Short communication

Plastic crystalline phases of crown ether:salt complexes and their utilization in lithium-metal batteries

Ali Abouimrane [a], Pierre-Jean Alarco [b], Yaser Abu-Lebdeh [a,*],
Isobel Davidson [a], Michel Armand [c]

[a] *National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*
[b] *Department of Chemistry, University of Montreal, P.O. Box 6128, Montreal, Quebec H3C 3J7, Canada*
[c] *LRCS, Université de Picardie Jules-Verne, UMR 6007 CNRS, 33 rue Saint-Leu, 80039 Amiens, France*

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Abstract

We have shown that crown ether complexes with the lithium salt, lithium bis-(trifluoromethanesulphonyl) imide (LiTFSI), are plastic crystals as evidenced by DSC and their mechanical properties. The conductivity of the complexes was measured and found to vary as a function of crown ether:salt molar ratio. Our study of the (18-Crown-6)–LiTFSI (1/1) solid complex showed that it has a high conductivity reaching $\sim 10^{-4}\,\mathrm{S\,cm^{-1}}$ at $50\,^\circ\mathrm{C}$ and an electrochemical stability of over 4 V enabling its use in a lithium-metal battery. A lithium battery with 1:1 (18-Crown-6)–LiTFSI as electrolyte was assembled, tested, and found to exhibit reversible Li$^+$ transport.
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1. Introduction

Polymer electrolytes, formed from a salt dissolved in a solvating polymer, such as those based on poly (ethylene oxide), –[CH$_2$CH$_2$–O–]$_n$–, PEO, are widely investigated for all solid-state electrochemical devices [1]. Those that conduct lithium ions are particularly important due to the stability of the ether unit of the polymer chains against reduction by metallic lithium. These PEO-salt electrolytes' stabilities are incurred by virtue of their ability to form a conducting interfacial film, hence rendering possible the fabrication of high voltage batteries ($\sim 3.5\,\mathrm{V}$) [2].

However, due to the many problems associated with the operation of such batteries, especially the low ambient temperature conductivity of these polymer electrolytes, many other modified polymers or even alternative systems such as glass electrolytes [3], crystalline electrolytes [4] or plastic crystal electrolytes [5,6] have been investigated. The latter have attracted much attention recently due to their liquid-like behavior within a crystalline lattice that gives rise to an exceptional set of properties, including high diffusivity of ions and plastic mechanical properties [7].

During the course of our work on plastic crystal electrolytes we have observed that crown ether complexes, the molecular analogue of PEO electrolytes, show a similar behaviour to common plastic crystals; most important of which are the extra peak in the DSC scan and the characteristic soft appearance. This has motivated us to conduct this study by preparing several crown ether complexes of different sizes mixed with the lithium salt, lithium bis(trifluoromethanesulphonyl) imide, which is often abbreviated as LiTFSI.

We report on the thermal behaviour and conductivity of the prepared complexes and the performance of a lithium-metal battery prepared using one of these complexes as the electrolyte.

2. Experimental

All reagents and solvents were commercially available and used without further purification. The crown ether-LiTFSI complexes were prepared by mixing 18-Crown-6 or 12-Crown-4 (Aldrich) with LiTFSI (Fluka) in dichloromethane (Aldrich). Conductivity measurements were performed using the impedance spectroscopy technique by varying the frequency between 1 MHz and 5 Hz using a conductivity cell with a cell constant of $1\,\mathrm{cm^{-1}}$. The temperature was varied between -20 and $100\,^\circ\mathrm{C}$ at intervals of $2\,^\circ\mathrm{C}$ allowing 20 min for thermal

* Corresponding author.
  E-mail address: Yaser.Abu-Lebdeh@nrc.gc.ca (Y. Abu-Lebdeh).

equilibration at each set point. Differential scanning calorimetric analysis was performed using a Perkin-Elmer Pyris 1. All the samples were sealed in aluminum DSC pans in an argon filled glove box and then scanned from -150 to $150\,^{\circ}C$ at $10\,^{\circ}C\,min^{-1}$.

Cyclic voltammetry measurements were made at a scan rate of $10\,mV\,s^{-1}$ using Li metal as a counter electrode and stainless steel as a working electrode. A Li–((18-Crown-4)–LiTFSI)–LiFePO$_4$ battery was tested on a VMP multichannel potentiostat (Bio-Logic Science Instrument). A typical composition of the cathode was: 85% of active material, 5% carbon mixture and 10% PVDF. A $30\,\mu m$ thick, porous separator (Celgard®) was inserted between the electrodes to prevent short-circuits. The cells were cycled in a potentiostatic mode between 3 and 3.7 V at $40\,^{\circ}C$.

3. Results and discussion

3.1. (12-Crown-4)–LiTFSI complexes

Fig. 1 shows the DSC scan of neat 12-Crown-4 crown ether, and five of its complexes with LiTFSI at different molar ratios. The neat compound showed a single peak corresponding to its melting at $22\,^{\circ}C$. When LiTFSI was added in a 1:1 molar ratio, two new peaks emerged at -109 and $88\,^{\circ}C$ with the melting point increased to $145\,^{\circ}C$. The two extra peaks correspond to a crystal-to-plastic crystal transition I and plastic crystal I-to-plastic crystal II transition, respectively.

When the molar ratio was varied from 1/1 to 1/0.95 in order to introduce ion-free crown ether rings, the DSC scan showed only a slight decrease of the melting point from 145 to $134\,^{\circ}C$. However, when the ratio was changed to 1/0.6, 1/0.5 and 1/0.4, a completely different behavior was encountered. In this case, the peak at $\sim-110\,^{\circ}C$ disappeared in all the three compounds, while another appeared at $\sim105\,^{\circ}C$, that is, most probably, attributable to the formation of a 2/1 complex [8]. It is also observed that the peak at $89\,^{\circ}C$ of the 1/1 decreased as a function of ratio to reach $67\,^{\circ}C$ at 1/0.4. The entropy of fusion of the 1/1 complex was calculated from the DSC scan and was found to be $44.5\,J\,K^{-1}\,mol^{-1}$, a value higher than the $20\,J\,K^{-1}\,mol^{-1}$ set by Timmermans for the existence of plastic crystalline behav-
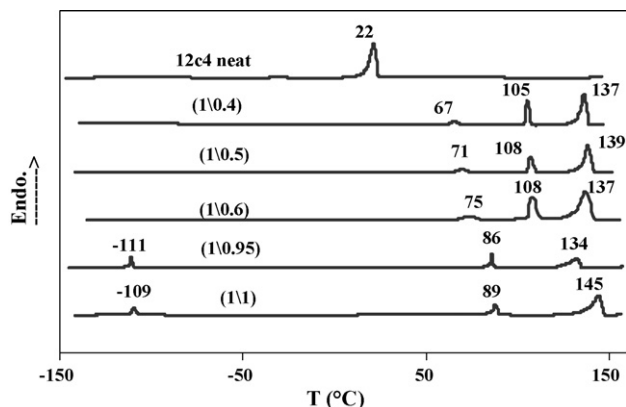
ior. However, such higher values have been observed previously and it was suggested to be normal in the case of plastic crystal electrolytes where other factors contribute to the total entropy like the flexibility of the anion, for example [9].

The plastic crystal phase has been recognized and given the name by Timmermans who also suggested that this metastable phase is exhibited by globular (spherical) molecules or planar molecules that become globular on rotating around one of the axes [10]. In the case of the crown ether complex we suggest that the formation of the plastic crystalline phase occurs when the highly flexible etheric ring becomes rigid, such as when its oxygen atoms bind to a lithium cation, forming a strong $O\cdots Li^+$ interaction, which in turn imparts an overall disc-like shape to the complex.

Molecular rotation of crown ether rings in the solid-state of their complexes has been reported by Ratcliffe et al. [11,12]. They have concluded from DSC and ^2H NMR line shape analysis that an onset of motion of the rings occurs rapidly at the phase transition where O–CH_2–CH_2 units exchange sites along the ring, with the necessary adjustment for their new conformation. This, however, indicates a rotation along the plane of the ring which does not result in a spherical-like shape of the molecule, as proposed by Timmermans. In order for that to be obtained, the dominant rotation should take place around the C_2 axis (in-plane). However, it should be noted that the shape of the molecule is not the only condition for the observation of the plastic crystal behavior, as succinonitrile, one of the most studied plastic crystals, is a well-known exception to this rule.

3.2. (18-Crown-6)–LiTFSI complexes

Neat 18-Crown-6 has a melting point of $40\,^{\circ}C$, evidenced as one endothermic peak in the DSC. However, when it was mixed with LiTFSI (1/1), the resultant compound exhibited two new peaks at -30 and $29\,^{\circ}C$, and an increase in melting temperature to $49\,^{\circ}C$ as shown in Fig. 2. The entropy of fusion of the 1/1 complex was found to be $4.5\,J\,K^{-1}\,mol^{-1}$ which in this case is in compliance with Timmerman's criterion. This low entropy can be attributed to the large entropy of transition at $-30\,^{\circ}C$ that most probably arises from the movement of O–CH_2–CH_2 units which are weakly bonded to the Li^+ cation due to the mismatch

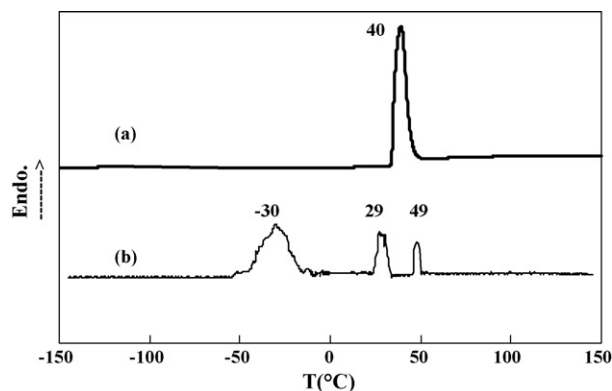Fig. 1. DSC scans of neat 12-Crown-4 and its LiTFSI complexes.

Fig. 2. DSC scans of the neat 18-Crown-6 (a) and its 18-Crown-6: LITFSI (1/1) complex (b).
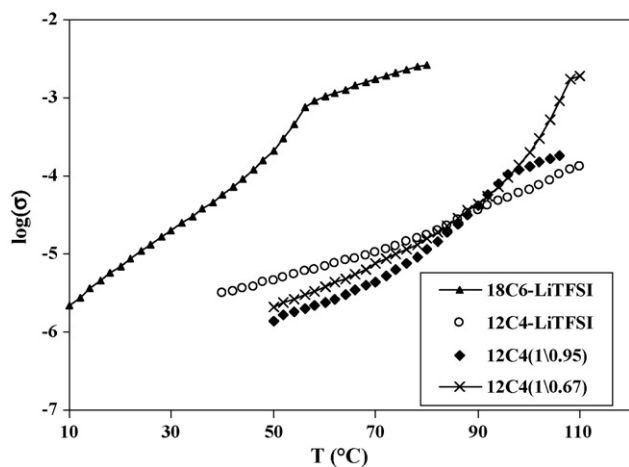
Fig. 3. Conductivity of the LiTFSI complexes of the 12-Crown-4 and 18-Crown-6.

between the size of the cation and that of the cavity size of the ring.

3.3. Conductivity of the complexes

Fig. 3 shows the temperature dependence of ionic conductivity of the (12-Crown-4)–LiTFSI complexes at (1/1, 1/0.95 and 1/0.67 molar ratios). At temperatures below the second plastic transition, ∼89 °C, the 1/1 complex showed the highest conductivity throughout the plastic range reaching 4.6×10^{-6} S cm^{-1} at 50 °C, a value close to the one reported by others [13]. The 1/0.95 complex showed lower conductivity than that of the 1/1 contradicting what we predicted that the availability of ion-free crown rings in the solid would provide a lower energy barrier for the Li ions to move from a complexed ring to an ion-free one. Moreover, the conductivity of the three compounds merged at the transition temperature (∼88 °C), reaching ∼3×10^{-5} S cm^{-1}.

The conductivity of the (18-Crown-6)–LiTFSI (1/1) was also measured and is shown in Fig. 3. This complex exhibited an ionic conductivity of 8.3×10^{-6} S cm^{-1} at 20 °C, that increased to 6.1×10^{-5} S cm^{-1} at 40 °C (in the plastic crystal phase), and to 1.8×10^{-4} S cm^{-1} at 50 °C (above melting). These values are lower than the ones reported by Shriver et al. [8] who obtained, for example, a conductivity of 3.5×10^{-5} at 20 °C. In general, the variation of conductivity with temperatures follows the binomial behavior already reported for other plastic crystals [14].

3.4. The lithium-metal battery

The (18-Crown-6)–LiTFSI (1/1) complex was chosen for the fabrication of the battery due to its ability to provide the highest conductivity within the plastic range at temperatures near ambient. For this purpose, we have first investigated the electrochemical stability window of the solid complex by cyclic voltammetry as depicted in Fig. 4. The cyclic voltametry showed the expected anodic and cathodic peaks corresponding to lithium stripping and deposition, respectively. Moreover, no more peaks were observed up to 4 V versus Li$^+$/Li, indicating an electro-

chemical stability window of at least 4 V for the solid complex. A cell was assembled using lithium-metal as an anode and LiFePO$_4$ as the cathode, and it was tested at 40 °C in a potentiostatic experiment (Fig. 5). The oxidation and reduction peaks were observed at 3.54 and 3.30 V, respectively. It can be observed from the figure that the reduction peak is much sharper than that of oxidation indicating faster kinetics and that crown ether complexes behave in a manner similar to their polymeric counterparts; PEO:Li salt complexes [15].

3.5. General remarks

DSC scans of crown ether complexes have been previously reported in the literature and the observed endothermic peaks before melting were either went un-identified or misinterpreted as extra melting points due to the relative infancy of the subject. Shriver and coworkers have reported on the thermal and conductivity behavior of many crown ether complexes with different cations and anions including Li and TFSI ions. Whenever they observed the crystal-to-plastic crystal transition peak, they misinterpreted it as a second melting. Moreover, after the re-interpretation of the DSC of the Li cation complexes we expect this finding to be valid for other metal cation complexes. For
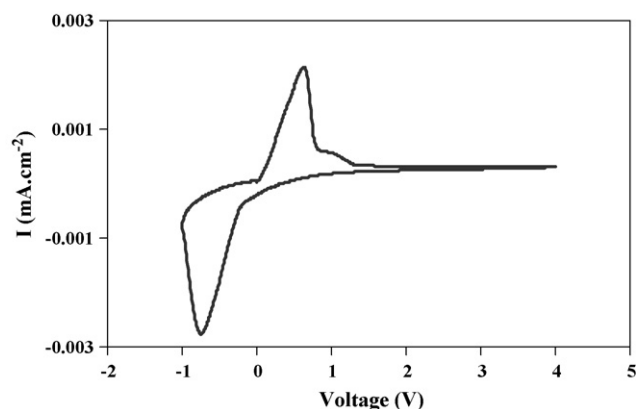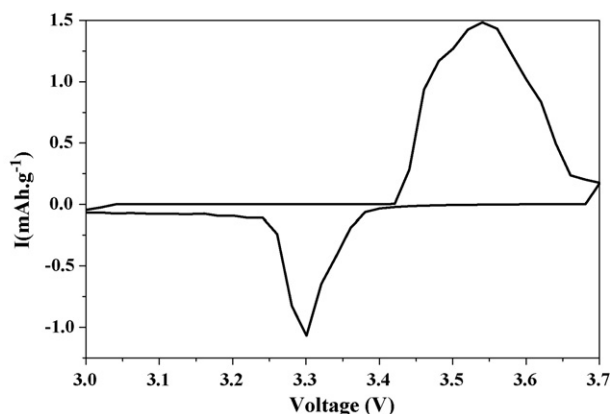

Fig. 4. Cyclic voltammogram of the (18-Crown-6)–LiTFSI (1/1) complex using lithium-metal as a blocking electrode and stainless steel as a working electrode at a scan rate of 10 mV s^{-1}.

Fig. 5. Slow scan cyclic voltammogram (50 mV h^{-1}) of the Li–((18-Crown-6)–LiTFSI) (1/1)–LiFePO$_4$ solid-state battery at 40 °C.

this purpose we have prepared a (18-Crown-6)–KBF$_4$ (1/1) salt and recorded its DSC scan, not shown here. It exhibited a peak of melting at 98 °C (*ca.* mp near 40 °C) and most importantly another peak at 54 °C corroborating what we predicted to be a plastic crystal transition, and also indicating a general plastic crystalline behavior in the crown ether complexes. Finally, current work involves the investigation of the plastic behavior in other crown ether complexes of different metallic cations.

4. Conclusions

Plastic crystal solid electrolytes based on crown ether complexes with a LiTFSI salt were prepared at different molar ratios. Their thermal, ionic conductivity and electrochemical properties were investigated. We have shown in this work that crown ethers can be envisaged as a new type of ion-conducting material due to their ability to form plastic crystalline phases when complexed with salts of alkali metal cations. We have also shed light on the current misunderstanding in interpreting extra thermal events in the DSC scans of such complexes as extra melting events instead of being recognized as a solid-solid transformation to the plastic crystalline phase. (18-Crown-6)–LiTFSI exhibited a small temperature range of plastic crystal behaviour between 29 and 49 °C and a high ionic conductivity of $\sim 10^{-4}$ S cm^{-1} at 40 °C. This particular electrolyte was tested in a Li/LiFePO$_4$ battery and showed promising results despite the low discharge capacity. This compound is an example of a plastic crystal solid electrolyte that is stable against reduction in contact with lithium-metal and as such it can be used as an electrolyte for lithium-metal or lithium ion batteries. Furthermore, the greater understanding of these complexes paves the way to the development of other types of plastic crystal electrolytes.

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