New Main-Chain Crown-Ether Polyimides for Lithium-Ion Battery Membranes

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ABSTRACT

Thin rugged membranes based on polyimides having a columnar liquid crystal (LC) morphology (nanotubules of crown ether) which rapidly conduct lithium ions between the anode and cathode is the objective. This preliminary report describes the synthesis and characterization of a novel lithium-ion conducting polymer containing crown ether segments in the backbone. Segments of fluorocarbon co-monomers were used to lower cohesive energy density relative to the hydrophilic crown ether segments in order to promote a microphase-separated morphology. However, no evidence of phase separation nor LC morphology are observed. The ionic conductivity of the polymer films was measured using the technique of electrochemical impedance spectroscopy (EIS) and two polished stainless steel electrodes with the polymer film coated on the working electrode.

Introduction

Polymer membrane technology for lithium-ion batteries is an attractive alternative for meeting the military's increased requirements for lightweight devices with increased power. Lithium-ion battery technology potentially offers a very high theoretical energy density. Additionally, this type of technology can be safer and may have lower life-cycle costs than existing battery technology. Efforts in developing this technology have been made by several research institutions over the past two decades (1). The initial discovery of ionic conductivity in polymers was reported by Wright in 1973 (2, 3). The idea of using ionic conducting polymers in batteries was proposed by Armand in 1978 (4, 5). Ion-conducting polyimide membranes are promising candidates for separating the electrodes because such a membrane has the mechanical stability to prevent shorts on rough handling, the chemical stability to prevent decomposition reactions that organic liquid electrolytes are prone to suffer at elevated temperatures, and the ability to resist penetration of lithium dendrites (6). Many types of polymers have been studied for this type of application including amorphous poly(ethylene oxide) (7, 8), polyphosphazene with ethylene oxide side chains (MEEP) (9), and various polysiloxanes with ethylene oxide side chains (10, 11). Such polymer membranes tested to date suffer from low conductivity compared to liquid electrolytes. The best of these films in the dry state do not have a lithium-ion conductivity much better than about 10^-5 S/cm at room temperature.

There have only been a few reports in the open literature on main-chain polymeric crown ethers. An early attempt was reported by Mathias in 1980 (12), in which main-chain polymers contained crown ethers in the backbone. However, this polymer did not exhibit LC properties. The first example of a main-chain polymer containing crown ethers which exhibited LC morphology was reported by Percec in 1989 (13). However, these polymers required large amounts of non-crown mesogens before LC behavior was observed. The most important polymers related to this study were reported by Fischer, Zuev and Karasz in 1994 (14, 15). Their polymers were polyamide-esters containing dibenzo-18-crown-6 ethers in the backbone and exhibited a “fine scaled” LC texture having the appearance of a smectic phase. However, ionic conductivities were not measured.

Our main objective is to develop thin rugged membranes based on main-chain crown-ether polyimides (PI) that can be formed into films having columnar liquid crystal morphology in which lithium ions can be rapidly transported.

Our idea is to design a polymer membrane in which the LC morphology forms stacks of crown ethers that are highly conducting channels for transporting lithium ions (Fig. 1). The driving force for the formation of the LC morphology will be due to microphase separation of the hydrophilic crown ether segments and the hydrophobic
fluorocarbon segments (both segments having high aspect ratios).

Several main-chain crown-ether polymers were made during this study and one such polymer is represented in Scheme I.

**Scheme I**

\[
\begin{align*}
\text{6FDA} & \quad + \quad \text{H}_2\text{N}-\text{CF}_3\text{CF}_3\text{NH}_2 \\
\text{Trimer-IImide Precursor} & \\
\text{anti-diaminodibenzo-18-crown-6} & \\
\text{6FDA/ABL-21/anti-DADB-18-crown-6-PI} \\
\text{Where } n > 1
\end{align*}
\]
Experimental

$^{19}$F Spectra were obtained on a Bruker AMX-200 NMR Spectrometer. $^1$H and $^{13}$C NMR Spectra were obtained on a Bruker AMX-400 NMR Spectrometer. Thermal characterization of the crown ether PI was measured by TA Instruments DSC and TGA under a nitrogen atmosphere at a heating rate of 10°C/min. Ionic conductivities of the polymer films were measured using the technique of Electrochemical Impedance Spectroscopy (EIS) consisting of a computer-controlled EG&G Model 273 potentiostat/galvanostat, EG&G Model 5210 lock-in amplifier and EG&G Model 398 EIS Software. The EIS measurements were made using two polished stainless steel electrodes with the polymer film coated on the working electrode. An added weight (generally 637 g) ensured good mechanical contact between the two electrodes. Measurements were conducted over the frequency range of 100 kHz to 1 Hz. The Bode plot (log $|Z|$, vs. log $\omega$) generally gave a straight line with the expected slope of $-1$. The film resistance was determined at high frequencies using the real portion of the impedance.

2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 2,2'-bis(trifluoromethyl)benzidine (ABL-21) were obtained from Chriskev Company and dibenzo-18-crown-6, sebacocyl chloride were obtained from Aldrich Chemical Co. All starting materials were used as received.

Synthesis of Crown Ether Monomer: Syn- and anti-dinitrodibenzo-18-crown-6 were prepared by the nitration (HNO$_3$/acetic acid) of dibenzo-18-crown-6 according to a literature procedure (16). The two isomers have very different solubilities which allowed for easy separation by fractional crystallization. Anti-Diaminodibenzo-18-crown-6 (anti-DADB-18-crown-6) was prepared by suspending unttdinitrodibenzo-18-crown-6 (1.00 g) and PtO$_2$ (50 mg) in 50 mL of N,N-dimethylformamide. Hydrogenation in a Parr Shaker yielded a yellow/orange solution which was evaporated to dryness under vacuum. The yellow residue was suspended in dichloromethane and filtered to give a yellow solid in high yield. Sublimation at 220°C, 0.1 mm Hg, gave the diamine (anti-DADB-18-crown-6) as a white solid in reduced yield.

$^1$H NMR (DMSO-$d_6$, $\delta$ PPM): 6.62 (d, 2 H), 6.23 (d, 2 H), 6.04 (dd, 2 H), 4.62 (s, 4 H) and 4.16-3.60 (m, 16 H).

Synthesis of Trimer-Imide Precursor: A round-bottom flask was charged with 20 mL 1-methyl-2-pyrrolidinone (NMP), 6FDA (1.5 g, 3.38 mmol) and ABL-21 (0.54 g, 1.69 mmol) (2 mol dianhydride:1 mol diamine). The contents were stirred at ambient temperature under a positive nitrogen blanket overnight. The solution was imidized at 170°C for 4 hours under a continuous positive nitrogen atmosphere. The cooled trimer solution was poured slowly into 200 mL hexane and the resulting oil was separated from the hexane. The oily product was dried under high vacuum (0.05 mm Hg, 80°C) for 3 days to give a brown powder in 85% yield (6FDA/ABL-21 PI).

$^{19}$F NMR (acetone-$d_6$, $\delta$ ppm): -56.00 (s, 6 F) and -61.61 to -61.34 (m, 12 F) confirmed the product was obtained in the proper stoichiometric amounts.

Synthesis of Main-Chain Crown Ether PI: A round-bottom flask was charged with 6 mL NMP, 6FDA/ABL-21PI (0.66 g, 0.56 mmol), and anti-DADB-18-crown-6 (0.22 g, 0.56 mmol). The contents were allowed to stir at ambient temperature under a positive nitrogen blanket overnight. The solution was imidized at 170°C for 6 hours under a continuous positive nitrogen atmosphere. The cooled polymer solution was precipitated slowly into 60 mL of absolute ethanol and the resulting polymer suspension was filtered and the cake was washed twice with ethanol. The crude polymer was Soxhlet-extracted with absolute ethanol at reflux temperature under a positive nitrogen blanket for 3 days. The polymer was dried under vacuum (0.05 mm Hg) overnight to give a purple powder (6FDA/ABL-21/anti-DADB-18-crown-6 -PI) in 88% yield. $^1$H NMR (DMSO-$d_6$, $\delta$ ppm): 8.25-7.62 (m, 15 H), 7.06-6.86 (m, 6 H) and 4.13-3.84 (m, 16 H). $^{13}$C NMR (DMSO-$d_6$, $\delta$ ppm): 166.33, 166.18, 147.95, 147.95, 147.76, 135.61, 132.97, 132.59, 130.20, 124.77, 124.19, 120.06, 112.47, 112.14, 68.71, 67.89, and 64.63. Thermal analysis: $T_g = 225°C$, $T_d$ (onset) = $>350°C$.

Film Preparation: The film preparation for the prepared PI was accomplished by incorporating a Li salt (lithium bis(trifluoromethyl sulfonyl) imide) into a 27 weight % polymer solution in NMP. The lithium salt was dissolved in tetrahydrofuran and then this Li salt solution was added to the polymer solution. The Li salt/polymer solution was filtered through a 0.5 µpore size membrane filter and doctor-blade coated onto stainless steel slides. The film was then dried under a dry nitrogen stream with increasing temperature to 200°C for 15 minutes. Final removal of solvent was accomplished under high vacuum. The dry films were smooth in appearance with average thickness of between 5-7µ.

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Results and Discussion

Initially, a copolyimide of 6FDA and anti-diaminodibenzo-18-crown-6 was prepared which had a glass transition temperature of 217°C. It exhibited no liquid crystalline transition. The 6FDA-ABL-6FDA trimer polymer was prepared with the idea that the longer fluorinated segment, because of its hydrophobicity and large geometric aspect ratio, would be likely to form liquid crystal morphology. However, no LC phase was observed for this polymer either. Its glass transition temperature was 225°C.

The film conductivities for the trimer PI at several different concentrations of the lithium salt are given in Table I. The salt concentration is expressed as the ratio of lithium atoms to oxygen atoms in the crown portion of the polymer. The ionic conductivities of the prepared films go through a maximum as a function of salt concentration. It is possible that aggregation of lithium salts in the polymer membrane may account for the decrease in conductivity at higher concentrations. The desired ionic conductivities are lacking at ambient temperature. This may be due to the non-LC morphology of the prepared films. Preliminary studies at higher temperatures have yielded an activation energy of 45 kJ/mol for the ionic conductivity.

Table I. Polyimide Film Conductivities from EIS Measurements at 23°C

<table>
<thead>
<tr>
<th>Salt Concentration</th>
<th>Film Thickness (µm)</th>
<th>Film Conductivity (S/cm)²</th>
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<tbody>
<tr>
<td>Li/O = 0.04</td>
<td>6.0</td>
<td>0.6 x 10⁻⁴</td>
</tr>
<tr>
<td>Li/O = 0.08</td>
<td>7.0</td>
<td>2.0 x 10⁻⁴</td>
</tr>
<tr>
<td>Li/O = 0.16</td>
<td>5.5</td>
<td>0.8 x 10⁻⁴</td>
</tr>
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² σ = L/R^²A; where σ is the film conductivity, L is the film thickness, R is the measured resistance, and A is the film area.

Future Work

Ongoing investigations will continue at China Lake to develop PI polymeric materials possessing LC morphology with the goal of improving the ionic conductivities by three orders of magnitude. Longer flexible spacers will be incorporated between crown-ether segments, and new dilithium salts will be synthesized.

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References