Chapter 5

Battery Studies
5.0 BATTERY STUDIES

High energy solid state polymer electrolyte rechargeable lithium batteries are under study in various academic and industrial laboratories [153-157]. Therefore, our main objective is to develop a polymer battery based on PVC electrolyte developed from the present study. Sample PC 7 which consists of PVC : LiCF$_3$SO$_3$ : LiBF$_4$ : EC : PC (9 : 2.7 : 6.3 : 12 : 70) was chosen for this purpose since it shows the highest electrical conductivity among all the films prepared. The thin film polymer battery was assembled into a battery casing with the polymer electrolyte sandwiched between the lithium anode and the graphite cathode under argon atmosphere in a glove box. The characteristics were studied using the BAS LG50 Galvanostat. A schematic representation of the cell fabricated is shown in Figure 5.1.

![Diagram](image)

Figure 5.1: Schematic representation of the fabricated cell.
The open circuit potential of the cell was measured and it was found to be 3.399V. The cell was discharged immediately. The first discharge current, \( I_d \) applied were 0.10mA and 0.50mA. The typical discharge curve for these two discharge currents are shown in figure 5.2 and 5.3.

![Graph showing discharge curve](image)

**Figure 5.2**: First discharge curve for the cell fabricated (\( I_d = 0.10\)mA)
The discharge curve for $I_d = 0.10\text{mA}$ shows a plateau potential at 3.1 V. This plateau potential is constant for at least 500 minutes. The discharge curve for $I_d = 0.50\text{mA}$ shows two plateau potential regions. The first plateau potential region occurs at 2.4 V and the second plateau region is seen at 1.6 V. It is observed that this potential comes to zero after prolonged time. From the discharge curves, the discharge capacity of the cell is calculated and the potential versus capacity curves were plotted (Figure 5.4 and 5.5).
Figure 5.4: Potential versus capacity curve for the cell fabricated (0.10mA).

Figure 5.5: Potential versus capacity curve for the cell fabricated (0.50mA).
The discharge capacity for the whole discharge curve is found to be 2.2 mAh for \( L_d = 0.50 \text{mA} \). It can be observed that when the discharge current is increased, the plateau voltage fell and the realizable capacity decreased. The cause of the above phenomenon was the lower ionic conductivity in the polymer electrolyte and the higher electrode/electrolyte interface resistance [62, 158]. From this, it can be noted that the better performance of the batteries can be obtained at lower discharge current values. Immediately after the discharge, the battery cycled for a long time.

The battery was charged at a constant current of 0.05mA for 60 minutes and discharged at a constant current of 0.10mA for 600 minutes. The cell was cycled between the range of 4V and 0V. Figure 5.6 and Figure 5.7 show the charge-discharge characteristics for the polymer electrolyte at 2\(^{nd}\) cycle and 3\(^{rd}\) cycle.

![Graph showing charge-discharge curve](image)

**Figure 5.6**: Charge - discharge curve of the polymer electrolyte (2\(^{nd}\) cycle)
Figure 5.7: Charge - discharge curve of the polymer electrolyte (3rd cycle)

It can be observed that after attaining the maximum potential, it begins to drop and maintains a plateau potential of around 2.5 V for the second cycle. As for the 3rd cycle, the plateau potential drops to 2.2 V and also shows a second plateau potential at around 1 V. Figure 5.8 shows the potential versus discharge capacity curves for these two cycles. The discharge capacity for the 3rd cycle is around 1mAh, which is lower than the discharge capacity for the 2nd cycle.
Figure 5.8: Potential versus capacity curve for the 2\textsuperscript{nd} and 3\textsuperscript{rd} cycle

Now the cell is charged with a higher current value (0.10mA) but the discharge current value (0.10mA) is maintained. Nagamoto \textit{et al.} [159] stated that the coulombic efficiency is high when the battery is charged and discharged at the same current. Figure 5.9 to 5.17 shows the charge-discharge characteristic for the polymer for the 2\textsuperscript{nd}, 3\textsuperscript{rd}, 4\textsuperscript{th}, 5\textsuperscript{th}, 6\textsuperscript{th}, 8\textsuperscript{th}, 10\textsuperscript{th}, 15\textsuperscript{th} and 20\textsuperscript{th} cycle.
Figure 5.9: Charge-discharge curve for the polymer electrolyte at 2nd cycle.

Figure 5.10: Charge-discharge curve for the polymer electrolyte at 3rd cycle.
Figure 5.11: Charge-discharge curve for the polymer electrolyte at 4th cycle.

Figure 5.12: Charge-discharge curve for the polymer electrolyte at 5th cycle.
Figure 5.13: Charge-discharge curve for the polymer electrolyte at 6th cycle.

Figure 5.14: Charge-discharge curve for the polymer electrolyte at 8th cycle.
Figure 5.15: Charge-discharge curve for the polymer electrolyte at 10th cycle.

Figure 5.16: Charge-discharge curve for the polymer electrolyte at 15th cycle.
Figure 5.17: Charge-discharge curve for the polymer electrolyte at 20th cycle.

From the discharge, it was observed that the potential comes to zero after a prolonged time. From the discharge part of the curves, the discharge capacity of the cell can be calculated. The potential versus discharge curve for the 2nd, 3rd and 4th cycle is shown in Figure 5.18.
Figure 5.18: Discharge behaviour at 2\textsuperscript{nd}, 3\textsuperscript{rd} and 4\textsuperscript{th} cycle.

Table 5.1 illustrates how the value of plateau voltage and discharge capacity varies with the number of cycles. Figure 5.19 shows the variation of discharge capacity with the number of cycles.
<table>
<thead>
<tr>
<th>Number of cycle</th>
<th>Plateau voltage/ V</th>
<th>Discharge capacity / mAh</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.2</td>
<td>0.490</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>0.292</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>0.232</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>0.185</td>
</tr>
<tr>
<td>6</td>
<td>2.0</td>
<td>0.133</td>
</tr>
<tr>
<td>7</td>
<td>2.0</td>
<td>0.097</td>
</tr>
<tr>
<td>8</td>
<td>1.9</td>
<td>0.087</td>
</tr>
<tr>
<td>9</td>
<td>1.7</td>
<td>0.075</td>
</tr>
<tr>
<td>10</td>
<td>1.6</td>
<td>0.068</td>
</tr>
<tr>
<td>15</td>
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<tr>
<td>20</td>
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</tr>
<tr>
<td>25</td>
<td>0.8</td>
<td>0.031</td>
</tr>
</tbody>
</table>

Table 5.1: Characteristic of the PVC - LiCF$_3$SO$_3$ - LiBF$_4$ - EC - PC cell. 
($I_c = 0.10mA$ and $I_d = 0.10mA$).
Figure 5.19: Discharge capacity versus number of cycling for the cell.

Since the discharge plateau potential curve is reduced to a very low value, the cycling of the battery was terminated after 25 cycles. It was observed that the discharge capacity for the 2nd cycle is 0.490 mAh. The capacity of the cell is slowly fades away after prolonged cycling. The capacity fading of the cell after cycling may be attributed to several reasons. The most important reason is the formation of a non-conducting passivation film on the surface of the lithium electrode [160-162]. The lithium metal which is used as an anode material in the present study will interact with the chlorine atom of the PVC polymer and form a LiCl surface layer on the lithium metal. This is because the lithium metal has more affinity towards chlorine atom of the PVC polymer. The formation of LiCl will automatically decompose the polymer electrolyte and thereby reduce the capacity of the thin film polymer battery [163].
The other possible reason for the decreased capacity of the assembled cell may be the low ionic conductivity of the polymer electrolyte and high electrode/electrolyte interface resistance. This may be related to the deterioration of interfacial contacts or contact losses at the electrode/electrolyte interfaces [162,164]. Figure 5.19 shows clearly the fact that the capacity of the battery does not decrease very much after the 7th cycle. This suggests the fact that the interface between the electrode and electrolyte interface probably improves with cycling [161].

From these studies, we observed that to develop a battery, many complications have to be overcome. These include the conductivity of the polymer electrolyte, the degradation of battery performance etc.