

Electrochemical characterization of poly(ethylene-*co*-methyl acrylate)-based gel polymer electrolytes for lithium-ion polymer batteries

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Abstract

Gel polymer electrolytes (GPE) composed of poly(ethylene-*co*-methyl acrylate) copolymer, LiBF₄-EC/EMC/PC, and silanized fumed silica are prepared. The ionic conductivity reaches $5.8 \times 10^{-4} \text{ S cm}^{-1}$ in the GPE containing 22% poly(ethylene-*co*-methyl acrylate), 65% LiBF₄-EC/EMC/PC and 13% silanized fumed silica at room temperature. GPEs are free-standing films and are used to prepare thin films for rechargeable lithium-ion polymer cells. Lithium-ion polymer cells, which consist of mesophase carbon fibre anode, poly(ethylene-*co*-methyl acrylate)-based GPE and LiCoO₂ cathode, are assembled, and their charge–discharge cycling characteristics are investigated. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In recent years, there has been an increasing need for rechargeable batteries with high specific energy for portable electronic equipment. As a result, lithium polymer batteries are now being widely studied and developed. These batteries can be produced in a variety of forms. This permits portable batteries of the required shapes to be produced readily, and enables customization of portable powered electronic equipment [1–3]. Conventional poly(ethylene oxide) (PEO)-based solid polymer electrolytes are the most commonly studied, and exhibit conductivities in the range 10^{-8} – $10^{-5} \text{ S cm}^{-1}$ at room temperature, which is not sufficient for practical application at ambient temperature [4]. Further, in order to increase the ionic conductivity by increasing the molecular motion, it is necessary to decrease the glass transition temperature or crystallinity of the polymer. This results in a large reduction in the mechanical properties of the polymer electrolyte. In this respect, most of the recent studies have been directed to the preparation and characterization of gel polymer electrolytes (GPE) which exhibit higher ionic conductivity at ambient temperature. GPEs are

prepared by incorporating liquid electrolytes into a matrix polymer such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC), poly(vinyl pyrrolidone) (PVP) and poly(vinyl sulfone) (PVS) [5–8]. Among these systems, there are some GPEs which exhibit ionic conductivity in excess of $10^{-3} \text{ S cm}^{-1}$, but the mechanical properties of the material are not sufficient to produce thin films, i.e., impregnation of liquid electrolyte into a polar polymer results in softening of the polymer. One way to solve this problem is to use a copolymer as a matrix polymer. In our group, the electrical properties of GPEs based on the poly(acrylonitrile-*co*-methyl methacrylate-*co*-styrene) (PAMS) have been prepared and the cycling performance of Li/GPE/LiMn₂O₄, Li/GPE/LiNi_{0.5}Co_{0.5}O₂ and carbon/GPE/LiCoO₂ cells employing a PAMS-based GPE has been reported [9–11]. These studies have demonstrated that the use of copolymer for GPEs allows optimization of the physico chemical properties such as ionic conductivity, mechanical properties and compatibility with the plasticizing electrolyte solution.

In this work, an investigation is made of the electrical properties of GPEs composed of poly(ethylene-*co*-methyl acrylate) copolymer as a matrix polymer, plasticizing liquid electrolyte solution, and silanized fumed silica. In the copolymer, the ethylene unit is a highly crystalline and non-polar phase, and the methyl acrylate unit is an amorphous and polar phase. Thus, liquid electrolyte is con-

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tained in the amorphous and polar phase to form ion conductive channels, and the crystalline and non-polar phase forms a supporting structural phase. Lithium-ion polymer cells are fabricated and are composed of a mesophase carbon fibre (MCF) anode, a poly(ethylene-co-methyl acrylate)-based GPE, and a lithium-cobalt oxide cathode. The characteristics and electrochemical performance of these lithium-ion polymer cells are presented and discussed.

2. Experimental

2.1. Preparation of GPEs

The matrix polymer for the GPEs was a poly(ethylene-co-methyl acrylate) (hereinafter abbreviated to PEMA) random copolymer with a methyl acrylate content of 29 wt.%. It was purchased from Aldrich Chemical, and purified by successive dissolution in tetrahydrofuran (THF) and precipitation with ethyl alcohol. The purified PEMA was then dried in a vacuum oven for 24 h. GPEs were made from PEMA, plasticizing electrolyte solution, and silanized fumed silica. PEMA was first dissolved in anhydrous THF. After the polymer was completely dissolved, a predetermined amount of liquid electrolyte and silanized fumed silica (Cabot) was added and the solution was further stirred. The organic liquid electrolyte was 1.2 M LiBF_4 in ethylene carbonate (EC)/ethylmethyl carbonate (EMC)/propylene carbonate (PC) (4:3:1 by volume) solution (Mitsubishi Chemical, battery grade). The resulting solution for the GPE was cast with a doctor blade apparatus onto a glass plate, and then left to evaporate the solvent slowly at room temperature. After evaporation of THF, the film was separated from a glass plate. The thickness of the cast film was in the range 40–60 μm . All procedures for preparing the GPEs were carried out in a dry-box filled with argon gas.

2.2. Fabrication of lithium-ion polymer cells

The composite carbon anode was prepared by coating a slurry of mesophase carbon fibre (MCF, Petoca), GPE and super-P carbon on a copper foil with a doctor blade. The composite cathode contained the same GPE and super-P carbon along with the LiCoO_2 (Japan Chemical) cathode material, which was cast on aluminum foil. The thickness of the composite electrodes ranged from 60 to 80 μm , and their active mass loading corresponded to a capacity of about 2.0 mA h cm^{-2} . A lithium-ion polymer cell of cross-sectional area 4 cm^2 was assembled by sandwiching the GPE between the composite carbon anode and composite LiCoO_2 cathode. The cell was then enclosed in a metallized plastic bag and vacuum-sealed to permit testing outside of a dry box. The assembly of all cells was performed in a dry-box filled with argon gas.

2.3. Electrical measurements

The AC impedance measurements were performed by means of Zahner Elektrik IM6 impedance analyzer over a frequency range of 10 Hz to 100 kHz for conductivity measurements of GPEs and from 1 mHz to 100 kHz for interface investigation of lithium-ion polymer cells. Blocking cells with stainless-steel (SS) electrodes were used for conductivity measurements. Cyclic voltammetry experiments were carried out on a SS working electrode with lithium electrodes as the counter and reference electrodes in the potential range -0.5 – 4.3 V vs. Li at a scanning rate of 5 mV s^{-1} . The charge and discharge cycling tests of carbon/GPE/ LiCoO_2 cells were conducted galvanostatically using Toyo battery test equipment (TOSCAT-3000U).

3. Results and discussion

PEMA copolymer consists of a polar unit(methyl acrylate) and a non-polar unit(ethylene). Liquid electrolyte is contained in the polar unit to form the ion conductive paths, and the non-polar unit provides a supporting structural phase. Thus, the capacity to retain electrolyte solution and the mechanical properties of the GPE film are dependent on the ethylene/methyl acrylate composition in the PEMA copolymer. To prepare GPEs with higher uptake of liquid electrolyte, the methyl acrylate composition in PEMA was fixed at 29 wt.% in this study. The polymer electrolyte was prepared by solution casting from a homogeneous mixture which contained 25 wt.% PEMA and 75 wt.% 1.2 M LiBF_4 -EC/EMC/PC.

The AC impedance spectrum of a SS/GPE/SS cell at room temperature is shown in Fig. 1. The plot consists of a spike displaced from the origin, which represents a resistor

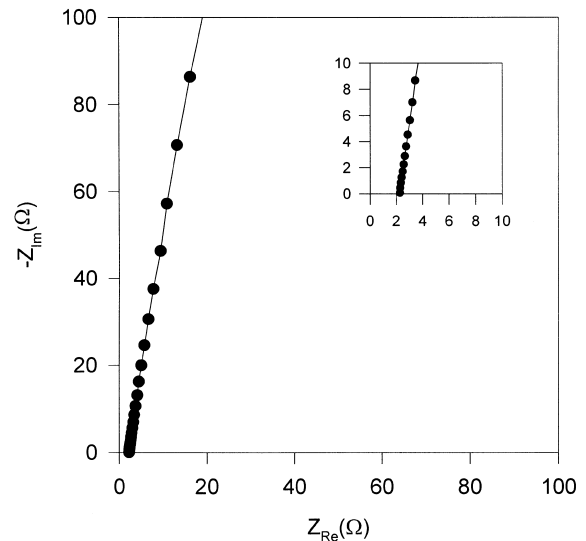


Fig. 1. AC impedance spectrum of SS/GPE/SS cell with GPE of 25 wt.% PEMA and 75 wt.% LiBF_4 -EC/EMC/PC at 25°C.

in series with a capacitor. The intercept (2.3Ω) on the real axis gives the resistance of the GPE. The ionic conductivity was calculated to be $5.5 \times 10^{-4} \text{ S cm}^{-1}$ from the electrolyte resistance with thickness and surface area of GPE film. It was observed, however, that liquid electrolyte incorporated in the matrix polymer slowly exuded due to the poor compatibility between the ethylene unit in the copolymer and aprotic solvents such as EC, EMC and PC. As previously reported [9,12], the addition of fine fumed silica powder is a useful method for increasing the capability to hold liquid electrolyte. To prevent solvent exuding from the GPE film, the silanized fumed silica was added to the previous GPE system. The influence of the silica content on the ionic conductivity is shown in Fig. 2. It is found that the ionic conductivity exhibits a maximum at 11 wt.% silica. An increase in conductivity with addition of silica up to 11 wt.% is related to enhancement of the capability to hold the liquid electrolyte, since silica powder has a high adsorption capability. This enables the plasticizing liquid electrolyte to be loaded into the GPE film. Beyond 11 wt.% silica, the addition of silica powder decreases the ionic conductivity due to the restriction of ionic motion. For the system under study, the optimum silica content is considered to be 9–13 wt.% in terms of both the ionic conductivity and the mechanical properties. For this range of silica content, the GPEs were films of thickness 40–60 μm and line was not exuding of solvent on long storage together with good mechanical strength.

It is well-known that the ionic conductivities of GPEs strongly depend on temperature. The temperature dependence of the ionic conductivity of a GPE containing 22 wt.% PEMA, 65 wt.% $\text{LiBF}_4\text{-EC/EMC/PC}$ and 13 wt.% silica is given in Fig. 3. The ionic conductivity reaches $5.8 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, and remains at a high value ($2.4 \times 10^{-4} \text{ S cm}^{-1}$) even at -15°C . This

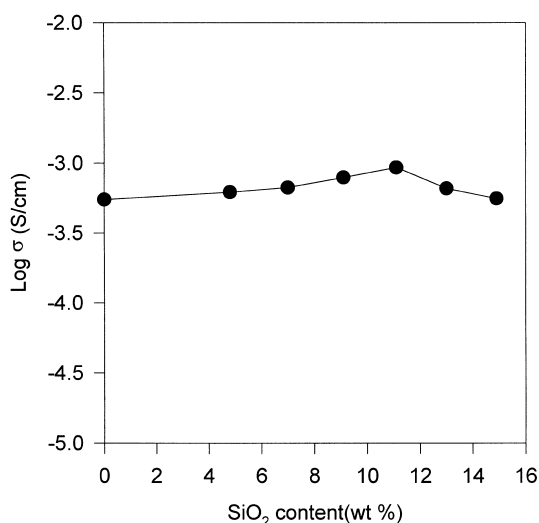


Fig. 2. Ionic conductivities of PEMA-based GPEs as function of SiO_2 content.

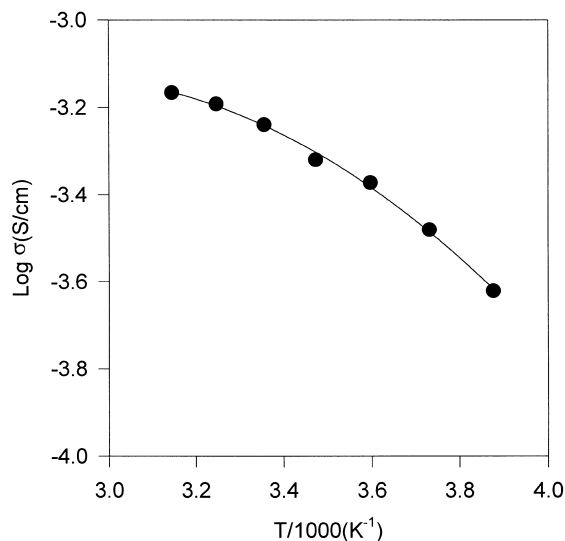


Fig. 3. Temperature dependence of ionic conductivity for GPE of 22 wt.% PEMA, 65 wt.% $\text{LiBF}_4\text{-EC/EMC/PC}$ and 13 wt.% SiO_2 .

performance at low temperature is due to the use of a selected ternary solvent mixture (EC/EMC/PC) with a low viscosity, a high dielectric constant and, above all, a low freezing point.

In order to investigate the cycling reversibility of the GPE, cyclic voltammetric measurements using a three-electrode cell were performed. The cyclic voltammograms for a Li/GPE/SS cell are given in Fig. 4. On scanning the electrode in a negative direction, a cathodic peak is observed at about -0.475 V , which corresponds to the plating of lithium on to the SS electrode. On the reverse scan, stripping of lithium is observed at about 0.376 V . The voltammograms ascribed to lithium deposition/dis-

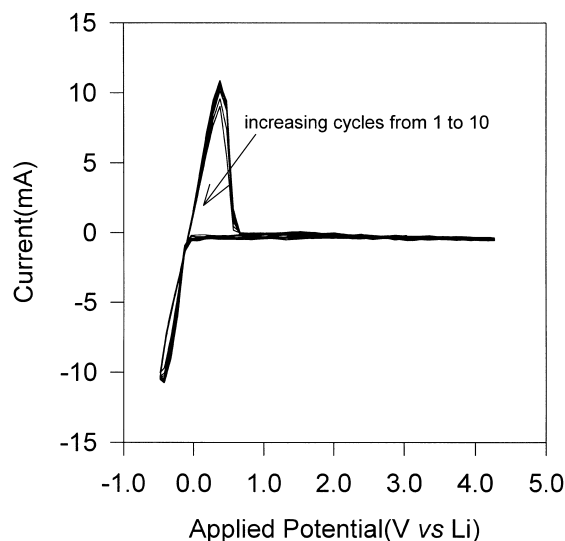


Fig. 4. Cyclic voltammograms of Li/GPE/SS cell at 25°C (scan rate: 5 mV s^{-1}), where SPE consists of PEMA (22 wt.%), $\text{LiBF}_4\text{-EC/EMC/PC}$ (65 wt.%) and SiO_2 (13 wt.%).

solution are highly reversible, because the peak currents remain fairly constant with repeated cycling. On sweeping the electrode to 4.3 V, there are no additional oxidation peaks related to the decomposition of the GPE, which means that the GPE system is electrochemically stable up to at least 4.3 V vs. Li.

In order to evaluate the electrochemical performance of a lithium-ion polymer cell using the GPE, a carbon/GPE/LiCoO₂ cell was fabricated with a GPE which contained 22 wt.% PEMA, 65 wt.% LiBF₄-EC/EMC/PC and 13 wt.% fumed silica. The assembled cell was subjected to cycle tests in the following order: preconditioning with a cut-off voltage of 4.2 V for the upper limit and 2.7 V for the lower limit at the C/20 rate (0.1 mA cm⁻²) for the first cycle, and the C/4 rate (0.5 mA cm⁻²) in subsequent cycles. A preconditioning charge–discharge cycle of a carbon/GPE/LiCoO₂ cell at the C/20 rate is shown in Fig. 5. The data show well-defined charge–discharge voltage profiles, which indicates a reversible cycling process. This cell delivered a discharge capacity of 126 mA h g⁻¹ for an active LiCoO₂ material in the composite cathode. The small voltage drop in passing from charge to discharge confirms the low internal resistance of the lithium-ion polymer cell. The coulombic efficiency in the preconditioning cycle is calculated to be 81%. The large irreversible capacity observed in this cycle is caused by the formation of a passivating film on the surface of the carbon electrode due to the decomposition of electrolyte, as reported previously by other authors [13,14]. The process of carbon passivation during the initial cycling is referred to as the ‘formation period’. This passivation film can prevent the electrolyte from further reduction by the active lithium, and thus limits the degradation of electrolytes.

After the preconditioning cycle, the cell was charged at a current density of 0.5 mA cm⁻² up to a target voltage of 4.2 V. This was followed by a constant–voltage charge

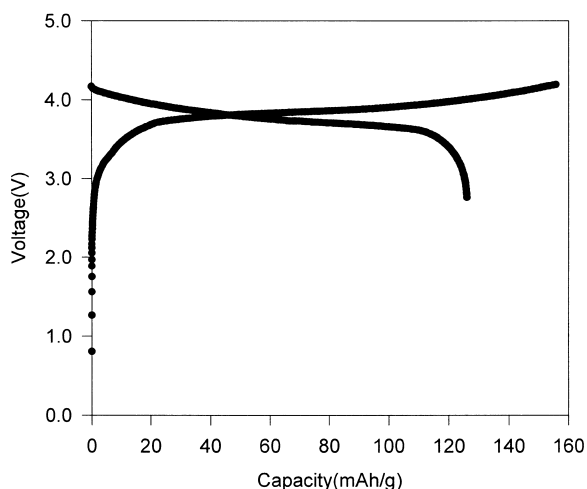


Fig. 5. First preconditioning cycle of lithium-ion polymer cell with GPE of 22 wt.% PEMA, 65 wt.% LiBF₄-EC/EMC/PC and 13 wt.% SiO₂.

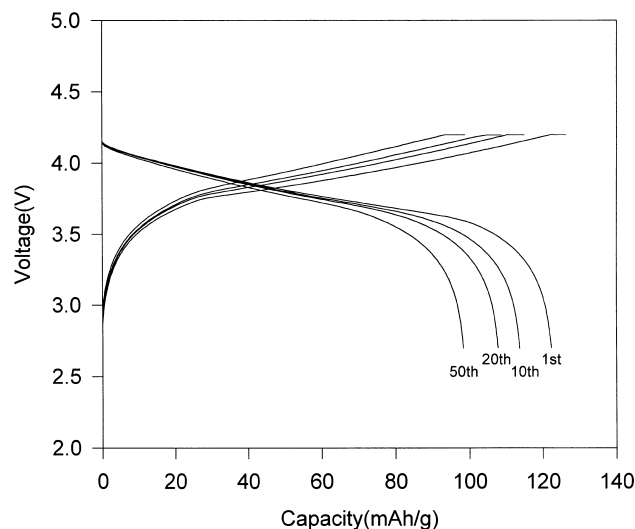


Fig. 6. Charge and discharge curves of lithium-ion polymer cell with repeated cycles at current density of 0.5 mA cm⁻² (C/4 rate).

with a decline in current until the final value has reached 20% of the charging current (i.e., 0.1 mA cm⁻²). It was discharged to a cut-off voltage of 2.7 V at the same current

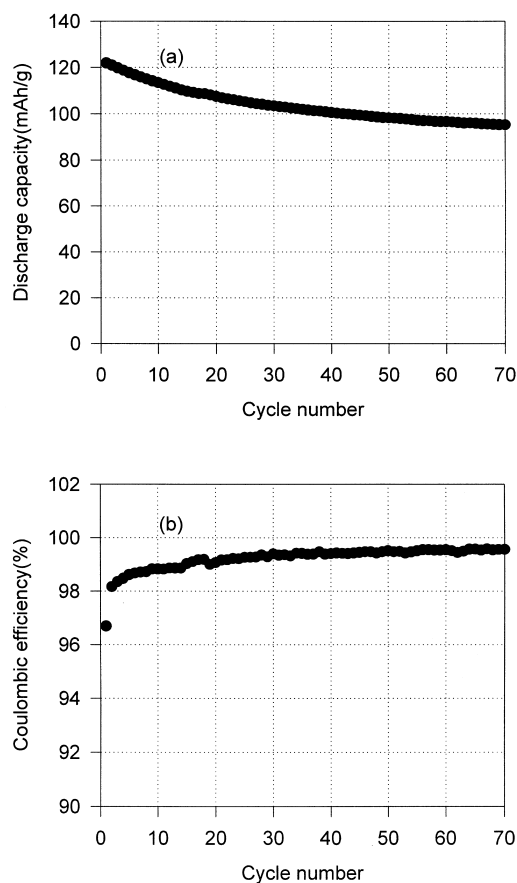


Fig. 7. Discharge capacity and coulombic efficiency of lithium-ion polymer cell as a function of cycle number at C/4 rate: (a) discharge capacity vs. cycle number; (b) coulombic efficiency vs. cycle number.

density. The charge–discharge curves for the 1st, 10th, 20th and 50th cycle of a carbon/GPE/LiCoO₂ cell are given in Fig. 6. The discharge capacity and coulombic efficiency as a function of cycle number is presented in Fig. 7. The discharge capacity of the carbon/GPE/LiCoO₂ cell declines from an initial value of 122 to 95 mA h g⁻¹ after 70 cycles. Decline in the capacity is probably due to the deterioration of the composite electrode/GPE interface, which gradually increases the cell internal resistance during the cycling. It is found that the coulombic efficiency steadily increases with cycle number; it reaches a value of 99.6% at the 70th cycle. A coulombic efficiency of less than 100% is probably associated with the oxidation of the solvent. Thus, the proper selection of solvent and solute in terms of stability against oxidation is necessary to achieve better cycling characteristics.

The AC impedance technique can provide useful information on the charge transfer and diffusion of lithium ions in lithium-ion polymer cells. The AC impedance spectra of a carbon/GPE/LiCoO₂ cell in a fully discharged state is shown in Fig. 8. For the freshly made cell, only one small arc appears. Thus, the equivalent circuit comprises the electrolyte resistance and the interface resistance. After the first preconditioning cycle, the spectrum displays two arcs. The first one is observed at middle frequency and can be associated with an ionically conducting surface layer which grows on the electrode. The low-frequency semicircle is

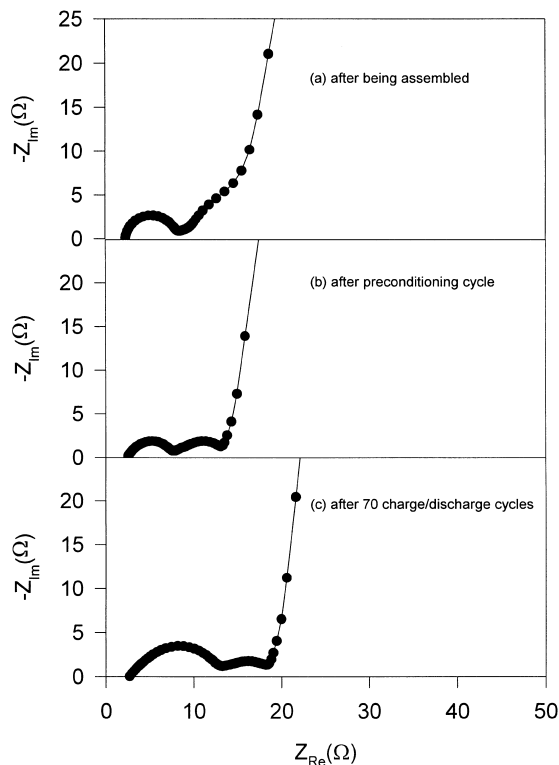


Fig. 8. AC impedance spectra of lithium-ion polymer cell at fully discharged state: (a) after assembly; (b) after preconditioning cycle; (c) after 70 cycles.

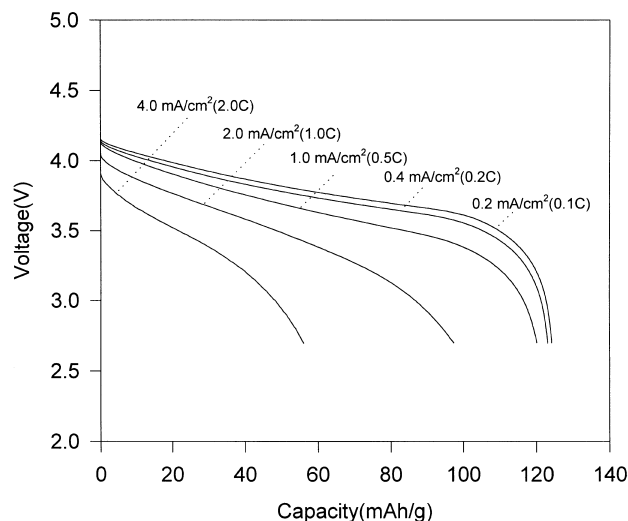


Fig. 9. Discharge profiles of lithium-ion polymer cell at different current rates. Charge rate is 0.2 C with 4.2 V cut-off.

related to a charge transfer between the surface layer and the electrode. This presumption was confirmed by the fact, that a low frequency semicircle is observed after the preconditioning cycle. This behaviour can be ascribed to an initial poor interfacial contact between the GPE and the composite electrodes before cycling, which means that current flow is necessary to activate the GPE/electrode interface, as previously reported for a Li/polymer electrolyte/LiV₃O₈ cell or Li/GPE/carbon cell [15,16]. The total interfacial resistance is greater than the electrolyte resistance, and it is thus of crucial importance to minimize these resistances for the practical applications. After 70 cycles, the middle-frequency semicircle is significantly increased, while the charge transfer resistance observed at low frequency remains unchanged. This would indicate formation of an ionically conducting surface layer at the electrode surface, which is usually caused by the decomposition of electrolyte solution, when the cell is successively charged and discharged. An increase in electrode resistance will cause a high cell polarization, which gives rise to incomplete charging and, therefore, apparent capacity losses.

The rate capability of a carbon/GPE/LiCoO₂ cell was evaluated. The discharge curves obtained at different current rates are given in Fig. 9. The cell delivered a discharge capacity of 124 mA h g⁻¹ at the C/10 rate. The discharge capacity slowly decreases with current rate, which is due to polarization. A useful capacity of 120 mA h g⁻¹ was obtained at the C/2 rate, which was 97% of the discharge capacity at the C/10 rate. The discharge capacity is found, however, to drop abruptly to 56 mA h g⁻¹ at the 2C rate. The reduced capacity in the carbon/GPE/LiCoO₂ cell at high rate may be primarily related to the lower diffusion rate of lithium ions in the GPE. Further research is being conducted in the author's laboratory to improve the high-rate performance of the lithium-ion poly-

mer cells by, e.g., incorporation of highly conductive liquid electrolyte into the PEMA matrix, improvements in the morphology of composite electrodes and optimization of the component ratio in the composite electrodes.

4. Conclusions

GPEs composed of PEMA, $\text{LiBF}_4\text{-EC/EMC/PC}$, and silanized fumed silica have been prepared. The ionic conductivity reaches $5.8 \times 10^{-4} \text{ S cm}^{-1}$ in a GPE which contains 22 wt.% PEMA, 65 wt.% $\text{LiBF}_4\text{-EC/EMC/PC}$ and 13 wt.% silanized fumed silica at room temperature to give free-standing films sufficient to prepare thin film ($\sim 40 \mu\text{m}$) for rechargeable lithium-ion polymer cells. Lithium-ion polymer cells which consisted of a MCF anode, a PEMA-based GPE and a LiCoO_2 cathode gave a discharge capacity of 126 mA h g^{-1} based on LiCoO_2 cathode material. With repeated charge–discharge cycling at a current density of 0.5 mA cm^{-2} , the cell maintained 78% of the initial capacity after 70 cycles. The cell yields a discharge capacity of 56 mA h g^{-1} at the 2C rate. Further improvements in cycle-life and high rate performance are essential for portable electronics applications.

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