

Preparation of porous, chemically cross-linked, PVdF-based gel polymer electrolytes for rechargeable lithium batteries

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Received 5 January 2004; accepted 2 March 2004

Available online 5 June 2004

Abstract

This study reports the development of a new system of porous, chemically cross-linked, gel polymer electrolytes based on poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF–HFP) copolymer as a polymer matrix, polyethylene glycol (PEG) as a plasticizer, and polyethylene glycol dimethacrylate (PEGDMA) as a chemical cross-linking oligomer. The electrolytes are prepared by a combination of controlled evaporation and thermal polymerization of PEGDMA. PVdF–HFP/PEG/PEGDMA gel polymer electrolytes with a composition of 5/3/2 exhibit both high ambient ionic conductivity, viz., $>1 \text{ mS cm}^{-1}$, and a high tensile modulus of 52 MPa, because of their porous and network structures. All the blends of electrolytes are electrochemically stable up to 5 V versus Li/Li⁺ in the presence of 1 M LiPF₆/ethylene carbonate–diethyl carbonate (EC–DEC). With these polymer electrolytes, rechargeable lithium batteries composed of carbon anode and LiCoO₂ cathode have acceptable cycleability and a good rate capability.

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Keywords: PVdF–HFP copolymer; Polyethylene glycol dimethacrylate; Chemical cross-link; Polymer electrolytes; Controlled vaporization; Lithium batteries

1. Introduction

Many gel polymer electrolytes comprising polymer matrices, plasticizing organic solvents and alkali metal salts have been intensively studied for applications in rechargeable lithium batteries and other electrochemical devices [1–3]. Electrolytes with reduced thickness and improved ionic conductivities are technical goals for increasing the power density. Gel polymer electrolytes in the form of very thin films act simultaneously as transport for lithium ions, separator, and binder between the negative (anode) and positive (cathode) electrodes. Although gel polymer electrolytes with high ionic conductivity ($>1 \text{ mS cm}^{-1}$) can usually be achieved by adding large amounts of organic solvents, they do not have sufficient mechanical ruggedness to withstand winding and stacking during manufacturing, or the stress that arises from morphological deformation of the electrode during repeated charge–discharge [3–6].

Various approaches to increasing the mechanical strength have been proposed recently. Inorganic fillers, such as fume silica, zeolite, clay, Al₂O₃ or glass fiber have been added to strengthen the dimensional stability of gel polymer electrolytes [7–11]. Microphase-separated method has also been adopted and found to be effective. Systems such as PEO/PMMA [12], PVdF/HDPE [13], PEG/PEO [14] and PMMA/PVC [15] fall into this category. Microporous membranes of polyolefins such as polyethylene and polypropylene, impregnated with gel polymer electrolytes have been developed [5,16]. In these membrane-supported electrolytes, polyolefins possess excellent mechanical properties and the gel can trap electrolyte solution without leakage. Another type has been prepared via the chemical cross-linking method [17–20]. Most gel systems today are prepared by forming temporary physical cross-links via physical interactions such as crystallites or hydrogen bonds between the chains. These gel polymer electrolytes may undergo solvent exudation from the physical cross-linked structure on long storage, and may also dissolve and lose their mechanical integrity at high temperature [21]. By contrast, chemically cross-linked gel polymer electrolytes possess chemical cross-links that are permanent and remain thermally stable up to the decomposition temperature of the components. Hence, the chemical cross-linking method

Abbreviations: PEO, polyethylene oxide; PMMA, poly(methyl methacrylate); PVdF, poly(vinylidene fluoride); HDPE, high density polyethylene; PEG, polyethylene glycol; PVC, polyvinyl chloride

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clearly shows not only better dimensional stability, but also thermal stability. It exhibits no solvent exudation and is easy to control [21,22]. Therefore, this method has been used in the present study to develop new gel polymer electrolytes.

Beside the concern over mechanical strength, the process to fabricate gel polymer electrolytes requires a moisture-controlled environment because of the high sensitivity of lithium salts to water, which amounts to high equipment cost and inconvenient operation. Researchers of Telcordia Technologies (formerly Bellcore) overcame these difficulties and developed microporous poly(vinylidene fluoride-co-hexafluoropropylene (PVdF–HFP)-based polymer electrolytes [23–26], in which the microporous structures made by the plasticization/extraction procedure can enhance the electrolyte uptake, thus improving the ionic conductivity and rate capability. Consequently, a critical moisture-controlled environment is only needed during the last activation step. Nevertheless, the extraction step is still inconvenient—it increases the production cost and presents safety concerns related to the handling of large volumes of extracting solvents. Therefore extraction-less processes to prepare microporous polymer electrolytes have been developed by using volatile plasticizers [27], a phase inversion process with controlled evaporation (solvent/non-solvent) [28–30], and liquid immersion [31–33].

In this study, an attempt is made to combine both the chemical cross-linking method and the controlled evaporation process to prepare porous, chemically cross-linked, gel polymer electrolytes. The advantage of this combined approach is that the ionic conductivity and mechanical properties can be controlled independently by designing properly the structure of the polymer electrolyte, and by selecting a suitable liquid electrolyte solution. Furthermore, the polymer membranes can be manufactured in an ambient environment.

2. Experimental

2.1. Preparation of gel polymer membranes and electrodes

For the preparation of chemically cross-linked PVdF–HFP (Elf Atochem, Kynar 2801)-based gel polymer electrolytes, the required amount of PVdF–HFP was first dissolved in acetonitrile (Riedel deHaën) to form a homogeneous solution. The solution was then mixed with plasticizer, polyethylene glycol (PEG, $M_w = 400$, Lancaster), and a cross-linking agent, PEGDMA oligomer (Aldrich, $M_w \sim 330$), at 50 °C for 1 h. An initiator, 2,2'-azobisisobutyronitrile (AIBN, Showa), was later added to the PVdF–HFP/PEG/PEGDMA solution. The resulting viscous solution was cast with a doctor blade on to a Teflon plate. After natural evaporation of the acetonitrile, self-supporting polymer membranes were formed. The polymer membranes were then heated in oven at 80 °C for 12 h to polymerize the PEGDMA. The porosity of the membrane was increased by means of both

vacuum evaporation and controlled evaporation. In the case of vacuum evaporation, the viscous polymer solution cast on the Teflon plate was heated immediately in a vacuum oven without natural evaporation of the acetonitrile.

For controlled evaporation, a 3:1 v/v mixture of acetone (Aldrich) and methanol (ALPS Chem) was used as the casting solvent in place of pure acetonitrile. The subsequent steps were the same as in the former process of natural evaporation. The resulting porous PVdF–HFP/PEF/PEGDMA blended films (50–70 μm thickness) were used as polymer electrolytes for electrochemical and mechanical studies.

The carbon anode was prepared by coating a slurry of meso-carbon micro-beads (MCMB 1028, Osaka gas), PVdF–HFP, super-P carbon (Erachem) and *N*-methyl-2-pyrrolidinone (NMP, Tedia) on to a copper foil. The cathode was a mixture of LiCoO₂ (Seimi), PVdF–HFP and acetylene black (Lonza) that was cast on to aluminum foil. The electrodes were dried at 110 °C overnight under vacuum. The electrodes were roll-pressed under an appropriate pressure to obtain uniform thickness. The active mass loading was adjusted to a capacity of about 3.0 mAh cm⁻². The anode and cathode electrodes were punched into discs of 13 or 12 mm in diameter and transferred into an argon-filled glove-box (VAC) for storage.

2.2. Morphology and electrolyte uptake

The cross-sectional morphology of the polymer membrane was observed by scanning electron microscopy (SEM) (JEOL, JSM-840) under vacuum (10⁻¹ Pa) after sputtering with gold at 10 mA for 1 min.

The polymer membranes were transferred to an argon-filled glove-box and soaked in an electrolyte solution containing 1 M LiPF₆ (Ferro) dissolved in EC–DEC (1:1 v/v, Ferro). The liquid electrolyte uptake was evaluated according to the relationship:

$$\text{uptake (\%)} = \frac{W - W_0}{W_0} \times 100 \quad (1)$$

where W and W_0 are the weights of the wet and dry membrane, respectively.

2.3. Electrochemical and mechanical measurements

The ionic conductivities of the polymer electrolytes were determined with an Autolab frequency response analyzer (Eco Chemie) at an ac amplitude of 10 mV over the frequency range of 1 kHz to 0.5 MHz at room temperature. The samples were sandwiched between two electrodes (0.5 cm² in area) that were made from 316 stainless-steel (SS) in a probe equipped with a thickness gauge. The ionic conductivity (σ) was then calculated from the electrolyte resistance (R_b) obtained from the intercept of the Nyquist plot with the real axis, the membrane thickness (l), and the electrode area (A) according to the equation $\sigma = l/AR_b$.

The electrochemical stability window was examined for a cell of configuration Li foil | polymer electrolytes | SS by linear sweep voltammetry (LSV) at 5 mV s^{-1} . The liquid electrolytes included different lithium salts, such as LiClO_4 , LiBF_4 and LiPF_6 .

The mechanical properties of the polymer membranes were measured by the ASTM D882 procedure with a universal tensile meter (IMADA). The test specimens were 5 mm in width and 10 mm in length. The tensile rate was controlled at 25 mm per min.

2.4. Cell testing

Lithium cells using porous, chemically cross-linked, gel electrolyte were assembled by sandwiching the polymer electrolyte (containing 1 M LiPF_6 in EC–DEC) between a LiCoO_2 cathode and an MCMB anode in coin cells (thickness = 3 mm and diameter = 20 mm). All assemblies were conducted in an argon-filled glove-box in which the water content was below 10 ppm. Cycling tests of the cells were performed with a Maccor battery tester (Maccor Series 4000) at the 1 C rate with voltage cut-off limits of 2.7 and 4.2 V. Rate capability tests were conducted charging the cells at 0.1 C to 4.2 V, followed by 0.1, 0.2, 0.5, 1 and 2 C to 2.7 V, respectively.

3. Results and discussion

3.1. Characterization

The cross-sectional morphology of a porous, chemically cross-linked, polymer electrolyte, e.g., PVdF–HFP/PEG/PEGDMA (5/3/2), was identified by SEM as shown in Fig. 1. It is found that both vacuum evaporation and controlled evaporation can produce porous structures in the electrolyte membranes. By contrast, membranes prepared by natural evaporation have a non-porous continuous structure. The formation of porous structures is kinetically controlled by the volatility of the casting solvent. These solvents in-

clude acetone, methanol and acetonitrile that boiling points of 56, 65 and 81°C , respectively. In the case of controlled evaporation (acetone/methanol = 3/1), the polymer solution becomes richer in methanol (non-solvent) when the acetone (good solvent) is evaporated, and then the polymer is precipitated in the non-solvent phase. A porous structure is formed in the polymer matrix after evaporation of methanol [30]. The formation of a porous structure was also obtained by rapid evaporation of acetonitrile in vacuum evaporation. In the case of natural evaporation, no porous structures were observed due to the slow evaporation of acetonitrile.

Furthermore, membranes prepared by controlled evaporation are found to exhibit higher porosity and a more uniform structure than those prepared by vacuum evaporation, as shown in Fig. 1(b) and 1(c). The software, SigmaScan Pro, was used to evaluate the pore size on the surface, and the porosity of the membrane can then be estimated by [5,34]:

$$\sigma_m = \sigma_s \frac{P}{T^2} \quad (2)$$

where σ_m and σ_s represent the ionic conductivity of the membrane electrolyte and the base electrolyte, respectively; P and T are the porosity and tortuosity of the membrane, respectively.

The porosity of the membranes prepared by controlled evaporation and vacuum evaporation was estimated to be about 15 and 5%, respectively. Usually, a larger porosity leads to higher ionic conductivity of the membrane [35]. Therefore, it might be expected that the gel polymer electrolytes prepared by controlled evaporation possess higher liquid electrolyte uptake and ionic conductivity than those prepared by vacuum evaporation or natural evaporation.

The liquid electrolyte uptake of PVdF–HFP/PEG/PEGDMA polymer membranes with various compositions is shown in Fig. 2. In order to estimate the influence of the chemical cross-linking structure on the electrolyte uptake of the membranes, PVdF–HFP/PEG/PEGDMA membranes without chemical cross-linking structure were prepared for comparison. Apparently, the liquid electrolyte uptake decreases when the PEGDMA content in the chemically

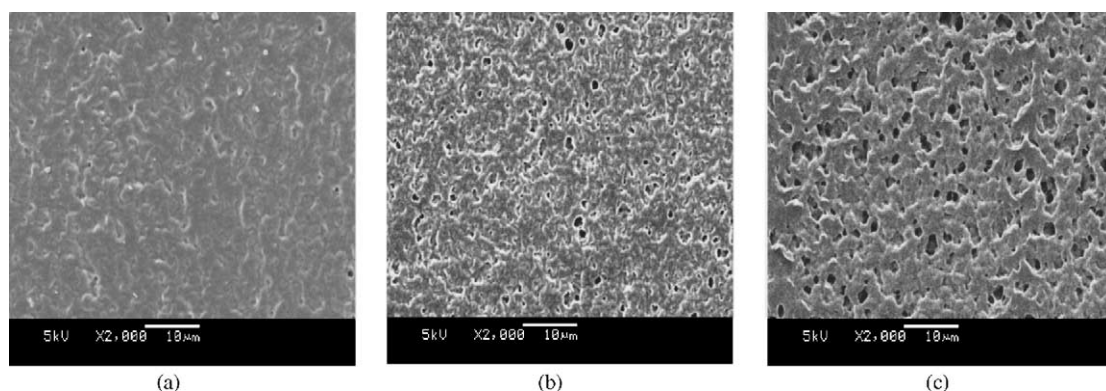


Fig. 1. Scanning electron micrographs of the surface morphology of chemically cross-linked PVdF–HFP/PEG/PEGDMA (5/3/2) gel polymer electrolytes prepared by (a) natural evaporation, (b) vacuum evaporation, and (c) controlled evaporation.

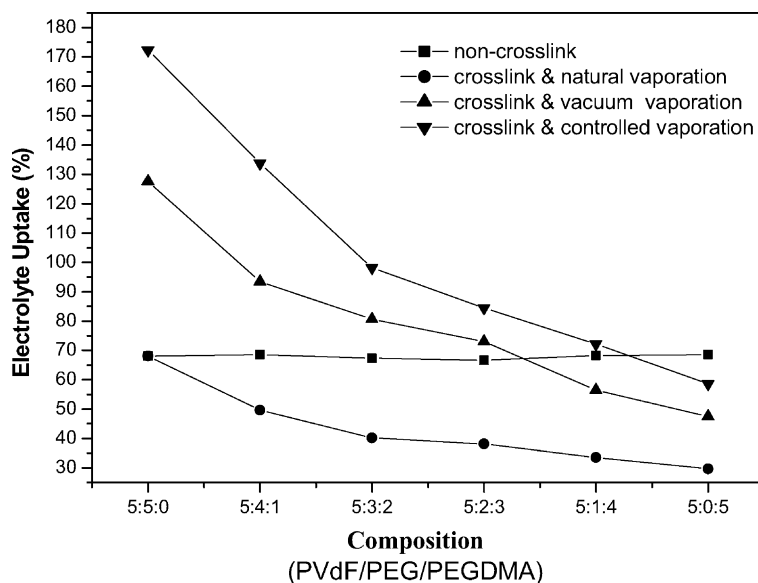


Fig. 2. Liquid electrolyte uptake as function of composition of PVdF–HFP/PEG/PEGDMA polymer membranes.

cross-linked membranes increases. By contrast, the electrolyte uptake remains almost constant in polymer membranes without a chemically cross-linked structure. This is related to the cross-linking density in the polymer membrane. A high density results in a dense structure that hinders the swelling of the polymer chain by liquid electrolyte. On the other hand, in the case of polymer membranes without chemical cross-linking structure, viscous PEGDMA oligomer acts as plasticizer, i.e., the same function as PEG. For this reason, the electrolyte uptake of the PVdF–HFP/PEG/PEGDMA membranes without a chemical cross-linking structure is almost constant and independent of the ratio of PEG to PEGDMA.

Membranes prepared by controlled evaporation exhibit higher liquid electrolyte uptake than those prepared either by vacuum evaporation or by natural evaporation. This difference in electrolyte uptake may be attributed to the porosity of the membrane. Saito and coworkers [36,37] proposed that the liquid electrolyte uptake was composed of two distinct steps in a porous, PVdF-based, gel polymer membrane. First, the liquid electrolyte entered the pores of the membrane from the outside. Then, the liquid electrolyte temporarily trapped in the pores penetrated into the polymer chain to form a swollen gel. It was also found that the electrolyte uptake in the membrane was controlled by the porosity. In the present study, however, the porosity of the gel polymer membranes is below 15%, and the polymer matrix constitutes above 85% of the volume. Thus, the liquid electrolyte absorbed in the matrix should not be ignored and, accordingly, the electrolyte uptake of the chemically cross-linked PVdF–HFP/PEG/PEGDMA membranes prepared by controlled evaporation or vacuum evaporation is affected by the PEGDMA content, as shown in Fig. 2.

3.2. Electrochemical properties

The ionic conductivity of PVdF–HFP/PEG/PEGDMA electrolyte containing 1 M LiPF₆/EC–DEC is shown in Fig. 3. The ionic conductivity of the electrolyte without a chemically cross-linked structure is above 1 mS cm⁻¹ at any composition. In the case of chemically cross-linked electrolytes, the ionic conductivity decreases with increase in PEGDMA content because of the network of chemically cross-linked PEGDMA. In addition, the ionic conductivity of an electrolyte with a porous structure is higher than that without a porous structure. Among these porous electrolytes, the ionic conductivity of PVdF–HFP/PEG/PEGDMA electrolyte prepared by controlled evaporation can reach above 1 mS cm⁻¹ if the PEGDMA content is below 20%.

According to Saito and coworkers [36,37], lithium ion migrates through the porous membrane via two different environments: the liquid state, which is within the porous structure, and the gel state, which is the swollen polymer matrix. Further, it was found that the migration of lithium ion in the porous gel was dominated by the gel state. This implies that the ionic conductivity of the porous membrane is mainly determined by the ionic mobility inside the gel state. The chemically cross-linked structure formed by thermal polymerization of PEGDMA results in a decrease in ionic mobility in the gel state, but this is compensated by the more porous structure obtained by controlled evaporation. The acceptable criterion of ionic conductivity for a polymer electrolyte is 1 mS cm⁻¹, so the PEGDMA content should be controlled below 20% in this system.

The electrochemical stability window of an electrolyte is generally determined by linear sweep voltammetry [38]. A polymer electrolyte for use in rechargeable lithium batteries must be stable within the range of its operating voltage,

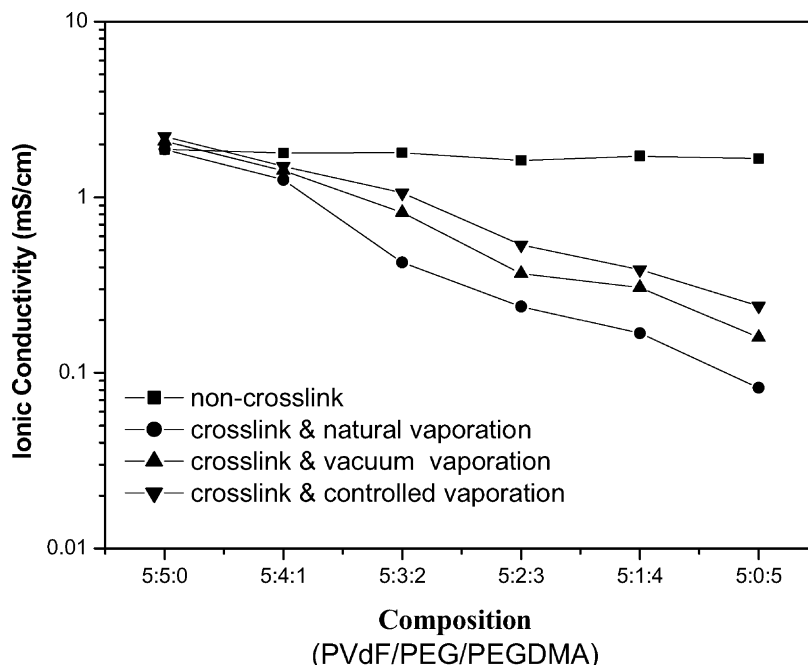


Fig. 3. Ionic conductivity of PVdF-HFP/PEG/PEGDMA gel polymer electrolytes containing 1 M LiPF₆/EC-DEC.

usually above 4.5 V versus Li/Li⁺, and show no oxidation peak due to decomposition over the voltage range. In this work, the electrochemical stability was examined by altering the composition of PVdF-HFP/PEG/PEGDMA containing 1 M LiClO₄/EC-DEC, or by altering the lithium salts (e.g., LiClO₄, LiBF₄ and LiPF₆) in the liquid electrolyte that was soaked in the PVdF-HFP/PEG/PEGDMA (5/3/2) membrane.

The electrochemical stability windows of porous polymer electrolytes containing 1 M LiClO₄/EC-DEC at room tem-

perature are presented in Fig. 4. For all compositions, the anodic potential limit almost always appears at about 4.8 V versus Li/Li⁺. This indicates the formation of ClO₂ and HCl from the decomposition of ClO₄⁻ ions above 4.5 V [39].

The electrochemical stability windows of polymer electrolytes containing various lithium salts, including LiClO₄, LiBF₄ and LiPF₆, are shown in Fig. 5. Among them, the anodic potential limit of the polymer electrolyte soaked in 1 M LiPF₆/EC-DEC is the most stable and reaches higher than 5 V versus Li/Li⁺. According to the results of Figs. 4

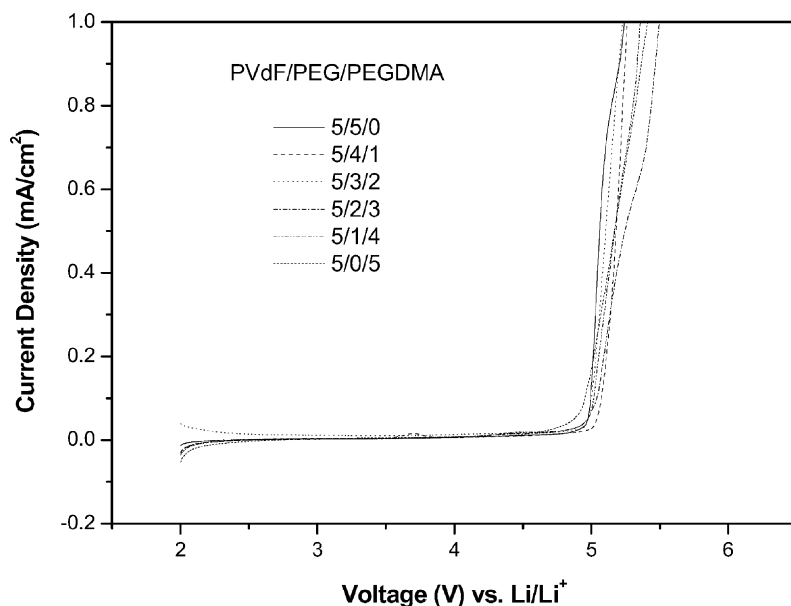


Fig. 4. Electrochemical stability window of porous, chemically cross-linked PVdF-HFP/PEG/PEGDMA gel polymer electrolytes containing 1 M LiClO₄/EC-DEC.

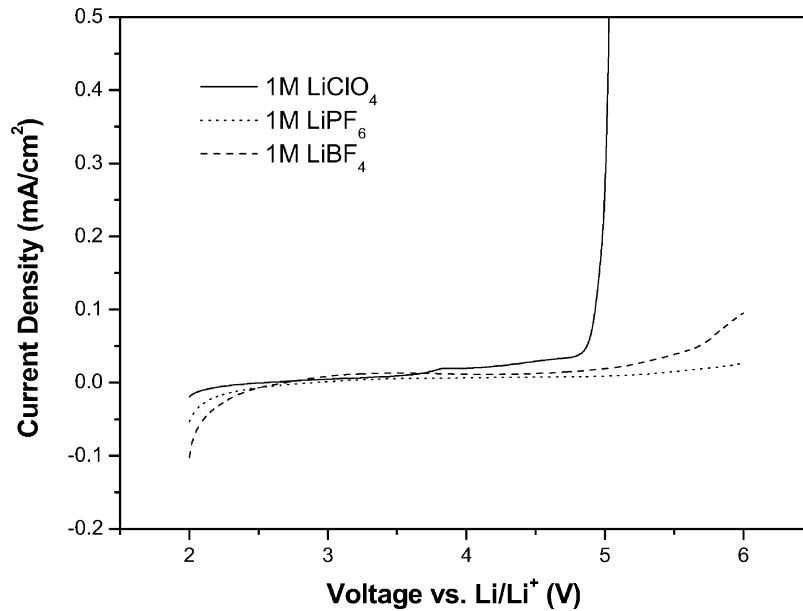


Fig. 5. Electrochemical stability window of porous, chemically cross-linked, gel polymer electrolytes (PVdF-HFP/PEG/PEGDMA = 5/3/2) as functions of various lithium salts including LiClO_4 , LiPF_6 and LiBF_4 .

and 5, the oxidation of polymer electrolytes depends mainly on different lithium salts, which suggests that the decomposition of lithium salts is a major factor. The decomposition potentials of these liquid electrolytes do not, however, clearly show whether the solvent or the salt, or both, are involved in the oxidation processes [40,41]. Nevertheless, the anodic potential limits of all liquid electrolytes are above 4.5 V, which demonstrates their potential for high-voltage lithium battery systems.

3.3. Mechanical properties

From a practical point of view, the required mechanical properties are high tensile modulus and better flexibility [3]. A high tensile modulus can withstand the stress induced by winding and stacking, and flexibility can make the polymer electrolyte more convenient to be rolled or folded into its finished shape. Data on the tensile modulus and tensile elongation at break are given in Figs. 6 and 7,

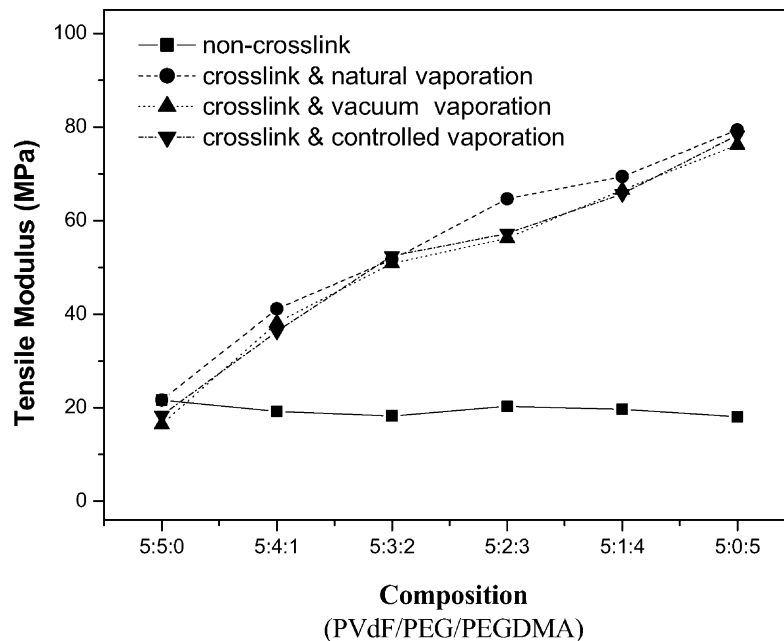


Fig. 6. Tensile modulus of PVdF-HFP/PEG/PEGDMA polymer membranes.

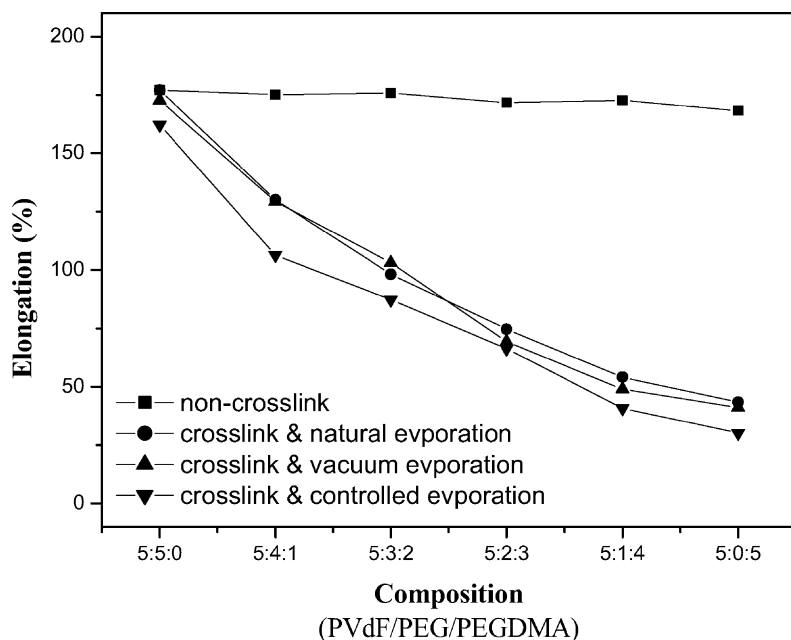


Fig. 7. Tensile elongation of PVdF-HFP/PEG/PEGDMA polymer membranes.

respectively, as a function of blend composition. The results demonstrate that the tensile modulus of this material can be enhanced when the PEGDMA content is increased. In the case of PVdF-HFP/PEG/PEGDMA (5/3/2) gel polymer membranes, the chemical cross-linking structure improves the tensile modulus from 20 to ca. 50 MPa. Nevertheless, the tensile elongation decreases when the PEGDMA content increased at the same time. The tensile elongation at break of the PVdF-HFP/PEG (5/5) is above 150%, but that of chemically cross-linked PEGDMA films is near zero due to their high brittleness. Therefore, the chemically cross-linked PVdF-HFP/PEG/PEGDMA gel polymer membranes prepared in this work reveal more flexibility than chemically cross-linked PEGDMA. In addition, the membrane exhibits a higher tensile modulus and lower elongation than the polymer membrane without a chemical cross-linking structure. The increase in the tensile modulus might be related to entanglement of the PVdF-HFP polymer chain and the PEGDMA network, i.e., the interpenetrating polymer network [42,43]. In this blend system, unraveled PVdF-HFP polymer chains with high molecular weight ($M_w = 4.77 \times 10^5$) are randomly mixed with liquid PEGDMA oligomer, which are then entangled with the PEGDMA network formed by the PEGDMA oligomer after curing. Therefore, the chemical cross-linking structure is eventually accompanied by physical cross-linking of the PVdF-HFP polymer chain.

In addition, the results also show that the tensile modulus of the electrolytes depends directly on the PEGDMA content, rather than on the existence of a porous structure. This implies that the interpenetrating polymer network with a physical and chemical cross-linking structure determines

the tensile modulus of the PVdF-HFP/PEG/PEGDMA gel polymer electrolytes.

3.4. Battery performance

According to the above observations on morphology, electrolyte uptake, ionic conductivity, electrochemical stability and mechanical properties, the porous chemically cross-linked PVdF-HFP/PEG/PEGDMA gel polymer electrolytes prepared by controlled evaporation exhibit superior potential for rechargeable lithium batteries. Among these polymer electrolytes, the PVdF-HFP/PEGDMA (5/3/2) electrolyte displays simultaneously high ionic conductivity (1.06 mS cm^{-1}), high tensile modulus (52 MPa), and a wide electrochemical window. It was therefore used to make coin cells for performance testing.

The rate capabilities of a MCMB|polymer electrolyte|LiCoO₂ cell at room temperature are presented in Fig. 8. It appears that a high-rate capability is realized for this type of electrolyte due to its high ionic conductivity and porous structure. At the 1 C rate, the cell can deliver about 91% of its C/2 capacity. Even at a high 2 C rate, the cell can still deliver about 80% of its C/2 capacity.

The cycleability of the MCMB|polymer electrolyte|LiCoO₂ cell at the C/2 rate between 2.7 and 4.2 V at room temperature is shown in Fig. 9. The initial capacity increases slightly to $120 \text{ mAh}^{-1} \text{ g}$ during the first few cycles. Then, the capacity decreases slowly during cycling and retained about 85% of the initial discharge capacity after 50 cycles. This result is essentially acceptable as compared with that using a commercial separator, such as Celgard[®] 2300.

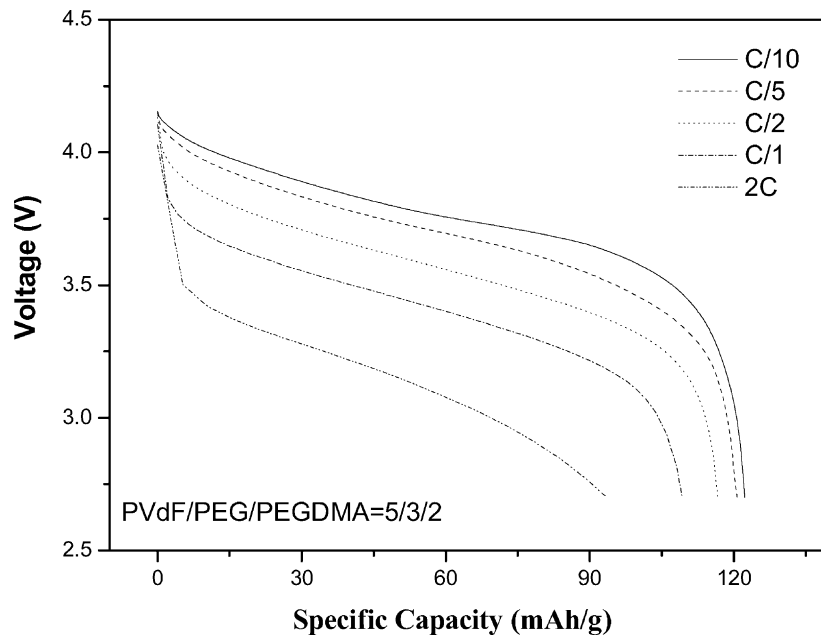


Fig. 8. Rate capability of MCMB|porous chemically cross-linked gel polymer electrolyte|LiCoO₂ cell with controlled evaporation and activated by 1 M LiPF₆ in EC–DEC (1:1 v/v) at room temperature.

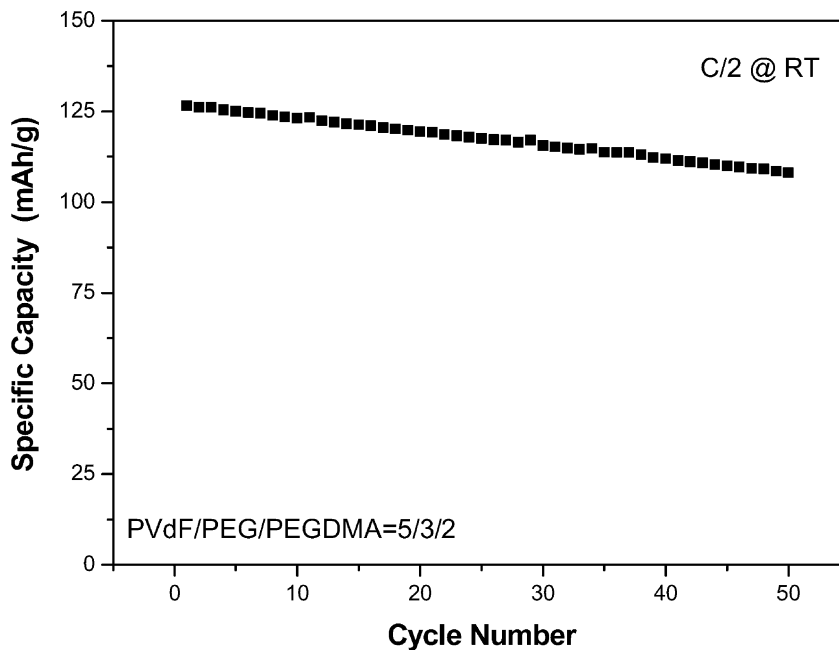


Fig. 9. Cycleability of MCMB|porous chemically cross-linked gel polymer electrolyte|LiCoO₂ cell with controlled evaporation and activated by 1 M LiPF₆ in EC–DEC (1:1 v/v) at C/2 rate at room temperature.

4. Conclusions

A new porous, chemically cross-linked, gel polymer electrolyte system based on PVdF–HFP/PEG/PEGDMA blend. The chemical cross-linking structures formed by PEGDMA oligomer support the mechanical strength of the polymer electrolytes. The polymer chains of PVdF–HFP plasticized by PEG become more flexible and improve the mobility of the lithium ions. Porous structures formed by

controlled evaporation instead of the inconvenient extraction process, which is currently practiced, can facilitate the absorption of liquid electrolytes and contribute to high battery performance. Furthermore, all the operations involved can be carried out under an ambient environment, and a critical moisture-controlled environment is only required during the last activation step. A so-prepared PVdF–HFP/PEG/PEGDMA (5/3/2) electrolyte containing 1 M LiPF₆/EC–DEC shows high ionic conductivity of about

1 mS cm⁻¹ at room temperature and an acceptable tensile modulus of 52 MPa. This polymer electrolyte also has a high electrolyte uptake of about 98% and wide electrochemical stability up to 5 V versus Li/L⁺. Thus, the polymer electrolyte developed in this study shows promise for application in rechargeable lithium batteries.

Acknowledgements

This work has been supported by the Materials Research Laboratories of Industrial Technology Research Institute. The authors would especially like to thank Dr. Yih-Song Jan and Dr. Mao-Sung Wu for helpful discussion and assistance.

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