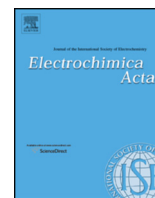




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Utilization of electrochemical impedance spectroscopy for experimental characterization of the diode features of charge recombination in a dye sensitized solar cell



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ABSTRACT

The anode-electrolyte interface is a primary location for charge recombination in a dye sensitized solar cell (DSSC), and hence acts as a major efficiency-limiting factor of the device. The electrical signature of this recombination effect is similar to that of a semiconductor diode, and at the same time serves as an indicator of the recombination mechanisms. The present work focuses on certain detailed aspects of the experimental detection and analysis of this diode-like behavior of a DSSC. The recombination process is activated in a forward biased dark cell containing a photo-anode of multilayered TiO₂ particles. The resulting reaction kinetics are probed with a combination of D.C. voltammetry and strategically designed electrochemical impedance spectroscopy (EIS). The voltage dependent impedance parameters of the multi-component solar cell are obtained from complex nonlinear least square analysis of the EIS data. Among these parameters, the characteristic frequency and the recombination resistance of charge transfer at the TiO₂-electrolyte interface follow the same diode-like voltage dependence as that of the cell's D.C. current. The experimental considerations for analyzing these effects in a quantitative approach are discussed. The ideality factor of the DSSC diode is dictated by charge recombination in the mesoporous TiO₂ photo-anode, and emerges with mutually agreeing values from independent D.C. and A.C. measurements. The results illustrate how the component-resolved analytical capability of EIS can be utilized for a detailed evaluation of the electrochemical performance of a DSSC.

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1. Introduction

The diode-like D.C. electrical response of a dye sensitized solar cell (DSSC) serves as a useful indicator of the mechanism of charge recombination that directly affects the cell's energy conversion efficiency [1–4]. The A.C. response of a DSSC also contains certain diode-like characteristics of the cell [5,6]. However, a DSSC contains several components, including a mesoporous TiO₂ film, a sensitizer dye adsorbed onto the TiO₂, a redox electron mediator in the electrolyte, and a catalytically active (typically Pt) counter electrode. The interfaces associated with these different cell components simultaneously affect the photochemical and electrical characteristics of the DSSC [7,8]. As a result, and depending on the detailed construction of the

device, quantitative analysis of the diode response of a DSSC can be difficult – unless the cell's conjointly interfering component effects are fully resolved from the experimental data. Thus experimental technique(s) employed for such analysis must be capable of resolving the electrochemical signatures of the individual cell-components. This criterion becomes further demanding for the DSSCs equipped with multilayered photo-anodes and/or light scattering layers [9–11] where additional active interfaces are introduced.

The technique of electrochemical impedance spectroscopy (EIS) offers a powerful tool for studying the component-specific functions of DSSCs, and can be employed to inspect the diode-like A.C. characteristics of these cells [12–16]. Nevertheless, to fully utilize the component-selective resolution of EIS, it is necessary to tactically extract the different relaxation frequencies of the reactions occurring at the different interfaces within the DSSC. The analytical framework of such an approach can be developed by employing D.C. bias dependent cell-equivalent circuit (CEC)

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models of the device, derived from complex nonlinear least square (CNLS) fitting of experimental EIS data [17]. The present work centers on this utility of EIS, and couples EIS with linear sweep voltammetry (LSV) to analyze the A.C. and D.C. diode characteristics of a DSSC containing a photo-anode of multilayered TiO₂ particles.

The experiments reported here utilize the underlying correlations between the A.C. impedance parameters and the diode-like D.C. current-voltage features of a DSSC. As shown in previous works, an un-illuminated DSSC under forward bias (FB) is ideally suited for this purpose [4,15]. By following this approach, and using a Grätzel cell of multilayered TiO₂ particles as a model test device [18], we examine here both the A.C. and the D.C. behaviors of the DSSC diode. The activated dark current is caused by the same interfacial reactions that also dictate charge recombination under illumination [2,19–22]. The electrical signatures of the individual DSSC components are resolved with EIS by using strategically selected experimental control variables and by applying sequential steps of CNLS analysis [23]. CNLS calculated uncertainties in the individual CEC elements [24] are employed as a composite measure of the uniqueness of the resulting CEC.

2. Experimental

2.1. Test cell and experimental set up

The components of the experimental DSSC (0.283 cm² active area) were obtained from Solaronix [25]. These included a Ruthenizer (N719 reference) dye, an Iodolyte electrolyte, an inner sealing spot gasket foil (Meltonix), outer sealing foil and cap, a dense transparent (multilayer) region of titania nanoparticles, a light scattering layer (LSL), a “spot Pt electrode” and fluorinated tin oxide (FTO) substrates pre-treated with TiCl₄. Fig. 1 schematically shows the main parts (not drawn to scale) of the DSSC under FB without illumination. Electrical connections to the cell were made through the FTO glass plates at the anode (A) and counter-electrode (C) sides. The cell was filled with an electrolyte containing an electron mediator I₃⁻/I⁻ redox couple. The anode film contained TiO₂ particles of progressively increasing sizes (9, 13, 20 and 37 nm diameters) in going from the FTO substrate to the

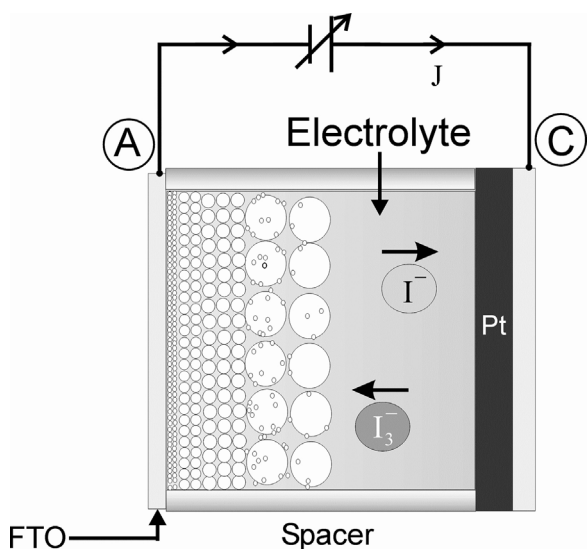


Fig. 1. Schematic of the forward biased un-illuminated DSSC (not drawn to scale) used in this work. The mesoporous TiO₂ photo-anode film contains nanoparticles of different sizes (open circles). I₃⁻ from the electrolyte is reduced by TiO₂, and I⁻ ions are oxidized at the Pt CE. The FTO substrates on the anode and the counter electrode (CE) sides are labeled as A and C, respectively.

electrolyte boundary. The largest (~400 nm) TiO₂ particles, placed immediately next to the electrolyte, formed the LSL [11]. The dye molecules adsorbed onto the TiO₂ particles are not shown here.

The multilayer structure of the photo-anode involving different sizes of TiO₂ particles was chosen for the test cell in view of the increased efficiencies reported for this type of anodes [26,27]. In this design, the LSL improves light collection efficiency by promoting photon confinement through multiple scatterings within the anode film [11,28]. The smaller particles provide large specific surface areas for effective dye adsorption [27]. The placement of the smallest particles at the FTO surface facilitates charge transfers between the FTO and TiO₂ films [26]. The permeation of the smaller TiO₂ particles in the layers of larger particles helps to lower the inter-particle contact resistance [29]. All these above factors contribute to boosting the solar cell's performance. Furthermore, this specific cell architecture serves another critical purpose in the present study, namely it provides a model photovoltaic system of multiple active interfaces that is suitable for exploring the component sensitive diagnostic capability of EIS. For data collection, the entire cell assembly was placed in a light-tight Faraday cage on an electrically grounded Optical Table, and controlled with a PAR Versastat-3 potentiostat/galvanostat using a four-lead two-electrode configuration [23]. The DSSC was maintained at 25° C using a TC-24–10 temperature controller from TE Technologies. D.C. current (*J*) vs. voltage (*V*) data were recorded with LSV scanned at a speed of 5 mV s⁻¹.

2.2. Component resolved impedance measurements

Both the range and the intervals of the A.C. perturbation frequencies of EIS were found to affect the experimental resolution necessary to detect all the individual impedance elements of the DSSC. To fully detect the fast reactions, it was necessary to set the high-frequency cut-off of the perturbation spectrum above the corresponding reaction frequencies (inverse of rate constants). Similarly, to identify the characteristic marks of the high-impedance CEC elements, it was necessary to set the low frequency perturbation sufficiently below the expected frequencies of the slowest interfacial reactions. An adequate packing of frequencies throughout the entire spectrum was also necessary to minimize uncertainties in the CNLS fits to the EIS data.

To meet these above criteria of component-resolved EIS, several initial experiments were performed using the same test cell and different combinations of D.C. voltages (*V*) and A.C. perturbation frequencies (ω). The results of these diagnostic tests were used to evaluate the spectral features of the cell's high- and low-impedance elements with respect to controlled variations of *V* and ω . CNLS calculations were performed to check the correlations between frequency-packing and uncertainties in the individual circuit elements detected from different spectral regions. From these results, the frequency ranges of the perturbation spectrum for EIS were adjusted depending on the bias voltages, and then the entire experimental spectrum (composed of sinusoidal voltages with 5 mV average amplitude) was evenly frequency-weighted.

In the medium to heavily FB voltage regions (>400 mV), 196 perturbation frequencies were selected for EIS in logarithmic intervals between 300 kHz and 0.1 Hz. At < 400 mV, a similar selection was made between 400 kHz and 0.1 Hz, but these EIS data were collected in two separate scans; the first scan was performed on a fixed 200 mA detection range of the potentiostat to prevent spectral distortion and to obtain a clear reading of the high-frequency Nyquist intercept on the real impedance axis. The second scan was performed on an auto-range of the potentiostat to reduce noise in the low-frequency spectra. The two scans were combined together to form a full Nyquist spectrum for the given bias voltage. At the OCP of the dark cell (0 V) the A.C. spectrum was

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