

# A novel composite polymer electrolyte containing room-temperature ionic liquids and heteropolyacids for dye-sensitized solar cells

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Received 20 August 2007; received in revised form 18 September 2007; accepted 19 September 2007

Available online 22 October 2007

## Abstract

A novel composite polymeric gel comprising room-temperature ionic liquids (1-butyl-3-methyl-imidazolium-hexafluorophosphate, BMImPF<sub>6</sub>) and heteropolyacids (phosphotungstic acid, PWA) in poly(2-hydroxyethyl methacrylate) matrix was successfully prepared and employed as a quasi-solid state electrolyte in dye-sensitized solar cells (DSSCs). These composite polymer electrolytes offered specific benefits over the ionic liquids and heteropolyacids, which effectively enhanced the ionic conductivity of the composite polymer electrolyte. Unsealed devices employing the composite polymer electrolyte with the 3% content of PWA achieved the solar to electrical energy conversion efficiency of 1.68% under irradiation of 50 mW cm<sup>-2</sup> light intensity, increasing by a factor of more than three compared to a DSSC with the blank BMImPF<sub>6</sub>-based polymer electrolyte without PWA. It is expected that these composite polymer electrolytes are an attractive alternative to previously reported hole transporting materials for the fabrication of the long-term stable quasi-solid state or solid state DSSCs.

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**Keywords:** Room-temperature ionic liquid; Heteropolyacid; Composite polymer electrolyte; Ionic conductivity; Dye-sensitized solar cells

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention over the past decade due to their high photo-energy conversion efficiencies and low cost cell fabrication processes [1,2]. For DSSCs, the electrolytes usually consist of an iodide/triiodide redox couple in organic solvents. However, the disadvantages of using liquid electrolytes are less long-term stability, difficulty in robust sealing, evaporation and leakage of electrolyte in case of breaking of the glass substrates [3,4]. Therefore, p-type semiconductor [5], hole-conductor [6], and polymeric materials incorporating triiodide/iodide as a redox couple [7–9] have

been attempted to substitute the liquid electrolytes for quasi-solid or solid state DSSCs.

Recently, growing attention has been paid to quasi-solid DSSCs using polymer gel electrolytes due to their unique hybrid network structure and favorable properties such as thermal stability, non-flammability, negligible vapor pressure and easy solidification, when compared with the liquid electrolytes [10,11]. To pursue high conversion efficiency of DSSCs, it is necessary and pivotal to enhance the ionic conductivities of these polymer gel electrolytes [7,12,13]. However, conventional polymer electrolytes exhibit very low ambient ionic conductivity because of the severe crystallinity of polymers. In this respect, most of the recent studies have been directed to the preparation and characterization of polymer gel electrolytes that have higher ionic conductivity at ambient temperature. It is known that room-temperature ionic liquids (RTILs) have

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wide liquid-phase range, non-flammability and very low vapor pressure at room temperature, wide electrochemical windows, high ionic conductivity, and excellent thermal and chemical stability [14,15]. One of the interesting developments in the field of RTILs is the combination of RTILs and polymers to form gel-like composites for the application in DSSCs [3,16], where the RTILs are both the ionic sources and the plasticizer. In addition, polymer electrolytes doped with proton donors have recently attracted much attention due to their high proton conductivity, chemical and electrochemical stability, and easier processing of polymer matrices. As one of the most attractive inorganic proton donors, heteropolyacids (HPAs) have been demonstrated to be highly conductive and structural stable [17,18]. These striking and significant observations have triggered our interest to explore the use of RTILs and HPAs as “gelator” to enhance the ionic conductivity of polymer electrolytes. To date, however, few work has been reported on composite polymers containing RTILs and HPAs as the polymer electrolytes for the fabrication of DSSCs. Hence, HPAs are combined with RTILs-based polymers to form polymer gel electrolytes for quasi-solid DSSCs in this paper.

## 2. Experimental

### 2.1. Materials

2-Hydroxyethyl methacrylate (HEMA) was purchased from Acros and further purified by distillation. 2,2'-Azobis-isobutyronitrile (AIBN) and tris(2,2'-bipyridyl)-ruthenium(II) chloride were purchased from Aldrich. 1-Butyl-3-methyl-imidazolium-hexafluoro phosphate (BMImPF<sub>6</sub>) was purchased from Solvent Innovation. Phosphotungstic acid (PWA) and other reagents were purchased from Beijing Chemical Reagent Factory and used as received.

### 2.2. Preparation of composite polymeric gels

Composite polymeric gels comprising PWA filler and BMImPF<sub>6</sub> in poly(2-hydroxyethyl methacrylate) (PHEMA) matrix were prepared by a similar method to our previous published procedures [19]. Typically, HEMA was mixed with AIBN in 0.5 wt% with respect of HEMA as initiator of the free-radical polymerization. The homogeneous mixture was kept in an oven of 60 °C for 0.5 h. Then BMImPF<sub>6</sub> were added at the volume ratio of 1:4 to the amount of monomer and kept at 60 °C for another 0.5 h. At last, PWA was added to the mixture, and sonicated for a few minutes to make a homogeneous phase. The resulting mixture was cast on polytetrafluoroethylene mould and heated first at 60 °C for 5 h, and then increased to 70 °C to initiate the free radical polymerization of HEMA for 20 h. The obtained products were further treated at 60 °C in a vacuum for 12 h to remove the residual monomer. For comparison, the PHEMA–RTIL composite polymeric gels without PWA was prepared in the same pro-

cedures and labeled as “PWA00”; accordingly, the composite polymeric gels with 3 wt% and 6 wt% PWA with respect to the weight of the HEMA monomer were labeled as “PWA03” and “PWA06”, respectively.

### 2.3. Fabrication of quasi-solid state DSSCs

Quasi-solid state DSSCs were assembled using a film of the composite polymer electrolyte sandwiched between the TiO<sub>2</sub> photoanode and the counter electrode. TiO<sub>2</sub> paste for the fabrication of photoanode was obtained by mixing 2 mL of ethanol and 300 mg of TiO<sub>2</sub> nanoparticles (Degussa P25) homogeneously. Nanocrystalline TiO<sub>2</sub> films were prepared by doctor blading of TiO<sub>2</sub> paste onto FTO conducting glass substrate (15 Ω/square F-doping SnO<sub>2</sub>), followed by heating in air at 450 °C for 2 h. The resultant ca. 4 μm thick TiO<sub>2</sub> films were coated with the sensitizer dye tris(2,2'-bipyridyl)-ruthenium(II) chloride by immersing the film in a 1.0 × 10<sup>-3</sup> M ethanol dye solution overnight. The transparent platinized counter electrode was prepared by the deposition of a drop of 0.05 M of H<sub>2</sub>PtCl<sub>6</sub> in isopropanol solution onto the FTO conducting glass followed by heating at 400 °C in air for 20 min. The composite polymer electrolyte comprised the as-prepared composite polymeric gel, containing 9% and 0.9% (w/w) of NaI and I<sub>2</sub>, respectively. For deposition, the suitable amount of composite polymeric gel (PWA00, PWA03 or PWA06) was added into an organic solvent mixture containing *N,N*-dimethylformamide (DMF), ethylene carbonate (EC) and propylene carbonate (PC) in the ratio of 5:3:2 (w/w) under stirring, followed by the addition of NaI and I<sub>2</sub>, respectively. Then the resulting mixture was heated in a closed flask at 120 °C to dissolve the polymer matrix, followed by cooling down to room temperature to form a homogeneous solution. Afterwards, about 500 μL of this solution was dropped over the sensitized TiO<sub>2</sub> electrode in steps, allowed to dry in air, and then pressed against the counter electrode. An external clamp maintained the mechanical integrity of the cell, without any further sealing.

### 2.4. Measurements

Attenuated total internal reflection Fourier transform infrared (ATR-FTIR) spectra were carried out using Perkin Elmer spectrometer in the frequency range of 4000–600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The thermal gravimetry (TG) analysis was performed with a STA 409C thermal analyzer (NETZSCH, Germany). Measurements were conducted by heating the as-prepared samples from 50 to 600 °C at a heating rate of 10 °C/min under flowing argon atmosphere. The SEM images of the samples were characterized by field emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F) operated at 1.0 kV.

The ionic conductivity of the composite polymeric gel was evaluated using electrochemical impedance spectra (EIS) method at ambient temperature and humidity. The impedance measurements were carried out on a PARSTAT

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