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Photo-electrochemical properties of variously-sized titanium dioxide nanoparticle-based dye-sensitized solar cells

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ABSTRACT

Titanium dioxide (TiO_2) of various particle sizes were employed for the fabrication of dye sensitized solar cells (DSSCs). The morphology and particle size dependent dye loading nature of the photoanodes were analyzed using scanning electron microscopy and UV–visible absorption spectroscopy respectively. Electrochemical impedance spectroscopy and current–voltage measurements were performed to investigate the effect of particle size, aging and temperature on the photo-electrochemical properties of the fabricated DSSCs. The parameter which affects the electron transport properties under various experimental conditions were obtained through fitting the Nyquist plot with an equivalent circuit.

1. Introduction

Titanium dioxide (TiO_2) nanostructure as the photoanode in dye sensitized solar cells has triggered intense interest among researchers around the globe owing to their low material cost and straightforward fabrication methods. Over 11% efficiency has been achieved with TiO_2 as photoanode, which is comparable to the commercial photovoltaic devices [1–3]. Generally, a typical DSSCs consist of dye sensitized wide band gap semiconductor photoanode, counter electrode and redox electrolyte. Even though each components of the DSSC has its own importance, the role of semiconductor oxide in the photoanode is emphatically crucial as the overall cell performance predominantly depended [4–6]. Light harvesting and electron collection are the two critical factors determining the efficiency of dye sensitized solar cells; these factors are directly related with the photoanode [7]. Apart from this, the dye loading and the electron transport path determining the photo-carrier collection are the crucial functions of the photoanode [8].

Recently, many work have been reported based on DSSCs using different morphological TiO_2 and various wide band gap semiconductors replacing porous TiO_2 nanostructures [9–13]. But these TiO_2 nanostructures are still dominating in the overall performances of DSSCs. Since various parameters like less electron transport properties, high recombination of photo-exited electrons, low stability of materials etc [14] forbid other materials and other forms of TiO_2 to compete against commercially used porous TiO_2 nanoparticles. Various particle sized TiO_2 paste are commercially available for the fabrication of DSSC photoanodes which show excellent photovoltaic performance than that of other forms of TiO_2 nanoparticles [15,16]. Even though, these TiO_2 pastes show good performance in DSSC, many efforts are in progress to achieve the theoretical efficiency. Since the size of the nanoparticle in the photoanode is a vital factor affecting the overall performance of the cell. So the detailed study on various sized TiO_2 nanoparticle is important from the application point of view.

Electrochemical impedance spectroscopy (EIS) has been a widely employed tool to study the kinetics of

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photoanode, electrochemical and photoelectrochemical processes occurring in the DSSC [17,18]. Bisquert et al. [19,20], Kern et al. [21] and Adachi et al. [22] have developed the general formulation of impedance models considering theoretical and experimental aspects of electron diffusion and recombination in a thin layer of porous electrodes in DSSCs. They have proposed detailed theoretical and experimental aspects for the DSSCs using impedance spectroscopy with reliable values of electron transport parameters in DSSCs and have been suggested as the requisites for making efficient DSSCs.

In our present study, we report the effect of different particle sized TiO_2 nanoparticles in the electrochemical and photo-electrochemical properties of DSSCs. Apart from this the effect of aging and temperature on different particle sized photoanodes were analyzed using impedance spectroscopy by fitting the Nyquist plot and discussed in detail.

2. Experimental

2.1. Cell fabrications

Ultrasonically well cleaned fluorine doped tin oxide (FTO) having sheet resistance of 10 Ω/square was used to fabricate both the photoanodes and counter electrodes. The photoanode electrodes were made from three different commercially available TiO_2 pastes of particle sizes ~9 nm (T9), ~20 nm (T20), ~400 nm (T400) (Ti-Nanoxide HT/SP (8–10 nm, 1800 USD/100 gm); Ti-Nanoxide D/SP (15–20 nm, 750 USD/100 gm); Ti-Nanoxide R/SP (>100 nm, 710 USD/100 gm) of Solaronix). These nanoporous TiO_2 pastes were coated on FTO by the doctor blade technique followed by an annealing at 450 °C for 30 min and the final thicknesses were 8 μm, 12 μm and 16 μm for T9, T20 and T400 respectively after the solvent evaporation (0.25 cm^2 active area). The obtained photoanodes were sensitized by soaking in N719 dye (Ruthenium 535 bis-TBA cis-bis (isothiocyanato) bis (2,2-bipyridyl-4,4-dicarboxylato)-ruthenium(II) bis-tetrabutyl ammonium) dissolved in anhydrous ethanol solution. Excess dye molecules were removed by soaking photoanode in 99.9% ethanol for 30 min. Platinum counter electrodes were prepared by depositing a commercial platinum paste (Solaronix, platinum catalyst T/SP) on a specially holed FTO glass substrate, which was subsequently heat treated at 400 °C for 30 min in air. The photoanode and counter electrodes were sealed together using a 25 μm hot-melt sealing sheet (SX 1170–25, Solaronix). The internal space of each cell was filled with a redox liquid electrolyte 0.5 M LiI, 0.05 M I_2 and 0.5 M 4-tertbutylpyridine in acetonitrile by capillary action. The cells were left few hours for the complete diffusion of electrolyte within the photoanodes before performing the photo-electrochemical test.

2.2. Characterizations

The surface morphologies of TiO_2 photoanodes were analyzed using field emission scanning electron microscope (FE-SEM, S-4200, Hitachi) operated at 15 kV. The film thicknesses were measured using a surface profiler meter (α-step, TENCOR P-2). The amount of dye loading in the photoanodes were determined using UV–visible spectrum (OPTIZEN 3220UV spectrophotometer) by desorbing dye using 0.1 M NaOH solution. The current–voltage characteristics of the DSSCs were performed under 1 sun illumination (AM 1.5 G, 100 mW cm^{-2}) with San Ei Electric (XES 301S, Japan) solar simulator having the irradiance uniformity of ±3%. The overall fill factor (*FF*) and conversion efficiency (η) can be calculated using the relations,

$$FF = P_{max}/(V_{oc} \times J_{sc}) \quad (1)$$

$$\eta = [(FF \times V_{oc} \times J_{sc})/P_{in}] \times 100 \quad (2)$$

where,

$$P_{max} = (V_{max} \times I_{max}) \quad (3)$$

and P_{in} are the maximum power density and input power density respectively. Electrochemical impedance spectroscopy (EIS) was performed using a BioLogic potentiostat/galvanostat/EIS analyzer (SP-150, France) under 1 sun illumination. The aging dependent photo-electrochemical properties were analyzed by selecting the best fabricated cells from each set of sample placed in an open condition at room temperature (~25 °C) and measured periodically up to 3 weeks. The temperature dependent EIS spectrum was recorded by placing the cells under unfiltered halogen lamp and the corresponding temperature was monitored using Infrared thermometer (model no: 383 accuracy ±2 °C). Five sets of best cells from each type of photoanodes were used for the experiment in various experimental conditions. The standard deviation of the overall experiment values are ~0.183, 0.172 and 0.141 for T9, T20 and T400 DSSCs respectively.

3. Results and discussion

The FE-SEM images of T9, T20 and T400 coated on FTO substrates are shown in Fig. 1 a, b and c. From the SEM image, the different particle size and the porous nature of the fabricated photoanodes can be easily observed. Fig. 2 shows the optical absorption spectrum of desorbed dye from the TiO_2 photoanodes. The spectrum clearly depicts particle size dependent absorption of the dye on the surface of photoanodes. Obviously, the sample T9 with very small particle size shows maximum dye adsorption owing to their large surface area than T20 and T400 photoanodes. Fig. 3 shows the current voltage behavior of three different particle size photoanoded DSSCs. The calculated photovoltaic parameters of the cells are shown in Table 1. The efficiencies of T9, T20 and T400 are 8.125%, 7.175% and 3.71%, respectively. The high efficiency of the T9 is due to large injection of photoelectron (current density 18.043 mA cm^{-2}) due to its dominant dye adsorption capability. However, the open circuit voltage (V_{oc}) of T20 and T400 is higher than that of T9 DSSC. This is believed to be large recombination of photo injected electron with the electrolyte in T9 DSSCs. Since, the electrons have to travel a long zigzag path which hampers the effective electron collection due to recombination with electrolyte than the larger size TiO_2 particle having less path length [23]. The aging dependent photovoltaic