

# Composite polymer electrolytes reinforced by non-woven fabrics

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## Abstract

Composite electrolytes composed of a blend of polyethylene glycol diacrylate (PEGDA), poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) together with a non-woven fabric have been prepared by means of ultra-violet cross-linking. As the non-woven fabric serves as a mechanical support medium, the composite electrolyte has good integrity up to an initial liquid electrolyte uptake of 1000% (ethylene carbonate (EC)–dimethyl carbonate (DMC)–ethylmethyl carbonate (EMC)–LiPF<sub>6</sub>). The ionic conductivity of the composite electrolytes reaches 4.5 mS cm<sup>-1</sup> at an ambient temperature of around 18 °C and are electrochemically stable up to about 4.8 V versus Li/Li<sup>+</sup>. The conductivity and interfacial resistance remain almost constant even at 80 °C. Scanning electron micrographs show that the high-temperature behavior is associated with structural stability that is induced by chain entanglement between PVdF, PMMA and PEGDA network. A MCMB|LiCoO<sub>2</sub> cell using the composite electrolytes retains >97% of its initial discharge capacity after 100 cycles at the C/2 rate (150 mA), and delivers more than 80% of full capacity with an average load voltage of 3.6 V at the 2C rate. The cell also shows much better cycle-life than one with a PVdF-coated composite electrolyte at high temperatures because of the better liquid electrolyte retention capability.

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## 1. Introduction

Rechargeable lithium batteries have become a key component of modern portable electronic devices since the remarkable commercial success of Li-ion cells distributed first by SONY in 1991 [1]. Li-ion batteries operate on the same principle as Li-metal batteries, but do not have critical problems associated with the unstable Li–metal interface because they utilize Li<sup>+</sup>-intercalated carbonaceous anodes instead of reactive metallic lithium [2]. In the next generation of lithium batteries, usually named Li-ion polymer batteries (LiPB), gel polymer electrolyte (GPE) technologies will play a major role to improve scale-up, safety, and design flexibility [3].

Even though various gel polymer electrolytes plasticized by organic liquid solvents eliminate the room-temperature conductivity limit of dry polymer systems based on poly-

ethylene oxide (PEO) [4], their mechanical strength is still not sufficient to allow high-speed battery manufacturing that would employ the lamination and packing processes commonly used in plastic industry [5]. Therefore, there have been several recent reports [6–10] on LiPBs with gel polymer electrolytes which include thin microporous polyolefin separator films [6–10]. The gelled polymers are accompanied with an inert separator film, the support film endows the final polymer electrolyte matrix with sufficient mechanical properties for practical battery assembly procedures. This concept is technically analogous to the outstanding Gore-Select<sup>TM</sup> membrane, a composite ionomer reinforced by microporous Teflon<sup>®</sup> film, that is used in hydrogen fuel-cell applications [11]. In any cases, these approaches may yield the best compromise between apparent areal resistance and mechanical integrity.

In gel-coated electrolyte systems poly(vinylidene fluoride) (PVdF) and its copolymers with hexafluoropropylene (PVdF–HFP) are commonly chosen as an ionic conductive gel layer because of their high electrochemical properties and better adhesion with electrode laminates that contain a

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PVdF homopolymer binder [12]. On the other hand, the flow properties of PVdF-based gel polymers at elevated temperature can lead to internal short-circuits and safety hazards [6]. They may also undergo severe exudation of solvent from the physically cross-linked polymer structure upon long storage.

To solve these problems, a miscible polymer solution of polyethylene glycol diacrylate (PEGDA), poly(methyl methacrylate) (PMMA) and PVdF has been prepared in the presence of organic liquid electrolytes, and cross-linked on a non-woven fabric support under ultra-violet (UV) irradiation. It is well known that the UV-crosslinking reaction produces more thermally stable polymer electrolyte matrices [13] and the final product can be directly cured on either Li-metal foil or electrode laminates within a few seconds. In previous works [14,15], we have reported that the chemically and physically cross-linked structure of the PEGDA–PVdF blend was responsible for better thermal stability at elevated temperature. As an inexpensive support medium has been impregnated with thermally stable polymer blends containing PMMA having high affinity with liquid electrolytes, the electrochemical properties, mechanical properties and mass productivity are expected to be fairly optimized. This paper presents the characterizations of UV-cured PEGDA–PVdF–PMMA composite electrolytes reinforced by non-woven fabric and their use in LiPBs.

## 2. Experimental

PVdF homopolymer (Elf Atochem, Kynar761) and PMMA (Polyscience,  $M_w = 450,000$ ) powders were dissolved in liquid electrolyte solutions at elevated temperature. A battery-grade liquid solution of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) containing Li salt (Merck, EC/DMC/EMC (1/1/1 vol.%) and 1 M  $\text{LiPF}_6$ ) was used as a liquid electrolyte. The PEGDA oligomer (Aldrich,  $M_w = 742$ ) was mechanically mixed with the PVdF–PMMA gel, then a photoinitiator, 2-chlorobenzophenone (Aldrich), and a curing accelerator, triethylamine (TEA, Junsei Chemical), were added to the mixture. The resultant polymer solution mixture was uniformly coated on non-woven fabric (PET viscous rayon, 85  $\mu\text{m}$ ) fixed on to a Mylar carrier film, and cured under UV irradiation (Sankyo Denki GL 20,  $\lambda = 375 \text{ nm}$ ) for 1 h.

Tensile tests were performed with an Instron Model 4201 tester, in accordance with ASTM D882-88. The test specimens were 6 mm in width and approximately 100  $\mu\text{m}$  in thickness. The grip distance was 50 mm and the cross-head speed was 25 mm/min. The cross-sectional morphology of blend films was examined with a scanning electron microscope (FE-SEM, Hitachi S-4300) at 10 kV. All samples were prepared by cryogenic fracture after immersion in liquid nitrogen for 5 min. To examine liquid electrolyte reten-

tion over time, the weight change of the gel films was monitored at 80 °C.

The ionic conductivity ( $\sigma$ ) of gel films was determined by ac impedance spectroscopy (Zalmer IM6 impedance analyzer). Sample films were sandwiched between two parallel stainless steel (SUS) discs ( $\phi$ : 1.5 cm). The frequency ranged from 1 MHz to 1 Hz at a perturbation voltage of 5 mV. The electrochemical stability window was studied by linear sweep voltammetry using an EG&G Model 273A potentiostat. A three-electrode T-cell configuration was applied and used Li-metal as a reference as well as a counter electrode.

Prismatic cells were assembled with reinforced composite electrolytes sandwiched between a  $\text{LiCoO}_2$  cathode (Seimi Co., 8 cm  $\times$  13 cm, 40 mg  $\text{cm}^{-2}$ ) and a graphite (Osaka Gas, MCMB1028) anode. The weight ratio of active material, carbon conductor (MMM Carbon, Super-P) and polymer binder (Elf Atochem, Kynar 761) was 100:10:6 for the cathode and 100:10:7 for the anode. The cathode and anode slurries were spread on to aluminum and copper foils, respectively, by means of an in-house tape-casting machine, and thoroughly dried at 100 °C for 48 h in a vacuum oven, followed by roll-pressing at 5 ton  $\text{cm}^{-2}$  to obtain uniform thickness. Finally, the MCMB| $\text{LiCoO}_2$  cells were enclosed in aluminum plastic pouch bags after heat lamination at 80 °C. All procedures were carried out in a dry room in which the moisture content was below 10 ppm. The galvanostatic charge–discharge performance was examined between 3.0 and 4.2 V (Toyo, TOSCAT-3000U).

## 3. Results and discussion

The tensile elongation at break of UV-cured blend gel films at different compositions is shown in Fig. 1. In immiscible polymer blends, the interfacial adhesion is usually not strong enough for stress to be efficiently transferred from one phase to another during yielding or fracture, which thus results in poor mechanical properties [16]. Therefore, measurement of the tensile properties of PEGDA–PVdF–PMMA (E/V/M) blends is an efficient way to estimate compatibility between parent polymers. In particular, tensile elongation at break is very sensitive to the strength of the interface and is commonly measured to examine the efficacy of the blend [17]. The elongation of PVdF and PMMA usually exceeds 200 and 400%, respectively, while that of UV-cured PEGDA films is near zero due to high brittleness. It is improved up to 300% at E/V/M (4/4/2 w/w) films when polymers and oligomer were dissolved in liquid electrolyte in a weight ratio of 1:6 (600 wt.% of EC–DMC–OMC– $\text{LiPF}_6$ ). These elongation values are higher than those predicted from the rule of mixture. Considering that polymer blends tend to have properties intermediate between those of the separate components, the positive deviation implies high compatibility between parent polymers. The E/V/M blend is somewhat different from conventional solution-blended ones. A completely miscible solution of PVdF and PMMA is

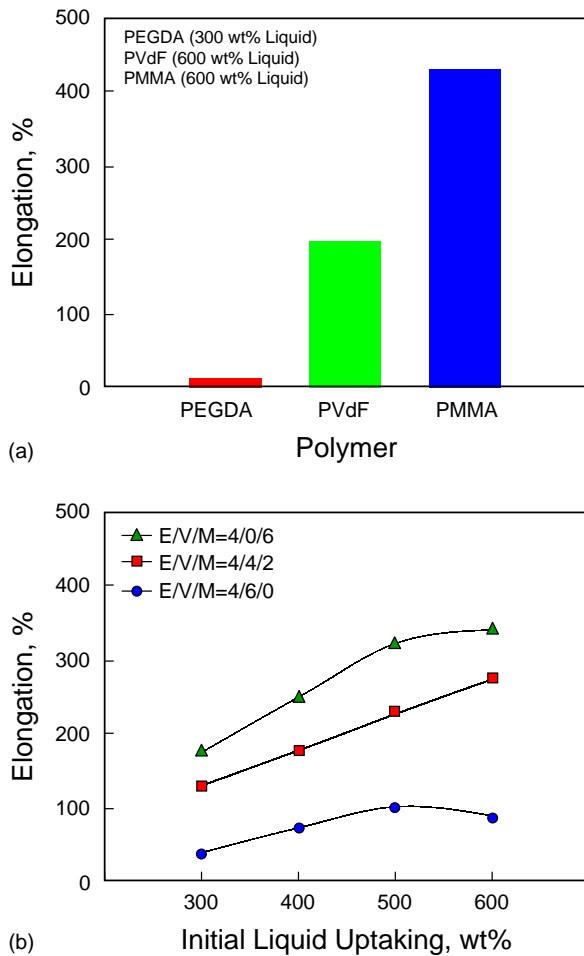


Fig. 1. Tensile elongation of gel polymer electrolytes: (a) parent polymers; (b) blend electrolyte at different compositions.

simply mixed with low viscous PEGDA oligomer. Thereafter, a chemical cross-linking reaction of PEGDA and a physical cross-linking of the polymers occur so that PVdF and PMMA chains are trapped in PEGDA network structure. This makes the resultant blend highly homogeneous.

Typical ac impedance spectra for composite electrolyte films using blocking electrodes are shown in Fig. 2(a). The bulk resistance ( $R_b$ ) was determined from the high-frequency intercept on the real axis in complex impedance spectra, and then  $\sigma$  is calculated from the equation  $\sigma = l/A R_b$ , where  $l$  is the nominal thickness ( $\sim 100 \mu\text{m}$ ) and  $A$  the electrode area. As shown in Fig. 2(b), positive curvatures of Arrhenius plots suggest that the ionic conduction mechanism obeys the Vogel–Tamman–Fulcher relationship, which describes the transport properties in a viscous matrix. Composite electrolytes exhibit higher conductivity than unmodified E/V/M blend electrolytes over the entire temperature range. In general, E/V/M (4/4/2) blend electrolytes cannot be obtained as a free-standing film above 600 wt.% uptake of the liquid electrolyte because of the dilution effect, but reinforced composite electrolytes are able to take up about 1000 wt.% liquid electrolyte while maintaining essential integrity and

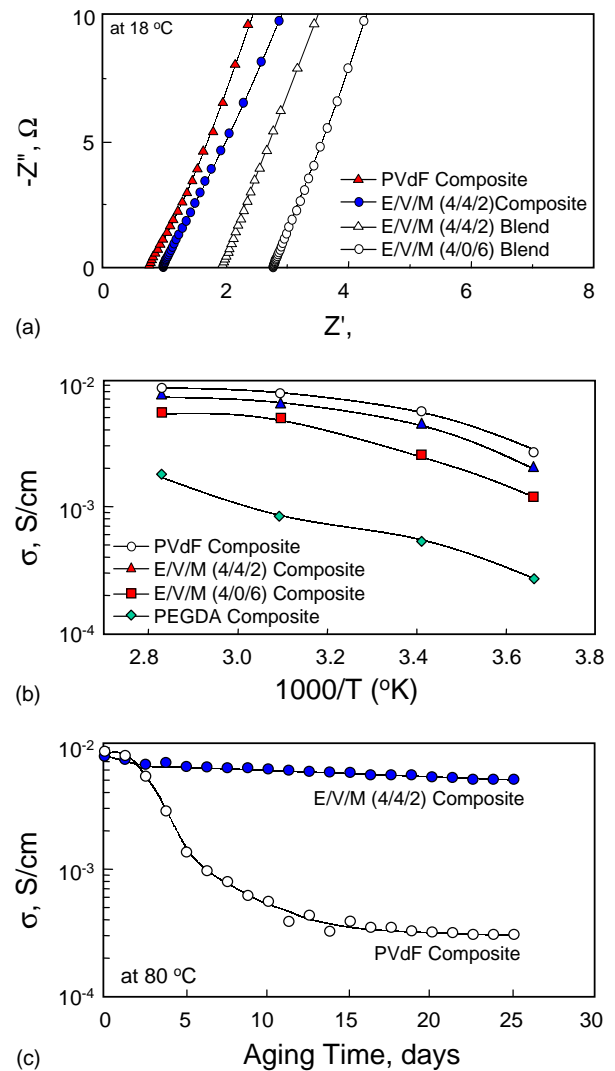


Fig. 2. Ionic conductivity of composite electrolytes: (a) ac impedance spectra; (b) Arrhenius plot; (c) conductivity change at 80 °C.

flexibility. This may be partly due to a high compatibility of the carbonyl group in PMMA units with carbonate solvents, and also due to the fact that a mechanical support with good affinity with liquid electrolytes operates as an additional liquid electrolyte reservoir. The isothermal conductivity measurements presented in Fig. 2(c) indicate that ionic conductivity of PVdF composite electrolytes gradually decreases at 80 °C. In contrast, the E/V/M (4/4/2) composite electrolyte displays a much more stable conductivity than the PVdF composite under the same conditions. Since the ionic conduction is mainly provided by the liquid electrolyte, such a variation is probably related to the polymer morphology and microstructure for liquid electrolyte retention.

Scanning electron micrographs of composite electrolytes impregnated with different gel polymers are presented in Fig. 3. It is seen that PVdF and E/V/M electrolytes are characterized by a similar porous structure, but there is minor

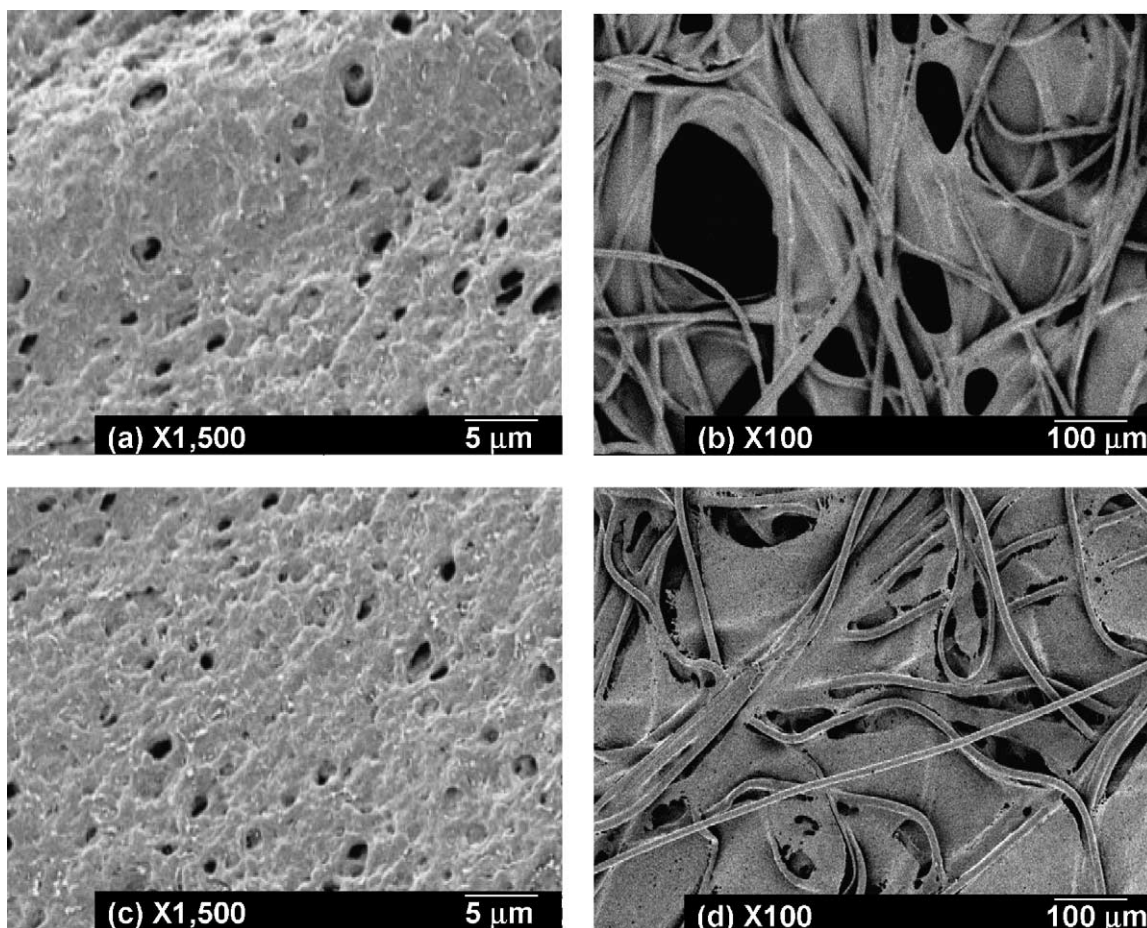


Fig. 3. Scanning electron micrographs of composite electrolytes: (a) PVdF composite; (b) PVdF composite after annealing; (c) E/V/M composite; (d) E/V/M composite after annealing.

difference in pore size because the E/V/M blend may tend to have a pore size that is intermediate between porous PVdF and dense PEGDA [14]. The morphologies are dramatically changed, however, when both samples are stored in liquid electrolyte solution at 80 °C for 2 h. The wetting of the polymeric components on non-woven fabrics is similar, but larger pores are formed in the PVdF-coated composite and may represent the coalescence of small pores due to dissolution of PVdF chains in the presence of EC-based liquid solvent at elevated temperature [18]. Accordingly, the conductivity loss of the PVdF composite at 80 °C is closely related to fast evaporation of liquid electrolytes through the larger microporous structure [19]. For a miscible E/V/M-coated composite, the strong chain entanglement of the PVdF, PMMA and PEGDA network may allow micropores to be retained. It appears that the structural stability has significant influence, particularly on the high-temperature conductivity of the E/V/M composite.

The weight change of different gel polymer electrolytes with time on exposure to the dry room atmosphere is given in Fig. 4. Each sample was pressed lightly between two sheets of filter paper to remove the excess of liquid electrolyte solution, and the weight change was monitored with time at

80 °C. The weight loss resulted mainly from evaporation of organic liquid electrolyte solutions from the electrolyte membranes. The rapid weight loss of PVdF-based GPE and composite are primarily attributed to evaporation of liquid electrolyte through large pores, and is in good agreement

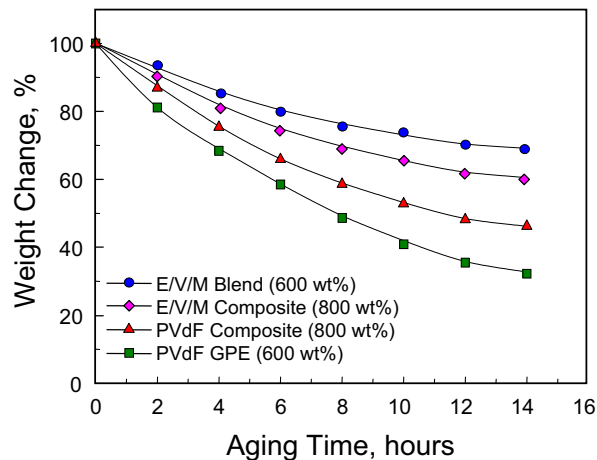


Fig. 4. Weight change of composite electrolytes at 80 °C.

with morphology studies. The liquid electrolyte retention was apparently improved for the E/V/M blend and the composite. Despite the higher initial uptake, liquid electrolyte soaked into the E/V/M composite is not likely to be exuded from the polymer host and the support medium. Thus, it is confirmed that a reinforced composite could be the most efficient way to obtain better retention ability over a broad temperature range and with a higher initial liquid electrolyte.

Impedance analysis was used to study the interfacial properties of non-blocking Li|GPE|Li cells. An ac impedance spectrum of a Li-metal–GPE interface under open-circuit condition is presented in Fig. 5(a). The intercept at high frequency can be assigned to electrolyte resistance ( $R_e$ ), and the intercept on the low-frequency side corresponds to interfacial resistance ( $R_i$ ). It is found that the  $R_e$  values of both PVdF–HFP and PEGDA–PVdF electrolytes are almost constant at room temperature within 90 h. The change of  $R_e$  and  $R_i$  with time at 80 °C is given in Fig. 5(b) and (c), respec-

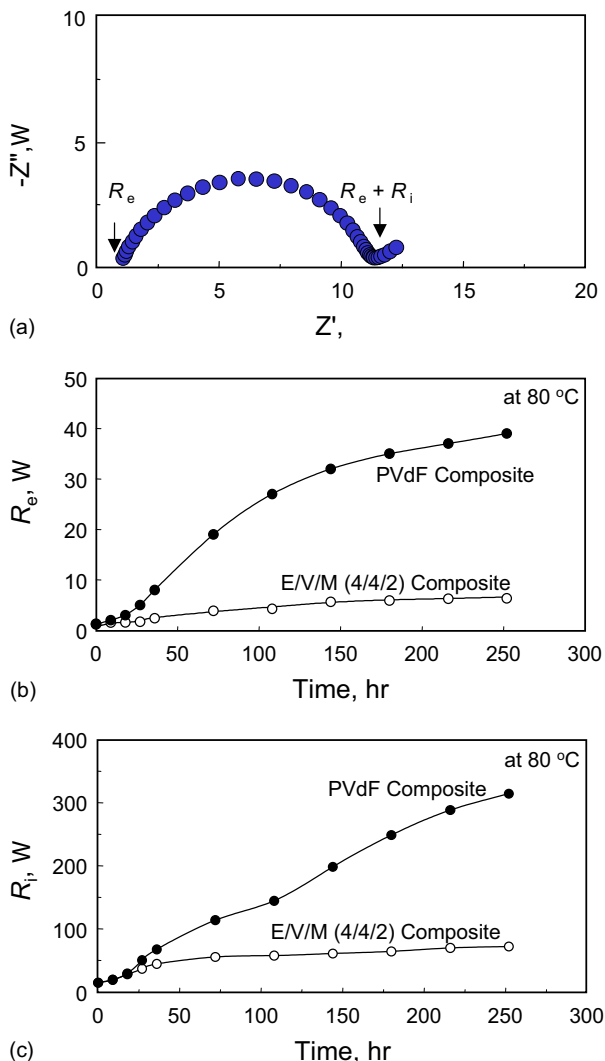


Fig. 5. Impedance behaviour of Li|GPE|Li cells: (a) typical impedance spectrum; (b) bulk resistance at 80 °C; (c) interfacial resistance at 80 °C.

tively. The value  $R_e$  of a E/V/M (4/4/2) composite electrolyte levels off at around 8  $\Omega$ , whereas the PVdF-coated composite exhibits a continuous increase in resistance. This may result from faster solvent depletion from PVdF gel polymer layer at high temperatures. In the case of interfacial resistance, the progressive increase in  $R_i$  for the PVdF-coated composite indicates the continuous growth of a passivation layer on the Li-metal surface [20]. This resistive layer is known to be caused by the reaction between aprotic solvents and the Li-metal electrode. It is supposed that the passivation layer is not uniform in both composition and density across the layer, and the middle-frequency semicircle is usually depressed [21]. For a E/V/M composite electrolyte, the rate of growth of  $R_i$  is significantly reduced after 36 h because there is no subsequent flow of corrosive solvents to the interface [22]. It is evident from impedance results that the E/V/M composite electrolyte exhibits good affinity with liquid electrolytes and is a better reservoir for EC-based liquid electrolyte solution than the PVdF-coated composite electrolyte over a wide temperature range.

Current–voltage responses of Li|GPE|SUS cells at room temperature are given in Fig. 6. The electrochemical stability window of a given polymer electrolyte is generally determined by means of linear sweep voltammetry of an inert electrode in the selected electrolyte [23]. The onset of current in the anodic high-voltage range is assumed to result from a decomposition process associated with the electrode [24]. The onset voltage, taken as the upper limit of the electrolyte stability range, is generally located as the point of intersection of the extrapolated linear current in the high-voltage region with the voltage axis. For all composite electrolytes, the current responses are negligible below  $\sim 4.7$  V versus Li/Li<sup>+</sup>. This is indicative of no decomposition of any components in this potential region. It is, therefore, concluded that UV-cured PEGDA–PVdF–PMMA composite electrolytes have suitable electrochemical stability to allow the use of high-voltage electrode couples such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub>.

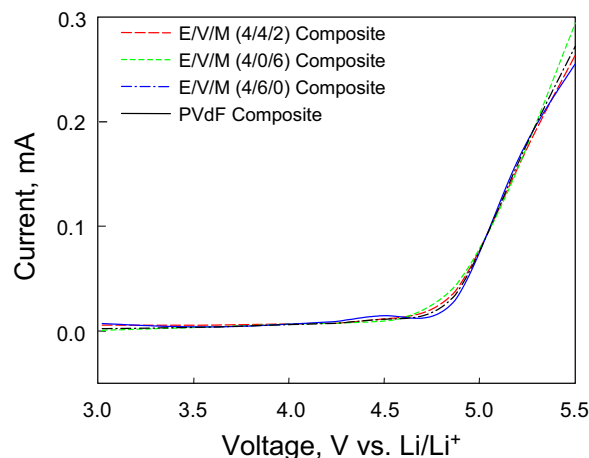


Fig. 6. Electrochemical stability windows of composite electrolytes.

MCMB|LiCoO<sub>2</sub> cells were assembled with different composite electrolytes. The cycleability of Li<sub>x</sub>CoO<sub>2</sub> is generally limited to  $x = 0.5$ , which gives a specific capacity of  $\sim 137 \text{ mAh g}^{-1}$ . For a value of  $x$  lower than 0.5, the oxidation of Co<sup>3+</sup> to Co<sup>4+</sup> becomes possible and this may also change the crystallinity of the LiCoO<sub>2</sub> cathode and thus affect the crystal structure and cause a decrease in reversibility [25]. A charge–discharge profile for a MCMB|LiCoO<sub>2</sub> cell using a E/V/M (4/4/2) composite electrolyte incorporating 800 wt.% liquid electrolyte at room temperature is given in Fig. 7(a). This cell was charged and discharged at the C/2 rate between 3.0 and 4.2 V. The observed capacities are very close to the theoretical value of  $\sim 3 \text{ mAh cm}^{-2}$ , corresponding to the value of  $x = 0.5$  in Li<sub>x</sub>CoO<sub>2</sub>, and slightly higher than that of a Li-ion cell. This may be related to the low internal tension inside the Li-ion cell when enclosed in a plastic pouch.

All composite electrolytes demonstrate excellent cycle-life at room temperature. In the case of cell operation at 80 °C, the capacity of a MCMB|LiCoO<sub>2</sub> cell with a PVdF-coated composite electrolyte steadily decreases after the first 10 cycles and falls below an initial capacity of 80% after 50

cycles. In contrast, the capacity of the E/V/M (4/4/2) composite electrolyte is almost equal to the initial capacity, as shown in Fig. 7(b). The capacity fading of a LiPB using a PVdF composite electrolyte could be caused by the continuing evaporation of liquid electrolytes and the higher solubility in liquid electrolytes at 80 °C. It can be concluded that the better structural and thermal stability of UV-cured E/V/M composite electrolytes improves high-temperature performance.

The rate dependency and low-temperature performance were also examined. Discharge profiles of MCMB|LiCoO<sub>2</sub> cells as a function of discharge rate are given in Fig. 8(a). The intercalation of Li cations into LiCoO<sub>2</sub> gives rise to a voltage plateau at about 3.7 V versus Li/Li<sup>+</sup>. It is clear that very good cycleability is displayed by the E/V/M composite electrolyte when cycled between 3.0 and 4.2 V. Assuming that the capacity at the C/5 rate is 100% capacity, this cell delivered about 91% of the nominal cathode capacity at the 1C rate with a load voltage of 3.6 V. The reduced capacity at high rates is due to the low value of the chemical diffusion coefficient of lithium ions in the LiCoO<sub>2</sub> lattice and the lower

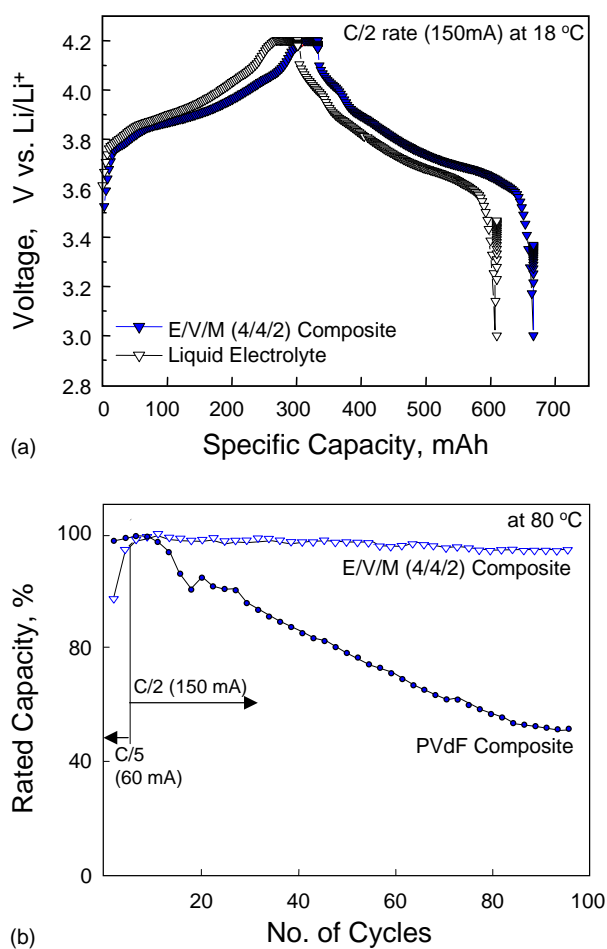


Fig. 7. Battery performance of a LiPB: (a) typical charge–discharge profile; (b) cycle-life at 80 °C.

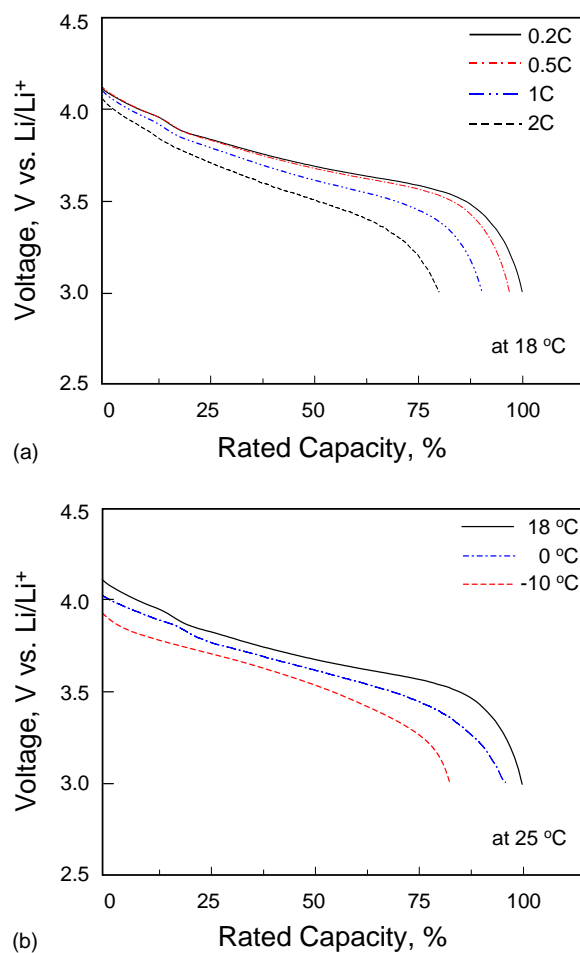


Fig. 8. Battery performance of a LiPB: (a) rate capability; (b) temperature dependence.

diffusion rate of lithium ions in GPE, as compared with that in liquid electrolyte. At the 2C rate, this cell delivered about 82% of the full capacity at an average load voltage of 3.5 V.

To measure low-temperature performance, each cell was stored at the test temperature for 24 h prior to charge–discharge. As shown in Fig. 8(b), the MCMB|LiCoO<sub>2</sub> cell using E/V/M (4/4/2) composite electrolyte retained 96 and 83% of the room temperature discharge capacity at 0 and –10 °C, respectively. The capacity loss at low temperature is generally induced by a large polarization of the lithium ions at the electrode–electrolyte interface [26], but the combination of high dielectric constant, low viscosity and low freezing point solvents could be favorable for low-temperature operation.

#### 4. Conclusions

An inexpensive mechanical support medium, i.e. a non-woven fabric, is simply impregnated with PEGDA–PVdF–PMMA polymer blend solution and plasticized by liquid electrolytes. The polymeric components are chemically and physically cross-linked. This procedure yields a mechanically stable composite electrolyte with a large uptake of initial liquid electrolyte. When the blend weight ratio was 4/4/2, the composite electrolyte showed a maximum conductivity of 4.5 mS cm<sup>–1</sup> at 18 °C and electrochemical stability up to 4.8 V versus Li/Li<sup>+</sup>. Conductivity and liquid electrolyte retention became much less sensitive at high temperature, compared with the characteristics of the PVdF composite. It is concluded that the chain entanglement between PVdF, PMMA and PEGDA network provides a composite membrane with structural stability in terms of solubility of PVdF in EC-based solvents and pore-size distribution. This enables UV-cured PEGDA–PVdF–PMMA composite electrolytes to maintain lower interfacial resistance even at 80 °C. As a result, 8 cm × 13 cm MCMB|LiCoO<sub>2</sub> cells using the composite electrolytes show good cycle-life and rate capacity at elevated temperature operation. The synergic results of the composite electrolytes are thought to be highly suitable for practical Li-ion polymer batteries.

#### Acknowledgements

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