On the Hysteresis of Current Density-Voltage Curves of Dye-sensitized Solar Cells

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ABSTRACT

Here, we report on the dependence of the current density-voltage (j-V) curves of dye-sensitized solar cells (DSSCs) on the condition of potential sweep – sweep direction and delay time. The phenomenon, termed as hysteresis, is ambiguously attributed to the capacitive nature of the mesoporous TiO_2 photoelectrode or diffusional pseudo capacitance of the electrolyte solution in DSSCs. To explain the hysteresis, here, we have developed a simple model translating fundamental processes: generation, transport and accumulation of charges in a working DSSC. The numerical solution of the corresponding time-dependent j-V equation allowed us to calculate the j-V curves for different sweep directions and delay time. The model calculation suggests that the hysteresis originates at open circuit region due to double layer capacitance at the counter electrode and maximum power due to the chemical capacitance of the TiO_2 film. Moreover, the double layer capacitance, at the exposed substrate/electrolyte interface, affects the j-V curves at short circuit region if the delay time is extremely short. All these capacitive elements are strongly related to the electrolyte; however, the mechanism needs to be explored further.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have progressively been attracting significant attention in the field of photovoltaics since the publication of the seminal *Nature* paper by Professor Michael Grätzel and his colleague in 1991 [1–3]. Generally, a DSSC is composed of a panchromatic dye-loaded nanoporous-nanocrystalline TiO_2 film on fluorine-doped tin oxide (FTO) as the photoelectrode (PE), an iodide/triiodide based electrolyte solution as the redox mediator and a Pt-coated FTO as the counter electrode (CE). Measuring photovoltaic performance is an essential step in characterizing DSSCs. The photovoltaic parameters – short-circuit current density (j_{sc}), open-circuit voltage (V_{oc}), maximum power (P_{max}), and fill-factor (ff) – are obtained from the analysis of current density-voltage (j-V) curve. The j-V curve of a DSSC is measured by sweeping the applied voltage either from short circuit (SC) to open circuit (OC) or vice versa and recording the corresponding current [4,5]. From the above parameters, the energy conversion efficiency (η) is calculated as $\eta = P_{max}/P_{in} = V_{oc}j_{sc}ff/P_{in}$, where P_{in} is the intensity of the incident light.

The shape of the j-V curve strongly depends on voltage sweep: the j-V curve measured by sweeping the voltage from SC to OC (normal scan) differs, especially around P_{max}, from that measured in the reverse direction (reverse scan); the hysteresis becomes more pronounced with the increase of the sweep rate or decrease of the delay time [4–9]. As a result, V_{oc}, P_{max}, ff as well as η obtained from the j-V curve in reverse scan become greater than that of the normal scan. The above phenomenon was attributed to the large time constant of the DSSCs that originates from the intrinsic capacitance of the porous TiO_2 electrode with internal surface area about 10^3 times greater than the active area of the PE [4,7]. However, such attribution was ruled out in other reports that showed the longer time constant of DSSCs was due to the sluggish ionic movement in the electrolyte [4–9].

The capacitance of the mesoporous nanocrystalline TiO_2 was investigated extensively using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) [10–13]. Professor Bisquert and his colleagues developed a model accounting for the charge accumulation, charge transport, and interfacial charge transfer processes to explain the CV response of nanoporous TiO_2 electrode in an aqueous electrolyte [11]. In this work, we have extended the model to explain the j-V curve of complete DSSCs and aimed to investigate the origin of the longer time constant of DSSCs as well as the hysteresis of their j-V curves.

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Here, we present several sets of experimental *j-V* curves of DSSCs (with and without dye-loaded ∼ 6 μm-thick TiO₂ film at the PE) measured at different potential sweep and illumination conditions. A DSSC with a thin layer of TiO₂ (∼ 1 μm-thick) at the PE was also explored to compare with that of the regular one. The hysteresis of the *j-V* curves was explained with the data obtained from numerical simulations of the model. All the parameters involved in the simulations were obtained from combined analysis of the *j-V* and EIS data of the DSSCs [14–16].

2. Experimental Results

2.1. Materials and Methods

A ∼ 6 μm-thick mesoporous TiO₂ film with an active area of 0.25 cm² was deposited on cleaned FTO glass (Pilkington TEC8, 8 Ω/square) substrates by screen printing a TiO₂ paste (TTP-20N, ENB, Korea) followed by sintering at 500 °C for 30 minutes in an electric muffle furnace. Dye loading was performed by dipping the TiO₂ electrodes in an ethanolic solution of 3.0×10^{-4} M N719 (Solaronix SA, Switzerland) for 16 hours. A regular type DSSC (**RD**) was fabricated by attaching the dye-loaded TiO₂ PE and a platinized CE together with a piece of 60 μm-thick Surlyn film (Meltonix 1170-60, Solaronix SA, Switzerland). A blank DSSC (**BD**), without any dye on TiO₂ electrode, was fabricated following the same procedure. A drop of liquid type electrolyte – 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M I₂, 0.1 M guanidinium thiocyanate and 0.5 M 4-tert-butylpyridine (TBP) dissolved in a mixture of acetonitrile and valeronitrile (volume ratio of 85:15) – was directly injected into the cell through the drilled holes at the counter electrode, and the holes were sealed with a piece of scotch tape. For a thin film DSSC (**TD**) with ∼ 1 μm-thick TiO₂ film at the PE, the FTO substrate was spin coated with the same TiO₂ paste diluted ten times in ethanol; rest of the procedure was the same as mentioned above for **RD**. The aperture area of the Surlyn film was considered as the active area of the **TD**.

Photovoltaic measurements were performed employing a solar simulator (XES-40S1, San-Ei Electric Co. Ltd., Japan) with an AM 1.5 filter. The intensity of the light was adjusted to simulate one sun intensity (100 mW cm⁻²) using a standard silicon photodiode. The *j-V* curves were measured with an all-purpose potentiostat (IviumStat, Ivium Technologies, The Netherlands) by applying linear staircase sweep voltage from SC to OC and vice versa with different delay times of 2 ms, 5 ms, 10 ms, 25 ms, 50 ms, 100 ms, and 200 ms that correspond to the scan rates of 5000 mV s⁻¹, 2000 mV s⁻¹, 1000 mV s⁻¹, 200 mV s⁻¹, 100 mV s⁻¹, 50 mV s⁻¹, and 25 mV s⁻¹, respectively. The measurement was performed in the dark condition also.

EIS spectra of the cells were measured by the same potentiostat, and the spectra were fitted to an appropriate equivalent circuit of DSSCs on Zview software (version 3.1, Scribner Associates Inc., USA). The EIS measurements were carried out at different steady states of the cells by applying forward bias from 0 V to V_{oc} of the cells with a step of 50 mV in the light (100 mW cm⁻²) and in the dark condition. The applied bias was synchronized with a modulated voltage of 10 mV with a frequency range of 100 kHz to 100 mHz.

2.2. Experimental j-V Curves

Fig. 1 shows *j-V* curves of the **RD** with N719 dye-loaded 6 μm-thick TiO₂ film. The *j-V* curves in reverse sweep showed a clear peak at P_{max} when the delay time was only 2 ms. The photovoltaic performance parameters: V_{oc}, j_{sc}, and *ff* obtained in the normal sweep were smaller than those in the reverse sweep (Fig. 2). The difference between the corresponding parameters became more
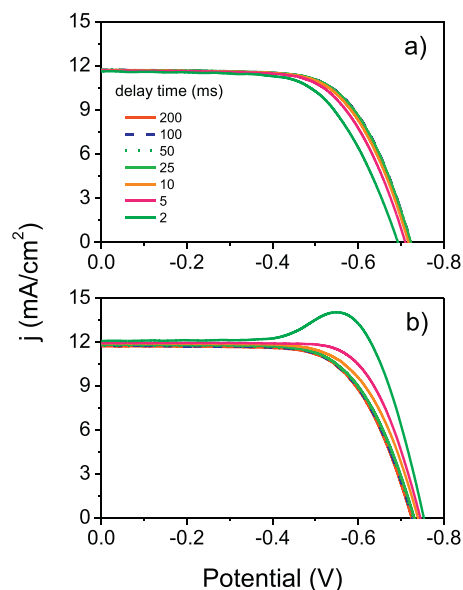

Fig. 1. *j-V* curves of the DSSC based on regular dye-loaded TiO₂ film (**RD**) measured under one sun condition (100 mW cm⁻²) by applying potential sweep in a) normal and b) reverse direction with delay times of 2 ms, 5 ms, 10 ms, 25 ms, 50 ms, 100 ms, and 200 ms.

pronounced with the decrease of delay time. As a result, η obtained from the *j-V* curves in normal sweep decreased and that in reverse sweep increased as the delay time decreased. Also, the **BD** with a 6 μm-thick TiO₂ film, without dye, showed similar hysteresis (see the Supporting Information, Fig. S1). However, the *j-V* curves of the **TD** with N719 dye-loaded 1 μm-thick TiO₂ film did not show such hysteresis (see the Supporting Information, Fig. S2) even though both the **RD** and the **TD** were composed of the same electrolyte solution. The above result suggests a strong correlation between
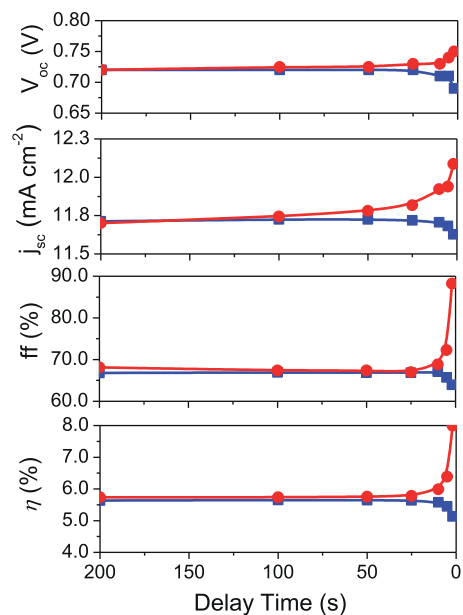

Fig. 2. Photovoltaic performance parameters of the DSSCs based on regular dye-loaded TiO₂ film (**RD**) measured under one sun condition (100 mW cm⁻²) by applying potential sweep in normal (blue squares) and reverse (red circles) direction with delay times of 2 ms, 5 ms, 10 ms, 25 ms, 50 ms, 100 ms, and 200 ms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)