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Silicotungustic acid incorporated gel polymer electrolyte as efficient redox mediator for dye sensitized solar cells

Nagaraj Pavithra, Sambandam Anandan*

Nanomaterials and Solar Energy Conversion Lab., Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India

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ABSTRACT

Silicotungustic acid (STA) modified gel polymer electrolytes (GPEs) with various wt% (0–5%) were prepared using Poly(ethylene oxide) as polymer and LiI/I_2 as redox couple. The conformational changes, by the addition of STA were studied using Fourier transform infrared spectroscopy, differential scanning calorimetry and scanning electron microscopy. Electrochemical properties like ionic conductivity (σ) and tri-iodide diffusion co-efficient ($D_{I_3^-}$) were studied using electrochemical impendence spectroscopy and linear sweep voltammetry experiments respectively. Photovoltaic properties of fabricated dye sensitized solar cells (DSSC) using such electrolytes were studied under 85 mW cm^{-2} illumination and the results were supported by Nyquist and bode phase plots from electrochemical impendence spectroscopy. A photovoltaic conversion efficiency of 6.26% was achieved for the GPE containing 3 wt% STA. Finally, the effect of LiI blocking layer for the DSSCs containing STA free and STA modified gel electrolytes was studied.

1. Introduction

For the past few decades, the two major problems that our planet earth is facing are energy demand and global warming, due to more consumption of fossil fuels. Finding a new renewable green energy source is the common solution for both the problems. Solar energy is the most promising renewable energy because the energy provided by the sun is enormous and it is available for whole year. Dye sensitized solar cells (DSSCs), which works on the principle of plant photosynthesis is one among the various types of solar cells and it have many advantages like low cost and easy room temperature fabrication process over other types of solar cells [1]. Apart from the advantages, use of liquid electrolytes (LE) in DSSCs, limits its long term stability and out-door applications due to evaporation, dye desorption and corrosion of counter electrolyte by the LE [2]. To increase the durability of DSSCs, the LE can be replaced either by solid or gel polymer electrolytes [3–6], room temperature ionic liquids (RTILs) [7,8], hole transport material (HTMs) [9–11], etc. Jihuai Wu et al. in his recently published review exemplify that one third of DSSC research is related to electrolytes [12]. In the midst of other type of electrolyte, polymer electrolytes have attracted attention due to their stability. But, for the DSSCs constructed using solid polymer electrolytes (SPEs) the efficiencies were quite low, due to poor ionic conduction in the solid matrix. To overcome this, gel polymer electrolytes (GPEs) were used because its ionic conductivity values comparable to LE and as well as its stabilities are comparable with SPEs [13,14]. Generally, GPEs were prepared by dissolving polymer network (polymer host) with stoichiometric ratios of electrolyte composition and then gelatized using either plasticizer, organic gelators, inorganic (ceramic fillers), co-polymerization, heat induced/UV-cured cross-linker or by soaking the polymer film in liquid electrolytes [15].

Poly(ethylene oxide) (PEO) is the more commonly studied polymer matrix to prepare polymer electrolyte. It shows excellent photochemical stability, even in the presence of platinum and TiO_2 nanoparticles and its high ionic dissociation leads to better ionic conductivity of the electrolytes [16,17]. Hetero-poly acids (HPAs), those with Keggin structure were well known for their electro catalytic activity and they possess good thermal stability [18,19]. In the literature, a number of researchers used various HPAs coupled with TiO_2 film as well as in polymer electrolytes to suppress the recombination reaction and thus improving the photo-conversion efficiency of DSSC [20–22]. Silicotungstic acid (STA) is one among the commonly exploit hetero-polyacids and well known for its electro catalytic properties [23–25]. In the case of DSSCs composed of polymer electrolytes an alkali halide layer was introduced in

* Corresponding author.
E-mail address: sanand@nitt.edu (A. Sambandam).

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order to modify the dye/electrolyte interface. Among various alkali metal halides, LiI is the more commonly encountered salt [26,27].

In this present work, we were concentrated to prepare PEO/LiI-I_2 based gel polymer electrolytes (GPEs) by the addition of various weight percentage of STA in the presence of propylene carbonate. Propylene carbonate acts as a plasticizer and as well as solvent [28]. The changes in conformational, electrochemical, and photo-electrochemical properties of prepared gel polymer electrolytes (GPEs) were examined. Finally, the effect of LiI blocking layer for LE, STA free and STA incorporated GPEs were studied.

2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO), $TiCl_4$, Acetyl acetone (99%), Triton-X (95%), Poly(ethylene glycol) (PEG, MW = 10,000), N719 dye, and Silicotungstic acid were purchased from Sigma-Aldrich, India. TiO_2 (P25) (Degussa), Nitric acid (Merck) and Propylene Carbonate (Alfa-Aesar) were also used. All purchased chemicals and reagents were of analytical grade and used as received without any further purification.

2.2. Preparation of gel polymer electrolytes

The gel polymer electrolytes modified with and without STA were prepared as follows: 0.264 g of PEO is dissolved in a solvent mixture of propylene carbonate and acetonitrile in the volume ratio of 1:20 by continuous stirring at 80 °C for 2 h. Then, the redox couple with the controlled concentration ratio of the iodine and the iodide salt, $[I_2]/[LiI]$ as 0.1 and various weight% (0–5) of STA with respect to PEO were added and stirred at 80 °C for another 2 h. The solution was then stirred for overnight and then evaporated at 80 °C. At this temperature only acetonitrile (B. Pt: 82 °C) will evaporate and propylene carbonate (B. Pt: 242 °C) will remain in the electrolyte. Thus, the STA free and STA modified gel polymer electrolytes were obtained. GPEs containing various weight% (0–5) of STA were denoted (A-F) respectively. For comparison, the liquid electrolyte containing same molar concentrations of LiI and I_2 in propylene carbonate was also prepared and it is represented as Liq.

2.3. Fabrication of dye sensitized solar cell

2.3.1. Preparation of photo anodes

TiO_2 paste was prepared by a reported procedure [29]. In short, 0.5 g of TiO_2 (P25) nanoparticles, 0.016 g of PEG (as binder), 0.21 mL of acetyl acetone and 0.04 mL of Triton-X were added to a solution of 1 M HNO_3. This mixture was sonicated for 1 h in an ultrasonic water bath and stirred continuously for 24 h. The above prepared paste was coated on pre-treated Fluorine doped Tin oxide (FTO) plates by doctor blade method. Pre-treatment was done by dipping the plates in a 40 mM solution of $TiCl_4$ for 30 min at 70 °C. Finally, the TiO_2 coated FTO plates were sintered at 450 °C for 30 min in a tubular furnace to obtain uniform films. Then, the films were sensitized by using a 3×10^{-4} M solution of N719 dye in 1:1 solvent mixture of acetonitrile and *tert*-butanol for 24 h. For the cell with LiI blocking layer, surface of the dye sensitized photoanode is treated with a dilute solution of LiI in acetonitrile [26]. The active area of the as prepared electrodes was 0.25 cm^2.

2.3.2. Preparation of counter electrodes

Pt coated counter electrodes were prepared by drop casting method, using a 5×10^{-4} M solution of $H_2[Pt(Cl)_6]$ in pre-cleaned FTO plates followed by sintering the plates at 450 °C for 30 min.

2.3.3. Cell assembly

DSSC were fabricated by sandwiching the electrolytes (LE/GPE) in between the photoanode and the Pt counter electrode. An adhesive tape of thickness ~50 μm was used to maintain the thickness of the electrolyte layer and to prevent short-circuiting of the electrodes.

2.4. Characterization techniques

The structural changes of prepared gel polymer electrolytes (GPEs) modified with and without STA were studied using Fourier transform infrared spectra obtained using a Thermo Scientific Nicolet iS5 FTIR spectrometer. Differential scanning calorimetry experiment was performed in the temperature range of −65 °C to 120 °C using Mettler Toledo DSC 822e model at the heating rate of 10 °C/min. Thermogravimetric analysis was performed using

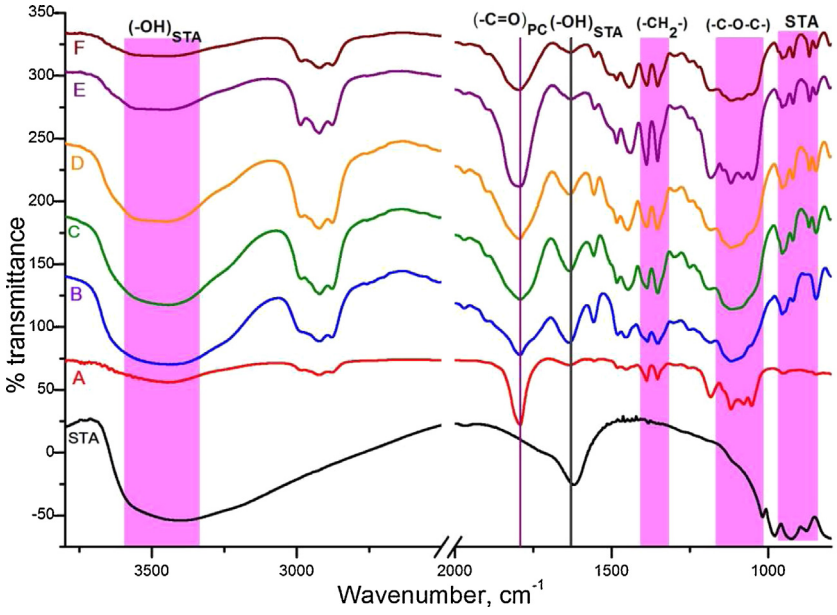

Fig. 1. FTIR spectra of prepared gel polymer electrolytes containing various weight% (0–5) of STA were denoted (A–F) respectively.