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Electrochemical properties of $\text{Li}_x\text{Mn}_2\text{O}_4$ composite electrode in cells based on glass–polymer composite electrolytes

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Abstract

Electrochemical behavior of $\text{Li}_x\text{Mn}_2\text{O}_4$ powders, prepared using different synthesis approaches, have been studied using $\text{Li}_x\text{C}_6/\text{Li}_x\text{Mn}_2\text{O}_4$ cells based on glass–polymer composite electrolytes. Results indicate that the $\text{Li}_x\text{Mn}_2\text{O}_4$ powders prepared by a xerogel technique have much smaller particle size, larger capacity utilization and less capacity fading during cycling in comparison to the powders prepared by solid state reactions. The electrochemical behavior of a composite positive electrode based on $\text{Li}_x\text{Mn}_2\text{O}_4$ is influenced not only by the microstructure of the $\text{Li}_x\text{Mn}_2\text{O}_4$ powders but also by the volume fractions of other constituent phases.

Keywords: Li-ion battery; $\text{Li}_x\text{Mn}_2\text{O}_4$; Xerogel process; Glass–polymer composite electrolyte

1. Introduction

Transition metal oxides with general formula Li_xMO_2 ($M = \text{Mn}, \text{Co}$ and Ni) have received much attention as prospective electrode materials for lithium batteries [1–14]. Among these intercalation compounds, the spinel LiMn_2O_4 has been perceived to be the most promising positive electrode materials because of its readily availability, low cost and environmental compatibility.

Powders of LiMn_2O_4 are typically prepared from mixtures of Li salts (such as LiOH , Li_2NO_3 and LiCO_3) and manganese oxides, acetates, or hydroxide powder [9–13]. The mixtures usually are calcined at either low temperatures (ranging from 300 to 600°C) or high temperatures (ranging from 800 to

900°C). Solution techniques [9,10,12] have been widely investigated to reduce the synthesis temperatures and particle size of LiMn_2O_4 powders, which will improve the morphology of the powder and reduce the diffusion length of Li ions in LiMn_2O_4 particles.

It has been reported [9,10,12] that the LiMn_2O_4 powders prepared at low temperatures (300–600°C) exhibit much better cycling behavior than the LiMn_2O_4 powders prepared at high temperatures (800–900°C). Others reported [11,13] that the LiMn_2O_4 prepared at high temperatures using solid state reaction degrades rapidly upon cycling although the initial capacity is satisfactory. Further, there are discrepancies in the literature as to what plays a dominant role in determining the capacity fading at 4.1 V. According to Manev et al. [12], the capacity loss is due primarily to the disturbed stoichiometry occurring at high temperatures as a result of oxygen

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loss. Therefore, the average Mn oxidation state would be less than 3.5 and result in a lower capacity. Later, Tarascon et al. [15] have reported that the particle size is the main factor influencing the capacity.

Although the behavior of $\text{Li}_x\text{Mn}_2\text{O}_4$ in cells based on liquid electrolytes has been widely studied, the electrochemical behavior of these electrode materials in cells based on solid state electrolytes has not been well characterized. Thus, the objective of this study is to characterize the cycling behavior of the $\text{Li}_x\text{Mn}_2\text{O}_4$ electrode materials using a newly-developed glass-polymer composite electrolyte (GPC) [16]. The GPC electrolytes exhibit high conductivities ($3 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at room temperature to $1.4 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 80°C), adequate mechanical flexibility and good electrochemical stabilities against $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xC_6 . An initial cycling of $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells has shown good cycleability between 3 V and 4.5 V [17]. In this study, we report the electrochemical behavior of positive electrodes based on $\text{Li}_x\text{Mn}_2\text{O}_4$ prepared using different synthetic approaches in an effort to improve cycling performance. In practice, it is important to determine the optimum conditions under which LiMn_2O_4 powders can be synthesized with desired electrochemical properties. These properties are typically sensitive to the morphology of resulting powders and hence to their preparation route.

2. Experimental

GPC electrolytes were prepared as described elsewhere [16]. $\text{Li}_x\text{Mn}_2\text{O}_4$ powders were prepared using two synthesis approaches: xerogel and solid state reaction. In a solid state process, Li_2CO_3 (Alfa) and Mn_2CO_3 (Cerac) powders were mixed at ratio of Li:Mn (1:2) and ball-milled for 12 h in ethanol. After evaporating ethanol at 80°C , the powders were reground and calcined at 800°C for 24 h. In a xerogel process [14], stoichiometric amounts of manganese and lithium acetates were added in methanol and a 1 mol of citric acid was dissolved by stirring. After complete dissolution of the added solution, homogenous gelatinous precipitates were obtained. Upon decomposition at 350°C for 12 h, $\text{Li}_x\text{Mn}_2\text{O}_4$ particles of sub-micron sizes were obtained. The spinel phase of the prepared powders obtained from

solid state reaction and xerogel were examined using X-ray diffraction (Phillips PW 1800 diffractometer and $\text{Cu K}\alpha$ radiation).

The composite positive electrode were prepared from LiMn_2O_4 powder mixed with GPC powder and carbon blacks (Alfa) at different weight ratios. The composite negative electrode was processed by mixing the GPC and graphite (Alfa) powders in a weight ratio of 50:50. Solid state cells, C/GPC/ $\text{Li}_x\text{Mn}_2\text{O}_4$, were then assembled by pressing the composite electrode, GPC electrolyte and the composite negative electrode into a three layered pellet. Cycling of cells and 4-probe impedance measurements [16] were carried out at 70°C using a Potentiostat/Galvanostat (EG&G 273A) and a lock-in amplifier (EG&G M5120). All impedance spectra of $\text{Li}_x\text{Mn}_2\text{O}_4$ were measured in the fully-discharged state (or as prepared).

3. Results and discussion

3.1. Microscopic characteristics of $\text{Li}_x\text{Mn}_2\text{O}_4$ powders

X-ray diffraction (XRD) patterns of $\text{Li}_x\text{Mn}_2\text{O}_4$ powders prepared by xerogel and solid state reaction are shown in Fig. 1. Although the peak positions and relative intensity of $\text{Li}_x\text{Mn}_2\text{O}_4$ prepared by the two

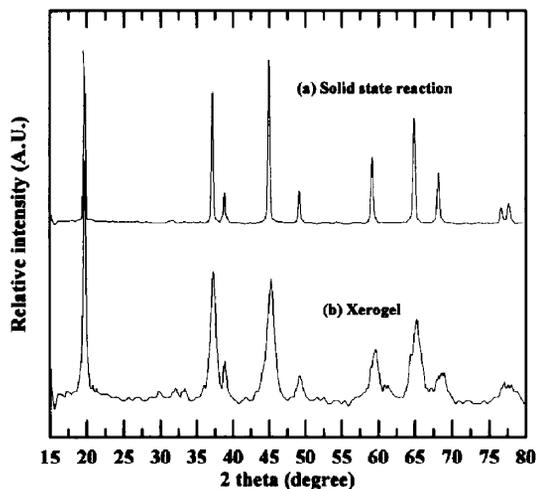


Fig. 1. X-ray diffraction patterns for powders synthesized using (a) solid state reaction at 800°C for 24 h and (b) xerogel process (heat-treated at 350°C for 12 h).

synthesis approaches are similar, the width of the peaks are much broader in the XRD pattern for the xerogel powder, indicating a somewhat smaller average particle size.

Fig. 2 shows the SEM pictures of agglomerates of the $\text{Li}_x\text{Mn}_2\text{O}_4$ powders prepared using a xerogel or a solid state process. The xerogel powders have much finer particle (0.1 μm) and agglomerate sizes (1 μm)

(a) solid state reaction



(b) xerogel process



Fig. 2. SEM pictures of $\text{Li}_x\text{Mn}_2\text{O}_4$ powders prepared using (a) solid state reaction at 800°C for 24 h and (b) xerogel (heat-treated at 350°C for 12 h).

in comparison to the powders obtained from solid state reaction.

3.2. Electrical properties of $\text{Li}_x\text{Mn}_2\text{O}_4$ composite electrodes

Shown in Fig. 3 are the cell configurations for 4-probe impedance measurements and an impedance spectrum of a GPC electrolyte layer. Fig. 4a shows the cell configuration for interfacial impedance measurements while Fig. 4b and 4c show the dependence of the $\text{Li}_x\text{Mn}_2\text{O}_4$ /GPC interfacial resistances on the way in which the $\text{Li}_x\text{Mn}_2\text{O}_4$ powders were prepared. The interfacial resistance are also influenced by the applied dc bias. The resistance of the $\text{Li}_x\text{Mn}_2\text{O}_4$ /GPC interface was 430 Ω (without d.c. bias) when the $\text{Li}_x\text{Mn}_2\text{O}_4$ was synthesized using the solid state reaction at 800°C and 265 Ω (without d.c. bias) when the $\text{Li}_x\text{Mn}_2\text{O}_4$ was synthesized using xerogel at 350°C. This is because the $\text{Li}_x\text{Mn}_2\text{O}_4$ powders obtained from a xerogel process would have larger contact area with the GPC electrolyte at the interface. Fig. 5 shows the dependence of the resistances of the $\text{Li}_x\text{Mn}_2\text{O}_4$ /GPC interfaces on the volume

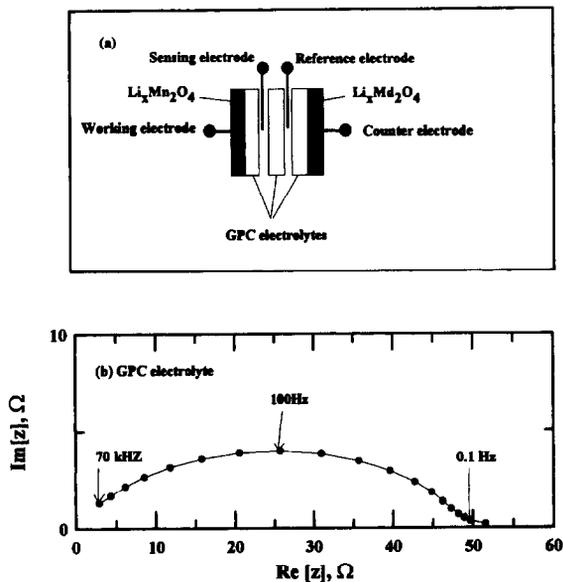


Fig. 3. (a) Cell configuration for 4-probe measurement and (b) an impedance spectrum measured at 70°C of a GPC composite electrolyte with composition of 87 vol% $(0.56\text{Li}_2\text{S} \cdot 0.19\text{B}_2\text{S}_3 \cdot 0.25\text{LiI})$ glass and 13 vol% $(\text{PEO})_6 \cdot \text{LiN}(\text{CF}_3\text{SO}_2)_2$.

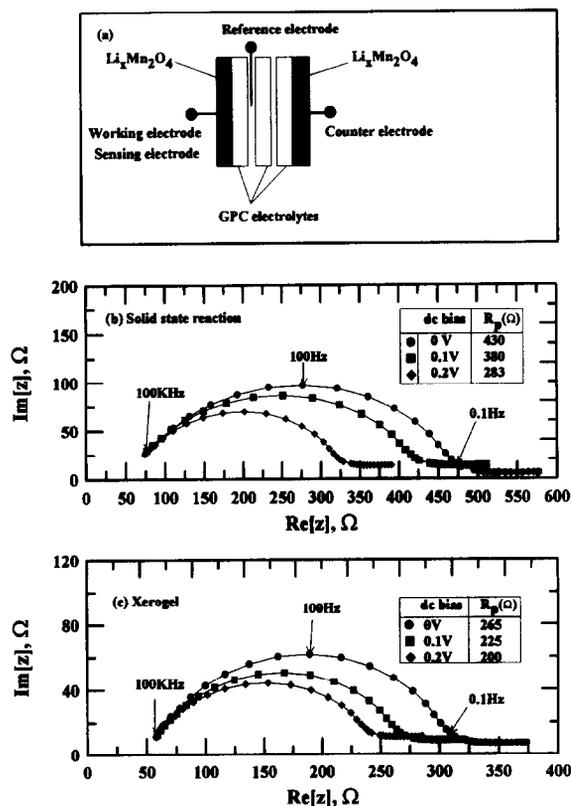


Fig. 4. Cell configuration for 4-probe measurement (a) and impedance spectra of $\text{Li}_x\text{Mn}_2\text{O}_4$ /GPC interfaces measured at 70°C: $\text{Li}_x\text{Mn}_2\text{O}_4$ was prepared using (b) solid state reaction and (c) xerogel process.

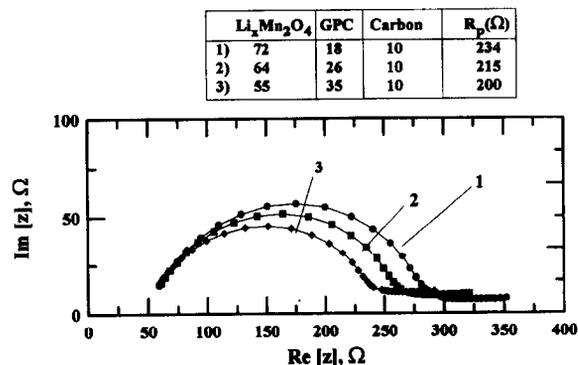


Fig. 5. Impedance spectra of composite positive electrodes measured (at 70°C) using a cell configuration of $\text{Li}_x\text{Mn}_2\text{O}_4$ /GPC/ $\text{Li}_x\text{Mn}_2\text{O}_4$.

fraction of each constituent phase. Among the 3 volume fractions studied, the composite positive electrode with a volume ratio of 55:35:10 exhibits a minimum interfacial resistance, suggesting that 35 vol% GPC electrolytes is necessary to improve Li ion transport in the composite electrode.

3.3. Cycling behavior

Fig. 6 shows the cycling behavior of the composite positive $\text{Li}_x\text{Mn}_2\text{O}_4$ electrode prepared using (a) solid state reaction and (b) xerogel. The cells were

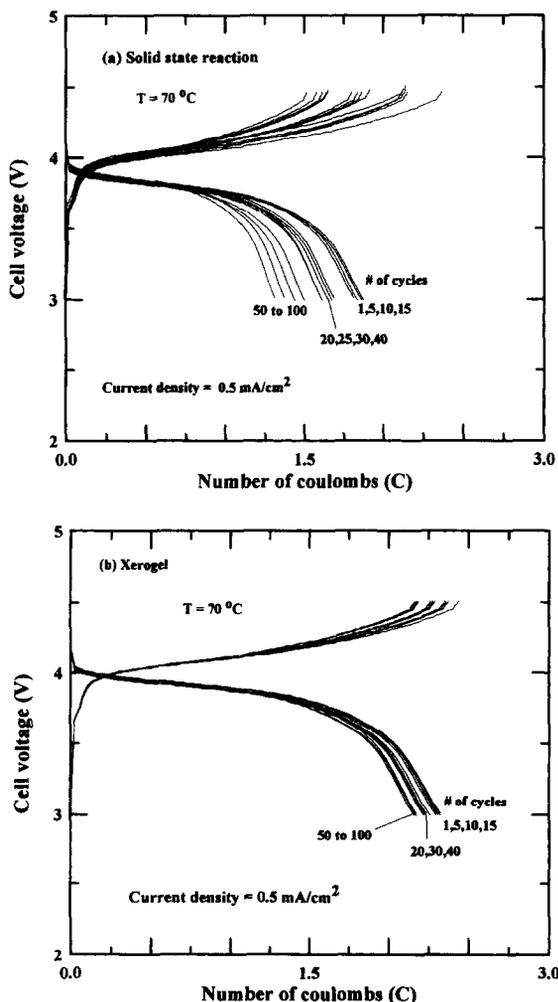


Fig. 6. Cycling behavior of $\text{Li}_x\text{C}_6/\text{Li}_x\text{Mn}_2\text{O}_4$ cells cycled at a current density of 0.5 mA/cm^2 : $\text{Li}_x\text{Mn}_2\text{O}_4$ was prepared using (a) solid state reaction and (b) xerogel.

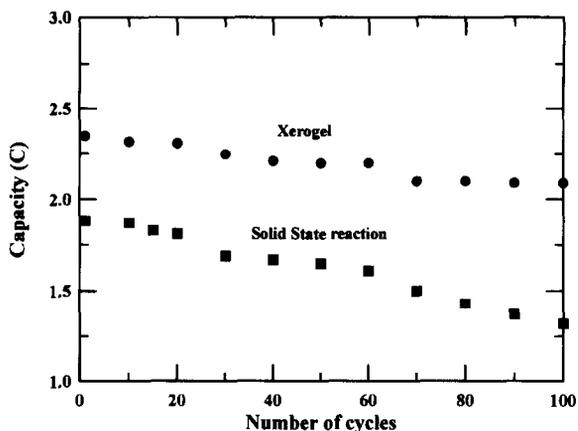


Fig. 7. Capacity fading of $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells (at 70°C) based on $\text{Li}_x\text{Mn}_2\text{O}_4$ powders prepared using different methods.

cycled between 3 and 4.5 V at a current density of 0.5 mA/cm^2 . The initial capacity of an electrode based on $\text{Li}_x\text{Mn}_2\text{O}_4$ powders from solid state reaction was 1.87 C and decreased rapidly down to 1.3 C after 100 cycles. In contrast, the capacity of the $\text{Li}_x\text{Mn}_2\text{O}_4$ powder prepared from xerogel process showed better capacity retention and the capacity decreased from an initial value of 2.3 C to 2.05 C after 100 cycles, as summarized in Fig. 7.

Fig. 8 shows the charge and discharge curves of the first cycle of each cell tested at 70°C at different current densities. The effect of discharge and charge

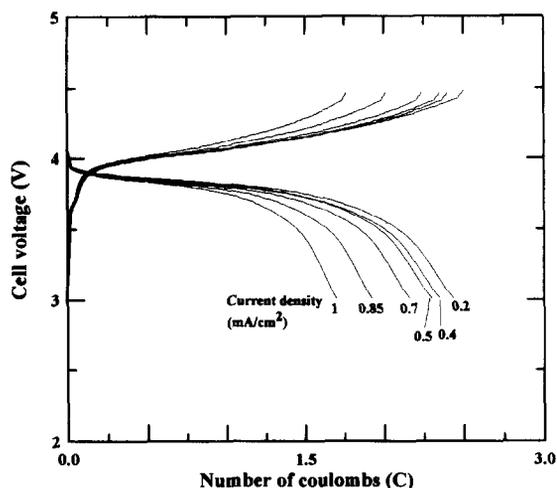


Fig. 8. First cycle of each $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell cycled (at 70°C) between 3 V and 4.5 V at different current densities ($\text{Li}_x\text{Mn}_2\text{O}_4$ was prepared using xerogel process).

current densities on the depth of cycling was studied using a cell based on $\text{Li}_x\text{Mn}_2\text{O}_4$ powder prepared using the xerogel process. When the discharge current density was increased from 0.5 to 0.85 mA/cm^2 , the discharge depth decreased 8%. When the current density was further increased to 1 mA/cm^2 , the depth of discharge was decreased by another 7%. This is due to slow diffusion of Li ions in $\text{Li}_x\text{Mn}_2\text{O}_4$, and the larger the particle size, the stronger the effect of current density on the depth of cycling. Thus, by reducing the particle size of $\text{Li}_x\text{Mn}_2\text{O}_4$ powders, the cell reversibility and capacity utilization were greatly improved.

4. Conclusions

The cycling behavior of the $\text{Li}_x\text{Mn}_2\text{O}_4$ prepared using a xerogel process (at 350°C) exhibited lower interfacial resistance, high rate capability and better capacity retention after 100 cycles than the powder prepared using solid state reaction at 800°C. This is attributed primarily to the preferred microstructure of the powders obtained from a xerogel process. Further, the overall behavior of a composite electrode based on $\text{Li}_x\text{Mn}_2\text{O}_4$ depends also on the volume fraction of each constituent phase.

Acknowledgments

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