Electrochemical impedance analysis of nanoporous TiO$_2$ electrode at low bias potential

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Abstract

TiO$_2$ colloid was prepared by the sol–gel method and was bladed on transparent conduction glass to made nanoporous electrode. The impedance performance of TiO$_2$ electrode was studied at various bias potential. A simplified equivalent circuit was proposed to investigate the charge transport impedance of TiO$_2$ film and good fitting results were obtained.
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Dye-sensitized solar cells (DSC) have attracted great scientific and technological interests as photovoltaic devices for their low production cost and simple preparation process [1,2]. The nanocrystal TiO$_2$ based DSC have achieved high photoelectric conversion efficiency up to 11% [3]. The electrochemical impedance spectroscopy (EIS) is a useful method for the analysis of these charge transfer and transport processes of DSC [4]. EIS could be used to evaluate the internal series resistance, catalysis performance of the counter electrode, the diffusion properties of I$^-$/I$_3^-$ and the electron recombination process at the surface of TiO$_2$ [5–8].

The injected electrons from excited dye are slowed down by trapping at the surface of the TiO$_2$ particles. The trapped electrons are more difficult to transport between the nanoparticles and might back react through the recombination with I$_3^-$ ions. To evaluate the transport impedance of TiO$_2$ electrode, suitable models are required for the analysis of EIS results. Bisquert and co-workers [9] described the impedance of a porous TiO$_2$ electrode by transmission line models and gave the equivalent circuit for a complete solar cell. For the predigestion of EIS models, the TiO$_2$ electrode was supposed to be a homogeneous electrode. Here, a new simplified equivalent circuit was used to study the EIS of TiO$_2$ based DSC at low bias potential.

1. Experimental

TiO$_2$ colloids were prepared by hydrolyzing the mixture of titanium (IV) isopropoxide (Aldrich) and isopropyl alcohol in the presence of distilled acetic acid (pH = 2) followed by autoclaving at 250 °C for 12 h. The TiO$_2$ colloidal

paste was doctor-bladed onto the clean transparent conduction glass sheets (FTO, 30 Ω cm^{-2}, F-doped SnO$_2$). After dried in air, the samples were heated for 30 min at 450 °C, resulting in anatase TiO$_2$ nanoparticle film electrodes.

The counter electrode was Pt coated transparent conduction glass sheets. The mixture of ethylene carbonate (EC, Acros) and propylene carbonate (PC, Acros) (EC:PC = 5:5, v/v) containing 0.5 mol/L KI and 0.05 mol/L I$_2$ was selected to be the electrolyte of DSC. A spacer about 20 μm was used between the working and counter electrode, which was pressed together with clips.

The electrochemical impedance spectra (EIS) were carried out with a potentiostat (Solartron SI1287) and a frequency response analyzer (Solartron 1255B). The impedance measurement of DSC was recorded over a frequency range of 0.01–1 M Hz with ac amplitude of 10 mV.

2. Results and discussion

The Bode diagrams of the measured impedance spectra at various bias potentials are presented in Fig. 1. There was an obvious change in the form of the phase angle *vs.* log frequency curves as the potential was changed, which indicated that different charge transfer processes appeared. Generally, the impedance spectrum of testing cells consisted of five components, which were attributed to charge transfer at Pt/electrolyte (ω_1), FTO/electrolyte (ω_2), TiO$_2$/electrolyte (ω_3), electron transport resistance (ω_4) and diffusion impedance of I$_3^-$ in electrolyte (ω_5) [9,10]. When the applied potential was more negative than −0.60 V, the three time constants appeared in the Bode diagrams should be corresponded to charge transfer at Pt/electrolyte (ω_1, 10^3–10^4 Hz), TiO$_2$/electrolyte (ω_3, 10–100 Hz), and diffusion impedance of I$_3^-$ in electrolyte (ω_5, 0.1–1 Hz) which was in consistent with other researchers [4].

When the bias potential was equal to or lower than −0.30 V, the Bode diagram comprised of a high-frequency and a low-frequency time constant at around 100 Hz and 0.5 Hz, respectively. The high-frequency time constant could be ascribed to the space-charge layer and the interfacial charge transfer process at the FTO/electrolyte (ω_2) interface. This was confirmed by the results of Fig. 2 which showed the Bode diagrams of the blank FTO. The characteristic frequency
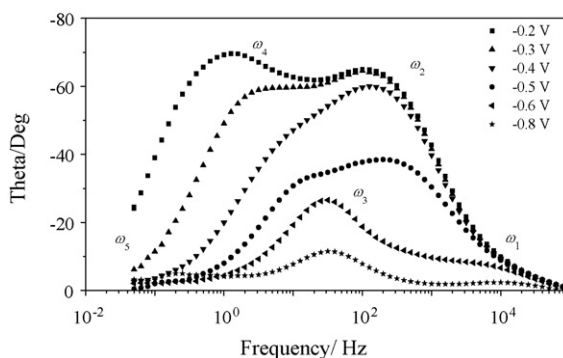

Fig. 1. Bode plots of EIS data recorded at various potentials for a nanoporous TiO$_2$ electrode in the mixture of ethylene carbonate (EC, Acros) and propylene carbonate (PC, Acros) (EC:PC = 5:5, v/v) containing 0.5 mol/L KI and 0.05 mol/L I$_2$.
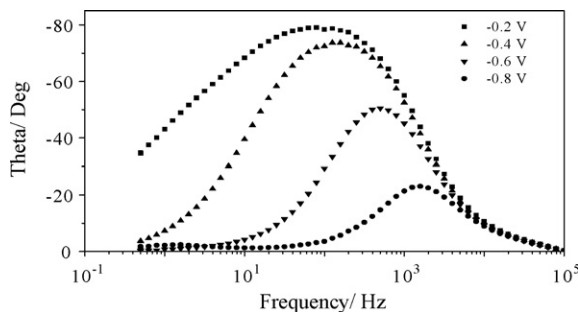

Fig. 2. Bode plots of EIS data recorded at various potentials for a blank FTO electrode in the mixture of ethylene carbonate (EC, Acros) and propylene carbonate (PC, Acros) (EC:PC = 5:5, v/v) containing 0.5 mol/L KI and 0.05 mol/L I$_2$.

of blank FTO was almost the same as that of the ω_2 of TiO$_2$ coated FTO. This region was no longer visible at more negative bias potential than -0.60 V for TiO$_2$ coated FTO. But for the blank FTO, the time constant remained evidently at -0.80 V (Fig. 2). This distinction could be contributed to the dramatically decrease of charge transfer and transport impedance and the aggrandizement of capacitance at the surface of TiO$_2$ nanoparticle with the negative shift of bias potential. The low-frequency part of the spectra might be attributed to the capacity behaviour at the TiO$_2$/electrolyte interface and the charge transport of TiO$_2$ film (ω_4). The characteristic frequency moved toward high-frequency obviously until the applied potential shifted negatively to -0.60 V.

Under high applied potential, the Fermi energy level in TiO$_2$ approached and was even more negative than the lower edge of the conduction band of TiO$_2$ film which resulted in the severe decrease of R_t. The charge transport impedance (R_t) and the surface impedance (R_{FTO} and Z_{CPE}) of FTO/electrolyte might be both omitted (shown in Fig. 1), thus it was difficult to investigate the charge transport impedance through EIS analysis under high bias potential. The analysis of the EIS of TiO$_2$ electrode at lower bias potential was useful for the evaluation of the charge transport impedance (R_t).

To quantify the impedance of the different charge transfer process of DSC, the equivalent circuit was a useful tool to deal with the EIS data. As the applied potential ranged from -0.10 V to -0.40 V, the recombination reaction at the TiO$_2$/electrolyte was so slow that the electrochemical reaction process (R_r) could be omitted. The equivalent circuit of TiO$_2$ electrode could be simplified to be Fig. 3. A constant surface element (CPE) was used to replace the pure capacitance for a better agreement between the fitting and experimental data. The value of CPE is defined as $Z_{CPE} = 1/T(j\omega)^P$, where T is the capacitance of the pure capacitor, P ($0 < P < 1$) represents the deviation of the pure ideal capacitance behaviour, which is related to the inhomogeneities at the surface [11]. The total impedance of the equivalent circuit from Fig. 3 can be given as:

$$Z = R_s + \left[\frac{1}{R_t + (1/T(j\omega)^P)_{TiO_2}} + (T(j\omega)^P)_{FTO} + \frac{1}{R_{FTO}} \right]^{-1} \tag{1}$$

The complex non-linear least-squares fitting method was used to fit Eq. (1) to the experimental EIS data obtained at the -0.30 V bias potential. The impedance spectra of the TiO$_2$ nanoporous electrodes without dye and with dye were shown in Fig. 4(a) and (b), inspectively. Experimental data are represented by symbols while the solid lines correspond to the fitting result. The fitting line overlapped almost all the experimental point. The best fit values of the equivalent circuit elements were listed in Table 1. The goodness of the fit could be judged by the estimated relative errors which represent the standard deviation in the fitting process listed in Table 1. The simulated results agreed very well with the experimental data for all the parameters of the equivalent circuit elements. The relative errors were less than 6%.

The EIS of a TiO$_2$ electrode was also studied after absorption of cis-bis(thiocyanato)-*N*,*N*′-bis(2,2-bipyridyl-4,4′-dicarboxylate) ruthenium (II). The test was carried out at -0.30 V under dark condition. The charge transport impedance (R_t) increased after the adsorption of dye (Table 1). The introduction of dye molecular without illumination might form a core–shell structure like the metal oxides, such as Al$_2$O$_3$, Nb$_2$O$_5$, which increased the surface resistance of TiO$_2$ electrode [12–14]. After the adsorption of dye, the capacitance at TiO$_2$/electrolyte surface increased by one order which might be related to the carboxylic acid groups in the dye molecule.
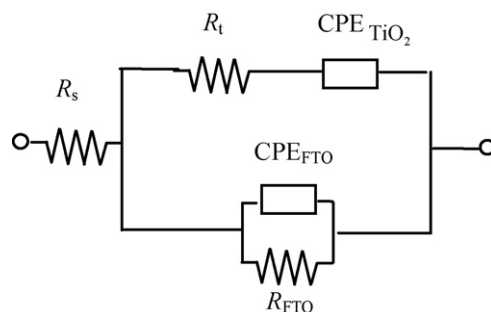

Fig. 3. Electrical equivalent circuit model used to simulate the EIS results of TiO$_2$ electrode at low bias potential.
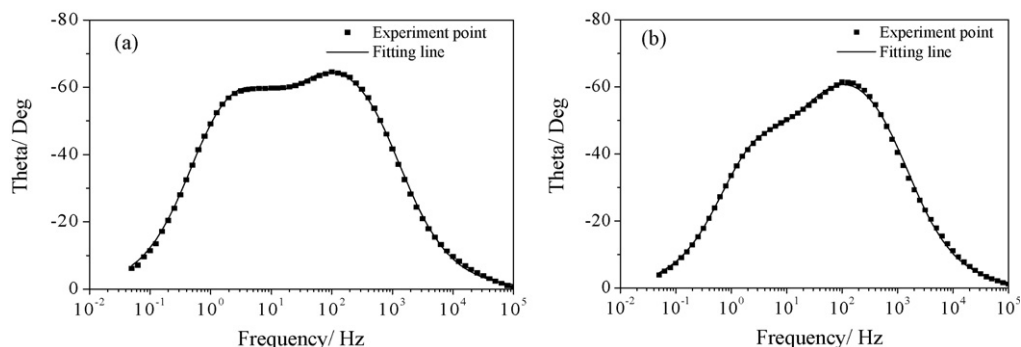
Fig. 4. Bode plots of EIS data recorded at −0.30 V for nanoporous TiO_2 electrodes: (a) without dye and (b) with dye.

Table 1
The values of the equivalent circuit elements presented in Fig. 3 obtained by fitting the experiment plots at the applied potential of −0.30 V and the corresponding relative percentage errors.

	R_s (Ω cm^2)		R_t (Ω cm^2)		$CPE_{TiO_2} - T$ (F cm^{-2})		$CPE_{TiO_2} - P$		R_{FTO} (Ω cm^2)		$CPE_{FTO} - T$ (F cm^{-2})		$CPE_{FTO} - P$	
	Data	Error (%)	Data	Error (%)	Data	Error (%)	Data	Error (%)	Data	Error (%)	Data	Error (%)	Data	Error (%)
FTO/TiO$_2$ no dye	40.96	0.25	3208	4.43	7.83E−6	4.35	0.87	1.14	18946	1.07	1.13E−5	1.89	0.86	0.28
FTO/TiO$_2$ with dye	44.39	0.36	4470	5.33	8.84E−5	5.83	0.88	1.77	20580	1.96	1.23E−5	2.22	0.83	0.34

3. Conclusions

The impedance performance of TiO_2 electrode was studied at various bias potential. At low bias potential, the Bode diagram was proposed to comprise of the impedance at FTO/electrolyte surface, the charge transport impedance (R_t) and the capacity behaviour at the TiO_2/electrolyte interface. A simplified equivalent circuit for the EIS at low bias potential was proposed and the good fitting results were obtained. This method provided an easy way to investigate the charge transport properties of TiO_2 electrode.

Acknowledgments

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