


Chapter VII  Electrochemical Impedance Analysis of Titania Nanostructures

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CHAPTER VII

Electrochemical Impedance Analysis of Titania Nanostructures

7.1 Introduction

Electrochemical impedance spectroscopy (EIS) has been widely recognized as a powerful tool for the investigation of electrochemical systems [1, 2]. It is used to characterize limitations and improve the performance of PEC cells. There are three fundamental sources of voltage loss in PEC cells: charge transfer activation or “kinetic” losses, ion and electron transport or “ohmic” losses, and concentration or “mass transfer” losses. Among other factors, EIS is an experimental technique that can be used to separate and quantify these sources of polarization. By applying physically-sound equivalent circuit models, wherein physiochemical processes occurring within the cell, are represented by a network of resistors, capacitors and inductors. One can extract meaningful qualitative and quantitative information regarding the sources of impedance within the cell. EIS is useful for research and development of new materials and electrode structures, as well as for product verification and quality assurance in manufacturing operations.

7.2 Theory

Electrochemical Impedance Spectroscopy involves a sinusoidal alternation of the applied potential, at low amplitudes, where the system will be linear with respect to current and potential. Measurements are conducted with an ac component $\Delta E_\sim$ passing through the working electrode given by
\[ \Delta E_\sim = \Delta E_m \sin \omega t \quad \text{(7.1)} \]

and \(\omega = 2\pi f\) \quad \text{(7.2)}

where

\[ E_m = \text{amplitude of the applied potential and} \]
\[ \omega = \text{angular frequency} \]
\[ f \text{ is the ac frequency.} \]

In an electrochemical impedance experiment, the frequency is varied in order to probe different processes that have different time constants. Figure 7.1 shows the schematic representation of a simplified equivalent circuit used to interpret impedance measurements of a metal [3].

**Fig. 7.1** Equivalent circuit representation of a metal with ohmic resistance (\(R_o\)), double layer capacitance (\(C_{d.l.}\)), charge transfer resistance (\(R_{c.t.}\)) and mass transport resistance (\(R_{m.t.}\)).

If an electrode behaves as a pure ohmic resistance, the relation between the change in potential and the instantaneous value of intensity will be

\[ \Delta E_\sim / \Delta I_\sim = E_m / I_m = R_o \quad \text{(7.3)} \]
This ideal situation does not exist in real electrodes; on the other hand, a phase shift ($\theta$) appears between alternating current and alternating potential. In electrochemical systems, the current changes can lag, lead or be in phase with the potential changes. The equation

$$\Delta E_\text{r} = \Delta E_m \sin(\omega t - \theta)$$  \hspace{1cm} (7.4)

can be represented by different simple electric circuit elements. The impedance is characterized by the modulus

$$|Z| \equiv \Delta E_m / \Delta I_m$$  \hspace{1cm} (7.5)

and the phase shift $\theta$.

There are two ways to represent the data [4]. One method is called the Nyquist plot. It is a diagram where the imaginary part of $Z$ is plotted versus the real part of $Z$. Another representation is called the Bode plot, which is a composite of two figures, one log $|Z|$ is plotted versus log $\omega$ and the other is $\theta$ versus log $\omega$, where:

$$|Z| = [\text{Re}(Z)^2 + \text{Im}(Z)^2]^{1/2}$$  \hspace{1cm} (7.6)

$$\theta = \tan^{-1}\left\{\frac{\text{Im}(Z)}{\text{Re}(Z)}\right\}$$  \hspace{1cm} (7.7)

Figure 7.2 represents a schematic of a Nyquist plot illustrating the different resistances present in Fig. 7.1 often used to depict the processes occurring at one electrode versus a reference. The Nyquist plot is usually a semicircle. The ohmic resistance can be found by reading the real axis value at the high frequency intercept. This is the intercept near the origin of the plot. The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the ohmic resistance. The diameter of the semicircle is therefore equal to the polarization resistance. The different impedances present in Fig.7.1 can be equated as follows
\[ Z = Z_{\text{ohm}} + \left[ \frac{1}{Z_{\text{d.l.}}} + \frac{1}{(Z_{\text{c.t.}} + Z_{\text{m.t.}})} \right] \]  

(7.8)

At high frequency the capacitive effect behaves as a closed circuit and the response is that of only an ohmic resistance, having no imaginary component. At the other extreme, at low frequency, the capacitive component acts like an open circuit and the impedance response reflected all the resistances in series: ohmic, charge transfer and diffusion. Diffusion is a slower process than charge transfer and so manifests itself at the lowest frequency. If the diffusion layer is not fixed, but changes with time, then the response is a straight line on the Nyquist plot at 45° angle. If the capacitance dominates then this is a vertical line on the Nyquist plot, in the imaginary plane. Typically charge diffusion.

Fig. 7.2 Typical shape of a Nyquist plot with: a) charge transfer and double layer limitations at the high frequency range, and b) mass transport limitation at the low frequency range. The intercept Re(Z) is \( R_{\text{ohm}} \)
transfer and capacitive effects occur at similar frequencies and this combination creates a semi-circular response [4].

7.3 Experiment

All electrochemical measurements were carried out in electrolyte solution of 1 M KOH, with halogen lamp illumination using three-electrode system at room temperature with the nanostructure titania electrode, a platinum plate, and a saturated calomel electrode (SCE) which served as the working, counter, and reference electrodes, respectively. The distance between the working electrode and the lamp was 3 cm. The EIS measurement was carried out by applying 1 MHz to 1 Hz frequency range with oscillation amplitude of 25 mV from VMP3 multichannel potentiostat.

7.4 Results and discussion

The Nyquist plots Fig. 7.3 of titania (LS1) are recorded in dark and light irradiation using modulated applied potential in a sinusoidal manner. Both measurements, in the dark and in the light, resulted in identical plots, where an ohmic resistance is found at high frequencies. It can be inferred that the response at high frequency is related to the interface between the electrode and the electrolyte, which is likely to accelerate the transfer of the carrier and even increase the photoelectric conversion. There is a decrease in the impedance values due to illumination, which suggests a faster charger transfer, or in other words a lower $R_{ct}$ the electrode-solution interface. On close inspection, the spectra for LS1 under dark contain two semicircles, although this is not distinctly seen at the first glance. The first semicircle corresponds to the Faradaic reaction which primarily arises from the slow kinetics of the $O_2$ reduction
reaction, while the second semicircle is attributed due to finite O$_2$ diffusion (onset of mass transfer limitations) [5]. Due to the overlapping of the two semicircles (kinetic and

Fig. 7.3 EIS of LS1 electrode under a) dark and b) light illumination.
transport loops) and since it is not complete, precise estimation of the parameters pertaining to Faradaic reaction and diffusion was difficult to achieve (with high sensitivity) and hence it is not reported. The EIS parameters are given in Table 7.1.

The Nyquist plots in Fig. 7.4 of titania (LS2) are recorded in dark and light irradiation by modulating the applied potential in a sinusoidal manner. The Nyquist plots are a semicircle-like characteristic in its complex plane when the electrode impedance is predominantly determined by the charge transfer resistance in a kinetics-controlled process [6]. Both measurements, in the dark and in the light, resulted in identical plots, where a small tail is found at low frequencies. The low-frequency tail appears to be the result of non-stationary behaviour during the time necessary to complete the scan. There is a decrease in the impedance values due to illumination, which suggests a faster charger transfer, or in other words a lower $R_{ct}$ the electrode-solution interface. The photocurrent originates from the photo-oxidation of water and the photocurrent density corresponds to the amount of free carriers under the same potential bias, which is related to the amount of photo-generated holes within the TiO$_2$ electrode [7]. The use of 0.05 M KF and ethylene glycol electrolytes to synthesize LS2, instead of 0.5 wt% of hydrofluoric acid electrolyte used in LS1, has lowered $R_{ct}$ value. In real systems, however, the picture is rarely as ideal as that shown for LS2 under dark condition in Fig. 7.4 since the results usually show deviations from an ideal semicircle with a small tail at the end. The main
problem which can be encountered is that the “arcs” can be rotated due to surface in-
homogeneity, roughness, surface morphology, some physicochemical processes [8].

Fig. 7.5 presents a larger radius distorted semicircle corresponding to higher TiO$_2$
resistance value of LS3. The larger theradius of semicircle, the smaller will be the

**Table 7.1 EIS measurements of nanostructured samples under dark and light illumination.**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Dark</th>
<th>Light</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_o$ $\Omega$</td>
<td>$R_{ct}$ $\Omega$</td>
</tr>
<tr>
<td>LS1</td>
<td>27.32</td>
<td>16.4</td>
</tr>
<tr>
<td>LS2</td>
<td>2.07</td>
<td>4313.64</td>
</tr>
<tr>
<td>LS3</td>
<td>2.28</td>
<td>2290.72</td>
</tr>
<tr>
<td>LS4</td>
<td>4.32</td>
<td>1.85</td>
</tr>
<tr>
<td>PS1</td>
<td>7.14</td>
<td>6333.97</td>
</tr>
<tr>
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<td>16.95</td>
<td>3993.05</td>
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<td>2441.01</td>
</tr>
<tr>
<td>PS4</td>
<td>2.70</td>
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<td>2526.85</td>
</tr>
<tr>
<td>CS3</td>
<td>5.27</td>
<td>2025.18</td>
</tr>
</tbody>
</table>
Fig. 7.4 EIS of LS2 electrode under a) dark and b) light illumination.
Fig. 7.5 EIS of LS3 electrode under a) dark and b) light illumination.
capacitive constant, which results in the higher value of the impedance of Faraday current [9]. Therefore, it is more difficult for the chemical reaction to take place on the electrode owing to the higher energy barrier [10]. Also, two overlapping semicircles occur. The second semicircle corresponds to the diffusion process of redox electrolyte while the first is the charge-transfer semicircle due to exchange reaction [11, 12]. However, it is found that the radius of the semicircle considerably decreases after light illumination. The most pronounced distortion is the additional inward tail at low frequencies. This feature has been attributed to adsorption-desorption phenomenon at the working electrode surface [13]. The use of 0.25 wt. % of NH₄F in ethylene glycol electrolytes to synthesize LS3, instead of 0.05 M KF and ethylene glycol electrolyte (LS2) has further lowered R_{ct} value than LS1 and LS2. The situation at the interface arcs shown in Fig. 7.5 reveals that the distorted semicircle may be due to the nanorod morphology confirmed by FEGSEM image.

Fig. 7.6 shows Nyquist plot of LS4 film electrodes. These curves represent kinetic-capacitive effects taking place in the dark and upon illumination. The impedance response under illumination is nearly a perfect semicircle while it is incomplete in the dark condition. Moreover, the smaller radius which indicates its lower R_{ct} corresponds to the optimal photo electrochemical performance. Due to the incomplete semicircle of LS4 under dark condition, precise estimation of the parameter pertaining to Faradaic reaction
was difficult to achieve and hence not reported. The use of non-fluoride based electrolytes of 0.5 M HCl + 0.4 M H₂O₂ in ethylene glycol to synthesize LS4, instead of 0.25 wt. % of NH₄F in ethylene glycol electrolytes (LS3) has still further lowered $R_{ct}$ value than the other nanostructures (LS1, LS2 and LS3).
The $R_{ct}$ value with light illumination varied in the sequence LS4 < LS3 < LS2 < LS1, and is shown in Table 7.1. This suggests that electron transport resistance of the electrodes under illumination is also in the same sequence.

Fig. 7.7 presents the incomplete semicircle of larger radius for dark and a smaller radius for illumination of PS1. During light illumination, the radius of the semicircle decreases since the chemical reaction takes place. Also, the difference in the response with and without irradiation is due to the shift in the governing process of the electrochemical anodic reaction in KOH. Under light illumination, a substantial fraction of the potential change appears across the Helmholtz layer (Fermi level pinning), which also changes the charge-transfer rate constant [14]. The impedance curves in the light and in the dark show similar shapes, and the shapes are characteristic of a kinetic-capacitive effect.

The Nyquist plots in Fig. 7.8 of titania (PS2) have a distorted semicircle-like characteristic. Two arcs overlap at interface under dark in anodic oxide layer due to cone-like inter phase structure while an inward tail is noticed in the low frequency region under illumination. A decrease in the impedance values is noticed due to illumination, which suggests a faster charge transfer, or in other words it lowers the electrode-solution interface resistance $R_{ct}$. Moreover in the semicircle a long tail is noticed. This result suggests that the metaphorical shutter speed of the impedance snapshot was not fast enough to capture the short interval behaviour of the system. The use of 0.05 M KF and
ethylene glycol electrolytes to synthesize PS2, instead of 0.5 wt. % of hydrofluoric acid electrolyte used in PS1 has lowered $R_{ct}$ value.

Fig. 7.7 EIS of PS1 electrode under a) dark and b) light illumination.
Fig. 7.8 EIS of PS2 electrode under a) dark and b) light illumination.
Fig. 7.9 presents an incomplete larger radius semicircle corresponding to higher TiO$_2$ resistance value PS3 electrode under dark condition. However, it is found that the radius of the semicircle significantly decreases after light illumination. The use of 0.25 wt. % of NH$_4$F electrolyte in ethylene glycol to synthesize PS3 has further lowered R$_{ct}$ value.

Fig. 7.10 shows Nyquist plot of a nearly semicircle of PS4 film electrode and is not closed at low frequency region under the dark condition. These curves represent kinetic-capacitive effects taking place in dark and upon illumination. In addition, the impedance response under illumination is a closed semicircle and decreased expressively. The non-fluoride based electrolytes of 0.5 M HCl + 0.4 M H$_2$O$_2$ in ethylene glycol used to synthesize PS4, instead of 0.25 wt. % of NH$_4$F in ethylene glycol electrolytes used in PS3, has still further lowered R$_{ct}$ value.

The circular radii with light illumination get varied and R$_{ct}$ value varies in the sequence PS4 < PS3 < PS2 < PS1, as shown in Table 7.1. This suggests that electron transport resistance of the electrodes under illumination is also in the same sequence.

Fig. 7.11 displays semicircle of larger radius which appears for dark and a smaller radius for light illumination of CS1. The sample under dark condition shows a pronounced distorted arc (semicircle portion) at lower frequencies in the EIS plane, whose diameter corresponds to the electron transfer resistance controlling the kinetics at the electrode interface [14, 15]. Significant changes in the EIS spectra are observed for
the TiO$_2$ nanotube electrode during light illumination, and a long tail appears. Also, the difference in the response with and without irradiation is due to the shift in the governing

![Fig. 7.9 EIS of PS3 electrode under dark and light illumination.](image-url)
Fig. 7.10 EIS of PS4 electrode under dark and light illumination.
Fig. 7.11 EIS of CS1 electrode under dark and light illumination.
process of the electrochemical anodic reaction in the KOH. The nanotube results in a marked decrease of the semicircle diameter, which justifies an analogous decrease of the electron-transfer resistance and relates directly to a faster charge transfer, or in other words a lower $R_{ct}$ at the electrode-solution interface. At the first glance, the impedance spectra denote the presence of two semicircles overlap, which can be ascribed to the response of the semiconductor space charge layer in series with the Helmholtz layer in the electrolyte side. The slight depletion is due to the inhomogeneity of the electrode which is at the origin of the dispersion of time constants of the RC circuit. Such behaviour can be due to various phenomena like surface states, the porosity of the electrode, the distribution of current and potential field as well as slow adsorption [16].

The Nyquist plots in Fig. 7.12 of titania CS2 are recorded in the dark and light irradiation by modulating the applied potential in a sinusoidal manner. The capacitive arc in the dark suggests that the Faradaic charge transfer was the limiting step for the oxidation process in the electrode surface. However, on close examination, under illumination, two capacitive arcs were observed in the Nyquist plot of CS2, the arc at higher (left) frequencies was correlated to the charge transfer resistance and the lower (right) frequencies was correlated to the mass transfer limitation. The capacitive arc in the bright condition was much smaller than the capacitive arcs in the dark condition, which suggested that the photoexcited carriers increase the conductivity of the titania nanostructures. Both measurements in the dark and in the light resulted in identical plots,
where an ohmic resistance is found at high frequencies. The EIS parameters are given in Table 7.1. The treatment of 0.05 M KF and ethylene glycol electrolytes to synthesize CS2, has diminished $R_{ct}$ value. This demonstrates that the CS2 TiO$_2$ nanotube array

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Fig. 7.12 EIS of CS2 electrode under dark and light illumination.
electrode exhibits a greater separation efficiency of photogenerated electron–hole pairs and a faster charge transfer than the CS1 TiO$_2$ nanotube film at the solid–liquid interface.

Fig. 7.13 displays larger radius of the semicircle corresponding to higher TiO$_2$ resistance value of CS3 electrode. The semicircle is distorted at the left side and the cell presents a high impedance. The high impedance exhibited by the cell in the dark can probably be related to the large resistance of the porous TiO$_2$ electrode [17]. However, after light illumination it is found that the semicircle is inclined inwards at lower frequencies and the radius of the arc decreases. The usage of 0.25 wt. % of NH$_4$F in ethylene glycol electrolytes to synthesize CS3, instead of 0.05 M KF and ethylene glycol electrolyte used in CS2, has further lowered the R$_{ct}$ value.

Fig. 7.14 shows the electrochemical impedance spectroscopy data in the dark and upon illumination of CS4. EIS shows two semicircles and the semicircle at high frequency is attributed to the charge transfer resistance at the anode, the TiO$_2$/electrolyte interface [18]. This indicates that a TiO$_2$ nanotube photoanode prepared in HCl + H$_2$O$_2$ in ethylene glycol has a smaller charge-transfer resistance. The use of non-fluoride based electrolytes to synthesize CS4, instead of fluorine based electrolytes used in CS3, has still further lowered R$_{ct}$ value. The semicircle at low frequencies is attributed to the diffusion of electro active species in the solution known as the Warburg impedance (Z$_w$), which indicates that the anionic diffusion prevails over the electron transfer. Since the ionic diffusion and the heterogeneous charge transfer occur as successive mechanisms, the
impedance $Z_W$ is in series with the resistance $R_{ct}$ [19]. Further, the impedance response under illumination is decreased more, which suggests that the photoexcited carriers

Fig. 7.13 EIS of CS3 electrode under dark and light illumination.
Fig. 7.14 EIS of CS4 electrode under dark and light illumination.
increase the conductivity [20]. Moreover, the smaller radius corresponds to the optimal performance of CS4.

The $R_{\text{ct}}$ value with light illumination varied in the sequence CS4 < CS3 < CS2 < CS1, as shown in Table 7.1. This suggested that electron transport resistance of the electrodes under illumination was also in the sequence CS4 < CS3 < CS2 < CS1. The use of non-fluoride based electrolytes to synthesize CS4, instead of fluorine based electrolytes used in CS3 still further lowered $R_{\text{ct}}$ value.

Under the dark condition, the EIS arc radii of LS4, PS4 and CS4 are much bigger than those under illumination because there are few electrons generated. In the presence of light irradiation, impedance radii reduce sharply due to the separation of photogenerated charge carriers, which means the charge transfer resistance at the electrode/electrolyte interface decreases greatly as a result of illumination. Moreover, the lower electrochemical impedance of CS4 nanotubes than those of the other samples is observed both under dark and illumination conditions. The result further indicates that TiO$_2$ nanotubes with longer tube length exhibit lesser recombination of photogenerated electron-hole pairs and faster charge transfer at solid/liquid interface.

7.5 Conclusion

On illumination the charge transfer resistance is reduced considerably due to the photo generated charge carriers. The decrease in the impedance values, due to illumination, suggests a faster charger transfer, or in other words a lower $R_{\text{ct}}$ the
electrode-solution interface. These results show that the nanostructure prepared by non-fluorine electrolyte has higher electrical conductivity and increases the cell’s efficiency.

References


