Short communication

Solid-state Mg/MnO$_2$ cell employing a gel polymer electrolyte of magnesium triflate

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Abstract

In view of the abundant resources, low costs and the relatively low reactivity of magnesium, solid-state batteries using this metal are worthy of investigation in comparison with solid-state lithium batteries. For such cells, a gel polymer electrolyte (GPE) is prepared using polyacrylonitrile, propylene carbonate, ethylene carbonate and magnesium triflate. The composition of GPE is optimized in view of the minimum liquid components required for gel formation and maximum ionic conductivity. This is achieved by preparing several films with varying concentration of the constituents and measuring their ionic conductivity by AC impedance spectroscopy. Mg/GPE/MnO$_2$ cells are assembled and their discharge behaviour is studied. A capacity value of about 40 mA h per gram of MnO$_2$ is obtained. Cyclic voltammetric experiments demonstrate qualitatively the reversible behaviour of the MnO$_2$ electrode. The Mg/GPE/MnO$_2$ cells are subjected to about 20 charge–discharge cycles with a consistent capacity of about 20 mA h g^{-1} Cycle-life data is limited by surface passivation of the magnesium negative electrode and poor rechargeability of the MnO$_2$ positive electrode. At present, the results show that the Mg/GPE/MnO$_2$ cells have an inferior performance in comparison with that of well-developed, lithium-based rechargeable batteries. Further extensive investigations are required to raise the performance of the magnesium-based rechargeable cells to practical levels. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Solid-state Mg/MnO$_2$ cell; Gel polymer electrolyte; AC impedance; Discharge capacity; Cycle-life

1. Introduction

Investigations related to the development of high-energy batteries, particularly lithium batteries and lithium-ion batteries, have gained in importance in recent years. Among these, solid-state batteries, which employ a solid polymer as electrolyte, possess special importance. By using a thin film of a solid polymer electrolyte (SPE), several advantages are expected, of which enhancement in specific energy occupies primary importance. Studies of Li$^+$ ion conducting SPE media, which originated with high molecular weight poly(ethyleneoxide) (PEO), have been numerous [1]. Although PEO is a suitable solid medium to form dimensionally stable thin films of SPE, the ionic conductivity at ambient temperature is very low, namely, specific conductivity, $\sigma \approx 1 \times 10^{-8}$ S cm^{-1}. Since this value is not suitable for battery applications, investigations have

been directed towards modification of PEO and also several other polymers. Gel polymer electrolytes (GPE) have emerged as suitable electrolytes for solid-state lithium batteries [2].

Magnesium is an attractive electrode material, and has been employed successfully in both aqueous primary batteries and reserve batteries [3]. Solid-state rechargeable magnesium batteries are interesting in comparison with lithium batteries on account of the following advantages: (1) The ionic radii of Li$^+$ and Mg^{2+} are 68 and 65 pm, respectively, i.e., comparable in magnitude [4]. Hence, easy replacement of Li$^+$ ions by Mg^{2+} ions in insertion compounds is possible. (2) Magnesium metal is more stable than the lithium. It can be handled safely in oxygen and humid atmospheres unlike lithium which requires a high purity argon or helium atmosphere. Therefore, safety problems associated with magnesium metal are minimal. (3) Global raw material resources of magnesium are plentiful and thus, it is much cheaper than the lithium. Investigations related to solid-state magnesium batteries, however, are scarce in the literature [5]. Recently, it has been

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reported that the reversibility of the Mg/Mg^{2+} couple occurs in a GPE [6]. In the present communication, a GPE of optimum composition is used to assemble solid-state $Mg/GPE/MnO_2$ cells and the results of electrochemical studies are reported.

2. Experimental

A GPE film (thickness ≈ 100 μm) was prepared by heating at 80°C a suspension of the required quantities of polyacrylonitrile (PAN), propylene carbonate (PC), ethylene carbonate (EC), and magnesium trifluoromethanesulfonate (MgTr). These chemicals were purchased from Aldrich. In order to use minimum liquid components and achieve maximum conductivity (σ), GPE films with different concentrations of the constituents were prepared. It was found that a GPE with mass ratio of PAN:PC:EC:MgTr at 1:2:2:0.4 gave a maximum value of σ at 20°C. GPE films of this composition were used in subsequent experiments. Specimens of magnesium (10×10 mm) were sectioned out of a sheet of Mg AZ 21 alloy (Dow Chemicals) and were polished with successive grades of emery paper to a smooth finish, washed thoroughly in acetone and dried at ambient temperature. The manganese dioxide electrodes were prepared using battery grade γ-MnO_2 (electrolytic manganese dioxide, EMD). A mixture of EMD (80 wt.%), graphite powder (10 wt.%) and PAN (10 wt.%) of the GPE composition as the binder was thoroughly ground in a mortar and applied to a nickel grid (10×10 mm). The nickel grid was subjected to prior degreasing in alkali and etching in dilute HCl. The grid along with the electrode material was heated at 80°C for about 5 min and then compacted at a pressure of 5 tons cm^{-2}. A $Mg/GPE/MnO_2/GPE/Mg$ cell (for brevity, hereafter referred to as a $Mg/GPE/MnO_2$ cell) was assembled in an argon atmosphere by sandwiching the respective electrodes and the GPE film in a sealed container. Several cells were assembled for the purpose of different experiments and to ensure reproducibility. The charge–discharge cycling of the cells was carried out at constant current, using a galvanostatic circuit that consisted of a regulated DC power source, a high resistance and an ammeter in series. Cell voltage was measured using a Philips multimeter model PP 9007. Cyclic voltammetry and AC impedance spectroscopy were carried out by means of EG and G PARC equipment and a Versastat model 6310, respectively. Experiments were carried out at 20 ± 1°C in an air-conditioned room.

3. Results and discussion

The AC impedance behaviour of a symmetrical $Mg/GPE/Mg$ cell is shown in Fig. 1. The data were fitted to an equivalent circuit, as shown in the inset of Fig. 1, using Boukamp NLLS fitting program. From the resistance
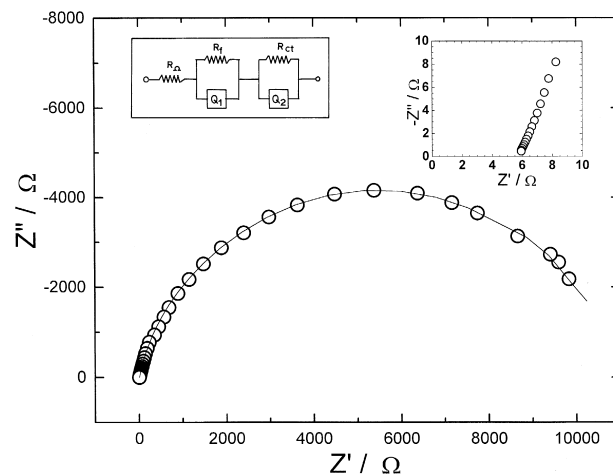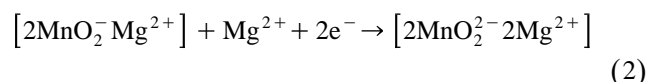

Fig. 1. AC impedance data as complex plane plot for a $Mg/GPE/Mg$ symmetrical cell measured at 20 ± 1°C. High frequency region is expanded and shown separately as an inset. Resistance of GPE film ($R_\Omega = 6.0$ Ω), resistance of surface film on Mg ($R_f = 243$ Ω) and charge-transfer resistance of $Mg = Mg^{2+} + 2e^-$ reaction ($R_{ct} = 10.46$ kΩ) are obtained by fitting experimental data to equivalent circuit shown in inset. Q_1 and Q_2 refer to constant phase elements corresponding to surface film capacitance and double-layer capacitance, respectively. Area of the magnesium electrode = 1.0 cm^2 and thickness of GPE = 100 μm. Experimental data are shown as symbols and theoretical data as solid curve.

value of the GPE, the value of σ obtained was found to be 2.1×10^{-3} S cm^{-1}. On repetition of the experiment, the value of σ was reproducible within $(1.9 \pm 0.2) \times 10^{-3}$ S cm^{-1}.

The open-circuit voltage of a $Mg/GPE/MnO_2$ cell was 2.3 V. After the assembly, a cell was allowed to equilibrate under open-circuit conditions for about 4 h before it was subjected to experiments. During this period, or even longer periods of open-circuit standing, the cell voltage remained constant.

The closed-circuit voltage curve of a $Mg/GPE/MnO_2$ cell during discharge to about 0 V is shown in Fig. 2. There are two distinguishable voltage plateau, the first plateau being above 1.0 V and the second one below 1.0 V. Akin to the reactions involved in a Li–MnO_2 cell with a non-aqueous liquid electrolyte [7], the following reactions can be considered to correspond to the voltage plateau of the $Mg/GPE/MnO_2$ cell discharge:

$$2MnO_2 + Mg^{2+} + 2e^- \rightarrow \left[2MnO_2^- \cdot Mg^{2+} \right] \qquad (1)$$

$$\left[2MnO_2^- Mg^{2+} \right] + Mg^{2+} + 2e^- \rightarrow \left[2MnO_2^{2-} 2Mg^{2+} \right] \qquad (2)$$

Reaction (1), which corresponds to the first discharge plateau, is the reduction of MnO_2 from Mn^{4+} to Mn^{3+}. This is accompanied by insertion of Mg^{2+} ions from the GPE into the MnO_2 lattice, which results in the formation of $[2MnO_2^- Mg^{2+}]$. This product undergoes another single electron reduction from Mn^{3+} to Mn^{2+} in reaction (2), which corresponds to the second voltage plateau (Fig. 2).
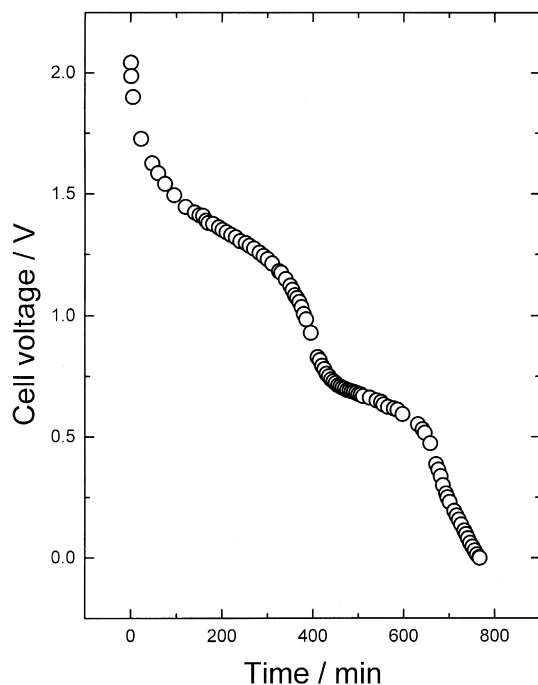
Fig. 2. Closed-circuit voltage of Mg/GPE/MnO$_2$/GPE/Mg cell as function of time during discharge at constant current of 0.2 mA. Area of each electrode = 1.0 cm^2; mass of MnO$_2$ = 26 mg; thickness of GPE = 120 μm.

Fig. 4. Discharge (●) and charge (○) curves of Mg/GPE/MnO$_2$/GPE/Mg cell at constant current of 0.2 mA. Area of each electrode = 1.0 cm^2; mass of MnO$_2$ = 16 mg; thickness of GPE = 100 μm.

The discharge behaviour of the Mg/GPE/MnO$_2$ cells suggested that the GPE films can be employed as the electrolyte. Since only the first plateau of the discharge (Fig. 2) encompasses a useful range of cell voltage, a cut-off voltage of 1.1 V was considered and a discharge capacity of 40 mA h g^{-1} of MnO$_2$ was obtained.

Since investigations on rechargeable magnesium batteries are more interesting, an attempt was made to examine the rechargeability of the Mg/GPE/MnO$_2$ cells. Studies of the magnesium electrode reaction, viz.,

$$Mg = Mg^{2+} + 2e^- \qquad (3)$$

in GPE revealed [6] that the reaction is reversible, although the exchange current density is low. Recently, it has been reported [8] that the reve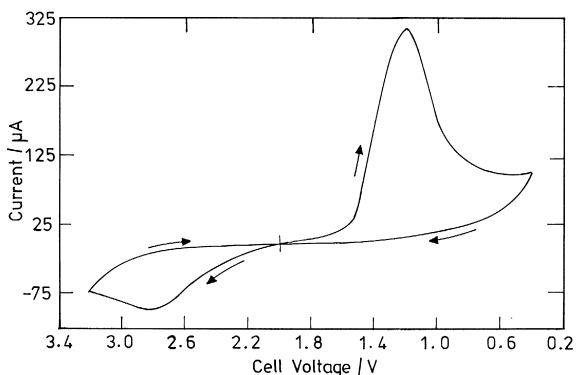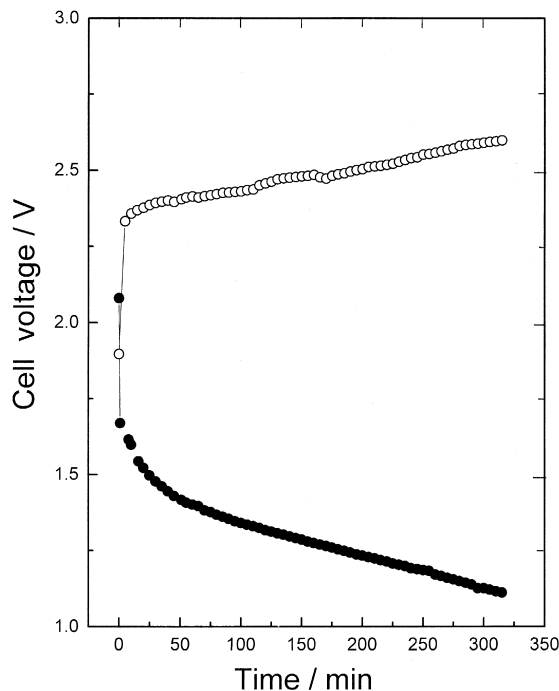rsible intercalation and de-intercalation of Mg^{2+} ions is possible in cobalt manganese oxide (Mn$_{2.15}$Co$_{0.37}$O$_4$). In view of these reports, Mg/GPE/

Fig. 3. Cyclic voltammogram of MnO$_2$ positive electrode of Mg/GPE/ MnO$_2$/GPE/Mg cell at scan rate of 0.1 mV s^{-1}.
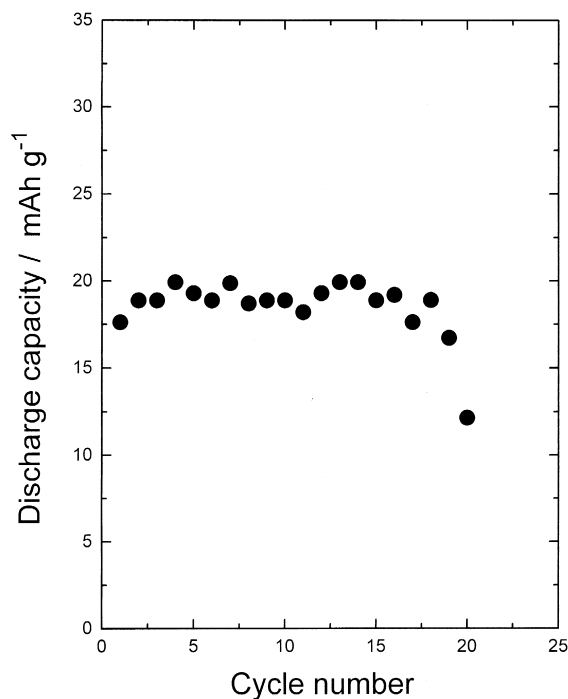

Fig. 5. Cycle-life data of a Mg/GPE/MnO$_2$/GPE/Mg cell at constant current of 0.2 mA. Area of each electrode = 1.0 cm^2; mass of the MnO$_2$ = 16 mg; thickness of the GPE = 100 μm.

MnO_2 cells were subjected to cyclic voltammetry and charge–discharge cycling. A cyclic voltammogram of the MnO_2 positive electrode of the Mg/GPE/MnO_2 cell is shown in Fig. 3. A reduction peak is present at a cell voltage of about 1.2 V in the forward scan. An oxidation peak appears at about 2.8 V during the reverse scan. Although the peak current values or charges associated with the cathodic and anodic peaks are not equal in magnitude, the voltammogram qualitatively suggests that the MnO_2 electrode undergoes the reduction and oxidation processes in the GPE medium.

The typical charge–discharge curves of a Mg/GPE/MnO_2 cell are shown in Fig. 4. On subjecting the cell to charging by a capacity equal to the discharge capacity, the cell voltage reaches a value of 2.6 V during the first cycle. With increase in the cycle number, however, it is found that the discharge curve exhibits a voltage dip, which is similar to the delay time of magnesium-based aqueous batteries [9]. Also, the charging voltage gradually increased. These processes are attributed to the Mg/GPE interface. With an increase in cycle number, the surface area of magnesium increases due to non-uniform deposition of Mg during charging. This is supported by SEM observations of a magnesium electrode, which was subjected to 20 cycles. Therefore, the reactivity of the magnesium surface in GPE increases with cycle number and results in increased passivation of the magnesium surface. The cycle-life data of a Mg/GPE/MnO_2 cell is shown in Fig. 5. A constant capacity of about 20 mA h per gram of MnO_2 is obtained for about 20 cycles. Cycling could not be continued further, as the cell voltage exceeded 5.0 V during charging. This value of voltage was a safe voltage window for the GPE.

4. Conclusions

Solid-state Mg/MnO_2 cells, which employ a GPE, have been assembled and their electrochemical behaviour studied. Although the capacity obtained is less than the theoretical value (308 mA h per gram of MnO_2 for a one-electron reduction), the studies suggest the usefulness of GPE, which utilizes magnesium triflate as the salt. It is attempted to extend the studies to examine rechargeability of the cells. The cycle-life limitation is due to progressive passivation of the Mg/GPE interface and poor rechargeability of the MnO_2 electrodes. At present, the results reflect the poor performance of Mg/GPE/MnO_2 cells in comparison with performance capabilities of the well-developed lithium-based rechargeable batteries. Further extensive investigations are required, however, to raise the performance of the magnesium-based rechargeable cells to practical levels.

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