DNA Based Electrolyte/Separator for Lithium Battery Application

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DNA based electrolyte/separator for lithium battery application

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ABSTRACT

In this study, we demonstrated the use of DNA-CTMA (DC) in combination with PolyVinylidene Fluoride (PVDF) as a host matrix or separator for Lithium based electrolyte to form solid polymer/gel like electrolyte for potential application in Li-ion batteries. The addition of DC provided a better thermal stability of the composite electrolyte as shown by the thermos-gravimetric analysis (TGA). The AC conductivity measurements suggest that the addition of DC to the gel electrolyte had no effect on the overall ionic conductivity of the composite. The obtained films are flexible with high mechanical stretch-ability as compared to the gel type electrolytes only.

Keywords: DNA-CTMA, PVDF, Li-ion battery, Separator, electrolyte

1. INTRODUCTION

The ever increasing demand for efficient, reliable, lighter, portable and more importantly safer batteries is the driving force behind the tremendous amount of research work directed towards solid state electrolytes nowadays. The many uses of secondary batteries range from portable electronics to hybrid and electric vehicles. Two general categories of secondary batteries are mainly explored: the first are liquid electrolyte metal-ion (Lithium-ion or sodium-ion) batteries and the second are the gel polymer electrolyte (GPE) metal-ion batteries also known as metal-ion polymer batteries. Polymer batteries are attractive due to their relatively long lifespan and highest cell voltage among secondary cell batteries. They also have other advantages over their liquid counterparts including their high electrical resistivity (no internal shorting), no electrolyte leakage and less chemical reactivity at the electrode surface [1-3]. The main disadvantage of solid state electrolytes is their poor ionic conductivity limiting the cycling performance of the corresponding cells to 200-300 cycles [4]. On the other hand, the gel polymer electrolytes possess both the cohesive properties of solids and the diffusive property of liquid electrolytes [5, 6]. In this study, we focus on the use of DNA-CTMA as a host material for a gel type polymer based on PVDF-LiAsF6. The new composite material is designed to offer a flexible, stretchable membrane with high ionic conductivity to be used as a solid electrolyte and a separator for Li-batteries.
2. Experimental

2.1. Materials

Deoxyribonucleic acid- cetyltrimethylammonium (DNA- CTMA) and PolyVinylidene Fluoride (PVDF) (supplier) were used in this study without further modifications. N- Methyl- 2 -Pyrrolidone (NMP) was chosen as solvents for DNA-CTMA and PVDF. The Lithium Hexafluoroarsinide (LiAsF6) in a mixture of Ethyl Carbonate (EC)/Ethyl Methyl Carbonate (EMC)/Dimethyl Carbonate (DMC) solvents was prepared in our lab to be used as liquid electrolyte.

2.1. Solution preparation and film casting

The 1:1 DNA- CTMA (DC): PVDF solution was prepared by dissolving equal parts by weight of DNA-CTMA and PVDF in NMP. Furthermore, control solutions were prepared by dissolving DNA-CTMA in NMP and PVDF in NMP. The dissolution process was activated by heating the solutions to 85°C on a hotplate. Free standing films of DC: PVDF were cast in a Petri dish. The film thicknesses were controlled by the volume of the solution dispensed in the casting dish. The DC: PVDF films were then dried in air at 85°C for 6-8 hours. The films were carefully peeled-off with tweezers.

2.2. Coin- cell Fabrication

Coin- cells were used as casings for the DC:PVDF films to run electrical measurements. A stainless steel disk was placed in the ‘can’ and a 17 mm cut-out of the DC:PVDF film was placed on top. A drop of LiAsF6 dissolved in a combination EC/EMC/DMC(1:1:1) solvent was applied to the DC:PVDF film. The ‘cap’ was placed over the ‘can’ and the film was left to absorb the liquid electrolyte for few hours. After 2 hours, a stainless steel disk was placed on top of the film and two springs were placed between the top stainless steel disk and the ‘cap’ (Fig. 2). The cell was sealed using a coin cell crimping press. This entire process was done in a glovebox under Argon gas.

2.3. Testing methods and equipment

Impedance testing using the Solartron 1260A Impedance/ Gain- phase Analyzer was performed on each cell at temperatures ranging from -20°C to 100°C in a controlled- environment chamber.

Thermogravimetric analysis (TGA) was run using a TA Instruments TGA 500 at temperatures up to 900°C to determine the thermal stability of the DC: PVDF based solid electrolyte.

Fourier- Transform Infrared Spectroscopy (FTIR) data was collected using a Thermo Scientific Nicolet 6700 to determine the physical/chemical interaction between the PVDF, DNA and liquid electrolyte (LiPF6 in EC/EMC/DMC).

![Figure 1: Schematic Diagram of Coin Cell Configuration](image-url)
3. Results and discussion

3.1. Impedance and Conductivity

The impedance measurements determined from the Nyquist plots showed high resistance at low temperatures, represented by a semi-circle, for all the DC:PVDF films which may indicate the freezing of the electrolyte at these low temperatures (<0°C). At higher temperatures, the variations of the $Z''$ vs $Z'$ appear to be linear suggesting a decrease of the DC: PVDF electrical resistance.

The measured resistance values and their corresponding temperatures were used to create Arrhenius Conductivity plots for each of the films (Table 1) and figure 3.

Table 1: Electrical Resistance of DC: PVDF (10, 20, and 50 μm) Film at Various Temperatures

<table>
<thead>
<tr>
<th>Cell Bulk Resistance (Ω)</th>
<th>T(°C)</th>
<th>10 um</th>
<th>20 um</th>
<th>50 um</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-20°C</td>
<td>2.77E+05</td>
<td>2.48E+05</td>
<td>2.00E+07</td>
</tr>
<tr>
<td></td>
<td>0°C</td>
<td>5.42E+03</td>
<td>4.50E+03</td>
<td>3.12E+05</td>
</tr>
<tr>
<td></td>
<td>15°C</td>
<td>13.403</td>
<td>5.42E+01</td>
<td>2.65E+04</td>
</tr>
<tr>
<td></td>
<td>25°C</td>
<td>12.019</td>
<td>4.4773</td>
<td>8.21E+03</td>
</tr>
<tr>
<td></td>
<td>35°C</td>
<td>8.3701</td>
<td>6.2658</td>
<td>3.83E+03</td>
</tr>
<tr>
<td></td>
<td>45°C</td>
<td>6.2892</td>
<td>34.749</td>
<td>1.37E+03</td>
</tr>
<tr>
<td></td>
<td>65°C</td>
<td>3.7336</td>
<td>17.644</td>
<td>22.472</td>
</tr>
<tr>
<td></td>
<td>100°C</td>
<td>2.4253</td>
<td>15.197</td>
<td>8.5512</td>
</tr>
</tbody>
</table>

The conductivity (Log $\sigma$) for the DC: PVDF films with 10 and 20 μm thickness as a function of temperature follow an Arrhenius behavior with two distinct slopes (activation energies) whereas for the 50 μm film only one activation energy is determined as shown in Figure 3. The activation energies for the 10 μm film were 1.7292 eV from -20°C to 15°C (indicative of solid electrolyte-like behavior) and 0.1990 eV from 15°C to 100°C (indicative of liquid-electrolyte-like behavior). The activation energies for the 20 μm film were 1.4829 eV from -20°C to 15°C (indicative of solid-electrolyte-like behavior) and 0.1604 eV from 15°C to 100°C (indicative of liquid-electrolyte-like behavior). The activation energy of the 50 μm film was 1.6462 eV from -20°C to 100°C (indicative of solid-electrolyte-like behavior).

Figure 2: Conductivity Plot for DC: PVDF (different thicknesses) in coin cell
3.2. TGA

TGA was performed in order to evaluate the thermal stability of the films. In this study, we run TG analysis on DC- only, PVDF- only, and DC: PVDF films, before and after soaking in the liquid electrolyte. The soaking in electrolyte was undertaken for few hours before the TGA was run to endure full intake of the electrolyte into the host matrix. As shown in figure 4, the degradation temperature of DC increases from \( \approx 260^\circ C \) to \( \approx 300^\circ C \) when it is soaked in LiAsF$_6$ solution (liquid electrolyte); On the other hand, the addition of the liquid electrolyte to PVDF rendered it thermally unstable as indicated by the lowering of its degradation temperature from 480°C to 420°C. Most importantly, the addition of the liquid electrolyte to the DC: PVDF film increased its overall stability by decreasing the degradation rate. The degradation temperature for the soaked and non- soaked DC: PVDF film remains, approximately, the same (Fig. 4). Note that the initial decrease in mass of the DNA-CTMA/PVDF/NMP film is due to the evaporation of the liquid electrolyte solvent.

![Figure 3](http://proceedings.spiedigitallibrary.org/)

Figure 3: Upper Left (first) to Lower Right (last); DNA- CTMA Plotted against DNA-CTMA-LiAsF$_6$, PVDF Plotted against PVDF- LiAsF$_6$, DNA- CTMA- LiAsF$_6$ Plotted against PVDF- LiAsF$_6$, DNA- CTMA/PVDF Plotted against DNA- CTMA/ PVDF- LiAsF$_6$

3.3. FTIR

Both DNA and PVDF show their characteristic FTIR peaks (Fig. 5): DNA doping by CTMA ion at 2926 and 2846 cm$^{-1}$, C=O stretching at 1647 cm$^{-1}$, C-N stretching at 1231 cm$^{-1}$, P=O at 1088 cm$^{-1}$, C-O at 1052 cm$^{-1}$, and C-O bending at 962 cm$^{-1}$. When combined, DNA and PVDF show a reduction in peak intensity, indicative of simple physical mixture. When the liquid electrolyte is added to the DNA-CTMA/PVDF film, the DNA doping by CTMA ion remains intact at 2926 and 2846 cm$^{-1}$, however, there is a major band shift at 1647 cm$^{-1}$ of DNA-CTMA due to C=O to \( >1750 \) cm$^{-1}$. This band shift indicates doping at C=O sites by LiAsF6 electrolyte, however, further tests would need to be done in order to differentiate the behavior of the individual polymer components from the liquid electrolyte.
4. Conclusion

DNA-CTMA/ PVDF films were fabricated and tested using impedance, thermal, and spectroscopic analysis to access their suitability as solid state electrolytes for advanced batteries. The test showed strong evidence that DNA-CTMA provided additional thermal stability to PVDF when the liquid electrolyte is added. The FTIR scan shows that there was an interaction between the DNA-CTMA/PVDF and the LiAsF$_6$. This can be further supported by the TGA data which shows that the addition of LiAsF$_6$ to the DNA-CTMA film improved the thermal stability by increasing degradation temperature while also decreasing the degradation rate. Furthermore, while the PVDF films were flexible, they would break if folded; the addition of the DNA enhanced the flexibility, allowing the films to be folded with high elasticity. While low temperature conductivity of DC-PVDF/LiPF$_6$ has been found inferior compared to the traditional liquid electrolyte, but the trend reversed at higher temperature. Lower thickness shows better ionic conductivity for DC-PVDF/LiPF$_6$ electrolyte films. Further characteristics of DC-PVDF/LiPF$_6$ electrolytes such as stability with lithium anode, resistance to dendrite formation and charge-discharge power capability will be determined later.
References: