**SODIUM ION CONDUCTING GEL POLYMER ELECTROLYTE USING POLY(VINYLIDENE FLUORIDE HEXAFLUOROPROPYLENE)**

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**Keyword: ionic conduction, gel polymer electrolyte, PVdF-HFP, electrochemical stability, sodium batteries.**

**Abstract**

Gel polymer electrolyte (GPE) films using polyvinylidene fluoride – hexafluoropropylene (PVdF – HFP) matrix were prepared for aim to achieve good sodium-ion conductivity at room temperature. GPE of PVF-HFP were formed by microporous PVDF-HFP membranes filled and swollen in different liquid electrolytes: GPEs were formed by microporous PVDF-HFP membranes filled and swollen in different liquid electrolytes: NaClO4, NaPF6 and NaTFSI salts dissolved in mixtures of carbonate solvents (propylene carbonate (PC), fluoroethylenecarbonate (FEC)) or ionic liquids (1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide and 1-butyl-3-methyl bis(trifluoromethanesulfonyl)imide). The effect of different electrolytes on the structure and morphology, electrolyte absorption and sodium ionic conductivity of activated membrane were investigated. GPEs showed “sponge-like” structure with high porosity of 80 – 85 % and large pore size. The ionic conductivity of GPEs reached 1-2 mS.cm-1 at room temperature. Sodium intercalation into Na0.44MnO2 electrode was performed in coin-cell type by using GPEs as conduction media. Cycling data of sodium cell using PVdF-HFP/NaClO4 1M-PC:2%FEC exhibited an excellent stable specific capacity of 100 mAh.g-1 at room temperature.

**Key words: gel polymer electrolyte, PVdF-HFP, liquid electrolyte, ionic liquid, ionic conductivity, electrochemical stability, sodium batteries.**

**1. Introduction.**

Nowadays, energy conversion and storage are central to research and development in the field of sustainable energy technology. Since lithium-ion batteries (LIBs) were first commercially released in 1991, they have given raises for the development of portable computers, mobile phones, electric cars, and many other electronic devices [1]. Although LIBs have been widely used due to its highest voltage and highest specific capacity, Li-metal abundance is limited and mostly concentrated in South America [2]. Therefore, it restricts the application of LIBs in large scale and significantly increases the cost of lithium resources. Hence, it is necessary to find the substitutable materials which can fulfil the abundant and environmental safety requirements.

Recently, sodium (Na) has attracted much attention as the most promising alternatives to the existing LIBs [3,4]. Na possesses several advantages against Li such as natural abundance, cost-effective and low-toxicity. Moreover, Na has a redox potential of -2.71 V vs. SHE (only 0.3 V above that of Li) and performed similar properties as Li [5]. Therefore, many efforts have been devoted to achieving better sodium-ion batteries (SIBs) for large-scale applications [3,4].

Many attempts to replace volatile and flammable organic solvents have been reported for rechargeable cells due to the liquid leakage, corrosion with electrodes, volatility and flammability of organic solvents [6-8]. Among various alternative electrolytes, gel polymer electrolyte (GPE) have been the subject of interests because of its relatively good conductivity and high ion transport number. GPE were firstly introduced for LIBs but are much less studied for SIBs application [9]. GPE is comprised liquid electrolytes immobilized in different polymer hosts, e.g. poly(vinylidene fluoride) (PVdF), poly(viny-lidene fluoride-co-hexafluoropropylene) (PVdF-HFP), poly(vinyl pyrrolidone) (PVP), poly(methyl methacrylate) (PMMA) or the blend polymer (PVdF-PVP; PVdF-PMMA,…) [10-15].

Many studies revealed that copolymer PVdF – HFP could be a promising polymer host for lithium-ion batteries [16-19]. In fact, the properties of PVdF-HFP copolymer include both PVdF and PHFP properties. The melting point of copolymer is about 130 - 140oC, lower than pure PVdF (170oC) [20]. In comparing with PVDF, PVdF-HFP possesses lower crystallinity and higher free volume due to the incorporation of an amorphous phase of HFP. Therefore, it keeps the balance between the mechanical properties and ionic conductivity of polymer membrane. Moreover, copolymer shows high flexibility as compared to PVdF, and dielectric constant of 8.4, which favors the large dissolution of lithium salts and subsequent support of high concentration of charge carriers [18]. The dispersion of ceramic filler is an important approach to reinforce mechanical and thermal properties of GPE, referred as “composite GPEs”. Generally, the ceramic fillers are Al2O3, SiO2, ZrO2, TiO2.The employed fillers are divided into two categories: active and passive type. The filler particles like Al2O3, SiO2, ZrO2 etc. do not directly participate in the ion transport, whereas the active fillers like Li3N, LiAlO2, Na-β-alumina, etc. are involved in the ion conduction process in composite GPEs [19-22].

Due to the high oxidation and high thermal stability of GPEs using PVdF-HFP matrix, this polymer has been proposed so far for SIBs application. In our knowledge, few studies on sodium – ion conducting using GPE containing organic solvents or ionic liquids have been reported for sodium metal or graphitizable anode rechargeable batteries [23, 24]. Herein, gel-polymer electrolytes based on PVdF-HFP with different liquid electrolytes embedded in polymer matrix were investigated to enhance the safety for long-term cycling in sodium battery application. The porous structure of PVdF-HFP membrane after swelling in liquid electrolytes ensures the mobility of ions through the pores and micrometer-sized channels and allow a favorable ionic conductivity at room temperature. The thermal properties and morphology of GPE were performed and compared for different embedded electrolytes. The electrochemical compatibility and performance related to sodium intercalation/extraction have been studied in sodium half-cell using Na0.44MnO2 as cathode material.

**2. Materials and methods**

*2.1 Preparation of PVdF-HFP copolymer*

The host co-polymer poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP, Sigma Aldrich, average molecular weight approximately 400.000 g/mol) was dissolved in an absolute acetone (Chemsol, analytical grade, Vietnam) by mechanical stirring under reflux at 40 oC. The concentration of PVdF-HFP is 5 %w/w in acetone solution. Deionized water (2 wt.%) was added into the solution as non-solvent. After 2-hours stirring, 5 mL homogeneous solution was poured on a well cleaned petri glass plate of 10 cm diameter. When the evaporation of acetone was completed, the homogenous white membrane was obtained. The membrane was dried under vacuum at 80 oC for 24 hours and stored in argon atmosphere.

*2.2 Preparation of gel polymer electrolyte*

1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide (EMITFSI, 99.8 %) and 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide (BMITFSI, 99.8 %) and sodium bis(trifluoromethane-sulfonyl)imide was purchased from Sigma Aldrich. The dried membranes were soaked in organic electrolytes (at room temperature) purchased from Kanto Chemical Co, Japan (1.0 M NaClO4 or NaPF6 solutions in propylene carbonate (PC) or mixture propylene carbonate: fluoroethylene carbonate (FEC) = 98:2 (% in volume)) to obtain the gel polymer electrolyte (GPE) for further characterization. For ionic liquid-based electrolyte, the membrane was soaked in solution of 0.5 M NaTFSI dissolved in EMITFSI or BMITFSI as solvent.

*2.3 Porosity and thermal characterization*

Porosity (P) of membranes was calculated from Eq (1):

Porosity = [1 – mreal/(dPVdF-HFP  Vmembrane)] 100% (1)

Where mreal is the weight of membrane after the absorption of electrolyte; is the density of pristine membrane (1.77 g/ml), and Vmembrane is the volume of the membrane, deduced from surface area (S = 0.785 cm2), thickness of membrane is measured after electrolyte uptake. For pristine membrane, mreal is the original weight.

Thermogravimetric analysis (TGA) coupled with Differential scanning calorimetry (DSC) of GPE membranes were carried out in argon atmosphere from room temperature to 800 oC with heating rate 10 oC/minute by utilizing a LabSYS Evo TG-DSC 1600. Before analysis, GPEs were weighed to calculate the weight loss. When the sample reach 800oC, the cooling step was started naturally in air without controlled-temperature.

*2.4 Structure and morphology of membrane*

Membrane structure was analyzed before and after swelling in the electrolyte by using a Bruker D8 Advance Diffractometer (Brucker) using a Cu Kα1 radiation source (λ = 1.5406 Å). The data were collected in the range of diffraction angle 2θ from 10 o to 80 o with the step size of 0.05o/step, 1 second per step.

Surface morphology of pure membrane and GPE was investigated by using S4800 HITACHI Field Emission Scan electron microscope (FE-SEM), Japan. The membranes were sputtered with platinum using a current of 30 mA, acceleration voltage of 3 kV in 10 minutes prior to SEM measurements. The pores size of polymer membrane could be manually estimated by using scale bar of acquired SEM images. Average values were calculated for whole pores on the SEM images.

*2.5 Ionic conductivity and electrochemical characterization*

The ionic conductivities of GPE were measured by Electrochemical Impedance Spectroscopy (EIS). AC impedance was applied with an oscillation of 8 mV and in the frequency range of 0.1 Hz to 100 kHz between 25 and 50 oC by utilizing a Biologic VSP 3 channels. In blocking type cells, the GPE membranes with 10 mm diameter saturated with the liquid electrolytes were sandwiched between two stainless steel (SS) electrodes. The ionic conductivity (σ) was calculated from Eq. (2):

σ = d/(SRb) (2)

Where Rb is the bulk resistance of GPE; d is the thickness of the polymer electrolyte, and S is the area of the stainless steel.

The cathode electrode formulation consisting of 80 wt.% synthesized Na0.44MnO2, 10 wt.% carbon black, and 10 wt.% polyvinylidene difluoride (PVdF) was dispersed in N-methyl-2-pyrrolidone (NMP) to form a slurry. Then, the electrode slurry was coated on Al foil and dried at 80oC under vacuum for 15 hours.

Cyclic voltammetry method is used to investigate electrochemical stability of GPE as well as Na+ ion diffusion mechanism in the electrode materials. Cyclic voltammetry was also performed in Swagelok cell with Na0.44MnO2 cathode and Na metal as the counter and reference electrodes. Both measurements are performed at 25 oC under scan rate of 0.1 mV.s-1 in a potential range of 2.0 to 4.0 V vs Na+/Na, respectively.

Charge – discharge test was carried out in half-cell containing lithium metal as anode, an electrode sheet of synthesized Na0.44MnO2 as cathode and gel copolymer PVdF-HFP electrolytes as membrane. The half-cell was assembled under argon atmosphere in glovebox. Cycling test was performed at galvanostatic regime with C/10 rate in potential range 2.0 to 4.0 V at room temperature by using Biologic MPG2 16 channels.

**3. Results and discussion**

*3.1 Structural analysis*

X-ray diffraction study is used to determine the degree of crystallinity of the polymer membranes in a qualitative manner. In order to investigate the influence of electrolyte uptake to the structure of pristine membrane, XRD analysis was performed for PVdF-HFP pristine and GPE with different electrolytes in Figure 1.

The diffraction patterns at 17.5 o, 18.5 o, 20.2 o and 39 o corresponding to (100), (020), (110) and (021) related to the semi-crystalline nature of PVdF-HFP shown in Figure 1. Previous studies reported the low crystallinity of pristine PVdF-HFP by the broad peak a at 2θ=18, 20, 27 and 39o and other minor peaks emerged in the noisy background [28-30]. The liquid electrolytes such as NaClO4/PC, NaClO4/EC embedded in PVdF-HFP membrane induced a slight decrease in the degree of membrane crystallinity, as evidently shown the enlargement of diffraction pattern peaks in Figure 1. GPEs based on ionic liquids (EMITFSI) exhibited the same crystallinity as the pristine membrane. Generally, the electrolyte uptake in membrane couldn’t suppress the semi-crystallinity phase of PVdF-HFP. Stephane et al. [9] reported the crystallinity decrease of GPE by the decrease of crystalline peaks and its broadness when the micron size particle of ceramic incorporated.

The decrease of crystallinity degree (in percentage, %) for the prepared sample has been calculated using the following relation mentioned by Pradeepa et al. [11]:

χ =

Where S is the sum of the area of all the crystalline peaks; S0 is the total area under the diffractograms. The degree of crystallinity for the samples in Figure 1 was found to be 24 %; 18 % ; 16 % and 23%.

*3.2 Morphology and electrolyte uptake*

The surface morphology of polymer membranes before and after soaking in different liquid electrolytes was examined by SEM images (Figure 2).

The pristine membrane was relatively porous with heterogenous pores size distribution; however, a limit number of pores was observed. After soaking, morphological changes in the host polymer of PVDF-HFP due to liquid electrolyte penetration and immobilization to form GPE. The polymer matrix appeared to be swollen, and many pores are seen, connected to each other through the polymer host. PVDF-HFP soaking in 1 M NaTFSI/PC and 1 M NaTFSI/EMIMTFSI exhibited the uniform pores as compared to soaking in other electrolytes. It can be principally resulted in the strong interaction between the C-F groups of bis(trifluoromethanesulfonyl)imide anion and C-F backbone of polymer matrix. Sanchez et al [31] reported the fluorinated anions with their high delocalization of the negative charge enhancing the interaction between the anion and C-F backbone of polymer matrix, thus the polymer was well swollen into the electrolyte providing the lace structure.

The ability to retain liquid electrolyte was evaluated by the amount of electrolyte uptake into polymer matrix. The maximum amount of electrolyte uptake and membranes porosity corresponding to different liquid electrolytes were reported in Table 1. The porosity of membrane before and after adsorption of electrolyte was calculated by equation (1). In addition, the pore size was also estimated by using the SEM images and given in Table 1.

The porosity of GPE membranes were the competition between two factors: the electrolyte penetration and retaining into the pores and the swelling of membrane. In general, the penetration of electrolyte into the pores results initially in decrease of soaked membrane porosity by embedding liquid. On the other hand, the membranes were also swollen because of the interaction between electrolyte and polymer membrane which increased the porosity. Therefore, the larger amount of electrolyte uptake, the higher degree of porosity is. Tang et al. [32] reported that EMIBF4 embedded in PVdF-HFP membrane increased the charge carriers (the ions) which interacted with the electron donors of the polymer and thus reduced the polymer – polymer intermolecular interaction. This could soften polymer chain resulting the amorphousness and porosity of the polymer electrolyte system.

Table 1 shows that the porosity of soaked membranes about 82 – 87 % for liquid electrolytes comparing to 55 % of pristine membrane. Hence, the value is consistent with the amount of electrolyte uptake for 1M NaPF6 /PC, 1M NaClO4/PC and 1M NaClO4/PC:2%FEC, which the viscosity of these electrolytes is nearly the same. However, viscous ionic liquid solution performed a lower amount of embedding electrolyte as well as a lower porosity. It could be explained that the penetration of electrolyte is the predominant factor because of high viscosity. Ionic liquids of EMIMTFSI, BMIMTFSI have a high viscosity: η = 35.6 mPa.s and 61.1 mPa.s as compared to PC solvent (η = 2.5 mPa.s), respectively. The higher viscous BMITFSI infiltrated through the membrane more difficultly than EMITFSI. Thus, PVdF-HFP/BMITFST showed the higher porosity than PVdF-HFP/EMITFSI.

Besides, the pore size of GPEs with different electrolytes were slightly changed when using carbonate-based electrolytes (Table 1) while ionic liquids embedded PVdF-HFP exhibited the larger pore size due to the strong interaction between TFSI- anion and polymer segmental motion.

*3.3 Thermal properties: TGA and DSC*

Thermal stability is a critical factor of using polymer electrolytes in batteries application. PVDF-HFP pristine membrane exhibited endothermic peaks related to the melting temperature of crystalline phase at 145 oC and degradation at 480 – 500 oC (including two-step: at 480oC and at 495 – 500 oC) on DSC curve (Figure 3A) [33]. The result is also corresponding to TGA curve, which consists two steps of weight loss (Figure 3B) [34].

Some changes in thermal properties of GPE were observed as compared to pristine membrane. The thermal stability of GPE was also compared with commercial separator, microfiber Whatman GF/C microfiber embedded in the same electrolytes. Free liquid electrolyte decomposed quickly at 85 oC with weight loss about 94.5 % due to the high flash temperature of propylene carbonate (Table 2). The gel polymer electrolyte is basically stable within 100oC. With the temperature rising, the mass of gel polymer electrolyte gradually declines and two significant mass losses between 120 and 500oC were observed [35, 36]. The first decomposition stage, about 40 – 50 % may be related to the evaporation of carbonate solvents but shifted to higher temperature as compared to the free liquid one (Table 2). PVDF-HFP is more efficient in keeping electrolyte slowly degraded than Whatman separator. Thus, this stability enhancement is a result of interaction between liquid – polymer backbone; a part of liquid retention capability by membrane pore sizes and porosity degree. The mass of gel polymer electrolyte begins to decrease significantly at 410oC; and it could be probably because of the decomposition of the great mass of PVdF-HFP. Even the thermal stability temperature of GPE is reduced to 410 oC but it’s still enough stable for batteries application. Usually, the operating range of lithium-ion battery is 40 – 70oC [37].

Figure 4 shows the comparison of different electrolytes embedded in PVDF-HFP membranes. As pure ionic liquid has a higher temperature degradation than liquid solvent (380 oC toward 100 oC), GPEs entrapped ionic liquids and sodium salt are more thermal stable than other electrolytes (Table 2).

*3.4 Electrochemical properties: ionic conductivity and electrochemical stability*

The ionic conductivities of gel-polymer electrolytes were determined by electrochemical impedance spectroscopy (EIS) using blocking electrodes configuration in Swagelok-cell type. The typical impedance plot of solid polymer electrolyte based on poly(ethylene oxide) consists of medium to high-frequency semicircle followed by low-frequency straight line, which corresponds to bulk/grain boundary ionic resistances of the membrane electrolyte and electrolyte/electrode double layer capacitance, respectively [18]. In case of GPE based on PVDF-HFP, the high-frequency semicircle does not appear due to facile ion mobility in liquid and gel electrolyte systems. Hence, ion possess a small relaxation time and a minor capacitance effect of the bulk electrolyte in the EIS spectrum [21] (Figure 5). The resistance of the bulk electrolytes was retrieved from the intercept of the straight line on the real axis and the ionic conductivity was calculated as equation 2 (Experimental section). In Table 3, the ionic conductivity of electrolytes reduced significantly, about 5 times when trapping in PVDF-HFP polymer matrix. The conductivity value of GPE based on organic liquid electrolyte is about 1 – 2.0 mS.cm-1 at 30oC. The value is higher than expected literature data, about 0.32 mS.cm-1 in case of LiPF6 embedded in PVdF-HFP or about 0.21 mS.cm-1 for Celgard commercial membrane which is suitable for rechargeable batteries application [38]. Ionic liquids electrolyte with EMITFSI or BMIMTFSI has advantages of high thermal stability, non-volatility, and large electrochemical window; however, its high viscosity restrains the mobility of sodium ion in the bulk and even in the polymer matrix. In addition, the interactions between different cations, anion in complex media (ionic liquid) as well as with polymer backbone are quite complicated and still an explored question to understand sodium ion conduction mechanism. Sodium ion in GPE based on ionic liquids suffered eventually the strong interactions with other ions, giving a low mobility and penalizing ionic conductivity [34, 39]. The values are five times lower, about 0.21 and 0.25 mS.cm-1 at 30oC as compared to GPE based on organic liquid electrolytes (Table 3). H. Ye et al. [40] reported the conductivity of 0.5 M LiTFSI/P13TFSI/PVdF-HFP about 0.27 mS.cm-1 at room temperature.

The ionic conductivity dependence on temperature in the range from 30oC to 50oC (Figure 6) indicated that the increase conductivity value is a function of temperature. The non-linearity indicates that ion transport in polymer electrolytes is dependent on different factors: interaction between ion – polymer segment, ion – solvent molecule [41] as higher temperature leads to decrease of entrapped liquid electrolyte viscosity as well as expansion of the polymer matrix, it provides a bigger free volume, high mobility of backbone and motion of polymer segments; and promoting charge carrier rate. Thus, the results may be described by the Vogel – Tammann –Fulcher (VTF) relation who describes the transport properties in a viscous matrix [42].

= A.T-1/2. exp [-E / (T - T0)]

Where σ is ionic conductivity, T0 is thought to be related to Tg and was regressed onto the conductivity data; T is the temperature of measurement, A and E are fitting constants [42].

The activation energy *E* for all prepared GPE is calculated by linear fit of VTF plot. The activation energy is represented the mobility of ions (Na+, anions) in the gel media, so that the highest value is the lowest mobility of sodium ion. As seen in Table 3, the highest value of GPE based on BMIMTFSI, Ea = 2.3 kJ.mol-1 is logically related to the highest viscous media of BMIMTFSI inducing a barrier that reduced the motion rate of Na+ sodium. Thus, its lowest conductivity was observed at any temperature in comparing to the other electrolytes.

The anodic and cathodic stability of GPE was determined by using cyclic voltammetry (Figure 7). The electrochemical stability window of an electrolyte is essential because a suitable voltage can be selected to apply on the cell during cycling to ensure the good performance. Therefore, the electrolyte must be electrochemically stable, or it must not show any redox reaction within the expected potential range. The limit potential of oxidation/reduction process at which the current flow begins is considered as the onset of electrochemical decomposition was given in Table 4. It is found that the onset current of reduction is nearly -0,2 V vs Na+/Na related to anion TFSI- for GPEs with ionic liquids (EMITFSI, BMIMTFSI). The reduction of propylene carbonate in electrolyte solution is 1,2 vs Na+/Na (0,9 V vs Li+/Li reported in literature). In Figure 7B, the highest oxidation limit was expectedly obtained for ionic liquids embedded in PVdF-HFP due to the nature of high stable oxidation resistance of EMITFSI and BMIMTFSI (almost > 5 V vs Li+/Li). In effect, the electrochemical window of GPE is perfectly compatible with 4V sodium electrode materials.

To confirm Na+ ion conduction and possible application of GPE in sodium batteries, cyclic voltammetry was performed in the asymmetric cells Na//GPE//Na0.44MnO2 and comparing to commercial Whatman membrane.

In potential range of 2.0 – 4.0 V, a typical voltammogram of Na0.44MnO2 consisting of reversible redox pairs at anodic and cathodic scans, indicating the complex reversible insertion/deinsertion of Na ion into/out of the structure Na0.44MnO2 within a multiphases evolution (Figure 8). In reduction process, sodium ion intercalated firstly in the site Na3 and Na2 (S-shaped tunnel), after that, sodium ion moved to the site Na1 (small tunnel) at end of intercalation [43]. Sodium cell using GPE as electrolyte showed the well-defined reversible redox pairs which are totally corresponding to the case of using commercial Whatman membrane. The higher current intensity of redox peaks was obtained for GPE than Whatman separator. The results indicated the good sodium conduction at room temperature which is suitable for sodium batteries application.

The cycling performance of sodium cell was evaluated in Swagelok cell-type with battery configuration of Na//GPE//Na0.44MnO2 under a constant current density of C/10 at room temperature. It was founded that charge/discharge curves of PVdF-HFP/NaClO4 PC:2% FEC exhibited nearly no increase of polarization after 20 cycles (Figure 9A) and the stable discharge capacity is about 100 mAh.g-1 (Figure 9B). In addition, there is still no evidence capacity fading. Sodium cell using PVdF-HFP/NaClO4 1M – PC (without FEC) exhibited a lower and less stable than one with using FEC. The addition of FEC with small amount helps to stabilize the electrode – electrolyte interface, hence the cycling capacity is much better improved [44]. Attempts to cycling the cell with PVdF-HFP/BMIMTFSI or EMIMTFSI + 0.5M NaTFSI at room temperature were unsuccessful due to low ionic conductivity and high viscosity of electrolyte medium, the specific capacity value is negligible in compared to GPE with different liquid electrolytes. Further studies of ionic conductivity enhancement by using carbonate co-solvent with ionic liquids in swelling PVDF-HFP membrane are still pursuing.

**4. CONCLUSIONS**

In summary, gel type polymer electrolytes of PVdF-HFP were successfully prepared by swelling porous membranes in different liquid electrolytes. GPEs with organic liquid solution exhibited a suitable sodium conductivity which the value about 1 – 2 mS.cm‑1 at room temperature. The highest ionic conductivity was observed for NaClO4 1M – PC:2%FEC/PVdF-HFP, about 1.91 mS.cm-1. The temperature dependent ionic conductivity shows the VTF behavior, which indicates that ion transport in gel medium together with mobility of backbone and polymer segment. When the electrolytes entrapped in PVdF-HFP membranes, its thermal stability significantly increased as evidently showed the higher temperature of degradation of liquid electrolyte comparing to its commercial microfiber membrane. The electrochemical stability window of GPE is compatible with 4 V sodium electrode materials due to high oxidation limit of about 4 V vs Na+/Na. Cyclic voltammogram and charge – discharge test of GPE in Na//GPEs// Na0.44MnO2 configuration cell exhibited a reversible intercalation/deintercalation of Na+ as well as a stable discharge capacity. NaClO4 1M – PC:2%FEC/PVdF-HFP exhibited a stable specific capacity of 100 mAh.g-1 without evidence of capacity fading after 20 cycles.

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