Structural Changes and Electrochemical Stability of Ionogel Incorporating Tetraethyl Orthosilicate and PVDF-HFP

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Abstract. Ionogels are emerging hybrid materials and are widely studied due to the combination of thermophysical properties from ionic liquid and mechanical integrity from the polymer matrix. Ionic liquid has received wide attention due to its promising properties, high ionic conductivity, and thermal stability. The liquid nature of ionic liquid has restricted its application. Thus, the confinement of ionic liquid within a polymer matrix has allowed ionogel to be applied in strain sensors and lithium-ion batteries. Nevertheless, the compatibility between the polymer matrix and ionic liquid is crucial for ionogel. Incompatibility between polymer host and ionic liquid results in low ionic conductivity, poor mechanical strength, and undesired for practical application. The interaction between polymer matrix and ionic liquid is studied in this study through optical microscopy. The addition of ionic liquid resulted in the disappearance of the polymer matrix's highly porous nature, as evidenced by the optical microscopy images. This disappearance of the porous nature suggests the compatibility of the polymer matrix with ionogel. Furthermore, the electrochemical stability of the ionogel is also examined through linear sweep voltammetry technique and achieved 2.3V.

Keywords: Structural Changes, PVDF-HFP, electrochemical stability, ionogel
1. Introduction

Ionic liquids (ILs) are organic salts or compounds completely comprised of cations and anions, which has a low melting point lower than 100 °C [1-4]. However, the melting point of ILs is lower than inorganic salts, resulting from large-sized-anion and cations. The ionic packing and coulombic interaction between ions are affected by the molecular structure of ILs, which determines the electrochemical properties of ILs [5]. ILs represent a category of materials, existing in liquid form with property profiles, that originate from different interaction such as van-der-Waals interaction, coulombic interaction and hydrogen bonding [6]. Compelling thermophysical properties as exhibited by ILs, including high conductivity, immiscibility and promising thermal stability, have made it possible for various applications [7]. With such properties, ILs are being utilized in different fields, such as solvents solvent application, drug delivery systems [8], and catalysts for batteries [9]. However, the liquid nature of ionic liquid will lead to problems such as leakage, which can be overcome by confining ionic liquid within the polymer matrix or polymer system [10]. Thus, immobilizing ionic liquid in a hybrid host is ascribed to forming a solid form with good stretchability and transparency. The resultant composite, also known as ionogel, which combines the properties of ionic liquid and mechanical integrity from the polymer matrix, has been applied in different areas such as proton-exchange membranes [11], strain sensors [12], temperature sensors [13], pressure sensor [14], and electric layer double capacitor [15].

Nevertheless, the polymer matrix has a strong impact as it provides adequate mechanical stability to ionogel. In contrast, the compatibility between the polymer system and ionic liquid would influence the performance of ionogel. For instance, incompatibility of the polymer system with ILs would exert difficulty in transportation, thus hindering ion transportation [4]. Incompatibility issues may arise due to the contrast in chemical functionalities between ILs and confining systems, which results in seepage under mechanical deformation [16]. At extreme temperatures, incompatibility would also cause macroscopic phase separation. Liu et al. reported that the compatibility between the host polymer (Chitosan) and ionic liquid (EMIM BF4) had improved the electrochemical stability of ionogel, and good mechanical strength of ionogel [17]. The ionogel has achieved a value of 33.97 kPa of mechanical strength.

On the contrary, Guo et al. demonstrated that the incompatibility between host polymer and ionic liquid results in a higher tendency of agglomeration upon the incorporation of nanoparticles [18]. This has led to the undesired performance of ionogel, such as poor interfacial stability between electrode and ionogel, poor battery cycling stability and low ionic conductivity. Furthermore, Tiruye et al. also found that the incompatibility between Poly(diallyl dimethylammonium) bis(trifluoromethanesulfonylimide) (PILTFSI) and 1-butyl-1-methylpyrrolidinium dicyanamide, (PYR14DCA) has resulted in difficult preparation of free-standing solid membranes [19]. Cowan et al. further clarified that the incompatibility between host polymer and ionic liquid is crucial for practical application that demands proton transport [20]. The incompatibility between the host polymer and polymer matrix causes poor interface stability and weak ionic conductivity, which is unfavorable for practical application.

In short, the compatibility between the host polymer and ionic liquid is essential in governing the performance of ionogel. Consequently, the compatibility of the polymer system and ILs must be scrutinized before proceeding to synthesize and characterize ionogel. In this study, we aim to investigate the compatibility between the electrolyte solution and polymer matrix. Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) is employed as the polymer matrix. In contrast, the polymer matrix changes are examined upon incorporating silica precursor, ILs through Optical Microscopy. Lastly, the electrochemical stability of ionogel is also tested using the linear sweep voltammetry method (LSV) via an electrochemical workstation.

2. Research Methodology

2.1 Materials

This study used Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) as the polymer matrix. Acetone was used as a solvent to dissolve the polymer, while tetraethyl orthosilicate (TEOS) was used as a silica precursor. Meanwhile, formic acid was used as a catalyst in the preparation of ionogel. The ionic liquid utilized in this study was 1-ethyl-3-methylimidazolium bis (trifluoromethyl sulfonate) (EMIM TFSI), lithium trifluoromethyl sulfonate (LiTf) was used as a lithium source.
2.2 Preparation of Polymer matrix and Ionogel.
Fig. 1 summarizes the preparation steps of polymer. For the preparation of polymer, PVDF-HFP is first dissolved in acetone in 10 wt% for 24-48 hours under continuous stirring conditions. Pure PVDF-HFP was produced by pouring the solution onto mould for characterization. For PVDF-HFP/TEOS preparation, TEOS was added into the PVDF-HFP solution at a weight ratio of 75:25. The synthesis of ionogel is performed by mixing the electrolyte solution with the polymer solution, followed by the addition of FA at a molar ratio of 7.8:1.

2.3 Characterisation of Polymer matrix
The Optical Microscopy images of the polymer matrix and ionogel are obtained by Nikon Eclipse LV 100N Pol Microscope. The linear sweep voltammetry (LSV) was performed using IVIUM Compact stat 10800 in a voltage range of 0-5V. To perform LSV characterisation, the sample is placed between two stainless steel electrodes, as shown in Fig. 1.

![Stainless Steel Electrode](image)

Fig. 1. Set-Up of the LSV test

3. Results and Discussion

3.1 Physical Appearance, and Optical Microscopy Image of Ionogel.

The images of ionogel are displayed in Fig. 2. The formation of ionogel implies the compatibility between the host polymer and electrolyte solution. However, this is further investigated through optical microscopy images. Thus, optical microscopy characterization was performed to understand the morphology changes. Fig. 3 shows the optical microscopy images for pure PVDF-HFP, while Table 1 summarizes the characteristic indication labeled in the optical microscopy images. The image shows that the pure PVDF-HFP exhibits porous morphology (labelled A). Fig. 4 shows the optical microscopy images of PVDF-HFP with the addition of TEOS (silica). After the addition of TEOS, no major differences were obtained in the morphology of PVDF-HFP/TEOS. The optical microscopy images for ionogel are shown in Fig. 5. After incorporating the electrolyte solution, the highly porous nature of PVDF-HFP has disappeared. This implies the compatibility of the polymer matrix with the electrolyte solution [21]. Moreover, Error! Reference source not found. also displays that the electrolyte solution is absorbed in the pores of PVDF-HFP, evidenced by the smooth surface (labelled C). From the microscopic images, the PVDF-HFP TEOS is compatible with ionic liquid, forming ionogel.

| Table 1. Characteristic Indication of Optical Microscopy Images |
|------------------|------------------|
| Labelled Parts  | Indications                  |
| A                | Porous Morphology as exhibited by Pure-PVDF-HFP |
| B                | Remaining Porous morphology in the ionogel after incorporation of ionic liquid |
Smooth surface after the addition of ionic liquid

Fig. 2. Image of Ionogel

Fig. 3. Optical Microscopy image of Pure PVDF-HFP
Fig. 4. Optical Microscopy image of PVDF-HFP/TEOS

Fig. 5. Microscopy Images of PVDF-HFP/TEOS/IL
3.2 Linear Sweep Voltammetry (LSV)

LSV is performed to understand the electrochemical stability of PVDF-HFP/TEOS and ionogel. The LSV plot is shown in Error! Reference source not found.. The electrochemical stability is identified from the graph, where a sudden spike is observed from the plot. From Fig. 6., PVDF-HFP/TEOS has a narrow electrochemical stability, but the electrochemical stability is widened upon the addition of electrolyte solution, which is 2.3V.

![Fig. 6. LSV Plot of PVDF-HFP/TEOS and Ionogel](image)

4. Conclusion

With the incorporation of electrolyte solution, the optical microscopy images show that the porous morphology of PVDF-HFP remains, where most of the electrolyte solution is absorbed in the pores of PVDF-HFP. This implies the compatibility between the host polymer and electrolyte solution. The optical microscopy images show that most of the pores disappeared upon addition of ILs/TEOS. Thus, this confirms that the polymer matrix PVDF-HFP is compatible with the silica precursor. The addition of TEOS into the polymer network has induced the efficient formation of a silica network, whereby this system can contain ionic liquid, producing ionogel. The electrochemical stability is also being examined, exhibiting electrochemical stability of 2.3V. Thus, future research direction will be devoted to exploring the electrochemical properties (ionic conductivity, specific capacitance) and mechanical strength of ionogel.

5. Nomenclature

<table>
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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>EMIM Bf4</td>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate</td>
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<tr>
<td>EMIM TFSI</td>
<td>1-ethyl-3-methylimidazolium bis (trifluoromethyl sulfonate)</td>
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Thus, future research direction will be devoted to exploring ionogel. The electrochemical stability is expected to enhance with the incorporation of electrolyte solution, which is 2.3V. The electrochemical stability is identified from the graph, where a sudden spike is shown in the LSV plot. The electrochemical properties of PVDF-HFP are compatible with the silica precursor. The addition of TEOS into the polymer network, whereby this system can contain ionic liquid, producing a robust and flexible electrochromic devices.

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**References**


