



# Ionic liquid-gelled polyvinylidene fluoride/polyvinyl acetate polymer electrolyte for solid supercapacitor



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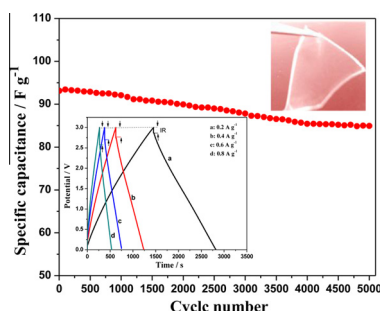
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## HIGHLIGHTS

- A novel PVDF/PVAc/IL GPE for solid-state electrochemical devices was successfully prepared.
- By tuning the IL contents, the GPE could form a uniform, translucent, and very flexible film.
- The GPE presented both good thermal stability and satisfactory electrochemical properties.
- A 3.0 V cell using this GPE showed both high specific capacitance and good cycling stability.

## GRAPHICAL ABSTRACT

A 3.0 V solid-state C/C capacitor cell using the fabricated flexible PVDF/PVAc/IL GPE film presents good electrochemical performance.



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## ABSTRACT

A promising ionic liquid-gelled polymer electrolyte (GPE) based on semi-crystal polyvinylidene fluoride (PVDF), amorphous polyvinyl acetate (PVAc) and ionic conductive 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF<sub>4</sub>) is successfully prepared via solution-casting method. The structures and morphologies of the GPEs are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the thermal stability of the GPEs is measured by thermogravimetric/differential scanning calorimetry (TG/DSC). Highly homogenous, translucent, and flexible GPE films are easily obtained by adjusting the ionic liquid (IL) contents. The PVDF/PVAc/IL (IL, 50 wt%) GPE film presents good thermal stability (~300 °C), wide electrochemical window (>4.0 V), and acceptable ionic conductivity ( $2.42 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature) as well. A 3.0 V C/C solid-state capacitor cell using this GPE film was assembled and measured. It is found that the capacitor cell shows specific capacitance of  $93.3 \text{ F g}^{-1}$  (based on activated carbon) at the current density of  $200 \text{ mA g}^{-1}$ , and can retain more than 90% of the initial capacitance after 5000 charge–discharge cycles.

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## 1. Introduction

Since the discovery of ionic conductivity in PEO-based polymer electrolytes by Wright [1] in 1973, the solid polymer-based electrolytes (SPEs) received considerable attention worldwide. Generally, the SPEs are composed of polymers and solid solution of inorganic salts embedded in polymer matrices, and are mechanically, thermally, and electrochemically stable. Additionally, there is no liquid leakage and much safer than traditionally used liquid electrolytes. Armand [2] firstly applied SPEs in batteries in 1978 and found their good stability and acceptable ionic conductivity. The SPEs were then widely explored and applied in batteries [3,4], fuel cells [5], and supercapacitors [6]. However, the poor compatibility of polymers with most inorganic salts usually causes miscellaneous phases and low ionic conductivity (lower than  $10^{-5}$  S cm<sup>-1</sup>) [7] that are obviously unfavorable for high-performance electrochemical devices. Therefore, it is necessary to further improve the homogeneity and conductivity of the SPEs in meeting the current needs.

The gel polymer electrolytes (GPEs) are proposed to replace the SPEs by adding a plasticizer component to polymer phases [8–10]. The plasticizer containing organic solvents with high dielectric constant (e.g. EC, PC) could not only enhance the dissolubility of salts, but also reduce the degree of crystallization of polymer, thus make the polymer-based electrolyte flexible. The GPEs constructed by polymer matrices filling with liquid electrolytes generally exhibit high room-temperature conductivity of  $\sim 10^{-3}$  S cm<sup>-1</sup> [11,12] and promising cycling stability for electrochemical energy storage [13–15]. However, the volatile solvents as plasticizers are supposed to cause safety problems at higher temperature circumstances. Therefore, a prospective insight into a novel medium with no/low volatility as an alternative to the current plasticizer is significant.

Ionic liquids (ILs) or room-temperature molten salts (RTMSs) which contain only liquid ions or ionic aggregates at room temperature [16] have attracted great interest in recent years. Their unique properties for electrochemical applications include negligible vapor pressure, wide voltage window, high ionic conductivity, and good thermal stability (typically up to 200–300 °C) [17]. Fuller [18] firstly synthesized IL-based GPEs which exhibited ionic conductivity of  $10^{-3}$  S cm<sup>-1</sup> at room temperature and  $10^{-2}$  S cm<sup>-1</sup> at 100 °C. A series of IL-based GPEs were investigated for supercapacitors [19–21] and Li-ion batteries [22], and they showed extremely stable electrochemical performance. Incorporation of ILs into polymer matrices as plasticizers not only enhances the flexibility of the skeleton supporter, but adds the mobile conductive ions within the networking [23,24]. More importantly, volatilization-free IL plasticizers are sure to minimize the latent risks from pressure leakage which used to occur in traditional liquid electrolyte systems.

Polyvinylidene fluoride (PVDF) has been widely used as a polymer material owing to superior overall properties. Generally, it appears semi-crystalline state, and contains 59.4 wt% fluorine and 3.0 wt% hydrogen [25], having high corrosion resistance. Compared with other hydrocarbon-based polymers, PVDF is more thermally stable regarding the high electronegativity of fluorine atoms and the high dissociation energy of the C–F bond [26]. In addition, PVDF exhibits good thermodynamic compatibility with other polymers such as polymethyl methacrylate (PMMA) [27], polyvinyl acetate (PVAc) [28] over a wide range of blend compositions. Especially, amorphous PVAc domains formed in PVDF/PVAc blends can effectively depress PVDF crystallization and improve the polymer flexibility.

In this case, we intend to prepare a well flexible PVDF/PVAc GPE film using a common ionic liquid i.e. 1-butyl-3-methylimidazolium tetrafluoroborate as the conductive plasticizer. To the best of our knowledge, this flexible GPE film has not been investigated so far.

## 2. Experimental

### 2.1. Chemicals

*N*-Methylimidazole (99%, Alfa Aesar), bromobutane (analytical pure, Sinopharm Chemical Reagent Co. Ltd., China), ethyl acetate (analytical pure, Tianjin Fuyu Fine Chemical Co. Ltd., China), tetrafluoroborate potassium (analytical pure, Changsha Shengyang Chemical Materials Co. Ltd., China), acetone (analytical pure, Hengyang Kaixin Chemical Reagent Co. Ltd., China), dichloromethane (analytical pure, Sinopharm Chemical Reagent Co. Ltd., China), Polyvinylidene fluoride (Shanghai 3F New Material Co. Ltd., China), polyvinyl acetate (Jiangsu Yinyang Gumbase materials CO. Ltd., China), activated carbon (Nanjing Zhengsen Environmental Science and Technology Co. Ltd., China), acetylene black (Jiaozuo Hexing Chemical Industry CO. Ltd., China), polytetrafluoro ethylene (PTFE, Shanghai Zhaozhi Nano Technology Co. Ltd., China). All the chemicals were used without further purification.

### 2.2. Preparation of materials

#### 2.2.1. Synthesis of BMIMBF<sub>4</sub>

In this paper, two-step synthesis method was applied to synthesize the ionic liquid. Firstly, 16.0 mL *N*-methylimidazole (0.2 mol) was added to 100 mL three flask and stirred under 70 °C oil bath. 23.6 mL bromobutane (0.22 mol) was added dropwisely into the flask. A light-yellow liquid was synthesized after 30 h reaction. The crude product was washed three times using ethyl acetate and distilled to remove solvent. The intermediate 1-butyl-3-methylimidazolium bromide (BMIMBr) was vacuum-dried at 70 °C to constant weight. Then, 3.15 g KBF<sub>4</sub> was dissolved in 50 mL acetone in flask and mixed with another acetone solution containing 5.478 g BMIMBr. The mixture was stirred under 30 °C for 24 h. After reaction, the product was filtrated to remove KBr and then distilled to eliminate ethyl acetate. The product was washed sequentially using equal volume of dichloromethane for 2–3 times and vacuum-dried at 70 °C for 12 h. The amount of water was determined by Karl Fischer titration (<30 ppm), No free Br<sup>-</sup> ions were detected by aqueous AgNO<sub>3</sub> solution. The structure of the obtained BMIMBF<sub>4</sub> was confirmed by <sup>1</sup>H-NMR with chemical shift  $\delta$  (ppm, relative to Me<sub>4</sub>Si): 9.15 (s, 1H), 7.79 (t, 1H), 7.72 (t, 1H), 4.17 (t, 2H), 3.82 (s, 3H), 1.76 (m, 2H), 1.27 (m, 2H), 0.89 (s, 3H).

#### 2.2.2. Preparation of PVDF/PVAc/IL GPEs

The GPEs contained fixed ratio of PVDF and PVAc (3:2 wt/wt) and different mass percentage of BMIMBF<sub>4</sub>. The solution-casting method was used to prepare GPEs. Briefly, PVDF and PVAc were dissolved in 30 mL acetone. The solution was stirred at room temperature for 30 min, then at 60 °C until solution became transparent and homogeneous. BMIMBF<sub>4</sub> was added in and vigorously stirred overnight. After degassing to remove air bubbles, the transparent slurry was carefully casted onto a pretreated glass-made plate mould. The mould was set into a drying cabinet at 40 °C for 48 h to evaporate most acetone, and then transferred into a vacuum drying chamber at 60 °C for 10 h. The obtained dried, off-plate films with thickness of 100–200  $\mu$ m are translucent and flexible.

#### 2.2.3. Preparation of electrodes

Commercially applied activated carbon (supercapacitor grade), acetylene black (battery grade), PTFE (5 wt%, battery grade) were used as received. Stainless steel sieves (60-mesh) were used as current collectors. Activated carbon, acetylene black and PTFE with the mass ratio of 85:10:5 were mixed and dispersed in absolute isopropyl alcohol to form uniform slurry. The slurry was casted

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