Review Article

Electrochemical Impedance Spectra of Dye-Sensitized Solar Cells: Fundamentals and Spreadsheet Calculation

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Electrochemical impedance spectroscopy (EIS) is one of the most important tools to elucidate the charge transfer and transport processes in various electrochemical systems including dye-sensitized solar cells (DSSCs). Even though there are many books and reports on EIS, it is often very difficult to explain the EIS spectra of DSSCs. Understanding EIS through calculating EIS spectra on spreadsheet can be a powerful approach as the user, without having any programming knowledge, can go through each step of calculation on a spreadsheet and get instant feedback by visualizing the calculated results or plot on the same spreadsheet. Here, a brief account of the EIS of DSSCs is given with fundamental aspects and their spreadsheet calculation. The review should help one to develop a basic understanding about EIS of DSSCs through interacting with spreadsheet.

1. Introduction

Impedance spectroscopy is a powerful method for characterizing the electrical properties of materials and their interfaces [1–4]. When applied to an electrochemical system, it is often termed as electrochemical impedance spectroscopy (EIS); examples of such systems are electrochemical cells such as fuel cells, rechargeable batteries, corrosion, and dye-sensitized solar cells (DSSCs) [2, 3]. Recently, EIS has become an essential tool for characterizing DSSCs [5–17]. Typically, a dye-sensitized solar cell (DSSC) is composed of a ruthenium dye loaded mesoporous film of nanocrystalline TiO_2 on fluorine-doped tin oxide (FTO) glass substrate as photoelectrode (PE), an iodide/triiodide (I^-/I_3^-) based redox electrolyte solution, and a Pt coated FTO glass substrate as counter electrode (CE) [14, 15, 18–20]. Analysis of EIS spectrum of a DSSC provides information about several important charge transport, transfer, and accumulation processes in the cell. These are (i) charge transport due to electron diffusion through TiO_2 and ionic diffusion in the electrolyte solution; (ii) charge transfer due to electron back reaction at the FTO/electrolyte interface and recombination at the TiO_2 /electrolyte interface and the regeneration of the redox species at CE/electrolyte interfaces; and (iii) charging of the

capacitive elements in the cells including the interfaces, the conduction band, and surface states of the porous network of TiO_2 [2, 7, 15, 21–23]. Even though there are many books and reports on EIS, it is often very difficult to explain the EIS spectra of DSSCs. Moreover, the details of EIS calculation always remain under several layers of programming abstraction and thus cannot be accessed by the user.

Calculating EIS spectra on spreadsheet can be a powerful approach as the user, without having any programming knowledge, can go through each step of calculation on a spreadsheet and get instant feedback by visualizing the calculated results or plot on the same spreadsheet. From our experience of learning EIS of DSSCs from scratch, we found that it was far more easy and fun to learn EIS through spreadsheet calculation than trying to decipher the abstract ideas of EIS on books or papers.

Here, a brief account of the general aspects of EIS is given with mathematical expressions and their calculation on spreadsheet (see the interactive Microsoft Excel 2010 file in the Supplementary Material available online at <http://dx.doi.org/10.1155/2014/851705>). Most importantly, we summarize the fundamental charge transfer processes that take place in working DSSCs and how those processes give rise to EIS spectra.

2. Electrochemical Impedance Spectroscopy

2.1. Fundamentals. Let us begin with the notion of an ideal resistor having resistance R . According to Ohm's law, current (I) flowing through the resistor and voltage (V) across the two terminals of the resistor is expressed by the following relation:

$$V = IR. \quad (1)$$

On the other hand, impedance is a more general concept than resistance because it involves phase difference [4]. During impedance measurement, a small-amplitude modulated voltage $V(\omega, t)$ is applied over a wide range of frequency ($f = \omega/2\pi$) and the corresponding currents $I(\omega, t)$ are recorded, or vice versa. The resultant impedance $Z(\omega)$ of the system is calculated as [1, 2, 4]

$$Z(\omega) = \frac{V(\omega, t)}{I(\omega, t)} \quad (2)$$

provided that $I(\omega, t)$ is small enough to be linear with respect to $V(\omega, t)$, or vice versa. At a certain frequency ω , $V(\omega, t)$ may have different amplitude and phase than that of $I(\omega, t)$ depending on the nature of the charge transfer processes in the system that results in impedance of the corresponding charge transfer process. When the frequency of the applied perturbation is very low, the system is said to be driven with dc current and the impedance of the system coincides with its dc resistance (R_{dc}), that is, impedance with zero phase difference [2, 10]:

$$Z(0) = \frac{V(0)}{I(0)} = R_{dc}. \quad (3)$$

It is to be noted here that there are other response quantities related to impedance such as admittance (Y), modulus function (M), and complex dielectric constant or dielectric permittivity (ϵ) [2, 4].

In complex number, a small-amplitude AC voltage can be described as $V(\omega, t) = V_0 \exp(j\omega t)$ and response to this potential is the AC current $I(\omega, t) = I_0 \exp\{j(\omega t - \theta)\}$, where θ is the phase difference between $V(\omega, t)$ and $I(\omega, t)$ and $j = \sqrt{-1}$. Therefore, (2) can be written as [1, 4]

$$Z(j\omega) = \frac{V_0}{I_0} \exp(j\theta). \quad (4)$$

Again, (4) can be rewritten in terms of magnitude (Z_0) as [1, 4]

$$Z(j\omega) = Z_0 \exp(j\theta). \quad (5)$$

Applying Euler's relationship and replacing Z_0 with $|Z|$, (5) can be expressed as [1, 4]

$$Z(j\omega) = |Z| (\cos \theta + j \sin \theta). \quad (6)$$

In general, impedance is expressed as [1, 4]

$$Z(\omega) = Z_{Re} + jZ_{Im} \quad (7)$$

or more simply as [1, 4]

$$Z = Z' + jZ'', \quad (8)$$

where $Z_{Re} = Z' = |Z| \cos \theta$ and $Z_{Im} = Z'' = |Z| \sin \theta$ are the real and the imaginary parts of the impedance, respectively. The real and imaginary parts of the impedance are related to the phase angle θ as

$$\theta = \tan^{-1} \left(\frac{Z''}{Z'} \right) \quad (9)$$

and the magnitude $|Z|$ as

$$|Z| = \sqrt{Z'^2 + Z''^2}. \quad (10)$$

EIS data can be displayed in different ways. In the complex plane, Z'' is plotted against Z' . The complex plane plots are often termed as Nyquist plots [4]. In Bode plot, both $\log |Z|$ and θ are plotted against $\log f$. Sometimes, it is helpful to plot $\log Z''$ against $\log f$ [1, 2].

In the frequency domain, current-voltage relations can be rearranged as (2). If a purely sinusoidal voltage $V(\omega, t) = V_0 \sin(\omega t)$ is applied across a resistor with resistance R then the current that flows through the resistor will be $I(\omega, t) = V(\omega, t)/R = V_0 \sin(\omega t)/R$, which can be written as $I(\omega, t) = I_0 \sin(\omega t)$. So, the impedance of the resistor, $Z_R(\omega)$, is [1]

$$Z_R(\omega) = \frac{V(\omega, t)}{I(\omega, t)} = R. \quad (11)$$

In this case, the applied voltage and the resultant current are in phase. If the voltage is applied to a capacitor having capacitance C then the resultant current is $I(\omega, t) = C dV(\omega, t)/dt = \omega C V_0 \cos(\omega t)$, where $I = dq/dt$ and $q = CV$. The above expression for the current passing through the capacitor can be written as $I(\omega, t) = \omega C V_0 \cos(\omega t - \pi/2)$ or $I(\omega, t) = I_0 \sin(\omega t)$, where $I_0 = \omega C V_0$. The impedance of the capacitor, $Z_C(\omega)$, is thus [1]

$$Z_C(\omega) = \frac{V(\omega, t)}{I(\omega, t)} = \frac{1}{\omega C}, \quad (12)$$

where $1/\omega C$ or in complex notation $1/j\omega C$ is the reactance of a capacitor and $-\pi/2$ is the phase difference. According to the above description, reactance for any electrical element can be deduced using fundamental relation between current and voltage for that element as summarized in Table 1 [2, 4].

Analysis of EIS data is central to the study of EIS of an electrochemical system. An overview of the system of interest facilitates the translation of the charge transfer, transport, and accumulation processes in the system to an electrical circuit composed of a lump of series and parallel combination of resistors, capacitors, inductors, and so forth. The equivalent model is used to deduce the physically meaningful properties of the system. Any equivalent circuit model can be constructed using Kirchhoff's rules [1, 2]. For example, if two elements are in series then the current passing through them are the same and if two elements are in parallel then the voltages across them are the same.

TABLE 1: Basic electrical elements and their current-voltage relation.

Component	Symbol	Fundamental relation	Impedance, $Z(\omega)$
Resistor	R	$V = IR$	R
Capacitor	C	$I = C \frac{dV}{dt}$	$\frac{1}{j\omega C}$
Constant phase element	Q_n	$I = Q_n \frac{dV}{dt}$	$\frac{1}{(j\omega)^n Q_n}$
Inductor	L	$V = L \frac{dI}{dt}$	$j\omega L$

	A	B	C	D	E	F	G	H	I	J	K
1	power	$f = 10^{\wedge} \text{power (Hz)}$	$\omega = 2\pi f \text{ (radian)}$	$s = j^* \omega$	Cdl (F)	$Z_{Cdl}(\omega) = 1/sCdl$	$Z' \text{ (}\Omega\text{)}$	$Z'' \text{ (}\Omega\text{)}$	$ Z \text{ (}\Omega\text{)}$	$\Theta \text{ (radian)}$	$\Theta \text{ (degrees)}$
2	-2	$=10^{\wedge} A2$	$=2^* \text{PI}()^* B2$	$=\text{COMPLEX}(0, C2)$	0.0001	$=\text{IMDIV}(1, \text{IMPRODUCT}(D2, E2))$	$=\text{IMREAL}(F2)$	$=\text{IMAGINARY}(F2)$	$=\text{IMABS}(F2)$	$=\text{IMARGUMENT}(F2)$	$=\text{DEGREES}(J2)$
3	5	$=10^{\wedge} A3$	$=2^* \text{PI}()^* B3$	$=\text{COMPLEX}(0, C3)$	0.0001	$=\text{IMDIV}(1, \text{IMPRODUCT}(D3, E3))$	$=\text{IMREAL}(F3)$	$=\text{IMAGINARY}(F3)$	$=\text{IMABS}(F3)$	$=\text{IMARGUMENT}(F3)$	$=\text{DEGREES}(J3)$

	A	B	C	D	E	F	G	H	I	J	K
1	power	$f = 10^{\wedge} \text{power (Hz)}$	$\omega = 2\pi f \text{ (radian)}$	$s = j^* \omega$	Cdl (F)	$Z_{Cdl}(\omega) = 1/sCdl$	$Z' \text{ (}\Omega\text{)}$	$Z'' \text{ (}\Omega\text{)}$	$ Z \text{ (}\Omega\text{)}$	$\Theta \text{ (radian)}$	$\Theta \text{ (degrees)}$
2	-2.0	1.00E-02	0.0628319	0.0628318530717959i	0.0001	-159154.943091895i	0.00	-159154.94	159154.94	-1.57	-90
3	5.0	1.00E+05	628318.5307180	628318.530717959i	0.0001	-0.0159154943091895i	0.00	-0.02	0.02	-1.57	-90

FIGURE 1: Screenshots of the spreadsheet calculation of impedance of a capacitor (C_{dl}) with capacitance of 100 μF at frequencies 10 mHz and 100 kHz showing formulas and corresponding results in MS Excel.

In spreadsheet, a complex number can be constructed using built-in function and the number can be operated with all the basic mathematical operators available in the spreadsheet as functions for complex numbers. Figure 1 shows such calculation implemented for impedance of a capacitor (C_{dl}). Thus, spreadsheet enables one to calculate EIS in its user friendly interface. Based on the above concept, all the EIS plots discussed in the present paper are calculated on spreadsheet (see the Microsoft Excel 2010 file in the Supplementary Material) unless otherwise mentioned.

2.2. Equivalent Circuit of Some Electrochemical Systems and Their Impedance

2.2.1. Ideally Polarizable Electrode in Contact with Electrolyte.

An ideally polarizable electrode behaves as an ideal capacitor because there is no charge transfer across the solution/electrode interface [1]. Impedance of such system can be modeled as a series combination of a resistor and a capacitor as shown in the inset of Figure 2(a). If R_s is the solution resistance and C_{dl} is the double layer capacitance then the total impedance of the system becomes

$$Z(\omega) = Z_{R_s}(\omega) + Z_{C_{dl}}(\omega), \quad (13)$$

where $Z_{R_s}(\omega)$ and $Z_{C_{dl}}(\omega)$ are the impedance for R_s and C_{dl} , respectively. Equation (13) can be written in terms of reactance as [1, 24]

$$Z(\omega) = R_s + \frac{1}{j\omega C_{dl}}. \quad (14)$$

Rearranging (14), one gets

$$Z(\omega) = R_s - \frac{j}{\omega C_{dl}}. \quad (15)$$

Here, the real (Z') and the imaginary (Z'') parts of the impedance are R_s and $-1/\omega C_{dl}$, respectively. Figure 2(a) shows complex plane plot of the impedance as a straight line perpendicular to the real or x -axis at R_s , in this case $R_s = 50 \Omega$, while the capacitive impedance contributes to the negative imaginary part of the impedance. At the low frequency limit ($\omega \rightarrow 0$) the capacitive impedance is so large that the total impedance is infinity. Therefore, the dc resistance, $Z(0)$, of the system is infinity and there is no dc current to flow through the system. As the frequency increases the capacitive impedance decreases. At the limit of very high frequency ($\omega \rightarrow \infty$), the capacitor becomes short-circuited and there remains the resistance R_s only. However, complex plane plot does not tell us about the corresponding frequency of the impedance explicitly. In the Bode plot (Figure 2(b)), $\log |Z|$ and θ are plotted against $\log f$. The plot of impedance (red circle) versus frequency has a breakpoint, which corresponds to the characteristic frequency $\omega = 1/R_s C_{dl}$ or characteristic time constant $\tau = 1/\omega = R_s C_{dl} = 0.005$ s of the system. On the other hand, the Bode phase plot (blue square) shows that the phase angle changes from 0° at high frequency to -90° at low frequency.

2.2.2. Nonpolarizable Electrode in Contact with Electrolyte.

If the electrode is nonpolarizable, then the system can be modeled by introducing a resistance R_{ct} parallel to the capacitance C_{dl} as shown in the inset of Figure 2(c), which

FIGURE 2: (a) Complex plane plot for the impedance corresponding to the equivalent circuit as shown in the inset with $R_s = 50 \Omega$ and $C_{dl} = 100 \mu F$ and (b) Bode magnitude and phase plot of the impedance. (c) Complex plane plot for the impedance corresponding to the simplified Randle's circuit with $R_s = 50 \Omega$, $R_{ct} = 100 \Omega$, and $C_{dl} = 100 \mu F$ as shown in the inset; (d) Bode magnitude and phase; and (e) Bode imaginary and phase plot of the impedance.

is known as simplified Randle's circuit [1, 24]. Eventually, the circuit consists of a series connection of a solution resistance R_s with a parallel combination of a charge transfer resistance R_{ct} and a double layer capacitance C_{dl} . The impedance of the system can be written as

$$Z(\omega) = Z_s(\omega) + Z_{pl}(\omega), \quad (16)$$

where $Z_s(\omega) = R_s$ and $Z_{pl}(\omega)$ is the impedance of the parallel combination of the R_{ct} and the C_{dl} .

Thus, (16) can be written in terms of reactance as [1]

$$Z(\omega) = R_s + \frac{R_{ct}}{1 + \omega^2 R_{ct}^2 C_{dl}^2} - j \frac{\omega R_{ct}^2 C_{dl}}{1 + \omega^2 R_{ct}^2 C_{dl}^2}. \quad (17)$$

Here, $R_s + R_{ct}/(1 + \omega^2 R_{ct}^2 C_{dl}^2)$ and $-j \omega R_{ct}^2 C_{dl}/(1 + \omega^2 R_{ct}^2 C_{dl}^2)$ are the real and imaginary parts of the impedance, respectively. Figure 2(c) shows the impedance of the system in complex plane plot. The plot has a semicircle, which is typical for a kinetic control system. When $\omega \rightarrow \infty$, the capacitive

impedance is short-circuited, and this eventually shunts the R_{ct} . Therefore, only the R_s remains at the high frequency intercept. As the frequency decreases the capacitive impedance increases. At the low frequency intercept the capacitive impedance is infinitely large but still there is the R_{ct} . So, the dc resistance $Z(0)$ of this system is $Z(0) = R_s + R_{ct}$. It can be noticed from (17) that the maximum of the Z'' occurs at $Z' = R_s + R_{ct}/2$, which corresponds to the characteristic frequency of the charge transfer process (ω_{max}).

In Figure 2(d), the Bode magnitude plot (red circle) of the system has two breakpoints [1]. From the high frequency edge, the first breakpoint corresponds to the time constant τ_1 :

$$\tau_1 = \frac{1}{\omega_1} = \frac{1}{2\pi f_1} = \frac{R_s R_{ct} C_{dl}}{R_s + R_{ct}}, \quad (18)$$

and the second breakpoint corresponds to the time constant τ_2 :

$$\tau_2 = \frac{1}{\omega_{max}} = \frac{1}{2\pi f_{max}} = R_{ct} C_{dl}. \quad (19)$$

Here, the frequency f_1 in the Bode magnitude plot (red circle, Figure 2(d)) can be calculated from (18) as $f_1 = \omega_1/2\pi = 1/2\pi\tau_1 = 47.75$ Hz. On the other hand, f_{max} is calculated to be 15.92 Hz for $R_{ct} = 100 \Omega$ and $C_{dl} = 100 \mu F$. The Bode phase plot (blue square, Figure 2(d)) has a maximum at around the frequency ω_{max} and 0° phase shift at both the high and low frequency limit. However, the maximum of the phase angle appears at, somewhat, higher frequency than the actual ω_{max} , which appears at the maxima of the Bode imaginary plot (Figure 2(e)) [1].

Figure 3(a) shows EIS spectra in complex plane for different values of R_{ct} . The semicircle progressively increased as the value of R_{ct} increased from 50 to 100Ω while C_{dl} remained the same. The Bode magnitude and phase plots depicted in Figures 3(b) and 3(c) clearly show increase of magnitude and decrease of characteristic frequency (ω_{max}) with the increase of R_{ct} . On the other hand, the complex plane plot (Figure 4(a)) remained unchanged for a fixed value of R_{ct} and different values of C_{dl} . Thus, $Z(0)$ changes as the R_{ct} changes while it remains fixed for all values of C_{dl} . For both cases, the Bode magnitude and phase plots depicted in Figures 4(b) and 4(c) clearly show that ω_{max} shifts towards the low frequency edge for increasing either R_{ct} or C_{dl} . It is to be noted here that phase angle at the maxima decreases with the decrease of R_{ct} while it is the same for different values of C_{dl} .

2.2.3. Inductance. So far we have seen that the imaginary part of the impedances for different combination of resistances and capacitors showed negative values and the spectra appeared in the first quadrant of the complex plane. However, the imaginary parts sometimes take positive values and thus the spectra appear in both first and forth quadrants due to the inductance of the contact wire, which often produces a tail at high frequencies (Figure 5(a)) [2]. On the other hand, impedances of several types of solar cells show similar phenomenon, however at low frequency region, as a loop that forms an arc in the fourth quadrant (Figure 5(b)), which is attributed to specific adsorption and electrocrystallization processes at the electrode [2, 4].

2.2.4. Constant Phase Element. In equivalent circuit model of an electrochemical system, the capacitance C_{dl} is often replaced by a constant phase element (CPE) to account for the deviation of the C_{dl} from an ideal capacitor. The impedance of the CPE is expressed as [2, 4, 25]

$$Z_{Q_n}(\omega) = \frac{1}{(j\omega)^n Q_n}, \quad (20)$$

where Q_n and n are the CPE prefactor and index, respectively. If the index n is equal to 1.0 the CPE coincides with a pure capacitor. Generally, n varies from 1.0 to 0.5 to fit an experimental data. The impedance corresponding to the simplified Randle's circuit with CPE (Figure 6(a)) can be expressed as

$$Z(\omega) = R_s + \frac{R_{ct}}{1 + (j\omega)^n R_{ct} Q_n}. \quad (21)$$

Figure 6(b) shows EIS spectra for the impedance corresponding to the equivalent circuit (Figure 6(a)) in complex plane for different values of CPE index n . As the value of n decreases from 1.0 to 0.5 the semicircle deviates to a depressed semicircle. In this case, the characteristic frequency ω_{max} is expressed as [2]

$$\omega_{max} = \frac{1}{(R_{ct} Q_n)^{1/n}}. \quad (22)$$

From (22), we can see that the CPE response decelerates with the decrease of n , which is evident at the second breakpoint from high frequency end of Figure 6(c). Moreover, the phase angle at the maxima decreases as well (Figure 6(d)). The equivalent capacitance (C_{dl}) of the electrochemical interface corresponding to the parallel combination of R_{ct} and Q_n of Figure 6(a) can be calculated by comparing (22) with (19) as

$$C_{dl} = Q_n^{1/n} R_{ct}^{1/n-1}. \quad (23)$$

2.2.5. Semi-Infinite Diffusion. There is another important impedance element that accounts for the impedance of redox species diffuse to and from the electrode surface. The impedance is known as semi-infinite Warburg impedance and is expressed as [1]

$$Z_W(\omega) = \sqrt{\frac{2}{j\omega}} \sigma. \quad (24)$$

Since $1/\sqrt{j} = (1-j)/\sqrt{2}$, (24) can be written as

$$Z_W(\omega) = \frac{\sigma}{\sqrt{\omega}} (1-j). \quad (25)$$

The coefficient σ is defined as [1, 24]

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right), \quad (26)$$

where C_O^* and C_R^* are the bulk concentration of oxidant and reductant, respectively; D_O and D_R are the diffusion coefficients of the oxidant and reductant, respectively; A is the

FIGURE 3: (a) Complex plane plot for the impedance corresponding to the simplified Randle's circuit with $R_s = 50 \Omega$, $C_{dl} = 100 \mu F$, and different values of R_{ct} as mentioned. (b) Bode magnitude and (c) phase plot for the impedance.

surface area of the electrode; and n is the number of electrons involved. The semi-infinite diffusion impedance cannot be modeled by simply connecting resistor and capacitor because of square root of frequency ($\sqrt{\omega}$) [1, 24]. A semi-infinite transmission line (TL) composed of resistors and capacitors (Figure 7(a)) describes the impedance as a distributed element. This impedance appears as a diagonal line with a slope of 45° in complex plane plot (Figure 7(b)). In the Bode plot (Figure 7(c)), the magnitude of the impedance (red

circle) increases linearly from a very low value at high frequency limit to a high value at low frequency limit and the phase angle (blue square) always remains at 45° , which is the characteristic of a diffusion process. This kind of diffusion phenomenon is seen where diffusion layer has infinite thickness.

2.2.6. Randle's Circuit. If the kinetic control process as discussed in Section 2.2.2 is coupled with mass transfer process

FIGURE 4: (a) Complex plane plot for the impedance corresponding to the simplified Randle's circuit with $R_s = 50 \Omega$, $R_{ct} = 100 \Omega$ and different values of C_{dl} as mentioned. (b) Bode magnitude and (c) phase plot for the impedance.

then the simplified Randle's circuit can be modified by introducing Warburg impedance (W) as shown in the inset of Figure 7(d) to model the mixed control process [1, 24]. The model of this mixed control system is known as Randle's circuit. The complex plane plot (Figure 7(d)) shows that the impedance of faradic process appears as a semicircle at high frequency edge and the diffusion process appears as a diagonal line with a slope of 45° at the low frequency edge. The Bode magnitude plot (red circles, Figure 7(e)) of the same system has three breakpoints, in the order of decreasing frequency; the first two breakpoints are similar to that of the case

for kinetic control process, which is modeled as simplified Randle's circuit, and the last one corresponds to the diffusion process. The Bode phase plot (blue squares, Figure 7(e)) is similar to the Bode phase plot for simplified Randle's circuit except at the low frequency region where phase angle gradually increases and at the limit of low frequency it reaches 45° due to diffusion process. If the time constant ($\tau_F = 1/\omega_{\max} = R_{ct}C_{dl}$) of the faradic or charge transfer kinetics is too fast compared to the time constant ($\tau_d = R_{ct}^2/2\sigma^2$) of diffusion process then the system is said to be under diffusion control. On the other hand, the system will be under kinetic control

FIGURE 5: Complex plane plots for the impedances that show inductive effects at (a) the high frequency and (b) the low frequency regions. Inset shows the corresponding equivalent circuits with $R_s = 10 \Omega$, $R_{ct} = 100 \Omega$, $R_1 = 160 \Omega$, $C_{dl} = 100 \mu F$, and $L_1 = 10 \mu H$ for (a) and $100 H$ for (b).

if the time constant associated with the kinetics is relatively slower than that of diffusion [1, 24].

2.2.7. Diffusion in a Thin Film. Diffusion occurs in a thin film also, for example, triiodide diffusion in the electrolyte solution of DSSCs. Moreover, diffusion can be coupled with reaction such as the electron diffusion-recombination at the PE of DSSCs. Impedance of such diffusion is known as finite-length diffusion impedance. The impedance of the diffusion and recombination or diffusion and coupled reaction can be modeled as a finite-length transmission line (FTL) composed of distributed elements r_m , r_k , and c_m as shown in Figures 8(a) and 8(b), where r_k is given by [26]

$$r_k = R_k L = \frac{1}{\omega_k c_m}. \quad (27)$$

In thin film diffusion, the diffusion layer is bounded and the impedance at lower frequencies no longer obeys the equation for semi-infinite Warburg diffusion [1, 2, 4]. Professor Bisquert has modeled various aspects of diffusion of particles with diffusion coefficient D in a thin film of thickness L , where the characteristic frequency ω_d is [26]

$$\omega_d = \frac{D}{L^2}. \quad (28)$$

In a reflecting boundary condition, electrons, being injected at the interface between a conducting substrate and a porous semiconductor film, diffuse through the film to the outer edge of the film where electron transport is blocked. This diffusion phenomenon can be modeled as a FTL with short-circuit at the terminus similar to that in Figure 8(a), however, without

r_k as the diffusion is not coupled with reaction. On the other hand, in an absorbing boundary condition, electrons are injected at p - n junction and are collected at the outer edge of the neutral p region of a semiconductor. The diffusion process can be modeled as a FTL with open-circuit at the terminus similar to that in Figure 8(b), of course, without r_k .

The diffusion impedance ($Z_{d,o}$) for a reflecting boundary condition is expressed as [26]

$$Z_{d,o}(\omega) = R_d \sqrt{\frac{\omega_d}{j\omega}} \coth \sqrt{\frac{j\omega}{\omega_d}}, \quad (29)$$

where $R_d (= r_m L)$ and $\omega_d (= 1/c_m r_m)$ are the diffusion resistance and characteristic frequency of diffusion, respectively. Complex plane plot of this impedance shows a straight line with 45° at high frequency and then vertically goes up at the low frequency (Figure 8(c)). The high and the low frequency regions clearly show two distinct features separated by the characteristic frequency ω_d . When $\omega \gg \omega_d$, the system behaves as a semi-infinite and (29) coincides with (24) as [26]

$$Z_{d,o}(\omega) = R_d \sqrt{\frac{\omega_d}{j\omega}}. \quad (30)$$

At the low frequency region, the impedance becomes [26]

$$Z_{d,o}(\omega) = \frac{R_d}{3} + \frac{R_d \omega_d}{j\omega}. \quad (31)$$

FIGURE 6: (a) Equivalent circuit with Q_n as CPE. (b) Complex plane, (c) Bode magnitude, and (d) phase plot for the impedance corresponding to the equivalent circuit with $R_s = 50 \Omega$, $R_{ct} = 100 \Omega$, and $Q_n = 100 \mu F \cdot s^{n-1}$ and different values of CPE index n as mentioned.

For absorbing boundary condition, the diffusion impedance ($Z_{d,c}$) can be expressed as [26]

$$Z_{d,c}(\omega) = R_d \sqrt{\frac{\omega_d}{j\omega}} \tanh \sqrt{\frac{j\omega}{\omega_d}}. \quad (32)$$

The impedance in complex plane plot appears as an arc at the low frequency region and a straight line with 45° showing semi-infinite behavior at high frequency region that follows (30) as shown in Figure 8(d).

The impedance of the diffusion and recombination for the reflective boundary condition ($Z_{dr,o}$) is expressed as [26]

$$Z_{dr,o}(\omega) = \sqrt{\frac{(R_d R_k)}{(1 + j\omega/\omega_k)}} \coth \sqrt{\left(\frac{\omega_k}{\omega_d}\right) \left(1 + \frac{j\omega}{\omega_k}\right)} \quad (33)$$

and the impedance for the absorbing boundary condition ($Z_{dr,c}$) is expressed as [26]

$$Z_{dr,c}(\omega) = \sqrt{\frac{(R_d R_k)}{(1 + j\omega/\omega_k)}} \tanh \sqrt{\left(\frac{\omega_k}{\omega_d}\right) \left(1 + \frac{j\omega}{\omega_k}\right)}, \quad (34)$$

where R_d and ω_d are the diffusion resistance and characteristic frequency for diffusion, respectively, as in (29) and (32). The additional terms R_k and ω_k are the resistance corresponding to homogeneous reactions and the characteristic frequency of the reaction, respectively. Equations (33) and (34) have three independent parameters, for example, R_d , ω_d , and ω_k . The relation among the physicochemical parameters is expressed as [26]

$$\frac{R_k}{R_d} = \frac{\omega_d}{\omega_k} = \left(\frac{L_n}{L}\right)^2, \quad (35)$$

FIGURE 7: (a) Semi-infinite transmission line depicting diffusion process. (b) Complex plane and (c) Bode plot for the Warburg diffusion where the coefficient $\sigma = 150 \Omega s^{-0.5}$. (d) Complex plane and (e) Bode plot for the impedance corresponding to Randle's circuit with $R_s = 50 \Omega$, $R_{ct} = 100 \Omega$, and $C_{dl} = 100 \mu F$ and the Warburg coefficient $\sigma = 150 \Omega s^{-0.5}$. Inset (d) shows Randle's circuit and magnitude and phase plot for Randle's circuit.

where L and L_n are the film thickness and the diffusion length, respectively. Comparing (28) and (35), one can write

$$L_n = \sqrt{\frac{D}{\omega_k}}. \quad (36)$$

Figure 8(e) shows EIS spectra for impedance of diffusion-reaction with reflective boundary condition in complex plane plot for different ratio of R_k/R_d . When R_k is very large (red circles, Figure 8(e)), (33) reduces to (30) of simple diffusion. In this case, the reaction resistor r_k in the transmission

FIGURE 8: Finite-length transmission line models of diffusion-reaction impedance with (a) reflective and (b) absorbing boundary condition. Complex plane plots of the impedance model for diffusion with the (c) reflective boundary condition and (d) the absorbing boundary condition. Complex plane plot of the impedance model for diffusion coupled with a homogeneous reaction with the (e) reflective boundary condition (inset shows magnified view of the high frequency region of the plot) and (f) the absorbing boundary condition.

line model (Figure 8(a)) is open circuit. For a finite R_k , the impedance takes two different shapes depending on the quotient of (35). If $R_k > R_d$ (blue squares, Figure 8(e)), the impedance at high frequency region ($\omega \gg \omega_d$) follows (30) and at the low frequency region ($\omega \ll \omega_d$) the expression is

$$Z_{dr,o}(\omega) = \frac{1}{3}R_d + \frac{R_k}{(1 + j\omega/\omega_k)}. \quad (37)$$

Thus, the complex plane plot of the impedance has a small Warburg part at high frequency and a large arc at low frequency. In this case, the dc resistance is expressed as

$$R_{dc} = Z(0) = \frac{1}{3}R_d + R_k. \quad (38)$$

When $R_k < R_d$ (green triangles, in the inset of Figure 8(e)), (33) gives the expression

$$Z_{dr,o}(\omega) = \sqrt{\frac{(R_d R_k)}{(1 + j\omega/\omega_k)}}, \quad (39)$$

where the reaction time is shorter than the time for diffusion across the layer ($\omega_k \gg \omega_d$). This is the case when diffusing species are lost before they reach the outer edge of the film. The model corresponding to (39) is called Gerischer's impedance and the dc resistance has the form

$$R_{dc} = Z(0) = \sqrt{R_d R_k}. \quad (40)$$

Figure 8(f) shows the complex plane plot of the impedance for diffusion-reaction with the absorbing boundary condition for different cases of R_k/R_d . For a very large value of R_k (red circles, Figure 8(f)), (34) turns into (32) of simple diffusion as in Figure 8(d). The dc resistance of the impedance equals R_d . If $R_k > R_d$ (blue squares, Figure 8(f)), (34) approximates to (32); however, the dc resistance is slightly less than that of the case for very large value of R_k due to additional contribution of r_k 's as in Figure 8(d). When $R_k < R_d$ (green triangles, Figure 8(f)), (34) reduces to Gerischer's impedance of (39) and the dc resistance of the impedance is given by (40).

3. EIS Spectra of DSSCs

The charge transfer kinetics, involved in working DSSCs based on liquid electrolyte containing I_3^-/I^- redox couple, are shown in Figure 9(a) with plausible time constants [19, 27, 28]. Within the frequency range of EIS measurement, several time constants are well dispersed in the frequency domain and they give rise to three distinct semicircles in complex plane plot (Figure 9(b)) or three distinct peaks in Bode plot (Figure 9(c)) of EIS of a DSSC at a certain steady-state, at around open-circuit voltage (V_{oc}) under illumination or at high potential under dark, attained by applying a voltage and illumination. These semicircles in the EIS spectra have been assigned to corresponding charge transfer processes by means of theoretical and experimental approach [5, 6, 12, 13, 29]. Among the three semicircles of the complex plane plot (Figure 9(b)), in the order of decreasing frequency, the first

semicircle corresponds to the charge transfer processes at the Pt/electrolyte and uncovered FTO/electrolyte interfaces with a characteristic frequency ω_{CE} , the second or middle semicircle corresponds to the electron diffusion in the TiO_2 film and electron back reaction with oxidized redox species at the TiO_2 /electrolyte interface, and the third semicircle at the low frequency region corresponds to the diffusion of I_3^- in the electrolyte solution with a characteristic frequency ω_D . The characteristic frequency for electron transport or diffusion (ω_d) appears at the high frequency region of the middle semicircle while the peak frequency (ω_k) of that semicircle corresponds to the electron back reaction. Similarly, the Bode plots (Figure 9(c)) show all characteristic frequencies except ω_d , which may appear as a break point at the high frequency limit of second semicircle in complex plane plot at certain steady-states but not in Bode plot. The above description is consistent with the time constants shown in Figure 9(a).

Several research groups have already demonstrated systematic approach to characterize EIS of DSSCs [7, 12, 13, 30]. Determination of physical parameters from EIS spectra of DSSCs is often done by fitting the spectra to an equivalent circuit. The most widely used equivalent circuit of the complete DSSCs is a transmission line model as shown in Figure 10(a), where r_{ct} is the charge transfer resistance of the charge recombination process at the TiO_2/I_3^- in electrolyte; c_μ is the chemical capacitance of the TiO_2 film; r_t is the transport resistance of electrons in TiO_2 film; Z_d is the Warburg element showing the Nernst diffusion of I_3^- in electrolyte; R_{Pt} and C_{Pt} are the charge transfer resistance and double-layer capacitance at the Pt CE; R_{TCO} and C_{TCO} are the charge transfer resistance and the corresponding double-layer capacitance at exposed transparent conducting oxide (TCO)/electrolyte interface; R_{CO} and C_{CO} are the resistance and the capacitance at TCO/ TiO_2 contact; R_s is the series resistance; and L is the thickness of the mesoscopic TiO_2 film [7]. At high illumination the equivalent circuit may be simplified to Figure 10(b). In addition to selecting an appropriate equivalent circuit, one must be able to estimate the parameters to a good approximation from the EIS spectra to initiate the fitting on a program that usually comes with every EIS workstation. Adachi et al. showed how to determine the parameters relating to charge (electrons and I_3^-) transport in a DSSC from EIS spectra [6]. The EIS spectra of DSSCs do not necessarily show three distinct arcs in the complex plane plot or three peaks in Bode plot; however, proper inspection of the experimental data may help to extract the important parameters efficiently. Even though the charge transfer processes in a working DSSCs are more complicated than the above description, we will mainly discuss most significant processes and how the impedance of those individual processes shapes the EIS spectra of complete DSSCs.

3.1. Ohmic Series Resistance. The sheet resistance of electrode substrate and the resistance of electrolyte solution are the main contributor to the Ohmic series resistance (R_{OS}) in DSSCs. The impedance (Z_{OS}) for the R_{OS} is

$$Z_{OS} = R_{OS}. \quad (41)$$

FIGURE 9: (a) Charge transfer kinetics involved in dye-sensitized solar cells where dark arrow shows loss mechanism: (1) injection of electrons, (2) diffusion of electrons in the TiO_2 , (3) regeneration of dye, (4) regeneration of redox mediator (I_3^-/I^-), (5) diffusion of I_3^- , (6) diffusion of I^- , (7) back reaction of TiO_2 conduction band electrons with I_3^- , (8) recombination of electrons with oxidized dye, and (9) back reaction of electrons from FTO to I_3^- . (b) Typical impedance spectra of a DSSC presented in complex plane and (c) Bode imaginary (blue solid line) and phase (green solid line) plot. In the order of decreasing frequency, the characteristic frequencies ω_{CE} , ω_d , ω_k , and ω_D correspond to the charge transfer processes at the Pt/electrolyte interface, electron diffusion in the TiO_2 film, electron back reaction with oxidized redox species in the electrolyte, and diffusion of redox species in the electrolyte solution, respectively.

FIGURE 10: (a) General transmission line model and (b) simplified model at high illumination intensities of DSSCs. Reprinted (adapted) with permission from [7]. Copyright (2014) American Chemical Society.

3.2. Charge Transfer at the CE. The charge transfer resistance (R_{Pt}) at the Pt CE is associated with the redox reaction involving I^- and I_3^- . The exchange current density (i_0) of the reaction is related to R_{Pt} by Buttlar-Volmer equation as [13]

$$R_{Pt} = \frac{RT}{nFi_0}, \quad (42)$$

where R is the ideal gas constant, F is the Faraday constant, T is the temperature, and n is the number of electrons involved in the reaction. The charge transfer process at the CE can be modeled as a R - C parallel circuit and the corresponding impedance (Z_{Pt}) can be expressed in terms of CPE as

$$Z_{Pt} = \frac{R_{Pt}}{1 + (j\omega)^{n_{CE}} R_{Pt} Q_{Pt}}. \quad (43)$$

So, the characteristic frequency of the charge transfer process (ω_{CE}) can be calculated as

$$\omega_{CE} = \frac{1}{(R_{Pt} Q_{Pt})^{1/n_{Pt}}} \quad (44)$$

and the equivalent capacitance of Q_{Pt} (C_{Pt}) can be calculated as

$$C_{Pt} = Q_{Pt}^{1/n_{Pt}} R_{Pt}^{1/n_{Pt}-1}. \quad (45)$$

3.3. Electron Diffusion and Recombination at the PE. In DSSCs, electron transport through diffusion in the TiO_2 is coupled with electron back reaction, generally termed as recombination, at the TiO_2 /electrolyte interface. The impedance of diffusion and recombination of electrons at the PE of DSSCs has been extensively studied by several

research groups [5, 12, 26, 31]. Impedance of this diffusion-recombination process (Z_{PE}) appears in the middle semi-circle of EIS spectra of DSSCs (Figure 9(b)) with characteristic frequencies ω_d and ω_k . The PE permeated with liquid electrolyte clearly resembles the electrochemical system with reflecting boundary as shown in Figure 8(a). Thus, the impedance of diffusion and recombination of electrons at the PE of DSSCs can be expressed by (33). In practice, the distributed capacitance c_m is replaced with distributed CPE to account for the nonideality in the diffusion-recombination processes. In this case, the characteristic frequency ω_k can be expressed in terms of CPE as [32, 33]

$$\omega_k = \frac{1}{(R_k Q_k)^{1/n_k}}. \quad (46)$$

Similarly, the characteristic frequency ω_d can be written as [32, 33]

$$\omega_d = \frac{1}{(R_d Q_k)^{1/n_k}} \quad (47)$$

and the impedance can be expressed as [32, 33]

$$Z_{PE} = \sqrt{\frac{(R_d R_k)}{1 + (j\omega/\omega_k)^{n_k}}} \coth \sqrt{\left(\frac{\omega_k}{\omega_d}\right) \left\{1 + \left(\frac{j\omega}{\omega_k}\right)^{n_k}\right\}}, \quad (48)$$

where R_d is the electron transport or diffusion resistance, R_k is the electron recombination resistance, and Q_k and n_k are the CPE prefactor and index, respectively. The chemical capacitance (C_μ) of the TiO_2 film permeated with electrolyte can be calculated from CPE as

$$C_\mu = Q_k^{1/n_k} R_k^{1/n_k-1}. \quad (49)$$

FIGURE 11: Complex plane plot for the impedance of a DSSC showing calculated impedance of individual components and complete DSSC using parameters as summarized in Table 2. The blue circle shows the EIS spectra simulated on Zview software using the same parameters and according to the equivalent circuit as shown in the inset, where DX is the extended element 11: Bisquert number 2 that corresponds to the impedance of the diffusion-recombination process at the PE of DSSCs (Z_{PE}).

According to (35) and (46), (48) can be rearranged as

$$Z_{PE} = \sqrt{\frac{(R_d R_k)}{1 + (j\omega)^{n_k} R_k Q_k}} \times \coth \sqrt{\left(\frac{R_d}{R_k}\right) \{1 + (j\omega)^{n_k} R_k Q_k\}}. \quad (50)$$

3.4. Diffusion of I_3^- in the Electrolyte Solution. In the electrolyte solution, concentration of I^- is much higher than that of I_3^- . As a result, only I_3^- contributes to the diffusion impedance that appears at the low frequency region [6, 12, 13]. The impedance of I_3^- diffusion can be modelled as FTL with short-circuit terminus and without r_k (Figure 8(b)) and the corresponding finite-length Warburg impedance (Z_{D1}) can be expressed as

$$Z_{D1} = R_{D1} \sqrt{\frac{D_1/\delta^2}{j\omega}} \tanh \sqrt{\frac{j\omega}{D_1/\delta^2}}, \quad (51)$$

where R_{D1} is the diffusion resistance, D_1 is the diffusion coefficient of I_3^- , and δ is the diffusion length, which is considered as half of the thickness of the electrolyte film [12]. Equation (51) is the same as (32), which expresses the impedance of finite-length diffusion with absorbing boundary condition provided that $\omega_D = D_1/\delta^2$ where ω_D is the characteristic frequency of the diffusion. The frequency maxima (ω_{max}) are related to ω_D as $\omega_{max} = 2.5\omega_D$.

3.5. Constructing EIS Spectra of Complete DSSCs. According to Figures 9(a) and 10(a), a simple electrical equivalent circuit

of DSSCs can be constructed by combining the elements that are involved in the impedances Z_{OS} , Z_{PE} , Z_{D1} , and Z_{Pt} [7, 13]. Thus, the impedance of complete DSSCs (Z_{DSSC}) can be calculated by summing up (41), (43), (50), and (51) as

$$Z_{DSSC} = Z_{OS} + Z_{PE} + Z_{D1} + Z_{Pt}. \quad (52)$$

Figure 11 shows complex plane plot for the impedance of a DSSC showing individual components calculated through (52) using the parameters obtained from an EIS spectrum of a DSSC with N719 loaded TiO_2 as a PE, I^-/I_3^- based liquid electrolyte, and a platinized CE measured at open-circuit voltage under 1 sun condition (Table 2). To compare the EIS spectrum calculated on spreadsheet (green solid line, Figure 11) with that obtained by commercially available software, EIS spectrum of DSSC (blue circle, Figure 11) was also calculated on Zview software (Zview version 3.1, Scribner Associates Inc., USA) according to the equivalent circuit shown in the inset. It is found that both spreadsheet calculation and Zview simulation generate exactly the same EIS spectrum of DSSC.

4. Conclusions

Spreadsheet calculation can successfully simulate EIS spectra of DSSCs. Calculation of EIS on spreadsheet allows one to get overall idea of how EIS spectra of DSSCs evolve from impedance response of individual components of DSSCs and how the properties of the EIS spectra are related to each other. Any kind of EIS spectra can be calculated on spreadsheet using the built-in function available in the spreadsheet provided that the corresponding impedance expression is known. This review should help one to learn EIS of DSSCs

TABLE 2: Parameters used to calculate EIS spectra of DSSC.

Description	Parameters	Value	Unit
Ohmic series resistance	R_{OS}	10.0	Ω
Charge transfer resistance at the Pt CE	R_{Pt}	3.5	Ω
CPE for capacitance at the Pt CE/electrolyte interface	Q_{Pt}	2.6×10^{-5}	$F \cdot s^{n-1}$
CPE index for capacitance at the CE/electrolyte interface	n_{Pt}	0.90	N/A
Electron diffusion resistance through TiO_2	R_d	0.8	Ω
Electron recombination resistance at the TiO_2 /electrolyte interface	R_k	9.0	Ω
CPE prefactor corresponding to the chemical capacitance (C_μ) of TiO_2 film	Q_k	1.0×10^{-3}	$F \cdot s^{n-1}$
CPE index corresponding to the chemical capacitance (C_μ) of TiO_2 film	n_k	0.95	N/A
Ionic diffusion resistance in the electrolyte	R_{DI}	5.0	Ω
Characteristic frequency of ionic diffusion	ω_{DI}	2.0	rad/s

as well as to develop a basic understanding of EIS in general from scratch.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] B. A. Lasia, "Electrochemical impedance spectroscopy and its applications," in *Modern Aspects of Electrochemistry*, B. E. Conway, J. O. M. Bockris, and R. White, Eds., pp. 143–248, Springer, New York, NY, USA, 2002.
- [2] J. Bisquert and F. Fabregat-Santiago, "Impedance spectroscopy: a general introduction and application to dye-sensitized solar cells," in *Dye-Sensitized Solar Cells*, K. Kalyanasundaram, Ed., p. 457, CRC; Taylor & Francis, Boca Raton, Fla, USA, 2010.
- [3] J. R. Macdonald, "Impedance spectroscopy," *Annals of Biomedical Engineering*, vol. 20, no. 3, pp. 289–305, 1992.
- [4] J. R. Macdonald and W. B. Johnson, *Impedance Spectroscopy*, John Wiley & Sons, New York, NY, USA, 2005.
- [5] F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, and A. Hagfeldt, "Influence of electrolyte in transport and recombination in dye-sensitized solar cells studied by impedance spectroscopy," *Solar Energy Materials and Solar Cells*, vol. 87, no. 1–4, pp. 117–131, 2005.
- [6] M. Adachi, M. Sakamoto, J. Jiu, Y. Ogata, and S. Isoda, "Determination of parameters of electron transport in dye-sensitized solar cells using electrochemical impedance spectroscopy," *The Journal of Physical Chemistry B*, vol. 110, no. 28, pp. 13872–13880, 2006.
- [7] F. Fabregat-Santiago, J. Bisquert, E. Palomares et al., "Correlation between photovoltaic performance and impedance spectroscopy of dye-sensitized solar cells based on ionic liquids," *The Journal of Physical Chemistry C*, vol. 111, no. 17, pp. 6550–6560, 2007.
- [8] J. Bisquert, F. Fabregat-Santiago, I. Mora-Sero, G. Garcia-Belmonte, and S. Giménez, "Electron lifetime in dye-sensitized solar cells: theory and interpretation of measurements," *The Journal of Physical Chemistry C*, vol. 113, no. 40, pp. 17278–17290, 2009.
- [9] E. M. Barea, J. Ortiz, F. J. Payá et al., "Energetic factors governing injection, regeneration and recombination in dye solar cells with phthalocyanine sensitizers," *Energy & Environmental Science*, vol. 3, no. 12, pp. 1985–1994, 2010.
- [10] J. Halme, P. Vahermaa, K. Miettunen, and P. Lund, "Device physics of dye solar cells," *Advanced Materials*, vol. 22, no. 35, pp. E210–E234, 2010.
- [11] S. R. Raga, E. M. Barea, and F. Fabregat-Santiago, "Analysis of the origin of open circuit voltage in dye solar cells," *Journal of Physical Chemistry Letters*, vol. 3, no. 12, pp. 1629–1634, 2012.
- [12] R. Kern, R. Sastrawan, J. Ferber, R. Stangl, and J. Luther, "Modeling and interpretation of electrical impedance spectra of dye solar cells operated under open-circuit conditions," *Electrochimica Acta*, vol. 47, no. 26, pp. 4213–4225, 2002.
- [13] Q. Wang, J.-E. Moser, and M. Grätzel, "Electrochemical impedance spectroscopic analysis of dye-sensitized solar cells," *Journal of Physical Chemistry B*, vol. 109, no. 31, pp. 14945–14953, 2005.
- [14] S. Sarker, H. W. Seo, and D. M. Kim, "Electrochemical impedance spectroscopy of dye-sensitized solar cells with thermally degraded N719 loaded TiO_2 ," *Chemical Physics Letters*, vol. 585, pp. 193–197, 2013.
- [15] S. Sarker, H. W. Seo, and D. M. Kim, "Calculating current density-voltage curves of dye-sensitized solar cells: a straightforward approach," *Journal of Power Sources*, vol. 248, pp. 739–744, 2014.
- [16] S. R. Raga and F. Fabregat-Santiago, "Temperature effects in dye-sensitized solar cells," *Physical Chemistry Chemical Physics*, vol. 15, no. 7, pp. 2328–2336, 2013.
- [17] J. Bisquert, L. Bertoluzzi, I. Mora-Sero, and G. Garcia-Belmonte, "Theory of impedance and capacitance spectroscopy of solar cells with dielectric relaxation, drift-diffusion transport, and recombination," *The Journal of Physical Chemistry C*, vol. 118, no. 33, pp. 18983–18991, 2014.

- [18] B. O'Regan and M. Graetzel, "Low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films," *Nature*, vol. 353, no. 6346, p. 737, 1991.
- [19] M. Grätzel, "Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 164, no. 1–3, pp. 3–14, 2004.
- [20] M. K. Nazeeruddin, F. de Angelis, S. Fantacci et al., "Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers," *Journal of the American Chemical Society*, vol. 127, no. 48, pp. 16835–16847, 2005.
- [21] E. M. Barea, C. Zafer, B. Gultekin et al., "Quantification of the effects of recombination and injection in the performance of dye-sensitized solar cells based on *N*-substituted carbazole dyes," *Journal of Physical Chemistry C*, vol. 114, no. 46, pp. 19840–19848, 2010.
- [22] F. Fabregat-Santiago, H. Randriamahazaka, A. Zaban, J. Garcia-Cañadas, G. Garcia-Belmonte, and J. Bisquert, "Chemical capacitance of nanoporous-nanocrystalline TiO_2 in a room temperature ionic liquid," *Physical Chemistry Chemical Physics*, vol. 8, no. 15, pp. 1827–1833, 2006.
- [23] F. Fabregat-Santiago, G. Garcia-Belmonte, J. Bisquert, A. Zaban, and P. Salvador, "Decoupling of transport, charge storage, and interfacial charge transfer in the nanocrystalline TiO_2 /electrolyte system by impedance methods," *The Journal of Physical Chemistry B*, vol. 106, no. 2, pp. 334–339, 2002.
- [24] L. R. F. Allen and J. Bard, *Electrochemical Methods: Fundamentals and Applications*, Wiley, 2nd edition, 2000.
- [25] J. Halme, "Linking optical and electrical small amplitude perturbation techniques for dynamic performance characterization of dye solar cells," *Physical Chemistry Chemical Physics*, vol. 13, no. 27, pp. 12435–12446, 2011.
- [26] J. Bisquert, "Theory of the impedance of electron diffusion and recombination in a thin layer," *Journal of Physical Chemistry B*, vol. 106, no. 2, pp. 325–333, 2002.
- [27] K. Hara and H. Arakawa, *Handbook of Photovoltaic Science and Engineering*, John Wiley & Sons, New York, NY, USA, 2005.
- [28] A. B. F. Martinson, T. W. Hamann, M. J. Pellin, and J. T. Hupp, "New architectures for dye-sensitized solar cells," *Chemistry: A European Journal*, vol. 14, no. 15, pp. 4458–4467, 2008.
- [29] A. Hauch and A. Georg, "Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells," *Electrochimica Acta*, vol. 46, no. 22, pp. 3457–3466, 2001.
- [30] L. Han, N. Koide, Y. Chiba, A. Islam, and T. Mitate, "Modeling of an equivalent circuit for dye-sensitized solar cells: improvement of efficiency of dye-sensitized solar cells by reducing internal resistance," *Comptes Rendus Chimie*, vol. 9, no. 5–6, pp. 645–651, 2006.
- [31] J. Bisquert, "Theory of the impedance of electron diffusion and recombination in a thin layer," *The Journal of Physical Chemistry B*, vol. 106, no. 2, pp. 325–333, 2002.
- [32] J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, and A. Compte, "Anomalous transport effects in the impedance of porous film electrodes," *Electrochemistry Communications*, vol. 1, no. 9, pp. 429–435, 1999.
- [33] J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, N. S. Ferriols, P. Bogdanoff, and E. C. Pereira, "Doubling exponent models for the analysis of porous film electrodes by impedance. Relaxation of TiO_2 nanoporous in aqueous solution," *Journal of Physical Chemistry B*, vol. 104, no. 10, pp. 2287–2298, 2000.