

Performance characteristics of LiMn_2O_4 /polymer/carbon electrochemical cells

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Abstract

This paper discusses the performance characteristics of two types of cells of configuration LiMn_2O_4 /chitosan/C. LiMn_2O_4 was prepared by the sol–gel method. The precursor obtained was heated at different temperatures to form LiMn_2O_4 . The performance of the LiMn_2O_4 compound prepared at different temperatures was investigated by studying the discharge characteristics of the LiMn_2O_4 /LiClO₄–EC–DMC/C cells. It was found that the cell utilising LiMn_2O_4 obtained by heating the precursor at 600°C, for 6 h gave the best performance. The LiMn_2O_4 compound was then used to fabricate cells using a chitosan-based electrolyte. In one of the cells, the chitosan polymer was doped with 32% salt to represent a salt-in-polymer electrolyte and in the other, the polymer was doped with 75% salt to form a polymer-in-salt electrolyte. The room temperature conductivity for the salt-in-polymer electrolyte was $1.3 \times 10^{-5} \text{ S cm}^{-1}$ and that of the polymer-in-salt electrolyte was $3.9 \times 10^{-3} \text{ S cm}^{-1}$. The cathode of all cells consists 80% active material 10% binder and 10% carbon by weight. The characteristics of the cells were measured and analysed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LiMn_2O_4 ; Electrochemical cells; Conductivity

1. Introduction

Solid state batteries have come a long way since Takahashi and Yamamoto demonstrated an all solid state cell [1]. With solid state batteries, problems in conventional liquid electrolyte battery systems such as spillage, difficulty in handling liquids during manufacturing, corrosiveness of liquid electrolyte with container and sealants [2], low power to weight ratio and limited shelf life [3] can be overcome. Liquid electrolytes also give the problems of gas formation and electrolyte vapour pressure [2] which is not present in solid state batteries. The discovery of new solid materials (organic and inorganic) with better conductivity values (10^{-3} – $10^{-2} \text{ S cm}^{-1}$) renewed interest in solid electrolytes [1]. The battery system first proposed by Armand [3] using thin film polymer electrolyte opens up practical possibilities of using polymeric materials. However, one major problem in solid state batteries is obtaining good interfacial contact between the electrolyte and the electrodes. The flexibility,

elasticity and adhesiveness of solid polymer electrolytes (SPE) present, to a certain extent, a solution to this problem [2]. The flexibility of the polymers also makes it possible to have batteries of different shapes and sizes. Thus, polymers present an ideal separator especially to thin film batteries [4].

The use of LiMn_2O_4 as cathodes and carbon as anodes has several advantages. LiMn_2O_4 has been quite extensively studied and characterised. Experimental results have shown that the material is a viable one for use as cathodes in rechargeable lithium batteries [5–27]. LiMn_2O_4 also has the advantage of being compatible with carbon anodes [7] and this avoids the use of pure lithium metal and thus eliminates the problems associated with its use. Manganese and carbon are relatively cheap materials [15–17] which is advantageous for the prospect of commercialising this type of battery.

The aim of this research is to use LiMn_2O_4 that has been synthesised using the sol–gel method. The best synthesis conditions that were determined in earlier studies were used in this work. The polymer electrolytes used will be a chitosan– LiCF_3SO_3 complex exhibiting the highest electrical conductivity at ambient temperature. The characteristics of the cells assembled are measured and discussed.

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2. Experimental

2.1. Synthesis of cathode material

Stoichiometric amounts of lithium acetate and manganese acetate were dissolved in ethanol and 1 M tartaric acid was added to the mixture until a gel was formed. The gel was slowly heated at 100°C until a black powder precursor was obtained. From thermogravimetric analysis (TGA) and battery charge/discharge studies, it was observed that sintering the precursor at a temperature of 600°C for 6 h gave good battery performance for the batteries using non-aqueous electrolytes, LiClO₄-EC-DMC.

2.2. Electrode fabrication

The cathode consisted of 80% LiMn₂O₄, 10% poly(vinylidene fluoride) (PVDF) and 10% activated carbon by weight and the anode consisted of 10% PVDF and 90% carbon blend by weight.

2.3. Electrolyte preparation

The polymer films of chitosan acetate-ethylene carbonate (EC)-lithium triflate (LiCF₃SO₃) were prepared by the solution cast technique. The composition of polymer-in-salt electrolyte is 25 wt.% of polymer and 75 wt.% of LiCF₃SO₃ and for the salt-in-polymer is 68 wt.% of polymer and 32 wt.% of LiCF₃SO₃. These were dissolved in 100 ml of 1% acetic acid solution by volume and dried to obtain the polymer films. Electrical conductivity measurements were performed with a HIOKI 3531-01 LCR bridge that had been interfaced with a computer in the frequency range 42 Hz to 5 MHz. The electrical conductivity of the sample, σ , can be calculated using the equation $\sigma = t/R_B A$, where t is the

thickness of the film, A the electrode-electrolyte contact area and R_B the bulk resistance [28]. The samples were placed in a desiccator during impedance measurement.

2.4. Battery assembly

The electrodes and the electrolyte were cut into circular shapes and assembled in a teflon holder in ambient conditions. For the cell with the polymer-in-salt electrolyte, the diameters of the cathode, the anode and the electrolyte were 1.8, 1.3 and 2.0 cm. The total weight of the battery components was 0.2728 g. For the cell with the salt-in-polymer electrolyte, the diameters of the cathode, the anode and the electrolyte were 1.8, 1.5 and 1.9 cm, respectively. The total weight of the battery components was 0.1590 g. The thickness of the batteries were between 0.79 and 1.02 mm. The battery was then tested using the Keithley 237 electrometer interfaced with a computer.

3. Results and discussions

The LiMn₂O₄ compound prepared at a sintering temperature of 600°C was used in the fabrication of the LiMn₂O₄/chitosan/C cells. The X-ray diffraction pattern of the prepared LiMn₂O₄ compound compares well with values from the JCPDS data and those reported in the literature [5,12]. The purity and stability of the cathode material was reliable, as obtained from earlier studies made on this material in non-aqueous lithium batteries. Chitosan was used in the present work because pure chitosan and chitosan-salt films can easily form films and are known to be amorphous [29,30] unlike PEO and its salt complexes. It can still form an amorphous film even when the salt content is higher than the polymer content.

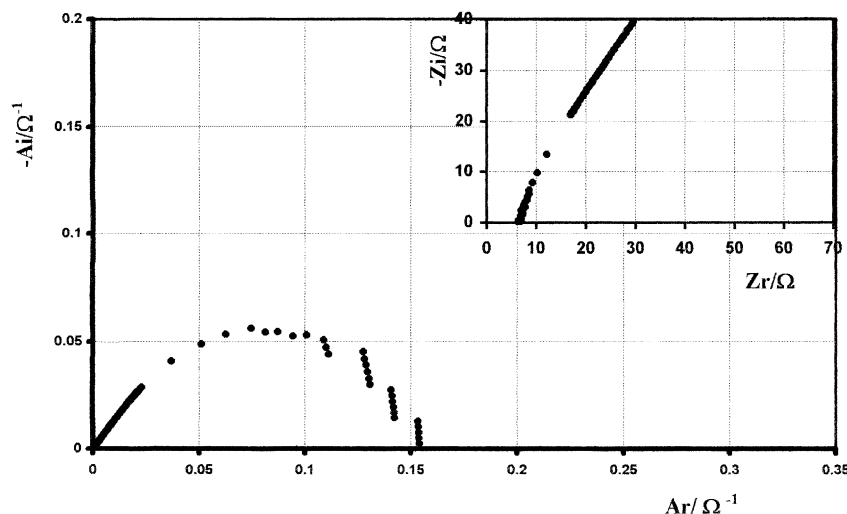


Fig. 1. Admittance and impedance (inset) plots for the chitosan-in-LiCF₃SO₃ electrolyte from which the bulk resistance was determined and consequently, the conductivity value calculated.

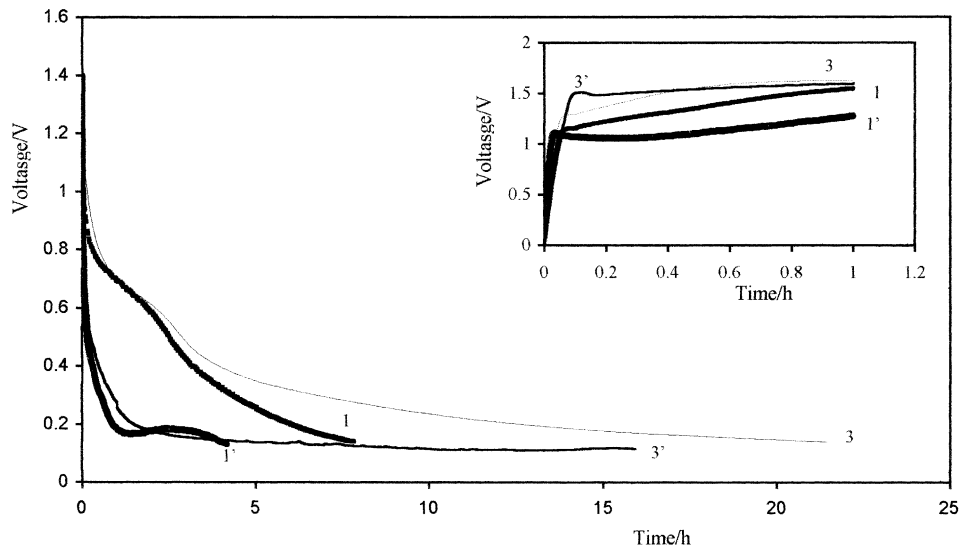


Fig. 2. Discharged characteristics of the first and third cycles. Inset shows charge characteristics of the first and third cycles. Numbers 1 and 3 indicate curves for the cell with the polymer-in-salt electrolyte and the numbers 1' and 3' for the cell with the salt-in-polymer electrolyte.

The ambient electrical conductivity of the salt-in-polymer electrolyte film was $1.3 \times 10^{-5} \text{ S cm}^{-1}$ and that of the polymer-in-salt film was $3.9 \times 10^{-3} \text{ S cm}^{-1}$. R_B was obtained from the plots shown in Fig. 1. Both the polymer-in-salt and the salt-in-polymer films were used to fabricate the $\text{LiMn}_2\text{O}_4/\text{chitosan}/\text{C}$ cell in open air. Since the cell had negligible voltage in the assembled state, it was charged at a constant current of 0.5 mA for 1 h. The cell only achieved a voltage of 1.5 V. A reasonable discharge characteristic showing a short plateau region could be observed when the cell was discharged at 0.001 mA (see curves 1 and 3, Fig. 2). When the cells were removed, the casings were

observed wet indicating that the cells had absorbed water when they were assembled in air. The presence of water could be the major cause for not obtaining a voltage of 4.2 V during charge which is typical for a $\text{LiMn}_2\text{O}_4/\text{C}$ cell. A back emf could have been established within the cell due to the presence of the water molecules resulting in a lower voltage when charged. The discharge curve resembles that of a polarisation current curve when the cells were discharged at a higher current, but when discharged at 0.001 mA, a short plateau can still be observed as shown by curves 1 and 3 for the cell with the polymer-in-salt electrolyte (Fig. 2). The plateau should evolve at $\sim 4 \text{ V}$ for a $\text{LiMn}_2\text{O}_4/\text{C}$ cell, but the

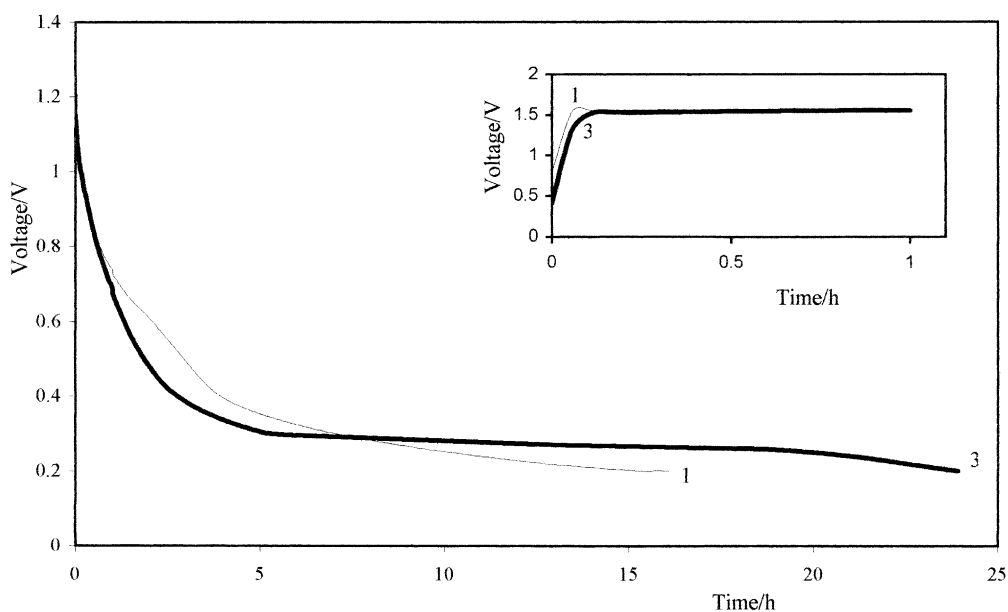


Fig. 3. Discharge characteristics of two cells connected in parallel. Inset shows charge characteristics of the same cell. Numbers 1 and 3 indicate cycle numbers.

back emf attributed to the water molecules reduced the plateau between 0.6 and 0.8 V for the cell with the polymer-in-salt electrolyte. For the cell with the salt-in-polymer electrolyte, even when discharged at such a low current, no “plateau-like” feature was observed. The lower ambient temperature electrical conductivity of the electrolyte could also be another factor for the discharge characteristic of the cell with the salt-in-polymer electrolyte. The discharge characteristics of two cells connected in parallel is shown in Fig. 3. The discharge time is about the sum of both the discharge times of the two individual cells.

4. Conclusions

Water absorbed by the components of the $\text{LiMn}_2\text{O}_4/\text{chitosan-LiCF}_3\text{SO}_3/\text{C}$ cell during its assembly in air could have established a back emf within the cell that reduced the plateau voltage of the cell and lowered its capacity. However, when discharged at a current of 0.001 mA, the “plateau-like” feature of an $\text{LiMn}_2\text{O}_4/\text{C}$ discharge characteristic can be observed provided the electrolyte has sufficient room temperature electrical conductivity.

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