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Electrochemical Properties of GeS₂-Based Glass-Polymer Composite Electrolytes for Lithium-Ion Batteries

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ABSTRACT

Electrochemical properties of glass-polymer composite (GPC) electrolytes, consisting of 0.4 $GeS_2 \cdot 0.3$ $Li_2S \cdot 0.3$ LiI glass and $P(EO)_8 \cdot LiN(CF_3SO_2)_2$ polymer, have been investigated using impedance spectroscopy and four-probe dc measurements. Results indicate that the GPC electrolyte with 13 vol % polymer exhibits conductivity of 4.5×10^{-5} Ω^{-1} cm^{-1} at room temperature, and 8×10^{-4} Ω^{-1} cm^{-1} at 80°C. Further, the GPC electrolyte is more stable against Li_1C_6 than against Li. The interfacial resistance of a GPC/Li_1C_6 interface remains constant at 80°C for 250 h. The cycling behavior of a cell consisting of carbon as the negative electrode and $Li_{1.05}Mn_2O_4$ as the positive electrode showed that the capacity decreased from an initial value of 110 to 100 mAh/g after 50 cycles.

Introduction

Lithium rechargeable batteries based on solid polymer electrolytes have been widely investigated for portable electronic and personal communication devices. However, the applications of these batteries seem to be limited by the low lithium-ion conductivity and poor electrochemical stabilities of the polymer electrolytes against Li or intercalation materials at high voltages.[1-3]

Recently, lithium-ion conducting sulfide glasses based upon B_2S_3, P_2S_5, and SiS_2 have exhibited conductivity of 10^{-3} to 10^{-4} Ω^{-1} cm^{-1} at room temperature. However, the problem with glass electrolytes is their lack of mechanical flexibility. To overcome the brittleness, small amounts of conducting polymers were added to the powders of the glassy electrolytes. The mixture of glass and polymer was then heated to a temperature above the glass transition temperature of the polymer so that the voids between the glass particles were filled with the polymer, leading to an improvement in packing density of the glass electrolyte.[4] The addition of a conducting polymer to a glass electrolyte may increase not only the mechanical flexibility, but also the ionic conductivity.

Recent studies[4] indicate that glass-polymer composite (GPC) electrolytes consisting of B_2S_3–based glass and poly(ethylene oxide) (PEO)– based polymers exhibit conductivities of 3×10^{-4} Ω^{-1} cm^{-1} at room temperature, and 1×10^{-3} Ω^{-1} cm^{-1} at 80°C. Furthermore, the lithium-ions transference number of the GPC electrolyte is 0.98, almost twice of that of PEO-based polymer electrolytes. However, to prepare B_2S_3 and a glass electrolyte with a composition of

0.56 $Li_2S \cdot 0.19$ $B_2S_3 \cdot 0.25$ LiI, carbon coated silica tubes must be used because an uncoated silica tube will react with B_2S_3 at elevated temperatures.[5] In addition, a B_2S_3-based glass electrolyte may react with polymer electrolytes at 80°C. Hence, it is necessary to develop new GPC electrolytes which have less reactivity and can be prepared using a simple synthesis procedure.

In this paper, GPC electrolytes based on a newly developed glass, 0.4 $GeS_2 \cdot 0.3$ $Li_2S \cdot 0.3$ LiI, are studied; their electrochemical properties such as ionic conductivity, transference number, and stabilities in contact with Li and Li_xC_6 are investigated as functions of the volume fraction of a polymer electrolyte. Further, the cycling behavior of $Li_xC_6/Li_xMn_2O_4$ cell based on the GPC electrolytes is also examined.

Experimental

Preparation and characterization of the GPC electrolytes, assembly of cells, and cell testing were all performed in a glove box under argon (Vacuum Atmosphere) with residual O_2 and H_2O less than 5 ppm. To prepare glassy GeS_2 (v-GeS_2),[6] stoichiometric amounts of Ge (99.9%, ESPI) and sulfur (99.999%, Alfa) were mixed in a mortar and pestle and the powder mixture was then transferred to a flame-dried bare silica tube. The tube was sealed under vacuum using a gas torch, and then slowly heated in a furnace to 900°C and held for 12 h, followed by quenching in air to room temperature. The obtained v-GeS_2 was homogeneous and yellow in color.[6]

The 0.4 $GeS_2 \cdot 0.3$ $Li_2S \cdot 0.3$ LiI glasses were prepared by mixing GeS_2 powder with appropriate amounts of LiI (99.999%, Aldrich) and Li_2S (99.9%, Cerac) powder in a

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mortar and pestle. The mixture was then transferred to a bare silica tube, vacuum sealed, heated to 750°C, and held for 25 min before being quenched in liquid N_2. The final product was transparent and yellow. The GPC electrolytes were then prepared by mixing and grinding (100-x) vol % (0.4 GeS_2·0.3 Li_2S·0.3 LiI) glass powder an x vol % [P(EO)$_8$·LiN(CF$_3$SO$_2$)$_2$] (x = 7, 13, 25) powder (3M). The powder mixtures were pressed into pellets of 100-200 µm thickness while holding at 80°C for 2 h to ensure that the voids between the glass particles were filled with the polymer.

$Li_{1.05}Mn_2O_4$ was prepared using a solid-state reaction. MnO_2 (Sedema, MMM) and LiOH·H_2O at a mole ratio of 1.05:2 were reacted at 800°C for 20 h and slowly cooled to room temperature at a rate of 2°C/min. A composite positive electrode was prepared by mixing $Li_{1.05}Mn_2O_4$, carbon black (Super P), and GPC electrolyte powder in a weight ratio of 40:10:50. Mesophase carbon fiber (MCF) and GPC electrolyte in a weight ratio of 50:50 were used as the negative electrode. To prepare a GPC/Li_xC_6 half cell, a cell consisting of lithium foil, the carbon electrode, and GPC electrolyte was assembled by laminating and pressing the three layers together. The Li/GPC/C cell was then discharged at a current density of 0.3 mA/cm² until the stoichiometry of the carbon electrode changed to approximately Li_1C_6, i.e., one lithium atom per six carbon atoms. Subsequently, the lithium foil was carefully removed from the cell to obtain a half cell of GPC/Li_1C_6. Two such GPC/Li_1C_6 half cells were then laminated (GPC to GPC) together to form a cell of Li_1C_6/GPC/Li_xC_6 for study of the stability of the GPC/Li_1C_6 interface.

A C/GPC/$Li_{1.05}Mn_2O_4$ cell was assembled by pressing two electrodes and a GPC electrolyte layer into a three-layered pellet at 80°C. The cell was cycled at a rate of 0.3C at 80°C. A potentiostat/galvanostat (EG&G 273A) and a lock-in amplifier (M5120) were used for four-probe impedance and dc polarization measurements.[4] The stability of the GPC electrolytes against Li and Li_xC_6 electrodes was determined from the impedance spectra of the interfaces. The cell design for characterization of transport properties of the GPC electrolytes is described elsewhere.[4] A Toyo battery cycler was used for measuring the cycling behavior of the C/GPC/$Li_{1.05}Mn_2O_4$ cell.

Results and Discussion

Total conductivity.—Figure 1 shows some typical impedance spectra of GPC electrolytes with x = 0, 7, 13, and 25 measured in a four-probe cell. When a current was applied through the counter and working electrodes, the voltages were acquired from the sensing and reference electrodes. Hence, the total resistance and total conductivity of the electrolytes can be determined from these impedance spectra.

Figure 2 shows the temperature dependence of the conductivities of the GPC electrolytes with different volume fractions of the polymer. Note that the conductivities of the GPC with x = 7 are nearly identical to those of x = 0, indicating that the addition of 7 vol % polymer to the glass powder does not affect the conductivity. The GPC consisting of 13 vol % P(EO)$_8$·(CF$_3$SO$_2$)$_2$ and 87 vol % [0.4 GeS_2·0.3 Li_2S·0.3 LiI] glass powder showed higher conductivity and better mechanical integrity and improved flexibility than the ones with x = 0 or 7. Also, the ionic conductivities of the GPC electrolytes with x = 13 ranges from 4.5 × 10⁻⁵ Ω⁻¹ cm⁻¹ at 25°C to 8 × 10⁻⁴ Ω⁻¹ cm⁻¹ at 80°C, because the added polymer filled up the voids in the glass powders. The conductivities of the GPC with x = 25 were smaller than those of the GPC with x = 13, suggesting that too much polymer was added to the glass electrolytes and reduced the total conductivity of the GPC electrolytes.

Lithium-ion transference number (t_{Li}).—When a constant current is applied through the working and counter electrodes in a four-probe cell in a steady-state, only lithium cations can transport through the cell, because electrons are blocked by the PEO electrolyte, and other ionic species are blocked by concentration polarization at elec-
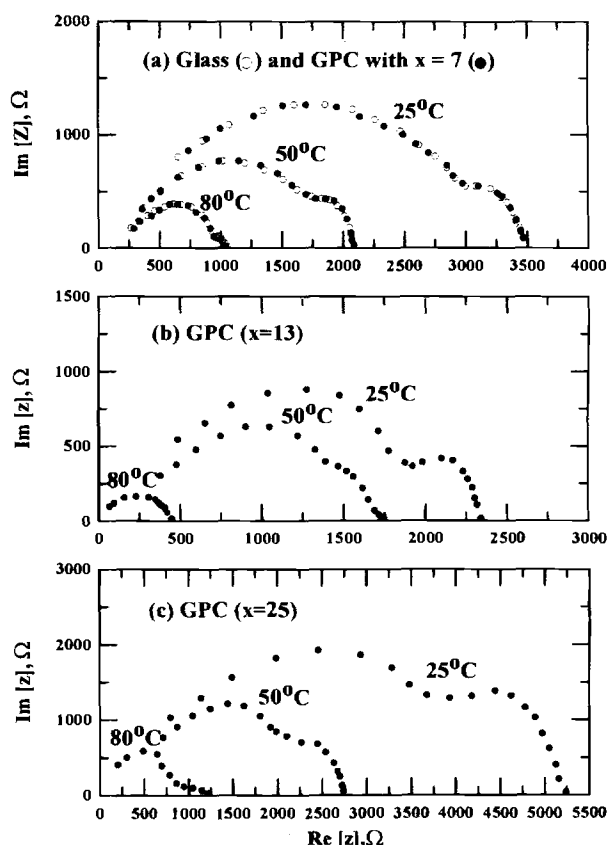

Fig. 1. Typical impedance spectra of (100-x) vol % (0.4 GeS_2·0.3 Li_2S·0.3 LiI) and x vol % [P(EO)$_8$·LiN(CF$_3$SO$_2$)$_2$] with x = 0, 7, 13, and 25 as measured in a four-probe cell.

trolyte-electrode interfaces. Hence, the resistance to the motion of lithium ion in the bulk pellet of the GPC electrolyte can be determined from

$$R_{Li} = V_{steady\ state}/I_{applied}$$

Figure 3 shows the dependence of the observed voltages between the sensing and the reference electrode on the

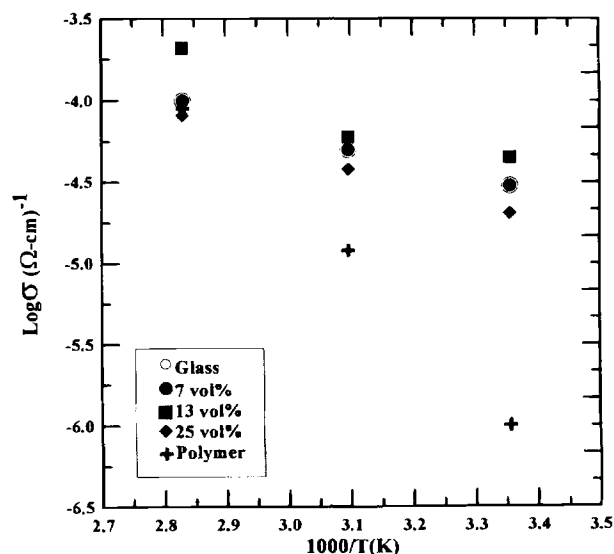**Fig. 2.** Total conductivity of glass (0.4 GeS_2·0.3 Li_2S·0.3 LiI), polymer [P(EO)$_8$·LiN(CF$_3$SO$_2$)$_2$], and GPC electrolytes with 7, 13, and 25 vol % polymer as determined from impedance spectra measured in a four-probe cell.
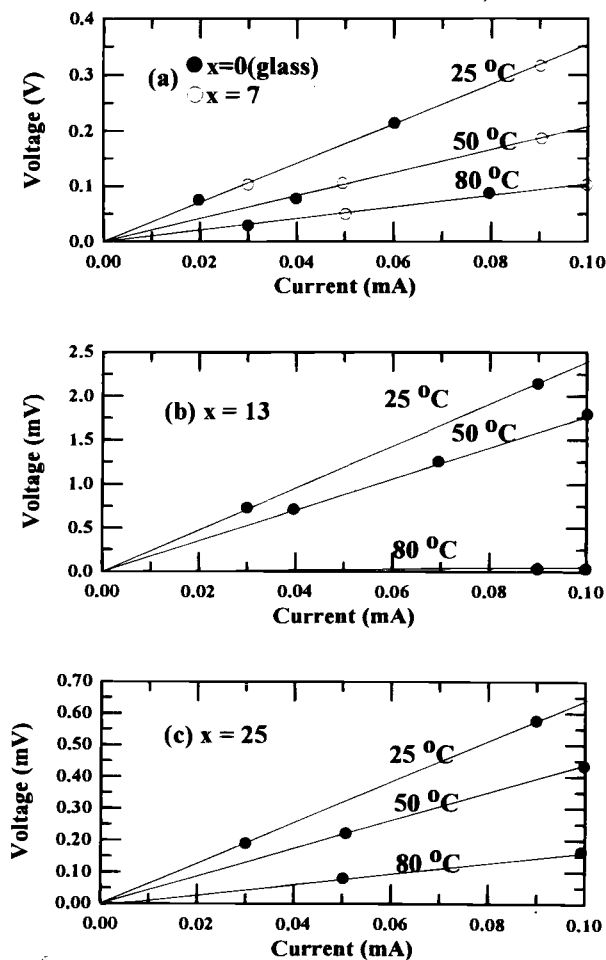
Fig. 3. Current vs. voltage plots from four-probe dc measurements at different temperatures for GPC electrolytes with x = 0, 7, 13, and 25.
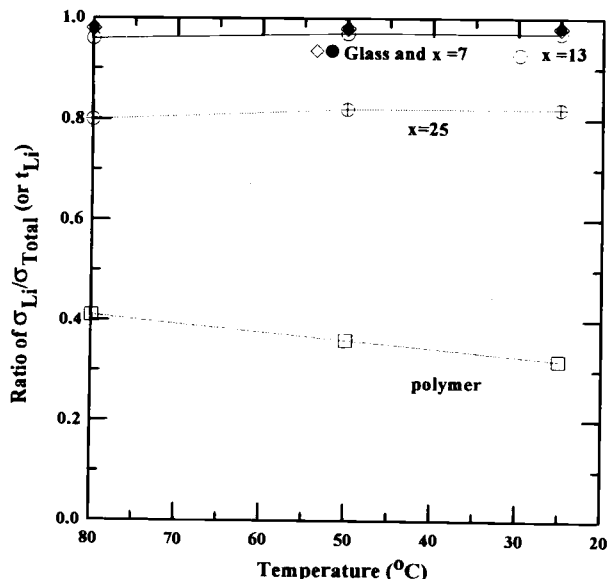
Table I. Total conductivities and ratios of $\sigma_{Li}/\sigma_{total}$ (or t_{Li}) for a glass electrolyte and GPC electrolytes with x = 7, 13, and 25.

Vol % polymer	Temperature (°C)	σ_T (Ω^{-1} cm^{-1})	t_{Li}
0 (glass)	25	3×10^{-5}	0.97
	50	5×10^{-5}	0.97
	80	1×10^{-4}	0.97
7	25	3×10^{-3}	0.97
	50	5×10^{-5}	0.97
	80	1×10^{-4}	0.97
13	25	4.5×10^{-5}	0.97
	50	6×10^{-5}	0.97
	80	8×10^{-4}	0.96
25	25	2×10^{-5}	0.82
	50	3.8×10^{-5}	0.82
	80	2.3×10^{-4}	0.8

where R_{total} is the total bulk resistance of the electrolyte between the reference and sensing electrode as determined from four-probe impedance measurements.

As seen in Fig. 4 and Table I, the calculated ratios of $\sigma_{Li}/\sigma_{total}$ for the pure glassy electrolyte and the GPC electrolyte with $x = 13$ are 0.97 and 0.96, respectively, which are similar to those reported in the literature for the glass electrolytes.[7,8] This indicates that the GPC electrolytes are single Li$^+$-ion conductors. However, upon further addition of polymer into the GPC electrolyte, i.e., when $x = 25$ vol %, ratios of $\sigma_{Li}/\sigma_{total}$ decreased to 0.82, indicating that 25 vol % polymer electrolyte in the glass electrolyte is too much, and disrupted the continuity of the glass phase and reduced the conductivity and lithium-ion transference number of the composite. Summarized in Fig. 5 are lithium-ion conductivities of various GPC electrolytes with different volume fractions of $P(EO)_8 \cdot (CF_3SO_2)_2$ polymer electrolytes.

Interfacial stabilities of the GPC electrolytes.—Because the GPC with $x = 13$ showed the highest lithium conductivities the GPC electrolytes studied, this electrolyte was further studied in terms of interfacial stabilities against Li and Li$_x$C$_6$. Shown in Fig. 6 is the evolution of the impedance spectra symmetric cells, Li/GPC/Li and Li$_1$C$_6$/GPC/Li$_1$C$_6$, and 80°C as a function of time. The resistances of the Li/GPC interface increased from 180 to 330 Ω after 250 h. This is probably due to the formation of passivation layer resulting from a reaction between the GPC and Li during storage at 80°C. In contrast, the resistance of the interface between Li$_1$C$_6$ and GPC remained constant after storage at 80°C for 250 h, indicating good stability of the composite electrolyte against the Li$_1$C$_6$ electrode.
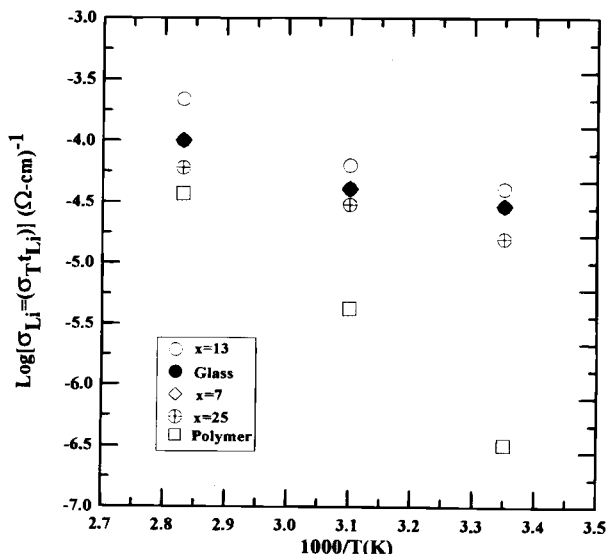
applied current through the working and the counter electrode. The t_{Li} of the electrolytes can then be estimated as

$$t_{Li} \cong \sigma_{Li}/\sigma_{total} = R_{total}/R_{Li}$$

Fig. 4. Ratios of $\sigma_{Li}/\sigma_{total}$ for composites consisting of (100-x) vol % (0.4 GeS$_2$·0.3 Li$_2$S·0.3 LiI) and x vol % [P(EO)$_8$·LiN(CF$_3$SO$_2$)$_2$] with x = 0, 7, 13, and 25.

Fig. 5. Li-ion conductivities of GPC consisting of (100-x) vol % (0.4 GeS$_2$·0.3 Li$_2$S·0.3 LiI) and x vol % [P(EO)$_8$·LiN(CF$_3$SO$_2$)$_2$] with x = 0, 7, 13, and 25.
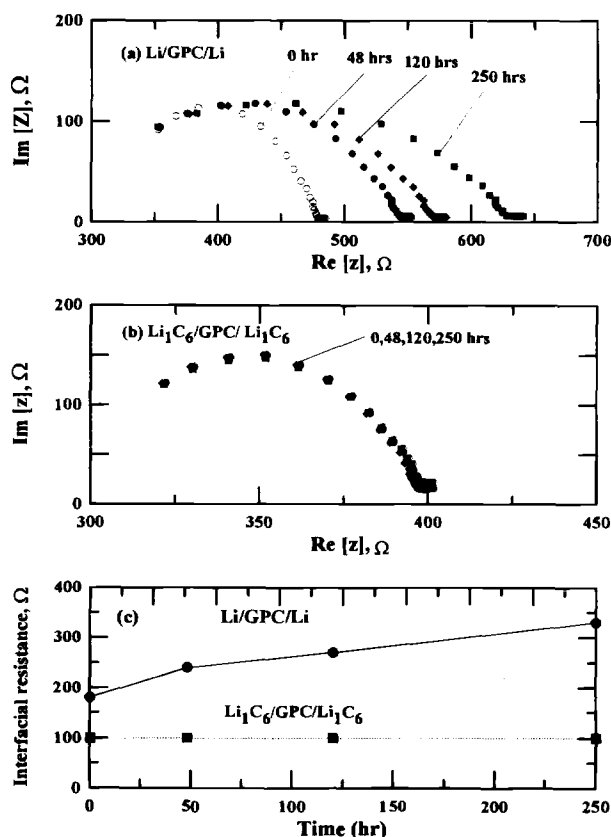
Fig. 6. Evolution of the impedance spectra of symmetrical cells based on GPC electrolytes with $x = 13$ at 80°C: (a) Li/GPC/Li, (b) $Li_2C_6/GPC/Li_1C_6$. Stabilities of the GPC electrolyte during storage at 80°C are shown in (c).

Fig. 7. Cycling curves of a $Li_xC_6/GPC/Li_{1.05}Mn_2O_4$ cell at 80°C with a charge and discharge rate of 0.3C.

Fig. 8. Variation of capacity as a function of cycle number for a C/$Li_{1.05}Mn_2O_4$ cell with liquid electrolytes (EC/DMC + LiPF$_6$) and a C/GPC/$Li_{1.05}Mn_2O_4$ cell. Both cells were cycled at a rate of 0.3C at 80°C with cutoff voltages 4.5 V for charge and 2.5 V for discharge.

Cycling behavior of a $C/Li_{1.05}Mn_2O_4$ cell.—A $C/Li_{1.05}Mn_2O_4$ cell based on a GPC electrolyte with $x = 13$ was cycled at 80°C at a charge and discharge rate of 0.3 C (0.75 mA/cm²). The charge and discharge curves of this cell are shown in Fig. 7. Note that after 50 cycles, the capacity of the cell fell from an initial value of 110 to 100 mAh/g while the cell resistance increased from an initial value of 120 to about 160 Ω. Because both GPC/Li_1C_6 and $GPC/Li_{1.05}Mn_2O_4$ interfaces appear to be stable, the observed capacity fading is due probably to degration of the electrode materials. This speculation is supported further by the data shown in Fig. 8, which indicate that the capacity retention of this solid-state $C/GPC/Li_{1.05}Mn_2O_4$ cell is better than that of a $C/Li_{1.05}Mn_2O_4$ cell using a liquid electrolyte under similar testing conditions at 80°C. The liquid electrolyte consisted of EC and DMC (each 50 vol %) with 1 M LiPF$_6$.

Conclusions

Results indicate that the addition of appropriate amounts of $P(EO)_8 \cdot LiN(CF_3SO_2)_2$ to 0.4 $GeS_2 \cdot 0.3$ $Li_2S \cdot 0.3$ LiI glass powder increased not only the mechanical integrity of the pellet, but also the ionic conductivity. The conductivities of the glass-polymer composite electrolyte containing 13 vol % of PEO vary from 4.5×10^{-5} Ω^{-1} cm^{-1} at room temperature to 8×10^{-4} Ω^{-1} cm^{-1} at 80°C, and the lithium-ion transference number of the GPC electrolyte is ~0.97. In addition, the stability of the GPC electrolyte against Li_1C_6 seems to be sufficient; an all solid-state, $C/GPC/Li_{1.05}Mn_2O_4$, exhibits better cycleability than a $C/Li_{1.05}Mn_2O_4$ cell using a liquid electrolyte.
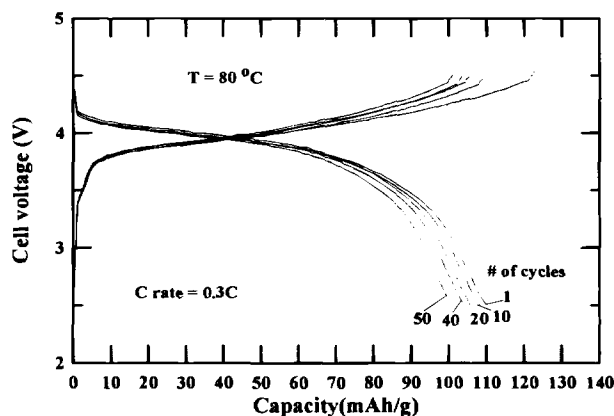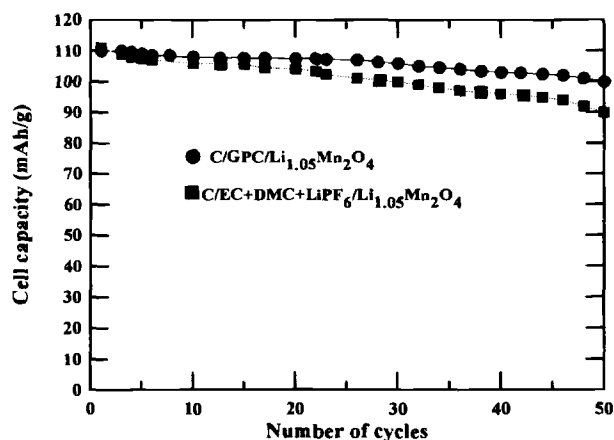
Acknowledgment

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