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Letter to the Editors

Characterization of interfacial stabilities of Li_xC_6 /glass–polymer composite/ $\text{Li}_x\text{Mn}_2\text{O}_4$ cells using in-situ four-probe measurements

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Abstract

The interfacial resistances of Li_xC_6 /GPC/ $\text{Li}_x\text{Mn}_2\text{O}_4$ cells with glass–polymer composite (GPC) electrolytes have been characterized using in-situ four-probe measurements during cycling. The evolution of impedance spectra of the cells shows that the kinetic stability of the GPC electrolyte against Li_xC_6 and $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes is reasonably good, although there is an initial increase in interfacial resistances. The resistance of a $\text{Li}_x\text{Mn}_2\text{O}_4$ /GPC interface increases from 370 Ω as prepared (in the fully discharged state) to 740 Ω after first cycle and then remains constant up to 80 cycles. The resistance of a GPC/ Li_xC_6 interface typically increases from an initial value of 380 Ω (as prepared) to 1020 Ω after 50 cycles. The interfacial resistances then stay relatively constant during cycling up to about 80 cycles. The observed discharge capacity fading of the positive electrode ($\text{Li}_x\text{Mn}_2\text{O}_4$) is about 8% after 80 cycles.

Keywords: In-situ four-probe measurement; Lithium-ion battery; Interfacial stability; Glass–polymer composite electrolyte

1. Introduction

Rocking chair batteries (RCBs) using intercalation compounds as electrodes (cathode and anode) have shown promising energy density and sufficient environment safety [1–7]. The negative electrode is typically based on graphite or petroleum coke [7,8]. While graphite exhibits a high capacity with a flat discharge characteristics [7,8,10,11], petroleum coke is stable against most of the electrolytes [7,8,10,11]. Among the best studied materials for the positive electrodes [9–16], LiMn_2O_4 -based materials are likely to be the materials of choice for RCBs because of their low cost, low toxicity and environmental compatibility [10–14].

The great advantage of RCBs is that there is no plating of metallic lithium during charge, effectively preventing lithium dendrite formation. In general, the growth of dendrites often leads to disconnection and electrical isolation of active lithium, resulting in loss of capacity, or to electrical shorting between electrodes and cell failure. To date, however, most RCBs are still based on liquid electrolytes, which may pose problems for some applications. For instance, some solvent may tend to cause exfoliation of the graphite and may form a passivating layer on the surface of the electrode that increases the polarization of the cell and lowers the cell voltage [9].

In this study, the viability of using a newly-developed glass–polymer composite (GPC) electrolyte for RCB with Li_xC_6 and $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes is investigated. In particular, the stability of the electrolyte and the interfaces of a Li_xC_6 /GPC/

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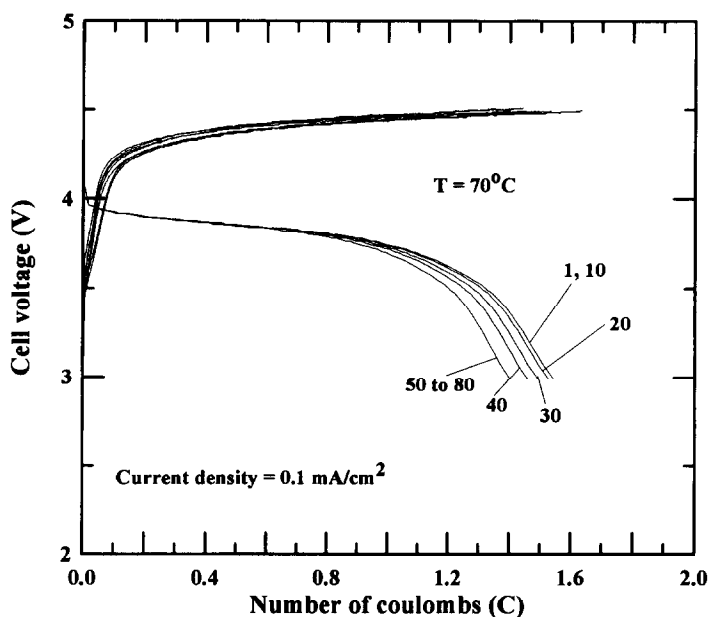


Fig. 1. Typical cycling behavior of a $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell charged and discharged at a current density of $0.1 \text{ mA}/\text{cm}^2$ at 70°C (the number adjacent to each curve is the number of cycle).

$\text{Li}_x\text{Mn}_2\text{O}_4$ cell during cycling is studied using four-probe measurements.

2. Experimental

The glass–polymer composite electrolyte used in this study has a 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 powder and 13 vol% $\text{P}(\text{EO})_6 \cdot \text{LiN}(\text{CF}_3\text{SO}_2)_2$ polymer electrolytes. The precursors for preparation of the GPC electrolyte were high purity $\nu\text{-B}_2\text{S}_3$, Li_2S , LiI and $\text{P}(\text{EO})_6 \cdot \text{LiN}(\text{CF}_3\text{SO}_2)_2$. All materials were handled in a glove box (Vac Atmosphere) with residual O_2 and H_2O less than 5 ppm. $\text{Li}_x\text{Mn}_2\text{O}_4$ powder was prepared using a modified xerogel process [1]. Stoichiometric amounts of manganese and lithium acetates were dissolved in methanol and 1 M aqueous solution of citric acid was then added and mixed with vigorous stirring. In the final stage, homogenous

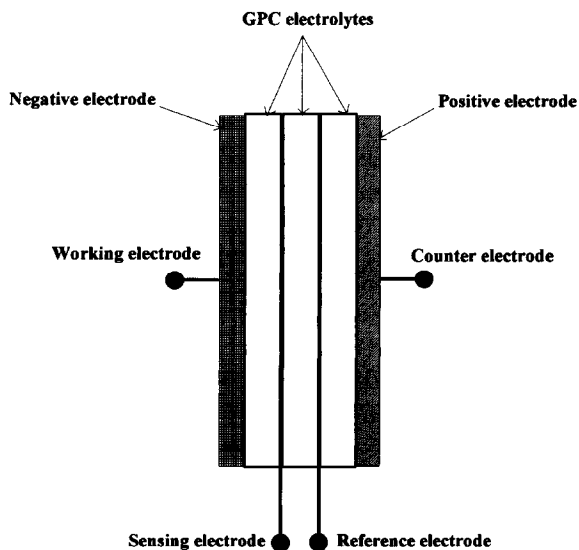


Fig. 2. A schematic showing the four-probe arrangement for impedance measurements during cycling.

and gelatinous precipitates consisted of metal hydroxide finely dispersed in the solution medium. When the solvents were evaporated slowly, xerogel-type powders were obtained. Upon decomposition at 350°C, $\text{Li}_x\text{Mn}_2\text{O}_4$ powder with sub-micron particle size was obtained.

The positive composite electrode was prepared from $\text{Li}_x\text{Mn}_2\text{O}_4$ mixed with the GPC powder and carbon blacks (Alfa) with a 40:50:10

($\text{Li}_x\text{Mn}_2\text{O}_4$:GPC:carbon) weight ratio. The composite anode was fabricated by mixing the GPC powder and carbon blacks in a weight ratio of 50:50. Cells of C/GPC/ $\text{Li}_x\text{Mn}_2\text{O}_4$ were prepared by pressing the GPC electrolyte and composite electrode powders into a three layered pellet (the typical thickness is about 1.3 mm). Impedance spectra and cycling measurements were obtained using an AG and G 273A potentiostat/galvanostat.

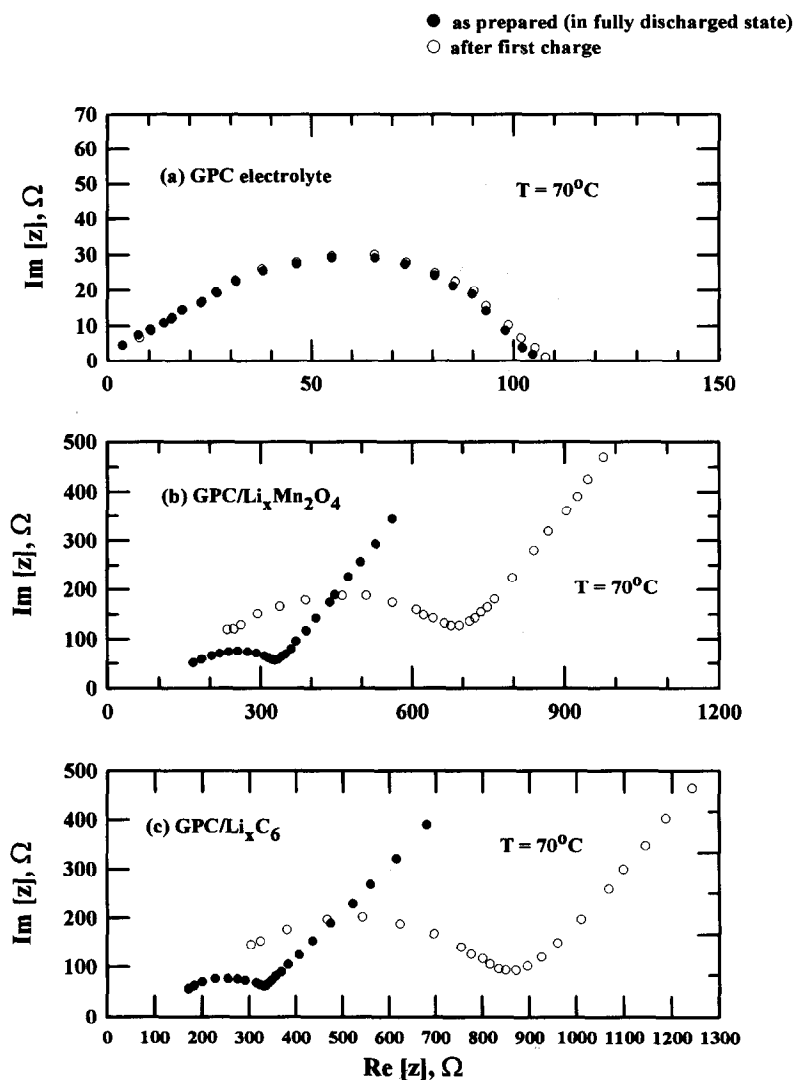


Fig. 3. Some initial impedance spectra of (a) GPC electrolyte, (b) $\text{Li}_x\text{Mn}_2\text{O}_4$ /GPC interface and (c) Li_xC_6 /GPC interface, acquired from a Li_xC_6 /GPC/ $\text{Li}_x\text{Mn}_2\text{O}_4$ cell at 70°C.

3. Results and discussion

3.1. Cycling behavior

Shown in Fig. 1 are some typical cycling curves for a $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell. The open cell voltage (OCV) of the cell as prepared (in fully discharged state) was around 0 V and the first charge took longer than the first discharge. The initial discharge capacity was 1.56 C, which reduced to 1.4 C after 80 cycles at a charge and discharge current density of $0.1 \text{ mA}/\text{cm}^2$ between 4.5 and 3 V.

3.2. Stabilities of GPC electrolyte and interfaces of $\text{Li}_x\text{C}_6/\text{GPC}$ and $\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}$

The advantages of four-probe measurements (Fig. 2) are the easiness in identifying the limiting factor to the performance of a cell. Shown in Figs. 3 and 4 are some typical impedance spectra of the GPC electrolyte and the interfaces of $\text{Li}_x\text{C}_6/\text{GPC}$ and $\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}$, which were acquired during the cycling of a $\text{Li}_x\text{C}_6/\text{GPC}(\times 3)/\text{Li}_x\text{Mn}_2\text{O}_4$ cell. When the cell is fully charged, the resistance of the GPC electrolyte showed only small initial increase. How-

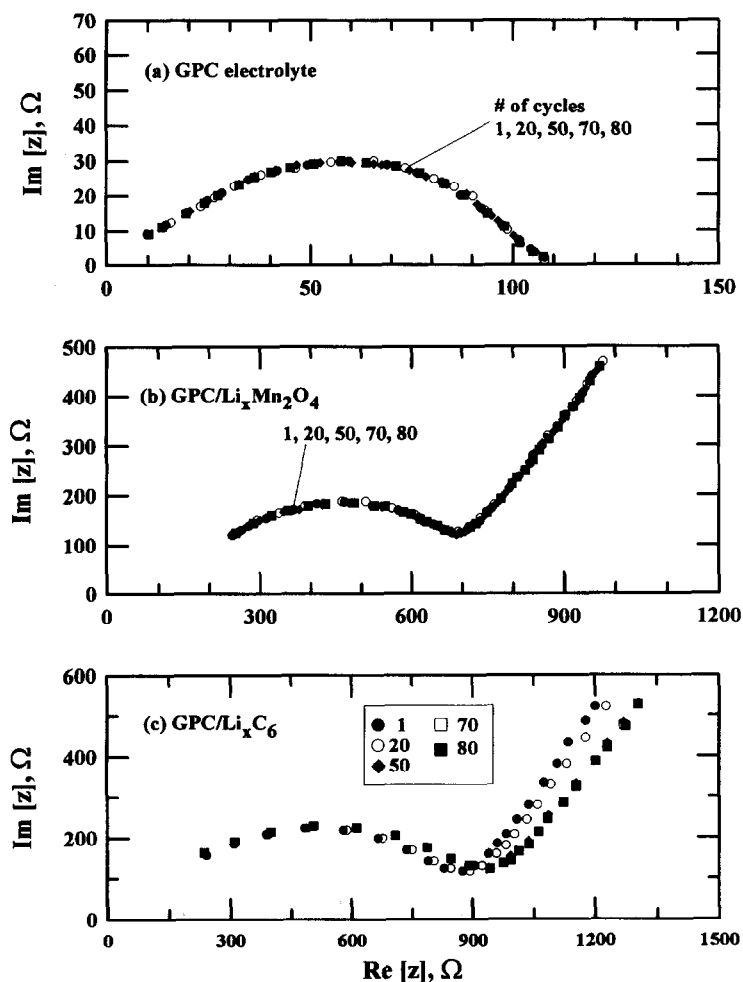


Fig. 4. Some typical impedance spectra of (a) GPC electrolyte, (b) $\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}$ interface and (c) $\text{Li}_x\text{C}_6/\text{GPC}$ interface, as determined from a $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell during cycling at 70°C .

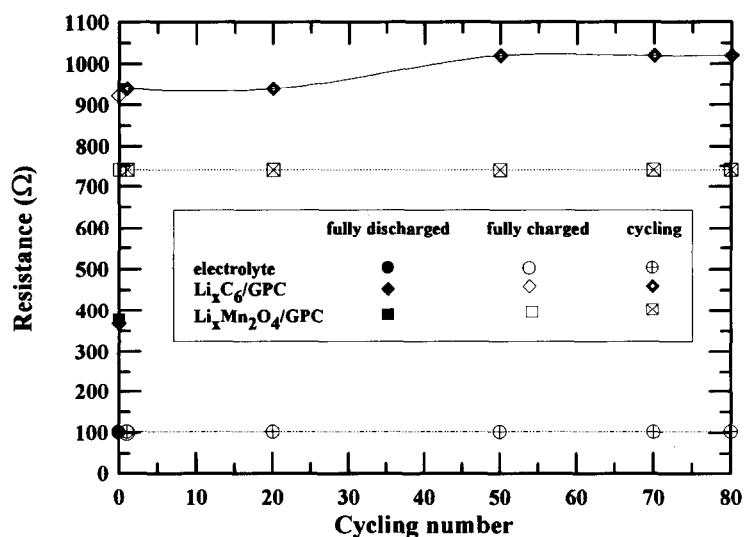


Fig. 5. Changes in resistances of (a) GPC electrolyte, (b) $\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}$ interface and (c) $\text{Li}_x\text{C}_6/\text{GPC}$ interface, at 70°C in a $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell during cycling at 70°C .

ever, the resistance of the $\text{Li}_x\text{C}_6/\text{GPC}$ interface increased from an initial value of $370\ \Omega$, as prepared in the fully discharged state, to $940\ \Omega$ after being fully charged for the first time; similarly, the resistances of the $\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}$ interface increased from 380 to $740\ \Omega$ in the cell as shown in Fig. 5. Upon cycling, the resistances of the $\text{Li}_x\text{C}_6/\text{GPC}$ interface increased from the initial value of $920\ \Omega$ after the first charge to $1020\ \Omega$ at the fully charged state after 50 cycles. The interfacial resistance then remained unchanged up to 80 cycles, while the resistances of the GPC electrolyte and $\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}$ interface stayed constant during cycling, as seen in Fig. 5. The initial increase of the resistances at the interfaces can probably be attributed to an increase in thickness of the passivating film between the electrodes and the electrolyte.

These results indicate that the formation of passivation layers at the $\text{Li}_x\text{C}_6/\text{GPC}$ and $\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}$ interfaces strongly influences the kinetics of the Li^+ ion insertion into or extraction out of the electrodes, and leads to an initial fading of the capacity of a $\text{Li}_x\text{C}_6/\text{GPC}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell.

4. Conclusions

Results indicate that the kinetic stability of the

$\text{Li}_x\text{Mn}_2\text{O}_4/\text{GPC}$ interface is much better than that of the $\text{Li}_x\text{C}_6/\text{GPC}$ interface during cycling, while the stability of the GPC electrolyte against both electrodes ($\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xC_6) during cycling seems to be excellent. Thus, the GPC electrolyte seems to be a viable electrolyte for solid state lithium-ion batteries.

Acknowledgments

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