

## Preparation and characterization of $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$ /polymer electrolyte/graphite cell

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Solid state batteries with lithium and an insertion material as active electrode components and a poly (ethylene oxide) based electrolyte, have proven to be feasible alternatives to the classical secondary battery systems. The solid state electrochemical cell  $\text{Li}_{1.1}\text{Mn}_2\text{O}_4 | \text{PEO}:\text{LiClO}_4 | \text{Graphite}$  was fabricated by sandwiching the thin electrolyte film between the cathode and anode pellets. This sandwich was pressed between suitable current collectors in a spring tight sample holder assembly. The complex impedance of electrolyte and  $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$  was measured and discharge characteristics were studied for various loads. Also energy densities were calculated. Constant current discharge curves were obtained at several load values. The observed energy density is 47 J/kg for 0.1 M ohm load. The lithium salt content of the polymer electrolyte is found to decrease at the positive electrode whilst increasing at the lithium side. The results predict that the critical charge at which the curves deviate should be inversely proportional to the current.

### 1 Introduction

In recent years, extensive work has been done on the research and development of lithium-ion batteries for portable electronic systems and electric vehicles<sup>1</sup>. As candidates for cathode materials, lithium manganese oxides are attractive and have the following advantages: low cost, ready availability and low pollution.  $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$  is a potential material for use in rechargeable lithium batteries, particularly as high voltage cathode material in lithium-ion cells using carbon-based anodes. Graphite exhibits a high capacity with a flat discharge characteristics<sup>2-5</sup>. The material offers a relatively high specific capacity at a potential exceeding approximately 2V vs.  $\text{Li/Li}^{+6\text{-eV}}$ . Solid state batteries with lithium and an insertion material as active electrode components and a poly(ethylene oxide) based electrolyte, have proven to be feasible alternatives to the classical secondary battery systems. Polymer electrolytes have occupied an important position in research towards developing new high energy density batteries. They have certain unique properties such as thin film forming property, good processibility, feasibility, light weight, elasticity and transparency as well as relatively high ionic conductivity and wide potential window in the solid state. This work reports on preparation and characterization of electrodes and electrolytes for lithium battery.

### 2 Materials and Method

#### 2.1 Sample preparation

$\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  (Sigma-Aldrich, USA) were used as starting materials. They were dried at 150°C for 6 hours. Appropriate amounts of  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  were taken, mixed together in Agate mortar and pestle and ground to fine powder.

The method of estimation of  $\text{Li}_{1.1}\text{Mn}_2\text{O}_4$  is given as follows :

$$\begin{aligned} \text{Amount of Li}_2\text{CO}_3 &= \frac{2 \times 1.81 \times (\text{Molecular Weight of Li}_2\text{CO}_3)}{2 \times 1.81 \times (\text{Molecular Weight of Li}_2\text{CO}_3) + 2 \times (\text{Molecular Weight of MnO}_2)} \\ \text{Amount of MnO}_2 &= \frac{2 \times (\text{Molecular Weight of MnO}_2)}{2 \times 1.81 \times (\text{Molecular Weight of Li}_2\text{CO}_3) + 2 \times (\text{Molecular Weight of MnO}_2)} \end{aligned}$$

The above mixture was kept in a furnace at 900 °C for 8 hours in order to enable the material to undergo solid state reaction with elimination of  $\text{CO}_2$  and  $\text{O}_2$ . Hence, a weight loss is observed after the first sintering. The completeness of the reaction is observed by the absence of weight loss during subsequent sintering. This mixture was ground to a fine powder and pelletized. This pellet was sintered in order to improve the packing density by keeping them inside the furnace at 400 °C for 3-4 hours.

$\text{LiMn}_2\text{O}_4$  is a poor anode, hence, we preferred  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  (nominal composition) as the anode<sup>12</sup>. Since it is easy to de-intercalate the excess lithium ion from  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  up to the stoichiometric limit. Further de-intercalation, i.e. any attempt to reduce the fraction of lithium ions would lead to formation of any of new phase other than  $\text{LiMn}_2\text{O}_4$  which causes the cell emf getting drastically reduced<sup>13</sup>. Not only the emf is reduced, but the electrode itself becomes more insulating, resulting in increasing the internal cell resistance.

The starting materials, PEO (MW 35,000) and  $\text{LiClO}_4$  were obtained from Aldrich (USA) and Fluka (Germany), respectively. Prior to the preparation of polymer electrolyte, the PEO and  $\text{LiClO}_4$  were dried under vacuum at about 65 °C and 180°C, respectively. The polymer and the salt were mixed at O/salt ratio of 8:1, because this ratio is known to yield good ionic conductivity as per the reported phase diagram<sup>14</sup> and this ratio indeed offers good mechanical strength to the polymer electrolyte also. A known weight of PEO and  $\text{LiClO}_4$  were dissolved in purified acetonitrile separately and then were mixed together to form  $\text{PEO}_8:\text{LiClO}_4$  blend. Polymer electrolyte blend thus prepared were then poured into the teflon die. The polymer electrolyte films were prepared by a standard solvent casting method<sup>15,16</sup>. High purity graphite was used as the negative electrode.

## 2.2 Preparation of the cell

The laboratory test cells  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  | Polymer electrolyte | graphite were fabricated by sandwiching the thin electrolyte film (weighted) between the cathode (weighted) and anode (weighted) pellets. This sandwich was pressed between suitable current collectors in a spring tight sample holder assembly for further characterization. This assembly were probably insulated and measurements were carried out under high vacuum conditions.

## 3 Results and Discussion

The method of calculation is to take the OCV as before and then shunt the battery with an external resistance  $R$  and note the instantaneous voltage reading. The internal resistance is now calculated by

$$R_{in} = \frac{(OCV - V) \times R}{V}$$

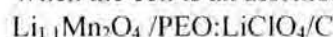
where  $R_{in}$  is expressed in ohms.

$$R_{total} = R_{in} + R_{load}$$

$$R_{in} = R_{total} - R_{load}$$

The discharge voltages of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  | Polymer electrolyte | graphite against discharge time at room temperature are shown in Fig. 1.

When the cell is in an assembled condition, then



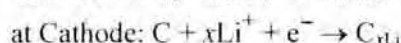
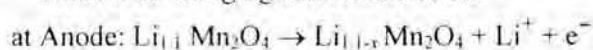
gives OCV = 0.85V appearing at graphite with respect to  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  and



After charging, gives OCV = 2.55V.

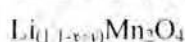
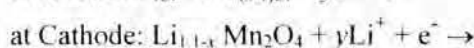
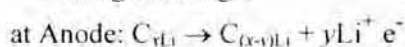
The electrochemical reactions of the discharge of the cell were expressed as:

At time of charging cell reactions are



When cell is charged such that the Li gets de-intercalated from  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  to get intercalate in C (graphite).

During discharge,



and the above all reaction gives OCV = 2.55V.

This reaction may continue till  $y = x$ . when  $y$  becomes  $x$  it means that the cell is fully discharged and the open circuit voltage is 2.55V as observed at the beginning of discharge.

Fig. 1 shows that OCV without any load measured as a function of time. While evaluating the cell performance under the ideal storage condition, OCV (= 2.55 V) has been found to be decreasing exponentially to a steady value of 0.75V after 100 minutes.

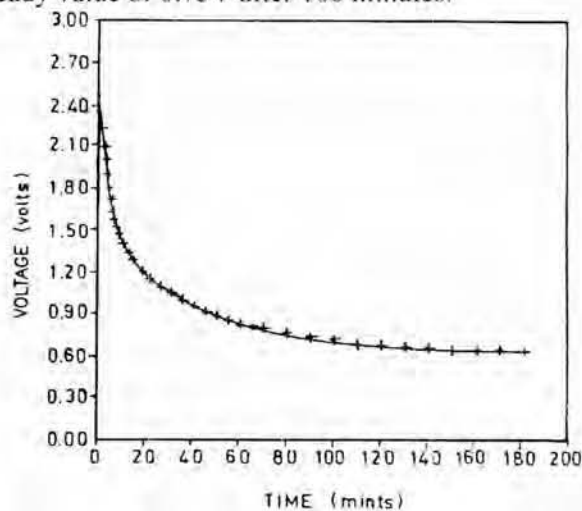


Fig. 1 — Open circuit voltage versus time

### 3.1 AC-impedance measurements

Room temperature electrode and electrolyte conductivities were determined separately from ac-impedance measurements using CHEN HWA 1061 LCZ meter with frequency range between 40 Hz and 200 kHz. The polymer electrolyte film was sandwiched between two well polished stainless steel disk electrodes attached with spring tight sample holder assembly.

The room temperature conductivity of the electrode and electrolyte was obtained from the standard complex impedance analysis method, used in solid state ionics. The room temperature conductivity of the electrode and electrolyte were found to be  $5.09 \times 10^{-4} \text{ S cm}^{-1}$  and  $1.23 \times 10^{-4} \text{ S cm}^{-1}$ , respectively.

### 3.2 Load characteristics

The important characteristics of the secondary cell are that the charge and discharge – the transformation of electrical energy to chemical energy and back again to electrical energy – should prove nearly reversibly, should be energy efficient, and should have minimal physical changes that can limit the cells cycle life.

The discharge curves presented for different loads shows that the slight variation in initial voltage is due to a slight spread in the initial open circuit voltage across an array.

At greater discharge currents the curve initially follows the EMF curve, so that any diffusional over potentials may be assumed to be insignificant. However, after the passage of a critical amount of charge, which depends on the current, the curves deviate sharply downwards. Such downward deviation at critical charge values are typical of diffusion limitation. The behaviour is due to bulk electrolyte transport number of less than

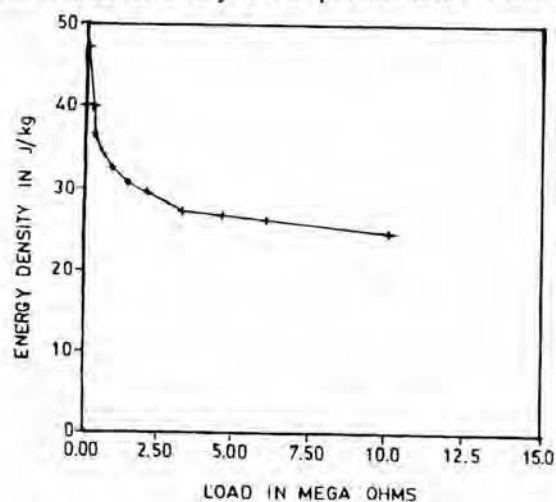


Fig. 2 — Energy density versus load

one for the ion which passes through the electrode/electrolyte interface.

The energy density can be calculated by  
 Energy density = Power density x hours of service  
 $\text{Whr/kg} = \text{W} / \text{kg} \times \text{hr} = (\text{A} \times \text{V} \times \text{hr}) / \text{kg}$

The energy densities of the secondary battery system for different load values are shown graphically in Fig. 2. The sharper slope, is indicative of superior retention of capacity with increasing discharge.

All the results reported here are those of cells operating at room temperature. Constant current discharge curve were obtained at several load values for 50 minutes time as shown in Fig. 3. The ohmic contribution is due to the resistances of the polymer electrolytes, the cathode material and the interfacial resistance between the electrolyte and the lithium.

In the cell described here, we would expect that the lithium salt content of the polymer electrolyte decreases at the positive electrode while increasing at the lithium side. These results predict that the critical change at which the curves deviate should be inversely proportional to the current. The results suggest that PEO based polymeric electrolytes can be considered as potential electrolytes for high energy density batteries.

### 4 Conclusion

Several chemical-synthesized conductive polymers have been examined for their characteristics as polymer electrolyte material for lithium secondary batteries. The poly(ethylene oxide) was found to have good charge/discharge characteristics. In the initial state of discharge, electrode over potentials are generated mainly by the electronic resistance path, which will be sufficiently low in all cases. However, after a partial

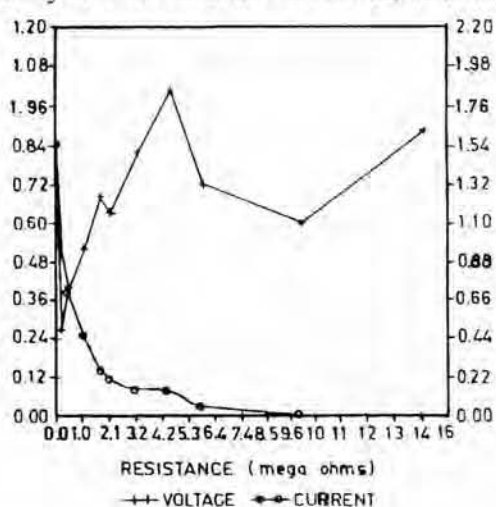


Fig. 3 — Discharge curve for the cell at 50 minutes

discharge of surface material, subsequent discharge requires conduction through the ionic resistance. These results indicate that the formation of passivation layers at the Graphite/PEO:LiClO<sub>4</sub> and Li<sub>1-x</sub>Mn<sub>2</sub>O<sub>4</sub>/PEO:LiClO<sub>4</sub> interfaces strongly influence the kinetics of the Li<sup>+</sup> ion insertion into or extraction out of the electrodes.

We have found that the graphite which functions as a lithium intercalation compound, has good characteristics for a negative electrode material. The ac impedance measurements also indicated that the interfacial properties for the electrode covering the upper voltage range are far superior to those for the lower voltage range. The current value is reduced due to interfacial resistance of the cell. The internal resistance of the cell arises as a result of poor interfacial contact between the electrode and the electrolyte due to semisolid nature of the electrolyte.

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