Short communication

Polymeric rechargeable solid-state proton battery

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Abstract

Rechargeable proton conducting polymeric solid-state batteries have been fabricated with the configuration $Zn + ZnSO_4 \cdot 7H_2O \parallel PEO:NH_4ClO_4 + PC \parallel V_2O_5 + PbO_2 + C + E$. The maximum cell voltage is ~ 1.57 V at full charge. The discharge characteristics of the cell have been studied at different loads. The cell remains stable for more than 180 h for low current drain ($\sim \mu A$) making it suitable for low current density application. The cell also showed a good rechargeability which was tested for nine cycles.
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1. Introduction

Rechargeable solid-state batteries, particularly Li^+ ion batteries, have recently attracted great attention for vehicular application (for a short review of earlier work and projection regarding likely developments in the future, refer to Vincent [1]). Rechargeability requires a good cathode material which show reversibility for the mobile lithium ion. The most successful approach is to use layered materials like TiS_2, PbO_2, V_2O_5, MnO_2, etc., or more recently developed $LiCoO_2$, $LiMnO_2$ or porous carbon [2–8]. The ionic radii of Li^+ ion are small and hence it could be intercalated into the layers of the layered materials. However, the ionic radii consideration also suggests that the proton (H^+) based rechargeable battery could also be an alternative to Li^+ ion battery. The electrochemical window for Li^+ ion batteries is generally high (~ 4 V) while that for proton battery it is (~ 1 V) which gives preferential advantage to the former on the basis of energy — density consideration. Nonetheless, because of the availability of low cost proton conductors, proton batteries appear a good alternative for low energy density battery applications [9,10]. For a successful proton battery, we need an anode capable of supplying or injecting H^+ ions into the battery electrolyte, a proton conducting electrolyte and a reversible cathode. Pandey et al. [9] and Singh et al. [12] have used composites of salt-hydrates as proton conducting solid electrolytes for their batteries while layered oxides MnO_2, PbO_2, V_2O_5 or V_6O_{13} were used as anodes. In the present paper, we have successfully used a "proton conducting polymer electrolyte" as electrolyte fabricating a rechargeable proton battery of configuration $MHx + Zn + ZnSO_4$ cathode | plasticized $PEO:NH_4ClO_4$ membrane as electrolyte | anode $V_2O_5 + PbO_2 + C$. The metal hydride (MHx) acted as the source of H^+ ion for the battery. The battery gives an open circuit voltage of ~ 1.5 V. The charge–discharge characteristics of the cell under different load conditions and its rechargeability over 9–10 cycles are also reported and discussed in this paper.

2. Experimental

2.1. Fabrication of battery

2.1.1. Preparation of the proton conducting polymer electrolyte membrane

Plasticized membranes of polyethylene oxide (PEO) complexed with NH_4ClO_4 was used as the electrolyte membrane for the proton batteries studied by us. For obtaining this, PEO ($M_w = 5 \times 10^5$, supplied by Aldrich) was first dissolved in dehydrated methanol to which weighed amount of NH_4ClO_4 was added so as to obtain $PEO:NH_4ClO_4$ ratio of 85:15 wt.%. It was stirred for 4–6 h for complexation. Stirring was continued

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till reasonably thick solution of the complex was obtained and then plasticizer propylene carbonate (PC) was mixed in this PEO:NH$_4$ClO$_4$ thick solution. It was again stirred till a highly viscous solution of (PEO:NH$_4$ClO$_4$) + PC was obtained. This was poured in a propylene Petri dish to obtain solution casted polymer electrolyte membrane (∼0.1 mm thick) after drying for 3–4 days in ambient. This was further dried in vacuum at 10^{-6} Torr.

2.1.2. Preparation of anode

(Zn + ZnSO$_4$·7H$_2$O + MHx) are taken in the ratio 10:5:2 by weight. Zn (polyforma, India) and ZnSO$_4$·7H$_2$O (CDH; India) were used. (MHx) stands for a lightweight hydrogen storage metal hydride. It is mischmetal (Mm)-based aluminum substituted penta-niekelide (MmNi$_{4.5}$Al$_{0.5}$) where Mm contains Ce-44.63%; La-21.63%; Na-21.36%; Pr-6.17%; Fe-4.0% and others 2.21%. It was synthesized by ball milling technique described by Singh et al. [12]. The "MmNi$_{4.5}$Al$_{0.5}$" was exposed to hydrogen for 24 h to obtain the metal hydride (MHx).

The three constituents (i.e. Zn, ZnSO$_4$·7H$_2$O and MHx) in the desired proportion were taken, mixed together and finally ground well. The mixture was subsequently put in a die and gently pressed (∼4 t cm^{-2}) to obtain the anode (of thickness ∼0.55 mm) in the form of a 13 mm diameter disc/pellet.

2.1.3. Preparation of cathode

The cathode material was principally a mixture of intercalating oxide PbO$_2$ (Lobachemic, India) and V$_2$O$_5$ (CDH, India), graphite (Residual, India) and plasticized polymer electrolyte. The layered oxides (PbO$_2$ + V$_2$O$_5$), acted as intercalation system, graphite C was added to introduce the electronic conductivity while the addition of the electrolyte helped in reducing the electrode polarization [9]. The compositional ratio of various constituents in the cathode mixture PbO$_2$:V$_2$O$_5$:C:polymer electrolyte, which gave the best results, was 8:2:1:0.5. This mixture was poured in a die and lightly pressed at 4 t cm^{-2} to get thin pellet/disc to be used as cathode (of thickness ∼0.87 mm).

2.1.4. Battery assembly

The polymer electrolyte membrane of thickness ∼0.12 mm (as described in "a" above) was placed between the loosely compacted anode and cathode pellets and the assembly was put in the palletizing die. This entire assembly was finally compacted to get a button shape polymeric solid-state proton battery. The cell, so obtained has the following configuration:

[anode]	||	solid polymer electrolyte (E)	||	[cathode]
Zn + ZnSO$_4$ · 7H$_2$O + MHx	||	PEO : NH$_4$ClO$_4$ + PC	||	V$_2$O$_5$ + PbO$_2$ + C + E
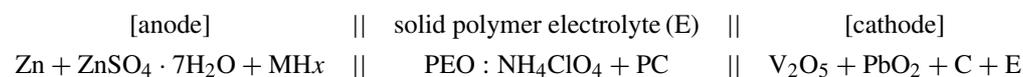
2.2. Measurement of conductivity of the polymeric membrane

Silver electrodes were deposited on the polymeric film (obtained by the process discussed in Section 2.1) by vapor deposition at a vacuum of ∼10^{-6} Torr. The standard complex impedance plot method was used for evaluating the conductiv-

ity. The measurement of real and imaginary parts of conductance was done by Hioki 2000 model in the frequency range 40 Hz to 100 kHz.

2.3. Cell characterization

The voltage and current was measured by a Keithley 2000 multimeter. In the voltage measuring mode, the input impedance of the multimeter is very high (1 GΩ) which is necessary for obtaining a reliable value of the voltage. For discharge studies, fixed load of 20, 57, 100 or 1 MΩ was connected to the battery. The current through the load and the voltage across the cell were monitored as a function of time. The cell was allowed to discharge till its voltage dropped to 20% of the initial value and then it was put to "charge" cycling. For this, the load is removed and the cell is charged using a constant current source to compensate for the charge withdrawn from the cell during its "discharge" cycle. This procedure was repeated for rechargeability studies over many cycles.

3. Results

3.1. Conductivity of polymeric membrane used as electrolyte

Proton transport in polyethene oxide complexed with NH$_4$ClO$_4$ has been earlier studied by Hashmi et al. (1990) [13]. They found that polymer complex having PEO:NH$_4$ClO$_4$ in the ratio of 85:15 wt.% possesses maximum conductivity $\sigma \sim 10^{-5}$ S cm^{-1} which is nearly four decades higher than pure PEO. They [13] also observed that apart from H$^+$, the anions (i.e. ClO$_4^-$) are also mobile in the bulk materiel but the transference number for H$^+$, i.e. t_{H^+} (≈0.85) is larger than $t_{ClO_4^-}$ (≈0.08). It may be noted that the value of $\sigma \sim 10^{-5}$ S cm^{-1} is low for battery application. Therefore, we made an effort to enhance the room temperature bulk conductivity of PEO:NH$_4$ClO$_4$ (85:15 wt.%) polymer electrolyte by adding plasticizer propylene carbonate (PC) to it. The variation of bulk conductivity at room temperature as a function of wt.% of PC is shown in Fig. 1. The curve shows that for low wt.% of PC, the conductivity initially increases and attains a maximum value $\sigma \sim 10^{-4}$ S cm^{-1} at 5 wt.% of PC. Further addition of PC (propylene carbonate) lowers conductivity and as prepared plasticized polymer electrolyte films were found to be porous and mechanically not stable. The decrease in the

conductivity at high PC concentration is an "artifact" because of the "soggy" nature of the film.

3.2. Open circuit voltage and short circuit current of the cell

As described in Section 2.1.4, the cell fabricated by us has the configuration Zn + ZnSO$_4$·7H$_2$O || PEO:NH$_4$ClO$_4$ +
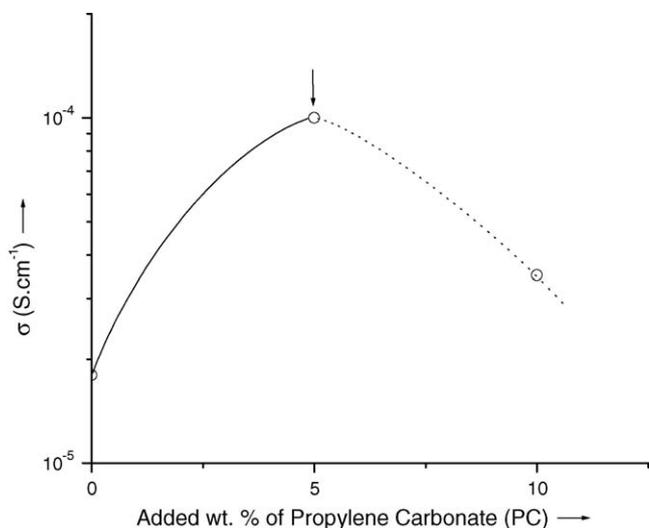
Fig. 1. Electrical conductivity of plasticized polymer electrolyte [PEO:NH$_4$ClO$_4$ (85:15 wt.%) + x wt.% PC)] as a function of x at 27 °C (relative humidity ~74%).

Fig. 2. Variation of open circuit voltage (OCV) with time.

3.3. Discharge characteristics at different loads

PC || V$_2$O$_5$ + PbO$_2$ + C + E. To check the initial voltage obtainable from the fabricated cell and to ensure proper electrode–electrolyte contacts, we measured open circuit voltage (OCV) by a high impedance (~GΩ) multimeter (Keithley, 2000) over a period of ~24 h. The results are given in Fig. 2. It can be seen that the initial voltage of 1.57 V, within 15 min of the fabrication of cell, stabilized to 1.55 V. The voltage remained constant (1.55 V) for a period of 24 h from which we can conclude about the fabricated cell is reasonably stable in open cell condition. For getting a qualitative idea of the internal resistance of the cell prepared by us, we measured short circuit current (I_{sc}) of the cell. The value of the I_{sc} so determined was approximately ~1.1 mA which indicates that the batteries have high internal resistance (~1 kΩ estimated from the measured value of dc voltage and I_{sc} and approximately checked by complex impedance plot under no discharge) which need to be improved by a suitable choice of electrode, electrolyte resistance, electrode–electrolyte interface resistance, electrode polarization, etc.

The discharge characteristics of the cell were studied for different loads, viz. 20 kΩ, 57 kΩ, 100 kΩ and 1.1 MΩ. The discharge characteristics are shown in Fig. 3. From Fig. 3(a), we can see that the discharge of the cell for load 20 kΩ is very rapid. The voltage drops from an initial voltage ~1.57 to ~0.47 V within half a minute, then slowly decreases to 0.4 V in 10 min and subsequently remains nearly constant for up to 40 min (labeled as "plateau region" after which it drops further. The same trend is seen in Fig. 3(a) for current drawn from the cell. However, the plateau region in the cell current (~10 μA) is not as well defined as the voltage "plateau region". For higher load resistances, the voltage drop is not so fast as that for the load of 20 kΩ. The higher the load, the longer is the time duration of stable performance of the cell. For example, the cell voltage at 57 kΩ load, as shown in Fig. 3(b), there appears a plateau region for 100 min after initial drop of voltage from 1.5 to 1.3 V. For this case also, a plateau region in the current is observed but now the plateau current is higher (~20 μA) than that for 20 ΩK load. For a still

Table 1
Energy densities of some H$^+$ ion solid-state batteries

S. No.	Battery configuration	Nature of electrolyte (El)	Energy density Wh kg^{-1}	References
1	Zn + El | El | MnO$_2$ + C	Polycrystalline solid composite NaH$_2$PO$_4$ + Na$_2$HPO$_4$	12	[14]
2	Zn + El | El | PbO$_2$ + C	Polycrystalline solid composite NaH$_2$PO$_4$ + Na$_2$HPO$_4$	4.64	[14]
3	Zn + El | El | V$_6$O$_{13}$ + C	Polycrystalline solid composite NaH$_2$PO$_4$ + Na$_2$HPO$_4$	1.76	[14]
4	Zn + El | El | MnO$_2$ + C	Polycrystalline solid composite P$_2$O$_5$ + SiO$_2$ + Al$_2$O$_3$	18	[15]
5	Zn + El | El | PbO$_2$ + C	Polycrystalline solid composite P$_2$O$_5$ + SiO$_2$ + Al$_2$O$_3$	4	[15]
6	Zn + El | El | V$_2$O$_5$ + C	Polycrystalline solid composite P$_2$O$_5$ + SiO$_2$ + Al$_2$O$_3$	2.6	[15]
7	Zn + ZnSO$_4$·7H$_2$O | El | El + PbO$_2$ + V$_2$O$_5$ + C	Polycrystalline solid composite phosphotungstic acid (PTA) + Al$_2$(SO$_4$)·16H$_2$O	0.8	[9]
8	Zn + ZnSO$_4$·7H$_2$O | El | El + PbO$_2$ + V$_2$O$_5$ + C	Polycrystalline solid composite phosphotungstic acid (PTA) + ammonium paratungstate	0.74	[11]
9	Zn + ZnSO$_4$·7H$_2$O | El | El + PbO$_2$ + V$_2$O$_5$ + C	Polymer electrolyte PEO:NH$_4$ClO$_4$ + 5 wt.% PC	0.56	Present work

Fig. 3. Discharge characteristics: cell voltage and cell current as a function of load resistance: (a) 20 kΩ; (b) 57 kΩ; (c) 100 kΩ; (d) 1.1 MΩ.

higher load of 100 kΩ, the plateau regions for nearly constant voltage (∼1.48 V) and current (∼12.5 μA) extend over a much longer time. For a load of 1.1 MΩ, in which the cell current drawn is low, the cell discharge characteristics shown in Fig. 3(d) are very good. The discharge curves show very small changes in the voltage and current with time. The cell voltage slowly decreases from 1.57 to 1.51 V in 20 h. Then a plateau region is observed extended well over ∼180 h. Similarly, the current versus time plot shows that the current initially decreases slowly from 1.38 to 1.32 μA within 20 h and then remains constant (a plateau region) for more than 180 h. The approximate energy density is 0.56 Wh kg^{-1} limiting the operation only up to the plateau region. Not many proton (H$^+$) batteries have been studied. For comparison, a few such batteries using solid–solid composites are listed in Table 1.

It may be noted that the discharge characteristics shown in Fig. 3(d) indicate that our cell configuration is good for low current density application and can work for several days. In this paper, we have demonstrated that a suitable polymer electrolyte can also be used to fabricate low weight batteries. Some more studies are required to improve the electrode–electrolyte interface, cathode and anode resistance.

Nonetheless, one of our cells was used in a wristwatch and it worked satisfactorily for nearly 2 weeks. This cell could be recharged and re-used. The rechargeability studies are described below.

3.4. Rechargeability studies

A typical experimental study of the rechargeability of the cell under 57 kΩ load resistance is shown in Fig. 4. The discharge was terminated after the cell voltage dropped by 20% of the initial voltage. The cell was then recharged using a constant current source. The results are shown in Fig. 4. It can be seen that the cell regains its initial value after recharging. We studied rechargeability up to 9–10 cycles without significant loss in the voltage. We estimate that the rechargeability cycle life may well be over 20 cycles up to which we did not see significant change in the "final" cell voltage (though point to point charge–discharge was not studied). It may be remarked that the layered materials like PbO$_2$ and V$_2$O$_5$ of the anode can intercalate the mobile H$^+$ ion (coming from the electrolyte during discharge) between its layers and de-intercalate the same during the charge cycle.
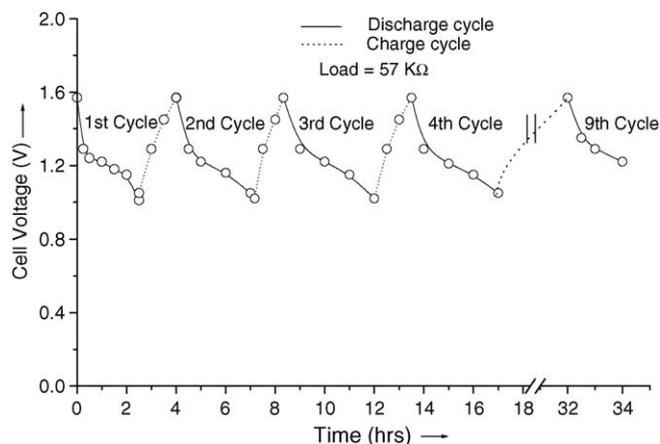
Fig. 4. Rechargeability studies on PEO:NH$_4$ClO$_4$ (85:15 wt.%) + PC 5 wt.% electrolyte based cell. The variation of cell voltage with time for nine discharge–charge cycle (load = 57 kΩ) is shown in the figure.

4. Conclusions

Polymeric rechargeable solid-state proton battery has been fabricated using polymeric proton conducting solid electrolyte, (PEO:NH$_4$ClO$_4$, 85:15 wt.% + 5 wt.% of propylene carbonate (PC)). A mixture of Zn + ZnSO$_4$·7H$_2$O + MHx was used as anode and the mixture of intercalating materials (PbO$_2$ + V$_2$O$_5$) + C + E as the cathode. The open circuit voltage (OCV) of the different cells is found to be approximately 1.57 V. The discharge characteristics of the cell have been studied at different loads. The cells remain stable for more than 180 h for low current drain (∼1 μA). However, it discharges quickly for large current drains or low load resistance. Thus, the cell is found suitable for low current density applications. The cell also showed a good rechargeability which was tested for nine cycles during which it did not show any loss of voltage.

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