Polyaniline nanofiber/carbon film as flexible counter electrodes in platinum-free dye-sensitized solar cells

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ABSTRACT

Efficient transfer of charges from a counter electrode to an electrolyte is a key process during the operation of dye-sensitized solar cells. Here, we develop a flexible counter electrode by electrochemical deposition of polyaniline nanofibers on graphitized polyimide carbon films for use in a tri-iodide reduction. As determined by the electrochemical impedance spectroscopy, the flexible counter electrode exhibited very low charge transfer resistance and series resistance. These results are due to the high electrocatalytic activity of the polyaniline nanofibers and the high conductivity of the flexible graphitized polyimide film. In combination with a dye-sensitized TiO2 photoelectrode and electrolyte, the photovoltaic device with the polyaniline counter electrode shows an energy conversion efficiency of 6.85% under 1 sun illumination. Short-term stability tests indicate that the photovoltaic device with the polyaniline counter electrode almost maintains its initial performance.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention due to their low production cost and high energy conversion efficiency [1]. As one of the most important components of the DSSC, the counter electrode can strongly influence the photoelectrochemical performance of the cell [2]. A counter electrode is commonly made of a thin layer of noble-metal platinum catalyst deposited on a transparent conducting oxide (TCO) substrate, such as fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO) glass. Previous work has shown that deposited platinum can disperse into the electrolyte and result in degradation of the DSSC [3]. To obtain a long lasting DSSC, many efforts have been devoted to exploring for a counter electrode with high stability and efficient electrocatalytic activity. It has been revealed that inexpensive organic conductive polymers and carbon materials are inert to the iodine-containing electrolyte and can exhibit comparable catalytic performances to that of platinum in the DSSCs and relative systems [4–16]. However, due to shortage of self-adhesion, introduction of binders, such as Triton X-100 and cellulose, and some inorganic materials are indispensable to obtain good contact of the catalytic materials with the TCO substrate [6,17,18]. Unfortunately, the organic agglomerants can also be dispersed into the electrolyte, resulting in the catalyst films peeling off [19]. Meanwhile, the introduction of the binders can increase the charge transport resistance in the counter electrode, which would negatively influence the overall energy conversion efficiency of the photovoltaic devices [17]. In situ electrochemical polymerization of organic monomers onto a conducting substrate seems a promising way to develop binder-free polymer counter electrodes for DSSCs. Electrochemically deposited polyaniline (PANI) has been employed as a counter electrode for DSSCs and exhibits good electrochemical activity [20–22]. However, several detailed electrochemical parameters, such as charge-transport resistance (RCT) in the catalyst, charge-transfer resistance (RCT) in the interface of the catalyst/electrolyte, and the diffusion of the electrolyte in the porous PANI electrode, have not been evaluated to date. The transport of charge in the polymer catalyst and the limitation of electrolyte mass transportation in the pore of the catalyst strongly influence the photovoltaic performance of the solar cells. Moreover, the large sheet resistance of the TCO substrate can increase the internal resistance of the photovoltaic device, resulting in a low fill factor and eventually a lower energy conversion efficiency. Lastly, the rigid and fragile TCO substrates limit the application of DSSCs. In the present work, a flexible counter electrode has been developed by the electrochemical deposition of aniline monomers onto graphitized polyimide carbon film (GPI). The GPI film is electrically conductive (conductivity: ~10,000 S/cm), flexible, compact, and is graphitized from a polyimide film. Besides, the stability of the DSSC with this type of counter electrode was also characterized.

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2. Experimental

2.1. Chemicals and materials

Aniline (analytical grade) was purchased from Sinopharm Chemical Reagent Co. Ltd., and prior to use, it was distilled under reduced pressure. 1-Propyl-3-methylimidazolium iodide (PMII, Aldrich), iodine (I₂, Aldrich), 4-tert-butylpyridine (TBP, Aldrich) were used as received. The N719 dye (cis-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetra-butylammonium)) was purchased from Solaronix. All other chemicals were of analytical grade. FTO glass was purchased from Nippon Sheet Glass Co. Ltd. (15 Ω/sq), and the biaxial oriented polyimide film (BOPI) was supplied from Kying Chemical Reagent Co. Ltd.

2.2. Preparation of counter electrode

The GPI film was prepared according to the literature [23,24]. First, BOPI was heated at 1000 °C under a nitrogen atmosphere for 0.5 h, with a heating rate of 3 °C/min, to achieve the desired carbonization. To prevent loss of the molecular orientation of the polymer film, the BOPI was sandwiched by two graphite plates during the carbonization procedure. Graphitization was performed by further heat treatment of the carbonized film at 2800 °C under an argon atmosphere for 1 h, with a heating rate of 10 °C/min. The PANI electrode was prepared by electrochemical polymerization of the aniline monomers onto the GPI film or the FTO glass using a tri-electrode system. Briefly, the GPI (or FTO glass) was used as the working electrode, a platinum sheet (2 cm × 2 cm in size) was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference. The aniline solution containing 0.1 M aniline was used as the electrolyte. Deposition of the aniline monomers on the working electrode was performed by electrochemical oxidation using a potentiodynamic method in the potential range from −0.2 to 1.2 V, versus the SCE where a sweep rate of 50 mV s⁻¹ was applied [25]. After the electrochemical polymerization, the PANI electrodes were washed with water and dried at 60 °C overnight under vacuum. For comparison with the PANI counter electrode, a conventional platinized FTO glass electrode was also employed. The platinized electrode was prepared by deposition of an 0.6 M H₂PtCl₆ solution (50 mM in isopropanol) onto the FTO glass, followed by heat treatment at 400 °C for 15 min.

2.3. Fabrication of the DSSCs

Fabrication of the DSSCs was performed according to a literature procedure [26]. TiO₂ nanoparticles were prepared by a hydrothermal synthesis starting from titanium (IV) n-butoxide. Briefly, 40 mL of titanium (IV) n-butoxide was added into 240 mL of 0.1 M HNO₃ under vigorously stirring. Next, the obtained slurry was rapidly heated to 80 °C for 8 h. After peptization, the colloidal solution was moved to a self-sealed, Teflon-lined autoclave, and the system was heated for 12 h at 230 °C to grow the TiO₂ nanoparticles. After that, polyethylene glycol (PEG, Molecular Weight 20,000) was added in a proportion of 50% of the TiO₂ weight. The TiO₂ paste was then deposited by doctor blade technique onto the FTO glass by preparing an active area (0.50 cm²). The TiO₂ film was sintered at 500 °C for 1 h. After cooling to 100 °C, the TiO₂ electrode was immersed into the N719 dye solution (0.5 mM in acetonitrile) for 24 h. After the sensitized TiO₂ electrode was rinsed with acetonitrile and dried, one drop of electrolyte was deposited onto the surface of the electrode and penetrated inside the TiO₂ film via capillary action. The electrolyte solution was composed of 0.6 M PMII, 0.05 M I₂, and 0.5 M TBP, which were dissolved in a mixture of acetonitrile and valeronitrile (85:15 by volume). Lastly, the sandwich type DSSC was fabricated by clamping the counter electrode onto the top of the TiO₂ photoelectrode.

2.4. Characterizations

The morphologies of the as-prepared PANI were characterized by scanning electron microscopy (SEM) using a JEOL JSM-5610 electron microscope. Electrochemical impedance spectroscopy (EIS) measurements were performed by a computer-controlled potentiostat (IM6ex, Zahner); the obtained spectra were fitted with Z-view software. The photocurrent–voltage (J–V) curves were recorded by a Keithley Series 2601A System (SourceMeter Instruments). The irradiation source was a solar simulator (San-Ei XES-301S) that gave an AM 1.5 G illumination on the surface of the solar cells. The incident light intensity (100 mW/cm²) was calibrated with a standard Si solar cell.

3. Results and discussion

3.1. Materials

Electrochemical deposition is a common method to grow conducting polymers. Many techniques, such as the galvanostatic method, the potentiostatic method, and cyclic voltammetry (CV) scanning, have been successfully developed to polymerize organic monomers [25,27–29]. CV is a simple and efficient way to grow PANI films onto a substrate. Specifically, PANI prepared by CV has the advantages of high electric conductivity, good adhesion to the substrate, and the ability to effectively avoid degradation during the growth procedure [30–32]. Fig. 1 presents the typical CV curves during the growth of the PANI films from the aniline monomers onto the GPI electrode in the electrolyte. It is obvious that the intensity of the peak current increased uniformly, which indicates that a continuous deposition of PANI on the GPI substrate occurred and that the films are conductive, electrochemically active and uniform.

Various electrodes with different morphologies were also obtained by changing the number of CV scanning cycles. Fig. 2 presents the SEM images of the PANI electrochemically polymerized by 3, 6, 10, and 20 cycles of CV scanning; these samples are denoted as PA-3, PA-6, PA-10, and PA-20, respectively. As the images show, the morphologies of the PANI varied from a particular shape to one of interconnected networks as the CV cycles increased, which means that the nanofibers nucleated and grew from the PANI particles. When the deposition amount was low, the GPI was only partially covered by the particular PANI (Fig. 2(a), PA-3). As the
deposition amount increased, the isolated particles became connected to the newly formed polymer. Continuously scanning the CV only increased the amount of deposition, but the diameter of the nanofibers remained unchanged from PA-6 to PA-10. For example, the samples prepared by CV scanning with 6 cycles (Fig. 2(b), PA-6) and 10 cycles (Fig. 2(c), PA-10) were both approximately 80 nm in diameter. On the other hand, when the CV scanning cycles were increased further, the diameter of the nanofibers became larger (Fig. 2(d), PA-20). Moreover, it is noteworthy that by increasing the number of CV cycles, the interconnected PANI network became denser and consequently the pores tended to tail off from the top view of the SEM images.

3.2. Electrocatalytic activity

To obtain the effects of the counter electrode and eliminate the impact of the photoelectrode, characterization of the electrochemical activity of the counter electrode was needed to be obtained with a symmetric cell [33]. The symmetric cell used consisted of two identical electrodes placed face to face in a sandwich configuration and had an effective electrode area of 1 cm². The electrolyte used in the symmetric cell is the same as that in the DSSC. For a conventional symmetric cell consisting of platinized electrodes, the electric circuit elements should have a constant phase element (CPE) connected in parallel with the \( R_{CT} \) \( W \) element. The \( R_{CT} \) \( W \) element represents the series connection of the charge transfer resistance \( R_{CT} \) for the \( \Gamma / \Gamma_3 \) redox reaction on the electrode surface with Warburg impedance \( W \) arises from the mass transport limitation of electrolyte diffusion. A series resistance \( R_s \) should also be added to the circuit to form the \( R_s(CPE(R_{CT}W)) \) network [33], as Fig. 3(a) shows. However, in the case of the polymer-based electrode, Warburg impedance originating from the charge transport in the catalyst cannot be ignored, due to its low electrical conductivity, compared with that of the platinum catalyst. Therefore, an element representing the Warburg impedance from the charge transport resistance in the PANI film should be introduced to the equivalent circuit. Fig. 3(b) shows the scheme of the equivalent circuit for the \( R_S(W_{CAT}(CPE(R_{CT}W))) \) network.

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![Fig. 2](image1.png)

**Fig. 2.** (a–d) SEM images of the electrochemically deposited PANI films on the GPI substrate. The number of CV scanning cycles for PANI films were as follows: 3 (a), 6 (b), 10 (c), and 20 (d). All scale bar lengths are 1 μm.

![Fig. 3](image2.png)

**Fig. 3.** Equivalent circuits for the symmetric cells consisted of platinum electrodes (a) and PANI electrodes (b). \( R_s \): series resistance; \( W \): Warburg diffusion impedance; \( R_{CT} \): charge transfer resistance on the electrode; CPE: constant phase element; \( W_{CAT} \): charge transport resistance in the PANI catalyst.

![Fig. 4](image3.png)

**Fig. 4.** Displays the Nyquist plots of the GPI electrode with and without deposition of the PANI. For comparison, impedance spectra of the cells consisting of conventional platinized electrodes and PANI/FTO electrodes were also recorded here. The detailed impedance parameters of the cells obtained by fitting the Nyquist plots with the equivalent circuit (Fig. 3(a) or (b)) are summarized in Table 1. The ohmic series resistance \( R_s \) can be determined by estimating the location of the intersection point of the abscissa axis of the Nyquist plots on the high frequency side where the phase

<table>
<thead>
<tr>
<th>Electrode</th>
<th>( R_{CT} ) (Ω cm²) (^a)</th>
<th>( W ) (Ω cm²) (^b)</th>
<th>( R_t ) (Ω cm²) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPI</td>
<td>61.50</td>
<td>0.74</td>
<td>–</td>
</tr>
<tr>
<td>PA-3</td>
<td>18.78</td>
<td>1.84</td>
<td>1.02</td>
</tr>
<tr>
<td>PA-6</td>
<td>1.78</td>
<td>1.09</td>
<td>1.60</td>
</tr>
<tr>
<td>PA-10</td>
<td>0.50</td>
<td>1.87</td>
<td>2.50</td>
</tr>
<tr>
<td>PA-20</td>
<td>0.58</td>
<td>6.52</td>
<td>6.82</td>
</tr>
</tbody>
</table>

\(^a\) \( R_{CT} \): charge transfer resistance.

\(^b\) \( W \): Warburg impedance arising from electrolyte diffusion.

\(^c\) \( R_t \): charge transport resistance in the catalyst.
is equal to zero. Due to their excellent electrical conductivity, the electrodes with the GPI substrate exhibited a very low series resistance, $R_S$. For example, the $R_S$ value for the raw or PANI modified GPI electrode-based cells were only $\sim 0.4 \Omega$, which is only about one percent of the $\sim 36-\Omega$ resistance for that of FTO substrate.

The catalytic performance of the electrodes can be evaluated by measuring the charge-transfer resistance ($R_{CT}$) in the symmetric cell configuration. By fitting the impedance spectra, the $R_{CT}$ of a single electrode can be taken as half the value of the real component of Nyquist plot at the intermediate frequency side semicircle for the PANI electrode, or the high-frequency side semicircle for the PANI-free electrode. For the raw GPI electrode, the $R_{CT}$ value is quite high, reaching almost $61.5 \Omega \text{cm}^2$ for a single electrode and indicating poor electrocatalytic activity for the redox reaction of the iodine species. When it was modified with the PANI film, the electrochemical behaviors dramatically changed. For instance, as the PANI loading on the flexible substrate increased (by increasing the CV scanning cycles from 3 to 10), the electrocatalytic activity of the electrodes also increased. The $R_{CT}$ values of the PA-3, PA-6, and PA-10 electrodes evaluated from the Nyquist plots were 18.78, 1.78, and 0.50 $\Omega \text{cm}^2$, respectively. This change of $R_{CT}$ in the PANI modified electrodes is due to the increasing surface area of the PANI film as the polymer loading increased. However, as the PANI loading continuously increased, the electrocatalytic activity decreased slightly; the $R_{CT}$ value of the PA-20 electrode evaluated from the impedance plots was 0.58 $\Omega \text{cm}^2$. This withdrawal in the electrochemical activity is probably due to the increased average diameter of the nanofibers (as shown in the SEM investigation), which would lower the effective area of the catalyst. In addition, the $R_{CT}$ value for the platinized FTO and PANI/FTO electrodes evaluated from the EIS data were 1.8 and 0.61 $\Omega \text{cm}^2$, respectively.

The Warburg impedance arises from limitations in the mass transportation of the electrolyte, especially when considering its transport in the pores of the PANI networks, cannot be ignored. The diffusion impedance information always appears on the low frequency side of the Nyquist plots, and it is exhibited as various shapes, such as semicircles, depressed arcs, and straight lines, which are depended on the characteristic frequency and its difference to the adjacent impedance element. Many publications indicate by increasing the catalyst loading, the resulting electrode with high surface area can exhibit a comparable electrocatalytic activity to that of platinum [34]. However, due to the increased film thickness, the diffusion length and resisting force of the electrolyte diffusion in the pores were consequently increased. Therefore, the Warburg impedance of the electrolyte increased. Here, in our experiment, the Warburg impedance from the diffusion of the electrolyte varied significantly with the catalyst loading, as shown in Fig. 4 and Table 1 (except for PA-3). According to the SEM images and the fact that the increase of Warburg impedance resulted from the increased PANI loading, the lengthening and narrowing of the pore hindered the mass transport of the iodine species.

In addition, due to the relatively low conductivity, compared with that of platinum particles, the charge transport resistance ($R_T$) in the catalyst also varied with the PANI loading. Table 1 indicates that the $R_T$ increased as the catalyst loading rose. This result may due to the increased charge transport length, which was determined as the length from the catalyst/electrolyte interface to the conducting substrate, GPI. Therefore, as the PANI films become thicker, the average charge transport length increased and, consequently, $R_T$ increased.

### 3.3. Photovoltaic performance

The photocurrent–voltage ($I–V$) behavior is the feature characteristic to determine the photovoltaic performance of solar cells. Many studies indicate that photovoltaic parameters, such as the open-circuit voltage ($V_{OC}$), the short-circuit photocurrent density ($J_{SC}$), and the fill factor (FF), can all be changed, and eventually the overall energy conversion efficiency ($\eta$) of the DSSCs varied when platinum on the counter electrode was replaced with other catalysts, such as carbon or conducting polymers. Fig. 5 presents the $I–V$ characteristics of the DSSCs with various electrodes, and the detailed photovoltaic parameters of the devices are summarized in Table 2.

Generally, the $V_{OC}$ value depends on the difference between the electronic Fermi level in the semiconductor and the formal potential of the redox couples on the counter electrode. Because the semiconductor photoelectrodes and the compositions of the electrolytes for all of the solar cells are the same, the $V_{OC}$ value of each photovoltaic device is dependent on the electrochemical properties of the counter electrode. It can be seen that the value for the $V_{OC}$ changed as the PANI loading varied. For example, the photovoltaic device with the raw GPI counter electrode showed a $V_{OC}$ of 901 mV, a value 81 mV higher than that of the platinum-
based DSSC. The increase to the open-circuit voltage is probably due to the positive shift in the formal potential for the I\(^{-}\)/I\(_3\)\(^{-}\) couple on the carbon electrode [35]. On the other hand, when PANI was applied onto the GPI film, the \(V\)\(_{OC}\) value slightly decreased. This result would be attributed to the slightly negative-shift in the formal potential of the redox couples on the PANI electrode, which resulted in a relatively small difference to the electronic Fermi level of the semiconductor. However, due to the very high electrochemical activity, the PANI-based cells still possessed relatively high \(V\)\(_{OC}\) values, compared with that of the platinized electrode [6].

The internal resistance of the DSSC strongly influences the value of \(FF\), and eventually affects the \(J\)\(_{SC}\) and \(\eta\). The internal resistance mainly consisted of series resistance from the substrate, the charge transport resistance, the charge transfer resistance on the counter electrode, and the impedance from the diffusion of the electrolyte. From Fig. 5 and Table 2, it is clearly seen that the catalytic activity of the counter electrode strongly influences the \(FF\) of the cell. Due to poor catalytic activity, the DSSC with raw GPI electrode exhibited the lowest \(FF\), \(J\)\(_{SC}\), and \(\eta\). However, when PANI was deposited onto the GPI substrate, the photovoltaic parameters dramatically changed. The \(FF\), \(J\)\(_{SC}\), and \(\eta\) for the GPI cell were 0.283, 9.68 mA/cm\(^2\), and 2.49%, while respective values for the cell with optimized PANI loading (PA-10) were 0.662, 12.40 mA/cm\(^2\), and 6.85%. Although PANI/FTO and Pt/FTO exhibited comparable electrochemical activities to PA-10, the \(FF\) and \(\eta\) were lower due to the large sheet resistance of the FTO. The \(FF\) decreased to 0.621 and 0.823, and the \(\eta\) decreased to 6.31% and 6.44% for the cells with the PANI/FTO and the Pt/FTO, respectively.

3.4. Long-term characterization

3.4.1. \(I\)-\(V\) characterizations

The major concern for the application of alternative counter electrodes to conventional platinized TCOs in DSSCs is long-term stability. Many publications indicate that during prolonged exposure in corrosive electrolyte, catalysts will detach from the substrate and deposit onto the surface of the semiconductor photocathode. These results aggravate the back transfer of the charge on the semiconductor/electrolyte interface (SEI) and decrease the catalytic activity of the counter electrode, resulting in lower charge collection efficiencies in the front TCO collector [3,19]. Fig. 6 shows the variations in the photovoltaic parameters of the DSSCs aged in the dark at room temperature. During the aging, both the \(J\)\(_{SC}\) and \(FF\) decreased slightly, compared with the fresh one. In contrast, the \(V\)\(_{OC}\) slightly increased after aging. As a result, the overall energy conversion efficiency of the photovoltaic device almost maintained its initial performance.

3.4.2. Electrochemical impedance spectroscopy

To gain further insight into the degradation of the photovoltaic performance of the DSSCs after aging, EIS was employed to characterize the electrochemical behaviors of an aged symmetric cell. No significant changes were found from the impedance and linear sweep voltammetry characterizations (not shown here). Thus, the only possible factor for the variation of the \(I\)-\(V\) characteristics would be attributed to the degradation of the photocathode. We therefore employed EIS to investigate the charge transport properties in the semiconductor film and to study the interfacial charge recombination on the SEI for the cell before and after aging.

Fig. 7(a) shows the impedance spectrum of the fresh DSSC at a bias of −0.6 V. It is clear that the electron transport in the mesoporous TiO\(_2\) film appears to have Warburg-like diffusion behavior in the high-frequency region, and the interfacial charge recombination process grew to a large semicircle in the low-frequency region. The electronic processes in the DSSC are well described by a transmission line model developed by Bisquert et al. [36–39], as shown in Fig. 7(c).

By fitting impedance data with the transmission line, we can obtain the characteristic elements that describe the 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 $I_3^-$ in the electrolyte, and chemical capacitance ($C_{Cu}$).

The conductivity of the TiO$_2$ network can be calculated from $R_t$ with geometric parameters. It has been established that the conductivity of the electrons in the TiO$_2$ network is exclusively dependent on the number of free electrons in the extended state [40]: $\sigma = \mu n e$ (where $e$ is the elementary charge and $\mu$ is the mobility). It is convenient to use the conductivity of the semiconductor as the variable to compare the change in potential, $R_{ct}$, and $C_{Cu}$ because $\sigma_0$ is decided by the position of the electronic Fermi level ($E_F$) with respect to the conduction band edge ($E_{cb}$) [40,41]:

$$\sigma = \sigma_0 \exp \left(\frac{E_F - E_{cb}}{k_B T}\right)$$  \hspace{1cm} (1)

where $\sigma_0$ is a constant, $k_B$ is the Boltzmann constant, and $T$ is the temperature. Because $\sigma_0$ relates only to the steady-state transport and reflects the rate of displacement in the transport band, the electron conductivity in a multiple trapping scheme is independent of the number of traps [42].

Fig. 8(a) shows the change of conductivity for the electrons in TiO$_2$ from a low to a high value as the Fermi level was shifted toward the conduction band. From the potential–conductivity relationship, it can be seen that the potential of the cell after aging slightly increased, which is in agreement with the slight increase to the $V_{OC}$ (Fig. 6). Because the electrochemical behaviors have not changed before and after aging, the larger difference between the $E_F$ and $E_{redox}$ (redox potential of $I/\Gamma$) can be attributed to the slight upshift of the conduction band of the cell after aging, rather than the downshift of the $E_{redox}$.

Fig. 8(b) shows the SEI charge transfer resistance, $R_{ct}$, of the DSSC before and after aging. It can be seen that the $R_{ct}$ values decreased exponentially as the Fermi level moved toward the conduction band, indicating that the charge transfer rate increased as the density of the electron increased. By comparing the two curves, it is clear that the charge transfer resistance decreased after aging. Moreover, the slope of the curves became smaller after aging, indicating that the transfer of electron was predominantly becoming intermediated by the surface sites.

Fig. 8(c) shows the chemical capacitance, $C_{Cu}$, of the TiO$_2$ films for the cell before and after aging. The capacitances of the semiconductor films exponentially grew as the potential shifted toward more negative values. Additionally, the capacitance became larger after aging. By linearly fitting the plots, it can be seen that the slope of the fresh cell is slightly higher than the aged one, which is very similar with the result found in the logarithmic relationship of the $R_{ct}$–conductivity in Fig. 8(b). The relatively low slope and large capacitance for the aged cell in the logarithmic $C_{Cu}$–conductivity plots indicate that the contribution from the intraband trap sites for the aged cell was much larger than in the case of the fresh one.

It should be noted that during the electrochemical polymerization of the aniline, chemical doping of the acid ($H_2SO_4$) molecules into the formed polymer also took place. Additionally, during the long operation period of the photovoltaic device, some of the sulfonic groups would dissociate into the electrolyte. The free sulfonic groups would anchor onto the surface of the semiconductor, and the oligomerization of the protons into the lattice of TiO$_2$ could not be avoided by the multi-process illumination and the photoelectrochemical and/or electrochemical redox processes. Intercalation of the protons into the lattice of the semiconductor can increase the density of surface state, which acts as the intermediate for the interfacial charge recombination, resulting in a degradation of the quality of the semiconductor. Moreover, the increase in the density of the electronic sites on the surface can also increase the chemical capacitance of the TiO$_2$ film. Meanwhile, intercalation of protons into the lattice can result in a local pH increase, which can cause a negative-shift in the conduction band edge, producing an increase in the cell potential difference [44,45].

The competition between the collection and recombination of electrons can be expressed in terms of the electron diffusion length. An effective diffusion length ($L_e$) for electrons can be obtained from impedance parameters ($L_e = \sqrt{R_{ct}/R_t}$). The effective diffusion length of electrons in the mesoporous semiconductor film for the
sites in the bulk and surface of the aged semiconductor film, the $\Delta n$ obtained from the impedance indicates that the aged cell possessed a relative short electron diffusion length, compared with the fresh one. A decrease in the electron diffusion length would lower the charge collection efficiency, resulting in a decrease to the photocurrent.

4. Conclusion

In summary, flexible counter electrodes were obtained by electrochemical deposition of polyaniline nanofibers onto graphitized polyimide carbon films. Additionally, various electrodes with different electrochemical performances were prepared by simply adjusting the number of scanning cycles during cyclic voltammetry. The polyaniline nanofibers exhibited promising properties as the catalyst in the counter electrode of the dye-sensitized solar cells. By fitting a developed equivalent circuit for the polyaniline electrode, the charge transfer resistance evaluated from the impedance data was 0.5 $\Omega$ cm$^2$, which is lower than that of 1.8 $\Omega$ cm$^2$ for a conventional platinum electrode. Due to high catalytic activity of the polyaniline nanofibers and the low sheet resistance of the graphitized polyimide carbon films, which lowered the internal resistance of the cell, the flexible counter electrode-based photovoltaic device exhibited relatively high open-circuit voltage, fill factor, and energy conversion efficiency.

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