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Electrochemical impedance spectroscopy of dye-sensitized solar cells with different electrode geometry

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ABSTRACT

Here, we report on the characterization of dye-sensitized solar cells (DSSCs) with different electrode geometry by analyzing their electrochemical impedance spectra along with current–voltage curves. The analysis shows a strong correlation between the photovoltaic performance and the series resistance (R_s) of the DSSCs. Among the component resistances of R_s, the Ohmic resistance (R_{OS}) is the largest that depends greatly on the geometry of the active area and the sheet resistance of the substrate. Other series resistive elements do not affect the R_s significantly. The study should help upscaling small unit DSSCs to large modules without compromising their photovoltaic performance.

Introduction

Dye-sensitized solar cells (DSSCs) have emerged as a promising technology in the field of photovoltaics due to their advantages – the low-cost manufacturing process, the use of abundant and non-toxic titanium dioxide, and the efficient generation of electricity even at diffuse light conditions – over other solar cells. The current record efficiency for the DSSCs under optimized laboratory conditions stands at 11.9% [1]. Moreover, a DSSC based on porphyrin dye showed 13% efficiency, whereas another variant of the DSSCs, perovskite solar cells, displayed efficiency more than 20% [2]. Recently, commercial production for DSSCs commenced to power accessories for electronic gadgets [3]. However, upscaling small laboratory scale DSSCs to large modules is a major concern for outdoor application of the cells that requires mass production of high-efficiency DSSCS modules [4–6].

The geometry of the active area of the DSSCs plays an important role in their photovoltaic performance [4,5]. A strong understanding of the resistive elements in terms of geometry is necessary to upscale the cell without compromising their performance. Electrochemical impedance spectroscopy (EIS) has become a ubiquitous tool for characterizing DSSCs since the analysis of EIS data allows one to determine the internal resistances separately [7–11].

Here, we have fabricated four different DSSCs with an active area of different geometry – shape and size. The resistive elements of the DSSCs were extracted from their EIS data. Analysis of the EIS data showed a strong correlation between the geometry and the photovoltaic performance of the DSSCs.

Experimental

All reagents and solvents were purchased from Sigma–Aldrich unless otherwise mentioned. Mesoporous films of nanocrystalline TiO_2 with an average thickness of 8 μm were deposited on cleaned FTO (Pilkington TEC8, 8 Ω/sq) substrates by screen printing a TiO_2 paste (TTP-20N, ENB Korea). The geometry of the TiO_2 films was controlled by using a screen having different masks patterned with rectangles of desired widths and lengths. After drying at 110 °C, the TiO_2 coated FTO substrates were sintered at 500 °C for 30 min. Then the TiO_2 electrodes were immersed in a 0.3 mM ethanolic solution of a ruthenium dye (N719, Solaronix SA, Switzerland) for 16 hr to obtain the dye loaded TiO_2 photoelectrodes (PEs). On the other hand, thermally decomposed Pt counter electrodes (CEs) were prepared by spin coating cleaned FTO glass substrates with an ethanolic solution of 50 mM chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) and then sintered at 380 °C for 20 min in an electric muffle furnace.

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The PEs and the CEs were put together with a piece of 60 μm thick Surlyn film (Meltonix 1170-60, Solaronix SA, Switzerland) as a spacer and sealing agent. A drop of a liquid electrolyte solution was directly injected into the cell through the drilled holes in the counter electrode, and the holes were sealed with a piece of scotch tape. The electrolyte solution was prepared by dissolving 0.6 M 1-butyle-3-methylimidazolium iodide (BMII), 0.03 M I_2, 0.1 M guanidinium thiocyanate and 0.5 M 4-tert-butylpyridine (TBP) in a mixture of acetonitrile and valeronitrile (volume ratio of 85:15).

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 one sun (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 short-circuit to open-circuit of the cells.

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 a forward bias from zero to open-circuit voltage (V_{oc}) in one sun condition. The applied bias was synchronized with a modulated voltage of 10 mV over a frequency range from 100 kHz to 100 mHz.

Results and discussion

The top view of a regular DSSC with an active area of 0.25 cm^2 is shown in Fig. 1a, where the area of the TiO_2 film of width S_{AW} and length S_{AL} is colored in red. In this work, four different DSSCs were fabricated by changing S_{AW} and S_{AL} (Fig. 1b); however, S_{PL}, the gap between the active area and the contact, was set to 0.5 cm for all cases. Here, we label the DSSCs based on the value of S_{AW} and S_{AL} in cm as 0.5 × 0.5, 1.5 × 0.5, 0.5 × 1.5, and 1.5 × 1.5.

The photovoltaic performance

Fig. 2a shows the current–voltage (i–V) curves of the DSSCs measured under one sun illumination condition. It was found that the short-circuit current (i_{sc}) increased linearly with the increase of the area of the TiO_2 films and the V_{oc} remained the same. The linear increase of i_{sc} is reflected in the almost similar short-circuit current density (j_{sc}) as shown in the current density–voltage (j–V) curves (Fig. 2b). Also, it was found that the maximum power density (P_{max}) decreased as the S_{AW} decreased and the S_{AL} increased for a given active area. The cell 0.5 × 0.5 showed highest P_{max} whereas 1.5 × 1.5 showed the lowest. Table 1 summarizes the photovoltaic performance parameters of the DSSCs. Both V_{oc} and j_{sc} were almost independent of the TiO_2 film geometry; the only difference in the fill-factor (*ff*) resulted in different power conversion efficiency (η) of the cells with different electrode geometry. The cell 0.5 × 0.5 being smallest with an active area of 0.25 cm^2 showed the highest efficiency whereas the cell 1.5 × 1.5 being largest with an active area of 2.25 cm^2 showed the lowest efficiency. Of the other two cells, 1.5 × 0.5 outperformed 0.5 × 1.5 even though the active area of the two cells was the same (0.75 cm^2).

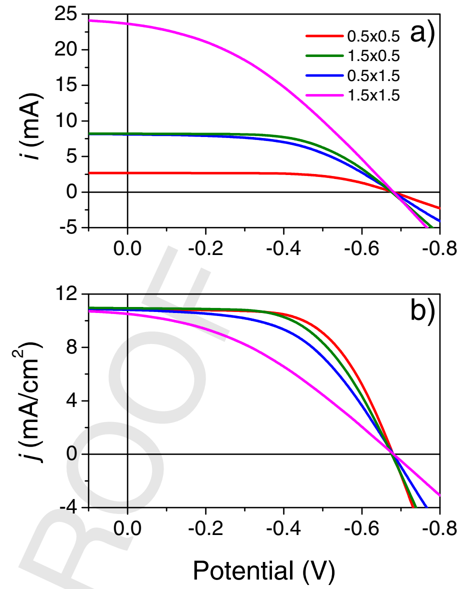
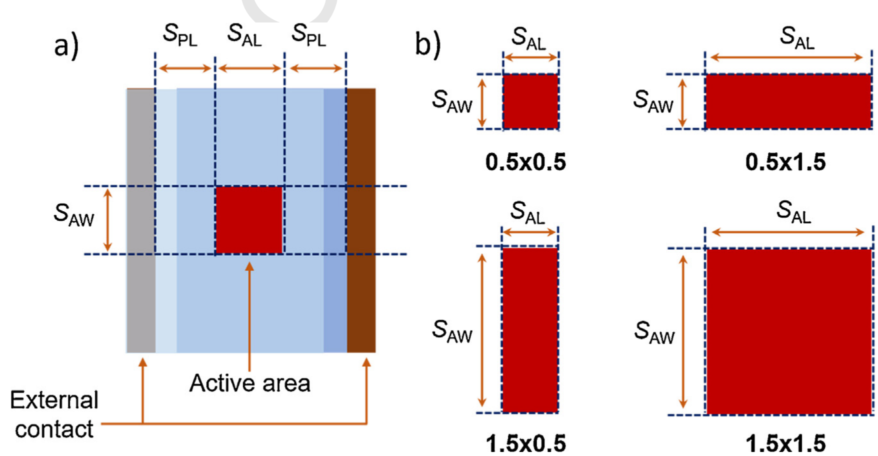


Fig. 2. (a) The i–V curves and (b) the corresponding j–V curves of the DSSCs measured at 1 sun condition.

Internal resistances

EIS spectra of the DSSCs were obtained at different potentials ranging from 0.0 V to 0.7 V (Figs. S1–S4 of the Supporting information). The spectra were fitted to an appropriate equivalent circuit of DSSCs to extract the resistive elements: the Ohmic series resistance (R_{OS}) corresponding to the solution resistance of the electrolyte and the sheet resistance of the FTO substrate, the charge transfer resistance (R_{CE}) at the CE, ionic-diffusion resistance



Q4 **Fig. 1.** Schematic of the geometry of (a) regular small size DSSC and (b) active area with shapes of 0.5 × 0.5 cm^2, 1.5 × 0.5 cm^2, 0.5 × 1.5 cm^2, and 1.5 × 1.5 cm^2. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)