EFFECT 15-CROWN-5 ON LI ANODE/ POLYMERIC ELECTROLYTE INTERFACE CHARGE TRANSFER

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Introduction

Crown ethers discovered by Ch. Pedersen in 1967 [1] possess some important properties which could affect both the increase of conductivity of Li ions in polymer electrolytes and the decrease of resistance of charge transfer in the Li/polymer electrolyte interface [2-4]. Crown ethers were introduced in polymer electrolytes and improved electrochemical properties of the interface with a lithium electrode were found. Crown ethers form complexes as a result of an ion-dipole interaction with a rigid Li cation, complex stability being dependent of a ratio of the Li⁺ ionic radius (1.2 Å) to the size of macrocyclic polyether cavity. The choice of certain crown ether was defined by the necessity of preparing not a very stable complex with Li⁺, which allowed Li ions to penetrate freely through the cavity of crown ether. 14-Crown-4 and 15-crown-5 have cavities of diameter of 1.2 Å and 1.7 Å, respectively [5]. Thus, 15-crown-5 was chosen.

This work reports on the study of the effect of 15-crown-5 on resistance of charge transfer in the Li/polymer electrolyte interface by applying liquid crown ether directly to a Li electrode surface. The polymer composition of oligourethane dimethacrylate and polypropylene glycol monomethacrylate studied by us previously [6] was used as a polymer matrix for gel electrolyte.

Experimental

Oligoure than e dimethacrylate ($M_n \approx 1400$; $M_w \approx 1600$):



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and polypropylene glycol monomethacrylate (MM = 376):



were used to prepare polymer gel electrolytes.

These ingredients polymerize via double bonds upon heating (a radical initiator is azobis(isobutyronitrile)) to form a three-dimensional network whose pores can keep a liquid electrolyte. The oligomer-monomer mixture at a 1:1 mass ratio was introduced in an aprotic liquid electrolyte (80 w/w.%), namely, 1 M LiClO₄ in γ -butyrolactone (GBL) and then the film was formed and thermally cured at 80^oC for 3 hours.

Electrochemical impedance was measured within $12 - 10^5$ Hz range at a measuring signal amplitude equal to 0.005 - 0.01 V using a LCR819 instrument (Goodwill Instruments Ltd.). The experimental data were processed in accordance with the model of adsorption relaxation of a double layer [7]. Symmetrical cells with reversible lithium electrodes were used as electrochemical ones.

The metallic Li surface was treated with liquid 15-crown-5 (1 min), an excess of crownether was removed with a filter paper. Some Li electrodes were kept in dry air for up to 6 months when Li-surface turned black. Thus, the metallic Li electrodes of 4 types were tested, namely:

- 1) Freshly rolled pure lithium (Li⁰);
- 2) Li covered by a passivating film (Li^{pass});
- 3) Freshly rolled pure lithium treated with 15-crown-5 (Li⁰_{crown});
- 4) Li covered by a passivating film and treated with 15-crown-5 (Li^{pass}_{crown}).

Results and Discussion

The Li/gel electrolyte interface was electrochemically tested depending on a kind of metallic lithium. The impedance spectra of the cells with reversible lithium electrodes are presented in Fig.1. Bulk conductivity of such an electrolyte is equal to $3.0 \times 10^{-3} \Omega/cm$ at room temperature.



Fig.1 Impedance spectra of gel electrolyte based on 1M LiClO₄/GBL and 20 w/w.% of polymer composition ($22^{\circ}C$, gel thickness is 0.048 cm, electrode area is 0.2 cm²) in a symmetrical cell with electrodes: 1) Li⁰; 2) Li^{pass}; 3) Li^o_{crown}; 4) Li^{pass}_{crown}.

The temperature dependence of resistance of charge transfer in the electrochemical parameters of the electrolyte was analyzed. The Li/gel electrolyte interface was studied for all 4 types of lithium surfaces. The activation energy was calculated for this interface parameter. The experimental data are summarized in Table 1.

Table 1 Temperature dependence of resistance of charge transfer in the interface of Li-gel electrolyte based on 1M LiClO₄/GBL and 20 w/w. % of polymer composition. Activation energies of charge transfer.

	Resistance of charge transfer ($\Omega \cdot cm^2$)				Activation
Temperature (⁰ C)	-8	5	22	50	energy
					(eV)
Li electrode					
Li ⁰	4 200	1 270	120	24	0.676 ± 0.074
Li ^{pass}	4 765	1 730	45	28	0.705 ± 0.180
Li ⁰ crown	1 660	320	68	10	0.693 ± 0.042
Li ^{pass} crown	700	200	66	42	0.390 ± 0.084

It is seen that at room temperature the least value of resistance of charge transfer in the the Li/gel electrolyte interface is that of Li covered by a black passivating film. It is known [8] that Li does not react with absolutely dry air without heating at room temperature. However, in wet air (water content is > 80 %) Li reacts with H₂O and CO₂ to form white LiOH and Li₂CO₃. We observed black Li₃N on the Li surface in minimally wet air. Li₃N has ionic conductivity of $(2\pm4)\times10^{-4}$ Ω/cm at room temperature [9]. Though R_F in Li^{pass}/gel electrolyte interface less than R_F in the Li⁰/gel electrolyte interface at room temperature, at other temperatures these values are approximately equal. Entirely other values of R_F are observed near interfaces after they were treated with crown-ether. These values are lower. The lowest value of R_F is that for the Li^{pass}_{crown}/gel electrolyte interface.

The activation energies of resistance of charge transfer in the Li/gel electrolyte interface are equal in the first three cases (Table 1) within the experimental error. For the Li^{pass}_{crown} /gel electrolyte interface the value of E_a is 1.8 times lower than those for the other interfaces.

Most possibly is that the (Li-crown)⁺ complex forms on the pure lithium surface [10]. The lithium surface covered by a passivating film provides the formation of complexes of 15-crown-5 molecules with lithium cations of the Li₃N - ionic conductor. Only in this case E_a of resistance of charge transfer decreases and can be interpreted by that in gel electrolytes Li⁺ ions have large solvate shells, which prevent from lithium ion approach to the metallic lithium surface. In solvents, particularly, GBL, relative distances between donor oxygen atoms and Li⁺ are not constant at Li ion solvation since solvating molecules are not linked with each other and have a high degree of freedom. On the contrary, binding oxygen atoms in crown ether complexes are located in a certain order at equal distances from a cation and, therefore, they are more stable in entropy. Thus, lithium ion loses its solvate shell, passes to a crown-ether cavity, and accepts an electron, i.e., Li⁺ + e \Leftrightarrow Li⁰ reaction is realized.

Conclusion

15-Crown-5 positively affects resistance of charge transfer in the interface of Li/gel electrolyte based on oligourethane dimethacrylate and polypropylene glycol monomethacrylate, provided the addition of 1 M LiClO₄ dissolved in GBL. The effect is stronger and the activation energy of resistance of charge transfer in Li⁺ + e \Leftrightarrow Li⁰ reaction in the Li/gel electrolyte interface decreases if the metallic lithium surface is passivated by Li₃N.

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