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Formation of highly conductive layers by crown ether molecules on the surface of a lithium anode at low temperatures

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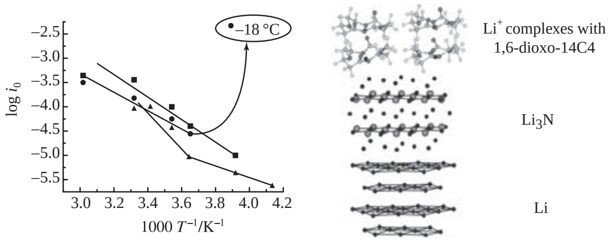
A sharp (250-fold) decrease in charge transfer resistance at the lithium anode/electrolyte interface in the presence of crown ethers in a range from 0 to –18 °C was found.



Crown ethers have useful properties that influence the Li$^+$ conductivity in lithium electrochemical systems. It has been shown[1–3] that the addition of 15-crown-5 and 18-crown-6 (18C6) increased the conductivity of liquid, gel and solid polymer electrolytes. In addition, charge transfer at the lithium/electrolyte interface was facilitated under the pretreatment of a Li surface by liquid 15-crown-5. This effect became more pronounced with lowering the temperature to –10 °C and coating the lithium surface with a thin layer of Li$_3$N.[4]

The promoting effect of charge transfer at the lithium/electrolyte interface at low temperatures is apparently caused by the formation of a so-called plastic crystal phase.[5] The metastable plastic crystal phase is usually formed by spherical or disk-shaped molecules. According to previously published data,[6] in the plastic crystal phase structure formed by 12-crown-4 (12C4) and 18C6 complexes with the Li$^+$ ion of LiN(SO$_2$CF$_3$)$_2$, ethereal rings lose their mobility due to the coordination of O atoms to lithium cations. As a result, the strongly bound Li$^+$–crown ether complex acquires a disk-like shape. DSC studies showed[6] that there are two new peaks at –109 and 88 °C for the 12C4–LiN(SO$_2$CF$_3$)$_2$ (1:1) complex, related to transitions of crystal → plastic crystal of type I and plastic crystal of type I → plastic crystal of type II. Melting point of 145 °C is significantly higher than that for pure 12C4 (–22 °C). Such a large distinction is caused by the contribution of other factors, for example, a decrease in anion mobility, to the total entropy.[7] There are similar transitions at –30 and 29 °C for the complex 18C6–LiN(SO$_2$CF$_3$)$_2$. Thus, the crown ether complexes with the lithium cation can exist in three phase states, which possess different conductivity. A higher conductivity of 10^{-4} S cm^{-1} at 40 °C[6] is observed in the case of 18C6, in contrast to 12C4, which forms a very strong complex with Li$^+$ with a lower mobility of Li$^+$.

Thus, we expect the formation of the conducting layers of crown ethers on a Li-metal electrode surface and a lithium electrode surface coated with Li$_3$N. To study this process, 1,6-dioxo-14-crown-4 was chosen. This crown ether is a by-product of the polymerization of 2-hydroxyethyl acrylate to polyester diacrylate (PEDA).[8,9] PEDA contains to 10 wt% 1,6-dioxo-14-crown-4. Polymer electrolytes based on this mixture have high electrochemical characteristics[10–12] apparently due to the presence of the crown ether.

The complete separation of 1,6-dioxo-14-crown-4 from the polymer fraction was impossible; therefore, an extract containing 80 wt% crown ether and 20 wt% PEDA, which was denoted as a cyclic structure (CS), was used for electrochemical studies. The CS was added to an organic liquid electrolyte of 1 M LiClO$_4$ dissolved in γ-butyrolactone (Li-GBL) in an amount of 8.2 wt%. Symmetric lithium cells contained a porous polypropylene separator impregnated with Li-GBL or Li-GBL + CS electrolytes.

With the use of freshly rolled lithium foil, the effect of the crown ether does not occur at –14 °C; in accordance with the results of previous studies,[1,3] the crown ether effect on a lithium surface was observed only during the storage of cells.

Thereafter, the cells with the Li$_3$N coated Li electrodes were collected. A lithium conductive Li$_3$N film[13] is successfully prepared on a Li metal surface by a reaction between Li and N$_2$ gas at a temperature of 100 °C in accordance with a published procedure.[14]

The results of electrochemical measurements[†] are shown in Figure 1. The exchange current i_0 (A cm^{-2}) was calculated using the formula

$$i_0 = RT/ZF\overline{R}_\mathrm{F},$$

where Z is the number of electrons involved in the elementary act of a reaction (this number is 1 for Li^0); F is Faraday's constant; T is the temperature (K); R is the universal gas constant; and R_F is the specific charge transfer resistance. $R_\mathrm{F} = R_\mathrm{ct}S/2$, where S is the contact area of the electrode/electrolyte interface, and R_ct

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[†] The electrochemical impedance of symmetrical cells with lithium electrodes was measured with a Z-2000 impedance meter (Electrochemical Instruments, Russia) in a frequency range from 10 to 1×10^5 Hz. The amplitude of the imposed sinusoidal perturbation was 10 mV. The components of the equivalent scheme were calculated by the Zview2 program.

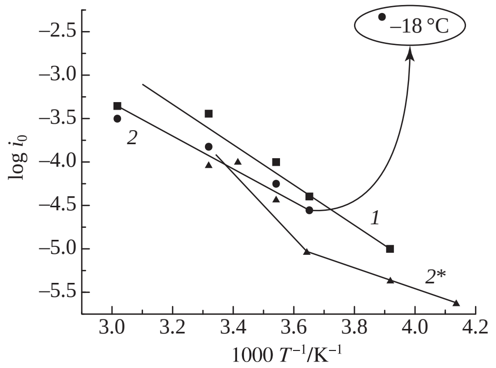

Figure 1 Arrhenius plots of the exchange currents (A cm^{-2}) at the Li/Li$_3$N interface (*1*) with a liquid electrolyte, (*2*) with the addition of CS under slow cooling, and (*2**) with the addition of CS under fast cooling.

is the charge transfer resistance calculated from the equivalent circuit.

The rate of cooling from 0 to –18 °C was 10 K h^{-1}. In a series of experiments with fast cooling, the cells were immediately placed in a vessel with a cooling liquid at –30 °C after assembling.

Figure 1 shows that, during the slow cooling of a Li/Li$_3$N cell with a liquid electrolyte and the CS additive to 0 °C, the line shape (curves *1* and *2*) is the same. However, there is jump of the exchange current by more than two orders of magnitude under slow cooling to –18 °C (curve *2*). During the rapid cooling of the Li/Li$_3$N cell with a liquid electrolyte and the CS additive (curve *2**), such a jump did not occur, and there was only a bending point at –10 °C. The impedance hodographs of the cells at 0 and –18 °C are shown in Figure 2.

The charge transfer resistance at the Li/electrolyte interface significantly decreased as the temperature was slowly decreased from 0 to –18 °C.

This is evidence for the formation of a new layer with a high Li$^+$ conductivity and a very low resistance at the interface. The equivalent circuits of cells that fit hodographs at 0 and –18 °C are shown in Figure 2. The second equivalent circuit, which was used in an analysis of the results of Li/Li$_3$N surface treated by liquid 15-crown-5,[4] consists of two parts responsible for two interfaces: the electrolyte/crown ether layers and the crown ether layers/lithium anode.

The layer of lithium nitride on the surface of lithium is very small, and its structure is compatible to the crystal structure of lithium; therefore, it was not determined on the hodograph.[4]

It is difficult to determine to which kind of interface each of the two semicircles in Figure 2 is attributed. Therefore, it is more accurately to discuss the total charge transfer resistance $R_{ct} = R_1 + R_2$, which is about 60 Ω. Taking into account the electrode surface (0.2 cm^2), the corresponding specific resistances are ~ 6 Ω cm^2, which is a very small value for such systems. For example, at 0 °C [Figure 2(*a*)], the charge transfer resistance of ~11000 Ω corresponds to a specific resistance of ~1100 Ω cm^2 at the same interface.

From the analysis of the other components of the equivalent circuit [Figure 2(*b*)], it can be assumed that R_{el} is resistance in a high frequency region corresponding to the electrolyte resistance; CPE1-P has a value of 1 and CPE1 corresponds to double layer capacitance. CPE2-P on value approaches to 0.5; therefore, it can be assumed that CPE2 refers to the diffusion difficulties of lithium ions.

The jump of exchange current was not observed under fast cooling (Figure 1, curve *2**). This indicates that the highly conductive complex of Li$_3$N with CS has no time to form. Nevertheless, Figure 1 shows that, in this experimental series, the slope of the Arrhenius curve below –10 °C decreased by a factor of 4 with the lowering of charge-transfer activation energy. In this case, the plastic crystals of crown ether may also be formed, but they have another microstructure different from that under slow cooling.

Based on the above data, we suppose that, in the case of Li/Li$_3$N–crown ether systems, a new phase of plastic crystals[6,7] is formed on the Li$_3$N surface if the temperature decrease is slow. With a further decrease in the temperature, the plastic crystal phase is transformed into a crystal phase. The transfer temperature depends on the crown ether structure and electrolyte composition. The same hypothesis explains why this effect does not occur at temperatures greater than 0 °C, when the crown ether crystals are melted.

The formation of a Li$^+$-ion conductive phase from crown ether molecules on the Li-metal surface is apparently difficult to expect due to the reactivity of lithium. This is confirmed by a study of the Li/liquid electrolyte + CS system using freshly cut Li metal.

Figure 3 schematically shows the structure of highly conductive layers on Li metal formed by lithium nitride and crown ether complexes with Li$^+$ ions at temperatures below

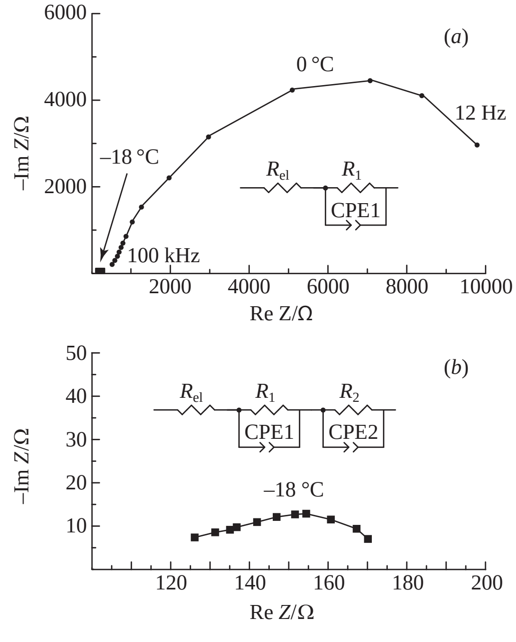

Figure 2 Impedance hodographs of the Li/Li$_3$N electrodes and Li-GBL electrolyte with the addition of 8 wt% CS symmetric cell under slow cooling (*a*) from 0 °C (*b*) to –18 °C.

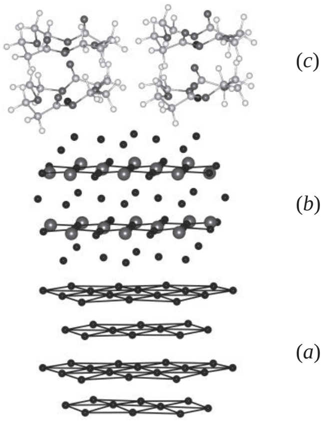

Figure 3 Highly conductive layers on Li metal at low temperatures: (*a*) a fragment of the Li-metal lattice; (*b*) a fragment of the Li$_3$N lattice; and (*c*) an adsorbed layer of Li$^+$–1,6-dioxo-14-crown-4 complexes.

–10 °C. The structures of Li-metal and lithium nitride fragments, as well as 1,6-dioxo-14-crown-4 molecules, have been optimized using quantum-chemical calculations by the PBE[15] density functional method and the extended basis H [6s2p/2s1p], C, O [10s7p3d/3s2p1d], Li [10s7p3d/4s3p1d].[‡]

The distances between layers in the Li-metal and lithium nitride lattices are 2.5 and 1.9 Å, respectively. Unfortunately, the structure of the total system consisting of crown ether–Li^+ complexes at the Li_3N/Li surface cannot be calculated due to a large number of atoms. Therefore, a constructed layer of crown ether–Li^+ complexes was imposed on the calculated fragment of Li_3N lattice. Recent theoretical studies showed that Li^+ movement through a layer of crown ethers requires the overcoming of a minor barrier of 22.6 kJ mol^{-1}.[17]

We assume that there is an energy barrier at Li^+ transport through the first interface of crown ether layer/Li_3N only, and it is practically absent from the second Li/Li_3N interface due to the presence of Li layers in the Li_3N structure that may be joined with Li-metal surface layers. For this reason, an appreciable charge transfer resistance appears that results in second semicircle on the impedance hodograph (Figure 2).

Thus, we suppose that the chemical adsorption of crown ethers on a Li_3N layer leads to the formation of a highly structured layer with a high conductivity at the electrolyte/Li/Li_3N interface at low temperatures. This occurs only on slow cooling with an increase of the total exchange current by more than two orders of magnitude. This effect opens up a possibility to improve the performance of a lithium battery at low temperatures.

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[‡] All calculations were performed using the PRIRODA[16] software package at the Joint Supercomputer Center of the Russian Academy of Sciences.

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