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Charge transfer and recombination kinetics in dye-sensitized solar cell using static and dynamic electrical characterization techniques

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Abstract

This study investigates the steady-state current–voltage characteristics, electronic and ionic processes and dynamic response of a TiO_2 nanoparticle based dye-sensitized solar cell (DSSC) using impedance spectroscopy and current–voltage measurements. A dye-sensitized solar cell is fabricated with 12.26 μm thick TiO_2 layer, having power conversion efficiency of 2.9% under AM1.5 spectrum with photo-generated current density (J_{SC}) of 7.2 mA cm^{-2} and open-circuit voltage (V_{OC}) of 672 mV. The observed electrochemical phenomenon at the TiO_2–electrolyte interface, in diffusion of electrolyte and in charge transfer at the counter electrode is mathematically modeled using alternating current (AC) electrical equivalent circuit. The effect of temperature and illumination on the steady state and dynamic parameters of dye-sensitized solar cells is also studied. The dynamic resistance of DSSC decreases from 440.7 Ω to 78.6 Ω with increase in illumination level from 20 mW cm^{-2} to 100 mW cm^{-2}.

Keywords: Dye-sensitized solar cell; Dynamic characterization; Two-diode model; Steady state characterization

1. Introduction

In last decade, dye-sensitized solar cells (DSSCs) based on nanocrystalline mesoporous TiO_2 films have attracted much attention as a potential low-cost alternative to single or polycrystalline p–n junction based solar cells. Recently, DSSCs have been studied and developed by many research groups in their work on photosensitizers (Chien and Hsu, 2013; Wu et al., 2012), plasmon induced efficiency enhancement (Ng et al., 2014; Muduli et al., 2012), solid electrolytes (Zhang et al., 2012; Wang et al., 2012), TiO_2 layer architecture (Mohammadi et al., 2012; Lamberti et al., 2013; Valdivia et al., 2013) and counter electrode materials (Chiang et al., 2012). DSSCs have demonstrated electrical energy conversion efficiencies above 12% (Yella et al., 2011), where electron injection from excited state of the dye to the conduction band of TiO_2 plays an important role (Franco et al., 1999; Cherepy et al., 1997). The injected electrons flow through the porous TiO_2 thin film to the transparent conducting oxide (TCO), depending on the incident intensity and trapping–detrapping effect (Peter and Wijayantha, 1999, 2000; Fredin et al., 2005; Duffy et al., 2000). The oxidized dye molecules are regenerated by redox mediators (I^-/I_3^-). Further, these oxidized redox mediators (I_3^-) are diffused to the back electrode where regeneration occurs for a complete DSSC operation cycle (Papageorgiou et al., 1996; Imoto et al., 2003).

The influence of electrode morphology, interfacial charge recombination and the charge transport on the

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output performance of DSSCs has been extensively studied by electrochemical impedance spectroscopy (EIS) Peter, 2007; Bay and West, 2005; Dloczik et al., 1997. Electrochemical impedance spectroscopy is a prominent method of measuring the current response to the applied alternating current (AC) voltage as a function of frequency to study the kinetics of electrochemical and photo-electrochemical behavior of devices. Despite the achievement of efficiency >10% in DSSCs, their effective exploitation has been limited due to: (a) unsystematic study of transport phenomenon, (b) inadequate performance analysis under actual test conditions, and (c) insufficient understanding of dynamic response towards varying temperature and illumination conditions, which is a major hindrance to put this technology in competition with the existing technologies. To surmount such issues, an in-depth understanding of morphology of DSSCs, transport of charge carriers, dynamic and steady-state behavior can offer an insight on how to develop and improve DSSC performance.

Keeping in view the above-mentioned shortfalls, we have undertaken a detailed study on: (a) development of AC impedance based electrical model to incorporate interfacial charge transport and recombination processes, (b) validation of the developed model using actual performance parameters of DSSC fabricated in our laboratory, (c) effect of illumination and temperature on the performance of the DSSC and (d) the effect of recombination mechanism during electrolytic charge diffusion. The developed theoretical model is validated by the obtained experimental results. For the design of a high performance power conditioning unit, it is essential to have accurate information about the static and dynamic characteristics of the solar cell (Yadav et al., 2013a). In our previous work, single-diode model was used to explore dynamic parameters of crystalline silicon solar cell (Yadav et al., 2013a,b). But DSSC is an electrochemical device which cannot be correctly modeled based on single-diode model, so a complete treatment of two-diode model is presented in this article to incorporate the calculations for dynamic resistance of DSSC.

2. Fabrication and assembling of DSSC

Fluorine doped tin oxide (F:SnO_2/FTO) coated glass substrates having sheet resistance ≈10 Ω/□ (Pilkington glass, India) were cleaned sequentially by ultrasonic treatment in detergent, deionized (DI) water, acetone and isopropyl alcohol and dried with nitrogen before film preparation. Anatase titanium (IV) oxide nanopowder having particle size <25 nm, 99.7% trace metals basis (Sigma–Aldrich) was used for preparing the front electrode of DSSC. The nanocrystalline TiO_2 paste was prepared by grinding TiO_2 nanopowder (12 g) in a mortar-pestle while adding solvent (about 20 ml acetic acid (pH adjusted to 3.5 in DI water)) dropwise. The paste preparation was done in ambient air at room temperature. The paste obtained was mixed with excess ethanol (150 ml) and magnetically stirred at 350 rpm for 2–4 h. To homogenize the TiO_2 paste, ultrasonication was performed for 15 min. The contents in the dispersion were concentrated by evaporator at 40 °C. The DSSC working electrodes were prepared by immersing the FTO glass plates into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 15 min and rinsed with water and ethanol. The rinsed working electrode was sintered at 450 °C for 30 min. A layer of nanocrystalline titania paste was deposited on the above FTO glass by doctor-blade method. The developed DSSC working electrodes were placed in ethanol for a few minutes to reduce surface irregularities, and then dried for 5 min at 130 °C. The samples were sintered at 450 °C for 30 min in ambient air. Further, the developed nanocrystalline TiO_2 electrodes were immersed in 40 mM $TiCl_4$ solution for 15 min and sintered at 450 °C for 15 min. After cooling, the TiO_2 working electrode was sensitized in 0.5 mM N-719 dye (Dyesol, Australia) solution (mixture of acetonitrile and methanol, volume ratio: 1:1) at 70 °C for 18–20 h in a dark room. Transparent platinum-coated counter electrodes with fill holes were procured from Dyesol (MBPT-38, Dyesol, Australia). The counter electrodes were heat treated at 400 °C for 15 min before assembling the DSSC. The dye-covered TiO_2 electrode and Pt –counter electrode were assembled into a sandwich type cell and sealed with Surlyn (25 μm). A drop of high-stability electrolyte (EL-HSE, Dyesol, Australia) was put on the hole in the back of the counter electrode. Finally the hole was sealed by using a hot-melt aluminum baked Bynel-thermoplastic sealant (Dyesol). The morphological and optical characterization data of the developed TiO_2 electrode for DSSC is given in supplementary information.

3. Theoretical modeling

3.1. Two-diode model of DSSC

An operating DSSC is principally governed by the relative kinetic rates of several charge transfer steps. The charge transfer taking place from the excited dye to a TiO_2 nanoparticle, from the electrolyte to the dye and from TiO_2 to the load terminals all play a very critical role in the performance of DSSC. Thus, it is very important to understand all the electronic processes taking place at the TiO_2 nanoparticle level, as well as the dynamics of charge separation and charge transport at the metal/oxide interface. The schematic band diagram of dye-sensitized solar cell is shown in the Fig. 1. For a DSSC, charge transfer related kinetics is discussed in detail in our previous work (Tripathi and Kumar, 2013; Tripathi et al., 2013a,b,2014).

Under a steady-state condition of illuminated DSSC, electron injection from the excited dye molecules, transport in the mesoporous semiconductor (TiO_2) thin film, and recombination with electrolyte at the TiO_2/electrolyte interface can be described by the following electron diffusion differential equation (Sodergren et al., 1994; Gomez and Salvador, 2005; Ni et al., 2008):