Research Article

Performance Degradation of Dye-Sensitized Solar Cells Induced by Electrolytes

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We investigated the change of the electric characteristics in dye-sensitized solar cell (DSSC) when the electrolyte has been injected and measured initially and lately for a period of time. It was found that the short-circuit current density decreased from 9.799 mA/cm² to 7.056 mA/cm² and the fill factor increased from 0.406 to 0.559 when the cell had stood for an hour, while the open-circuit photovoltage did not change due to fixed difference between the Fermi level of TiO₂ and the oxidation-reduction potential of electrolyte. The results can be explained by using the variation of the series resistance in the equivalent circuit of the DSSC.

1. Introduction

Dye-sensitized solar cells (DSSC) have attracted much attention ever since Grätzel et al. demonstrated the possibility to convert solar energy to electricity with a photoelectrochemical dye-sensitized device [1]. The DSSC provides a technically and economically credible alternative concept to present day p-n junction photovoltaic devices. The development of these new types of solar cell is promoted by the increasing public awareness that the earth's oil reserves will run out during this century. Because the energy needs of the planet will at least double within the next 50 years, the stage is set for a major shortage of energy supply unless renewable sources can cover the substantial deficit that fossil fuels can no longer furnish.

This accomplishes the optical absorption and charge separation processes by the association of a sensitizer as a light-absorbing material with a wide-band-gap semiconductor of mesoporous or nanocrystalline morphology [1–3]. It also offers the prospect of very low cost fabrication without expensive and energy-intensive high-temperature and high-vacuum processes, compatibility with flexible substrates, and variety of presentations and appearances to facilitate market entry, both for domestic devices and in architectural or decorative applications. Generally, the semiconductor, which accepts the electron from the sensitizer and transfers

it to the electrode, is nanocrystalline anatase TiO₂ which is mesoporous because of high surface area. High surface area of TiO₂ thin film improves the adsorption of sensitizer and hence increases the light-harvesting capacity of the mesoporous film. However, the electrolyte may penetrate into the mesoporous film and contact the dye-free TiO₂ and the electrode surface, resulting in the increase of the reverse saturation current. On the other hand, it also increases the contact area between the electrolyte and the sensitizer so that facilitates the reduction of I₃[−] by the combination of the hole. It was found that the short-circuit photocurrent decreased and the fill factor of the dye-sensitized solar cell increased as time goes on.

In this study, the change of the electric characteristics in dye-sensitized solar cell (DSSC) when the electrolyte has been injected and measured initially and lately for a period of time was investigated. The short-circuit photocurrent density (J_{sc}) and the fill factor (F.F.) were varied and the results can be explained by using the variation of the series resistance in the equivalent circuit of the DSSC.

2. Experimental Apparatus and Procedure

2.1. Preparing the Working Electrode. A TiO₂ thin-film electrode was designed and fabricated for use in a dye-sensitized solar cell. This TiO₂ thin-film was deposited on the top of

FIGURE 1: The procedure of preparing the working electrode.

an FTO-glass (Fluorine doped tin oxide, $\text{SnO}_2\text{:F}$) substrate, which has a size of $20 \times 20 \times 3$ mm and a sheet resistance of $8 \Omega/\text{sq}$. The TiO_2 particles (P-25) are composed of 30% rutile and 70% anatase, with a particle size range (<100 nm).

Figure 1 shows the procedure of preparing the working electrode of DSSC with a layer of TiO_2 particles and the steps are described as follows. (1) Diluting $40 \mu\text{L}$ of acetylacetone in 1 mL of de-ionic (DI) water; (2) mixing 1 g of TiO_2 particles with the diluted acetylacetone, and stir well to make the colloid of TiO_2 particles; (3) adjusting the glutinosity of the colloid of TiO_2 particles by adding 1.5 mL of DI water and $40 \mu\text{L}$ of surfactant (Triton-100, $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH}$), and then homogenize the colloid of TiO_2 particles for 30 minute in a mortar; (4) dropping the quantitative colloid of TiO_2 particles on the top of the F:SnO₂ (FTO) glass substrate, and then spin coat the working electrode with rotational speed of 3000 rpm; (5) drying the working electrode with a layer of TiO_2 particles at room temperature for 10 minute, and then sinter this working electrode at 500°C for 30 minutes in a high-temperature furnace; (6) immersing the FTO-glass substrate with a layer of TiO_2 particles into the (3×10^{-4} mol/L) solution of N-719 dye (Ruthenium, $\text{RuL}_2(\text{NCS})_2$) and ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$, 95%) for 24 hours at room temperature. A conventional working electrode with a layer of nanocrystalline TiO_2 on the FTO-glass substrate was fabricated using above procedures to demonstrate the feasibility and advantages of the working electrode with a layer of TiO_2 particles. An α -step (Dekeak 6 M) surface profiler was utilized to obtain the surface profile of the thin film and the average thickness of the thin film on the FTO-glass substrate of the working electrode. The thickness of the TiO_2 thin films was about $10 \mu\text{m}$. Figure 2 shows the practical working electrode.

2.2. Assembling the DSSC. Figure 3 shows the schematic of the DSSC. The thin film on the FTO-glass substrate of the working electrode was fringed using the Scotch magic transparent tape (3 M). Then, the working electrode and the counter electrode that a thin film of platinum was deposited on the FTO-glass substrate using a ion sputter (Hitachi E-1010) were fitted together, such that the space between the

FIGURE 2: The photograph of the working electrode.

two electrodes was adjusted to approximately $160 \mu\text{m}$ for embarking the liquid electrolyte. After sealing, the liquid electrolyte, which was composed of 0.5 M lithium iodine (LiI) and 0.05 M iodine (I_2) in 3-methoxypropionitrile, was injected into the cell through a hole on the cell that was prepared in advance.

2.3. Testing. A home-made I - V measurement system was adopted to measure the open-circuit photovoltage and short-circuit photocurrent of the DSSC. A solar simulator with a 500 W halogen lamp and a light intensity of $100 \text{ mW}/\text{cm}^2$, was employed to illuminate the DSSC. In addition, the power conversion efficiency η of the DSSC was determined by

$$\eta(\%) = \frac{V_{oc} J_{sc} FF}{P_{in}} \times 100. \quad (1)$$

In (1), V_{oc} , J_{sc} , and P_{in} represent the open-circuit voltage, the short-circuit current density, and the incident light power ($100 \text{ mW}/\text{cm}^2$), respectively. Moreover, the fill factor FF is given by

$$FF = \frac{V_{max} J_{max}}{V_{oc} J_{sc}}. \quad (2)$$

In (2), V_{max} and I_{max} represent the voltage and the current at the maximum output power point, respectively. The I - V characteristics of the prepared DSSC were measured at initial assembling stage and at one hour lately.

3. Results and Discussion

Figure 4 shows I - V characteristics of the DSSC when the electrolyte is just injected into the space between the working electrode and the counter electrode. The measured V_{oc} , J_{sc} , and F.F. are $9.799 \text{ mA}/\text{cm}^2$, 0.658 V , and 0.406 , respectively. Figure 5 shows I - V characteristics of the dye-sensitized solar cell after the electrolyte has been injected and stay for one hour. The measured V_{oc} , J_{sc} , and F.F. are $7.056 \text{ mA}/\text{cm}^2$, 0.668 V , and 0.559 , respectively. as Comparing Figure 4 to Figure 5, it is found that the J_{sc} decreases from $9.799 \text{ mA}/\text{cm}^2$ to $7.056 \text{ mA}/\text{cm}^2$ and F.F. increases from 0.406 to 0.559 . The V_{oc} does not change due to the fixed difference between

FIGURE 3: Schematic of the dye-sensitized solar cell.

FIGURE 4: I - V curve of DSSC when the electrolyte is just injected. FIGURE 5: I - V curve of DSSC when the electrolyte has been injected and stay for one hour.

the Fermi level of TiO_2 and the oxidation-reduction potential of electrolyte. To understand the difference in their J_{sc} for the measurement at initial assembling stage and at one, two, three and so forth hours lately. We conduct the standard I - V curve of the solar cell and discuss the change of the series resistance and the shunt resistance.

It has been known that the tangent slope of vertical part (near V_{oc}) is proportional to the reciprocal of the series resistance ($1/R_s$) and the tangent slope of transverse part (near J_{sc}) is proportional to the reciprocal of the shunt resistance ($1/R_{sh}$). When R_{sh} increase or/and R_s decrease, F.F. will become better. The tangent slope of V_{oc} part in Figure 5 is larger than that in Figure 4, which means R_s decreases as time goes on. However, the tangent slope of J_{sc} does not change obviously so that R_{sh} is almost the same. We thus discuss the factor that affects the series resistance R_s and ignores the shunt resistance R_{sh} .

The series-internal resistance of DSSCs was investigated by some researchers based on an equivalent circuit of DSSCs [4, 5]. It was found that series-internal resistance correlates with the charge-transfer at Pt counter electrode, TCO substrate resistance, and Nernstian diffusion in the

electrolyte. According to these, the equivalent circuit of DSSCs is constructed as shown in Figure 6. The series resistance is the sum of the charge transfer resistance at Pt/electrode interface (R_1), the diffusion resistance of I_3^- ions in electrolyte (R_2), and the sheet resistance of TCO (R_h). Because R_1 and R_h relate to the property of the material, they cannot change as time goes on. We think the major factor that influences R_s must be R_2 . The probable explanation is that the electrolyte only contacts the top surface of TiO_2 thin film when the electrolyte is just injected. However, the electrolyte may permeate into the mesoporous film after an hour and the contact area with dye-adsorbed TiO_2 will increase, so the charge-transfer from the electrolyte to the oxidized dye will be accelerated. The large contact area between the electrolyte and the dye-adsorbed TiO_2 film improve the rate of I_3^- reduction and hence decrease R_s .

According to the diode equation that correlates with Figure 6:

$$I = I_{ph} - I_0 \left\{ \exp \left[\frac{q(V + IR_s)}{nkT} \right] - 1 \right\} - \frac{V + IR_s}{R_{sh}}, \quad (3)$$

FIGURE 6: Equivalent circuit based on current-voltage characteristics of DSSCs. The sum of R_1 , R_2 , and R_h corresponds closely to the series resistance of DSSCs. C_1 is capacitance elements.

where I_{ph} is the ideal photocurrent, I_0 is the reverse saturation current, n is the ideality factor whose value is between 1 and 2 for the DSSC, R_s is the series resistance which is the sum of R_1 , R_2 , and R_h , and R_{sh} is the shunt resistance. The gain in open circuit voltage can be calculated from (3):

$$V_{oc} = \frac{nkT}{q} \ln \left[\frac{I}{I_0} - \frac{V_{oc}}{I_0 R_{sh}} + 1 \right]. \quad (4)$$

As R_{sh} increase, V_{oc} will also increase. as comparing Figure 4 to Figure 5, it is found that V_{oc} does not change obviously. Since $1/R_s$ is unchanged, it confirms that the shunt resistance in DSSCs is almost the same as time goes on.

The short circuit current can be obtained from (3) when $V = 0$, and it can be found that I_{sc} will increase as R_s decreases. However, I_{sc} decreases from 9.799 mA/cm² in Figure 4 to 7.056 mA/cm² in Figure 5. It must be the influences of the dark current which correlates with the recombination of charge carriers by reduction of I_3^- at dye-free TiO₂ surface and bare FTO surface exposed to electrolyte through porous electrode [6]. As we discussed before, the electrolyte will permeate into the mesoporous film when DSSC has been staid for an hour. It may apply the electrolyte to contact the dye-free TiO₂ surface and even the FTO surface, so that accelerates the recombination of the charge carriers from the conduct band of TiO₂ to the electrolyte and produces the reverse saturation current. The increase of the dark current lowers I_{sc} seriously so that it is important to modify the working electrode surface to decrease the reverse charge flow.

Based on the above discussion, it is known how to improve the performance of DSSCs by modifying the interface between the working electrode and the electrolyte, as investigated by some research workers [7–9]. Su et al. fabricated layer-by-layer Au nanoparticles, which were prepared using chemical reduction method, onto the working electrode as a Schottky barrier in a water-based DSSC [10]. It was found that an interfacial blocking layer could suppress the interfacial recombination between TiO₂ and excited dye molecules or I^-/I_3^- couple, which led to an improvement on cell performance [7–9]. Moreover, in order to improve the performance of DSSCs, it is also necessary to suppress the dark current. The reverse charge flow, recapture of the electron by the electrolyte, could be impaired by judicious design of the sensitizer. It can also form a tightly packed insulating monolayer blocking the dark current.

Consequently, decreasing the recombination of charges in the dye or electrolyte is one of the important issues to increase the conversion efficiency of DSSC and is worthy of ongoing study.

4. Conclusion

In this study, we discussed the change of the current-voltage characteristics in DSSCs as time goes on and found that fill factor (F.F) got better but short circuit current density J_{sc} decreased. The results were explained by using the variation of the series resistance in the equivalent circuit of the DSSC. The increase of F.F. may result from the decrease of series resistance R_s due to the electrolyte permeating into the mesoporous working electrode and hence increase the contact area with the dye-adsorbed TiO₂. However, it also applies the electrolyte to contact the dye-free TiO₂ surface and even the FTO surface, so that accelerates the recombination of the charge carriers from the conduct band of TiO₂ to the electrolyte and produces the reverse saturation current.

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