Chapter 6

Results & Discussion IV

6. Battery Characteristics

6.1 Battery Studies

There is a need for the development of rechargeable lithium polymer batteries with both high voltage and high energy density as a new type of energy supply [177-178]. Therefore, our main aim is to develop polymer batteries based on the electrolyte developed from the present study. Recent past, intensive research is focussed on to develop polymer batteries based on various polymer electrolytes [122-126, 179-185]. The thin film polymer batteries, which has been reported in the literature is based on PVDF polymer electrolytes with polyacetylene and lithium transition metal oxide electrodes [122,125]. we employed lithium metal as a anode and graphite as a cathode material. The polymer batteries were assembled as per the method described in chapter 2. The characteristics were analyzed with the help of BAS LG 50 galvanostat. Although it has been noted that Li metal has its disadvantages such as dentrite formation but to achieve higher capacity Li metal is used in the present study. Moreover the dentrite formation can be suppressed in the case of polymer electrolytes [67].

The assembled cell shows 3.36 V, 3.06 V and 3.01 V respectively for DMF, MF and EC plasticizer based polymer electrolyte. The cell was assembled inside an argon filled glove box. The cell was discharged immediately at room temperature. The first discharge curve for all the three batteries are shown in Fig 6.1 to 6.3. The first discharge currents are 0.1 mA, 2 μA and 5 μA respectively for DMF, MF and EC plasticizer based polymer electrolytes.

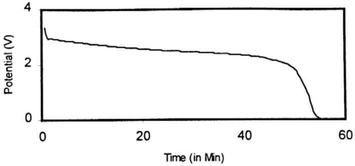

Fig.6.1. First discharge curve for DMF based cell, The plateau region begins at 2.7 V. The internal resistance is ~3.7 kΩ

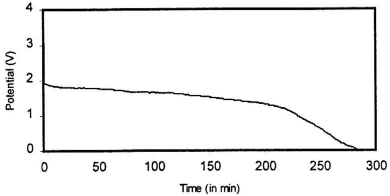

Fig.6.2. First discharge curve for MF based cell. The drop in voltage is about 1.06 V upon discharge. The internal resistance is ~ 530 kΩ

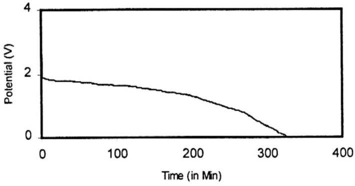

Fig.6.3. First discharge curve for EC based batteries. The drop in voltage is ~1.01 V upon discharge. The internal resistance is ~200 kΩ

From the discharge curves the discharge capacity of the batteries are calculated. The discharge capacities are found to be 92 μAh, 9.4 μAh and 27.4 μAh respectively for DMF, MF and EC plasticizer based polymer electrolytes. This is shown in Fig 6.4 to 6.6.

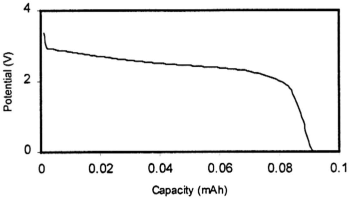

Fig.6.4. Capacity versus potential for DMF based cell (1st discharge)

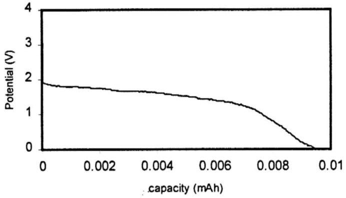

Fig.6.5. Capacity versus potential for MF based cell (1st discharge)

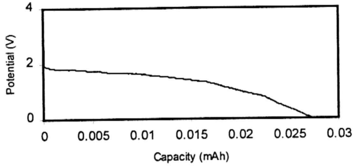

Fig 6.6. capacity versus potential EC based cell (1st discharge)

The discharge capacity is found to be high in the case of polymer batteries based on DMF plasticizer. The reason behind the high capacity in the case of DMF based polymer electrolyte is due to its high ionic conductivity at ambient condition. The capacity of the battery is very low when compared with the theoretical capacity of the cells. This is attributed to the high internal resistance of the cells which could be attributed to the low ionic conductivity of the polymer electrolyte and the interfacial resistance between the solid anode and electrolyte. It can be observed that the capacity shown by the cells is in accordance with the conductivity of the polymer electrolytes.

6.1.1 DMF Based Polymer Electrolyte System

The DMF plasticizer based polymer electrolyte cell is cycled with the charging current of 10 μA for 30 minutes and discharging current of 5 μA for 600 minutes. It was observed that after attaining the maximum potential of 4 V, it begins to fall and maintains a plateau potential at around 3 V. This plateau potential is constant until 600 minutes. Fig 6.7 shows the charge-discharge characteristic for the DMF plasticizer based polymer electrolyte. The behaviour is constant even at the 10^{th} cycle.

The cell is again discharged at a higher current i.e., 10 μA but the charging current value is kept constant. The discharge curve is shown in the Fig 6.8. Assuming that the plateau time is 10 hours then the discharge capacity is 100 μAh. If upon 10 cycles the discharge curve shows the same behaviour as in Fig 6.7 then a digital clock consuming 1 μA current can be expected to run for 100 hours for each cycle for a total of 1000 hours for the 10 cycles. This is equivalent to about 42 days.

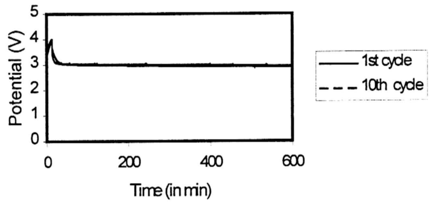

Fig 6.7. Charge/discharge curve for DMF based cell (charging at 10 μA and discharging at 5 μA)

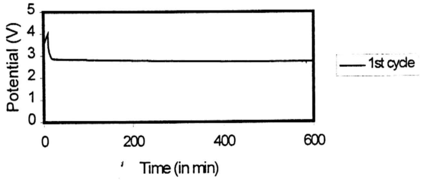

Fig. 6.8. Charge/discharge curve for DMF based cell at 10 μA

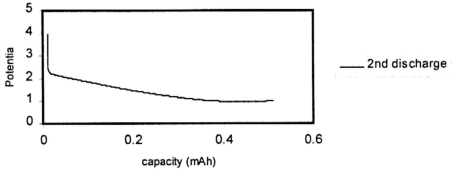

Fig. 6.9. Charge/discharge curve for DMF cell (charging at 10 μA and discharging at 50 μA)

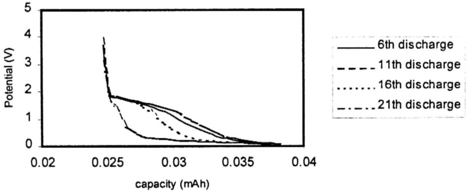

Fig 6.10: Charge/discharge curve for DMF cell (charging at 10 μA and discharging at 50 μA)

Fig. 6.9 shows the cell discharge curve for a current drain of 50 μA. The curve reaches a constant value of 1 V after about 5 minutes. Fig 6.10 shows the potential versus discharge capacity for the 2nd, 6th, 11th, 16th and 21st cycles. Since the discharge plateau potential curve is reduced to a very low value, the experiment was terminated after the 25th cycle.

From the discharge capacity of the cell, it can be observed that the 1st discharge curve has a capacity close to 0.5 mAh. After cycling, the 6th cycle shows very poor capacity (0.04 mAh). This sudden decrease in capacity of the cell after cycling may be attributed to variety of reasons. The most important reason is the formation of a non-conducting passivation film on the surface of the lithium electrode [186-187]. Since lithium metal is used as an anode material in the present study, it interacts with the fluorine atom of the PVDF polymer and forms the LiF surface layer on the lithium metal. This is because lithium metal has a great affinity towards the fluorine atom of the PVDF polymer [125]. The formation of such a layer increases the internal resistance of the cell.

The possible other reasons for the decreased capacity of the cell may be due to the low ionic conductivity of the polymer electrolyte and high electrode/electrolyte interface resistance [188]. The capacity versus potential curve shows very clearly the fact that the capacity of the battery is not decreased much in the 11th cycle when compared with the capacity of the 6th cycle. The capacity is almost same for the remaining cycles. This implies that the interface between the electrode and electrolyte interface improves after cycling.

From this study, it can be observed that the discharge capacity of the cell is more in the case of second cycle than the first cycle. It may be due to the low current discharge values for the second cycle than the first cycle. From this, it can be observed that the better performance of the batteries can be obtained at lower discharge current values. It is also observed from the capacity versus potential curve that the plateau potential value is decreased to 2 V for final cycle values. This decrease in plateau potential may be due to the fact that the discharging current is more than that of the charging current and the battery can not attain the maximum potential of 4 V. Thus the fall in the plateau potential value.

6.1.2 MF Based Polymer Electrolyte System

Fig 6.11 shows the discharge capacity versus potential curve for the MF plasticizer based polymer electrolyte cell for various cycles. The cell was cycled by charging it with 100 nA and discharged with 1 nA. From the Fig, it can be observed that the battery also shows similar kind of nature for the 2^nd^ and other cycles. For the 2^nd^ discharge, it gives a capacity of 0.9 μAh. The capacity of the cell decreased to 0.8 μAh in the 6^th^ cycle. The capacity decrease in this case is low when compared with the DMF plasticizer based batteries. This decrease in capacity for the cycles may be attributed to the formation of the surface layer on lithium metal anode and also to the conductivity of the electrolyte.

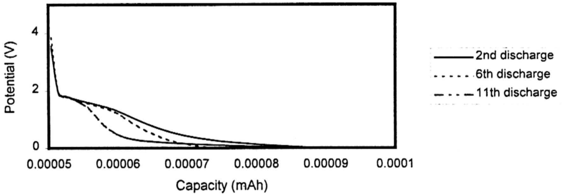

Fig 6.1.1 Discharge capacity versus potential for MF plasticizer based cells

6.1.3 EC Based Polymer Electrolyte System

The Fig 6.12 and 6.13 show the discharge capacity versus potential curve for various cycles. The cell was charged at 10 μA and discharged at 1 μA. The potential versus capacity curve shows similar behaviour as that of the DMF and MF based batteries.

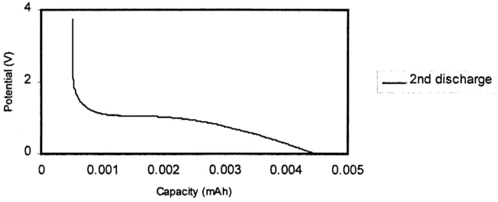

Fig 6.12: Discharge capacity versusu potential for EC plasticizer based cell

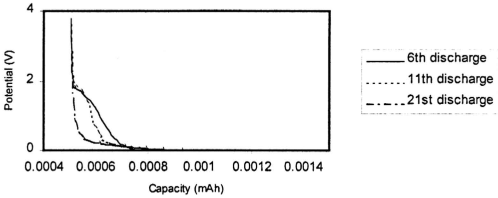

Fig 6.13. Discharge capacity versus potential curve for EC based cell.

A large drop in the potential was observed upon discharge. The plateau potential has been maintained close to 2 V. From galvanostatic analysis, it can be observed that all the batteries show good response in charge/discharge characteristics. Of all the cells analysed in the present study, the cell based on DMF plasticized electrolyte gives good response than the other cells made up of MF and EC plasticizer. These battery studies also confirmed the results obtained from the other studies.

Form the studies, it can be observed that the plateau potential range is high in the case of DMF plasticizer based cell. The DMF plasticized electrolyte cell gives the plateau potential in the range of 2.4 V and the other cells gives the plateau potential in the range close to 2 V. In all the batteries, it can be observed that the cells give two plateau potential. The first plateau potential is close to 2 V and the second plateau potential is close to 1.6 V.

6.2. Summary

Polymer batteries were developed based on highest conducting polymer electrolytes from all the three plasticizers. The capacity for all the batteries are in the order of μAh. This low capacity of the cells may be attributed to the low ionic conductivity, high interfacial resistance of the electrode/electrolyte interface and the formation of non-conducting surface films on lithium electrode. In the present investigation, DMF plasticizer based cell gives higher capacity than the other plasticizers used in the present study.