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To prepare miscible polyethylene glycol diacrylate/polyvinylidene fluoride (PEGDA/PVdF) blend gel polymer electrolytes, low molecular weight ($M = 742$) liquid PEGDA oligomer was mixed with PVdF-HFP dissolved in ethylene carbonate/dimethyl carbonate/LiPF₆ liquid electrolytes, and then cured under ultraviolet irradiation. Room temperature conductivity of PEGDA/PVdF blend films was found to be comparable to that of PVdF-HFP gel polymer electrolytes, and they were electrochemically stable up to 4.6 V vs. Li/Li⁺. Scanning electron micrographs revealed that PEGDA/PVdF blend electrolytes have pore size intermediate between dense PEGDA and highly porous PVdF-HFP. It was confirmed by weight change measurement that liquid electrolyte was likely to evaporate through large pores in PVdF-HFP at 80°C, while PEGDA/PVdF blend showed better liquid electrolyte retention ability. This result was in good agreement with more stable interfacial properties of PEGDA/PVdF blend at 80°C in ac impedance analysis. Consequently, both PVdF-HFP and PEGDA/PVdF gel polymer electrolytes delivered similar discharge capacity at room temperature, but PEGDA/PVdF blend gel polymer electrolyte showed much better cycle performance than pure PVdF-HFP at 80°C.

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A number of reports have been given recently on gel polymer electrolytes (GPEs) such as polyacrylonitrile (PAN),¹ polymethyl methacrylate (PMMA),² and polyvinylidene fluoride (PVdF),³ etc. Among them, PVdF and its copolymer with hexafluoropropylene (HFP), PVdF-HFP, are of considerable practical interest in view of industrial mass production as well as their high electrochemical properties. PVdF-HFP gels are usually prepared by dissolving the polymer host in organic liquid electrolyte solutions at elevated temperature.⁴ Microporous PVdF-HFP films swollen with liquid electrolyte solutions can be also prepared by PLiON technology developed by Bellcore (now Telcordia)⁵ and phase inversion method.⁶

For a gel polymer electrolyte to be effective, it needs to maintain high ionic conductivity over a wide temperature range and remain structurally stable during manufacturing, cell assembly, storage, and usage.⁷ PVdF-HFP copolymers were found to have high quality for these requirements, but HFP comonomers make them more soluble in ethylene carbonate (EC)-based liquid electrolyte solutions when the cell temperature is raised to over 60°C by abusive cell operation.⁸ This might lead to the concentration gradient of liquid electrolyte in gelled polymer matrix, as the cell temperature oscillates. Moreover, they undergo severe exudation of liquid electrolytes from porous gel polymer structure upon long storage, known as syneresis effect, and a high temperature facilitates the evaporation of volatile liquid solvents through large pores.⁸ Thus, it seems that these intermixed problems might be associated with capacity fading at high temperature operation above 60°C.⁹

On the other hand, ultraviolet (UV)-curing methods are well established to obtain chemically crosslinked polymer electrolytes at ambient temperature. Even though the resultant three-dimensional network structures do not show flow property in the presence of EC-based solvents even at higher temperature,^{7,10} they cannot maintain mechanical integrity under external pressure or elongation for practical cell assembly procedures. However, it was lately reported that their mechanical properties were significantly improved when UV-curable oligomers, represented by polyethylene glycol diacrylate (PEGDA), were mixed with PVdF-HFP dissolved in dimethyl-

formamide (DMF) before crosslinking reaction.¹¹ In addition, we found that PEGDA components modified the microstructure of porous PVdF-HFP, which allow PEGDA/PVdF blends to enhance liquid electrolyte retention ability. It is also expected to improve heat resistance of PVdF-HFP in EC-based solvents because the PVdF-HFP chains can be randomly entangled with PEGDA network frames in the miscible blend.

In this work, we prepared UV-cured PEGDA/PVdF blend gel polymer electrolytes without additional solvent (DMF), and studied the effect of structural change of blend membranes on their liquid electrolyte retention and electrochemical properties at different temperature. Finally, Li ion-polymer battery performances using PEGDA/PVdF blend gel polymer electrolytes are tested at various conditions.

Experimental

PVdF-HFP copolymer (Elf Atochem Co., Kynar2801) was dissolved in liquid electrolyte solutions at elevated temperature. A battery grade liquid electrolyte solution of EC and dimethyl carbonate (DMC) containing Li salt (Merck, EC/DMC = 50/50 vol %, 1 M LiPF₆) was used as a liquid electrolyte. PEGDA oligomer (Aldrich, $M = 742$) was mechanically mixed with PVdF-HFP gel in the presence of additional liquid electrolytes, then a photoinitiator, 2-chlorobenzophenone (Aldrich), and a curing accelerator, triethylamine (TEA, Junsei Chemical), were added to the mixture. The resultant solution was coated on Mylar substrate and cured under UV irradiation (Sankyo Denki GL 20, $\lambda = 375$ nm) for 1 h.

Thermal properties were examined by differential scanning calorimeter (Perkin Elmer DSC7). All the thermograms are calibrated against indium metal. Tensile test were carried out on an Instron model 4201 tester, in accordance with ASTM D882-88. The test specimens were 6 mm wide and approximately 100 μ m thick. The grip distance was 50 mm and the crosshead speed was 25 mm/min. Cross-sectional morphology of blend films was obtained by scanning electron microscope (SEM, Hitachi S-2500C) at 10 kV. All samples were prepared by cryogenic fracture after immersion in liquid nitrogen for 5 min. To examine liquid electrolyte retention over time, weight change of gel films was monitored at 80°C.

The electrochemical stability window was measured by linear sweep voltammetry using an EG&G model 273A potentiostat. Li metal (Cyprus Foote Mineral Co.) was used as counter and reference

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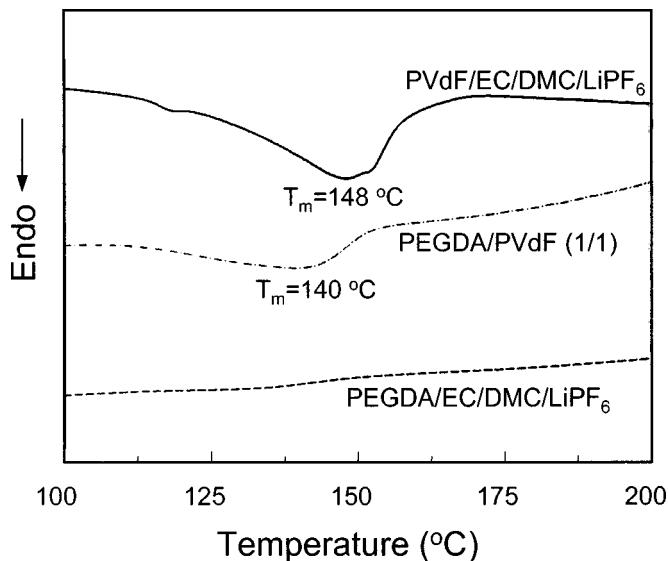


Figure 1. DSC thermograms of gel polymer electrolytes.

electrode, and stainless steel (SUS) disk ($\phi = 1 \text{ cm}^2$) was used as working electrodes. Ionic conductivity (σ) of blend films was determined by ac impedance spectroscopy (Zahner IM6 impedance analyzer). Sample films (ca. $50 \text{ }\mu\text{m}$) were sandwiched between two parallel SUS disks ($\phi = 1 \text{ cm}^2$). The frequency ranged from 100 kHz to 1 Hz at a perturbation voltage of 5 mV. Li metal/GPE interface behavior was also analyzed by impedance analysis. Impedance spectra of symmetrical Li/GPE/Li cells were measured under open circuit potential (OCP) condition with time at different temperature.

Prismatic Li ion-polymer cells were assembled by sandwiching PEGDA/PVdF gel polymer electrolyte films between LiCoO₂ cathode (Seimi Co., $2 \times 3 \text{ cm}^2$, 40 mg/cm^2) and mesocarbon microbead (MCMB)1028 (Osaka Gas) anode. The weight ratio of active material, carbon conductor (Lonza Co., graphite/acetylene black = 7/3 wt/wt) and polymer binder (Elf Atochem, Kynar 761) was 100/10/6 for cathode and 100/10/7 for anode. Cathode and anode slurry were coated onto aluminum and copper foils, respectively, and dried at 100°C for 48 h in a vacuum oven. Electrode laminates were roll pressed under appropriate pressure to obtain uniform thickness. Finally, MCMB/(PEGDA/PVdF)/LiCoO₂ cells were enclosed in an aluminum plastic pouch bag by a vacuum sealer. All procedures were carried out in a dry room where the moisture content was below 10 ppm. The galvanostatic charge/discharge performance was examined between 3.0 and 4.2 V (WonA Tech Co., Battery Cycler 3000) after preconditioning at C/10 for several cycles.

Results and Discussion

Figure 1 shows differential scanning calorimetry (DSC) thermograms of gel polymer samples without Li salts. The glass transition temperature (T_g) of neat PVdF-HFP copolymers usually spans a very wide range between -130 and -50°C , which implies random distribution of HFP domains,¹² and that of PEGDA is around -60°C . For miscible polymer blend systems, it is expected to be intermediate between those of the two polymer components. T_g for the blend sample was not definitely detected in blend compositions studied, but its melting peak shifted to lower temperature and heat of fusion was suppressed. The melting point depression and decrease in heat of melting means high compatibility of PVdF-HFP with PEGDA network. This indicates that the formation of PVdF-HFP crystals was suppressed by the interaction with PEGDA phase. PEGDA/PVdF blend is somewhat different to typical polymer solution blend process. PVdF-HFP solution is simply mixed with liquid PEGDA oligomer, and then PVdF-HFP chains were just trapped in

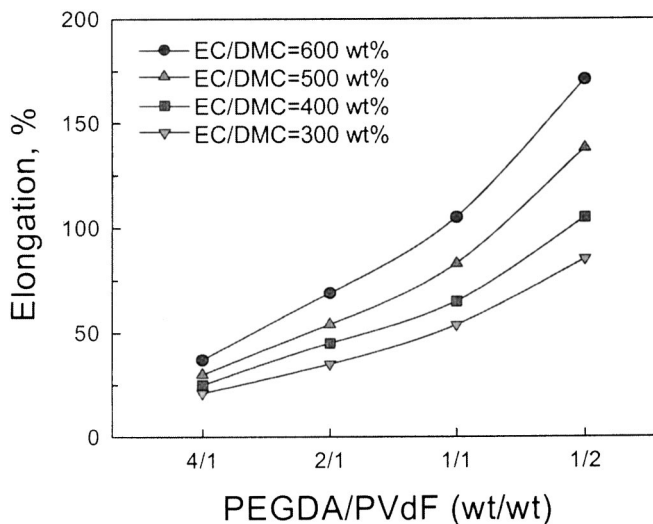


Figure 2. Tensile elongation at break of gel polymer electrolytes at different blend ratios.

PEGDA network during crosslinking of PEGDA. It means that the chemical crosslinking of PEGDA were simultaneously accompanied by physical crosslinking of PVdF with liquid electrolyte. This process makes the resultant blend highly compatible, as expected.

Figure 2 shows the tensile elongation at break of PEGDA/PVdF blend films at different blend compositions. In immiscible polymer blends, the interfacial adhesion is usually not strong enough for stress to be transferred efficiently from one phase to another one during yielding or fracture, thus resulting in poor mechanical properties.¹³ Therefore, the measurement of tensile properties of PEGDA/PVdF blends is another way to estimate compatibility of PEGDA with PVdF. Especially, tensile elongation at break is very sensitive to the strength of the interface and commonly measured to examine the efficiency of blend.¹⁴ The tensile elongation of commercial Kynar 2801 usually exceeds 200% but that of UV-cured PEGDA films is near zero due to high brittleness. However, it was improved up to 100% at PEGDA/PVdF (1/1, wt/wt) blend film incorporating 600 wt % of EC/DMC/LiPF₆ electrolyte solution with respect to the total weight of dry PVdF-HFP polymer and liquid PEGDA oligomer. Generally, UV-cured PEGDA gel electrolytes cannot be obtained as a freestanding film above EC/DMC/LiPF₆ = 400 wt % even at high concentration of photoinitiator because of the dilution effect, but UV-cured PEGDA/PVdF blend films showed good mechanical integrity above EC/DMC/LiPF₆ = 600 wt %, and the amount of initial liquid electrolyte was fixed at 600 wt % in further studies.

To clarify the change in initial liquid electrolyte uptaking, the polymer morphology was studied. As shown in Fig. 3, a pure PEGDA film has glassy and dense cross-sectional morphology. As PVdF-HFP content increases, the morphology of PEGDA/PVdF blend film becomes more porous and finally close to PVdF-HFP itself at PEGDA/PVdF = 1/2 (wt/wt). This strongly suggests that the structural change is mainly responsible for initial larger liquid electrolyte uptaking in blend films than PEGDA while maintaining mechanical integrity. Another important problem is liquid electrolyte retention over time. For physically crosslinked PVdF-HFP gels, liquid electrolyte solution is likely to evaporate and leak from gel polymer structure through large pores with time, which increases electrolyte resistance detrimentally, while Blonsky claimed that dense PEGDA film had better liquid retention with time despite initial low liquid solution uptaking.⁷ Figure 4 illustrates the weight change of gel polymer electrolyte with time upon exposure to dry room atmosphere. Each gel polymer sample was pressed lightly between two sheets of filter paper to remove the excess of liquid elec-

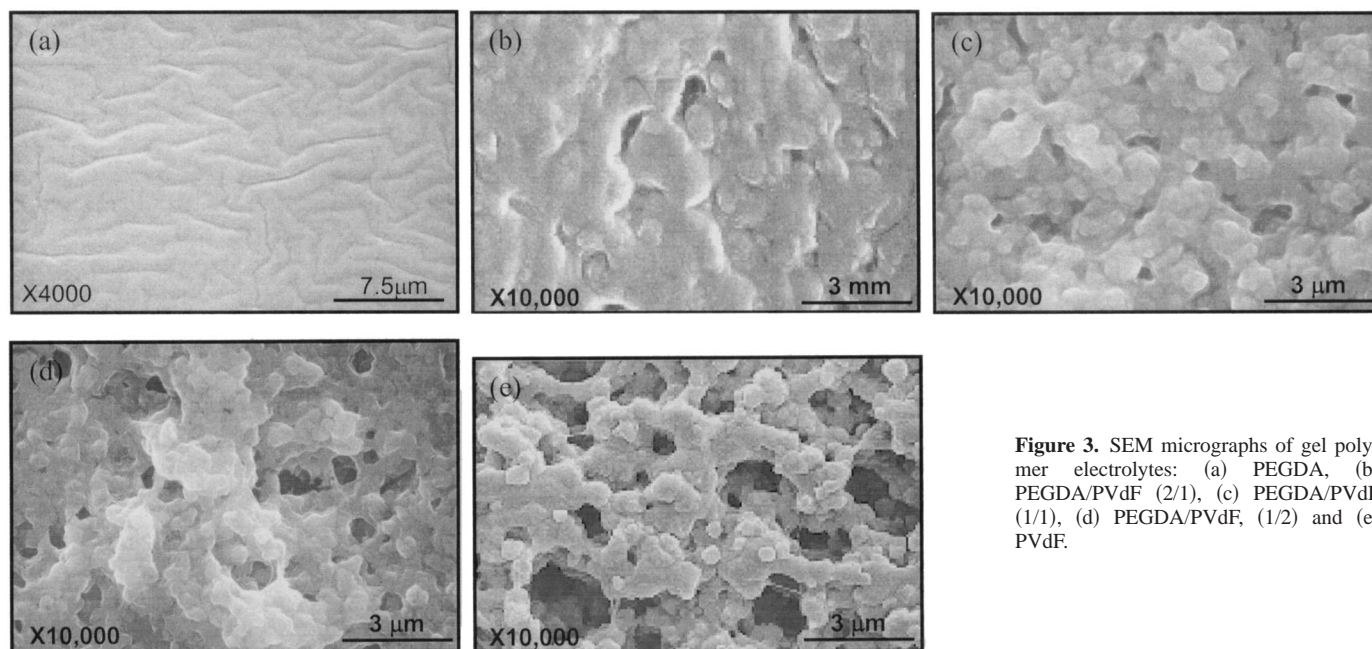


Figure 3. SEM micrographs of gel polymer electrolytes: (a) PEGDA, (b) PEGDA/PVdF (2/1), (c) PEGDA/PVdF (1/1), (d) PEGDA/PVdF (1/2) and (e) PVdF.

trolyte solution and their weight changes were monitored with time at 80°C. The weight loss resulted from evaporation of organic liquid electrolyte solutions from polymer gels. Considering scanning electron micrographs in Fig. 3, the fast weight loss of PVdF-HFP gels is primarily attributed to drying of liquid electrolyte through large pore size above 3 μm.¹⁵ On the contrary, liquid electrolyte retention was apparently improved for PEGDA/PVdF (1/1) blends where no large pore exists. It is obvious that they tend to have pore size intermediate between those of the separate components. Thus, if the blend ratio is optimized, it is possible to obtain the best compromise between initial liquid electrolyte uptaking and retention ability even at high temperature.

Figure 5 shows typical current/voltage curves of the Li/GPE/SUS cells at a scan rate of 1 mV/s. Electrochemical stability window of a given polymer electrolyte is generally determined by linear sweep voltammetry of an inert electrode in the selected electrolyte.¹⁶ The onset of the current in the anodic high voltage range is assumed to result from a decomposition process associated with electrode¹⁷ and this onset voltage is taken as the upper limit of the electrolyte sta-

bility range. This voltage is generally located as the point of intersection of the extrapolated linear current in high voltage region with the voltage axis. For all blend electrolytes, the current responses were negligible below 4.6 V vs. Li/Li⁺. This implies that there is no decomposition of any components in this potential region and PEGDA/PVdF blend electrolytes have suitable electrochemical stability to allow the use of high voltage electrode couples such as LiCoO₂, LiNiO₂, and LiMn₂O₄.

Figure 6 shows an Arrhenius plot of ionic conductivity (σ) for UV-cured PEGDA/PVdF blend gel electrolytes at different blend compositions. The bulk resistance (R_b) was determined from high frequency intercept on the real axis in complex impedance, then σ is calculated by the equation $\sigma = l/AR_b$, where A is the area and l is the thickness of membrane. In Fig. 6, the positive curvature indicates that ionic conduction obeys the Vogel-Tamman-Fulcher (VTF) relationship (Eq. 1), which describes the transport properties in a viscous matrix.

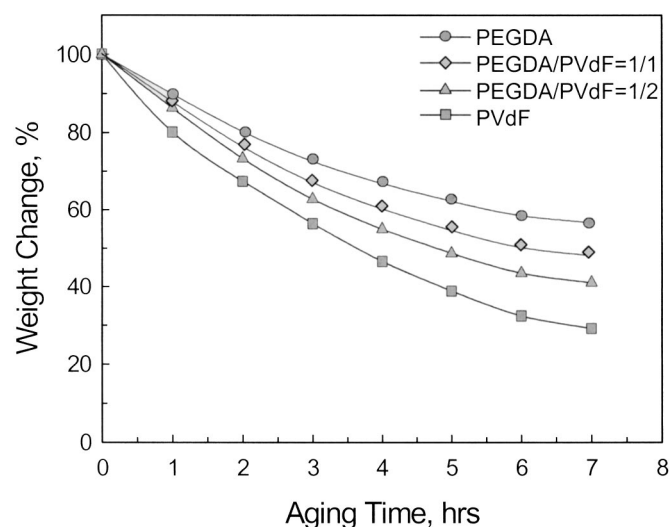


Figure 4. Weight change of gel polymer electrolytes with time at 80°C.

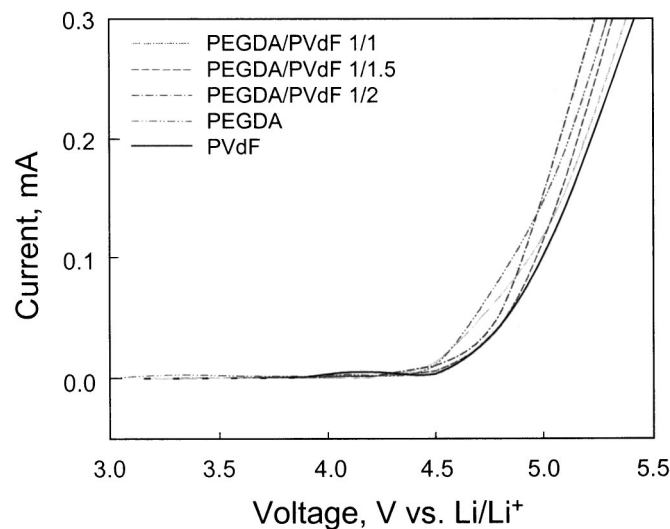


Figure 5. Stability window of gel polymer electrolytes containing 600 wt % of EC/DMC/LiPF₆.

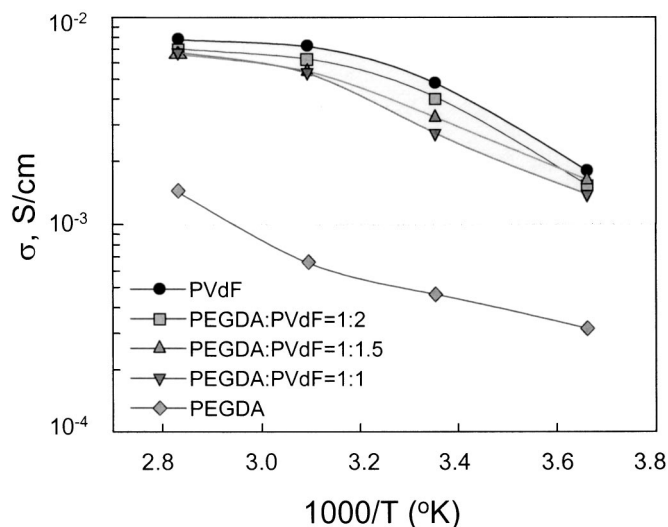


Figure 6. Ionic conductivity of gel polymer electrolytes at different temperatures.

$$\sigma(T) = AT^{-1/2} \exp[-B/k(T - T_0)] \quad [1]$$

where A is a constant proportional to the number of charge carriers, B is the pseudo-activation energy related to polymer segmental motion, k_B is the Boltzmann constant, and T_0 is a reference temperature associated with ideal T_g .¹⁸

Compared with the room temperature conductivity, around 1×10^{-2} S/cm, of EC/DMC/LiPF₆ liquid electrolytes, conductivity of pure PEGDA film was below 1×10^{-3} S/cm until the temperature reached about 60°C, but that of PEGDA/PVdF (1/2) film was as high as *ca.* 4×10^{-3} S/cm at ambient temperature and close to PVdF-HFP gel film. Note that the increase in ionic conductivity at higher PVdF content is related to better initial liquid solution retention in porous structure.

Impedance analysis was used to study interfacial phenomena of nonblocking Li/GPE/Li cells. Figure 7a shows a typical impedance spectrum of Li metal/GPE interface under open circuit condition. The interception 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). Figure 7b and c summarizes the change of R_e and R_i with time at 80°C. It is found that the R_e value of both PVdF-HFP and PEGDA/PVdF electrolytes were almost constant at room temperature within 90 h. PEGDA/PVdF blend electrolyte showed a slight increase in R_e even at 80°C, whereas PVdF-HFP displayed a rapid resistance increase after 24 h. This might result from faster solvent depletion from PVdF-HFP gel polymer structure at high temperature. In the case of interfacial resistance, the progressive expansion of R_i for PVdF-HFP indicates the continuous growth of a passivation layer on the Li metal surface.¹⁹ This resistive layer is known to be caused by the reaction between aprotic solvents and Li metal electrode. It is supposed that the passivation layer is not uniform in composition and density across the layer and the middle frequency semicircle is usually depressed.²⁰ For PEGDA/PVdF blend electrolyte, the rate of growth of R_i is reduced significantly after 24 h. It implies that there was no subsequent flow of corrosive solvents to the interface.²¹ It is evident from impedance results that PEGDA/PVdF blend electrolyte exhibits good affinity with liquid electrolytes and it is better reservoir for EC-based liquid electrolyte solution than pure PVdF-HFP gel electrolyte at high temperature.

MCMB/LiCoO₂ cell of 2×3 cm² area were assembled with PEGDA/PVdF blend electrolyte. The cycleability of Li_xCoO₂ is generally limited to $x = 0.5$, giving a practically specific capacity of

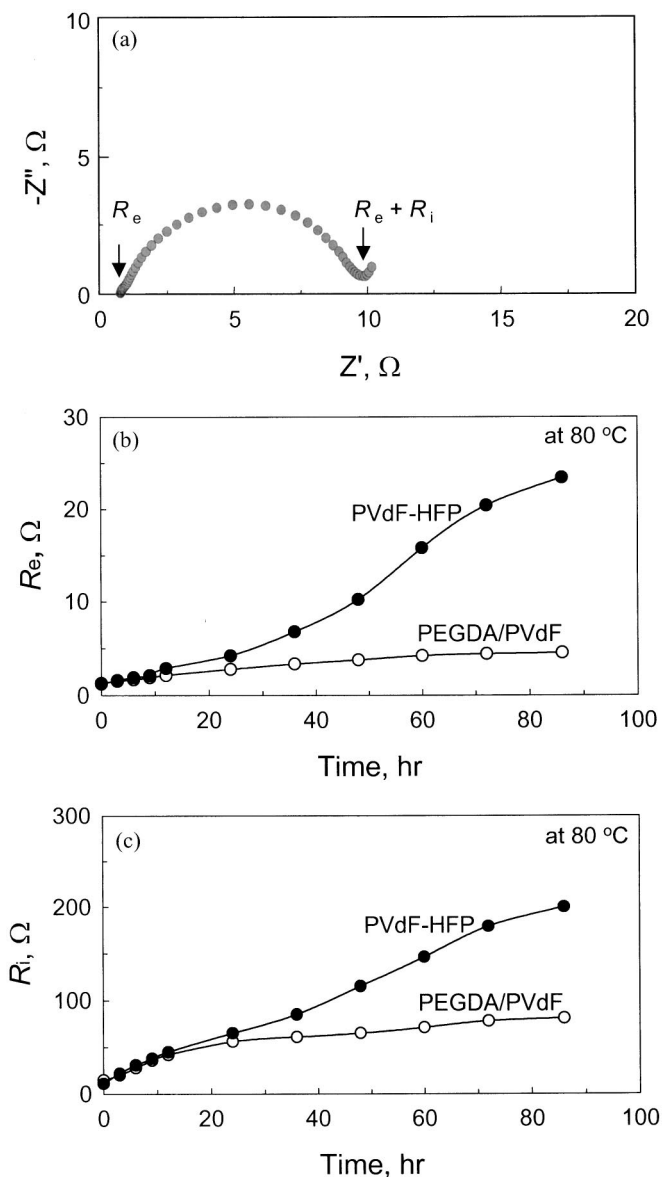


Figure 7. AC impedance spectra of Li/GPE/Li cells at 80°C: (a) PVdF and (b) PEGDA/PVdF (1/1).

ca. 120 mAh/g. For the value x of lower than 0.5, the oxidation of Co³⁺ to Co⁴⁺ becomes possible which may also transform the crystallinity of LiCoO₂ cathode affecting the crystal structure and thus cause decreasing in reversibility.²² Figure 8a shows cycle performance of MCMB/LiCoO₂ cells using different gel polymer electrolytes at room temperature. This cell was charged and discharged at C/2 rate (*ca.* 1.66 mA/cm²) between 3.0 and 4.2 V. The initial capacity of MCMB/PEGDA/LiCoO₂ was slightly increased up to 90 mAh/g in first few cycles because of initial poor interfacial contact between electrolyte and electrodes before cycling but the discharge capacity decreases rapidly in the following cycles. Both PVdF-HFP and PEGDA/PVdF (1/1) blend electrolytes display excellent cycle performance at room temperature. In the case of cell operation at 80°C, the capacity of the MCMB/PVdF-HFP/LiCoO₂ cell decreased steadily after the first 5 cycles and dropped below 70 mAh/g after 50 cycles whereas that of the PEGDA/PVdF blend was almost same to room temperature performance as shown in Fig. 8b. The capacity fading of PVdF-HFP could be caused by the continuing evaporation of -HFP liquid electrolytes and higher solubility in liquid electro-

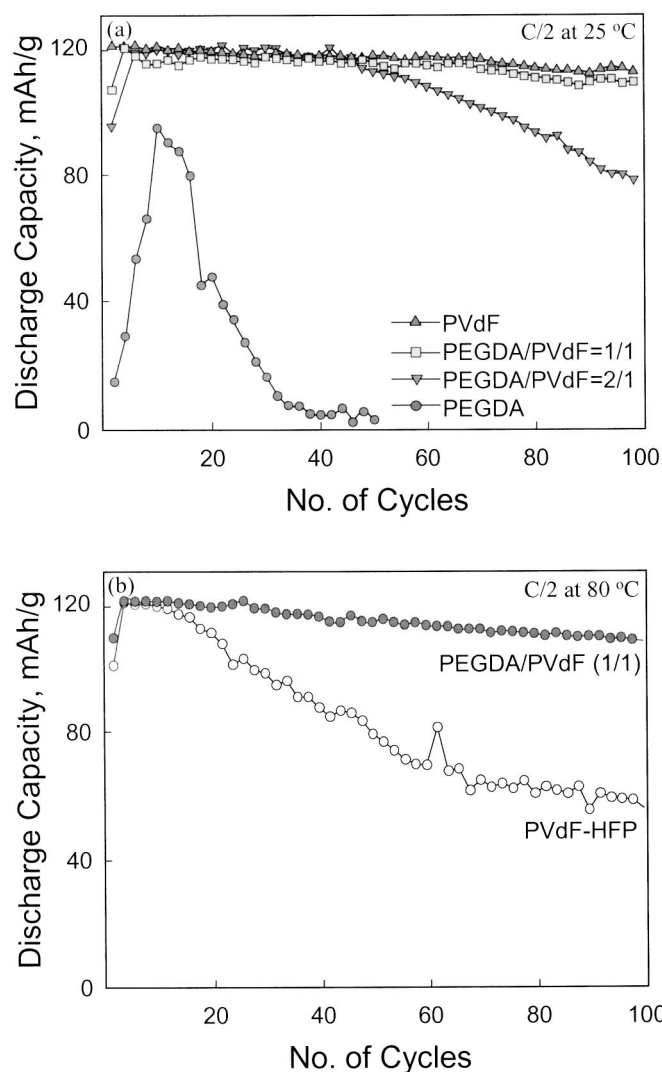


Figure 8. Cycle performance of MCMB/LiCoO₂ cell at 80°C: (a) PVdF and (b) PEGDA/PVdF (1/1).

lytes at 80°C, and it can be concluded that better structural and thermal stability improved high temperature performance for PEGDA/PVdF blend.

Rate dependency and low temperature performance were also tested. Figure 9 shows discharge profiles of the Li/(PEGDA/PVdF)/LiCoO₂ cells as a function of C rate. The intercalation of Li cation to LiCoO₂ gives rise to a voltage plateau at about 3.7 V vs. Li/Li⁺. It is clear from Fig. 9 that very good cycleability was realized for the PEGDA/PVdF (1/1) blend electrolyte when cycled between 3.0 and 4.2 V. The capacity at C/5 rate was assumed to be 100% capacity. At 1C rate, this cell delivered about 91% of the nominal cathode capacity at 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 lattice of LiCoO₂ and lower diffusion rate of lithium ions in the solid polymer electrolyte as compared with that in liquid electrolyte. At 2C rate, this cell delivered about 72% 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 condition for 24 h prior to charge/discharge reaction. As shown in Fig. 10, Li/(PEGDA/PVdF)/LiCoO₂ cell retained 92 and 76% of the room temperature discharge capacity at 0 and -10°C, respectively. The capacity loss at low temperature is

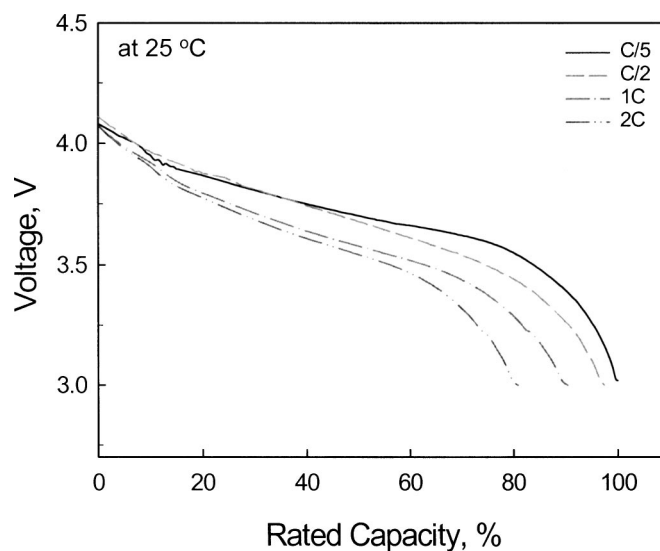


Figure 9. Rate capability of MCMB/(PEGDA/PVdF)/LiCoO₂ cells.

generally caused by large polarization of the lithium ions at the electrode/electrolyte interface.²³

Conclusion

Despite highly desirable ionic conductivity and mechanical properties of conventional PVdF-HFP gel polymer electrolytes, their poor liquid electrolyte retention and thermal instability appear to be major limitations to become a commercially viable alternative. It is known that the large pores in microporous PVdF-HFP films are responsible for fast evaporation of liquid electrolyte from the gel polymer structure.

We found that UV curing of a solution mixture of PEGDA oligomer and PVdF-HFP dissolved in EC-based liquid electrolyte produced miscible PEGDA/PVdF blends and they tended to have pore size intermediate between those of the separate components because PEGDA has dense morphology contrary to highly porous PVdF-HFP films. PEGDA/PVdF (1/1, wt/wt) blend gel electrolytes showed ionic conductivity of 4 mS/cm at room temperature, which is comparable to pure PVdF-HFP/EC/DMC/LiPF₆, and they were also electrochemically stable up to 4.6 V vs. Li/Li⁺. The weight

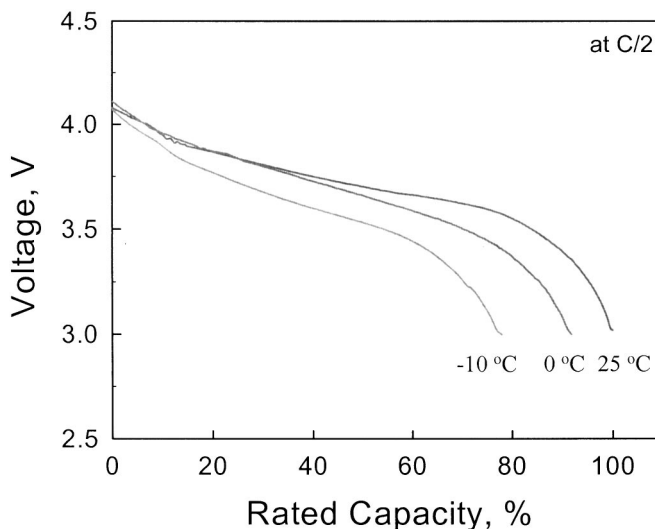


Figure 10. Low temperature performance of MCMB/(PEGDA/PVdF)/LiCoO₂ cells.

change measurement indicated that high temperature rapidly depleted liquid electrolyte from PVdF-HFP gel films, while structurally modified PEGDA/PVdF blend electrolytes showed much better liquid electrolyte retention. This enabled PEGDA/PVdF blends to maintain stable interfacial properties even at 80°C. As a result, both PVdF-HFP and PEGDA/PVdF gels delivered similar discharge capacity at room temperature, but PEGDA/PVdF showed much higher cycle performance than PVdF at 80°C. Thus, the synergetic results of PEGDA/PVdF blend system are thought to be highly suitable for commercial use.

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