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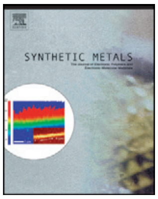

Letter

Solid-state dye-sensitized solar cells constructed with an electrochrome impregnated elastomeric electrolyte

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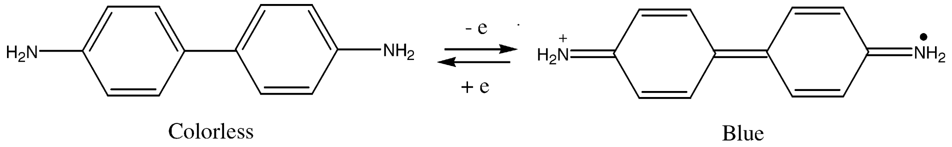
ABSTRACT

A new type of hybrid polymer electrolyte matrix based on benzidine impregnated polyepichlorohydrine (PEC) with TiO_2 nanofiller was developed for dye-sensitized solar cells (DSSCs). The polymer electrolytes were characterized by scanning electron microscopy (SEM), TGA, XRD and FT-IR, and the assembled DSSCs by photocurrent density–voltage and energy conversion efficiency (η) measurements. The ionic conductivity and the interfacial contact with dye attached TiO_2 particles were enhanced markedly by the addition of electrochrome impregnated polymer electrolyte, resulting in very high overall energy conversion efficiency.

1. Introduction

The search for alternate sources of energy has gained momentum in recent years in the light of our present energy needs. Sunlight is an abundant source one can tap into for electricity generation (photovoltaics) or to utilize as a driver for production of clean fuels (hydrogen generation). At present, if any one thinks of solar energy immediately dye-sensitized solar cells (DSSCs) came into their mind. Thus, the most promising DSSCs have been shown to operate with power conversion efficiencies of up to 10% when nanocrystalline TiO_2 electrodes have been used as a solid substrate and organometallic ruthenium complexes as sensitizers [1]. As highly efficient solar cells can be prepared dye-sensitized TiO_2 that also show remarkable long-term stability, sensitization of wide band gap oxide semiconductors by dye molecules, in general has regained considerable interest in experiments such as ultrafast electron transfer from the dye to the electrode and suppression of back-electron transfer to the dye (recombination) or the electrolyte as compared to hole transfer from the dye to the electrolyte are further prerequisites for efficient and chemically stable electrodes [2–9]. The practical problem in using TiO_2 is the undesired electron/hole recombination, which, in the absence of proper electron acceptors or donors, is extremely efficient and thus represents the major energy wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron-hole pair recombination is to add other (reversible) electron acceptors/donors to the reaction mixture. They have several effects such as (1) to increase the number of trapped electrons, and consequently, avoid recombination, (2) to generate more radicals and other oxidizing species and (3) to increase the oxidation rate of intermediate compounds. To attain such compatibility recently the research concerning the science of new materials with adequate properties for solar cells has increased mainly due to the growing energy demand and environmental impact caused by its production. Recently, in this regard, we also made an attempt to impregnate electron acceptor (heteropoly tungstic acid) in polyvinylidene fluoride as a solid polymer electrolyte for DSSC in order to effectively decrease the back-electron transfer reactions taking place [10].

Currently, research is now directed towards the assembly of solid-state electrochromic devices by mixing conducting polymers with thermoplastics and elastomers to produce polymeric blends which show the electrochromic properties of the conducting polymers (i.e., colored in the oxidized form and transparent in the neutral form) associated with the mechanical properties of common polymers [11,12]. Although some attempts [13,14] have been done in this regard, the use of interface between polymers and dye adsorbed TiO_2 coated conducting glass is still open for investigation. The current study is aimed to study the charge separation at the interface by modifying an elastomer (polyepichlorohydrine; PEC) by incorporating an electrochrome (benzidine), that in addition may act as an electron donor in the photosystem [15] (Fig. 1). The reason for choosing benzidine (Bz) is because rapid and reversible reduction occurs when bound to an electrode surface [16]. Benzidine (λ_{max} = 283 nm, see Ref. [17]) is an extensively studied class of redox chromophores [16,18,19], which on reduction generates a highly reversible and intensely colored blue monoradical cation and yellow diradical cation (see Eqs. (1) and (2)), which is supposed to absorb in the visible region (λ_{max} = 370 and 565 nm, see Ref. [17]) of the solar spectrum and in turn enhance the efficiency of the fabricated solar cells. In addition to electrochromophores, TiO_2 nanofillers were added to polymer electrolytes to induce consistent improvement in the transport properties.



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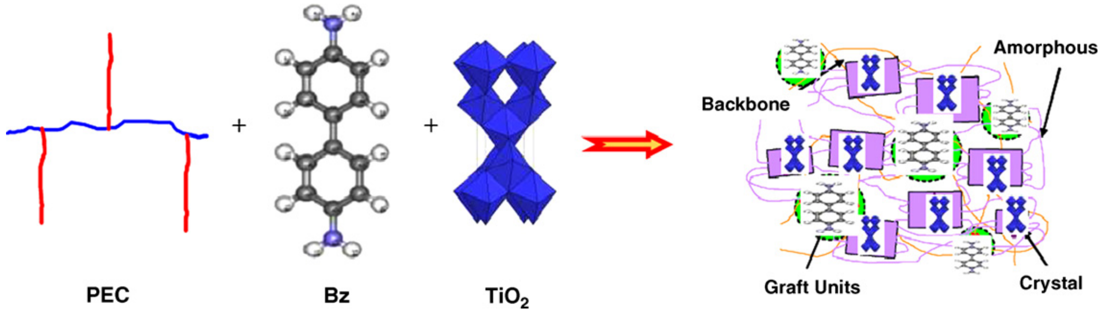
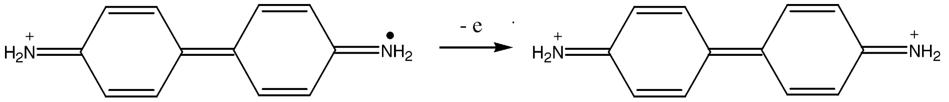


Fig. 1. Schematic illustration of benzidine impregnated PEC with TiO_2 nanofillers.



(2)

2. Experimental

Polymer electrolyte (E1) is prepared by dissolving about benzidine (1 wt.%) in 5 ml of DMF which is then added to desired amount (0.3 g) of polyepichlorohydrine (Aldrich; Mw = 9×10^5), KI (0.03 g) and I_2 (0.003 g) in 15 ml of DMF and heated at 80 °C for certain period of time to get homogeneous liquid. Polymer electrolyte (E2) is prepared as mentioned above but by adding 0.0383 g of nano-TiO_2 fillers (Degussa; 13 nm particle size). For characterization studies (XRD, IR, TGA and SEM analysis), thin polymer electrolyte membranes were cast by vacuum evaporation of solvent at 80 °C. Further, the conductivity of these thin films was performed by complex impedance analysis using Autolab PGSTAT with FRA module coupled to a computer over the frequency domain 1 MHz to 10 Hz with amplitude of 5 mV and in the temperature range 300–373 K with an aid of a pair of silver plates (1 cm^2) as electrodes. The thickness of the film used for electrochemical impedance technique is measured by air-wedge technique [20]. Detailed DSSC fabrication and characterization procedures are well described in recent publications by us [10].

3. Results and discussion

Scanning electron microscopy (SEM) was applied to establish the homogeneity of the nanocomposite materials. Fig. 2 exemplifies the high degree of dispersion of the benzidine and TiO_2 within the polymeric matrix, while few agglomerates with a 2–3 μm characteristic size are detected in certain areas of the PEC:Bz:TiO_2:KI/I_2 sample (Fig. 2b). These nanofillers, due to their hydrophilic properties, act as liquid-adsorbing centers, promoting liquid uptake and retention in the membrane without adversely affecting its mechanical properties.

The impedance diagrams for benzidine impregnated PEC with and without TiO_2 nanofillers systems are in general, slightly dephased semicircles at high frequencies (electrolyte) and straight lines at low frequency (capacitive behavior of electrode/electrolyte interfaces), inclined as function of the roughness and superficial oxides. For example, this may be confirmed by seeing the representative raw data (inset of Fig. 3) for the benzidine impregnated PEC with and without TiO_2 nanofillers at room temperature. The ionic conductivity can be calculated based on the following equation:

$$\sigma\ (\mathrm{S/cm}) = \frac{L}{RS}$$

where σ, L, R and S denote the ionic conductivity, thickness of the membrane, the resistance of the membrane and the cross-sectional area of the membrane, respectively. At 300 K, the ionic conductivity was determined to be much higher for benzidine impregnated PEC with and without TiO_2 nanofillers ($29.13 \times 10^{-5}\ \mathrm{S\,cm^{-1}}$ and $1.78 \times 10^{-5}\ \mathrm{S\,cm^{-1}}$) compared to pure benzidine ($1.58 \times 10^{-8}\ \mathrm{S\,cm^{-1}}$) and pure epichlorohydrin ($20 \times 10^{-6}\ \mathrm{S\,cm^{-1}}$). The value ($29.13 \times 10^{-5}\ \mathrm{S\,cm^{-1}}$) reached is in the same order of the best values obtained by the system (mixing conducting polymers with thermoplastics and elastomers to pro-

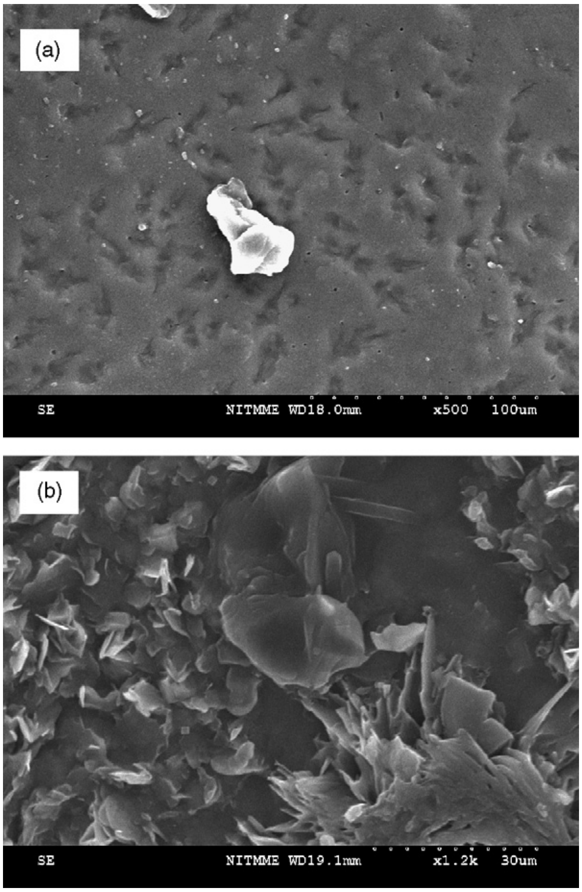


Fig. 2. SEM images of (a) benzidine impregnated PEC with iodine/iodide. (b) Benzidine impregnated PEC with iodine/iodide and TiO_2.