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Ionic liquid and nanoparticle based magnetic electrolytes: Design, preparation, and electrochemical stability characterization

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ABSTRACT

In this work, ionic liquid (IL) and nanoparticle (NP) based magnetic electrolytes are developed for the first time. The electrochemical stability of electrolyte is a crucial property for utilization in solar cells and batteries. The electrochemical stability behavior of the samples of pure ILs, ILs + NPs, ILs + NPs + iodide redox (I_3^-/I^-), and ILs + H_2O is investigated. It is shown that there is no significant electrochemical reaction in the pure ILs sample when direct current (DC) voltage ranging from 2 V to 40 V is applied. The results suggest that pure ILs have good electrochemical stability as electrolytes under DC voltage as high as 40 V. NPs are utilized in order to improve the performance of ILs as electrolytes. It is found that the presence of NPs does not influence the electrochemical stability of the electrolytes under the DC electrical field. Moreover, I_3^-/I^- is added to form samples of ILs + NPs + I_3^-/I^-. It is shown that the presence of I_3^-/I^- reduces the electrochemical stability of most of the IL + NP + I_3^-/I^- electrolytes utilized in this work. The presence of water can also reduce the electrochemical stability of the IL based electrolytes. Furthermore, the effect of a magnetic field on the NP concentration gradient in the samples of ILs + NPs and ILs + NPs + I_3^-/I^- is investigated. It is shown that there is a NP concentration gradient in the samples when an external magnetic field is applied. This discovery is useful when utilizing the IL and NP based magnetic electrolytes in solar cells and batteries. Finally, electrodes of the samples of $BmimPF_6$ + Fe_2O_3 NPs, and $BmimPF_6$ + Fe_2O_3 NPs + I_3^-/I^- after electrophoresis deposition experiments are compared. The findings in this work can enhance the development of utilization of IL and NP based magnetic electrolytes in solar cells and batteries.

1. Introduction

Ionic liquids (ILs) are environmentally friendly materials, which are hot research topic. ILs have many excellent properties, including high thermal and chemical stability, low vapor pressure, low melting point, modifiable phase behavior and polarity, excellent solubility, designable task-specific functional groups, and excellent electrochemical properties. Due to the excellent properties, ILs have been utilized as novel and promising materials in many research fields, including CO_2 capture, [1–7] catalysis science, [8–12] solar cells, [13–18] and batteries [19–22].

Many researchers focus on utilizing ILs as electrolytes in solar cells and batteries [23–26]. ILs can improve the electrical conductivity and thermal stability of electrolytes [27]. ILs based electrolytes are utilized in dye-sensitized solar cells (DSSC). In 1991, Grätzel et al. reported about a low cost, high-efficiency dye-sensitized solar cell [28]. Afterwards, new IL based green electrolytes are developed in his group for DSSC applications. For example, Wang et al. developed a polymer gel electrolyte for dye-sensitized nanocrystalline solar cells [29]. In addition, Wang et al. reported IL based electrolytes containing silica nanoparticles for quasi-solid-state DSSC applications [30]. Other types of electrolytes containing ILs are also developed in this group [31–36]. Many IL based electrolytes are designed and utilized in DSSC by the researchers worldwide. IL based electrolytes can also be utilized in batteries, including Li-ion battery, Li battery, Li-oxygen battery, and Al-ion battery [27,37]. For example, Bansal et al. reported the effect of ILs on the conductivity and transport properties of electrolytes in Li-ion batteries [37]. Nanoparticles (NPs) have a range of interesting properties, such as finite-size effects, and surface effects. NPs are utilized to enhance the performance of ILs as electrolytes in this work. For example, the IL and magnetic NP based electrolytes will show magnetic properties in the presence of an external magnetic field.

A new concept of IL and NP based magnetic electrolytes is released in this work. The electrochemical stability of ILs and NPs is crucial during the process of utilization of ILs and NPs in solar cells and batteries. Therefore, in this work, the electrochemical stability under DC voltage ranging from 2 V to 40 V in the samples of pure ILs (1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-methyl-3-octylimidazolium tetrafluoroborate, and 1-methyl-3-octylimidazolium chloride), ILs + NPs ($BmimBF_4$ + Fe_2O_3 NPs, $BmimPF_6$ + Fe_2O_3 NPs, $BmimPF_6$ + R711 NPs, and OmimCl + Fe_2O_3 NPs), ILs + NPs + I_3^-/I^- ($BmimBF_4$ + Fe_2O_3 NPs + I_3^-/I^-, $BmimPF_6$ + Fe_2O_3 NPs + I_3^-/I^-, and OmimCl + Fe_2O_3 NPs + I_3^-/I^-) and ILs + H_2O ($BmimBF_4$ + H_2O and $BmimPF_6$ + H_2O) is investigated. The

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results in this work will benefit the utilization of IL and NP based magnetic electrolytes in solar cells and batteries.

2. Experimental section

2.1. Materials

1-butyl-3-methylimidazolium tetrafluoroborate (CAS R.N. 174501-65-6, $BmimBF_4$), 1-butyl-3-methylimidazolium hexafluorophosphate (CAS R.N. 174501-64-5, $BmimPF_6$), 1-methyl-3-octylimidazolium tetrafluoroborate (CAS R.N. 244193-52-0, $OmimBF_4$) and 1-methyl-3-octylimidazolium chloride (CAS R.N. 64697-40-1, OmimCl) are obtained from Sigma-Aldrich. The mass fraction purity of the 4 ILs are ≥97%. Toluene (Purity ≥99.9%), 5 mg/mL Fe_3O_4 MNPs in toluene, and Fe_2O_3 nano powder (average size: <50 nm) are also purchased from Sigma-Aldrich and utilized in this work. R711 NPs are received from Evonik Industries AG, Germany. The physical properties of R711 NPs and Fe_2O_3 nano powder are shown in Tables 1 and 2 [38–40]. Millipore water is also utilized in the experiments.

2.2. Sample preparation

Samples of ILs + NPs are prepared, including $BmimBF_4$ + Fe_2O_3 NPs, $BmimPF_6$ + Fe_2O_3 NPs, $BmimPF_6$ + R711 NPs, and OmimCl + Fe_2O_3 NPs. In addition, ILs + NPs + I_3^-/I^- are prepared, including $BmimBF_4$ + Fe_2O_3 NPs + I_3^-/I^-, $BmimPF_6$ + Fe_2O_3 NPs + I_3^-/I^-, and OmimCl + Fe_2O_3 NPs + I_3^-/I^-. R711 NPs can be dispersed in $BmimBF_6$ very well. However, the dispersion property of Fe_2O_3 NPs in the samples utilized in this work is not as good as expected. The Fe_2O_3 NPs can precipitate from the samples after a long time quiescent process. Therefore, it is necessary to improve the dispersion property of magnetic NPs in IL based samples in the future work by, for example, modifying the surface property of NPs, utilizing other types of NPs and ILs, or utilizing additives. What's more, 5 mg/mL Fe_3O_4 MNPs in toluene is diluted as 1 mg/mL Fe_3O_4 MNPs in toluene using toluene. Moreover, $BmimBF_4$ + H_2O, and $BmimPF_6$ + H_2O, are prepared in this work.

2.3. Electrochemical stability characterization

Electrochemical stability of electrolytes is investigated using electrophoresis deposition instrument shown in Scheme 1. The instrument consists of a DC power source and electrodes. A sample is added in the beaker. Subsequently, a voltage applied on the sample and the current passing through the liquid can be measured during the electrophoresis deposition experiment process. The applied voltage can be controlled ranging from 2 V to 40 V.

3. Results and discussions

3.1. Electrochemical stability characterization

3.1.1. Effect of electrical field on pure ILs

Electrochemical stability of pure ILs of $BmimBF_4$, $BmimPF_6$, $OmimBF_4$ and OmimCl are investigated using electrophoresis deposition instrument. As shown in Fig. 1, the current of the samples is 0 A with the applied DC voltage ranging from 2 V to 40 V. It means that there is no significant electrochemical reaction in these pure ILs utilized in this work with the applied DC voltage as high as 40 V. The results illustrate that these pure ILs have high electrochemical stability during the experimental process. This property is important when utilizing ILs as electrolytes. Subsequently, IL and NP based systems are prepared for utilizing as magnetic electrolytes in this work. The NPs utilized in this work are Fe_2O_3 NPs, Fe_3O_4 NPs and R711 NPs. Fe_2O_3 NPs and Fe_3O_4 NPs exhibit strong magnetic properties while R711 NPs do not show significant magnetic properties. The presence of magnetic Fe_2O_3 NPs in ILs makes the electrolytes magnetic, which is a promising property for utilization as electrolytes in novel concept solar cells and batteries.

Table 1
Physical and chemical properties of R711 NPs [39,40].

Properties	Test value
Appearance	Powder
Specific surface area (BET, m^2/g)	125–175
Particle size (nm)	ca. 15
pH value (4% dispersion)	4.0–6.0
C content (%)	4.5–6.5
SiO_2 content based on ignited material (%)	≥5 wt.%

Table 2
Physical properties of Fe_2O_3 nano powder [38].

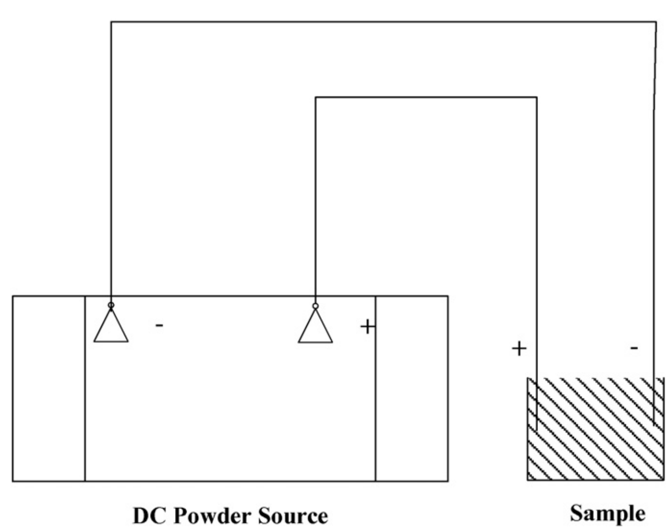
Properties	Test value
Appearance	Powder
Surface area (BET, m^2/g)	50–245
Particle size (BET, nm)	<5
Relative density (g/cm^3)	5.120

3.1.2. Effect of electrical field on IL + NP systems

Electrochemical stability characterization experiments are performed in the IL + NP systems, including the samples of $BmimBF_4$ + Fe_2O_3 NPs, $BmimPF_6$ + Fe_2O_3 NPs, $BmimPF_6$ + R711 NPs, and OmimCl + Fe_2O_3 NPs. As shown in Fig. 2a, the current in these samples is still 0 A when DC voltage ranging from 2 V to 40 V is applied. It illustrates a good electrochemical stability.

3.1.3. Effect of electrical field on IL + NP + I_3^-/I^- systems

I_3^-/I^- is an important component in many electrolytes for DSSC. Therefore, in this work I_3^-/I^- is added into three IL + NP samples to form the samples of $BmimBF_4$ + Fe_2O_3 NPs + I_3^-/I^-, $BmimPF_6$ + Fe_2O_3 NPs + I_3^-/I^-, and OmimCl + Fe_2O_3 NPs + I_3^-/I^- for further DSSC fabrication experiments. The current of these three samples is also measured when DC voltage ranging from 2 V to 40 V is applied. The experiments show that there is a significant current flowing in the samples of $BmimBF_4$ + Fe_2O_3 NPs + I_3^-/I^-, and $BmimPF_6$ + Fe_2O_3 NPs + I_3^-/I^-. In addition, the current in the two samples changes during the experimental process. The maximum current during the experimental process is shown in Fig. 2b. The maximum current of the sample of $BmimBF_4$ + Fe_2O_3 NPs + I_3^-/I^- is as high as 0.6 A at the voltage ranging from 2 V to 40 V. It means that the presence of I_3^-/I^- reduces the electrochemical stability of the electrolyte. In addition, the



Scheme 1. The sketch of electrophoresis deposition instrument.