Photovoltaic performance enhancement of dye-sensitized solar cells by formation of blocking layers via molecular electrostatic effect

Bo Li\textsuperscript{a,b}, Jiazang Chen\textsuperscript{b}, Jianfeng Zheng\textsuperscript{b}, Jianghong Zhao\textsuperscript{b}, Zhenping Zhu\textsuperscript{b}, Huanwang Jing\textsuperscript{a,b,*}

\textsuperscript{a} Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization, Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China
\textsuperscript{b} State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

\textbf{A R T I C L E   I N F O}

Article history:
Received 23 June 2011
Received in revised form 28 September 2011
Accepted 19 October 2011
Available online 25 October 2011

Keywords:
Dye-sensitized solar cells
Electrolyte
Blocking layers
Electrochemical impedance spectroscopy
Charge transfer

\textbf{A B S T R A C T}

The improvement in photovoltaic performance of dye-sensitized solar cells was found after aging in the dark and was analyzed by linear sweep voltammetry and electrochemical impedance spectroscopy. The promotion was found to arise from the formation of blocking layers on the surface of nanocrystalline TiO\textsubscript{2}, resulting most likely from the intermolecular electrostatic action between the 4-tert-butylpyridine and the 1,2-dimethyl-3-propylimidazolium ions. These blocking layers can retard the interfacial reaction of the electron with I\textsubscript{3}~ ions without deteriorating the rate of regeneration of the oxidized dye molecules. By virtue of the blocking layers, the retarding recombination of electrons with the I\textsubscript{3}~ ions significantly increased the electron lifetime and enlarged the electron diffusion length, resulting in a higher open-circuit voltage and an improvement in charge collection efficiency, and eventually an enhancement of the energy conversion efficiency.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention due to their low production cost and relatively high energy conversion efficiency [1]. Typically, a DSSC is constructed with a dye-anchored wide bandgap semiconductor supported on a transparent conducting oxide (TCO) substrate, an electrolyte containing redox couples (usually I\textsuperscript{-}/I\textsubscript{3}~ couple), and a platinized counter electrode. During the operation of the DSSC, electrons are injected from the photoexcited dye into the conduction band of semiconductor following with diffusing toward the TCO substrate. The oxidized dye molecules are regenerated by oxidizing I\textsuperscript{-} to I\textsubscript{3}~ ions. Photoelectrode becomes one of the key components in the DSSC, since many crucial steps take place in the bulk of semiconductor network or on semiconductor–electrolyte interface (SEI), which can significantly influence the photoelectrochemical performance of the photovoltaic cells.

In the short-circuit condition, the yield of charge extraction of a DSSC is basically indicative of the competition between the transport of electron through the porous semiconductor and the recombination of electrons with I\textsubscript{3}~ ions in electrolyte [2–6]. Improvement of the charge transport properties of the porous semiconductor electrode means reducing the electron recombination during the diffusion processes, and thus enhancing the electron collection efficiency of the photovoltaic cells. While in many cases, this way merely results in an increase of the short-circuit photocurrent density (J\textsubscript{SC}), the contributions to the increase of open-circuit voltage (V\textsubscript{OC}) or fill factor (FF) are often insignificant [7–9]. As another way to enhance the performance of a DSSC, suppression of the charge recombination on the SEI by passivating the surface state of the electrodes not only improves the collection efficiency of electrons, but the V\textsubscript{OC} and FF of the cell also can be enhanced [10–12]. Passivation of the surface can be realized by formation of physical thin films on the surface of porous electrodes [12–14], and/or by adding additives into the electrolyte [15]. The function of this way is to block and retard the interaction between electrons in the semiconductor and electron-acceptors in the electrolyte [10–13], and cover the defect of semiconductor [16], resulting in an increase of electron lifetime and band edge shift.

It is reported that the treatment of DSSC by electrolyte additives, light exposure, thermal aging, and storing in the dark has significant effects on the electron transport properties of semiconductor electrode and the situation of the SEI, and eventually influence the photovoltaic performance and stability of the cells [17–23]. One of the most attractive phenomena is the recovery or even improvement in the photovoltaic performance of DSSC following post-treatment. In the present work, we employed voltammetry and electrochemical impedance spectroscopy (EIS)
to investigate the change of photoelectrochemical properties of a Zn(II)-5,10,15,20-tetra(4-carboxyphenyl) porphyrin (TCPPZn) sensitized nanocrystalline TiO₂ based solar cell, which was treated in the dark at room temperature by various periods of aging. We attempt to elucidate the improvement of the photovoltaic performance of the cell after aging. We believe that our results could provide a deeper understanding of the electronic process in the semiconductor photoelectrochemical system and some useful information for improvement of DSSC.

2. Experimental

2.1. Chemicals and materials

N,N-Dimethylformamide (DMF) was purchased from Sinopharm Chemical Reagent Co. Ltd., prior to use, it was distilled from CaH₂. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII, TCI), iodine (I₂, Aldrich), 4-tert-butylpyridine (TBP, Aldrich) were used as received. All other chemicals were of analytical grade. FTO glass was purchased from Nippon Sheet Glass Co. Ltd. (15 ohm per square).

2.2. Synthesis of TCPPZn

TCPP (5,10,15,20-tetra(4-carboxyphenyl) porphyrin) was synthesized following the procedures of Alder [24]. TCPPZn was prepared by metallation of TCPP in a DMF solution containing Zn(OAc)₂ under reflux condition within 12 h. When the system cooled down to room temperature, water was added and the mixture was acidified with concentrated HCl. Then the precipitate was filtered, washed several times with water, dried, and column chromatographed [25].

2.3. Fabrication of photovoltaic cells

Fabrication of DSSC was mainly according to a literature procedure [26]. TiO₂ nanoparticles were prepared by hydrothermal synthesis starting from titanium (IV) n-butoxide. After that, polyethylene glycol (PEG, Molecular Weight 20000) was added in a proportion of 50% of the TiO₂ weight. The TiO₂ paste was then deposited by doctor blade technique on FTO glass and its active area is 0.50 cm². The TiO₂ film was then sintered at 500 °C for 1 h. After cooling to 100 °C, the TiO₂ electrode was immersed into the TCPPZn solution with a concentration of 0.5 mM in DMF for 24 h. After the sensitized TiO₂ electrode was rinsed with DMF and dried with nitrogen stream, one drop of electrolyte was deposited onto the surface of the electrode and penetrated into the TiO₂ film via vacuum perfusion. The electrolyte solution was composed of 0.6 M DMPII, 0.05 M I₂, and 0.5 M TBP that were dissolved in a mixture of acetonitrile and valeronitrile (85:15 by volume). The sandwich type DSSC was fabricated by clamping the platinum counter electrode onto the top of the TiO₂ photoelectrode.

2.4. Photoelectrochemistry and electrochemistry

The photocurrent–voltage (I–V) curves were recorded by a Keithley Series 2601A System Source Meter. The irradiation source is a solar simulator (San-Ei XES-301S) giving AM 1.5 G illumination on the surface of the solar cells. The incident light intensity was 100 mW/cm² calibrated with a standard Si solar cell. The measurement of the incident photon-to-current conversion efficiency (IPCE) was carried out with a Crown instrument. Linear sweep voltammetry curves were recorded using a CH Instrument (CHI 660D potentiostat). Electrochemical impedance spectroscopy (EIS) measurements were carried out by performing a computer-controlled potentiostat (IM6ex, Zahner) with a frequency of 0.005–500kHz. The obtained spectra were fitted with Z-view software.

3. Results and discussion

3.1. Photovoltaic characterization

In this work, we adopted Zn(II)-5,10,15,20-tetra(4-carboxyphenyl) porphyrin (TCPPZn) as the sensitizer, which is a common porphyrin dye for DSSC. Under the illumination of 100 mW/cm², AM 1.5 G (same as our experimental condition), the common efficiency for this type of cells is around 0.1% [27,28]. Fig. 1 presents the photocurrent–voltage characteristics of the cell before and after aging, and the detail photovoltaic parameters were summarized in Table 1. It is clear that the photovoltaic behaviors of the cell significantly changed after aging. Under one sun illumination, the photovoltaic parameters of the fresh cell, including open-circuit voltage (V_OC), short-circuit photocurrent density (I_SC), and fill factor (FF), and overall energy conversion efficiency (ƞ) were 406 mV, 0.530 mA/cm², 0.554, and 0.119%, respectively, which is similar with the reported results [28]. After aging for one week in the dark, the corresponding values (V_OC, I_SC, FF, and ƞ) of the cell became 415 mV, 0.762 mA/cm², 0.639, and 0.202%, respectively. Moreover, the photovoltaic performance of the cell was further improved by continuously aging (one month). By investigating the I–V curves, the corresponding values (V_OC, I_SC, and FF) of the cell after one month aging were 433 mV, 1.29 mA/cm², and 0.671, respectively, and the value of ƞ augmented to 0.374%, that is at least 2 times larger than that of the fresh one. While the energy conversion efficiency remain unchanged by further aging the cell.

The incident photon-to-current conversion efficiency (IPCE) of a DSSC can be defined as: IPCE = jεηₑ = ƞₑ/ηₑο = (where j is the photocurrent density, ɛ is the charge of an electron, l₀ is the incident photon flux, ƞₑ is the light harvesting efficiency of the sensitized

<table>
<thead>
<tr>
<th>Cell</th>
<th>V_OC (mV)</th>
<th>J_SC (mA/cm²)</th>
<th>FF</th>
<th>ƞ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>406</td>
<td>0.530</td>
<td>0.554</td>
<td>0.119</td>
</tr>
<tr>
<td>One week</td>
<td>415</td>
<td>0.762</td>
<td>0.639</td>
<td>0.202</td>
</tr>
<tr>
<td>One month</td>
<td>433</td>
<td>1.290</td>
<td>0.671</td>
<td>0.374</td>
</tr>
</tbody>
</table>
TiO$_2$ layer, $\eta_{inj}$ is the efficiency of electron injection from the excited sensitizer to TiO$_2$, and $\eta_{col}$ is the electron collection efficiency. Clearly the IPCE curve of a DSSC contains information about light absorption, electron injection, and electron collection efficiency. Fig. 2 presents the IPCE curves of the cell before and after aging (one week and one month). In the visible range, all the IPCE curves exhibit four characteristic bands, respectively, centered at ~430, ~570, ~610, and ~680 nm, which is in good agreement with the absorption feature of TCPZn, though the values for three curves are rather different. The IPCE values for the fresh cell are 6.9%, 0.39%, 0.30%, and 0.17% (respectively locate at wavelength of 430, 570, 610, and 670 nm). Then it becomes 11.0%, 0.83%, 0.61%, and 0.36% in the corresponding wavelength of illumination after the cell was aged for one week. By further aging the cell, the peak values of the IPCE reached 16.2%, 1.45%, 1.06%, and 0.39% in the four wavelength positions.

We assume that after aging, the light absorption would not be changed, since the dye in the system was not changed. For the electron injection efficiency, generally, the injection rate for electrons from the excited dye to semiconductor depends on the energy level difference between the conduction band of semiconductor and the dye excited/ground state oxidation potentials [29,30]. On the other hand, the charge collection efficiency is related to the competition between transport of electron through porous semiconductor and the charge recombination on SEI. In order to gain an insight into this enhancement in the IPCE and the photocurrent of the cell, we next investigate the characteristics of semiconductor and the transport/transfer properties of electrons in semiconductor electrode by voltammetry and impedance studies.

3.2. Electron transport and interfacial transfer

3.2.1. Linear sweep voltammetry

The dark current has a dominant influence on the study of the performance of a DSSC. The voltammetric behaviors are highly dependent on the distribution and density of local states, and influenced by the surface absorption species. Under forward bias, cathodic current arises from the reduction of the I$_3^-$ ions in the electrolyte by electrons injected from the FTO substrate into the mesoporous semiconductor, while the voltammetric behaviors in the reverse bias provide the information for the regeneration process of dye molecules ([Fig. 3(a)] [23]. The cathodic current can provide a reference to the position of the electronic Fermi level ($E_F$) with respect to the conduction band edge ($E_{cb}$). The forward bias is mainly depended on the difference between the electronic Fermi level ($E_F$) and the redox potential of electrolyte ($E_{redox}$), and the value of $E_{redox}$ is a constant in a given system. So according to the relationship between the current and forward bias, the onset potential (the corresponding potential of onset current at the knee point of curve in Fig. 3(b)) can imply the position of the conduction band edge ($E_{cb}$) [31]. The voltammetry curves of the cell before and after aging (one month) were shown in Fig. 3(b). As it shows, the onset potentials for cathodic current under the forward biases are almost same for the two curves, indicating that the conducting band (edge) position of semiconductor electrode for the cell before and after aging are not changed. By investigating the current values of two curves, it can be seen that in the region of forward bias (from less negative to more negative, in the right half of the curves in Fig. 3(b)), the cathodic current of aged cell is much lower, as compared with that of fresh one. The decrease of the current under forward bias suggests the interfacial reaction of electrons with I$_3^-$-ions is retarded after the cell aging in the dark. In the region of reverse bias (from less positive to more positive, in the left half of the curves in Fig. 3(b)), the very similar voltammetric behaviors of the fresh and aged cell indicate that the regeneration of dye in the cell after aging is not deteriorated.

3.2.2. Electrochemical impedance spectroscopy

In order to obtain further insight into the improvement in photovoltaic performance, we will employ EIS to investigate the charge transport properties in semiconductor film and interfacial charge recombination on SEI for the cell before and after aging. Fig. 4(a) shows the impedance spectra of the cell at a bias of ~0.5 V. It is clear that the electron transport in the mesoporous TiO$_2$ film appears as Warburg-like diffusion behavior in the high-frequency region and the interfacial charge recombination process grows to a large semicircle in the low-frequency region. As it shows, under the bias of ~0.5 V, the semiconductor electrodes for the fresh and aged cell exhibit similar electron transport resistance, while the charge recombination resistance is much larger for the cell after aging. The electronic processes in DSSC are well described by a
transmission line model developed by Bisquert et al. [32–35], as shown in Fig. 4(c). By fitting impedance data with the transmission line, we can obtain characteristic elements that describe electronic process occurring in the cell. The main elements that have been analyzed are electron transport resistance ($R_t$), charge recombination resistance ($R_{ct}$) on the SEI between the electron and the I$_3^-$ions in the electrolyte, and chemical capacitance ($C_m$).

Transport of electrons in the semiconductor is mainly driven by diffusion due to the effective screening of electrons by high ionic strength electrolyte. Conductivity of electrons in TiO$_2$ network is exclusively dependent on the number of free electrons in extended state [36]: $\sigma = e \mu$ (where $e$ is the elementary charge and $\mu$ is the mobility). And thus it provides a reference of the position of the electronic Fermi level ($E_F$) with respect to the conduction band edge ($E_{cb}$) [36,37]: $\sigma = \sigma_0 \exp\left[\frac{E_F - E_{cb}}{k_B T}\right]$ (where $\sigma_0$ being a constant, $k_B$ is the Boltzmann constant, and $T$ the temperature). In a DSSC, the bias potential of the cell is dependent on the difference between $E_F$ and $E_{\text{redox}}$ of I$^-$/I$_3^-$, then one can obtain:

$$\sigma = \sigma_0 \exp\left[\frac{e}{k_B T} \left(V + \frac{E_{\text{redox}} - E_{cb}}{e}\right)\right]$$  \hspace{1cm} (1)

The electron transport resistance, $R_t$, is reciprocal to the conductivity, thus the relationship between $R_t$ and bias potential can described as follows:

$$R_t = R_0 \exp\left[-\frac{e}{k_B T} \left(V + \frac{E_{\text{redox}} - E_{cb}}{e}\right)\right]$$  \hspace{1cm} (2)

**Fig. 5.** Electron transport resistance of the cell before and after aging. These data were obtained by fitting the impedance spectra of the cell measured in the dark under various forward biases.

**Fig. 5** shows the $R_t$ of the cell before and after aging. As it shows, the $R_t$ change from a very high to a very low value when the bias potential is displaced toward negative values. By carefully investigating the two plots, it can be seen that the electron transport resistance of semiconductor electrode almost unchanged before and after aging, indicating the position of the conduction band is not changed.

The capacitance measured by impedance spectroscopy is mainly contributed by the chemical capacitance, $C_m$, since the other contributions from the space charge, the Helmholtz layer, or the surface adsorbed ionic species are very small. Thus $C_m$ reflects the density and distribution of the electronic sites in the bandgap of the semiconductor. Fig. 6 presents the chemical capacitance, $C_m$, of the cell before and after aging in the dark for one month. It can be seen that the density and distribution of electronic sites in the bandgap of semiconductor are not changed for the cell before and after aging.

Electron transport in DSSC is driven mainly by diffusion, due to the effective electrolyte shielding of space charge [38]. It was found that the electron transport in DSSC depends strongly on occupation of the broadly distributed bandgap traps [39]. The electron diffusion coefficient, $D_m$, which was described as electron transport properties of semiconductor electrode, can be calculated from the
impedance parameters in terms of \( D_n = L_d^2/R_t \cdot C_p \) (where \( L_d \) is the thickness of the TiO2 film). Fig. 7 presents the diffusion coefficient of electrons in the semiconductor electrode in the cell before and after aging. It shows that the semiconductor electrode exhibits similar electron diffusion coefficient for the fresh and aged cell, since both of the \( R_t \) and \( C_p \) of the cell remain almost unchanged after aging.

The values of \( R_t \), \( C_p \) of and \( D_n \) obtained from the impedance spectroscopy are almost same for the cell before and aging, due to the density and distribution of electronic state for the semiconductor electrode was not changed. Our results are rather different from that obtained from cell treated by light soaking, adding electrolyte additives, or thermal aging, in which the electronic sites in the bandgap and band edge of the semiconductor are changed [19,23,40,41].

Since the charge transport properties in the mesoporous network of the semiconductor are unchanged for the cell after aging, we therefore pay our attention to the recombination characteristics for interpreting the improvement of the photovoltaic performance of the DSSC.

Due to the relatively slow transport through the TiO2 electrode, recombination of electrons with \( I_3^- \) ions in the electrolyte cannot be ignored. The recombination process always competes with the collection of electrons. The charge recombination on the SEI can be described by \( R_{ct} \) value, which can be obtained from impedance results. Fig. 8 presents the charge transfer resistance, \( R_{ct} \) of the cell before and after aging in the dark for one month. It is obvious that the \( R_{ct} \) value of cell after aging is much larger than that of the fresh one, indicating a retarding interaction of electrons with \( I_3^- \) ions in the aged cell.

The electron lifetime, \( \tau_n \) in DSSC is a central quantity to determine the recombination dynamics in the cell. Electron lifetime can be measured by small perturbation techniques at a fixed steady state such as intensity modulated photovoltaic spectroscopy (IMVS), impedance spectroscopy, and transient technique, like OCVD [42]. Here, we obtained the lifetime of electron in semiconductor under various bias potentials by impedance spectroscopy. The value of \( \tau_n \) can be calculated using the expression: \( \tau_n = R_{ct} \cdot C_p \). Fig. 9 exhibits the lifetime of electron in the semiconductor of the cell before and after aging as a function of bias potentials. Because of the retarding interaction between electrons and \( I_3^- \) ions (relatively large value of \( R_{ct} \)), the cell after aging exhibits a relatively long electron lifetime.

Electron collection efficiency is vitally important to determine the photovoltaic performance of a DSSC. Electron collection in the conducting substrate can be described in terms of electron diffusion length, \( L_d \). Using the electrochemical parameters from the impedance results and the thickness of TiO2 film, \( L_d \) can be calculated from the expression: \( L_d = (R_{ct} \cdot R_t)^{1/2} s = (D_t \cdot \tau_n)^{1/2} \). Fig. 10 presents the \( L_d \) of electrons in the semiconductor electrode for the cell before and after aging. Due to the relatively large value of \( R_{ct} \) and electron lifetime, the aged cell exhibits relatively large \( L_d \), which is in good agreement with the \( I-V \) characteristics and the IPCE result.

### 3.3 Molecular electrostatic effect

As investigated above by the linear sweep voltammetry and impedance spectroscopy, the regeneration of dye and the diffusion coefficient of electrons in the semiconductor network were not changed, so the only possible reason for the improvement in the photovoltaic performance of the cell after aging is the retarding interaction between electrons and \( I_3^- \) ions, which would be attributed to the formation of special blocking layers on the surface of nanocrystalline TiO2.

It is well known that the additives play a crucial role in influencing the photoelectrochemical performance of DSSCs. The adsorbed species on the TiO2 surface can result in modification of the redox
couple potentials, band shifts of the semiconductor materials, and effects of surface blocking. TBP is one of the most common additives added to the electrolyte, which can bind to the surface of the TiO₂ [10]. Here in our case, because the composition of the electrolyte contains TBP and DMPII, according to the discussion above, we suppose that the negative-charge enriched heterogeneous of TBP will interact with the 1,2-dimethyl-3-propylimidazolium ions (DMPI⁺) in the electrolyte due to the electrostatic action, resulting a special blocking layers on the surface of the TiO₂, as shown in Fig. 11. The formed blocking layers can occupy the naked TiO₂ surface and retard the interaction between electrons and I₃⁻ ions.

4. Conclusion

In this work, it was found that the cell after aging in the dark has a better performance comparing with the fresh one. To investigate this improvement, linear sweep voltammetry and electrochemical impedance spectroscopy were employed. The reason for the improvement was attributed to the retarding interaction between electrons and I₃⁻ ions in the electrolyte, which would be caused by the formation of blocking layers on the surface of nanocrystalline TiO₂. At last, we proposed that the formation of the blocking layers arise from the slow intermolecular electrostatic action between the 4-tert-butylpyridine and the 1,2-dimethyl-3-propylimidazolium ions.

We believe that the investigation for this enhancement by the formation of blocking layers occurred on the semiconductor–electrolyte interface of DSSC will help us to better understand the work principle of the cell. The finding in improvement of the photovoltaic performance of DSSC might provide important hints to adopt the electrolyte and open up a way to further improve the photovoltaic performance of the cells.

Acknowledgements

This work was financially supported by State Key Laboratory of Coal Conversion, China. B. Li and J. Chen thanks Dr. Yinghua Xu (Zhejiang Univ. Technol.) and Dr. Tiancheng Xu (HzCell Electrochem. Corp.) for the helpful discussion on EIS study.

References