

HALF - CELLS BASED ON SOLID VITREOUS ELECTROLYTE AND THERMO EXPANDED GRAPHITE

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Introduction

Lithium ion accumulators (LiA) are widely used in the different electronic devices due to the significant advantage of their properties as compared with the traditional ones.

At the same time, further development of LiA is hindered by a number of disadvantages: degradation of the LiA system at recharging and storage, the limited higher temperatures range, irreversible self-discharge, deposition of metal lithium on graphite electrode at recharging, electrolyte oxidation at a positive electrode and its reduction on a negative electrode at power source charging, chemical and electrochemical dissolution of electrode materials [1]. From the constructional stand-point, the possibility of liquid electrolyte leakage through hermetic sealing is also problematic. Substitution of liquid conducting electrolytes by the solid ones (SE) can help to solve both some design (e.g., quality of hermetic sealing) and the technological problems for lithium ion accumulators. Using the solid inorganic electrolytes will enable significant widening the working temperature range upwards the high values. For example, maximum operation temperature of liquid and polymer electrolytes does not exceed 60...70°C [2]. At the same time, solid vitreous electrolytes developed by the authors are stable up to the softening point (200...250°C) [3].

Practical use of solid electrolytes requires production process optimization of the electrochemical cells with SE.

In the work, effect of the solid electrolytes based on $\text{Li}_2\text{O-Li}_2\text{SO}_4\text{-B}_2\text{O}_3\text{-MoO}_3$ on the electrochemical properties of graphite electrode in the process of lithium ion intercalation/deintercalation has been investigated. Aim of the carried out investigations was determination of the possibility to use the half-cells solid electrolyte/graphite electrode (SE/Graphite) in lithium ion systems.

Experimental

For the investigations, natural graphite (25 μm fraction) modified by the original procedure [4] was used. Selection of solid glassy electrolyte based on the system $\text{Li}_2\text{O-Li}_2\text{SO}_4\text{-B}_2\text{O}_3\text{-MoO}_3$ [3] is conditioned by the high value of ionic conductivity (at 25°C, $4.3 \cdot 10^{-6} \text{ S/cm}$), wide electrochemical stability range (0.0...4.5.V vs Li/Li^+ electrode), and by high manufacturability.

Solid electrolyte was applied on graphite electrode by the specially developed technology. Thickness of SE layer was determined by the possibilities of technological equipment and

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was 50...150 μm . It should be noted that the possibilities of the applied method, in principal, allow to produce the layers of solid electrolytes with the thickness $\sim 10\ \mu\text{m}$.

Metal lithium was used as a counter- electrode. This was a 2325-size coin cell. Diameter of graphite electrodes is 16 mm. Between the solid electrolyte covering graphite surface and lithium electrode, in separator pores there was a liquid electrolyte. The solution 1M LiClO_4 was used as the electrolyte in the mixture of solvents EC/DMC=1:1.

Galvanostatic cycling was carried out on the automatic stand within the predetermined voltage range (0.0...1.5 V). Potentiodynamic cycling of graphite electrodes was carried out within the range from -0.1 up to 1.5 V against lithium reference electrode. Potential scanning rate was 0.1 mV/sec.

Results and Discussion

It is known that inorganic glass melts practically do not moisten graphite [5]. Nevertheless, during carrying out the work, we established good spreading of the melt of the developed solid electrolyte on graphite. This enables production of half-cells, graphite electrode/solid electrolyte, investigation and optimization of their electrochemical properties. The above phenomena can be conditioned both by abnormally high wettability of glass melts in the system $\text{Li}_2\text{O}-\text{Li}_2\text{SO}_4-\text{B}_2\text{O}_3-\text{MoO}_3$ [6] and the availability of sorbed oxygen [7] on the developed graphite surface.

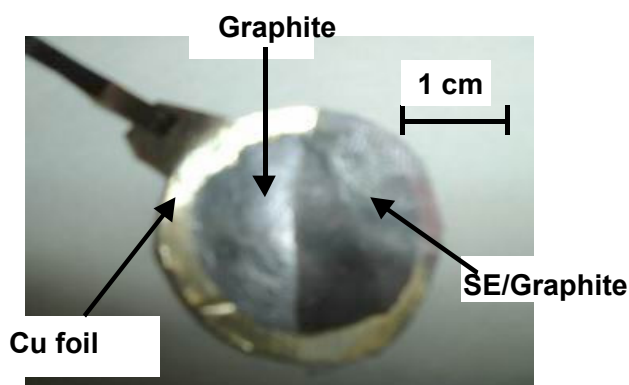


Fig. 1 Photography of the half-cell SE / graphite (#G8). Thickness of SE layer is 50 μm .

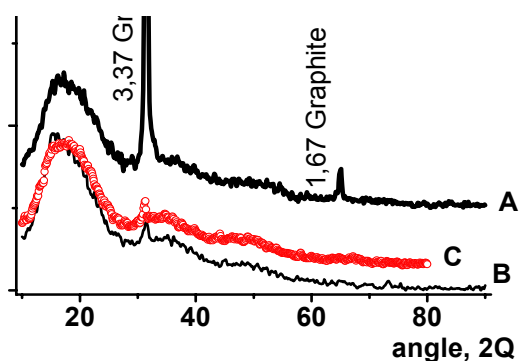


Fig. 2 X-ray pattern of half-cell SE/graphite (#G8). A – half-cell (X-ray radiation on graphite), B - half-cell (X-ray radiation on SE), C – flake of $\text{Li}_2\text{O}-\text{Li}_2\text{SO}_4-\text{B}_2\text{O}_3-\text{MoO}_3$ solid electrolyte.

At the first stage of work, to evaluate the quality of the applied SE layer, the half-cell SE/Graphite was manufactured, one of its half was coated with SE, and another was not coated. The photograph of such a sample is shown in Fig.1. As it evident from the figure, a solid electrolyte is absolutely transparent, and graphite surface as well as a copper current collector are visible rather well through it.

Then the half- cell SE/Graphite (G8) was investigated by the XRD analysis. Two different investigations were carried out: 1- radiation from the side of SE, 2 – radiation from graphite side. In Fig.2 there are presented the X-ray patterns of a half-cell, and on their basis we may conclude that when SE applied on graphite its X-ray amorphism remains. In the case of radiation penetration through SE, the intensity of diffraction graphite peaks decreases sharply due to the shielding effect of SE coating. In this case, diffraction peaks position does not change that indicates graphite structure stability.

For galvanostatic and potentiostatic investigations, series of the half -cells

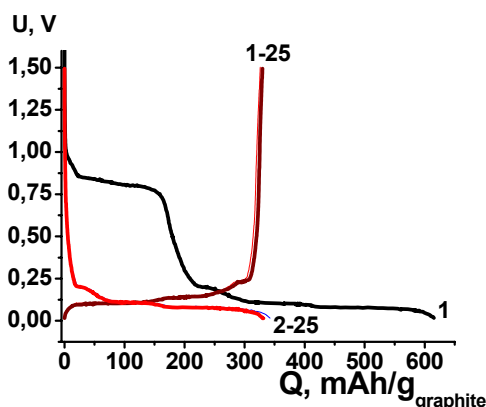


Fig. 3 Charge-discharge curves of Li - graphite (#Gt2) coin cell 2325 at 20°C. Charge/discharge current density is 50 $\mu\text{A}/\text{cm}^2$. Cycling range: 0.0...1.5 V. Graphite content is 5 mg/cm^2 . Numerals on curves correspond to a cycle number.

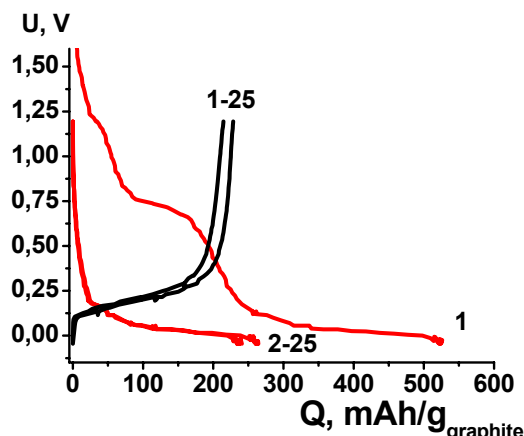


Fig. 4 Charge-discharge curves of Li - SE/graphite (#TM3) coin cell 2325 at 20°C. Discharge current density is 25 $\mu\text{A}/\text{cm}^2$. Charge current density is 50 $\mu\text{A}/\text{cm}^2$. Cycling range: 0.0...1.5 V. Thickness of SE layer is 140 μm . Graphite content is 1.85 mg/cm^2 . Numerals on curves correspond to a cycle number.

with liquid and solid electrolytes coating graphite electrode surface has been manufactured.

OCV of the all assembled cells is 2.8...3.0 V. OCV is determined by the potential of graphite electrode against metal lithium and is independent on the layer of solid electrolyte.

In Figs. 3, 4 there are presented the cycling results of graphite and graphite/SE electrode together with lithium electrode, respectively. The primary charging capacity is the order of 615 and 530, and discharge capacity at the 2...25 cycles is stable and is 330 and 240 $\text{mAh}/\text{g}_{\text{graphite}}$, respectively.

In Figs. 5, 6 potentiodynamic characteristics of the electrodes of graphite and graphite/SE together with the lithium electrode, respectively, are presented. In Table 1 the typical indices are summarized.

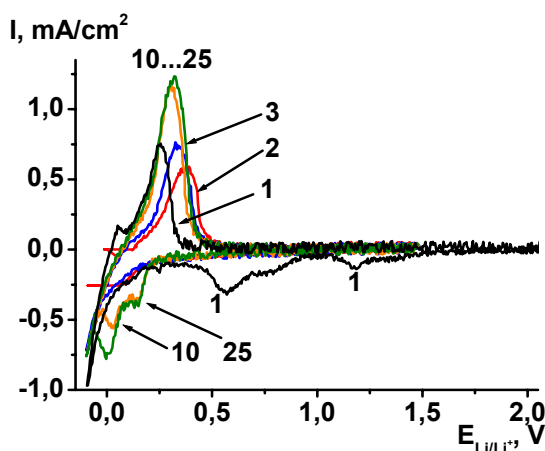


Fig. 5. Potentiodynamic characteristics of Li-Li-Graphite cell (#Gt7). Scanning rate is 0.1 mV/sec . Graphite content is 2.3 mg/cm^2 . Numerals on curves correspond to a cycle number.

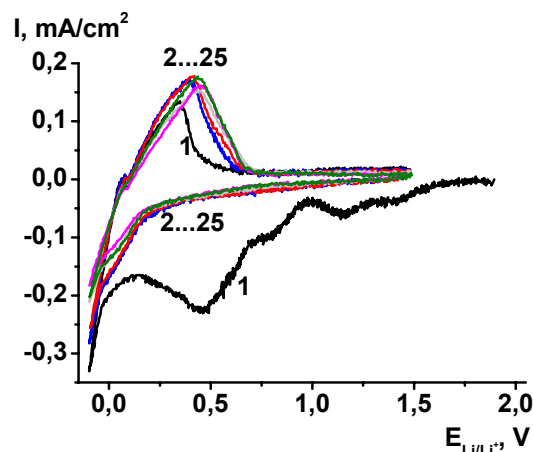


Fig. 6. Potentiodynamic characteristics of Li-Li-SE/Graphite cell (#G16). Scanning rate is 0.1 mV/sec . Thickness of SE layer is 120 μm . Graphite content is 2.25 mg/cm^2 . Numerals on curves correspond to a cycle number.

Analysis of the data presented in Table 1 allows to conclude that :

1. For the first cathode and anode curve in the both cases 3 and 1 peaks are typical, respectively. The difference consists in the 7-fold decrease of the anode peak value and the 2.5- fold decrease of cathode peak value for the system with a solid electrolyte as compared with liquid electrolyte.
2. For the 25-th cathode curve, 3 and 1 peak are typical for Graphite and SE/Graphite, respectively. The difference consists in the 6-fold decrease of anode peak value and in 3.5- fold decrease of cathode peak value for the system with solid electrolyte as compared with liquid electrolyte.
3. Decreasing current density value corresponding to the anode and cathode peaks, and displacement of anode peak potentials toward the more positive range at introducing solid electrolyte is resulted from the ohmic resistance of SE layer.

Table 1 *Electrode potentials of peaks on IU-curves*

Curve	Cycle number	Current density (mA/cm ²)		Potential vs Li/Li ⁺ , (mV)	
		Graphite	Graphite/SE	Graphite	Graphite/SE
Anodic	1	0,74	0,13	240	340
		-0,14	-0,06	1180	1160
Cathodic	1	-0,31	-0,23	560	470
		-0,97	-0,32	-100	-100
Anodic	25	1,21	0,18	310	450
		-0,37	---	140	---
Cathodic	25	-0,76	---	10	---
		-0,76	-0,19	-100	-100

Conclusions

The developed solid vitreous electrolyte based on the system $\text{Li}_2\text{O-Li}_2\text{SO}_4\text{-B}_2\text{O}_3\text{-MoO}_3$ is technologically compatible with the graphite electrode.

Character of the electrochemical processes in the systems with liquid and solid electrolytes is similar.

Due to the comparatively large thickness of the used solid electrolyte, voltage drop on it is great, that results in decreasing the current value and displacement of the potentials of anode and cathode processes.

The obtained results allow to suppose that optimization of the process of applying rather thin layer of solid electrolyte on electrode will enable increasing the range of working currents in the system of solid electrolyte/graphite anode, that will condition the possibility of its application in lithium-ion accumulators.

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