowledgments

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Redox Mediators for Li–Oxygen Batteries

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Li–oxygen (Li–O₂) batteries offer high theoretical energy density, but sluggish Li₂O₂ formation/decomposition and parasitic reactions limit reversibility. Soluble redox mediators lower polarization by enabling solution-mediated pathways; however, mediator crossover to lithium causes redox shuttling, mediator loss and anode corrosion. This presentation summarizes strategies to preserve mediator activity while stabilizing the Li interface. A Mn_xCo_{3–x}O₄-decorated separator promotes I[–]/I₃[–] and I₃[–]/I₂ redox coupling and restricts shuttling in LiI-mediated cells. Benzyltriethylammonium iodide and 4-fluoro-2-iodoaniline act as self-defensive mediators, coupling Li₂O₂ oxidation with in situ protective interphase formation. Complementary AgTFSI pretreatment and a polymeric ionic-liquid additive generate lithiophilic or cationic shielding layers on lithium; the latter extends cycling from 38 to 105 cycles at 200 mA g^{–1}. Operando synchrotron X-ray diffraction and X-ray computed tomography reveal mediator kinetics and electrode-interface evolution. These results demonstrate that co-designing mediator chemistry, separator functionality and dynamic Li-metal interfaces is essential for durable Li–O₂ batteries.

Standardized Infrared Thermography for High-Reliability Photovoltaic Systems

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In the maturing global solar market, the maintenance of photovoltaic (PV) assets has undergone a profound shift. What was once a reactive "fix-on-failure" approach evolved into a sophisticated regime of preventative maintenance where production availability and fire protection are paramount. Outdoor infrared (IR) thermography is no longer a luxury for specialized troubleshooting; it is a normative requirement for ensuring the long-term bankability and safety of PV plant.

Introduction

The IEC TS 62446-3 technical specification provides the essential framework for this transition, establishing rigorous, non-negotiable protocols for the thermographic inspection of operational PV modules and Balance-of-System (BOS) components. By distinguishing between Simplified Inspections (basic functional verification during commissioning) and Detailed Inspections (comprehensive analysis involving absolute temperature measurement and root-cause determination), the standard ensures that diagnostics are fit-for-purpose.

Standardizing these procedures transforms volatile thermal snapshots into reliable, traceable metrics. Without adherence to these normative requirements, raw data remains anecdotal and legally indefensible. For lead auditors and asset managers, the shift from qualitative "heat maps" to quantitative thermal analysis is the only path toward maintaining the structural integrity and performance warranties of large-scale solar assets.

The Hardware

Generic thermal cameras are insufficient for scientific-grade PV analysis. To ensure data accuracy and traceable results, the hardware must meet specific thresholds to avoid misleading artifacts caused by material physics.

The Spectral Response Mandate: A critical distinction must be made regarding wavelength. Mid-wave cameras (2 μm to 5 μm) shall only be used for electrical BOS components like fuses. Due to the partial transparency of glass in the 3 μm range, using mid-wave equipment on PV modules leads to catastrophic measurement errors, as the sensor captures temperatures from behind the front glass.

TABLE I: Minimum Requirements for IR-Cameras (per IEC TS 62446-3)

Feature	Minimum Requirement
Spectral Response	8 μm to 14 μm (Long-Wave) for modules; 2 μm to 5 μm (Mid-Wave) BOS ONLY
Object Temperature Range	-20 °C to +120 °C
Thermal Sensitivity (NETD)	$\leq 0.1 \text{ K}$ at 30 °C
Geometric Resolution	Max. 3 cm per pixel at module edge (5x5 pixels per cell)
Absolute Error	$<\pm 2 \text{ K}$
Adjustable Parameters	Emissivity (ϵ), Reflected Temperature (T_{ref})
Calibration	Traceable calibration required at least every two years

Geometric Resolution and IFOV: To detect microscopic failures, the standard requires a minimum resolution of 5x5 pixels per 6-inch cell. This is governed by the Instantaneous Field of View (IFOV). For example, a camera with an IFOV of 3.0 mrad at a distance of 10 m yields a pixel edge length (L_{pixel}) of 30 mm ($3.0 \text{ mrad} \times 10 \text{ m}$), which just meets the 5×5 pixel-per-cell requirement for a standard 15.24 cm cell. Any resolution lower than this renders the inspection non-compliant.

The Environmental Envelope: The Non-Negotiable Conditions for Data Integrity

Thermal signatures are volatile and dependent on external flux. Data validity is predicated on maintaining a specific "environmental envelope" to ensure the system is in a thermal steady state.

Normative Inspection Conditions

- Irradiance: A minimum of 600 W/m² in the plane of the module.
- BOS Load: For cables and connectors, the measured operating current must be at least 30% of the rated system current.
- Wind Speed: Maximum of 4 Beaufort ($\cong 28 \text{ km/h}$). High wind introduces convection cooling that masks critical defects.
- Cloud Coverage: Maximum of 2 okta (cumulus clouds). The Cirrus Nuance and Steady State: The presence of cirrus clouds can cause irradiance shifts exceeding 10% per minute. Per the standard, any shift of this magnitude triggers a mandatory 15-minute waiting period before resuming measurements to ensure the module returns to a thermal steady state. Failure to respect this waiting period results in "thermal ghosting," where residual heat patterns produce false positives.

The Drone Dilemma: Smearing Effects and Aerial Resolution

Unmanned Aerial Vehicles (UAVs) offer speed but risk data "smearing." The time constant of common bolometer detectors limits the effective moving speed of the camera.

As shown in Figure 1 of the standard, smearing becomes unacceptable at speeds exceeding 3 m/s. While aerial surveys are efficient for "Simplified Inspections" (identifying string-level outages), they frequently lack the resolution for "Detailed Inspections." A fast-moving drone survey carries an inherent risk of "false negatives." Consequently, aerial findings of concern must be validated by ground-based personnel

certified under ISO 9712 to perform absolute temperature measurements and root-cause analysis.

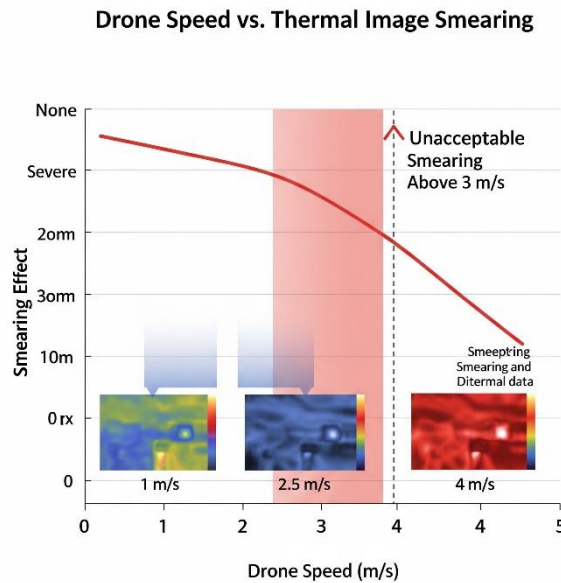
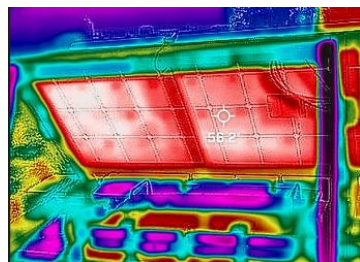


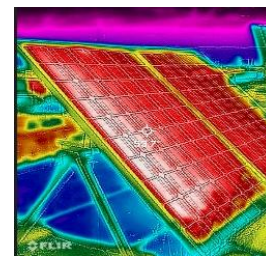
Figure 1: Drone speed vs. Thermal Image Smearing

Surface Physics: The Variable Nature of Glass Emissivity

Measuring temperature through glass—a material with a non-constant emissivity—requires advanced understanding of geometry and reflected radiation. The camera should ideally be perpendicular to the module. If the viewing angle drops below 30°, glass emissivity (ϵ) falls significantly (from ≈ 0.85 to 0.75 or lower). At these low angles, the camera no longer measures the module temperature; it measures the reflected background radiation, often the sky temperature, which can be as low as $-30\text{ }^{\circ}\text{C}$. This reflection leads to a massive underestimation of defect severity, potentially misclassifying a fire-risk component as a minor performance issue.



a) Back side



b) Front side

Figure 2: Example of thermograph analysis results during measurement

A common mistake in maintenance is reacting to the "raw" temperature shown on an IR camera. A 10-degree "hot spot" measured when the sun is at 600 W/m^2 is mathematically more severe than the same 10-degree difference at 1000 W/m^2 . To compare findings across different days or times, we must "project" the measured temperature difference to nominal conditions (1000 W/m^2) using the following formula:

$$\Delta T_1 = (G_2 / G_1)^x \cdot \Delta T_1$$

In this calculation, ΔT_1 is the measured temperature difference, G_1 is the actual irradiance, and G_2 is the standard 1000 W/m^2 . The exponential factor (x) is where the science of heat transport comes in:

For extended area abnormalities (like a whole warm cell), $x = 1$, representing a linear dependence. For point abnormalities (like a localized hot spot), x is typically between 1.5 and 1.8. An x value of 2.0 represents the theoretical limit: current-induced heat from a point spot with zero heat dissipation by radiation. By applying this math, we can determine the "true" severity of a defect as if it were operating under maximum load, allowing for accurate prioritization of repairs.

Conclusion

Thermal imaging in the solar industry is often reduced to a marketing gimmick—pretty pictures of blue and orange arrays. But as we have seen, true thermography is a rigorous engineering discipline. Without following the 600W rule, the 5x5 pixel mandate, and the mathematical normalization to 1000 W/m², you aren't performing a technical inspection; you're taking a high-priced photo. The implementation of the IEC TS 62446-3 framework elevates infrared diagnostics from qualitative imagery to a rigorous scientific discipline. By enforcing hardware precision, controlling the environmental envelope, and applying mathematical projections, the solar industry can ensure the long-term bankability and safety of global assets. The transition to standardized thermal analysis is not merely a best practice - it is the only professional standard for ensuring the reliability of the global energy transition.

Acknowledgments

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Effect of Reflow Profile Shape Above the Melting Point at a Constant Heating Factor on the Shear Strength of Solder Joint Systems for Battery Management System Applications

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The increasing deployment of Battery Management Systems (BMSs) in electric mobility and energy storage applications places growing demands on the reliability of electronic assemblies and their solder joints. The heating factor combines the time and temperature above the solder melting point into a single parameter for characterizing thermal exposure during reflow soldering. However, different time–temperature profiles can result in similar heating factor values and may affect different solder joint systems differently. This study compares the shear force of two 0805 solder joint configurations processed using two reflow profiles with different shapes above the solder melting point but approximately identical heating factors. Zero-ohm SMD resistors were soldered using Sn42Bi57Ag1 solder paste, while SAC305 solder preforms were assembled using the same paste, forming a solid–liquid soldering system. The triangular profile resulted in higher shear force for the resistor joints, with a statistically significant difference between the profile groups. In contrast, no statistically significant effect of profile shape was observed for the SAC305 preform joints. Flat-side-down preforms exhibited higher shear force than flat-side-up preforms, with a statistically significant difference between the two orientations. These results indicate that approximately identical heating factors do not necessarily produce equivalent mechanical responses across different solder joint systems.

Introduction

The rapid growth of electric mobility and stationary energy storage has significantly increased the demand for reliable Battery Management Systems (BMSs). Since BMS electronic assemblies contain numerous solder joints responsible for electrical interconnection, understanding the influence of reflow soldering parameters on solder joint properties is important for the manufacture of reliable BMS electronic assemblies. The thermal profile used during reflow soldering significantly affects solder joint formation and the resulting mechanical properties. Two of the key process parameters are the temperature reached during reflow and the time for which the solder is maintained above its melting point. To describe their combined effect, the heating factor Q_{η} can be used as an integral parameter representing the thermal exposure of the solder above its melting point. The principle of the heating factor is illustrated in Figure 1. Previous studies have demonstrated relationships between the heating factor, intermetallic compound formation, and the mechanical properties of solder joints [1][2][3].

However, a similar heating factor can be obtained using different combinations of temperature and time above the melting point. Consequently, reflow profiles with approximately identical heating factors may differ considerably in their thermal trajectories. Previous research has shown that the heating factor can be a useful parameter for predicting solder joint formation, particularly when the preheating conditions remain unchanged and only the reflow region is varied [3]. Nevertheless, an identical heating factor does not necessarily imply identical solder joint properties.

This issue becomes particularly relevant when different solder joint systems are considered. In conventional surface-mount assembly using low-temperature Sn-Bi-based solder paste, the solder is fully molten during reflow. In contrast, combining the same low-temperature solder paste with a SAC305 solder preform creates a solid–liquid soldering system because the SAC305 preform remains below its melting temperature. Previous studies have shown that interactions between molten Sn-Bi-based solder and solid SAC material depend on reflow conditions and can affect the resulting microstructure and mechanical properties of the joint [4][5][6].

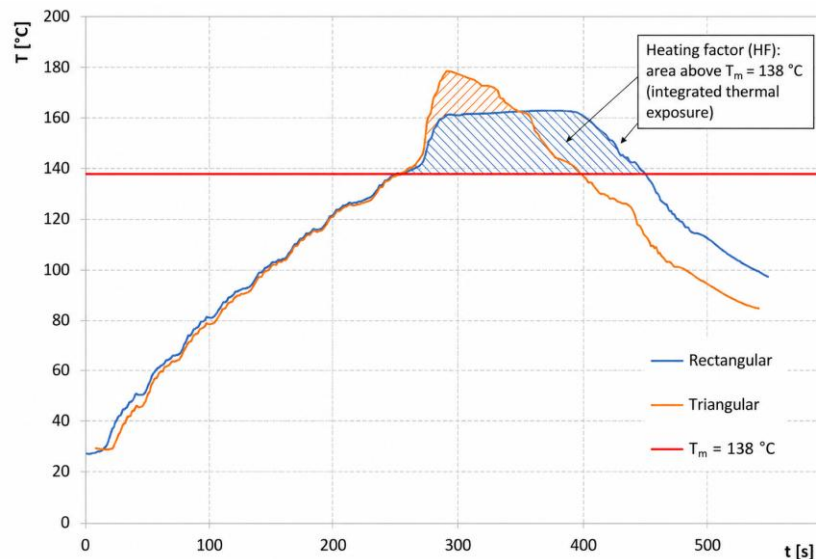


Figure 1. Measured reflow temperature profiles with different shapes above the solder melting temperature of 138 °C. The heating factor (HF) is represented by the area between the temperature profile and the melting temperature line for $T > 138$ °C.

Therefore, this study investigates whether two reflow profiles with different shapes above the solder melting point but approximately identical heating factors produce equivalent mechanical responses in two different solder joint systems using nominal 0805-sized test specimens. The two systems were compared by shear testing.

Experimental

Two different solder joint systems based on nominal 0805-sized test specimens were investigated. The first consisted of zero-ohm SMD resistors (Multicomp Pro MCWR08X000 PTL) with a height of 0.5 mm, soldered onto immersion tin (ImSn)-finished printed circuit boards using Sn42Bi57Ag1 solder paste with a melting temperature of 138 °C. The second system consisted of SAC305 solder preforms with a nominal 0805 size assembled onto ImSn-finished PCBs using the same Sn42Bi57Ag1 solder paste. Since the peak temperatures of both reflow profiles remained below the melting temperature of SAC305, the preforms did not undergo bulk melting during reflow, forming a solid–liquid soldering system with the molten Sn42Bi57Ag1 solder.

Due to the asymmetric geometry of the SAC305 preforms, two assembly orientations were distinguished: flat-side-down and flat-side-up.

The samples were soldered using two reflow profiles with different shapes above the Sn42Bi57Ag1 melting temperature and a target heating factor of approximately 1470 s°C. The rectangular profile reached a peak temperature of 162.4 °C and remained above the melting temperature for 86.8 s, whereas the triangular profile reached 177.6 °C with a time above the melting temperature of 69.1 s. The measured temperature profiles are shown in Figure 1.

The mechanical strength of the solder joints was evaluated by shear testing using a Dage PC-2400T tester. The test height was set to 25 µm and the test speed to 500 µm. The maximum shear force was used for evaluation.

Results and Discussion

The shear test results are summarized in Table I. The triangular profile resulted in a higher mean shear force for the 0805 resistor joints, and the difference between the two profiles was statistically significant (Welch's t-test, $p = 0.007$).

For the SAC305 solder preforms, two-way ANOVA with profile shape and preform orientation as factors showed no statistically significant effect of profile shape ($p = 0.891$). Flat-side-down preforms exhibited higher mean shear forces than flat-side-up preforms, with a statistically significant difference between the two orientations ($p = 0.0016$). No statistically significant interaction between profile shape and orientation was observed ($p = 0.545$).

TABLE I. Shear force results for the investigated solder joint systems.

Solder joint system	Profile shape	Orientation	Mean shear force [N]	SD [N]
0805 resistor	Rectangular	-	66.31	10.36
0805 resistor	Triangular	-	70.80	12.73
SAC305 preform	Rectangular	Flat-side-down	97.33	3.93
SAC305 preform	Triangular	Flat-side-down	96.58	5.29
SAC305 preform	Rectangular	Flat-side-up	90.78	5.51
SAC305 preform	Triangular	Flat-side-up	92.13	3.62

The different responses of the investigated solder joint systems suggest that sensitivity to the thermal trajectory above the melting point is system-dependent. Unlike the conventional resistor joints, the preform system involved interaction between solid SAC305 and molten Sn42Bi57Ag1 solder. Previous studies have shown that this interaction is affected by reflow conditions [4][5][6]. Under the investigated conditions, no statistically significant effect of profile shape on the shear force of the preform joints was observed, whereas flat-side-down preforms exhibited higher shear forces than flat-side-up preforms. Further microstructural analysis is required to identify the mechanisms responsible for the observed differences.

Conclusion

The solder joint systems based on nominal 0805-sized resistors and SAC305 solder preforms exhibited different responses to reflow profiles with approximately identical heating factors. The triangular profile resulted in higher shear force for the zero-ohm resistor joints, with a statistically significant difference between the profile groups, whereas no statistically significant effect of profile shape was observed for the SAC305

preform joints. Flat-side-down preforms exhibited higher shear force than flat-side-up preforms, with a statistically significant difference between the two orientations. These results indicate that the heating factor alone does not necessarily predict equivalent mechanical responses across different solder joint systems, even when the same solder paste and PCB surface finish were used.

Acknowledgments

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Multi-Species Multi-Reaction Model Parametrization of a Commercial NCA Positive Electrode from Half-Cell Open-Circuit Potential Data

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The Multi-Species Multi-Reaction (MSMR) model describes the open-circuit potential (OCP) of a lithium-ion electrode with a few thermodynamically meaningful parameters, but no parameter set has been published so far for nickel-cobalt-aluminum oxide (NCA). Here we parametrize the MSMR model for the NCA cathode of a commercial 18650 cell, using half-cell quasi-OCP (qOCP) data measured on material harvested from a pristine cell and from cells cycle-aged to the end of life under two state-of-charge windows. A peak analysis across aging states shows that the thermodynamic signature of NCA is essentially unchanged by aging.

Introduction

Battery management systems heavily rely on models of the cell open-circuit voltage (OCV), which is the difference between the open-circuit potentials (OCPs) of the two electrodes. Empirical fits such as polynomials or look-up tables are simple but offer no physical insight. Physics-based models, instead, rely on physically meaningful parameters, whose evolution can be linked to degradation mechanisms. Among them, the Multi-Species Multi-Reaction (MSMR) model [1][2] treats intercalation as a set of independent reactions, or “galleries”, each described by a standard potential U_j^0 , a site fraction X_j and a disorder parameter ω_j , and each corresponding to one peak of the differential-capacity curve [2][3]. The model has been parametrized for graphite, silicon, lithium iron phosphate, spinel manganese oxide and nickel-manganese-cobalt oxide (NMC) [1][2][3] but, to our knowledge, not for nickel-cobalt-aluminum oxide (NCA), despite its abundance in automotive cells [4]. Moreover, the common practice of modeling aging with gallery parameters frozen at their beginning-of-life (BOL) values [5] assumes an OCP shape invariant under aging, verified for NMC-811 [6] but not for NCA. This work fills both gaps.

Experimental and Model Fitting

The cells under study are commercial silicon-graphite/NCA cylindrical cells (Molicel INR-18650-M35A) selected from a larger cycle-aging campaign [7], in which eight cells were cycled at C/2 and 25 °C over four state-of-charge (SOC) windows. The cells cycled over the full (0–90%) and low (0–30%) SOC windows reached their end of life at a state of health (SOH) of 76% and 65%, respectively. A pristine cell and one end-of-life cell from each aging path were disassembled, and circular cathode samples

punched from the harvested electrode sheets were assembled into CR2032 coin cells against lithium metal, with 1 M LiPF₆ in EC/DMC (1:1 v/v) as electrolyte. The half-cells were cycled four times between 3.0 and 4.3 V at 36 μ A (about C/100), and the quasi-OCP (qOCP) was extracted from the fourth, most stable cycle.

Smooth differential-capacity curves are obtained using the histogram-counting method of Lu et al. [3], which avoids the noise amplification inherent in differentiating the raw voltage numerically. In the MSMR framework, the electrode stoichiometry θ follows from the condition that all galleries share the same electrode potential U_{ocp} :

$$\theta(U_{\text{ocp}}) = \sum_j X_j / (1 + \exp[f(U_{\text{ocp}} - U_j^0) / \omega_j]), \quad f = F/RT \quad [1]$$

and each gallery contributes a bell-shaped differential-capacity peak centered at U_j^0 , with a width governed by ω_j and an area set by X_j . Initial guesses of all parameters are read from the measured peaks and refined with a trust-region constrained optimizer, together with the stoichiometry window $[\theta_{\min}, \theta_{\max}]$ accessible between the voltage cut-offs. Each U_j^0 is constrained within ± 30 mV of its initial guess, keeping every gallery anchored to a visible peak, while normalizing the cost function by $(\theta_{\max} - \theta_{\min})^2$ prevents the optimizer from collapsing the stoichiometry window. The charge and discharge branches are fitted separately and averaged gallery by gallery, assuming a purely dynamic hysteresis [3].

Results and Discussion

Figure 1 overlays the differential-capacity curves of the charge branch at the three aging states. The BOL cathode and the cathode aged over the full SOC window display four peaks, whose standard potentials shift by less than 40 mV between aging states, while the site fractions and disorder factors vary by less than 50%; the discharge branch behaves analogously. The most degraded cathode also shows a splitting of the peak associated with the hexagonal-to-monoclinic phase transition of the Ni-rich layered oxide [8], attributed to aging-induced inhomogeneity. We therefore model NCA with four galleries at all aging states.

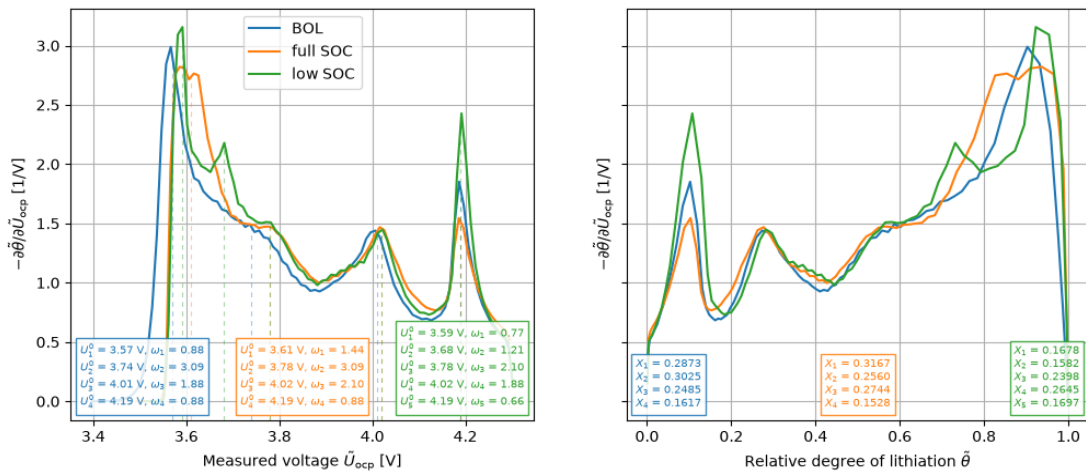


Figure 1. Differential capacity of the cathode charge branch versus measured voltage (left) and relative degree of lithiation (right) at the three aging states. Dashed lines mark the standard potentials U_j^0 ; boxes report the initial parameter guesses read from the peaks.

Figure 2 compares the MSMR model fitted on BOL data with the experimental qOCP curves at the three aging states, for the charge direction. At BOL, fit and measurement are almost indistinguishable, with a root-mean-squared error (RMSE) of 2.5 mV, while the same unaltered model still reproduces the qOCP of the aged cathodes, with the RMSE growing only to 17.4 mV at 76% SOH and to 27.5 mV at 65% SOH. The thermodynamic signature of NCA is thus largely preserved upon aging, supporting the practice of freezing the gallery parameters at BOL and ascribing OCV changes to electrode-level capacity and alignment shifts [5], as reported for NMC-811 [6].

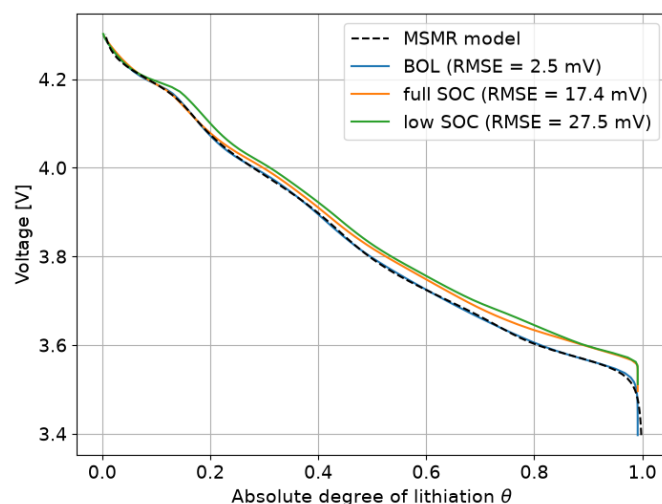


Figure 2. The MSMR model fitted on BOL data is compared with the experimental qOCP curves of the three aging states, for the charge direction. The RMSE of each comparison, computed over $\theta \in [0.02, 0.95]$, is reported in the legend.

The complete fitted and averaged MSMR parameter set, to our knowledge the first reported for an NCA electrode, will be tabulated in the full conference paper and presented at the meeting.

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Workflow for SEM Characterization of Battery Cross-Sections

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This contribution presents a complete workflow for preparing lithium-ion battery samples for operando scanning electron microscopy (SEM). The workflow combines broad ion beam (BIB) cross-section preparation, inert sample transfer, battery assembly inside an argon glovebox, and operando SEM analysis. Individual preparation steps are discussed with emphasis on preserving the native state of battery materials and ensuring reproducible experimental conditions.

Introduction

Lithium-ion batteries (LIBs) remain the dominant electrochemical energy storage technology for portable electronics, electric vehicles, and stationary energy storage systems. Continuous development of new electrode materials, solid-state electrolytes, and advanced cell architectures requires characterization techniques capable of resolving structural features over multiple length scales [1].

Operando scanning electron microscopy (SEM) enables direct observation of structural changes in battery materials during electrochemical cycling and has become an important technique for studying degradation mechanisms and validating emerging battery chemistries [2]. In contrast to conventional post-mortem analysis, the investigated structure remains electrochemically active throughout the experiment, allowing direct correlation between electrochemical response and microstructural evolution.

Reliable operando characterization requires considerably more than SEM imaging alone. Battery materials are highly sensitive to oxygen and moisture, while preparation of representative cross-sections requires minimizing mechanical damage introduced during sample preparation. Furthermore, all battery components must remain in a controlled environment throughout sample preparation, transfer, and assembly in order to preserve their native state [3][4]. These requirements make the complete preparation workflow a critical part of any operando experiment.

Workflow

The proposed workflow is designed for operando SEM experiments on pre-assembled battery systems. Depending on the investigated battery architecture and experimental objective, the specimen may consist of a complete battery or a partially assembled cell prepared for subsequent operando characterization.

The assembled battery is transferred under an inert atmosphere to a broad ion beam (BIB) system, where a representative cross-section area is prepared. Depending on the application, the cross-section may expose the complete battery thickness, allowing simultaneous observation of all layers and interfaces, or only the investigated electrode,

reducing preparation time while preserving the electrochemical functionality of the cell. The preparation strategy can therefore be adapted to the specific requirements of the experiment.

After BIB preparation, the subsequent workflow depends on the battery configuration. For liquid-electrolyte systems, the specimen is transferred back into an argon-filled glovebox, where the electrolyte is introduced through the protruding separator. The electrolyte gradually infiltrates the separator and porous electrodes by capillary action while minimizing disturbance of the prepared cross-section. Battery systems containing a solid electrolyte or other vacuum-compatible architectures do not require this step and can be transferred directly to the SEM.

The prepared battery is mounted into the operando SEM holder and transferred to the microscope using an inert gas transfer system, ensuring that air-sensitive materials remain protected throughout the workflow. Before electrochemical cycling, the battery is allowed to stabilize inside the SEM chamber. For liquid-electrolyte cells, this conditioning period enables complete wetting of the porous structure and establishment of stable electrochemical conditions. Operando imaging and electrochemical cycling are therefore typically initiated after an overnight equilibration period, whereas solid-state systems can generally be examined immediately after installation.

Conclusion

The presented workflow integrates sample preparation, inert handling, battery assembly, and operando SEM characterization into a unified methodology for investigating battery systems under controlled conditions. By combining broad ion beam cross-section preparation with protected sample transfer and SEM-compatible instrumentation, the workflow minimizes preparation-induced artifacts and environmental degradation while preserving the electrochemical functionality of the battery. Its modular design allows adaptation to various battery architectures, including both liquid- and solid-electrolyte systems, providing a versatile platform for operando studies of battery materials and interfaces.

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AI Declaration:

OpenAI ChatGPT was used to assist in drafting and language editing of this conference abstract. All scientific content, interpretations, and conclusions are the responsibility of the authors.

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Reducing Charging Stress and Cold-Charging Exposure in CubeSat Batteries

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CubeSat batteries in low Earth orbit are repeatedly charged within sunlight intervals while their temperature changes along the orbit. High charging currents, especially in combination with low temperatures, can accelerate ageing. A predictive energy-management method is proposed that combines solar-power forecasting with battery heating control. The forecast is used to distribute charging over the available sunlight period, while a separate controller compares predicted temperature trajectories with the heater switched on and off. Three strategies are assessed in two cold operating scenarios: conventional charging with threshold heating, forecast-based charging with threshold heating, and forecast-based charging with predictive heating. Charging-current spreading lowered the root-mean-square charging current by 42–53% compared with the conventional strategy. Predictive heating removed the remaining cold-charging intervals in both cases, with no relevant increase in charging-current severity, but required 2.2–2.4 Wh more heater energy than threshold control.

Introduction

In low Earth orbit, a CubeSat battery supplies power for the spacecraft during eclipse and is recharged during the following sunlit period. The available recharging time is limited, while surplus solar power varies with spacecraft payload demand and orbital conditions. Directing all available surplus power to the battery can produce brief intervals of high charging current, possibly resulting in an elevated battery stress. Meanwhile, CubeSat and battery temperature also change along the orbit. Charging while the battery is cold may accelerate harmful degradation mechanisms [1][2].

These two operating stresses are often treated separately. Electrical energy management can limit current, but often in a static way, whereas a thermostat typically activates the heater only after the measured temperature crosses a prescribed boundary. Such a reactive arrangement does not provide effective energy handling and provides a space for improvements. Earlier work showed that a long short-term memory (LSTM) forecast can be used to distribute CubeSat battery charging over the sunlight period and reduce current peaks [3]. The present contribution further extends this improved charging strategy via temperature-aware heater scheduling, so that the charging in cold conditions is reduced or eliminated, helping to prevent the occurrence of lithium plating.

Methodology

The assessment is simulation-based and uses orbital power and temperature behavior derived from CubeSat telemetry studies [4]. The electrical part is represented by a temperature-dependent one-RC equivalent-circuit model with hysteresis. A lumped thermal model propagates battery temperature from the orbital thermal trend, battery losses, and heater input. This combination retains the main temperature variation observed in orbit while providing a dynamic state that can be used by the heater controller.

Solar power is predicted one step ahead by an LSTM model at a sampling interval of 10 s. At every update, the controller recalculates how much energy still has to be stored and distributes the corresponding charging demand over the estimated remaining sunlight.

Three strategies are compared. Strategy A1 represents conventional operation: the battery receives the available charging power, and the heater follows threshold logic. Strategy A2 keeps the same heater rule but applies forecast-based charging-current spreading. Strategy A3 uses the same charging algorithm as A2 and replaces the thermostat with predictive heater control. Separating the cases in this manner allows the influence of charging control to be identified from A1 to A2, and the additional influence of heater scheduling from A2 to A3.

For A3, two temperature trajectories are calculated at each control update, one with the heater off and one with it on. The prediction interval is bounded by a selected maximum horizon and by the remaining sunlit time. For each trajectory, the controller accumulates the predicted temperature deficit below its reference level. Heating is requested when the reduction in this deficit is large enough to justify the action. The method is deliberately simple: it anticipates the slow thermal response but does not require a continuous optimization of heater power.

Two representative operating conditions are evaluated: a nominal cold case and a harsher cold case. Performance is reported through root mean square (RMS) charging current, heater energy, time spent charging below the reporting temperature, and an electro-thermal severity indicator. The last quantity accumulates charging current multiplied by the temperature shortfall during cold charging. It is used only to compare control strategies and is not interpreted as a cell ageing or lifetime model.

Results and Discussion

Table I shows that the forecast-based charging method provides the main reduction in electrical stress. In the nominal case, A2 lowers RMS charging current from 0.34 A to 0.16 A, corresponding to a 53% decrease. In the harsher case, the reduction is from 0.33 A to 0.19 A, or 42%. The A3 values remain nearly identical to A2: 0.17 A in the nominal case and 0.19 A in the harsher case. Predictive heating, therefore, does not cancel the benefit obtained from spreading the charging demand.

TABLE I. Key effects of predictive charging and predictive heating

Case	RMS A1 [A]	RMS A2 [A]	RMS A3 [A]	Cold time A2 / A3 [min]	Heater energy A2 / A3 [Wh]
Nominal	0.34	0.16	0.17	0.2 / 0	4.97 / 7.39
Harsher cold	0.33	0.19	0.19	3.5 / 0	12.94 / 15.10

The difference between A2 and A3 is most evident in the low-temperature indicators. Threshold heating leaves 0.2 min of cold charging in the nominal scenario and 3.5 min in the harsher scenario. With predictive heating, both values fall to zero, and the electro-thermal severity indicator is also reduced to zero. The controller achieves this by starting the heater before the temperature boundary is reached, using the remaining sunlight as advance information.

The improvement has an energy cost. Relative to A2, A3 increases heater consumption by 2.42 Wh in the nominal case and 2.16 Wh in the harsher case. The relative increase is about 49% and 17%, respectively. This is the central trade-off of the proposed coordination: a modest amount of additional electrical energy is used to remove the residual charging exposure below the selected temperature. The preferred setting will depend on the spacecraft energy margin, heater sizing, battery chemistry, and the temperature at which charging restrictions are imposed. However, the heater's energy is primarily sourced from surplus solar power, thus, not significantly impacting the overall spacecraft energy budget.

Conclusions

Coordinating charging-current distribution with anticipative heating addresses two battery stresses that occur together in cold CubeSat operation. Forecast-based charging reduced RMS current by 42–53% compared with conventional charging. Adding the predictive heater removed the remaining cold-charging intervals in both evaluated scenarios while preserving the current reduction. The required heater energy increased by approximately 2.2–2.4 Wh relative to threshold heating. These results support a control architecture in which charging and thermal management share the same forecast and orbital timing information, rather than acting as independent subsystems.

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The European Lithium-Ion Battery Market: Challenges and Opportunities

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The aim of this work is to present an overview of the global and European Li-ion battery market. The analysis aims to assess future market opportunities and technological challenges while addressing original equipment manufacturer (OEM) expectations and European Union sustainability standards. Based on excessive market data and industry forecast, the report highlights the rapid growth of Li-ion battery demand driven primarily by electric vehicles and increasingly by stationary energy storage systems supporting renewable energy integration. Global battery demand is expected to expand significantly with market value projections exceeding USD 300 billion and production capacities reaching several terawatt-hours annually.

The rapid development of electromobility, renewable energy systems, and digital technologies has significantly increased the global demand for lithium-ion batteries, making them one of the most strategic technologies supporting the transition toward a low-carbon economy. Within the framework of the European Green Deal and the objective of achieving climate neutrality by 2050, the European Union has recognized battery production as a key industrial sector essential for ensuring energy security, industrial competitiveness, and technological sovereignty. At the same time, the European battery market faces numerous economic, technological, geopolitical, and environmental challenges that may determine its future development.

This presentation aims to analyze the current state of the European lithium-ion battery market by identifying its main drivers, challenges, and future opportunities. Particular attention will be paid to the structure of the European battery value chain, covering the extraction and processing of critical raw materials, the production of battery components and cells, battery pack assembly, second-life applications, and recycling processes. The presentation will discuss the European Union's efforts to establish a resilient and competitive battery ecosystem while reducing its dependence on imported raw materials and battery technologies, particularly from Asian markets.

The analysis will address several critical issues affecting the sector. These include limited domestic availability of lithium, cobalt, nickel, and graphite, growing global competition, rising energy and manufacturing costs, supply chain disruptions, and increasingly stringent environmental and sustainability regulations.

The presentation will also consider the position of Poland within the European battery ecosystem. As one of the leading battery manufacturing locations in Europe, Poland plays an increasingly important role in the production of lithium-ion batteries and battery components, while simultaneously facing challenges related to innovation, supply chain resilience, and sustainable industrial development.

Moreover, a significant challenge in the battery market is the implementation of requirements arising from the Battery Regulation (EU) 2023/1542, which introduces a comprehensive framework supporting the transition toward a sustainable and circular battery economy. The regulation establishes requirements concerning battery durability, carbon footprint, responsible sourcing of raw materials, recycled content, collection efficiency, and recycling performance. It also defines ambitious recovery targets for critical materials, including lithium, and promotes improved battery design to facilitate repair, reuse, and recycling.

The study concludes that although Europe continues to face considerable structural challenges, the ongoing transformation of the battery sector creates substantial opportunities for technological innovation, industrial growth, and sustainable economic development. Strengthening domestic production capacities, diversifying critical raw material supplies, promoting circular economy practices, and investing in advanced battery technologies will be essential for enhancing Europe's strategic autonomy and maintaining its global competitiveness in the rapidly evolving battery industry.

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Safety Requirements and Standards for Lithium-Ion Cells Batteries

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Lithium-ion batteries have become essential components of electric vehicles, renewable energy storage systems and portable electronic devices. Despite their widespread use, Li-ion batteries are classified as dangerous goods (UN Class 9) due to potential hazards such as fire, explosion, thermal runaway, toxic gas release and environmental contamination. Consequently, their manufacture, testing, transport, use and end-of-life management are subject to extensive international and European regulatory frameworks designed to ensure safety and sustainability throughout the battery lifecycle. This presentation provides an overview of the principal standards and regulations governing lithium batteries with particular focus on transportation safety, certification requirements, sustainability criteria and the implementation of the new EU Battery Regulation.

Lithium-ion batteries have become the dominant energy storage technology for portable electronics, electric vehicles, and stationary energy storage systems due to their high energy density, long cycle life, and excellent electrochemical performance. However, their widespread deployment has also highlighted the critical importance of ensuring operational safety throughout the entire battery lifecycle. Failure mechanisms such as thermal runaway, internal short circuits, mechanical damage, overcharging, and exposure to extreme environmental conditions may result in severe safety hazards, including fire and explosion.

This presentation provides an overview of the fundamental safety requirements governing lithium-ion cells and battery systems, with particular emphasis on internationally recognized standards and testing procedures. European regulations are largely aligned with international standards while incorporating additional requirements related to quality management, environmental protection, and product traceability. Key standards include EN IEC 62281 for the safe transport of lithium cells and batteries or IEC 62660 series applicable to electric vehicle batteries. These standards define test procedures and acceptance criteria for battery performance, reliability, electrical safety, abuse tolerance, and post-crash safety. International transport requirements are based on the United Nations Manual of Tests and Criteria (UN 38.3), which mandates comprehensive safety testing before lithium cells and batteries can be transported by road, rail, sea or air. These tests are intended to demonstrate battery resilience under conditions that may occur during transport. Examples include altitude simulation, thermal cycling, vibration testing, mechanical shock, external short-circuit testing, impact and crush testing, overcharge testing, and forced-discharge testing. In addition, manufacturers often conduct abuse tests such as nail penetration, thermal runaway, fire exposure, and crush tests to evaluate battery behavior under extreme failure conditions [1][2][3].

This work further discusses the introduction of the Battery Passport, which will become mandatory from February 2027 for electric vehicle batteries, industrial batteries above 2 kWh, and batteries used in light means of transport. The Battery Passport will provide digital access to detailed information regarding battery origin, material composition, manufacturing data, carbon footprint, recycled content, safety characteristics, state of health, and lifecycle history through a QR-code-based system. This digital traceability tool is expected to enhance transparency, regulatory compliance, resource efficiency, and sustainable supply chain management across the European battery industry.

Finally, battery safety evaluation methodologies are reviewed, including UN transport testing and the EUCAR Hazard Level classification system, which is widely used to assess the severity of battery failures during abuse testing. Together, these regulations and standards establish a comprehensive framework that integrates safety, environmental responsibility, performance, and traceability, supporting the safe deployment and sustainable development of lithium battery technologies in Europe and beyond.

Acknowledgments

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Electrochemical Impedance Spectroscopy for Battery Systems: Transport, Kinetics, and Aging

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Introduction

Electrochemical impedance spectroscopy (EIS) is a powerful tool for characterizing batteries, enabling deconvolution of transport and reaction processes across wide time scales. However, quantitative interpretation remains challenging due to the intrinsic coupling of multiple physical processes—charge transfer, solid-state diffusion, ionic migration, and double-layer charging – all contributing simultaneously [1][2][6].

Our group developed a physics-based Transmission Line Model (TLM) derived from Poisson-Nernst-Planck equations, accounting for transport of electrons, lithium ions, and anions on three separate, coupled rails [1][3]. This contribution presents a systematic methodology for extracting physically meaningful parameters from impedance spectra of Ni-rich NMC cathodes, covering model development, verification, tortuosity determination, and cell format effects relevant to aging studies.

Experimental

Ni-rich NMC cathodes ($\text{LiNi}_{0.84}\text{Mn}_{0.06}\text{Co}_{0.10}\text{O}_2$) were harvested from commercial LG 18650 cells. Symmetric NMC-NMC cells were prepared by pre-cycling two cathodes in pouch half-cells against Li metal to SoC = 0.5, followed by reassembly into symmetric coin or pouch cells [4]. Coin cells used 14 mm electrodes, glass microfiber separators, and 72 μL of 1 M LiPF_6 in EC/EMC = 3:7 wt%. Non-intercalating salt experiments used TBAClO_4 in EC:DMC = 1:1 at 10 - 700 mM [4].

EIS was performed from 1 MHz to 0.1 mHz (5 mV) at 24.0 °C. Microstructural characterization included SEM-EDX, FIB-SEM, and X μ CT (1.0 μm voxel size). Impedance data were analyzed using our physics-based TLM [1][3], which accounts for R_A , R_{CT} , C_{dl} , ionic migration resistances (R_{03} , R_{05}), chemical capacitances (C_{04} , C_{14}), separator resistances (R_{13} , R_{15}), and solid-state Warburg diffusion (R_W , C_W). Fitting was performed in Python, with R_W and C_W pre-determined to overcome non-identifiability [2][4][6].

Results and Discussion

Model Validation and Scaling Verification

The TLM was validated through systematic experiments at three LiPF_6 concentrations (1 M, 0.1 M, 0.01 M). Decreasing salt concentration deconvoluted coupled low-frequency features, enabling identification of all six theoretically predicted impedance sections. Only the upgraded TLM (uTLM), which includes anion transport and chemical capacitances, reproduced the full low-frequency response—including

diffusional contributions from electrolyte in electrode pores and separator – while the conventional de Levie model could not [3].

Using NMC cathodes with mass loadings from 2 to 58 mg per 2 cm², we verified theoretically predicted scaling laws for all model parameters [2][6]. Electrode geometry governs detectability of individual impedance contributions; only a subset emerges above the measurement sensitivity threshold for a given mass loading. An unexpected additional diffusion feature—predominantly visible in thin electrodes—was attributed to ion diffusion within micropores inside NMC aggregates. The scaling-based normalization enabled rapid estimation of total chemical insertion capacitance (C_{total}) from mass-normalized Nyquist plots. We confirmed that C_{total} from low-frequency EIS quantitatively equals differential capacitance $C_d(x)$ from the equilibrium OCV curve, demonstrating that low-frequency EIS directly probes thermodynamic properties of single-phase insertion materials.

Tortuosity Determination and Diagnostic Capabilities

A key application is direct determination of electrode tortuosity from standard Li-ion cells without specialized reaction-blocking conditions [4]. Traditional methods require non-intercalating salts or extreme states of charge, which do not reflect functional battery chemistry. Our Full Insertion TLM decouples transport and reaction processes at any SoC. Through sensitivity analysis, we identified R_W and C_W as the primary source of non-identifiability; by pre-determining these values, we achieved stable extraction of all remaining parameters.

Validation through three independent pathways showed excellent agreement: X μ CT analysis gave $\tau_{\text{geo-eff}} = 4.2\text{--}4.4$ (accounting for pore constriction); non-intercalating salt EIS gave $\tau_{\text{EIS}}^0 = 3.5 \pm 0.2$; and Full Insertion TLM gave $\tau_{\text{EIS (LiPF}_6\text{)}} = 3.0 \pm 0.3$. The agreement confirms reliable tortuosity determination from functional cells. The method simultaneously extracts R_{CT} , C_{DL} , R_A , and chemical capacitances—providing a comprehensive diagnostic profile.

Cell Format Effects and Aging Implications

Pouch cells showed higher apparent tortuosity ($\tau \approx 5.2$) than coin cells ($\tau \approx 3.0$) despite identical electrodes and electrolyte. Controlled vacuuming confirmed that EMC evaporation during pouch sealing alters electrolyte composition, artificially increasing tortuosity. This provides a model for aging-related electrolyte decomposition, where similar changes occur in aged cells. Importantly, TLM analysis can distinguish genuine electrode degradation (increased R_{CT} , R_W) from electrolyte-related changes.

Cell Format Effects and Aging Implications

For quantitative interpretation, we address the relation between PNP-based TLM and Concentrated Solution Theory (CST). PNP-based models are strictly valid under ideality and infinite dilution assumptions—violated in real concentrated electrolytes [5]. We developed a framework for translating PNP-derived electrolyte parameters into CST-consistent quantities. The cation transference number, for example, differs between frameworks due to non-ideal interactions. Using representative Li-ion electrolytes, we demonstrate that this alignment is essential for physically sound interpretation of impedance-derived parameters.

Conclusions

We developed and validated a physics-based TLM for quantitative EIS analysis of porous battery electrodes. The upgraded TLM captures low-frequency diffusional contributions overlooked by conventional models. Scaling laws were verified using electrodes with varying mass loadings. Tortuosity was determined directly from functional cells ($\tau = 3.0 \pm 0.3$), validated against X μ CT ($\tau \approx 4.2 - 4.4$) and non-intercalating salt methods ($\tau = 3.5 \pm 0.2$). The method simultaneously extracts R_{CT} , C_{DL} , R_A , and chemical capacitances. Solvent evaporation during pouch sealing was identified as a source of artificially increased tortuosity, providing a model for aging-related electrolyte decomposition. A framework for translating PNP-derived parameters into CST-consistent quantities was established. The methodology offers a practical toolkit for in-situ characterization of transport and reaction processes in working battery electrodes.

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Design and Development of an Electrochemical Test Cell for Energy Storage Research

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The development of electrochemical energy storage systems relies on new and advanced electrode, electrolyte, and separator materials that offer higher energy density, longer cycle life, improved power capability, and safety. Consequently, there is an increasing need not only for the synthesis of novel materials but also for reliable methods to characterize their electrochemical properties. In this work, we would like to show the features of a unique test device, EMU, and compare it to commercially available test cell. The device matches the qualities of high-end commercial test devices and even offers additional features and advantages.

Introduction

Continuous improvements in batteries (BT) and supercapacitors (SC) rely on the development of advanced electrode, electrolyte, and separator materials that offer higher energy density, longer cycle life, improved power capability, and safety. Consequently, there is an increasing need not only for the design and synthesis of novel materials but also for reliable and standardised methods to characterise their electrochemical properties [1]. A wide variety of commercial instruments from different manufacturers are currently on the market. However, none of these systems fully satisfied our experimental requirements. For a complex development of BT and SC materials and full cell testing we formulated following requirements: BT and SC galvanostatic cycling, characterization via fundamental electrochemical techniques, adjustable applied force with force and temperature monitoring, the possibility of cycling in a climate chamber, in situ thickness measurement, conductivity measurement of powder materials and separators [2][3].

The test cell we developed is a Swagelok type cell, and we call it the EMU cell. It is equipped with built-in heating, interchangeable cartridges for faster manipulation, and the possibility to press samples into pellets with a pressure of over 30 MPa. The cartridges are airtight, meaning they can be taken out of the glovebox once they are assembled. This design received a positive review for patent claims and is expected to receive national patent protection.

In this work, we would like to compare it to commercially available test cell for BT and SC materials research and show the features of the device we developed.

Experiment

To verify the electrical response and test the design of the EMU cell, several key measurement methods were compared using the EMU cell and a commercially available Controlled Environment Sample Holder (CESH-e) from Biologic.

The two cells were measured under short circuit conditions to establish the intrinsic resistance of the devices. The series resistance was comparable at 185 and 249 m Ω in EMU and CESH-e, respectively. With the CESH-e cell measured in a 4-terminal setup, the inductive component was eliminated and the resistance dropped to 1.4 m Ω (Figure 1C). This is particularly important for very low resistivity materials and cells.

Testing of SCs and BTs in full-cell configuration was one of the essential requirements for the device. The SC was activated carbon-based with 6M KOH aqueous electrolyte. Both shape of the CV curve and capacitance values obtained from the cells are comparable confirming good functionality of EMU cell in real conditions (Figure 1D, E).

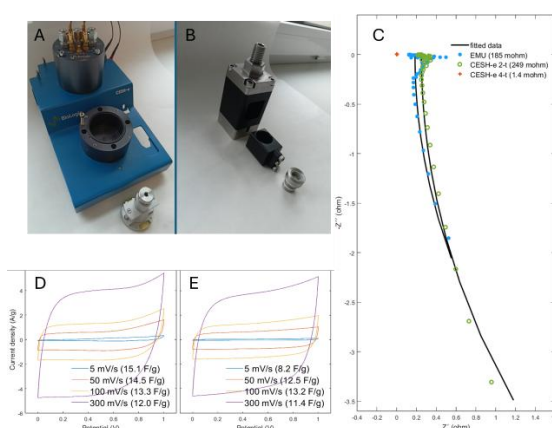


Figure 1. Picture of CESH-e (A) and EMU (B). Nyquist plot of CESH-e and EMU cells under short circuit conditions (C). CV curves of SCs in CESH-e (D) and EMU cell (E).

Based on the verification measurements, some improvements will be made to the design of the EMU cell. It will be equipped with 4 terminals for very high conductivity samples, and a ground connection will be added to ensure safety.

Other than that, the EMU compares to the commercial device and offers some additional functionalities. A simple modular design of the EMU also allows modifications of the size and geometry of the inner cell, or the material of the cell to fit specific experimental requirements.

Once the functionality was established, the measurement capabilities of this device were explored. Since the instrument's measurement techniques are numerous, we have only managed to use and test some of its functionalities so far and they are presented below.

Separator is a key component of any BT or SC. The MacMullin number (N_m) was measured for filter paper and glass fiber separators. CESH-e was used again to verify the results. The separators were measured in the presence of 6M KOH. The conductivity values and subsequently the N_m provided by EMU and CESH-e are comparable, as shown in Table I. The difference in conductivity values provided by EMU and CESH-

e is about 10 % and CESH-e provided slightly higher conductivity values, which could be explained by its 4-terminal setup with lower intrinsic resistance (Figure 1C).

TABLE I. MacMullin number of Filter paper and Glass membrane in EMU and CESH-e.

Separator	Cell	Conductivity [mS cm^{-1}]	N_m
Glass membrane	EMU	585	0.99
	CESH	636	0.91
Filter paper	EMU	131	4.42
	CESH	158	3.66

The pressure applied during assembly is a critical parameter for the overall performance of supercapacitors. During this experiment, the external pressure varied from 0.2 to 11 MPa. The capacitance increases steadily with the applied pressure up to 5.5 MPa. When the pressure is doubled from 5.5 to 11 MPa, capacitance increases only from 19.9 to 20.9 F/g (Figure 2A). Optimal assembly pressure was found to be 5.5 MPa.

The conductivity of non-activated and activated carbon powders was measured in the temperature range of 20 – 100 °C. The conductivity of both materials increases with temperature (Figure 2B, C), which is consistent with literature (4).

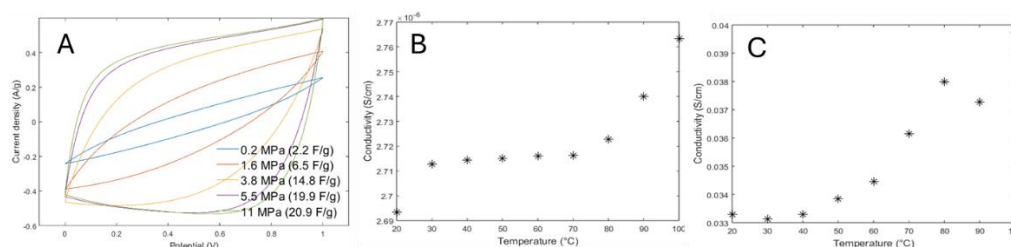


Figure 2. CV curves at different pressures of AC based SCs (A). Conductivity of non-activated (B) and activated carbon (C) at various temperatures.

Conclusion

The presented EMU cell is a device suitable for BT and SC research, as demonstrated by numerous results and comparative testing. It provides functionalities of several devices, offering BT and SC galvanostatic cycling, characterisation via fundamental electrochemical techniques, adjustable external force with force and temperature monitoring, in situ thickness measurement and multiple interchangeable cartridges, among other features. The device matches the qualities of a high-end commercial test device and even offers some advantages.

The objective of developing a testing device for the research and evaluation of BT and SC materials was successfully achieved, and the device will continue to be further developed and utilised in future research.

Acknowledgements

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Cathode Materials Development Using In-Situ Scanning Electron Microscopy

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In-operando scanning electron microscopy (SEM) has emerged as an effective approach for investigating Li-ion batteries [1]. By allowing direct, real-time visualization of dynamic reactions occurring within battery materials, this technique provides valuable insight for improving Li-ion battery performance. Within the broader range of operando methods, in-situ heating is particularly useful because it enables observation of structural evolution in materials, which is essential for clarifying growth mechanisms [2][3]. Nevertheless, relatively little attention has been given to the synthesis of Li-ion battery materials under in-operando SEM conditions. One major limitation is that conventional heating stages generally cannot introduce reactive gases during experiments, making it difficult to reproduce realistic synthesis environments.

This work presents the use of a MicroReactor device (Figure 1) [4][5], which enables source materials to be heated under controlled gas atmospheres, to investigate the synthesis pathway of single-crystal $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) cathode materials. The system uses a MEMS heating plate (Figure 1(a) and (b)) to heat the sample, while an aperture in the MicroReactor lid serves as an observation window (Figure 1(c) and (d)). This configuration allows SEM imaging of the sample while preventing residual gases in the SEM chamber from entering the in-situ reaction environment. The MicroReactor can sustain pressures of up to 300 Pa in the sample region during reaction while keeping the main SEM chamber isolated at pressures below 1.5×10^{-2} Pa. For battery materials that are sensitive to air or moisture, the MicroReactor also supports an inert-gas sample transfer workflow to minimize contamination during handling and transfer (Figure 1(e)). To demonstrate the applicability of the MicroReactor for studying single-crystal NMC growth, a three-stage experimental strategy was used. First, $\text{Ni}_{0.9}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$, hereafter referred to as $\text{TM}(\text{OH})_2$, was heated under 300 Pa oxygen to examine its decomposition into $\text{Ni}_{0.9}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (TMO). As shown in Figure 2, the precursor was successfully converted from $\text{TM}(\text{OH})_2$ to TMO, and the final morphology matched the expected TMO structure [6].

Next, the synthesis of single-crystal $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) was investigated by combining TMO with the conventional lithium source LiOH on the MEMS heating plate, followed by heating in 300 Pa oxygen. Figure 3 presents the heating sequence and shows the formation of an NMC monocystal from the TMO–LiOH mixture. The development of a large agglomerated single-crystal cluster through repeated heating steps using LiOH as the lithium source is consistent with previous findings [7]. These observations further demonstrate that the MicroReactor is suitable for developing and analyzing cathode synthesis processes.

Finally, Li_2O , which has a high melting point of 1438 °C and is typically regarded as unsuitable for cathode synthesis, was evaluated as a lithium source for single-crystal NMC formation [8]. Figure 4 captures the in-operando reaction between Li_2O and $\text{TM}(\text{OH})_2$. Unexpectedly, Li_2O was observed to begin sublimating above 700 °C. The resulting Li_2O vapor was able to penetrate the pores of TMO and promote the formation of crystalline NMC811 at temperatures far below the melting point of Li_2O . Based on these observations, a distinct growth mechanism is proposed in which Li_2O vapor assists the formation and separation of single crystals. This approach was also

successfully applied to convert spent polycrystalline NMC811 into well-separated single crystals.

Overall, this study demonstrates that in-situ SEM performed within the clean and well-controlled environment of the MicroReactor is a powerful method for investigating and optimizing both manufacturing and recycling processes for battery materials. The small quantity of required source materials, rapid adjustment of experimental parameters such as gas composition, gas pressure, and sample temperature, and the ability to image sample responses in real time make in-situ SEM a highly efficient platform for advancing research in this field.

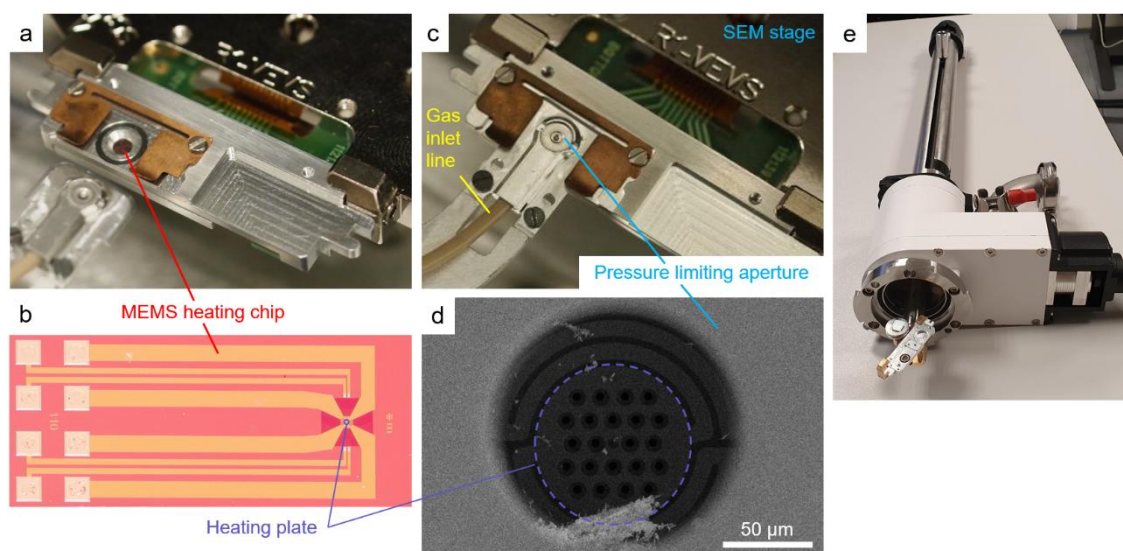


Figure 1. (a) MicroReactor base mounted on the SEM stage; (b) MEMS chip for sample heating and biasing; (c) removable lid equipped with a gas delivery line; (d) pressure-limiting aperture in the lid used as an SEM imaging window; and (e) CleanConnect transfer device enabling transfer of the MicroReactor base into the SEM under argon atmosphere.

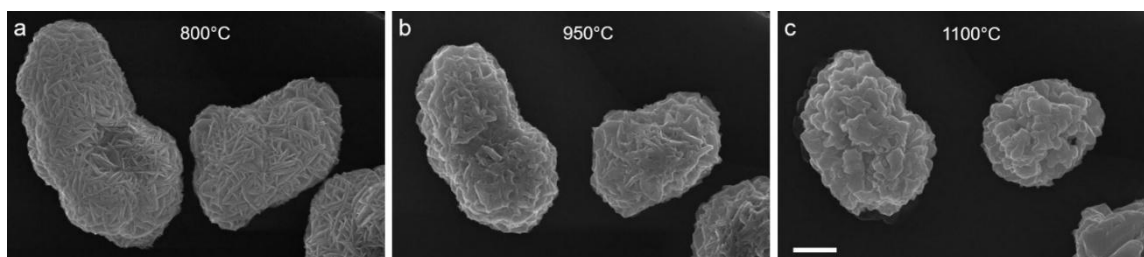


Figure 2. Heating TM(OH)₂ under an oxygen atmosphere of 300 Pa leads to its decomposition into TMO. The experiment was performed using the MicroReactor in a Helios UC DualBeam system. Secondary electron signals were acquired with a TLD (in lens) detector at a landing energy of 20 keV and a primary beam current of 200 pA. The scale bar corresponds to 1 μm. [9]

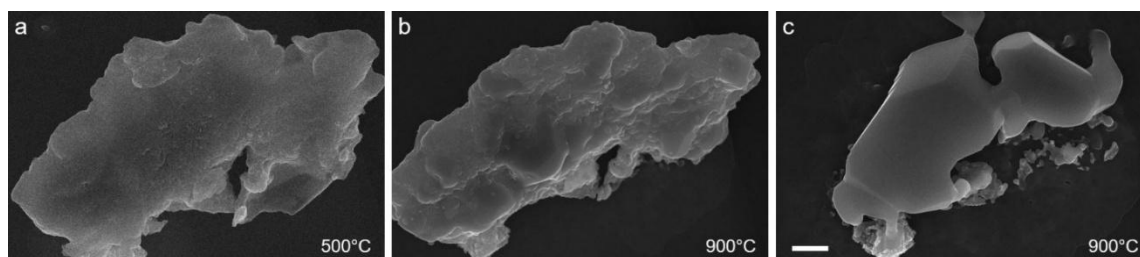


Figure 3. A TMO + LiOH sample prepared by high-temperature melting was heated under 300 Pa oxygen to synthesize single-crystal NMC. (a) No notable morphological changes were observed during heating from room temperature to 500 °C; (b) crystal formation began at 900 °C; and (c) after 70 min at 900 °C, most of the starting material had transformed into monocrystalline NMC811. The scale bar corresponds to 1 μm . SEM imaging conditions: Helios UC, TLD-SE, 20 keV, 25 pA. [10]

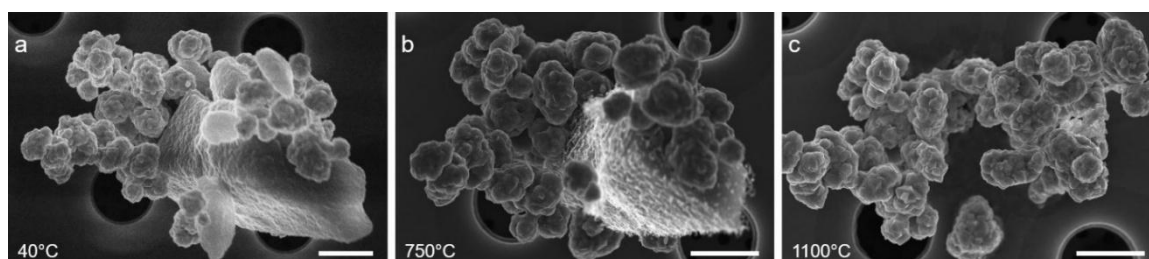


Figure 4. TMO particles and a Li_2O particle were heated under an oxygen atmosphere of 300 Pa. (a) Initial mixture of TMO and large Li_2O particles; (b) Li_2O sublimation at 750 °C; and (c) fully transformed single-crystalline NMC. The scale bar corresponds to 5 μm . SEM imaging conditions: Helios UC, TLD-SE, 15 keV, 25 pA. [11]

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Degradation-Resolved Electro-Thermal Characterization of High-Power Lithium Ion Cells for Physics-Informed Sensorless Internal Temperature Estimation

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Accurate internal temperature estimation requires electro-thermal models that remain valid throughout battery aging. This work addresses this challenge through a degradation-resolved electrothermal characterization of high-power lithium-ion cells. Molicel P45B cells (silicon–graphite anode, NCA cathode) were investigated at four states of health (100%, 90%, 85%, and 80% SOH). Across all degradation levels, resistance increased linearly by 1.5 mΩ per 10% SOH loss, revealing a single consistent ohmic trajectory. This enables SOH-aware internal temperature estimation from measured resistance alone. A two-dimensional thermal model was developed using only these electro-thermal parameters. Blind prediction of core temperature achieved an RMSE of 0.68 °C, while surface temperature across eight cells under dynamic drive-cycle loading was reproduced with an RMSE of 0.58–0.73 °C. Together, these results provide the experimental foundation for a physics-informed neural network for sensorless internal temperature estimation.

Introduction

In commercial lithium-ion batteries, battery management systems (BMSs) can typically measure only the cell surface temperature (T_{surf}), while the internal cell temperature (T_{int}) remains inaccessible. However, T_{int} governs degradation rates, lithium-plating risk, and the onset of thermal runaway. In high-power cylindrical cells, the core-to-surface temperature gradient can reach up to 10 °C during high-rate operation, highlighting the importance of accurate core-temperature estimation (1,2). A key limitation of existing estimators, including Kalman-filter observers based on lumped-parameter models and machine-learning approaches, is that they are typically parameterized and validated using fresh cells (2,3). As cells age, increasing internal resistance (R_{int}) leads to greater heat generation and reduced temperature-estimation accuracy, precisely when accurate T_{int} estimation is most critical (4). This paper addresses this gap by providing a degradation-resolved characterization of high-power cells. A measurement-parameterized thermal model is validated using internally instrumented reference cells and serves as the foundation for a physics-informed neural network (PINN) for T_{int} estimation.

Methodology

Eight MoliceL INR21700-P45B (P45B) cells (4.3 Ah min, 45 A rated) were prepared at four States of Health (SOH) levels (two cells for each level): [100, 90, 85, 80] %. Cells were aged by elevated-temperature cycling (40 °C) and characterized using a Neware CT-9008 inside a thermal chamber equipped with three spatially distributed ambient temperature probes and surface thermocouples calibrated to ± 0.2 °C using the ice-point method.

The experimental campaign comprised quasi-OCV mapping (C/20, 10% State of Charge, SOC increments), reference capacity tests, hybrid pulse-power characterization (12 A/6 A pulses at 10% SOC decrements), convection calibration from chamber transition transients, axial temperature mapping during a 12 A discharge, and constant current (CC) and WLTP-like drive-cycle tests at 25 °C. Two additional P45B cells instrumented with embedded thermocouples were independently tested at Coventry University for model validation.

Results

Electro-thermal characterization reveals that cell degradation follows a single, path-independent mechanism. The normalized aging marker collapses onto a common trend across all examined degradation states (Figure 1a). Both ohmic resistance (R_{1s}) and heat generation ($\dot{q}$) increase linearly with capacity loss, with resistance rising by 1.5 m Ω per 10% SOH loss (Figure 1b). This predictable behavior implies that SOH-aware internal temperature estimation can be formulated as a well-posed problem relying solely on noninvasive resistance observables.

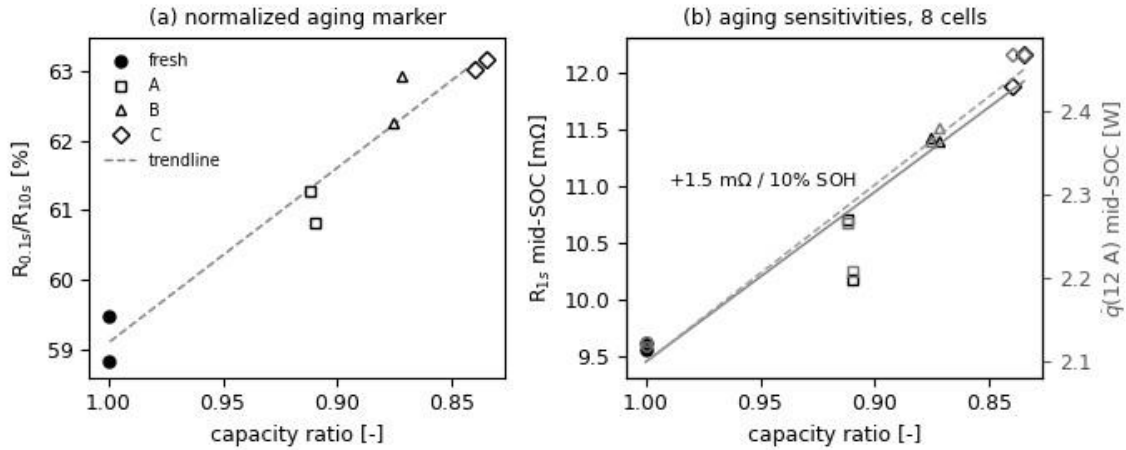


Figure 1. Characterization of the aging mechanism. (a) Normalized resistance marker showing a unified trend across all degradation levels. (b) Ohmic resistance and heat generation sensitivities demonstrate a consistent linear increase of +1.5 m Ω per 10% SOH drop.

In cross-lab blind validation, the model predicted the core temperature of an internally instrumented cell under 3 C-rate pulse loading with an RMSE of 0.68 °C, accurately reproducing the transient thermal response (Figure 2a). The model further generalized across all eight cells during dynamic drive-cycle testing, reproducing surface temperature with an RMSE of 0.58–0.73 °C without cell-specific tuning (Figure 2b). These results establish a validated framework for generating pseudotags and physics constraints for physics-informed neural network estimators.

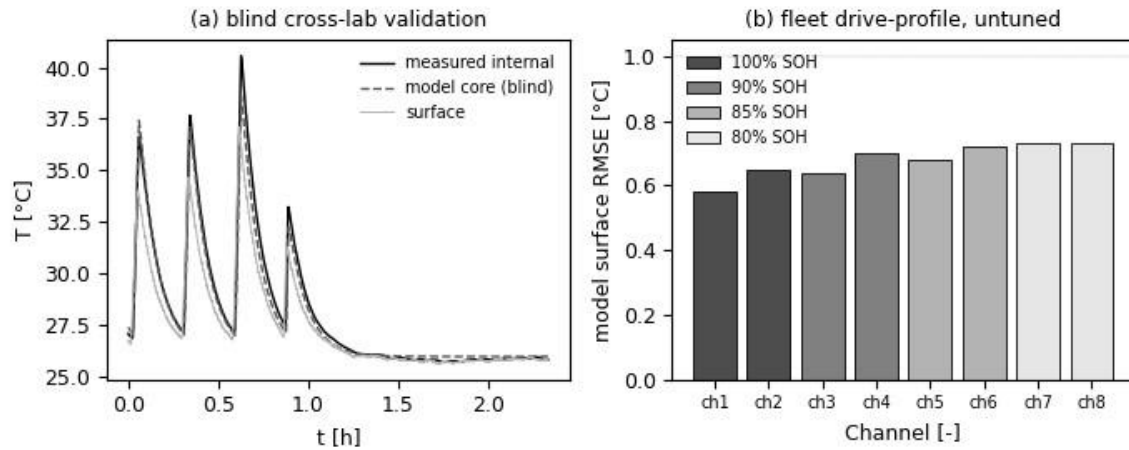


Figure 2. Validation of the electro-thermal model. (a) Blind prediction of the core temperature against an internally instrumented cell under pulse loads (0.68 °C RMSE). (b) Untuned fleet validation demonstrating 0.58–0.73 °C surface temperature RMSE across eight degraded cells during dynamic drive cycles.

Conclusion

This study presents a degradation-resolved electro-thermal characterization and validated thermal model for high-power 21700 cells. The derived thermal model was crossvalidated internally using twin cells and externally through blind prediction of instrumented cells, achieving a core-temperature RMSE of 0.68 °C. Cell aging followed a single, consistent ohmic trajectory, enabling SOH-aware internal temperature estimation from surface measurements. The validated model provides pseudolabels and physics constraints for training a physics-informed neural network. The performance of the resulting estimator under unseen conditions will be presented at the conference.

Acknowledgments

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Life Cycle Assessment of Industrial Black Mass Production from Spent Lithium-Ion Batteries

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The recycling of spent lithium-ion batteries (LIBs) is essential to secure critical raw materials and support circular battery value chains. This study evaluates the environmental performance of industrial black mass (BM) production through a gate-to-gate life cycle assessment using primary operational data from a Polish recycling facility. The climate change impact was estimated at 1.37 kg CO₂-eq/kg BM. Electricity consumption was the main environmental hotspot, contributing approximately 78% of total greenhouse gas emissions, while mechanical separation, shredding, and evaporation-drying were identified as the most impactful process stages. Replacing grid electricity with photovoltaic electricity reduced climate change impacts by approximately 91%, highlighting the importance of renewable energy integration for improving the environmental performance of LIB recycling and supporting circular battery value chains.

Introduction

The rapid expansion of electric mobility, energy storage technologies, and the ongoing electrification of energy systems is leading to a significant increase in the demand for lithium-ion batteries (LIBs). Consequently, large quantities of spent batteries are expected to emerge over the coming decades as batteries currently in use reach their end of life, creating both environmental challenges and opportunities for the recovery of critical raw materials. Efficient recycling of spent LIBs is therefore essential to support the transition towards circular battery value chains and reduce dependence on primary raw materials. Mechanical pretreatment constitutes a key step in battery recycling, producing black mass (BM), a valuable intermediate material enriched in graphite, lithium, nickel, cobalt, and manganese, which serves as the primary feedstock for downstream recovery processes.

Although several environmental assessments of LIB recycling have been reported in the literature, most rely on laboratory-scale data or generic life cycle inventories. Industrial-scale studies based on primary operational data remain scarce. Therefore, the present work aims to evaluate the environmental performance of industrial-scale black mass production at a recycling facility in Poland and identify the main environmental hotspots and improvement opportunities associated with the process.

Methodology

Study Goal and Scope

This study evaluates the environmental performance of black mass (BM) production from spent lithium-ion batteries (LIBs) using the Life Cycle Assessment (LCA) methodology in accordance with ISO 14040 [1] and ISO 14044 [2]. A gate-to-gate approach was adopted, covering the recycling process from the reception of spent LIBs at the recycling facility to the production of BM. The functional unit (FU) was defined as 1 kg of dry black mass, representing the main product of the mechanical pre-treatment process. Whenever possible, Polish conditions were used.

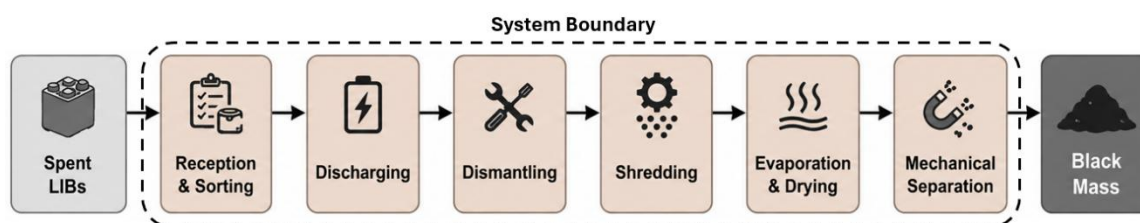


Figure1. System boundary for this study of black mass production from spent lithium-ion batteries.

Life Cycle Inventory

The inventory model was developed using primary operational data obtained from a recycling facility located in Poland. The recycling process comprises six main stages: (i) reception and sorting, (ii) discharging, (iii) dismantling, (iv) shredding, (v) electrolyte evaporation and drying, and (vi) mechanical separation. Material and energy flows associated with each operation were quantified and normalised to the defined functional unit. The use of primary industrial data enhances the representativeness of the assessment and enables a realistic characterisation of current industrial black mass production practices. Background data, including electricity generation and other upstream processes, were obtained from the ecoinvent v3.12 life cycle inventory database.

Life Cycle Impact Assessment

Environmental impacts were assessed using SimaPro v10.2 and the Environmental Footprint (EF) 3.1 method, following the recommendations of the Carbon Footprint Rules for Electric Vehicle Batteries (CFB-EV) [3]. The assessment included all impact categories recommended for battery systems under the EF 3.1 framework.

Results and Discussion

The life cycle inventory showed that approximately 1.35 kg of spent LIBs are required to produce 1 kg of dry BM. In addition to BM, the process generated Cu-Al fractions, polymeric materials, and fine dust as secondary output streams.

The climate change impact associated with the production of 1 kg of dry BM was estimated at 1.37 kg CO₂-eq. Electricity consumption was identified as the dominant contributor, accounting for approximately 78% of the total greenhouse gas emissions. Hazardous solvent treatment associated with electrolyte-related streams contributed approximately 13%, while compressed-air generation accounted for around 8%.

Mechanical separation was identified as the most environmentally intensive process stage, representing the largest contribution across most environmental impact categories. Shredding and evaporation-drying were the second and third largest contributors, respectively. Together, these three process stages accounted for approximately 80-90% of the total environmental impacts across all the assessed impact categories.

To investigate potential improvement opportunities, an alternative electricity supply scenario was evaluated. Replacing grid electricity with photovoltaic electricity resulted in a reduction of approximately 91% in climate change impacts. Substantial reductions were also observed in other impact categories, including acidification, eutrophication, freshwater ecotoxicity, and fossil resource depletion.

Conclusions

This work provides an industrial-scale environmental assessment of black mass production from spent lithium-ion batteries based on primary operational data. Electricity consumption was identified as the main environmental hotspot, followed by the treatment of electrolyte-derived streams and compressed-air generation. Mechanical separation, shredding, and evaporation-drying were identified as the most environmentally intensive process stages and should therefore be prioritised for process optimisation.

The scenario analysis demonstrated that integrating photovoltaic electricity can substantially reduce environmental impacts, particularly those related to climate change and fossil resource depletion. Overall, improving energy efficiency and increasing the share of renewable electricity are expected to deliver the greatest environmental benefits, while optimisation of compressed-air systems and electrolyte recovery technologies offers additional improvement potential. These strategies can contribute significantly to improving the environmental performance of black mass production and supporting the transition towards circular battery value chains.

Acknowledgments

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On Diagnostics of Automotive Battery Module by Electrochemical Impedance Spectroscopy: Influence of State of Charge

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This work investigated the influence of state of charge on dynamic EIS measurements of automotive NMC battery modules. The results confirmed that several equivalent circuit modeling parameters are affected by SOC, with the strongest and most consistent dependence observed for Q_2 and n_2 . The results show that EIS-based diagnostics should either be performed at a constant SOC or include SOC-dependent compensation.

Introduction

Lithium-ion batteries are an essential component of battery energy storage systems and have enabled the massive expansion of electromobility. One of the persistent challenges is their accurate and fast diagnostics. Due to manufacturing tolerances, cells exhibit different degradation behavior even under identical loading conditions. One of the methods that can be utilized for battery diagnostics is electrochemical impedance spectroscopy (EIS). This method allows to analyze the ongoing electrochemical processes separately, thereby obtaining comprehensive information about the battery state.

A drawback of this method is its sensitivity to both the environmental parameters of the measurement setup and the state of the battery itself. Y. Xiao¹ reports that as temperature increases from -20 °C to 20 °C, the absolute value of impedance decreases. A. Barai et al.² present that another parameter influencing the measurement results is the battery relaxation time. The State of Charge (SOC) of the battery at the time of measurement also affects the measured impedance values. S.S. Zhang³ and Q. Zhang⁴ state that the SOC is reflected in the impedance values measured at frequencies lower than 1 Hz, whereas the effect of SOC is negligible at frequencies above approximately 1 Hz. This contradicts the findings of Y. Xiao¹, who presented the influence of SOC across the entire measured frequency range (1 mHz – 10 kHz). Given these contradictions in the literature, this work focuses on the influence of SOC on the impedance response of the battery.

Methodology of testing

Experimental measurements were conducted on two Stellantis automotive battery modules with a capacity of 2.74 kWh, consisting of 12 NMC battery cells. To ensure a defined initial state, the entire module was first fully charged to 100% SOC. The module was then discharged using a constant current of 1C, which corresponded to 123 A.

EIS measurements were performed at predefined SOC levels, specifically at 10% intervals from 90% down to 10% SOC. During each EIS measurement, the continuous discharge current was reduced to 20 A. The EIS was performed using an AC current excitation signal with an amplitude of 10 A. The impedance spectra were recorded over

a frequency range from 0.1 Hz to 3000 Hz, with a measurement resolution of 10 points per decade.

The measured data were fitted using an equivalent circuit model (ECM) consisting of a series resistance, a series inductance and two parallel R-CPE elements.

Results

EIS spectra and ECM fitting

The measurement described above resulted in a total of 540 EIS datasets. The results show that the real part of the impedance in Nyquist plot increases at higher SOC levels, while the shape and size of the impedance arc change non-linearly. Larger arcs are observed at the extreme SOC levels, particularly at 10% and at 80–90% SOC.

SOC dependence of fitted parameters

The SOC dependence of each fitted ECM parameter was evaluated using a third-order polynomial regression. Table I shows that the most consistent SOC dependence was obtained for Q_2 , which reached high normalized R^2 values for the combined dataset and for both modules separately. A strong dependence was also observed for n_2 . These results indicate that the SOC-dependent variation is strongly reflected in the second R-CPE element. However, the physical interpretation of CPE-related parameters is less straightforward than for the resistance parameters.

The parameter R_1 also showed clear SOC dependence. The R_1 SOC dependence is illustrated together with Q_2 and n_2 in Figure 1.

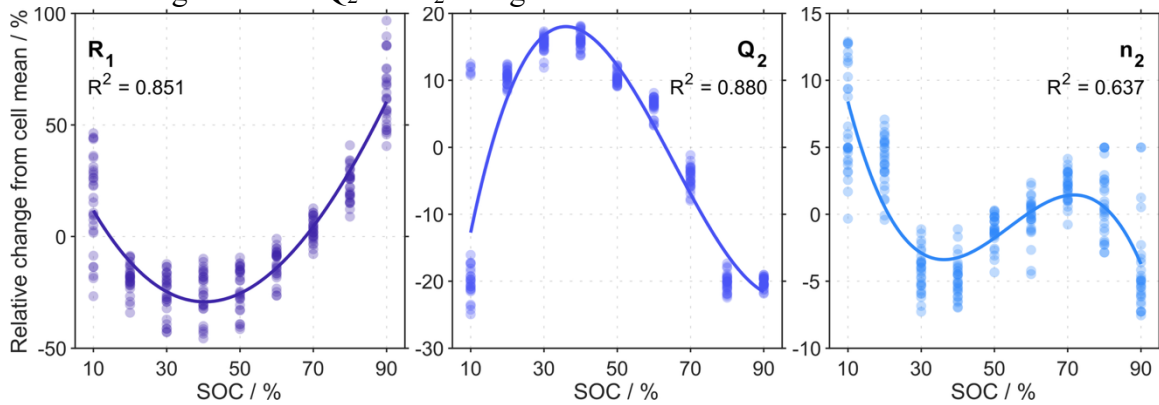


Figure 1. Normalized SOC dependence of ECM parameters R_1 , Q_2 , and n_2 , module A.

TABLE I. Normalized R^2 values of cubic SOC-dependent fits

Parameter	Modules A&B	Module A	Module B
R_s	0.126	0.643	0.29
L_s	0.007	0.045	0.149
R_1	0.32	0.851	0.427
Q_1	0.157	0.687	0.152
n_1	0.412	0.686	0.405
R_2	0.142	0.168	0.131
Q_2	0.909	0.88	0.959
n_2	0.66	0.637	0.728

SOC compensation model

For possible SOC compensation, cubic models were reported only for selected normalized parameters in the combined dataset. Therefore, Q_2 and n_2 were included due to their high normalized R^2 values, while R_1 was included because of its clearer physical interpretation and relation to charge-transfer processes.

The selected normalized parameter trends were described by

$$p_{\text{norm}}(\text{SOC}) = a\text{SOC}^3 + b\text{SOC}^2 + c\text{SOC} + d \quad [1]$$

where $p_{\text{norm}}(\text{SOC})$ is the normalized ECM parameter and (a), (b), (c), and (d) are the fitted coefficients. These models can be used to estimate the SOC-dependent contribution to the fitted parameters and may serve as a basis for future SOC correction. Table II shows calculated coefficients for both modules.

TABLE II. Cubic model coefficients of selected normalized ECM parameters for both modules combined

ECM parameter	a ($\times 10^{-4}$)	b ($\times 10^{-2}$)	c	d
R_1	-2.95	8.78	-5.80	78.5
Q_2	4.85	-9.16	4.64	-51.3
n_2	-2.57	4.07	-1.92	25

Conclusions

The results confirmed that several ECM parameters are affected by SOC, with the strongest and most consistent dependence observed for Q_2 and n_2 . The R_1 parameter also showed a clear SOC-related trend, especially in module A, and remains diagnostically relevant due to its clearer physical interpretation and relation to charge-transfer processes.

The results show that EIS-based diagnostics should either be performed at a constant SOC or include SOC-dependent compensation. However, the observed differences between modules indicate that a single global correction model may not be sufficient for all modules or cell groups.

Acknowledgments

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Coupling of CFD and PBM Techniques for Enhanced Particle Dynamics Modelling of Slurry Mixing

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Optimising the cell manufacturing process for Lithium-ion (Li-ion) batteries requires robust mathematical modeling and deep insight into internal physical processing phenomena. This work focuses on the proposed application of semi-analytical population balance modeling (PBM) coupled with computational fluid dynamics (CFD) to optimize electrode slurry production. We present semi-analytical PBM solutions to achieve high temporal accuracy and mesh-free computational efficiency during multi-compartmental slurry mixing. Bidirectional PBM-CFD coupling dynamically updates particle size distributions (PSD) and aggregation/breakage rates, offering a framework to reduce manufacturing costs and enhance electrode coating homogeneity.

Introduction

Lithium-ion batteries are a critical component in meeting global sustainable development goals and electric mobility targets [1][2]. However, key hurdles remain regarding processing efficiency and raw material waste during cell production. Refining the early roll-to-roll processing stages, specifically slurry mixing, drying, and calendaring; offers substantial opportunities to reduce material waste, energy consumption, and operational expenditure [1][3][4]. In slurry mixing, achieving a uniform particle size distribution directly impacts active material dispersion, slurry rheology, and subsequent coating quality on current collectors [4][5]. Capturing these physical phenomena requires advanced multi-scale models capable of handling both localized fluid dynamics and non-linear particle interactions. Thus, the proposed CFD-PBM coupling method can unify the inter- and intraparticle dynamics into a single model [6].

Semi-Analytical PBM-CFD Slurry Optimization

Coupled PBM-CFD models are essential for capturing particle interactions during mixing. Standard numerical discretisation schemes (e.g., Finite Volume or Fixed Pivot methods), however, incur prohibitive computational costs when embedded directly into CFD environments. To address this, we propose mesh-free semi-analytical methods to solve the continuous Smoluchowski aggregation equation:

$$\frac{\partial f(x,t)}{\partial t} = \frac{1}{2} \int_0^x \beta(x-y, y) f(x-y, t) f(y, t) dy - \int_0^\infty \beta(x, y) f(x, t) f(y, t) dy. \quad [1]$$

where $f(x, t)$ represents the particle size density and $\beta(x, y)$ is the interaction kernel.

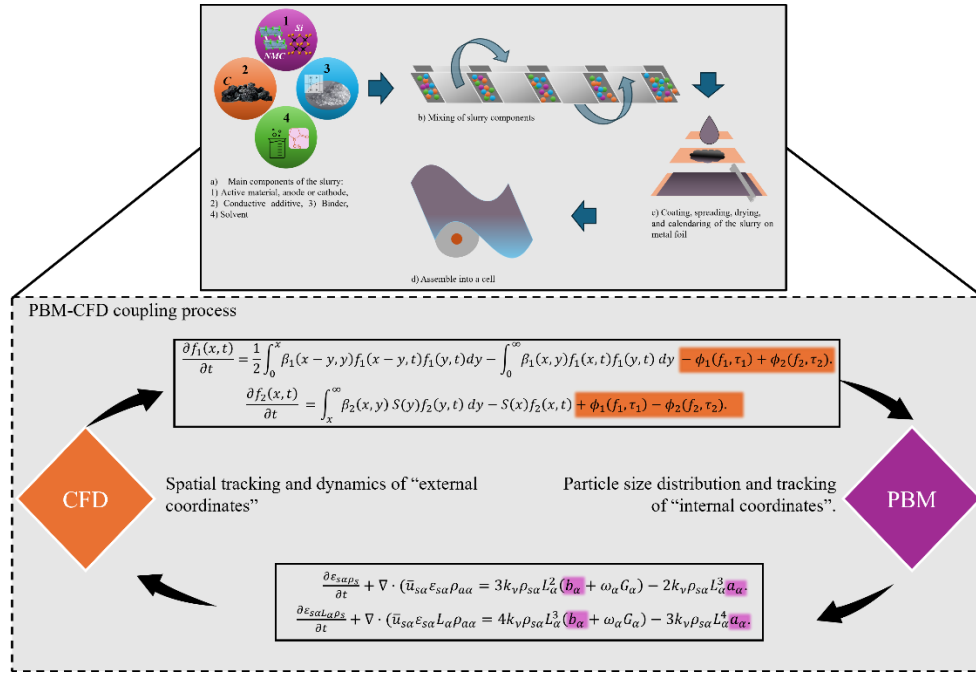


Figure 1. Graphical abstract of research workflow and strategy. The mathematical modelling of the li-ion slurry mixing phase in R2R manufacturing (top) by the combination of PBM and CFD techniques in a bidirectional system of partial differential and integro-partial differential equations with overlapping terms (highlighted) to link the mathematical equations

Comparative Performance of Semi-Analytical Schemes

We evaluated several semi-analytical techniques including the Homotopy Perturbation Method (HPM), Adomian Decomposition Method (ADM), Variational Iteration Method (VIM), and Modified Variational Iteration Method (MVIM); to identify optimal formulations for extended temporal stability. Comparative analysis demonstrates that MVIM yields superior accuracy over extended temporal domains ($t \geq 1.5$) where standard decomposition techniques diverge or lose accuracy. The performance was measured using the combination of relative error and computational time for several values of t with each method to calculate n terms of the series solution. Thus giving a practical performance evaluation to compare each method as it was applied to the Smoluchowski equation. The results indicate that MVIM has the greatest accuracy for extended temporal conditions when using 5+ terms but also the greatest computational expense (2652 seconds for 5 terms with relative error of 7.5×10^{-8} at $t = 1.5$). The VIMHe shows improved extended temporal accuracy similar to the MVIM when using 13+ terms and significantly lower computational cost (300 seconds for 13 terms with relative error of 1.8×10^{-3} at $t = 1.5$). A comprehensive summary of the qualitative performances of each model can be seen in Table 1.

The mesh-free framework removes traditional spatial and temporal discretisation bottlenecks, drastically reducing computational overhead during bidirectional coupling with CFD hydrodynamics. Beyond forward simulations, this mesh-free formulation

provides an efficient mathematical foundation for solving inverse problems to extract physical aggregation/breakage kernels ($\beta(x, y)$) directly from empirical slurry mixing data.

Conclusions

Implementing mesh-free MVIM semi-analytical PBMs within CFD frameworks provides a highly efficient computational approach for modelling battery electrode slurry mixing. By removing standard discretisation constraints while maintaining strict accuracy across extended temporal domains, this modelling framework enables refined optimization of particle size distributions, directly contributing to improved manufacturing efficiency and electrode quality.

Acknowledgments

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From Ageing to Thermal Runaway in Battery Energy Storage Systems

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This study investigates the thermal behavior of a stationary second-life battery pack containing cells with different degradation levels using electro-thermal modelling. The analysis focuses on identifying critical operating conditions and evaluating the influence of degraded cells on the overall temperature distribution and thermal safety of the battery system. The obtained results provide valuable insights for the safe integration, thermal management and risk assessment of second-life battery energy storage systems.

Introduction

The increasing adoption of stationary Battery Energy Storage Systems (BESS) has driven growing interest in the reuse of second-life lithium-ion (Li-ion) batteries retired from electric vehicles. While economically and environmentally attractive, these battery packs often consist of cells with different levels of degradation, resulting in significant variations in State of Health (SoH), internal resistance and heat generation. Consequently, the thermal behavior of the entire battery pack becomes increasingly non-uniform, with highly degraded cells acting as localized heat sources under elevated current loads. Such temperature inhomogeneity may accelerate further degradation and under insufficient cooling conditions increase the likelihood of thermal propagation and thermal runaway initiation.

The thermal behavior of Li-ion batteries is closely coupled with their electrochemical state and represents one of the key factors determining both performance and operational safety [1]. Most commercial Li-ion chemistries achieve optimal performance within a relatively narrow temperature range of approximately 15–35 °C [2][3]. Operation outside this range accelerates degradation processes and alters the electrochemical characteristics of the cells [4][5]. As batteries age, the growth of the solid electrolyte interphase (SEI), loss of active lithium, structural changes in the electrodes and increased internal resistance lead to higher irreversible heat generation during charge and discharge [3][4][6]. Consequently, aged cells dissipate more heat than fresh cells when subjected to identical operating conditions, making thermal management increasingly important, particularly in second-life battery systems where cells with different degradation levels coexist [7][8].

If the generated heat cannot be removed efficiently, local temperature rises may further accelerate degradation through positive thermal feedback, creating thermal hotspots within the battery pack [7][9]. Elevated temperatures promote parasitic side reactions, electrolyte decomposition, gas generation and continuous SEI growth, all of which further increase heat generation [3][4][6]. Under severe abuse conditions or insufficient cooling, this self-accelerating process may trigger thermal propagation and

eventually thermal runaway, accompanied by venting, fire, or explosion [3][6][10]. These risks become particularly important in second-life battery packs, where thermal non-uniformity caused by heterogeneous ageing may significantly reduce the overall safety margin.

Although the thermal behavior and thermal runaway mechanisms of Li-ion batteries have been extensively investigated [8][9][10], most studies focus on battery packs composed of homogeneous cells with similar ageing conditions or on abuse testing of individual cells. In contrast, the thermal behavior of second-life battery packs containing cells with heterogeneous degradation levels remains insufficiently understood, particularly under realistic operating conditions encountered in stationary BESS. Since degraded cells exhibit higher heat generation than first life cells, their influence on the overall temperature distribution and thermal safety of the battery pack requires further investigation.

Therefore, this work investigates the thermal behavior of a second-life battery pack integrated into a stationary Battery Energy Storage System designed for electric vehicle charging applications. A three-dimensional electro-thermal model developed in ANSYS Fluent is used to evaluate the influence of degraded cells on the temperature distribution within the battery pack. The battery pack is subjected to a realistic operating profile representative of a stationary energy storage system supplying an EV charging station, together with a more demanding loading scenario representing a worst-case operating condition. The objective is to identify critical temperature hotspots, assess the influence of cell degradation on thermal non-uniformity, and evaluate whether heterogeneous ageing may increase the risk of thermal runaway initiation.

Experimental

The experiment was conducted on a battery pack composed of NMC-based pouch cells arranged in an 8s3p configuration. Electrical behavior is described by semi-empirical model, based on an Equivalent Circuit Model (ECM), was characterized using the Galvanostatic Intermittent Titration Technique (GITT) method, which involves discharge pulses at 0.3 C followed by hourly rest periods, continued until the cut-off voltage of 2.65 V. This procedure enables the extraction of dynamic responses to current changes and allows identification of the RC elements across the full State-of Charge (SoC) range. These elements provide a simplified representation of the underlying electrochemical processes occurring within the battery. The thermal model is formulated using the Finite Element Method (FEM), while the battery behavior in ANSYS Fluent is also described using the ECM-based approach.

To investigate the thermal response under abuse conditions, thermal runaway was modelled using the four-equation kinetic model available in ANSYS Fluent. The model describes the main exothermic reactions occurring within a Li-ion cell, namely the decomposition of the SEI, negative electrode-electrolyte reactions, positive electrode-electrolyte reactions, and electrolyte decomposition. The reaction kinetics are represented by Arrhenius-type expressions, where the reaction rate depends on temperature through the activation energy and pre-exponential factor.

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Effect of Polystyrene Carbon on Degradation Processes of Fe-Mg-C Composites

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This work investigates a newly developed iron-based biodegradable material for potential use as a bone implant. High mechanical strength was achieved by high-temperature sintering of iron powder with varying amounts of polystyrene (PS) to produce C-Fe composite pellets, while magnesium was added to increase the corrosion rate. Corrosion behavior in physiological NaCl solution and simulated body fluid (SBF) at 37 °C was evaluated using potentiodynamic polarization and immersion tests. Changes in pH, conductivity, morphology (SEM), and chemical composition (EDS) were monitored throughout the degradation process. Long-term immersion revealed the formation of magnetite in NaCl solution and hematite in SBF. Analysis of both pristine composite samples and corrosion products formed in the immersion media provided insight into the degradation mechanisms of Fe-Mg-C composites prepared by high-temperature sintering with different PS contents.

Introduction

Biodegradable materials (BDMs) have attracted considerable attention as temporary bone implants because they can gradually degrade in the body, eliminating the need for implant removal while supporting tissue regeneration and bone healing [1][2]. Among the most promising systems are Fe- and Mg-based materials, which offer complementary advantages and limitations. Pure Fe provides excellent mechanical properties and biocompatibility but suffers from an excessively slow degradation rate, limiting its clinical use [3-6]. In contrast, Mg-based materials degrade too rapidly in physiological environments, leading to premature loss of mechanical integrity and hydrogen evolution, although released Mg²⁺ ions are generally well tolerated by the human body [7-10].

A promising strategy to optimize degradation behavior is the development of Fe-Mg composites, where Mg promotes galvanic corrosion of the Fe matrix [11]. In the present study, polystyrene (PS) was used as a carbon precursor to modify the microstructure.

The aim of this work was to perform a long-term comparative study of sintered Fe-Mg composites containing different amounts of PS-derived carbon. The study focused on (i) changes in morphology, porosity, and chemical composition during long-term degradation; (ii) the effect of carbon content on corrosion behavior; (iii) temporal changes in pH and electrical conductivity of the immersion media; and (iv) differences

in degradation mechanisms in physiological saline (0.9 wt.% NaCl) and simulated body fluid (SBF) at 37 °C.

Experimental

Materials, sample preparation, and immersion test

Reduced Fe powder (99%, average particle size 5 μm) and Mg powder (99.8%, particle size 100–300 μm) were used as starting materials. Expanded polystyrene (PS) spheres (EPS 100, 1–3 mm) served as the carbon precursor. Analytical-grade chemicals were used for the preparation of physiological saline (0.9 wt.% NaCl) and simulated body fluid (SBF, Hank's solution), while all solutions were prepared using deionized water.

All samples containing 9 g of Fe and 1 g of Mg with different PS contents (0.5; 1.0; 1.5 and 2.0 g of PS) were prepared using the same material procedure, which included mixing both powders with the polymer, their compaction, and sintering (1000 °C in argon atmosphere). Sintered pellets were immersed in physiological saline (0.9 wt.% NaCl) or SBF at 37 °C for up to 10 months. These media were selected to simulate physiological conditions and to evaluate the long-term degradation behavior of the composites.

Sample characterization

Surface morphology before and after immersion was examined by scanning electron microscopy (SEM, Thermo Fisher Scientific Quattro C and Tescan Vega3XMU). Elemental composition was determined using energy-dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 20 kV.

The pH and electrical conductivity of the immersion solutions were monitored periodically using an InoLab IDS Multi 9420 instrument (WTW) equipped with SenTix 980 pH and TetraCon 925 conductivity probes.

Corrosion behavior was evaluated by potentiodynamic polarization (PDP) using a $\mu\text{AUTOLAB}$ Type II potentiostat with GPES 4.7 software. Measurements were performed at a scan rate of 10 mV s^{-1} in a conventional three-electrode cell consisting of a paraffin-impregnated graphite working electrode (PIGE), a platinum counter electrode, and a saturated calomel reference electrode (SCE). The corrosion parameters were determined from Tafel polarization curves.

Results and discussion

The pH of the immersion solutions was monitored to evaluate changes in the corrosion process and the release of degradation products. Both media exhibited a rapid increase in pH during the first 14 days, indicating initial alkalization. Subsequently, NaCl solution showed larger pH fluctuations among the samples, whereas SBF maintained a more stable pH due to its buffering capacity, with a slight decrease observed at the end of the immersion period. A complementary experiment to pH was the temporal monitoring of the electrical conductivity of both immersion solutions. Since the solutions acquire higher pH values over time, the mobility of OH^- ions should contribute significantly to the conductivity. However, a decrease was observed, which suggests that OH^- ions are bound to poorly soluble metal hydroxides. The effect is stronger in the case of saline NaCl solution than in the case of SBF containing buffering agents.

Potentiodynamic polarization (PDP) was used to determine the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of Fe–Mg–C composites after immersion in NaCl and SBF. In both media, E_{corr} shifted toward less negative values and i_{corr} gradually decreased with immersion time, indicating a reduced corrosion rate due to the formation of protective Fe/Mg oxide and hydroxide layers on the composite surface. The changes were more pronounced in NaCl than in SBF, reflecting the buffering effect of SBF and its lower corrosivity. Corrosion products also differed between the media, with predominantly magnetite (Fe_3O_4) forming in NaCl and hematite (Fe_2O_3) in SBF, while higher PS-derived carbon contents promoted the release of corrosion products into solution.

SEM coupled with EDS was used to evaluate the morphological and compositional changes of Fe–Mg–PS composites and their corrosion products after immersion in NaCl and SBF. The analyses confirmed Fe, Mg, C, and O as the dominant elements, with increased oxygen content after immersion indicating the formation of oxide and hydroxide corrosion products. SEM revealed distinct degradation mechanisms in the two media: the original globular morphology was largely preserved in NaCl, whereas SBF promoted the formation of characteristic flower-like surface structures that became more pronounced with increasing immersion time and PS content.

Conclusion

Based on the morphological, chemical, and electrochemical analyses, the degradation mechanisms of Fe–Mg–C composites with different PS-derived carbon contents in physiological NaCl solution and SBF were proposed. The results demonstrate that both the immersion medium and carbon content significantly influence corrosion behavior, surface morphology, and the composition of degradation products. These findings provide a comprehensive understanding of the long-term degradation of Fe–Mg–C composites and support their further optimization for biodegradable implant applications.

Acknowledgments

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Data-Driven State-of-Health Estimation of Li-Ion Batteries Using Gaussian Process Regression and Kalman Filtering

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The growing utilization of lithium-ion batteries in electric vehicles and stationary energy storage systems increases the demand for accurate State-of-Health (SoH) estimation. Data-driven methods represent a promising alternative to conventional model-based approaches due to their ability to capture complex degradation behavior from experimental data. This paper presents a SoH estimation method based on Gaussian Process Regression using the NASA Battery Aging Dataset. Diagnostic features extracted from charge, discharge, temperature, and electrochemical impedance measurements are used as model inputs. The regression results are further refined by Kalman filtering to improve the stability of the estimated SoH trajectory. The proposed approach is evaluated using the Leave-One-Battery-Out validation strategy and compared with a linear regression model. The obtained results demonstrate improved estimation accuracy while maintaining low computational complexity, indicating the suitability of the proposed approach for battery diagnostics and Battery Management System applications.

Introduction

Lithium-ion (Li-ion) batteries have become the dominant energy storage technology in applications ranging from portable electronics to electric vehicles and stationary energy storage systems. [1] Their widespread deployment is primarily driven by their high energy density, long cycle life, and relatively low self-discharge. However, battery performance gradually deteriorates during operation due to calendar and cycle aging, resulting in capacity fade and increased internal resistance. These degradation processes reduce the available energy, decrease system reliability, and may compromise operational safety. [2]

To ensure reliable battery operation, Battery Management Systems (BMS) continuously monitor key battery parameters, among which the State of Health (SoH) is one of the most important. Accurate SoH estimation enables predictive maintenance, improves operational safety, and supports optimal utilization of battery systems throughout their service life. Since the degradation process is influenced by numerous electrochemical and environmental factors, accurate SoH estimation remains a challenging task. [2][3]

Conventional approaches rely on electrochemical or equivalent circuit models requiring detailed knowledge of battery characteristics and parameter identification. In contrast, data-driven methods have recently attracted considerable attention because

they can learn degradation patterns directly from experimental measurements without explicitly describing the underlying physical processes. [3]

This work presents a data-driven SoH estimation approach based on Gaussian Process Regression (GPR). The proposed model is developed using the NASA Battery Aging Dataset and combines electrical, thermal, and electrochemical impedance features to estimate battery health. The robustness of the estimated SoH is further improved by applying a Kalman filter, while the overall performance of the proposed methodology is evaluated using the Leave-One-Battery-Out validation strategy. [4]

Experimental

The proposed data-driven State-of-Health (SoH) estimation methodology was developed using the publicly available NASA Battery Aging Dataset. The dataset contains long-term experimental measurements of four commercial lithium-ion cells (B0005, B0006, B0007, and B0018) subjected to repeated charge–discharge cycling until end-of-life conditions were reached. For each cycle, the dataset provides synchronized measurements of voltage, current, temperature, discharge capacity, and electrochemical impedance spectroscopy (EIS), allowing comprehensive characterization of battery degradation. [5]

The overall workflow of the proposed methodology is illustrated in Figure 1. The processing chain consists of data preprocessing, diagnostic feature extraction, Gaussian Process Regression (GPR) model training, Kalman filter post-processing, and final model validation using the Leave-One-Battery-Out (LOBO) strategy.

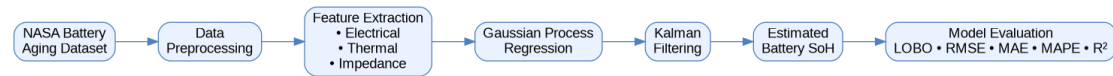


Figure 1. Workflow of the proposed data-driven methodology for lithium-ion battery State-of-Health estimation using Gaussian Process Regression and Kalman filtering.

Figure 2 presents the degradation behaviour of all four battery cells used in this study. As expected, all investigated cells exhibit a gradual reduction in discharge capacity with increasing cycle number, although the degradation rate differs slightly between individual batteries. This variability makes the dataset suitable for evaluating the generalization capability of data-driven prediction models.

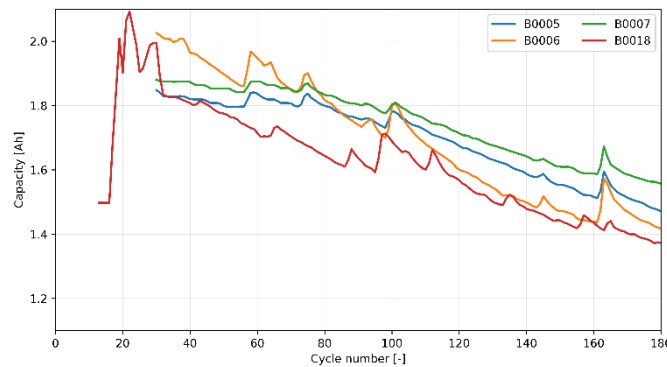


Figure 2. Capacity degradation of the NASA Battery Aging Dataset cells B0005, B0006, B0007, and B0018.

Representative electrical, thermal and impedance-related diagnostic features were extracted from the measured data and used as predictor variables for the regression model. The feature selection was based on quantities commonly available within

Battery Management Systems while simultaneously reflecting the electrical, thermal and electrochemical state of the battery throughout its lifetime (see Table 1).

TABLE I. Representative input features used for SoH estimation.

Feature group	Representative features
Electrical	Mean voltage, voltage slope, voltage variance
Thermal	Mean temperature, maximum temperature, temperature rise
Impedance	Ohmic resistance (R_e), charge transfer resistance (R_{ct}), impedance-based parameters

The predictive model was implemented in MATLAB using Gaussian Process Regression (GPR), which enables nonlinear mapping between diagnostic features and battery State of Health while simultaneously providing prediction uncertainty. To improve temporal consistency and suppress cycle-to-cycle fluctuations caused by measurement noise, the regression output was subsequently processed using a one-dimensional Kalman filter.

The predictive capability of the proposed methodology was evaluated using the Leave-One-Battery-Out (LOBO) cross-validation strategy. During each validation iteration, three batteries were used for model training, whereas the remaining battery served exclusively for testing. This validation procedure provides an unbiased assessment of model generalization to previously unseen battery data.

Model performance was quantified using the Root Mean Square Error (RMSE), Mean Absolute Error (MAE), Mean Absolute Percentage Error (MAPE), and the coefficient of determination (R^2). In addition to numerical evaluation, representative prediction results are presented in Figure 3, while the average prediction accuracy obtained over all LOBO validation runs is summarized in Table 2.

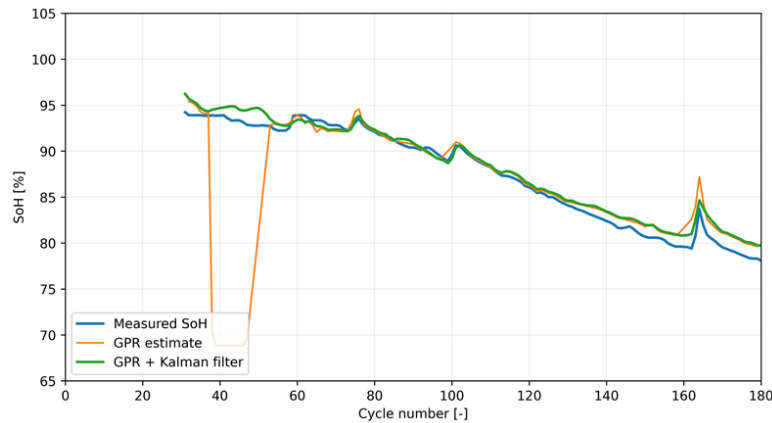


Figure 3. Measured and estimated State of Health of cell B0007 using Gaussian Process Regression and subsequent Kalman filtering under LOBO validation.

TABLE II. Average prediction performance across all Leave-One-Battery-Out validation runs

Model	RMSE	MAE	MAPE [%]	R^2
Baseline linear regression	0.0448	0.0407	5.2856	0.6899
GPR	0.0177	0.0155	2.0267	0.9640
GPR + Kalman filter	0.0174	0.0151	1.9781	0.9651

Conclusion

This paper presented a data-driven methodology for State-of-Health (SoH) estimation of lithium-ion batteries based on Gaussian Process Regression combined with Kalman

filtering. The proposed approach utilizes electrical, thermal, and electrochemical impedance features extracted from the NASA Battery Aging Dataset to estimate battery degradation under various aging conditions.

The representative prediction results demonstrate that the proposed model accurately follows the measured SoH trajectory throughout the battery lifetime, while Kalman filtering improves the temporal consistency of the estimated degradation curve by reducing cycle-to-cycle fluctuations. Compared with the baseline linear regression model, the proposed methodology achieved substantially lower prediction errors and a higher coefficient of determination during Leave-One-Battery-Out validation. The best overall performance was obtained using the combined GPR–Kalman approach, reaching an average RMSE of 0.0174, MAE of 0.0151, MAPE of 1.98%, and R^2 of 0.9651.

The obtained results indicate that the proposed methodology provides an accurate and computationally efficient solution for battery State-of-Health estimation. Owing to its ability to generalize across previously unseen battery data and its relatively low computational complexity, the proposed approach represents a promising candidate for future Battery Management System applications and further research on data-driven battery diagnostics.

Acknowledgments

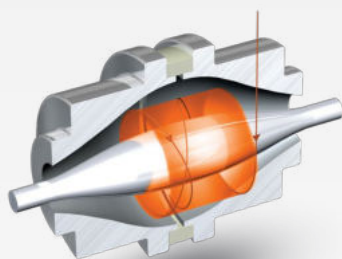
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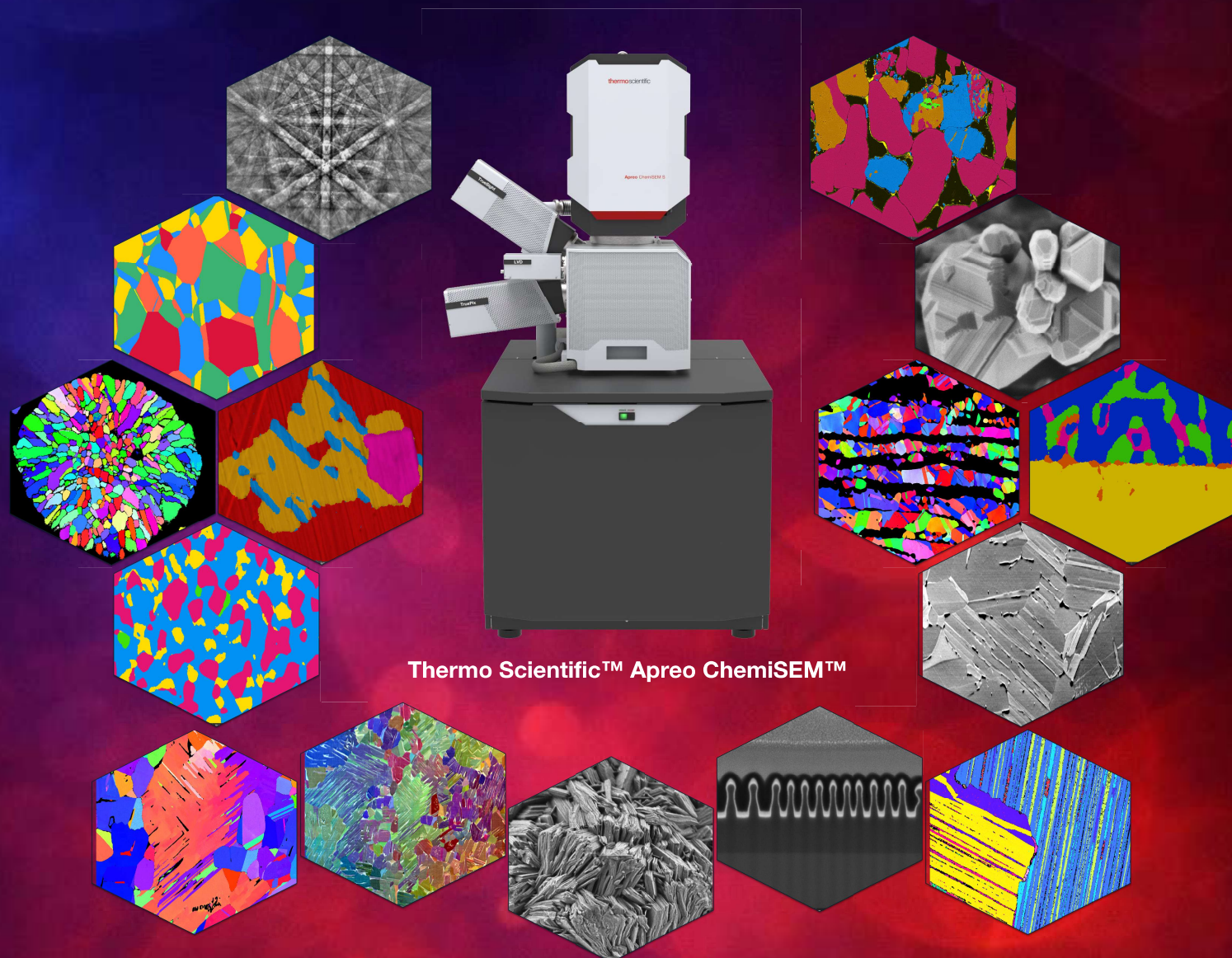


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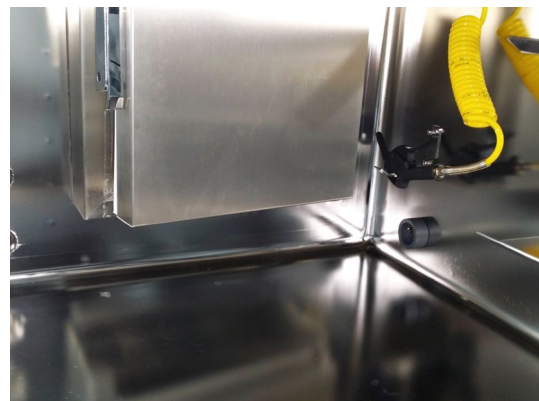
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