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Gel-coated membranes for lithium-ion polymer batteries

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Abstract

A membrane-supported gel polymer electrolyte for a lithium-ion polymer battery was prepared and characterized. This electrolyte was prepared by coating a gel polymer electrolyte onto a porous polyethylene membrane. The gel-coated membrane electrolytes exhibited a high ionic conductivity, and excellent mechanical and good adhesive properties. The gel polymer electrolyte coated on both sides of the membrane was demonstrated to encapsulate organic solvent within the porous membrane. With these gel-coated membrane electrolytes, lithium-ion polymer cells composed of a carbon anode and a $LiCoO_2$ cathode were assembled, and their cycling performances were evaluated. These lithium-ion polymer cells exhibited electrochemical performances similar to regular lithium-ion batteries with liquid electrolyte.

Keywords: Cycling performance; Gel-coated membrane; Lithium-ion polymer battery; Polymer electrolyte; Porous membrane

1. Introduction

In recent years, there has been an increasing need for high energy density rechargeable batteries for portable electronic equipment. Among them, lithium polymer batteries are now being widely studied and developed, because they can be produced in a variety of forms, thus permitting portable batteries of the required shapes to be produced readily, and enabling customization of portable power driven electronic equipment to be produced [1–3]. Conventional poly(ethylene oxide) (PEO)-based solid polymer electrolytes are the most commonly studied, and exhibit conductivities ranging from 10^{-8} to 10^{-5} S/cm at room temperature, which is not sufficient for practical applications 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, resulting in a large reduction in the mechanical properties of the polymer electrolyte. In this respect, most of the recent research has been directed

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towards the preparation and characterization of gel polymer electrolytes (GPEs) which exhibit higher ionic conductivity at ambient temperature. Gel polymer electrolytes are prepared by incorporating an organic liquid electrolyte into matrix polymers such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinyl pyrrolidone) (PVP), poly(vinyl sulfone) (PVS) and poly(acrylonitrile-co-methyl methacrylate-co-styrene) (PAMS) [5–11]. Among these systems, there are some GPEs that exhibit ionic conductivity in excess of 10^{-3} S/cm at room temperature, but their mechanical properties are not sufficient to produce thin films, because the impregnation of a liquid electrolyte into a polar polymer results in softening of the polymer. One of the ways to solve this problem is to use a mechanical support such as porous polyolefin membranes to prepare the gel polymer electrolytes. In previous works, poly(ethylene glycol) diacrylate (PEGDA)-based electrolyte solution was impregnated into porous polyolefin membranes and polymerized to form a solid polymer electrolyte [12]. Such membrane-supported polymer electrolytes show excellent mechanical strength for the fabrication of lithium polymer batteries.

With the aim of developing highly conductive polymer electrolytes with sufficient mechanical strength for preparing thin films, we tried to coat gel polymer electrolytes prepared with PAMS onto a microporous polyethylene (PE) membrane and investigate the electrochemical properties of these gel-coated membrane (GCM) electrolytes. A porous PE separator is used to give mechanical integrity and structural rigidity to the electrolyte system, while the gel polymer electrolyte coated on both sides of the membrane is adapted to encapsulate organic solvent within the porous membrane and to further assist in adhering the electrodes to the PE separator. With these GCM electrolytes, we fabricated lithium-ion polymer cells composed of a mesophase carbon fiber (MCF) anode and a lithium–cobalt oxide cathode. The characteristics and electrochemical performance of these lithium-ion polymer cells are presented and discussed. This study is an extension of the work we have previously carried out on gel polymer electrolytes based on PAMS [11,13].

2. Experimental

2.1. Polymer synthesis

PAMS was synthesized via emulsion polymerization with distilled water at 60°C in a glass reactor equipped with a nitrogen inlet, a reflux condenser, an additional funnel and a mechanical stirrer. The molar ratio of co-monomers in the reaction feed was varied with a total monomer concentration of 1 mol/l. Potassium persulfate ($K_2S_2O_8$) was used as a free-radical water-soluble initiator, and sodium lauryl sulfate was used as an emulsifier. The polymerization was continued for 6 h with vigorous agitation. The polymer was isolated by filtration and washed successively with distilled water at 80°C to remove any impurities such as residual monomers and initiator. The product was then dried in a vacuum oven at 100°C for 24 h. White powder was obtained as the final product. The synthesized PAMS will be designated PAMS ($x/y/z$) in this work, where x, y and z indicate the mol% of AN, MMA and ST units in the terpolymer, respectively.

2.2. Characterization

^{1}H-NMR spectra were obtained in DMSO-d_6 solvent on a Bruker-DRX-400 NMR spectrometer with tetramethylsilane (TMS) as an internal standard reference. Gel permeation chromatography (GPC) measurements were carried out using a Waters CV-150 instrument equipped with three μ-Styragel columns (10^3, 10^4, 10^5 Å) and the system was calibrated with monodisperse polystyrene standards in THF. Differential scanning calorimetry (DSC) thermal analysis was carried out to measure the glass transition temperatures with a heating rate of 10°C/min from −100 to 200°C. The morphology of the microporous PE membrane was examined using a scanning electron microscope (Hitachi, S 4500II).

2.3. Preparation of gel-coated membranes

PAMS was first dissolved in an anhydrous liquid electrolyte. The organic liquid electrolyte was 1.0 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 by volume, Samsung General Chemical Co., battery grade). The amount of PAMS was 5 wt% based on the total weight of the gel electrolyte solution consisting of PAMS and liquid electrolyte. A porous PE separator (Asahi Kasei, thickness 25 μm, porosity 40%) was then immersed in the gel electrolyte solution at 60°C. The membrane was taken out and slowly cooled to room temperature. During cooling, the impregnated material is physically crosslinked and the coated solution is gelled to form an ionic conductive layer. The thickness of the gel-coated membrane was 30–35 μm, and the amount of gel electrolyte consisting of PAMS and liquid electrolyte in the gel-coated membrane was about 85 wt%. All procedures for preparing the gel-coated membrane were carried out in a dry box filled with argon gas (99.999%).

2.4. Fabrication of lithium-ion polymer cells

The carbon anode was prepared by coating a slurry of mesophase carbon fiber (MCF, Petoca), poly(vinylidene fluoride) (PVdF) and super-P carbon onto a copper foil with a doctor blade. The cathode slurry containing the same binder (PVdF) and super-P carbon along with $LiCoO_2$ (Japan Chemical) cathode material was cast on aluminum foil. The thickness of the electrodes ranged from 100 to 120 μm, and their active mass loading corresponded to a capacity of about 3.6 mAh/cm^2. The lithium-ion polymer cell (active planar area 20 cm^2) was assembled by sandwiching the gel-coated membrane electrolyte between the MCF anode and $LiCoO_2$ cathode, as illustrated in Fig. 1. The cell was then enclosed in a metallized plastic bag and vacuum sealed in order to permit testing outside of a dry box. All assemblies of the cell were carried out in a dry box filled with argon gas.

2.5. Electrical measurements

The gel-coated membrane electrolyte was cut into 4 cm^2 squares and sandwiched between two stainless steel (SS) electrodes (SS/PAMS-GCM/SS cell) for conductivity measurements. In order to investigate the interfacial phenomena at the lithium electrode/GCM electrolyte interface, this sample was also sandwiched between two lithium electrodes (Cyprus Foote Mineral Co., 50 μm thick). The a.c. impedance measurement was performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range from 10 Hz to 100 kHz for conductivity measurements of the GCM electrolytes and from 1 mHz to 100 kHz for interface investigation of Li/PAMS-GCM/Li cells. The electrochemical stability window of the gel-coated membrane electrolyte was measured by linear sweep voltammetry at a scanning rate of 0.5 mV/s. Charge and discharge cycling tests of the MCF/PAMS-GCM/$LiCoO_2$ cells were conducted galvanostatically using Toyo battery test equipment (TOSCAT-3000U).

3. Results and discussion

The molar composition of PAMS was determined from the ^{1}H-NMR spectrum, as described in previous work [11]. The calculated molar compositions of the synthesized PAMS are summarized in Table 1. The average molecular weights and glass transition

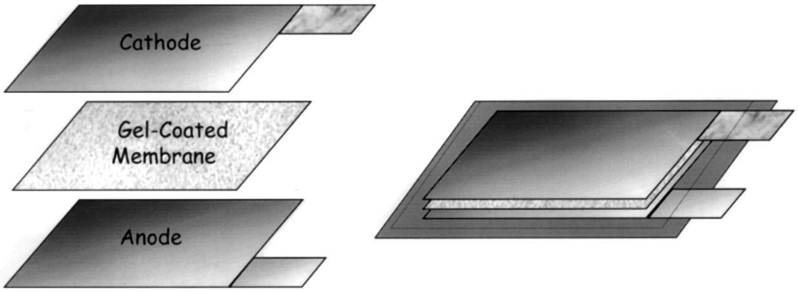


Fig. 1. Schematic diagram of the lithium-ion polymer cell.

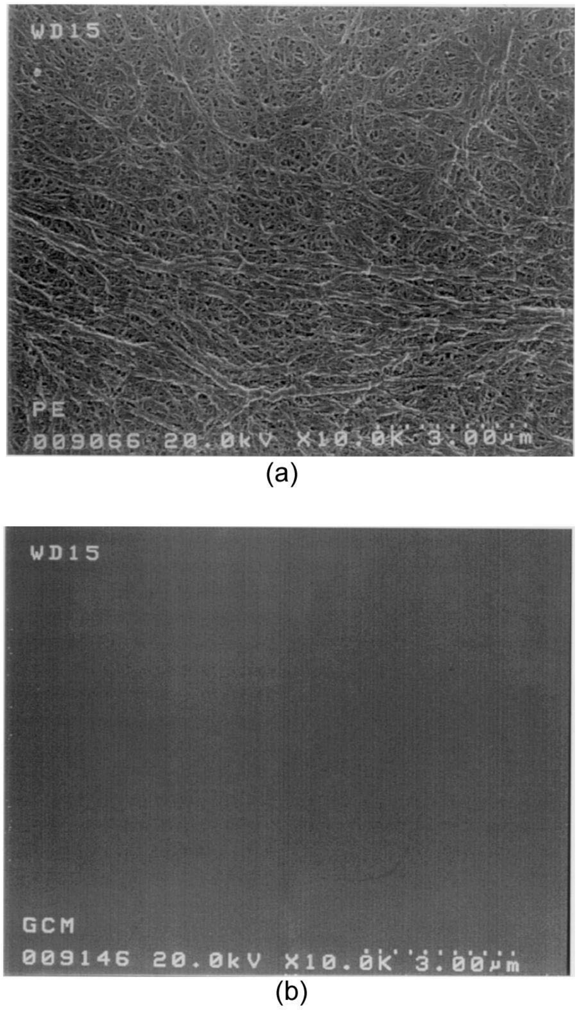
Table 1
Molar composition, average molecular weight and glass transition temperature of PAMS

Polymer	Molar composition (AN/MMA/ST)	Molecular weight		T_g (°C)
		M_n	M_w	
PAMS (59/31/10)	59/31/10	1 081 000	2 319 000	101.3
PAMS (59/12/29)	59/12/29	1 209 000	2 581 000	98.4
PAMS (32/31/37)	32/31/37	1 179 000	2 454 000	102.1

temperatures of PAMS terpolymers are also given in Table 1. The measured molecular weights are very high, and the polydispersity indexes are in the range 2.08–2.15. Only one glass transition for each PAMS was observed in the temperature range 98–102°C, which can be thought of as the arithmetic mean of the glass transition temperatures for the corresponding homopolymers.

Fig. 2 shows a typical scanning electron micrograph of the porous PE membrane used in this study. This membrane shows a uniform submicron pore structure. It has a nominal thickness of 25 μm and its porosity is 40%. When the PAMS-based gel is coated onto the membrane, the pores of the membrane become fully covered by the gel polymer electrolyte. The PAMS gel-coated membranes revealed a smooth pore-free morphology with a thickness of about 30–35 μm. Compared to the typical thickness of 50–200 μm for conventional gel polymer electrolytes in lithium-ion polymer cells [14,15], the thin GCM electrolyte is expected to increase the energy density of the lithium-ion polymer battery. The mechanical strength of the PAMS gel-coated membrane electrolyte was of the same order as that of the PE membrane itself.

Fig. 3 shows a typical a.c. impedance spectrum of SS/PAMS-GCM/SS at room temperature. The matrix polymer for preparing GCM was PAMS (59/31/10). The intercept on the real axis gives the electrolyte resistance. The ionic conductivity was estimated to be 1.1×10^{-3} S/cm from the bulk resistance with the thickness and surface area of the GCM electrolyte. Table 2 lists the ionic conductivity obtained from a.c. impedance spectra for the PAMS-GCM prepared with PAMS having different molar compositions. It was found that the ionic conductivity is dependent on the molar composition of PAMS in the GCM, which may be due to the ability of PAMS to take up electrolyte. The methyl methacrylate unit is able to trap a large amount of organic solvent due to the good compatibility between the large side functional group $-COOCH_3$ and carbon-



(a)
(b)

Fig. 2. Scanning electron micrograph of a microporous PE membrane.

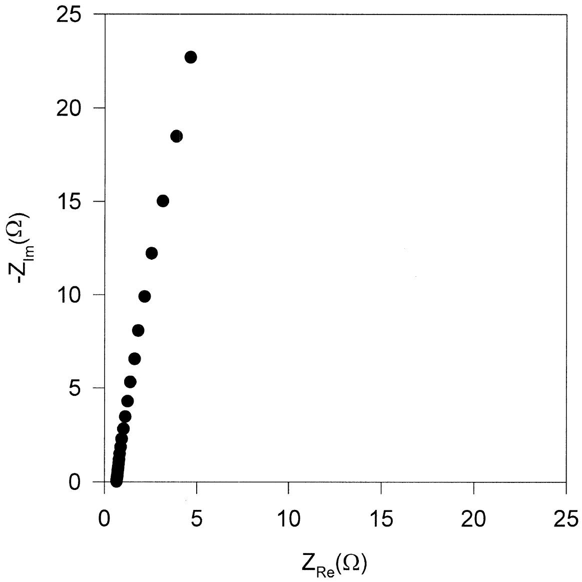


Fig. 3. Typical a.c. impedance spectrum of a PAMS (59/31/10)-based gel-coated membrane electrolyte at room temperature.

Table 2
Ionic conductivity and amount of liquid electrolyte uptake by PAMS-GCM

PAMS in GCM	Ionic conductivity (S/cm)	Wt% of liquid electrolyte
PAMS (59/31/10)	1.1×10^{-3}	85
PAMS (59/12/29)	1.0×10^{-3}	84
PAMS (32/31/37)	8.6×10^{-4}	81
Without PAMS	5.9×10^{-4}	54

ate-based organic solvents, such as EC, DMC and EMC, in the liquid electrolyte. On the other hand, the styrene unit in PAMS has poor compatibility with organic solvents from thermodynamic considerations [16]. The highest conductivity is thus found for PAMS-GCM using PAMS (59/31/10) as matrix polymer. For the PE separator system without the PAMS-gel polymer electrolyte, the amount of liquid electrolyte encapsulated in the membrane is low compared with PAMS-GCM. In order to investigate solvent exudation upon long storage in PAMS-based GCM, the bulk resistance of GCM was measured as a function of storage time in the sealed cells. Fig. 4 illustrates the time dependence of the ionic conductivity for GCM prepared with different PAMS. It can clearly be seen that the ion conduction behavior with time depends on the composition of PAMS. The difference in the ionic conduction behavior with time is believed to be due to the change of the quantity of electrolyte in the gel-coated membrane, which results from solvent leakage. Since the capacity of electrolyte uptake for PAMS (32/31/37) is relatively low, the solvent moves to the electrode surface. The consequences are a loss of liquid electrolyte encapsulated in the porous membrane, and a continuous decrease in the ionic conductivity. After a.c. impedance measurements, liquid electrolyte exuding from the gel-coated membrane was observed in the cell. The ionic conductivity of GCM with PAMS (59/31/10) remains nearly constant over the same period of time, which may be due to the strong attractive forces between PAMS and the electrolyte solution. From these results, the capacity to retain the electrolyte solution in the porous membrane is found to be strongly dependent on the molar composition of the polymer coated onto the porous membrane. In further discussions, the molar composition of PAMS will thus be restricted to 59/31/10.

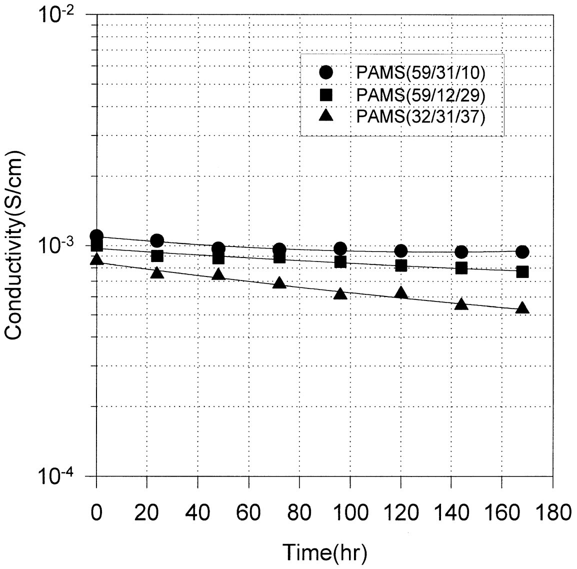


Fig. 4. Time evolution of the bulk resistance for PAMS-based GCM at 25°C.

We investigated the interfacial behavior of a lithium electrode in contact with the PAMS-based GCM electrolyte. Fig. 5 shows the time evolution of the a.c. impedance spectrum of a Li/PAMS-GCM/Li

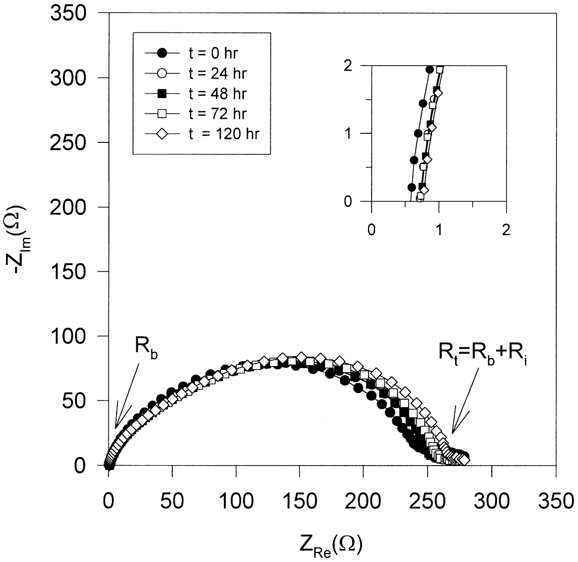


Fig. 5. A.c. impedance spectra of a Li/PAMS (59/31/10)-GCM/ Li cell as a function of storage time at 25°C.

cell under open-circuit potential conditions at 25°C. The bulk resistance (R_b) of GCM is obtained from the intercept on the real-axis at high frequency, and the interfacial resistance (R_i) is calculated from the difference between the intercept (R_t) at low frequency and R_b. It is found that the resistance of the GCM electrolyte maintains a constant value irrespective of time. However, the interfacial resistance showed a slight increase with time and reached a steady-state value after 120 h. This phenomenon reveals that the lithium electrode is passivated in a similar way as shown in other gel polymer electrolyte systems [17–19]. Passivation is known to be caused by reaction between aprotic solvents and lithium electrodes [20–22]. It should be noted that the initial value of the interfacial resistance is high compared with those of other gel polymer electrolyte systems, and the difference in the interfacial resistance at the initial and steady state is small. This means that most of the lithium electrode is passivated at an early stage, and there is no subsequent flow of corrosive solvents to the lithium surface.

For a lithium-ion polymer battery, the cell potential can approach 4.5 V vs. Li/Li^+, implying that the gel polymer electrolyte should be electrochemically stable up to at least 4.5 V. The electrochemical stability of PAMS-based GCM was evaluated by linear sweep voltammetric measurements. Experiments were performed by applying an anodic voltage to a cell composed of a PAMS-GCM sandwiched between a lithium electrode and an inert SS electrode. The voltage was swept from the open-circuit potential (3.3 V) of the cell towards more anodic values until a large current due to electrolyte decomposition at the inert electrode interface was observed. The decomposition voltage limit was defined as the potential at which a rapid rise in current was observed and continued to increase as the potential was swept, since the onset of the current flow may be associated with the decomposition of the electrolyte. Fig. 6 shows a typical linear sweep voltammetry curve of the cell prepared with PAMS (59/31/10)-based GCM. As can be seen, the decomposition voltage was found to be sufficiently high, at +5.0 V, which is acceptable for high voltage cathode materials such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. The electrochemical stability of PAMS-GCM was observed not to be substantially influenced by the molar composition of PAMS.

In order to evaluate the electrochemical performance of a lithium-ion polymer cell using the PAMS gel-coated membrane, a MCF/PAMS-GCM/$LiCoO_2$ cell was fabricated. The assembled cell was subjected to cycle tests in the following order: preconditioning with cut-off voltages of 4.2 V for the upper limit

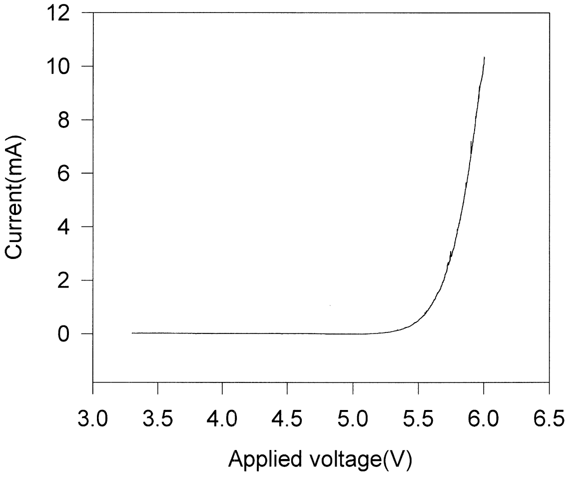


Fig. 6. Current–voltage curve of a Li/PAMS (59/31/10)-GCM/ SS cell at 25°C (sweep rate 0.5 mV/s).

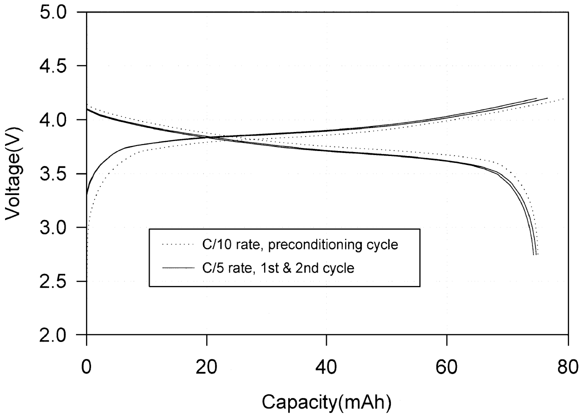


Fig. 7. Charge–discharge curves for a MCF/PAMS-GCM/$LiCoO_2$ cell.

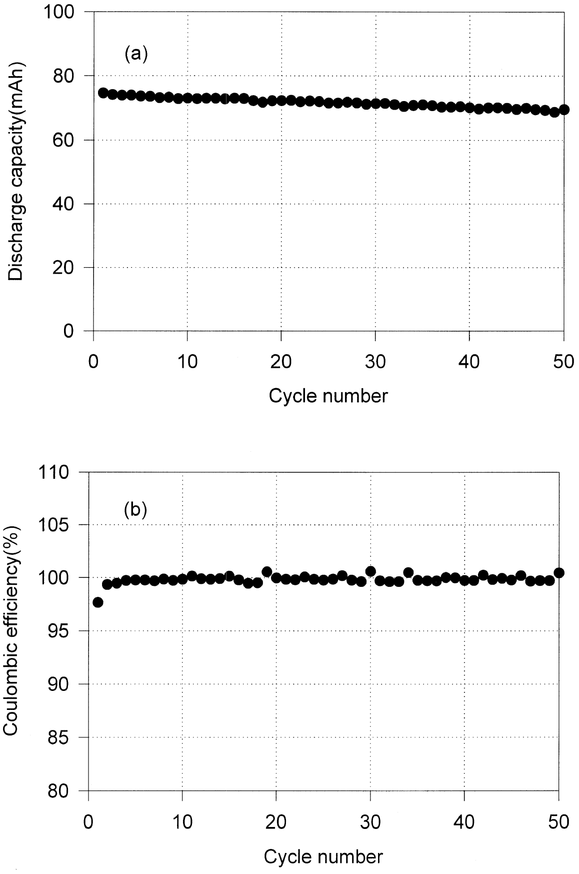


Fig. 8. Discharge capacity and coulombic efficiency of a MCF/PAMS-GCM/$LiCoO_2$ cell as a function of cycle number at $C/5$ rate. (a) Discharge capacity vs. cycle number; (b) coulombic efficiency vs. cycle number.

and 2.75 V for the lower limit at $C/10$ rate (7.2 mA) for the first cycle and subsequent $C/5$ rate (14.4 mA) cycles. Fig. 7 shows a preconditioning charge/discharge cycle of the lithium-ion polymer cell at $C/10$ rate, and subsequent two charge/discharge cycles at $C/5$ rate. This cell delivered a discharge capacity of 75 mAh during the first preconditioning cycle. This value is equivalent to a capacity of 143 mAh/g for active $LiCoO_2$ material in the cathode. The coulombic efficiency, which is defined as the ratio of the discharge capacity to the charge capacity, is 94% in the first cycle. The low coulombic efficiency observed during the initial cycle is caused by the formation of a passivating film, often called the solid electrolyte interphase (SEI), on the surface of the carbon electrode due to the decomposition of the electrolyte [23,24]. Such surface films provide good stability to the carbon anode toward electrolyte reduction in the subsequent lithium intercalation–deintercalation cycles. With further charge–discharge cycles at $C/5$ rate, an increase of cycling efficiency can clearly be seen. Fig. 8 shows the discharge capacity and the coulombic efficiency as a function of cycle number at $C/5$ rate. The MCF/PAMS-GCM/$LiCoO_2$ cell initially delivered 74.7 mAh and the discharge capacity of the cell decreased slightly with cycling. The decline in capacity is primarily due to the physical changes in the active materials and interfaces, which gradually increase cell internal resistance during cycling. The discharge capacity was maintained at 69.6 mAh for the 50th cycle, which was 93% of the initial capacity. The charge/discharge efficiency was about 100% after three cycles. This is convincing evidence of the good capacity retention of a lithium-ion polymer cell employing a PAMS gel-coated membrane electrolyte. Fig. 9 shows the discharge curves obtained at different temperatures. Both the voltage and the capacity are found to decrease gradually with decreasing temperature, which is due to an increase of the internal resistance of the cell. However, it showed good performance at −10°C, where the discharge capacity was 88% compared with that obtained at room temperature. The good performance at low temperature is related to the use of organic solvents with a high dielectric constant, low viscosity

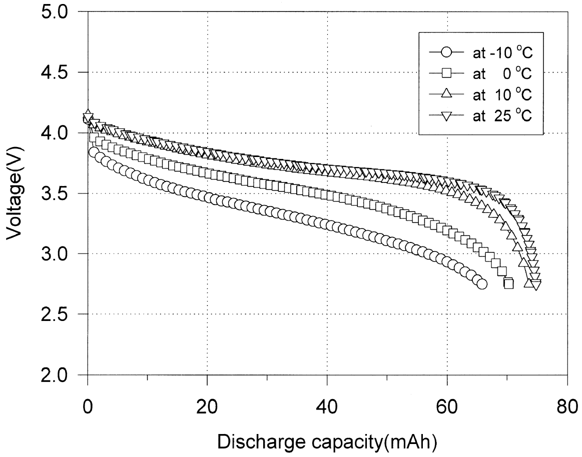


Fig. 9. Discharge profiles of a MCF/PAMS-GCM/$LiCoO_2$ cell obtained at different temperatures. Charge rate 0.5*C* with 4.2 V cut-off.

and low freezing point, in preparing the PAMS gel-coated membranes. In other words, an equivolume ternary mixture of EC, DMC and EMC in the GCM could provide the synergistic effects of EC (high dielectric constant), DMC (low viscosity) and EMC (low melting point) if present in appropriate proportions, which reduces the internal cell resistance at low temperatures. From the results described above, it is expected that the PAMS gel-coated membrane is a promising material as a polymer electrolyte for a lithium-ion polymer. More detailed studies on the battery performance of lithium-ion polymer cells employing PAMS gel-coated membrane electrolytes are in progress.

4. Conclusions

PAMS-based gel polymer electrolytes were coated onto porous PE membranes and their electrochemical characteristics were investigated. The relative molar composition of AN/MMA/ST in the PAMS proved to play a critical role in determining the capacity to retain electrolyte solution within the porous membrane. The ionic conductivity and electrochemical stability window of the optimized GCM were found to be 1.1×10^{-3} S/cm and 5.2 V vs. Li/Li^+, respectively. Gel polymer electrolytes coated onto PE membranes possess both the cohesive properties of the gel and the diffusive transport properties of the liquid. Gel-coated membrane electrolytes showed excellent mechanical strength, which is one of the most important factors to be considered when battery manufacturing technology moves from the laboratory to the pilot or mass production level. Lithium-ion polymer cells composed of a MCF anode, PAMS-GCM and a $LiCoO_2$ cathode showed a high discharge capacity of 142 mAh/g based on active $LiCoO_2$ material, and their charge–discharge cycles after a few initial cycles were demonstrated to be 100% efficient. These cells also exhibited good low temperature performance, showing 88% of the room temperature capacity at −10°C. These noteworthy battery performances have shed light on the possible practical application in high energy density rechargeable lithium-ion polymer batteries.

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