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Viologen impregnated PVDF with TiO_2 nanofiller as a solid polymer electrolyte for dye-sensitized solar cells

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Abstract

Dye-sensitized solar cells were fabricated using viologen impregnated PVDF with TiO_2 nanofiller as a solid polymer electrolyte sandwiched in between N3 (*cis*-di(thiocyanato)*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)-ruthenium(II)) dye adsorbed over TiO_2 nanocrystalline film as anode and conducting carbon cement coated over conducting glass as cathode to mainly impede the back-electron transfer processes. The prepared polymer electrolytes were well characterized before using them in solar cells. The functioning of the solar cells fabricated was monitored and the current–voltage characteristics were measured.

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Keywords: Dye-sensitized solar cells; Polymer electrolytes; Nanofillers; Methyl viologen

1. Introduction

Energy is an important as well as the basic need for every moment of life. The extraordinary consumption of fossil fuels is driving to the fast depletion of natural resources and hence there is an urgent need for the search for alternative sources of energy, which can supplant or supplement the existing energy for the survival of the future generation. Further more, the burning of fossil fuels for the production of energy releases hazardous gases into the atmosphere. To avoid both environmental pollution and the future energy crisis, much attention has to be devoted to convert the everlasting solar energy into other useful forms of energy. Hence the search for renewable sources of energy has led to an increasing interest in solar cells because of their possible role as transducers of solar to electrical energy. Further, from the pioneering results published at the outset of the nineties [1,2] dye-sensitized photoelectrochemical solar cells (DSSC) have been the subject of a large number of experimental investigations to improve their efficiency and stability. Since the category of dye-sensitized solar cells fall in between solid-state photovoltaics and classical regenerative photoelectrochemical cells, a lot of research groups have tried to replace the liquid electrolyte with other solid materials [3–13]. These solid electrolytes can carry the current up to the redox electrode, and they are capable not only to offer hermetic sealing and stability but also to reduce design restrictions and endow the cell with shape choice and flexibility. 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. In this regard, attempt has been made to impregnate heteropolyacid in polyvinylidene fluoride as a solid polymer electrolyte for dye-sensitized solar cell in order to effectively decrease the back-electron transfer reactions taking place [14]. Although some attempts 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. In the present paper, charge separation at the interface between

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PVDF and dye adsorbed TiO_2 coated conducting glass were studied by incorporating ionic sensitizer, methyl viologen that in addition may act as an electron relay. The reason for choosing viologen is because rapid and reversible reduction occurs when bound to an electrode surface [15]. Viologens are an extensively studied class of redox chromophores [16–18], which on first reduction generates a highly reversible viologen dication and secondly leads to the formation of the intensely colored radical cation all are supposed to absorb in the visible region of the solar spectrum and in turn enhance the efficiency of the fabricated solar cells. Further, the initial rate of viologen radical formation for the self-assembling system is higher than that for methyl viologen in the analogous homogeneous system [17,18] and hence in this context, viologen is impregnated into polymer membrane. In addition to ionic sensitizer, TiO_2 nanofillers were added to polymer electrolytes to induce consistent improvement in the transport properties.

2. Experimental

The starting materials used are poly(vinylidene fluoride) (Good Fellow), TiO_2 (Degussa) and methyl viologen (Aldrich). All the other chemicals used are the purest research grade available. The TiO_2, 13 nm particle size (Degussa) nanofiller was dried at 250 °C under vacuum for 4 h before use. A typical synthesis of modified polymer electrolytes was carried out as follows. Polymer electrolyte (E1) is prepared by dissolving about methyl viologen (1 wt%) in 2 ml of water which is then added to desired amount of PVDF (0.3 g), KI (0.03 g) and I_2 (0.003 g) in 25 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.

For characterization studies, thin polymer electrolyte membranes were cast by vacuum evaporation of solvent at 80 °C. The samples are well characterized by XRD, IR, TGA and SEM analysis. Further, the complex impedance analysis of these thin films was performed 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 gold plates (1 cm^2) as electrodes. The thickness of the film used for electrochemical impedance technique is measured by air-wedge technique [19].

3. Results and discussion

The phase identification for the prepared polymer electrolytes were carried out using powder X-ray diffraction (PANalytical). XRD patterns (Fig. 1) obtained for TiO_2 nanofillers added sample showed a mixture of anatase and rutile peaks in addition to the lines of PVDF. The bare PVDF membrane exhibits a group of lines in the region of 2θ from 17° to 21°, which overlaps with X-ray scattering from the amorphous region of the membrane at lower Bragg angles (1 0 0, 0 2 0, 1 1 0). The addition of methyl viologen and TiO_2 to PVDF polymer modifies the relative ratio between the crystalline and amorphous structures of cast PVDF with respect to bare PVDF.

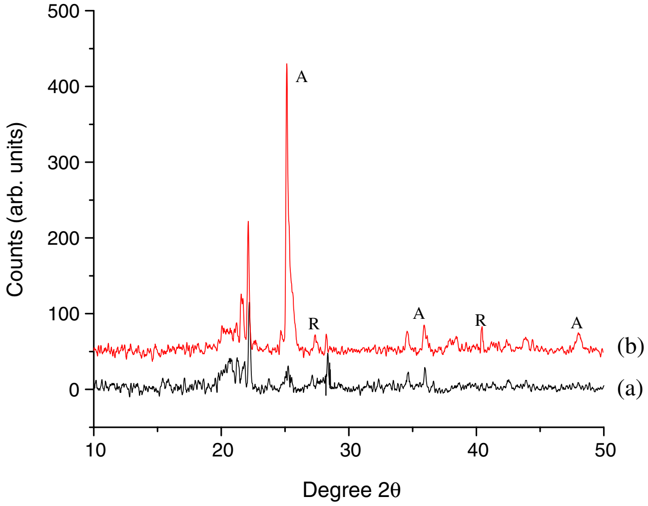

Fig. 1. XRD spectra of (a) viologen impregnated PVDF without TiO_2 nanofillers and (b) viologen impregnated PVDF with TiO_2 nanofillers.

The chemical compositions for the prepared polymer electrolytes were analyzed using FT-IR spectroscopy (Perkin–Elmer). For methyl viologen impregnated PVDF with and without nanofiller, almost all the stretching vibrations (C–H, C=C) of methyl viologen overlap with respect to PVDF (figure not shown) as follows. That is, the characteristic absorption bands of the symmetric and asymmetric vibration of the CH_2 group are observed for both the PVDF membranes at 2921 and 2850 cm^{-1} as published in the literature earlier [20,21]. Similarly CH_2 rocking vibration [21] at 879 cm^{-1} is observed for both the PVDF membranes. In addition, fluorine atoms attached to carbon double bonds have the effect of shifting the C=C stretching vibration to a higher frequency near 3020 cm^{-1} and is noticed for both the samples. For TiO_2 nanofiller added sample, Ti–O stretching vibration was noticed at 1073 cm^{-1}. The fact that all the peaks are found to be overlapped one over the other leads to conclude that both the methyl viologen and TiO_2 nanofiller are present in the polymer membrane.

The TGA thermograms of the methyl viologen impregnated PVDF with iodine/iodide and with TiO_2 nanofiller were displayed in Fig. 2. From Fig. 2, it is seen that all the membranes retain more than 95% of their weight up to a temperature of about 300 °C. Above 300 °C, all the membranes started to decompose in a rapid manner. In order to ensure the above findings in detail, the DTA analysis on the membranes will be more helpful. The melting endotherm corresponding to PVDF is observed at 161 ± 2 °C for all the prepared polymer electrolytes. The exothermic transformations above 450 °C on DTA curve of membranes were due to decomposition of polymer. It is believed that the addition of TiO_2 nanofillers may favour the formation of complexes with the polymer and in turn