MALEIC ANHYDRIDE AS FILM-FORMING ELECTROLYTE ADDITIVE IN GAMMA BUTYROLACTONE SOLUTIONS BASED LITHIUM-ION BATTERIES

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Introduction

Li-ion batteries are becoming more and more important for energy storage. They are now being considered as a potential energy source for space and military applications, both requiring a wide temperature range of reliable operation. However, Li ion cells are often limited at moderate temperatures because the electrolyte must remain liquid with a low viscosity and a high dissociation power for good conducting properties. An interesting solvent in the field of Li-batteries is therefore gamma-butyrolactone (GBL). The good physical properties of GBL that include among other things a wide liquid range from -45 °C (m.p.) to 204 °C (b.p.) and a good solubilizing power for lithium salts leads to an attractive electrolyte system for electrode research and development [1,2]. However, graphite anodes show in GBL-based electrolytes, with LiClO₄ as conductive salt, a large irreversible charge capacity in the first cycle and a poor cycleability. The reason is that the reductive decomposition of GBL forms a solid electrolyte interphase (SEI) layer different to a "standard" one. Since a good SEI layer covering the entire graphite surface is essential for reversible lithium intercalation/extraction, chemical modification of the graphite surface (which includes the modification of the SEI film as well) has attracted wide attention. Our present work described the influence of maleic anhydride (MA) as additive in GBL to improve the SEI (solid electrolyte interphase) of Li ion batteries with GBL based electrolytes. Standard electrochemically methods like impedance spectrometry and charge discharge measurements had been used to characterise the system. Moreover, additional and complementary information about the SEI formation inclusive the evolution of volatile reduction products was gained from subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS).

Experimental

Electrochemical experiments were performed in standard cells by room temperature described elsewhere [3]. Working electrodes were prepared by doctor blading natural graphite (LBG1025, Superior Graphite) with polyvinilidene fluride (SOLEF 1015, Solvay SA) binder onto a copper current collector. The electrodes were vacuum dried at 120 °C and contained ca. 10 mg of graphite (95 % (wt) LBG 1025 + 5 % (wt) PVDF). Li foils were used for both the reference and counter electrode. *In situ* SNIFTIRS was performed with a 12 mm polished glassy carbon (GC) as working electrode and a Li strap as counter and reference electrode. A schematic presentation of our SNIFTIRS setup has already been

Corresponding author: P. Novák Phone Number: + 41 56 310 2457 Fax Number: + 41 56 310 4415 E-mail: petr.novak@psi.ch published [4]. The cell was dried, assembled, filled with electrolyte and hermetically sealed in the glove box before adjusting it in the FTIR instrument. Spectra were measured at a resolution of 4 cm⁻¹ by accumulating 40 scans with a Perkin-Elmer 2000 Fourier transform infrared (FTIR) spectrometer equipped with a DTGS detector.

Results and Discussion

SNIFTIRS spectra from GBL with 1 M LiClO₄ and 2 % MA at different potentials are shown in Figure 1.



Fig. 1 SNIFTIR spectra from a polished GC electrode in GBL, 1M LiClO₄ with 2% MA at different potentials vs. Li/Li⁺.

Positive bands represent a decrease in concentration and negative bands represent an increase in the concentration of the species on the electrode and/or in the thin layer electrolyte layer between the electrode and the optical window. The negative band at 2340 cm⁻¹ is assigned to CO_2 . We relate the formation of CO_2 to the reduction of MA because no CO_2 was detected in experiments without MA. The other negative signals appear at 2.3 V and because no significant changes occurred below 1.7 V we assign them to reduction products of MA. However, we were not able to unambiguously attribute the peaks to known compounds but conclude that the electrochemical reduction of MA in GBL based electrolytes forms in addition to CO_2 also reductive decomposition products forming the SEI. The positive bands agree with them of MA, therefore we dedicated them to the consumed MA.

Half-cells composed of graphite and lithium metal with a glass fleece as separator to separate the anodic and cathodic compartments were used for the electrochemical experiments. Impedance spectra of graphite electrodes were measured at 0.4 V vs. Li/Li^+ . The shape of the spectra (Figure 2)



Fig. 2 Electrochemical impedance spectra at 0.4 V vs. Li/Li^+ of graphite electrodes in GBL and 1M $LiCIO_4$ with and without MA.

depends on the presence of MA. The highest frequency semicircle is attributed to Li-ion migration through passivating surface films and the lower frequency semicircle to charge transfer processes. The low frequency domain reflects the solid state diffusion of lithium into/from the graphite and the very low frequency domain reflects the (pseudo)capacitive behaviour, assigned to the accumulation of lithium into graphite. The plots in Figure 2 demonstrate the positive impact of MA on the electrode impedance behaviour, illustrating



Fig. 3 Cycling behaviour of electrodes in GBL with 1M LiClO₄ as solute with different MA concentrations.

that the overall electrode impedance is smaller independently of the frequency range. Interestingly, the highest frequency semi-cycle vanishes or is much smaller in the presence of MA, suggesting faster Li-ion migration through the surface SEI film. In Figure 3 the charge capacity and the irreversible charge loss are reported vs. the cycle number at 25 °C. It is obvious, that the behaviour of the cells has been improved by the addition of MA. This is due to the fact that charge capacity remains more constant and converges towards a constant value over the entire cycling test. Furthermore the irreversible charge loss is significantly reduced with use of MA.

Conclusions

The presence of MA in GBL based electrolytes containing $LiClO_4$ reduces the irreversible capacity of lithiated graphite electrodes and improves their stability during prolonged cycling. During the first charge cycle MA is reduced at rather positive potentials under CO_2 evolution. Therefore a protective film (SEI) is formed on the graphite surface which hinders the reductive decomposition of GBL at potentials of about 0.9 V vs. Li/Li^+ that otherwise causes much higher irreversible capacity of graphite electrodes in GBL based electrolytes. In conclusion the charge/discharge cycling tests of the graphite electrodes described above indicates that the presence of MA in solution has two positive impacts, decrease of the irreversible capacity of the electrodes and improvement of their cycleability [5].

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