

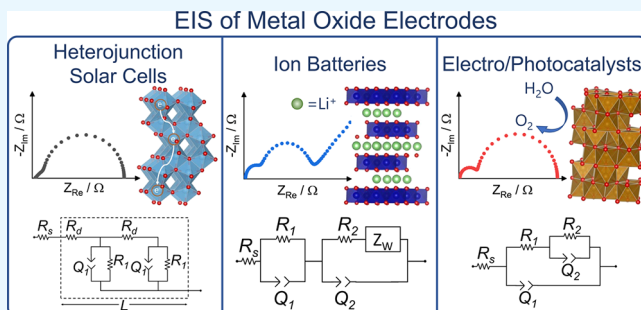
Electrochemical Impedance Spectroscopy of Metal Oxide Electrodes for Energy Applications

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ABSTRACT: Metal oxides have been of great importance to the development of energy conversion and storage technologies including heterojunction solar cells, Li-ion batteries, and electrocatalysts/photocatalysts for water splitting and CO₂ reduction. The role of metal oxides in these devices has been diverse, from charge transport layers to catalytic surfaces to protective blocking layers. Understanding the fundamental structural and electronic properties of these materials will continue to allow for advancement in the field of renewable energy. Electrochemical impedance spectroscopy (EIS) is one of the most utilized methods to characterize these electrodes in the context of energy applications. The utility of EIS stems from its ability to differentiate multiple interfaces (i.e., solid/electrolyte, solid/solid) within devices on the basis of their frequency response to a modulated potential and the subsequent decoupling of resistive and capacitive circuit components. In this review, the fundamental theory of EIS is first described with a physical and mathematical basis, followed by a discussion of equivalent circuit modeling. The review then covers examples from the literature where EIS has been particularly important in the understanding of electronic properties related to metal oxide electrodes within energy conversion and storage devices. A specific focus is placed on metal oxides that are used as heterojunction solar cells, ion batteries, and photocatalysts/electrocatalysts. Common themes are discussed within each application such as the study of electron and hole diffusion in solar cells, the dependence of recombination reactions and catalysis on surface defect/trap states for solar cells and photocatalysts, and the formation of passivation layers at the solid electrolyte interface in Li-ion batteries.

KEYWORDS: impedance, metal oxide, solar energy conversion, energy storage, photoelectrocatalysis



1. INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is a versatile technique for the study of electrode materials relevant to energy applications such as heterojunction solar cells, Li-ion batteries, and electro/photocatalysis.^{1–6} Metal oxide electrodes have been highly studied in these fields due to their stability, ease of synthesis, and diverse range of structures and metal atoms which allow for tunable applications based on optoelectronic properties. Metal oxides can behave as insulators, semiconductors, or metals depending on their atomic nature, crystal structure, and extent of doping. In general, the conduction band for metal oxides is defined by metal-based s- and d-orbitals depending on the metal atom. The symmetry of these orbitals along with the crystal structure of the oxide determine the extent of overlap with strong overlap leading to larger electron mobilities. The valence band of metal oxides consists of largely localized oxygen p-orbitals. This makes p-type conduction through metal oxides difficult without mixing metal d-orbital character into the valence band such as in the case of NiO, Cu₂O, and copper delafossites.

For energy applications, metal oxides with semiconductor and metallic properties are of interest because of the need to conduct charge through an electrical device. These materials are therefore found ubiquitously throughout energy applica-

tions including solar-to-electrical and solar-to-fuel energy conversion as well as energy storage in batteries and supercapacitors. For example, wide band gap semiconductor metal oxides such as TiO₂, ZnO, and NiO have been heavily studied as n-type and p-type electrodes in heterojunction solar cells such as dye-sensitized solar cells (DSSCs), organic photovoltaics (OPV), quantum-dot-sensitized solar cells (QDSCs), and perovskite solar cells (PSCs).^{7–11} Likewise, narrow band gap semiconductor metal oxides such as Fe₂O₃, Cu₂O, BiVO₄, and CuFeO₂ have been studied as direct light absorbers capable of driving photocatalytic H₂O oxidation, H⁺ reduction, and CO₂ reduction.^{2,5,12,13} Metal oxides with more metallic character have shown promise in electrocatalytic applications, where certain spinels and perovskites have been targeted toward electrochemical fuel production. In terms of electrical energy storage, metal oxides are heavily featured as cathodes in Li-ion batteries where the crystal structures of materials such as LiCoO₂ and LiMn₂O₄ create ion channels for lithium intercalation.^{3,14–17}

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As an alternating current (AC) technique, EIS is capable of distinguishing between resistive and capacitive responses of metal oxide interfaces based on the frequency dependence of the observed current. Central to this is the fact that the impedance of a resistor does not depend on the frequency of the modulated voltage; however, the impedance of a capacitor is inversely proportional to this frequency.^{1,6,18} Therefore, EIS offers the ability to study these components independently over a selected voltage range based on a frequency dependent current response. By comparison, a direct current technique such as cyclic voltammetry (CV) shows capacitive and resistive features simultaneously, such that differentiating the two can sometimes be difficult.¹⁹

Figure 1 shows the simplest equivalent circuit used to model metal oxide interfaces, called a Randles circuit. The parallel

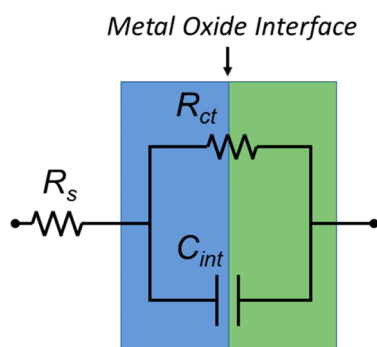


Figure 1. Simple circuit model which describes the flow of current across a metal oxide interface. Faradaic current is correlated with a charge transfer resistance (R_{ct}) while non-Faradaic current is correlated with an interfacial capacitance (C_{int}). A series resistance term (R_s) is shown to represent resistance due to wires, contacts, and solutions which complete the circuit.

combination of charge transfer resistance (R_{ct}) and interfacial capacitance (C_{int}) describes the flow of Faradaic and non-Faradaic current through the interface, respectively. The nature of the metal oxide interface may be a solid/solid or solid/liquid interface where one side is the metal oxide electrode and the other is a dissimilar material depending on the application. For metal oxide electrodes in energy applications, R_{ct} is associated with electron transfer reactions such as electron–hole recombination with a chromophore/semiconductor or catalysis by metal oxide surface sites. Interfacial capacitance is an equivalent capacitance that considers the series combination of

the capacitances for the metal oxide and the dissimilar material with which it is in contact. This material may be an electrolyte in either a solution or solid/gel form or a semiconductor as in the case of QDSCs, OPVs, and PSCs.

Here we present a review of how EIS has been used to characterize metal oxide electrodes specifically used in energy applications. Other reviews of EIS in the context of DSSCs, emerging photovoltaics, and thin films have previously been published.^{1,6,18} We specifically discuss EIS in the context of modulating an applied potential and measuring the magnitude and phase angle associated with the resulting current. This is by far the most common method used in the field of EIS; however, it should be noted that similar methods of modulating an illumination intensity, such as intensity modulated photocurrent and photovoltage spectroscopies (IMPS/IMVS), have been reported but are not discussed here.^{20,21} The applications covered in this review include heterojunction solar cells such as DSSCs, QDSC, and PSCs; ion batteries such as Li-ion, Na-ion, and Zn-ion; and electro/photocatalysts used to drive water oxidation and oxygen reduction reactions. In each case, the discussion is focused on what properties of the metal oxide can be elucidated by EIS. Common themes emerge within each application such as the study of electron (e^-) and hole (h^+) diffusion in solar cells, the dependence of recombination reactions and catalysis on surface defect/trap states for solar cells and photocatalysts, and the formation of passivation layers at the solid electrolyte interface in Li-ion batteries. Particular interest is placed on morphological changes to the electrode materials and how EIS can be used to better understand these complex interfaces. A high degree of attention is also placed on the modeling of EIS data using equivalent circuits, which can often be the most debated aspect of EIS studies, to shed light on which models are most effective at describing the observed data. To do this, we first begin with a brief background on EIS as an AC technique, discussing how different circuit elements such as resistors, capacitors, and constant phase elements are used to describe EIS data.

2. EIS BACKGROUND

EIS is fundamentally an AC technique in which an applied potential $E(t)$ is modulated over time with a small amplitude ($|E_0| \sim 5\text{--}10\text{ mV}$) at a controlled frequency (ω) according to eq 1. Here, ω is an angular frequency defined by $\omega = 2\pi f$, and f is the frequency in Hz. The small perturbation in potential

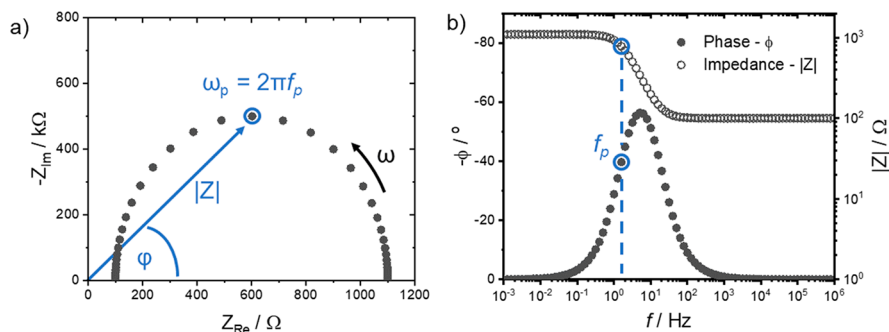


Figure 2. (a) Nyquist and (b) Bode plots representing the same EIS data simulated by the circuit shown in Figure 1 ($R_s = 100\ \Omega$, $R_{ct} = 1000\ \Omega$, $C_{int} = 100\ \mu\text{F}$). In the Nyquist plot, the modulus $|Z|$ and phase angle ϕ define the position of each frequency dependent data point in a complex plane. In the Bode plot, $|Z|$ and ϕ are plotted against the modulation frequency. The angular frequency associated with the $-Z_{im}$ peak in the Nyquist plot is labeled ω_p and corresponds to points labeled f_p in the Bode plot.

defined by $|E_0|$ is required to ensure linear behavior of the current following the Butler–Volmer model.²² The measured current response $I(t)$ is matched in frequency but offset by a phase angle (φ) depending on the parameters of the electrochemical circuit, eq 2. Impedance is defined as the AC analogue to resistance and is thus related to the alternating potential and current through Ohm's law shown in eq 3 and is expressed in units of ohms (Ω).

$$E(t) = |E_0|\sin(\omega t) \quad (1)$$

$$I(t) = |I_0|\sin(\omega t + \varphi) \quad (2)$$

$$Z(\omega) = E(t)/I(t) \quad (3)$$

In a typical EIS experiment, the modulation frequency is sampled over a wide range (~ 1 mHz to 1 MHz) for a fixed applied potential (E_{app}) on top of which the small modulation amplitude $|E_0|$ is applied such that $E(t) = E_{\text{app}} + |E_0|\sin(\omega t)$. When the frequency range is completed, E_{app} is shifted to a new value and the process is repeated. For a single potential, experiments may take anywhere from a few seconds to tens of minutes depending on the frequency range of interest. Therefore, it is not uncommon for experiments to take many hours to fully collect EIS data over a wide potential range and/or with a small step size between applied potentials.

Collected data is then interpreted using a variety of plots. The most important is the Nyquist plot, in which impedance is plotted as a complex number ($j = \sqrt{-1}$) according to eq 4 with Z_{Im} (Z'') along the y-axis and Z_{Re} (Z') along the x-axis (Figure 2). The characteristic semicircle arc arises from the parallel combination of a resistor and capacitor described in Figure 2. Each data point in a Nyquist plot represents a different frequency with ω decreasing from left to right. At infinitely low frequencies, the applied potential is essentially constant, and this condition is considered the DC limit where $Z_{\text{Re}} = R_s + R_{\text{ct}}$. This condition is often relevant when relating EIS data to other DC electrochemical techniques such as cyclic voltammetry. For each frequency, the impedance is defined by a vector originating from the origin with magnitude $|Z|$ and phase angle φ . These two terms are defined with respect to Z_{Re} and Z_{Im} by eqs 5 and 6.

$$Z(\omega) = |Z|(\cos(\varphi) - j \sin(\varphi)) = Z_{\text{Re}} - jZ_{\text{Im}} \quad (4)$$

$$|Z| = (Z_{\text{Re}}^2 + Z_{\text{Im}}^2)^{1/2} \quad (5)$$

$$\tan \varphi = Z_{\text{Im}}/Z_{\text{Re}} \quad (6)$$

Another method of graphing EIS data is the Bode plot, which is a combination of two plots that show the magnitude of impedance $|Z|$ and the phase angle φ on the y-axis and the modulation frequency f along the x-axis. Again, each data point represents a unique frequency which can now be correlated directly with $|Z|$ and φ . The Bode plot therefore allows for the frequency dependence of impedance to be more clearly observed than what is shown in the Nyquist plot. Sometimes, $|Z|$ and φ are combined into a single Bode plot with two different y-axes while at other times they are separated into Bode- Z and Bode-phase plots. A simulated Bode plot is shown in Figure 2 with the same parameters used in the Nyquist plot for comparison. Note that although the peak shape observed for φ results from the semicircle arc shown in the Nyquist plot, the frequencies associated with each peak are not identical. The peak in the Nyquist plot is directly related to R_{ct} and C_{int}

at the electrode surface according to $f_p = 1/R_{\text{ct}}C_{\text{int}}$ where $R_{\text{ct}}C_{\text{int}}$ is known as the time constant for the parallel circuit. The peak in the Bode-phase plot, however, does not correlate with f_p and can sometimes be difficult to interpret directly due to the presence of additional circuit elements such as series resistance. We caution the use of Bode plots to directly interpret EIS data and instead encourage all data to be fit according to a well-defined circuit model (discussed further below).

EIS data can also be interpreted in terms of frequency dependent and potential dependent capacitance. Just like impedance, capacitance can be defined as a complex number and determined from $Z(\omega)$ based on eq 7. Plotting C_{Re} vs frequency reveals direct information about capacitance at the electrode surface. This method of analysis has become particularly useful in the area of PSCs where accumulation of mobile ions (e.g., iodide, methylammonium) in the perovskite material at the interface with metal oxide electrodes results in large capacitances at low-frequencies.^{23–27} Figure 3 shows an

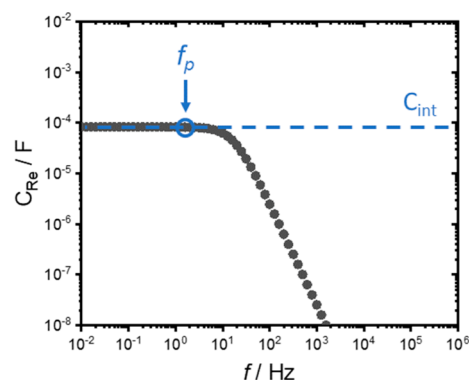


Figure 3. Capacitance vs frequency plot showing a plateau at $C_{\text{int}} = 100 \mu\text{F}$. C_{Re} was calculated from eq 7 based on the same data simulated in Figure 2. The peak frequency observed in the Nyquist plot is shown here for reference at f_p .

example plot of C_{Re} vs frequency for the same data shown in Figure 2. Note that the plateau in capacitance occurs at $C_{\text{Re}} = 100 \mu\text{F} = C_{\text{int}}$, thus allowing for the interfacial capacitance to be obtained directly from the plot.

$$C(\omega) = 1/j\omega Z(\omega) = C_{\text{Re}} - jC_{\text{Im}} \quad (7)$$

2a. EIS Modeling. In order to understand and extract meaningful information from EIS data, it must be fit to an equivalent circuit model which combines fundamental elements such as resistors, capacitors, inductors, constant phase elements, and diffusion elements. The impedance of each element is discussed below, and these are summarized in Table 1.

Resistors. Resistors are important elements which describe Faradaic charge transfer reactions across interfacial layers. The prime example is electron transfer from the electrode surface into an electrolyte solution or vice versa. The term resistance may also be used to describe movement of mobile charges through solid and liquid phases; however, these features are best modeled using diffusive elements described below. The impedance of a resistor (Z_R) is simply equal to its resistance in units of Ω , $Z_R = R$.

Capacitors. The non-Faradaic charge which accumulates at solid/solid and solid/liquid interfaces is modeled as a capacitance. Important interfaces include contacts between

Table 1. Summary of Circuit Elements Used to Model EIS Data

Resistor (R)		$Z_R = R$
Capacitor (C)		$Z_C = 1/j\omega C = -j/\omega C$
Inductor (L)		$Z_L = j\omega L$
Constant Phase Element (CPE)		$Z_{CPE} = 1/(j\omega)^\beta Q$
Warburg Diffusion (W) ^a		$Z_W = \frac{\sigma\sqrt{2}}{(j\omega)^{1/2}}$

^aOnly the equation for infinite diffusion is shown. See eqs 8 and 9 for finite diffusion.

adjacent metal oxide particles or nanocrystals, contacts between a metal oxide and a conductive substrate, and the double-layer which forms at the solid/solution interface. In the latter case, measured capacitance is often correlated with the density of electronic states at the metal oxide surface. The impedance of a capacitor (Z_C) varies inversely with ω via the relation $Z_C = 1/j\omega C = -j/\omega C$, and therefore, Z_C is largest at low frequencies and smallest at high frequencies.

Inductors. Inductors often need to be included in EIS models due to metallic contacts or leads being too close to one another. This is sometimes the case in small devices where anodes and cathodes are in close proximity as is the case in heterojunction solar cells where both electrodes are sandwiched together and only separated by a small distance.¹ The impedance of an inductor (Z_L) is equal to $j\omega L$. Thus, the impedance of an inductor is exactly opposite that of a capacitor. It is for this reason that the signature feature of an inductive circuit element is EIS data which crosses into the lower quadrant of the Nyquist plot as Z_{Im} becomes positive.

Constant Phase Elements (CPEs). Inhomogeneities in the surface of metal oxide electrodes result in nonideal capacitance in the double-layer at the solid/electrolyte interface. For this reason, CPEs are routinely used in place of pure capacitors to model this interfacial layer. The impedance of a CPE is defined by the relation $Z_{\text{CPE}} = 1/(j\omega)^\beta Q$ where Q is a nonideal capacitance and has units of $\text{F s}^{\beta-1}$ and β is an ideality factor which ranges from 0 to 1. When $\beta = 1$, $Z_{\text{CPE}} = Z_C$, and the interface is said to behave as an ideal capacitor ($Q = C$). Normally, β is found to be in the range 0.8–1, indicating nonideal behavior that is attributed to surface roughness and irregularities in surface termination, porosity, and complexity in the double-layer structure.

Warburg Diffusion. Diffusion of mobile charges within metal oxide electrodes and in solution is an important factor in EIS data analysis. The impedance of diffusion (Z_W) is called Warburg diffusion and can be described by finite and infinite diffusion models. Choosing the right form can be important for accurately describing the data. Equations 8 and 9 show two equations which describe Warburg diffusion in a finite thickness layer (i.e., a metal oxide electrode or a solution phase pore) for the case of open and shorted contacts at the solid/electrolyte interface, respectively. Sometimes these contacts are referred to as reflecting (open) and absorbing (shorted) boundaries and are discussed in more detail below.^{1,28,29} The two equations are similar and only differ in the use of either $\coth(x)$ and $\tanh(x)$ functions to describe the impedance. The $\omega^{1/2}$ dependence gives rise to a characteristic linear relationship between $-Z_{\text{Im}}$ and Z_{Re} for the Nyquist plot with slope = 1 and $\varphi = 45^\circ$. The σ term describes the resistance associated with diffusion as a function of

concentration of charge carriers and their diffusion coefficients. Equation 10 provides an expression for σ in terms of solution phase electrolyte species. The term $L/D^{1/2}$ describes the lifetime for diffusion ($\tau_d^{1/2} = L/D^{1/2}$) where L is the finite thickness of the diffusion layer and D is the diffusion coefficient of the mobile charge carrier. The diffusion lifetime is often called a carrier lifetime when the mobile species is e^- or h^+ charges. If L is known, then a diffusion coefficient for charge diffusion can be obtained. These parameters become important for describing diffusion through semiconductor metal oxides. In the case of electroactive or electro-inactive ions in fluid solution, the diffusion layer is often very large, and eqs 8 and 9 are condensed to a common limiting form shown in eq 11. This form of Warburg diffusion is most often observed with metallic electrodes where the applied potential is sufficient such that electron transfer at the metal oxide interface is not rate limiting, and therefore, current becomes dependent on diffusion of electroactive species to the surface. In this case, a diffusion coefficient of the mobile ion can be measured from the σ term.

$$Z_{\text{WO}} = \frac{\sigma\sqrt{2}}{(j\omega)^{1/2}} \coth\left[\frac{L}{D^{1/2}}(j\omega)^{1/2}\right] \quad (8)$$

$$Z_{\text{WS}} = \frac{\sigma\sqrt{2}}{(j\omega)^{1/2}} \tanh\left[\frac{L}{D^{1/2}}(j\omega)^{1/2}\right] \quad (9)$$

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_{\text{ox}} D_{\text{ox}}^{1/2}} + \frac{1}{C_{\text{red}} D_{\text{red}}^{1/2}} \right) \quad (10)$$

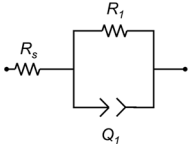
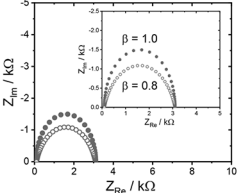
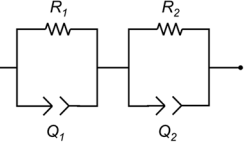
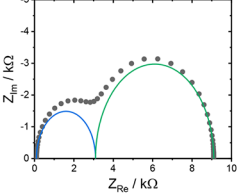
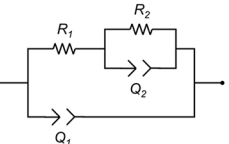
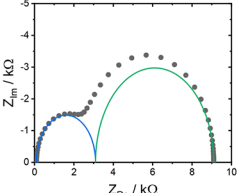
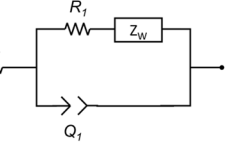
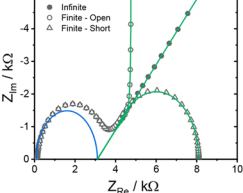
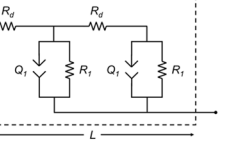
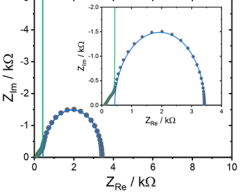
$$Z_W = \frac{\sigma\sqrt{2}}{(j\omega)^{1/2}} \quad (11)$$

Equivalent Circuits. Assembling fundamental circuit elements together into a logical and physically relevant circuit which describes the flow of charge across metal oxide interfaces is often the most challenging and debatable topic within the field of EIS. The challenge comes from the fact that many different equivalent circuits will often provide equally good fits to EIS data. Therefore, physical relevancy of the model and supporting characterization of the electrode material are strong requirements for the chosen model to be accurate.

A wide range of equivalent circuits have been used to model EIS data for metal oxide electrodes with many of the models depending on the application. Table 2 shows a collection of common equivalent circuits along with simulated Nyquist plots for reference. In each case, CPEs are used in place of ideal capacitors as is often the case for metal oxide electrodes. For simplicity, $\beta = 1.0$ was used for all simulations except for model A which provides a comparison between $\beta = 1.0$ and 0.8. Each model is briefly discussed below.

Model A. The simplest circuit, and often the most employed, is called a Randles circuit. The Randles circuit captures the most fundamental description of an electrode surface where both Faradaic (charge transfer resistance, R_1) and non-Faradaic (double-layer capacitance, Q_1) currents flow through the solid/electrolyte interface. These two elements are represented in parallel to reflect the fact that total current is the sum of Faradaic and non-Faradaic pathways. The R_s term is included in series to account for any and all resistances associated with solution resistance, wires, clips, or other

Table 2. Summary of Common Equivalent Circuits for Analyzing EIS Data of Metal Oxide Electrodes^a

Circuit	Simulated Data
Model A 	
Model B 	
Model C 	
Model D 	
Model E 	

^aValues used to generate simulations: $R_1 = 3 \text{ k}\Omega$, $R_2 = 6 \text{ k}\Omega$, $Q_1 = 1 \text{ }\mu\text{F s}^{\beta-1}$, $Q_2 = 10 \text{ }\mu\text{F s}^{\beta-1}$, $R_d = 1 \text{ k}\Omega$, $\sigma = 5 \text{ k}\Omega \text{ s}^{-1/2}$, $L/D^{1/2} = 1 \text{ s}^{1/2}$, $\beta = 1.0$ unless otherwise indicated. Blue lines show specifically where R_1 and Q_1 terms appear in the overall data. Green lines show how R_2 , Q_2 , R_d , or Z_W terms appear in the data.

contacts. The total impedance of an equivalent circuit is calculated by Kirchhoff's laws where Z is treated as a resistance. Therefore, the total impedance $Z(\omega)$ of a Randles circuit is shown in eq 12. The real and imaginary components of $Z(\omega)$ are then solved algebraically. Even for the simple Randles circuit, Z_{Re} and Z_{Im} are quite complicated functions.²² Therefore, computer software is routinely used to calculate Z_{Re} and Z_{Im} on the basis of the given equivalent circuit model.

$$Z(\omega) = R_s + \frac{R_1}{1 + R_1 Q_1(j\omega)^\beta} = Z_{\text{Re}} - jZ_{\text{Im}} \quad (12)$$

Given the frequency dependence of capacitive impedance (Z_C or Z_{CPE}), the semicircle arc of the Nyquist plot shown in Figure 2a can be readily explained. At high frequency, $Z_C \rightarrow 0$

and all current is non-Faradaic with $Z(\omega) = R_s = 100 \text{ }\Omega$ as is shown in the Bode-Z plot of Figure 2b. However, as frequency is decreased, Z_C becomes larger and forces current toward the Faradaic channel; thus, $Z(\omega)$ increases and forms the characteristic arc shape in the Nyquist plot. At the other extreme of infinitely small frequency, $Z_C \rightarrow \infty$; therefore, $Z(\omega) = R_s + R_{\text{ct}} = 1100 \text{ }\Omega$, and R_{ct} is defined by the width of the arc along the Z_{Re} -axis. The plateau in $|Z|$ at low frequency in Figure 2b is also diagnostic of this condition. At low frequency, all current passing through the solid/electrolyte interface is Faradaic. This situation is similar to holding an applied potential for an extended period of time in a chronoamperometry experiment where the non-Faradaic current has decayed to zero at very early times.

Table 2 provides a comparison of simulated data for the Randles circuit with an ideal ($\beta = 1$) and nonideal ($\beta = 0.8$) capacitor using a CPE in place of the capacitance. For an ideal capacitor, the capacitance can be calculated directly from the frequency associated with the peak in the Nyquist plot ω_p . This point is indicated in Figure 2a. The frequency ω_p is directly related to R_1 and $C_1 (= Q_1)$ through the relation $\omega_p = (R_1 C_1)^{-1} = 1/\tau$ where τ is the characteristic RC time constant for the parallel circuit. Often, the EIS literature will discuss Nyquist data in terms of time constants for each observed semicircle. For a nonideal capacitor, a depressed semicircle is observed in the Nyquist plot, and the peak observed in the Bode-phase plot is spread over a wider range of frequencies. This is called frequency dispersion and requires fitting EIS data to an equivalent circuit to accurately measure values such as β and Q .

Model B. The simple Randles circuit can be extended to include multiple parallel $R||C$ circuits in series to account for multiple semicircle arcs observed in the Nyquist plot. Model B considers only the inclusion of two parallel $R||C$ circuits, but higher numbers have been used to describe experimental data.⁴ This model is often invoked to account for the presence of surface passivation layers on metal oxide electrodes where current must first pass through the outside layer before reaching the underlying electrode. Such features are commonly encountered in the area of Li-ion batteries.^{14,15,30}

Model C. Another commonly used equivalent circuit is that of model C where one parallel $R||C$ circuit is embedded within a second parallel $R||C$ circuit. This model is one of the most useful at fitting a wide range of EIS features; however, this also means it is one of the most debated in terms of physical relevance to the metal oxide electrode. Derivatives of model C have been used to explain surface layer formation much like model B,³ the presence of defect states within semiconductor metal oxides,^{2,5,31–33} and resistance to charge transfer between metal oxides and conductive substrates, often called contact resistance.^{34,35} The physical relevance of each explanation hinges on the magnitudes of the resistor and capacitor elements. In the limit where $Q_1 > Q_2$, model C resembles a Randles circuit (model A) and exhibits a single arc in the Nyquist plot defined by the total resistance $R_1 + R_2$. This is the situation often invoked to characterize surface layers and defects states as Q_2 is defined as the capacitance of these layers/states and Q_1 is defined as the bulk capacitance of the metal oxide electrode. If Q_1 and Q_2 are similar in magnitude (within 1 order), the shape of the arc can appear warped or misshapen due to overlapping frequency responses from each capacitor. If $Q_1 \gg Q_2$, then model C is indistinguishable from model A and the single arc is defined only by Q_1 and $R_{\text{ct}} = R_1 +$

R_2 . In the opposite limit of $Q_1 < Q_2$, model C resembles model B with two distinct arcs. This limit has been used to describe porous electrodes with a contact resistance (R_1) between the metal oxide and the conductive substrate.^{34–36} The porosity of the electrode is accounted for by assigning Q_2 to the metal oxide capacitance and Q_1 to the capacitance of the conductive substrate exposed to the electrolyte due to incomplete coverage by the porous metal oxide. The condition of $Q_1 < Q_2$ has also been used to describe large concentrations of surface defect states in the case of Fe_2O_3 photoanodes used for water oxidation.^{2,5,12,31,32,37} Here, Q_1 is the capacitance of the bulk metal oxide, and Q_2 is the capacitance of surface defects.

Figure 4 shows a comparison of simulated data for model C and model B with ideal capacitors to highlight their similarities

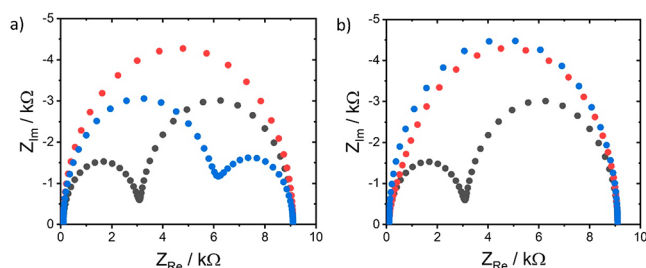


Figure 4. Simulated Nyquist plots comparing equivalent circuits with model B (a) and model C (b). Different colors represent different magnitudes for the capacitor C_2 in each model with $C_2 = 100 \mu\text{F}$ (black), $1 \mu\text{F}$ (red), and $0.01 \mu\text{F}$ (blue). In all cases, $R_s = 0.1 \text{ k}\Omega$, $R_1 = 3 \text{ k}\Omega$, $C_1 = 1 \mu\text{F}$, and $R_2 = 6 \text{ k}\Omega$.

and differences. In both cases, $R_1 = 3 \text{ k}\Omega$, $R_2 = 6 \text{ k}\Omega$, and $C_1 = 1 \mu\text{F}$ while C_2 was varied from 100 to $0.01 \mu\text{F}$. The two models are identical for the case of $C_2 = 100 \mu\text{F}$ ($C_2 \gg C_1$) but are distinct for the other two conditions. When $C_2 = C_1$, both models display a single arc with $R_{ct} = R_1 + R_2$; however, the arc for model C is slightly warped. As C_2 becomes smaller, model B again shows two semicircles arcs in the Nyquist plot with distinct C_1 and C_2 capacitances. At the same condition, model C displays only a single arc defined by C_1 .

Model D. The diffusion of mobile charges in the electrolyte is often described using the equivalent circuit shown in model D. This circuit is a modification to the Randles circuit where a Warburg diffusion (Z_W) term has been included in series with the charge transfer resistance. This arrangement is meant to describe the physical reality of diffusion of electroactive species to the surface of the electrode where they undergo oxidation or reduction via charge transfer. Such diffusion limitations form the bedrock of many electrochemical techniques where a diffusion layer builds up over time as the concentrations of electroactive species are depleted at the electrode surface.²² The diffusion of redox-inert species such as counterions can also be described by model D if the charge transfer event is within the metal oxide electrode and the counterions are necessary to balance charge. This is the case of ion intercalation batteries where the redox event is centered on a transition metal within the metal oxide electrode, but the diffusing ions are necessary for the event to occur.³

The equation used to describe Warburg diffusion in model D could be eqs 8 and 9 or eq 11. The most common form is to use the infinite form of Warburg diffusion (eq 11). The more general forms of eqs 8 and 9 are encountered when mobile charges exist within the metal oxide electrode structure. This

may be due to mobile carriers (i.e., electrons or holes) diffusing through conduction and valence bands, as is the case for many semiconductor metal oxides, or due to diffusion of small ions within porous channels, as in the case of Li-ion batteries. In these examples, the finite thickness of the metal oxide electrode defines L at a relatively small value. Choosing between eqs 8 and 9 depends on the magnitude of charge transfer resistance with the electrolyte solution. The terms reflecting and absorbing boundaries refer to the ability of the solid/electrolyte interface to reflect charges back into the metal oxide solid (infinite charge transfer resistance) vs absorbing charges into the electrolyte (zero charge transfer resistance).^{28,29}

Model E. A special case of thin layer diffusion for mobile carriers within porous metal oxide semiconductors is commonly evaluated using the equivalent circuit shown in model E. This circuit describes the diffusion of mobile carriers by the resistance R_d in series with a parallel $R_1||Q_1$ circuit meant to represent the solid/electrolyte interface. The inclusion of distributed r_d and $r_1||q_1$ elements along a chain indicates the porosity of the electrode where there are multiple interfaces between the metal oxide and electrolyte where Faradaic or non-Faradaic current may pass. The distributed elements are defined with respect to the overall terms as follows: $r_d = R_d/L$, $r_1 = R_1/L$, and $q_1 = Q_1/L$. An important feature of this model which cannot be described graphically is that the diffusion of carriers and charge transfer reactions at the solid/electrolyte interface are linked by assuming a steady-state concentration of mobile carriers. This model is called the diffusion-recombination model and was derived and popularized by Bisquert for the study of mesoporous TiO_2 electrodes used in dye-sensitized solar cells.²⁸ The expression for the total impedance is shown in eq 13. The effect of linking R_d and R_1 mathematically is to essentially allow for a variable degree of charge transfer through the solid/electrolyte interface, as opposed to completely reflecting ($R_{ct} = \infty$) or absorbing ($R_{ct} = 0$) conditions. Therefore, the semicircle arc associated with $R_1||C_1$ appears at lower frequency than charge diffusion. The simulated Nyquist plot in Table 2 clearly shows the linear Warburg behavior at high frequency. This is notably different than combining a finite Warburg diffusion term (eqs 8 and 9) in series with a parallel $R_1||C_1$ where the linear Warburg behavior would appear at low frequency following the $R_1||C_1$ arc at high frequency.

$$Z(\omega) = \left(\frac{R_d R_1}{1 + R_1 C_1 j \omega} \right)^{1/2} \coth \left[\left(\frac{R_d}{R_1} \right)^{1/2} (1 + R_1 C_1 j \omega)^{1/2} \right] \quad (13)$$

3. HETEROJUNCTION SOLAR CELLS

3a. Overview. Nanocrystalline, polycrystalline, and single crystalline metal oxide materials have been of great importance for their utilization in devices for solar-to-electric energy conversion.³⁸ Specifically, n-type and p-type wide band gap oxides are used as selective contacts for electron and hole transport, respectively, between a light absorber and the external circuit. Oxides that have been utilized in heterojunction devices as charge transport layers include TiO_2 ,^{39–41} ZnO ,^{42,43} SnO_2 ,^{44–46} Nb_2O_5 ,^{47–49} SrTiO_3 ,^{49–51} ZnSn_2O_4 ,^{52–54} CeO_2 ,^{55,56} NiO ,^{57,58} and CuGaO_2 .^{59,60} This list gives a small taste of the variety found in metal oxides: from

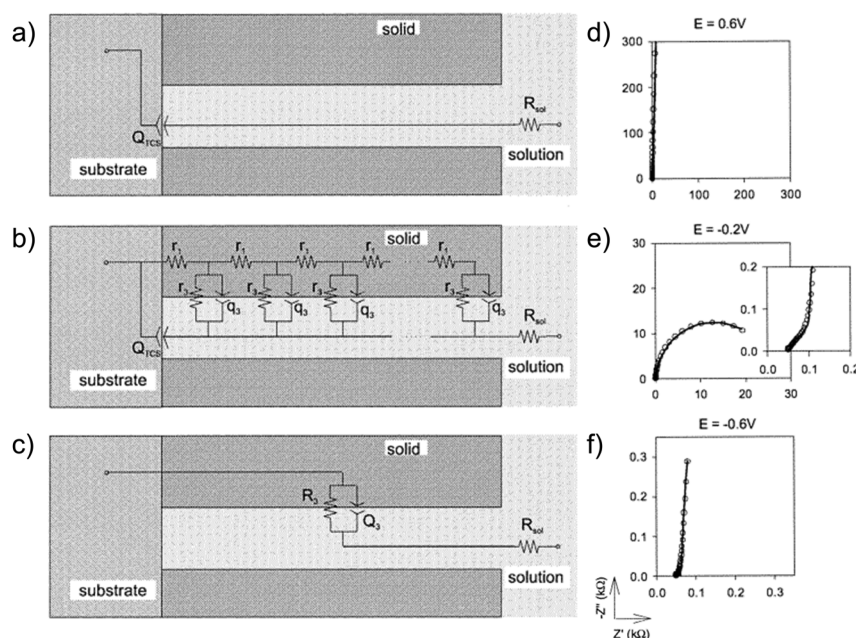


Figure 5. Equivalent circuit models used to analyze EIS data for mesoporous TiO_2 electrodes as a function of applied potential. Going from positive to negative potentials, TiO_2 is modeled as an (a) insulator, (b) semiconductor, and (c) metal. Nyquist plots (d–f) obtained at different applied potentials to show the behavior of each equivalent circuit. Reproduced with permission from ref 36. Copyright 2002 American Chemical Society.

using transition metals to lanthanides, from binary to ternary, and from n-type to p-type.

In some cases, the metal oxide facilitates charge separation from the light absorber at the metal oxide interface such as in dye-sensitized solar cells where a molecular chromophore is bound directly to the metal oxide surface.^{7,61} However, for heterojunction solar cells in which the light absorber is a semiconductor material of considerable thickness (e.g., quantum dot solar cells,^{8,9} organic photovoltaics,^{10,62} and perovskite solar cells^{11,23–27}), charge separation of e^- and h^+ may occur within the semiconductor and the metal oxide serves only as an electrode selective for e^- or h^+ . In the former case, the EIS data can be readily interpreted in terms of the electronic properties of the metal oxide because an electrolyte with a large Helmholtz capacitance is present at the interface. In the latter case, the significantly lower capacitance of the semiconductor makes interpretation of EIS data more challenging because the measured interfacial capacitance is a series combination of the semiconductor and metal oxide. This is perhaps why EIS studies focusing on metal oxides in the latter devices are not found often in the literature. Notable exceptions include studies on QDSCs which compare SnO_2 and TiO_2 where electron diffusion in the metal oxide can be observed^{63,64} and PSCs where the nature of the metal oxide makes a significant difference in the magnitude of the interfacial capacitance observed at low frequencies.^{23–27}

EIS is a powerful tool to characterize metal oxide electrodes, either in simple electrochemical cells, or in the context of complete solar cells. While CV on heterogeneous systems is useful, EIS can provide a distinction between specific interfaces such as the metal oxide/electrolyte and metal oxide/substrate interfaces as well as significant information on the band structure, density of states, number and type of charge carrier, and conductivity of the metal oxide electrode.⁶ In this section we describe metal oxides used for solar-to-electric energy conversion, the results of their EIS data, and the models that have been used to understand their properties. The under-

standing of heterogeneous electrochemistry using EIS is significant in the literature for TiO_2 , ZnO , and SnO_2 for electron transport (n-type), and NiO and CuGaO_2 for hole transport (p-type). In most cases, a metal oxide/electrolyte interface is specifically studied; however, a discussion of metal oxide/semiconductor interfaces is also included in the section on TiO_2 as it relates to recent work in the area of PSCs. The specific resistors and capacitors discussed in this section are related to the resistance to charge diffusion/transport (R_d , R_t , or Z_w) through the metal oxide, resistance to charge transfer (R_{ct}) or charge recombination (R_{rec}) at the metal oxide interface, and the chemical capacitance (C_μ) of the metal oxide. Importantly, C_μ can also be represented as a density of states (DOS) of the metal oxide, which gives insight into the distribution of defect/trap states at the metal oxide interface. Metal oxide morphology and doping are also shown to influence C_μ due to surface area changes, exposure of surface states, and changes in conductivity/introduction of defects.

3b. n-Type Metal Oxides. *TiO₂.* The most significant use of EIS to study a metal oxide in the context of heterojunction solar cells has been done on TiO_2 because of its use in the original Grätzel cell.⁶¹ Bisquert and co-workers, in particular, have published a significant body of work on mesoporous films of TiO_2 nanocrystals, as they are the most relevant in the context of dye-sensitized solar cells for their high surface area.^{19,36,65–67}

Bisquert has shown that, depending on the applied potential to a bare TiO_2 electrode in a three-electrode setup, different models can be used to understand the electronic properties of the metal oxide.³⁶ Specifically, the electrode can behave as an insulator at potentials very positive of the conduction band edge, and as a metal at potentials very negative of the conduction band edge. In these regimes, the equivalent circuits are simplified as shown in Figure 5. The corresponding Nyquist plots next to each circuit demonstrate that the impedance at positive potentials resembled a Randles circuit with an infinitely large R_{ct} due to the low level of electronic

states in the band gap. As the potentials became more negative and conduction band states began to be populated by electrons, R_{ct} decreased, and a semicircle arc was observed at low frequencies. At these conditions, the resistance for electron diffusion through the film could be observed, shown by the linear behavior at high frequencies, and the capacitance associated with conduction band states could be estimated. The transmission line equivalent circuit shown as model E was developed to model EIS data such as this for TiO_2 mesoporous films. As the applied potential was pushed further negative, the diffusional resistance decreased such that the linear feature was no longer observed. The capacitance of the metal oxide also increased such that the full semicircle arc was not fully resolved over the frequency range. These changes were explained by an exponential increase in the density of conduction band states in TiO_2 . As these states were populated at more negative potentials, the diffusional resistance decreased on the basis of its inverse relationship with conductivity and the capacitance increased as the concentration of charges went up. Overall, this work demonstrated the ability of impedance to differentiate insulator, semiconductor, and metallic behavior in metal oxide films, while considering the unique contributions of the mesoporous structure.

Bisquert and co-workers have also modified the transmission line model from above to include interfaces specific to DSSCs. Features were added that take into account the unique properties of electrolyte diffusion, charge recombination at the metal oxide/electrolyte interface, and the electrolyte/counter electrode interface.⁶⁷ Other models have been proposed that are specific to DSSCs in other operating conditions.^{68,69} Prior to Bisquert, Kern et al. derived a model that allowed for elucidation of EIS behavior for DSSCs at open circuit conditions under illumination where the modeling of electron diffusion and recombination was done with differential equations, as opposed to RC circuit elements.⁷⁰ It was later elucidated by Adachi et al. that, despite the different physical assumptions made by Kern and Bisquert for their models, they are each mathematically the same.⁷¹

One aspect of TiO_2 that researchers have sought to understand is the presence and distribution of trap/surface states present at potentials below the conduction band edge. The presence of these states influences the measured chemical capacitance and the charge transfer/recombination events that take place at the metal oxide surface. A study by Mora-Sero and Bisquert showed that the Fermi-level of electrons in surface states was distinct from the Fermi-level of free electrons in the conduction band of TiO_2 .⁷² Due to recombination of the electrons in the surface state with the electrolyte, the Fermi-level of the surface states is always below that of the bulk Fermi-level. The charge transfer resistance was measured by EIS and plotted vs the Fermi-level energy of the surface states and the bulk. It was revealed that surface state recombination is dominant due to the low concentration of conduction band electrons when the Fermi-level of the surface state is below that of the surface state energy and conduction band energy. As the Fermi-level of the surface state surpasses the energy level of the surface state, and the bulk Fermi-level approaches the conduction band, conduction band recombination becomes the dominant pathway.

Results of EIS investigations of nanoparticle TiO_2 mesoporous films in many studies have indicated the presence of such surface/trap states.^{73–79} Gimenez et al. studied surface states for a bare TiO_2 electrode in aqueous electrolyte by

modeling the charge transfer resistance and chemical capacitance using the transmission line model (model E).⁷⁵ A monoenergetic trapping model was developed in the paper and was validated by simulations and experimental data. EIS data showed an exponential increase in C_μ as the monoenergetic trap state was approached (around -0.85 V vs Ag/AgCl) followed by a decrease at more negative potentials, then an exponential increase at the trap state tail. The opposite trend was observed for R_{ct} where recombination resistance decreased as the trap states were populated with electrons. Illumination of the electrode resulted in similar behavior for C_μ , but R_{ct} was constant over the applied potential range. This was explained by a saturation of recombination events from photogenerated charges. EIS has also been used to differentiate between monoenergetic trap states and exponential trap states. Bertoluzzi et al. elucidated the contribution of exponential and monoenergetic trap states to the total chemical capacitance by comparing nanoparticle TiO_2 with submicron TiO_2 , which had more defined crystal facets to expose the surface states (Figure 6).⁷⁸

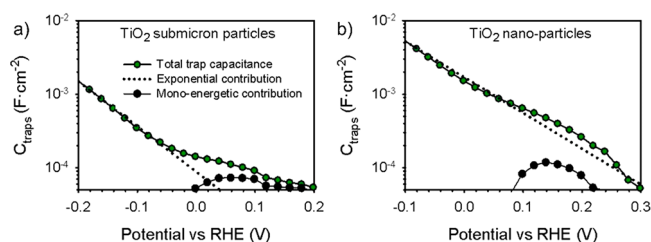


Figure 6. Total capacitance of trap states measured via EIS for (a) submicron TiO_2 and (b) nanoparticle TiO_2 . The contribution of monoenergetic traps was confirmed by the peak feature in the capacitance as a function of potential. The contribution of exponential trap states is shown by the dashed line. Reproduced with permission from ref 78. Copyright 2014 American Chemical Society.

Other studies have shown that passivation of trap/surface states can be achieved by adding blocking layers.^{77,80–83} Blocking layers are a standard component of heterojunction solar cells because of their ability to limit charge recombination. Pascoe et al. showed with EIS that atomic layer deposition of Al_2O_3 improved recombination by increasing R_{ct} while C_μ stayed consistent.⁷⁷ However, it was also shown that the conduction band states were being suppressed by the blocking layer treatment. Góse et al. used EIS to understand the improvements and limitations of blocking layers in DSSCs.⁸²

The desire to change the charge transport properties and surface area of TiO_2 electrodes has led to an exploration of different nanocrystalline morphologies. There are two notable aspects to the areas which have been investigated. The first is exploration of different crystal phases of TiO_2 , such as anatase, rutile, and brookite, to understand the relationship between crystal structure and charge transport. The most studied of these phases is anatase TiO_2 because of its larger band gap and higher conductivity,⁸⁴ but interest in rutile and brookite has been reported in the literature.^{84–93} EIS has been used to understand the fundamental charge transport properties of rutile and anatase crystal phases directly,^{94,95} as well as in solar cells.^{96–99} Growth of the rutile phase thermodynamically favors nanorods and can be seen in a study by Kim et al. to function well as a scaffold for perovskite nanocrystals in solid-

state PSCs.⁹⁸ Using EIS the authors determined the effect of rutile nanorod length on device performance. Under both an applied potential and illumination, it was determined that the impedance fitting could be simplified from the transmission line model (model E) to a simple two-arc model (model B), because the midfrequency Nyquist arc did not have a linear feature indicating diffusion limited charge transport, believed to be due to the large applied potential. The midfrequency arc was the result of the recombination resistance and the chemical capacitance. The authors showed that nanorod length had little effect on the chemical capacitance or recombination resistance in these devices, as neither of these parameters were changing significantly with applied potential, which was consistent with previously reported rutile PSC measurements. However, the photocurrent and photovoltage decreased in devices with increasing nanorod length.

Brookite solar cells have typically shown lower efficiencies than anatase TiO₂ but have had large open circuit potential (V_{oc}).^{92,93,96,97,100} Pourjafari et al. used EIS to study anatase TiO₂ and brookite samples synthesized under acidic and basic conditions to compare how morphology and surface structure affected electron injection into TiO₂.⁹⁶ EIS was measured at the open circuit potential under illumination, and Nyquist plots were fit to the transmission line model (model E). Synthesis and nanoparticle treatment both showed an effect on the measured chemical capacitance, recombination resistance, and electron lifetime in the TiO₂ electrodes. C_{μ} showed exponential dependence on V_{oc} for each sample, consistent with surface states, but base-synthesized brookite C_{μ} was considerably lower than anatase TiO₂. R_{rec} for brookite DSSCs was lower than anatase, but acid treatment increased R_{rec} in brookite DSSCs. Base-treated brookite also had the shortest electron lifetime, consistent with a small R_{rec} .

Kusamawait et al. had previously done a similar study on brookite TiO₂ photoelectrodes and showed high V_{oc} for brookite devices.⁹⁷ They also showed a higher recombination resistance and slower charge transport. The same EIS model was used in both studies (model E). Hsiao et al. also explored the effect of brookite and rutile defects in anatase TiO₂ with EIS in a DSSC.⁹⁹ The authors emphasize that the presence of trap states in TiO₂ has been tied to crystal defects, and intentionally adding those defects helps study the influence of trap states on charge transport. Measured EIS of pure and defect-rich anatase reveals an increased C_{μ} for defect-rich anatase, which is consistent with the surface traps acting as electron sinks.

The second aspect of morphological studies of TiO₂ using EIS has focused on changing the shape of the nanocrystal.^{101,102} With exploration of different particle shapes, control over electron transport and surface area can be achieved. Morphologies that have been explored for TiO₂ with EIS include nanoparticles,^{36,65,67–71,73–76,78,99,103–110} nanowires/nanotubes/nanorods,^{102,111–122} and other irregular shapes.^{79,123} Several of these morphologies have been studied in conjunction with synthetic, photochemical, and electrochemical doping. The most popular structure, besides nanoparticles, in the literature is the nanowire/nanotube/nanorod structure. To briefly differentiate these structures, nanorods are solid particles oriented specifically on the substrate, nanotubes are also oriented specifically but are hollow, and nanowires are solid but do not have a specific orientation. Their popularity is due to the idea that electron flow in a metal oxide could potentially be directed vectorially

toward the conductive substrate for improved charge transport and extraction from the solar cell.¹¹⁴ For this reason, one-dimensional TiO₂ nanostructures have been investigated in solar cell devices.^{102,111,117,118} Wu et al. used EIS to measure and deconvolute all aspects of a nanotube DSSC, including resistances associated with diffusion, electron, and charge transfer, as well as capacitances associated with the double-layer, contact, and chemical capacitances in the device.¹¹⁸

One of the first studies of TiO₂ nanotubes by Fabregat-Santiago et al. used EIS to compare the charge transport properties and chemical capacitance to those of TiO₂ nanoparticles.¹¹² Whereas TiO₂ nanoparticles typically show low charge carrier densities with a Fermi-level that is well below the conduction band edge, different morphologies of TiO₂ can display more metallic behavior (i.e., high carrier density). To explore if this phenomenon is observed in TiO₂ nanotubes were synthesized with widths of 20 nm, reflective of the size of TiO₂ nanoparticles synthesized for films, but had variable lengths from 200 to 1000 nm. The Nyquist plots display a single arc at low frequency with a high-frequency linear feature, indicative of electron diffusion through the TiO₂ nanotube. The widths of these TiO₂ nanotubes did not show a depletion capacitance consistent with band bending, which is the same behavior observed in nanoparticles.

Furthermore, it was demonstrated in the study by Fabregat-Santiago et al. that the nanotubes were susceptible to electrochemical doping, when exposed to an extremely negative potential for an extended time in basic media. This caused a significant change in the chemical capacitance and transport resistance. Figure 7 shows that, in the “fresh”

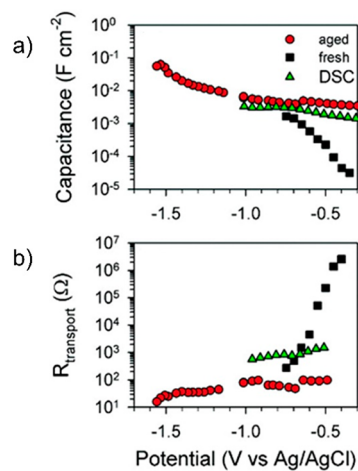


Figure 7. Potential dependence of (a) capacitance and (b) transport resistance for TiO₂ nanotubes measured by EIS as a function of applied potential. The “aged” nanotube electrode showed a large, uniform C_{μ} and low R_t indicating that H⁺ intercalation into the TiO₂ electrode had occurred. Reproduced with permission from ref 112. Copyright 2008 American Chemical Society.

nanotubes, the transport resistance measured by EIS exhibited an exponential dependence on applied potential, indicative of a low number of charge carriers when the applied potential is far from the conduction band edge. A similar trend was observed for the chemical capacitance, consistent with an increase in electronic states as the conduction band edge was approached (Figure 7). TiO₂ nanotubes that were “aged” by long exposure to an applied negative potential showed a significant decrease

in transport resistance and increase in capacitance that varied less with applied potential. This indicated an increase in charge carriers in the nanotubes resulting in Fermi-level pinning near the conduction band edge. The increased carrier concentration was attributed to reduction of Ti^{4+} sites coupled to intercalation of H^+ into the TiO_2 lattice. It was also demonstrated that the capacitance measured was variable with the length of the TiO_2 nanotube, indicating the role of surface area in proton intercalation. Comparative studies of nanotubes in acidic media showed R_t and C_μ values similar to “aged” samples in basic solution. Thus, a high concentration of protons immediately induced the reduction of TiO_2 and increased carrier density. Interestingly, studies of TiO_2 nanoparticles in acidic media did not demonstrate this intercalation behavior, which demonstrated that nanotube morphology was an important factor for proton intercalation.

Doping is a very common way to control defects and electronic properties of metal oxide electrodes.¹²⁴ EIS studies on TiO_2 electrodes have revealed a wide range of changes in charge transport resistance and chemical capacitance based on the chemical nature of the dopant and the method with which the dopant is introduced (e.g., photoinduced^{115,116} or electrochemically¹¹² induced). Niobium, tantalum, cerium, and tin have each been doped into TiO_2 and the resulting effects studied with EIS.^{125–128} Collectively, these studies point to the same result where increased concentration of dopant atoms led to decreased charge transport resistances due to the higher concentration of free carriers in the TiO_2 conduction band.

Discussion up to this point has focused on TiO_2 /electrolyte interfaces where the interfacial capacitance is directly related to the chemical capacitance of the TiO_2 electrode. However, when these electrodes are used as electron transport layers in lead halide perovskite solar cells, the capacitance at the metal oxide/semiconductor interface is more closely related to that of the perovskite material due to the formation of a depletion layer.^{23–27} Nonetheless, the nature of the metal oxide in contact with the perovskite has been shown to influence the presence of an ionic capacitance at the metal oxide/perovskite interface.^{129,130} This “extra” capacitance is due to mobile ions within the perovskite such as iodide and methylammonium which accumulate at the interface. This ionic capacitance is also problematic in PSCs as it leads to a hysteresis in photoinduced current–voltage measurements which are used to determine solar-to-electrical conversion efficiency, leading to uncertainty in these measurements.²⁵ Kim et al. has provided direct evidence for this assignment by examining the capacitance vs frequency data collected by EIS for PSCs with a TiO_2 electron transport layer in the “normal” configuration (electrons directed toward the transparent conductive oxide (TCO)) and with an organic electron transport layer in the “inverted” configuration (electrons directed away from the TCO).¹³⁰ Figure 8 shows that the TiO_2 /perovskite interface results in significant capacitance in the low-frequency region due to the accumulation of ions at the interface. The use of the organic electron transport layer removes much of this capacitance and yields a more reproducible current voltage curve. Studies have shown the use of SnO_2 as an n-type selective contact and/or NiO as a p-type selective contact can also decrease this low-frequency ionic capacitance, although the physical origin of the metal oxide dependence is not yet fully understood.^{129,130}

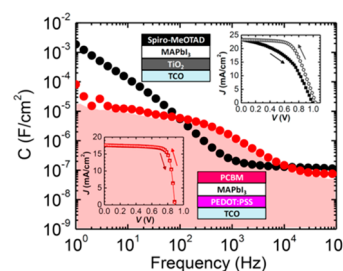


Figure 8. Capacitance vs frequency measured for PSCs with (black) and without (red) a TiO_2 electron transport layer. The inclusion of the TiO_2 layer results in ionic capacitance at low frequencies which results in hysteresis in the illuminated J – V curve (inset). The use of an organic electron transport layer, PCBM, does not show this ionic capacitance, and therefore, there is no hysteresis in the J – V curve. Reprinted with permission from ref 130. Copyright 2015 American Chemical Society.

Figure 8 also highlights an important aspect of understanding capacitance at metal oxide interfaces. The frequency dependence shows that the ionic capacitance occurs in the low-frequency region while the bulk capacitance of the perovskite occurs at high frequency. Therefore, in order to obtain meaningful information about the depletion layer capacitance of the perovskite, a high frequency can be used to isolate this feature from the ionic capacitance. Almora et al. have highlighted this technique in distinguishing true depletion layer capacitance using Mott–Schottky analysis from erroneous assignments due to the influence of the ionic term.²⁷

ZnO. Zinc oxide was one of the first metal oxides employed in heterojunction solar cells,^{131,132} but these never surpassed the efficiencies of TiO_2 solar cells. In comparison studies of TiO_2 and ZnO solar cells, the TiO_2 devices typically have better performance.^{133–135} Interest in ZnO has been maintained because of the ease with which different morphologies of ZnO can be synthesized.^{136,137} While different morphologies have been explored in TiO_2 , the crystal structure of ZnO gives rise to synthetic simplicity and a large level of variability to explore many unique structures. EIS has been used to study ZnO nanoparticles, but nanorods/nanotubes are the main ZnO structures studied with EIS, for the same reasons stated above for TiO_2 .

Before different ZnO morphologies are discussed, it is useful to compare ZnO systems that are similar to TiO_2 to understand if they can, electrochemically, be treated the same. A study by Guillén et al. addressed the issue of transport resistance measurement in ZnO nanoparticulate DSSCs that did not show the diffusion feature in their Nyquist data.¹³⁸ By combining time constants measured with IMPS and capacitance values measured from EIS, the authors used the relationship $\tau_{\text{tr}}\gamma = R_t C_\mu$ where γ is an illumination factor, to calculate R_t . EIS measurements were performed at short-circuit conditions, so as to be comparable to the IMPS data, and these were then converted to R_t from the given relationship. To check their method, the R_t values obtained from EIS + IMPS were compared to data collected using EIS only, and the values are comparable until high-Fermi-level conditions are reached, as expected.

An early EIS study on a ZnO nanowire array demonstrated that EIS could characterize the film by mathematically modeling the nanowire.¹³⁹ First, via Mott–Schottky measurements, Mora-Sero et al. demonstrated that by appropriately defining the particle geometry of the ZnO nanowires, band

bending was demonstrated at their surface (Figure 9). This has not been observed in anatase TiO₂ nanoparticles or nanotubes.

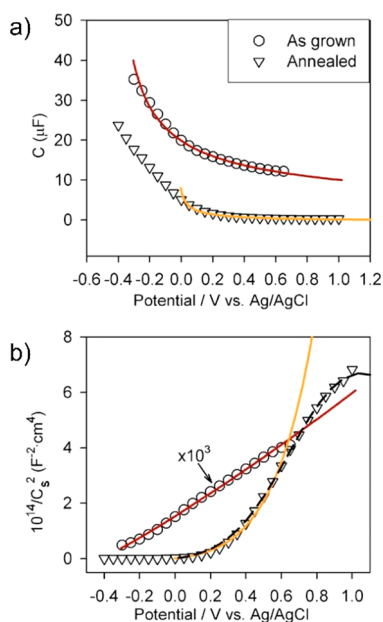


Figure 9. (a) Capacitance measured by EIS for a ZnO nanowire array before and after annealing at 450 °C in air. (b) Mott–Schottky representation of capacitance showing linear behavior for the as grown ZnO nanowire electrode. Reproduced with permission from ref 139. Copyright 2006 AIP Publishing.

The Mott–Schottky equation predicts a linear trend between C^{-2} and the applied potential (E_{app}) when band bending at the semiconductor/solution interface is present, eq 14. Here, ϵ is the relative dielectric constant of the semiconductor, ϵ_0 is vacuum permittivity, A is surface area of the interface, e is the fundamental charge, N is the doping density, k_B is Boltzmann's constant, and T is temperature. If a linear trend is observed, then the measured capacitance is that of the depletion layer formed at the metal oxide interface, and the flat band (E_{fb}) and doping density of the semiconductor may be determined. The small linear slope observed in the Mott–Schottky data indicated a high density of charges (N) in the nanowires, behavior that was attributed to the synthetic method. A decrease in charge density and capacitance was observed when nanowires were annealed under air at 450 °C, which indicated a remediation of defects that resulted in surface states. The change in capacitance with annealing was also seen in a study by Tena-Zaera et al. where ZnO nanowires were synthesized via electrodeposition and the same EIS model (model A) was used.¹⁴⁰

$$C^{-2} = (2/\epsilon\epsilon_0 A^2 eN)(E_{app} - E_{fb} - k_B T/e) \quad (14)$$

Characterization of ZnO nanorod DSSCs using EIS has also been reported. Martinson et al. used the transmission line model (model E) to measure the chemical capacitance and charge transfer resistance, as well as charge lifetimes and charge extraction time.¹⁴¹ Briefly, charge lifetime is defined as the amount of time the photogenerated charge survives before recombination with the electrolyte and is calculated from the relationship $\tau_n = R_{rec} C_{\mu}$. Charge extraction time is the amount of time it takes for the photogenerated charge to be collected in the external circuit and is calculated from the relationship τ_d

$= R_{ct} C_{\mu}$. EIS of the film was measured in the dark, with a bias such that the charge transport resistance feature is visible in the Nyquist plot. Conductivity is elucidated from the charge transport resistance and shows significantly lower conductivity compared to that of nanoparticle TiO₂. The ZnO nanorod film also shows lower capacitance and charge transfer resistance (Figure 10). However, the charge extraction time for the ZnO

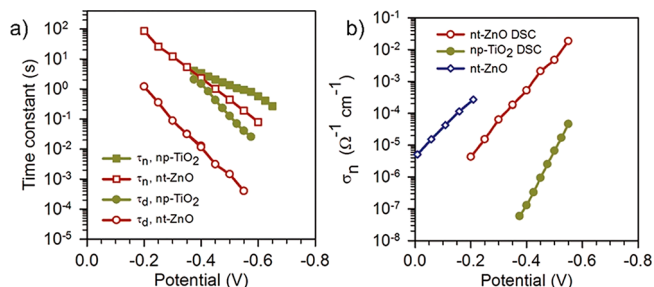


Figure 10. (a) Electron recombination lifetimes (τ_n) and extraction lifetimes (τ_d) calculated from resistance and capacitance values measured by EIS for DSSCs assembled from a nanoparticle TiO₂ electrode and a nanotube ZnO electrode. (b) Conductivity of a nanoparticle TiO₂ DSSC, a nanotube ZnO DSSC, and the bare ZnO nanotube array electrode as a function of applied potential. Reproduced with permission from ref 141. Copyright 2009 American Chemical Society.

nanotube DSSC is 2 orders of magnitude shorter than for nanoparticle TiO₂, displaying the influence of morphology on charge transport. EIS of a ZnO nanorod DSSC has also been studied under illumination and elucidates the contribution of trap states to the device performance.¹⁴² Fit to model E, the chemical capacitance under illumination showed exponential dependence at low bias potentials, consistent with a tail of surface trap states. At high bias potentials, the capacitance shows no dependence on illumination, which the authors attribute to a depletion layer capacitance related to the geometry of the electrode. R_{ct} also loses its linearity upon the bias potential reaching the onset of a trap state tail, indicating a contribution of the surface states to recombination. R_t remained consistent, regardless of whether the EIS was measured in the dark or under illumination. The authors state this is consistent with electron transport occurring within the nanorod core.

EIS has been used to compare the size and morphological aspects with regard to the electronic behavior of other ZnO structures.^{143–154} To briefly highlight some unusual structures, ZnO aggregates made from sintered nanowires showed a relationship between sintering temperature and charge transport resistance, elucidated from EIS.¹⁵³ Parthasarathay et al. used EIS to show surface-state-mediated electron transfer in ZnO multipods.¹⁴⁴ Hosni et al. investigated the electrochemical properties of ZnO electron transport layers when made of nanospheres or nanorods.¹⁵⁴ Three different nanosphere sizes and one size of nanorod were studied with EIS. The smallest ZnO nanospheres had the highest capacitance and the largest density of trap states. The other nanospheres and the nanorods had a similar C_{μ} and trap state density. The capacitance measurements correlated with the measured R_{ct} , as the smallest nanospheres had the lowest charge transfer resistance, consistent with having the highest trap state density. The other nanoparticle morphologies had very similar R_{ct} values.

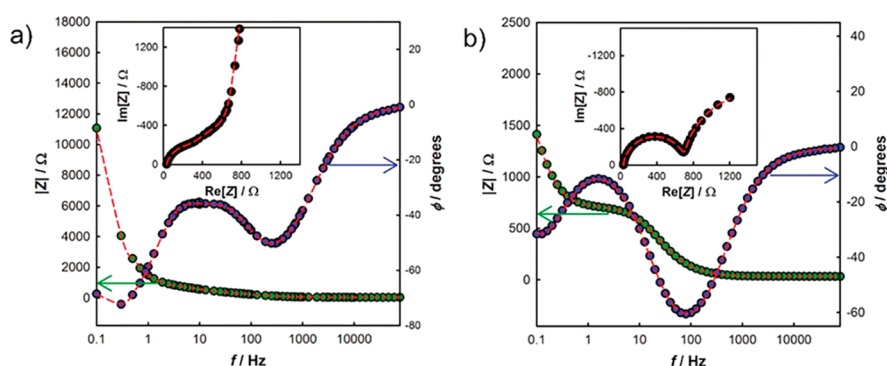


Figure 11. Nyquist and Bode plots for (a) TiO_2 and (b) SnO_2 QDSCs measured at their respective V_{oc} and 1 sun illumination. SnO_2 does not display the Warburg diffusion feature seen in the midfrequency range for TiO_2 indicating rapid transport of electrons in the SnO_2 electrode. Reproduced with permission from ref 64. Copyright 2011 American Chemical Society.

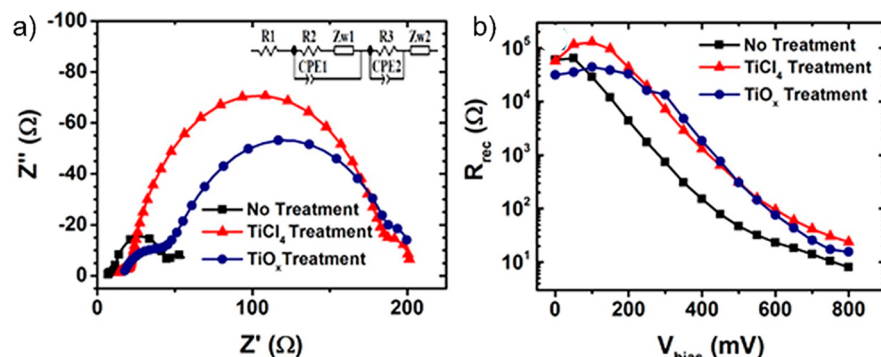


Figure 12. (a) Nyquist plots obtained at the open circuit condition for DSSCs assembled with SnO_2 electrodes which were untreated, treated with TiCl_4 , and treated with TiO_x to determine the impact of blocking layers on R_{rec} . The equivalent circuit used to fit the data is shown as an inset. (b) An increase in the midfrequency arc was consistent with an increase in R_{rec} following TiCl_4 and TiO_x treatment. Reproduced with permission from ref 63. Copyright 2016 Springer Nature.

Like TiO_2 , the effects of defects and doping have been studied in ZnO using EIS.^{155–163} The contribution of native defects in ZnO on its electrochemical performance was assessed by Das et al., where they showed remediation of defects after postsynthetic annealing.¹⁶¹ Cations doped into ZnO vary from alkali and alkaline earth metals to transition metals. Co-doped ZnO has been studied using EIS to assess the change in the dielectric of the material¹⁵⁸ and has also been shown to change the morphology of ZnO depending on doping level, which lowered recombination resistance and increased the charge lifetime.¹⁶⁴ EIS was used to explore the effect of tin doping on ZnO particle grain boundaries and the resulting electronic properties.¹⁶⁰ Li is one of the most well-studied metal oxide dopants. In a study by Cheng et al., ZnO doped at 5% and 20% was used as an electron transport layer in an inverted OPV.¹⁶² Data was fit with model C, and 5% Li- ZnO showed the largest recombination resistance and an electron lifetime that was over 2 times longer than that for 20% Li- ZnO . Li-doped ZnO has also been used as an electron transport layer in perovskite solar cells.¹⁶³ The authors acknowledge that Li^+ is more likely to interstitially dope in the ZnO structure as opposed to substituting into Zn sites in the structure. Mott–Schottky measurements show a positive shift in the conduction band edge compared to the undoped device. Nyquist plots fit with model B showed that recombination resistance is higher and charge transport resistance is lower for the doped solar cell.

SnO_2 . Along with TiO_2 and ZnO , SnO_2 is a heavily investigated metal oxide for heterojunction solar cells. However, its device efficiencies are consistently lower than those measured for devices utilizing TiO_2 .¹⁶⁵ Relative to TiO_2 , it has been shown that SnO_2 has faster electron transport, which is good for charge transport to the external circuit, but it suffers from fast recombination with the oxidized chromophores and redox mediators.¹⁶⁶ EIS has been used to explore these challenges to further improve devices using SnO_2 .

Hossain et al. studied QDSCs with SnO_2 and compared them directly to the same device architecture using TiO_2 .⁶⁴ Figure 11 shows a comparison of Bode and Nyquist plots for these devices. An important feature of these data was the lack of Warburg diffusion in the SnO_2 electrodes, as seen by the inset Nyquist plots where a linear increase in impedance is observed in the midfrequency range for TiO_2 , and no such feature is observed for SnO_2 . Analysis of the TiO_2 data required a transmission line model (model E) whereas SnO_2 data was analyzed using a series of two parallel RLC elements (model B). This behavior is consistent with other literature on SnO_2 where rapid charge transport properties have been observed; thus, R_d is small and not a major factor in the EIS data.^{167,168} The chemical capacitance and charge transfer resistance were also shown to be higher for SnO_2 than TiO_2 over the same potential range. Efforts to visualize R_t for SnO_2 were unsuccessful, but the authors used the transport time of the device cathode to make a rough estimate of the diffusion length of the device. In a similar study of QDSCs with SnO_2 ,

EIS was used to determine the contribution of the nanoparticle film structure to recombination and capacitance by changing the porosity of the electrode.¹⁶⁹ As expected, the more porous structure had a higher capacitance and a lower recombination resistance, explained by increased recombination via surface trap sites.

As with every metal oxide discussed thus far, the role of surface states has also been investigated for SnO₂. Huang et al. investigated the effect of surface states on the function of QDSCs employing SnO₂ and compared with TiO₂.¹⁷⁰ As with the study discussed above, Warburg diffusion was found to be present for TiO₂ whereas it was absent in the case of SnO₂. Treatment of SnO₂ with TiCl₄ was shown to decrease the contribution of surface states to the C_{μ} of the electrode, which in turn led to an increase in R_{rec} . This was attributed to formation of a passivation layer, thus blocking surface states from participating in recombination reactions. EIS has also been used to explore blocking layer treatment of SnO₂ in DSSCs with similar results.⁶³ SnO₂ electrodes were treated with either TiO_x or TiCl₄ and the EIS data compared with an untreated electrode. All treated solar cells showed a larger midfrequency arc in the Nyquist plots than the untreated cell (Figure 12), indicative of increased recombination resistance at the SnO₂/chromophore/electrolyte interface. The smaller arc at low frequency was assigned to the cathode/electrolyte interface. When R_{rec} is plotted over the entire applied potential range, it was shown that the treatment increased R_{rec} universally for both treatment methods.

Morphological changes of SnO₂ electrodes have been investigated in similar ways to TiO₂ and ZnO. Along with one-dimensional nanostructures (e.g., nanorods), hierarchical structures (e.g., nanoflowers) and nanofibers have been investigated in SnO₂-containing solar cells using EIS.^{171–175} Elumalai et al. and Kumar et al. investigated the charge transport properties of SnO₂ nanoflowers and nanofibers in DSSCs.^{171,172} In both studies, R_{rec} was larger for the nanoflowers compared to the nanofiber DSSCs. Interestingly, a higher capacitance was also seen for the nanoflowers, which usually leads to a lower R_{rec} . This indicates a larger surface area for the nanoflowers but a lower contribution of trap states to the recombination process.

Regardless of the inherent high conductivity of SnO₂, doping has still shown interesting effects on its electrochemical properties.^{176–181} A study by Dou et al. studied SnO₂ nanoflowers doped with Zn in DSSCs.¹⁷⁶ They also studied the effect of a blocking layer on their devices, and all of their data was compared to TiO₂ nanoparticles. The chemical capacitance is lower for Zn-SnO₂ compared to TiO₂, but upon TiCl₄ treatment the Zn-SnO₂ nanoflowers and TiO₂ have a similar capacitance, due to the increase in surface states from the treatment. Charge recombination is also increased upon TiCl₄ treatment for the SnO₂ films and surpasses the recombination resistance for TiO₂. Bisquert has pointed out that charge recombination can be affected by variations in the conduction band at different carrier concentrations,¹⁸² so to compensate the authors also plotted R_{rec} vs C_{μ} , which has been shown to allow for comparison of R_{rec} at the same density of states. The plot revealed significant inhibition of recombination events upon TiCl₄ treatment in the Zn-SnO₂ nanoflowers. An increase in electron lifetime was also observed in the treated nanoflowers. It should also be noted that charge transport resistance was very similar in each film, which

revealed that doping had a larger impact on transport than morphology.

3c. p-Type Metal Oxides. Metal oxides discussed up to this point behave as n-type semiconductors; however, in order to expand the range of heterojunction solar cell devices, p-type metal oxides have also been explored. The challenge of p-type oxides is the movement of charge (i.e., holes) through the valence band, which consists mainly of oxygen p-orbitals that are not highly delocalized, resulting in a large effective mass for holes.¹⁸³ Therefore, the best p-type metal oxides consist of metals that have 3d-orbitals that can energetically overlap with the oxygen 2p-orbitals, helping with delocalization and charge transport.

NiO. Nickel oxide is the most heavily explored p-type metal oxide used as a hole transport material in heterojunction solar cells.⁵⁷ A great deal of electrochemical properties of NiO have been elucidated from EIS, including charge transport, interfacial recombination, and density of states.^{184–193} Huang et al. measured the impedance of a NiO based DSSC and compared those results to those of a TiO₂ electrode to demonstrate the differences between p-type and n-type devices.¹⁸⁵ Nyquist data for the p-type device showed only two semicircles arcs, assigned to the NiO/electrolyte interface at low frequency and counter electrode/electrolyte interface, with no signs of Warburg diffusion. This was attributed to the low thickness of the NiO electrode. Comparing the two solar cells at the same potential showed a smaller recombination resistance for NiO than TiO₂. This result indicated that recombination events are more significant at the NiO/electrolyte interface.

In order to study the charge transport through the NiO electrode, Huang et al. did a follow-up study with a thicker NiO nanocrystalline film. The net result was that a Warburg diffusion feature could now reasonably be observed in the midfrequency range, although it was somewhat masked by the semicircle arc assigned to the counter electrode/electrolyte interface at high frequency (Figure 13).¹⁸⁹ This required fitting of their data using the transmission line model (model E). When EIS was measured under illumination of the solar cell, R_t and C_{μ} showed a mild exponential dependence on the measured open circuit potential. The authors tied this behavior to a hopping mechanism for the charge transport, where the holes are localized between Ni²⁺ and Ni³⁺ atoms. Consistent with their previous study, the authors also showed that illumination greatly affected R_{rec} , decreasing with higher light intensity and higher open circuit potential. Figure 13b shows a comparison of these data with data collected from intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) to show similar lifetimes for hole recombination ($\tau_h = R_{\text{rec}}C_{\mu}$) and hole transport ($\tau_{\text{tr}} = R_tC_{\mu}$).

There have been quite a few studies done on NiO doping, but only a few have used EIS to study the results.^{194–197} One in-depth study of a Li-doped NiO electrode using EIS was performed by D'Amario et al.¹⁹⁶ Their exploration was inspired by the fast charge recombination lifetimes measured in previous studies, which indicated a high conductivity for NiO and/or a high density of surface states that contribute to this recombination. The goal of this study was to shift the position of the valence band edge using Li⁺ doping, thereby achieving a higher open circuit potential for the p-type solar cell. EIS results indicated a strong dependence of charge diffusion and chemical capacitance on the percent Li⁺

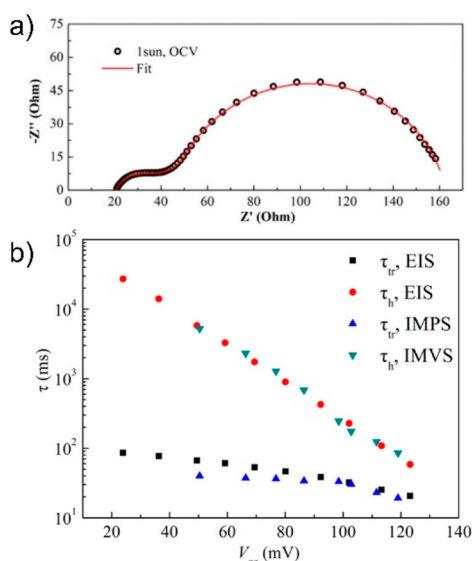


Figure 13. (a) Nyquist plot of a p-type NiO DSSC measured at open circuit potential under 1 sun illumination. (b) Hole lifetimes (τ_h) and hole extraction times (τ_{tr}) calculated from resistance and capacitance data measured from EIS compared to lifetimes measured from IMPS and IMVS. Reproduced with permission from ref 189. Copyright 2012 American Chemical Society.

concentration present during synthesis of NiO nanoparticles. In terms of capacitance, NiO synthesized with 0% Li^+ displayed a prominent peak at potentials near the valence band edge assigned to defect states in the NiO lattice. However, when NiO was synthesized with 1% Li^+ , this peak was dramatically smaller, and the overall capacitance was shifted to more positive potentials (Figure 14). The authors

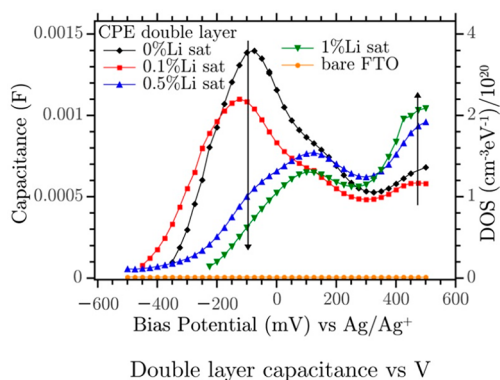


Figure 14. Capacitance and density of states (DOS) of NiO electrodes measured by EIS over a range of applied potentials. The effect of Li-doping NiO is readily seen by the decrease in defect states near -100 mV vs Ag/Ag^+ . Reproduced with permission from ref 196. Copyright 2014 American Chemical Society.

proposed that the inclusion of Li^+ results in passivation of defect states, and thus, a lower contribution to the overall chemical capacitance is observed. p-type DSSC measurements supported these results by showing an increase in the open circuit potential from 60 mV (0% Li^+) to 115 mV (1% Li^+).

CuGaO_2 . Delafossite copper metal oxides ($\text{Cu}^{\text{I}}\text{M}^{\text{III}}\text{O}_2$) have also been investigated as hole transport layers in p-type heterojunction solar cells due to their wide band gaps and large hole mobilities.^{198,199} The first EIS study on CuGaO_2

nanoparticles was used to show that these mesoporous electrodes could behave in a semiconductor or metallic manner.³⁵ Data was analyzed using a modified transmission line model (model E) with the addition of a contact resistance between the CuGaO_2 electrode and the conductive substrate. This feature was important due to the plate-like morphology of the nanoparticles. The nanoparticles showed low conductivities (σ), calculated from charge transport resistance, that increased moderately as the applied potential was stepped positive toward the valence band edge (Figure 15). CuGaO_2

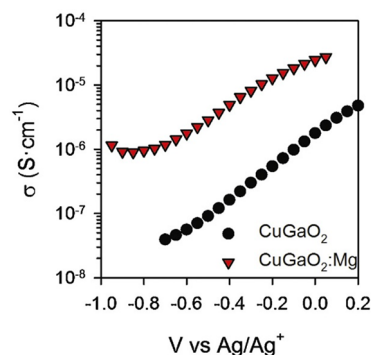


Figure 15. Conductivity (σ) of undoped and Mg-doped CuGaO_2 electrodes plotted vs applied potential showing the increase in conductivity with doping. Conductivity was calculated from the equation $\sigma = L(R_d A(1 - p))^{-1}$, where L is the film thickness, A is geometric area of the film, and p is porosity (assumed to be 50% for a mesoporous film). Reproduced with permission from ref 35. Copyright 2013 Elsevier.

nanoparticles were then doped with Mg^{2+} , which resulted in an order of magnitude increase in conductivity. Mott–Schottky analysis of the measured chemical capacitance allowed for the hole carrier density of the Mg-doped CuGaO_2 to be measured at 10^{19} cm^{-3} compared with 10^{17} cm^{-3} for undoped nanoparticles.

Another study by Bredar et al. also showed EIS of CuGaO_2 nanoparticles which displayed high conductivities without the need for dopant atoms.³⁴ Figure 16 shows Bode and Nyquist plots for CuGaO_2 mesoporous electrodes where solid lines represent fits to the same modified transmission line circuit described above. Hole diffusion can be clearly observed in the -0.8 V trace by the linear feature in the midfrequency range. As the potential is stepped to 0.8 V, this feature is diminished as R_d decreased. The overall change in R_d (and σ) over the applied potential range was small in comparison to the undoped CuGaO_2 example above and more in line with the Mg-doped example. These changes were also found to be independent of annealing conditions, thus ruling out interstitial oxygens as the source of charge carriers. Through elemental analysis and XPS measurements, the source of doping was determined to be copper vacancies in the crystal lattice. Elemental analysis revealed a 4% deficiency in Cu atoms, which equated to an acceptor density of 10^{21} cm^{-3} . A notable difference in the two EIS studies was the synthetic conditions for preparation of the CuGaO_2 electrode, suggesting that electrochemical properties of these metal oxides are highly sensitive to their growth environment.

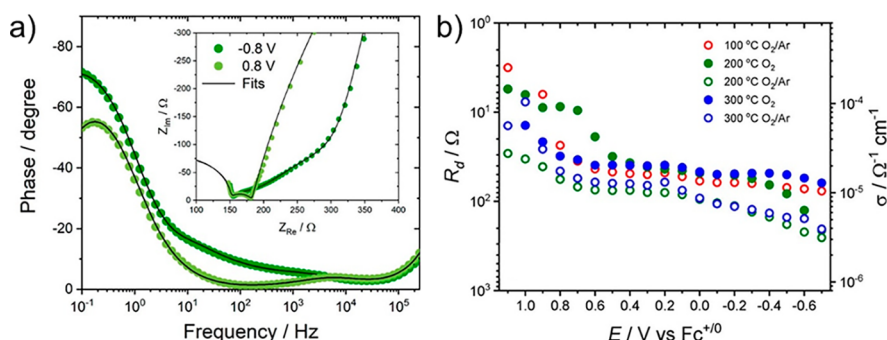
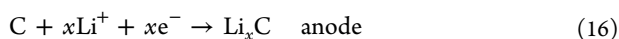
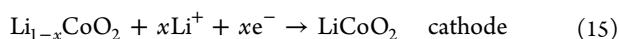


Figure 16. (a) Bode-phase and Nyquist (inset) plots shown for a CuGaO₂ mesoporous electrode highlighting the decrease in the linear diffusion feature observed at −0.8 V as potential is stepped to 0.8 V. (b) Hole diffusion resistance and conductivity plotted vs applied potential (referenced to ferrocene, Fc^{+/0}) showing that annealing conditions of the electrode have little effect on R_d . Reproduced with permission from ref 34. Copyright 2019 American Chemical Society.

4. ION BATTERIES

4a. Overview. A variety of metal oxides have been studied as cathodes and anodes in rechargeable ion batteries used for electrochemical energy storage.^{3,14,15,30,200–245} EIS can be a useful technique for researching these materials by providing insight into the corrosion rate of the metal oxide electrode during multiple charge and discharge cycles (i.e., long-term cycling efficiency) and ion diffusion into the metal oxide. The most well-studied type of ion battery using EIS is the Li-ion battery^{15,30,219–224,246–252} due to its commercialization in many portable electronics; however, other Na-ion^{200,205,214,225,229,253} and divalent ion batteries, particularly Zn-ion batteries,^{244,245,254–256} have also been investigated using this technique. Lithium-ion batteries primarily consist of a cathode, anode, and lithium-containing electrolyte present in the form of a solution, solid, or gel electrolyte.¹⁶ The cathode material consists of a lithiated transition metal oxide, and the anode is typically graphite; however, researchers have also explored anodic metal oxides.²⁵⁷ Upon charging the battery, oxidation of the transition metal oxide cathode is coupled with deintercalation of Li⁺ ions. Concomitantly, reduction of the anode results in Li⁺ intercalation between graphite layers. Redox half reactions for each of these processes are shown in eqs 15 and 16 for the case of a LiCoO₂ cathode and graphite (C) anode. As lithium ions are transferred between electrodes, electrochemical energy is stored as the potential difference between the electrodes is increased. During discharge, intercalation of Li⁺ occurs at the cathode upon reduction, and deintercalation occurs at the anode upon oxidation.



The reversibility of this process depends greatly on the structure and electrochemical properties of the metal oxide cathode. Oxides such as LiCoO₂, LiNiO₂, and LiMnO₂ possess layered structures where Li⁺ ions are able to diffuse in and out of the host oxide.^{3,14,201,236,238,253} Other important oxides such as spinel LiMn₂O₄ and its substituted derivatives (e.g., LiNi_{0.5}Mn_{1.5}O₄) possess interstitial sites where the occupancy by Li⁺ is variable.^{30,220,258–261} Importantly, the charge storage capacity of a metal oxide host is limited by the reversible solid-solution range of Li⁺ intercalation in the cathode host structure for a given redox potential of the transition metal cation.¹⁶

Important features of ion battery electrodes which have been studied by EIS include formation of passivation layers at the surface of cathodes and anodes, charge transfer to the metal oxide electrode, and Li⁺ diffusion in the solid state. Passivation layers, also known as solid electrolyte interface (SEI) layers in the Li-ion battery literature, are routinely observed on the cathode and anode surface due to chemical reactivity between the electrodes and electrolyte. The SEI layer can have both detrimental and beneficial effects, including loss in battery capacity over time but enhancement of the cycling efficiency. The formation of passivation layers is modeled using additional parallel R||C circuits such as models B and C discussed above.³ Importantly, the resistance of the SEI layer is believed to be the result of Li-ion migration through the layer; the growth of such layers over extended cycles leads to higher resistance.^{206,220,221,235,248–250} The impedance of solid-state ion diffusion, on the other hand, is described by a Warburg element at low frequency.^{4,215,228,236,239} Figure 17 shows a

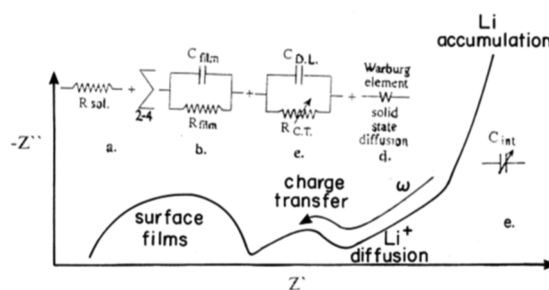


Figure 17. General impedance spectra illustration for lithiated electrode and the equivalent circuit analogue. Reproduced with permission from ref 4. Copyright 2000 Elsevier.

description of this behavior provided by Aurbach et al. where the additional arc assigned to formation of a passivation layer (i.e., surface film) occurs at high frequency while the charge transfer resistance associated with energy storage appears in the midfrequency range.⁴ Note that the linear portion at low frequency reveals information about Li⁺ diffusion as described by Warburg impedance.

In the following sections we discuss specific examples of EIS studies on metal oxides used as cathode and anode materials. We do not cover every example available in the literature and instead give a brief discussion of examples which use EIS to

elucidate particularly important features of metal oxide electrodes in the context of ion batteries.

4b. Li-Ion Cathode Materials. Lithium cobalt oxide is the archetype cathode material for Li-ion batteries.^{16,17,262} This layered oxide allows for a variable number of Li^+ ions to intercalate between layers of edge-shared cobalt oxide octahedra upon local redox changes in the cobalt oxidation state.^{14,263–265} Early studies by Goodenough revealed the presence of passivating surface layers that form by adsorption/decomposition of the electrolyte on the surface of LiCoO_2 .³ The observed EIS data revealed two semicircles (Figure 18), a

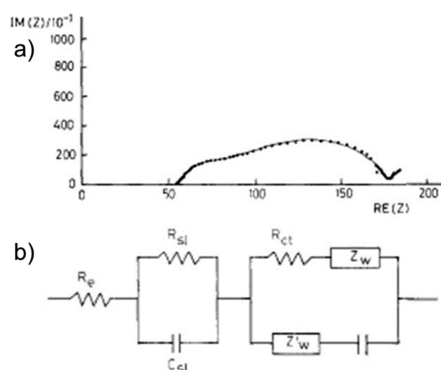


Figure 18. (a) Nyquist plot showing EIS data for a $\text{Li}_{0.65}\text{CoO}_2$ cathode at potentials up to 4.5 V vs lithium and (b) the equivalent circuit used for fitting. The parallel $R_{sl}||C_{sl}$ circuit describes the presence of a surface layer on the electrode with a high-frequency response. Reproduced with permission from ref 3. Copyright 1985 Electrochemical Society.

deviation from the expected response of one semicircle representing charge transfer to the transition metal and a high-frequency linear region describing diffusion of Li^+ . The new semicircle appeared at high frequency and increased in size over time. A thorough comparison of equivalent circuit models to account for the second arc resulted in the proposed equivalent circuit shown in Figure 18. Here, a second $R||C$ circuit is included to account for surface layer formation (R_{sl} , C_{sl}), and a second Warburg diffusion element is included to account for diffusion of Li^+ within the porous electrode structure (Z_w'). The surface layer formation was attributed to polymerization of propylene carbonate at the electrode surface with R_{sl} increasing over a 22 h period as the layer grew in thickness.

Another common observation of Li-ion battery cathodes is an increase in R_{ct} associated with oxidation/reduction of the transition metal over an extended number of charge–discharge cycles.^{14,15,221} This observation has been attributed to decomposition of the cathode material, which leads to losses in energy storage. Zhang et al. studied LiCoO_2 with a $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid-state electrolyte where EIS was used to analyze capacitance fade and increased impedance at the cathode/solid electrolyte interface after being subjected to long-term cycling.¹⁵ Overall, batteries experienced a loss of $\sim 10\%$ storage capacity over the first 100 cycles. Figure 19 shows Nyquist plots collected at the beginning and end of this cycling range where all three semicircle arcs are observed to increase in size after 100 cycles. The midfrequency arc was assigned to charge transfer with the LiCoO_2 cathode which increased from 9 to $118 \, \Omega \, \text{cm}^2$ along with a decreased capacitance. Scanning electron microscopy found that LiCoO_2

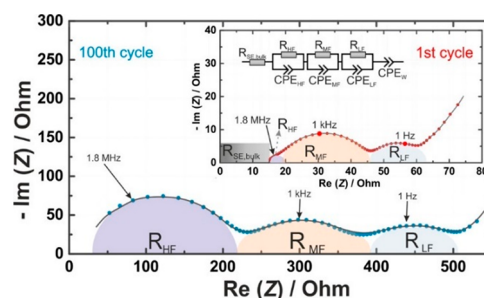


Figure 19. Nyquist plots after 1 charge cycle (inset) vs 100 charge cycles at 3.6 V vs In/InLi. After 100 cycles, decomposition of the LiCoO_2 cathode during cycling was observed as an increase in resistance for the semicircle arc in the midfrequency region, while formation of a surface layer at the LiCoO_2 /electrolyte interface was observed as an increase in resistance for the arc at high frequency. Reproduced with permission from ref 15. Copyright 2018 American Chemical Society.

particles were fractured following extended cycling, hypothesized to result in a loss of contact with the solid-state electrolyte. Electron energy loss spectroscopy also showed migration of cobalt ions from LiCoO_2 into the SEI layer which grew in size over the cycling range. This growth can be observed by a large increase in resistance for the high-frequency arc in the Nyquist plot. The low-frequency arc was assigned to the anode/electrolyte interface.

Lou et al. has followed the decomposition of LiCoO_2 and formation of surface layers using energy dispersive spectroscopy (EDS) and EIS as a function of cycle number.²²¹ Batteries were charged and discharged at 0.6 C (C = charge rate) with a 30% depth of discharge for 100, 400, 800, 1600, 2000, and 2400 cycles. The O:Co ratio rose from 2.34 to 2.96 as the cycling proceeded which suggested slow SEI growth as the cycle number increased. The SEI layer was hypothesized to consist of Li_2CO_3 on the basis of FTIR data in conjunction with the increase in oxygen content. We note that the ratio may also be explained by a loss of cobalt from the metal oxide. Consistent with results discussed in other studies, the Nyquist plots for EIS data showed a steady increase in both the high-frequency arc assigned to resistance (R_p) of the SEI layer and the midfrequency arc assigned to charge transfer with LiCoO_2 (R_{ct}). The linear feature at low frequency was assigned to Warburg diffusion of Li^+ ions; however, this feature was not modeled in this study.

Efforts to stabilize cathodes from decomposition and formation of passivating surface layers have focused on the use of additives to the battery electrolyte.^{14,30,221,227,228,234} As a recent example, Wu et al. compared EIS data of LiCoO_2 cathodes and graphite anodes with and without the additive 4-propyl-1,3,2-dioxathiolane-2,2-dioxide (PDTD) over multiple charge–discharge cycles. As seen in Figure 20, there was a significant increase in surface layer resistance (R_f) and R_{ct} over 150 cycles for both LiCoO_2 and graphite. However, the presence of PDTD as an additive stabilized both electrodes, exhibiting smaller increases in R_f and R_{ct} over the same cycling period. The influence of PDTD is thought to help stabilize the LiCoO_2 surface from leaching cobalt ions and forming surface layers.¹⁴

In other studies of LiCoO_2 , controlling the porosity and grain size of the electrode has been found to influence the EIS results.^{201,212,222} Annealing Co_3O_4 and CoO at 350°C resulted in optimal Li storage performance with high discharge

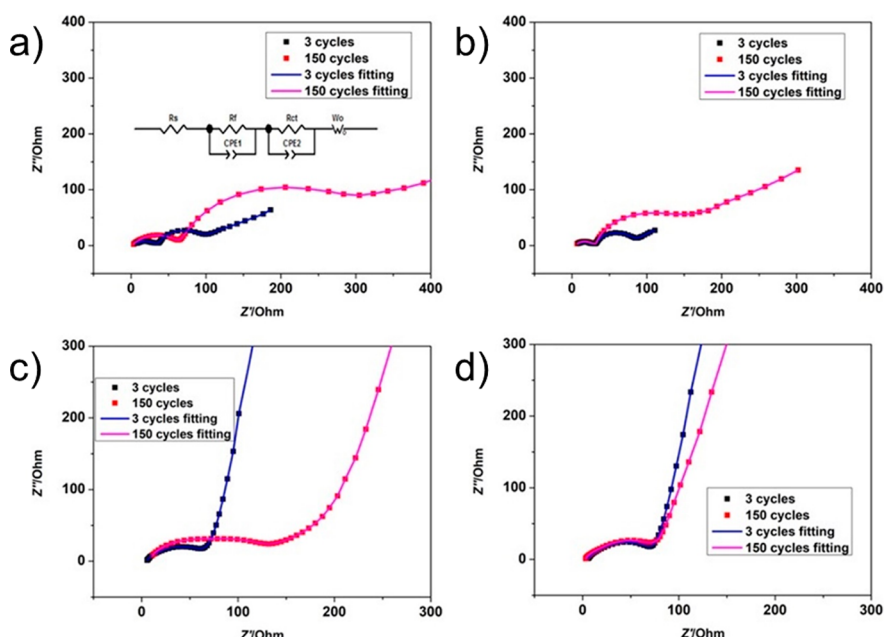


Figure 20. Nyquist plots showing discharge of LiCoO₂ cathodes (a, b) and graphite anodes (c, d) collected in electrolytes without (a, c) and with (b, d) the additive PDTD at the discharge state (~ 3.0 V). Large increases in R_f and R_{ct} without PDTD indicated decomposition of the electrodes over extended cycles. Inclusion of PDTD limited these increases over the same cycling period. Reproduced with permission from ref 14. Copyright 2019 American Chemical Society.

capacities and good long-term cycling stability; at higher annealing temperatures, a larger grain size was attainable which led to a smaller semicircle in the EIS data indicating low resistance from surface film formation.²⁰¹

Electron transport through the metal oxide may also be observed by EIS; however, most electrodes are designed to be highly conductive by mixing the metal oxide with carbon black as a composite. Zhuang et al. was able to observe electron transport for LiMn₂O₄ as a function of both charging voltage (3.5–4.3 V) and temperature using EIS.³⁰ As with other Li-ion battery studies, three features were generally observed in the Nyquist plot: two semicircle arcs at high and middle frequencies and a linear Warburg feature at low frequency. These features were assigned to Li-ion migration through the SEI film, charge transfer through the electrode/electrolyte interface, and solid-state diffusion of Li⁺ ions in the electrode matrix, respectively. However, over the potential range 3.5–3.7 V, an additional semicircle arc in the middle-to-high-frequency region was observed. To investigate the origins of this feature, EIS experiments were performed as a function of temperature. Below 20 °C, the middle-to-high arc frequency could be well-resolved; however, above 20 °C, the semicircles in the high- and middle-to-high-frequency ranges began to overlap. This suggested that the semicircle observed in the high-frequency region at room temperature may actually be composed of two distinct features, as seen in Figure 21. These two features were proposed to be due to Li-ion migration through the SEI film at high frequency, as is typically discussed, and electronic transport through the cathode at middle-to-high frequency. Also notable in this study is the predictable dependence of charge transfer resistance and Warburg diffusion as a function of temperature. For low temperatures, R_{ct} is quite large, and therefore, Warburg diffusion cannot be observed over the finite frequency range. However, as temperature is increased, R_{ct} drops precipitously, and the Warburg feature can be clearly observed.

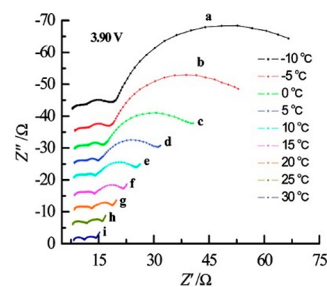


Figure 21. Nyquist plots at various temperatures for a spinel LiMn₂O₄ cathode at 3.90 V. At low temperatures, a third semicircle arc was observed in the middle-to-high-frequency range assigned to electron transport inside the cathode. Reproduced with permission from ref 30. Copyright 2010 American Chemical Society.

4c. Li-Ion Anode Materials. Copper(II) oxide has been studied as an anode material for Li-ion batteries where the reduction of copper(II) to copper metal results in reversible formation of Li₂O according to the reaction $\text{CuO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Cu} + \text{Li}_2\text{O}$. The morphological dependence of the CuO electrode has been a particular area of focus in terms of EIS studies.^{228,229,232,249,266} Wang et al. have investigated the difference in electrochemical behavior of leaf-like, oatmeal-like, and hollow-spherical CuO structures.²³² Charge storage capacity and long-term cycling efficiency were found to be weakest for the oatmeal-like structure, which showed the lowest porosity based on scanning electron microscopy. EIS was able to provide justification for these results where a noticeably larger R_f resistance was observed for the oatmeal structure ($R_f = 321.1 \, \Omega$) than for the leaf ($R_f = 45.7 \, \Omega$) and hollow-sphere ($R_f = 43.8 \, \Omega$) structures. Similar to the discussion above for cathode materials, the R_f resistance is attributed to the formation of a passivation layer at the solid/electrolyte interface, which is attributed to decreased charge storage capacity. The lower porosity of the oatmeal structure

was proposed to be the main culprit in the higher surface film resistance.

While the morphology of the anode can impact the charge storage capacity and cycling efficiency, the nanostructure of the SEI layer on the anode also affects the electrochemical behavior of the battery during cycling and can be analyzed using EIS. Huang et al. studied the formation of the SEI layer on CuO nanowires following the conversion of CuO to Cu and Li_2O .²³⁵ A Nyquist plot is shown in Figure 22 where the

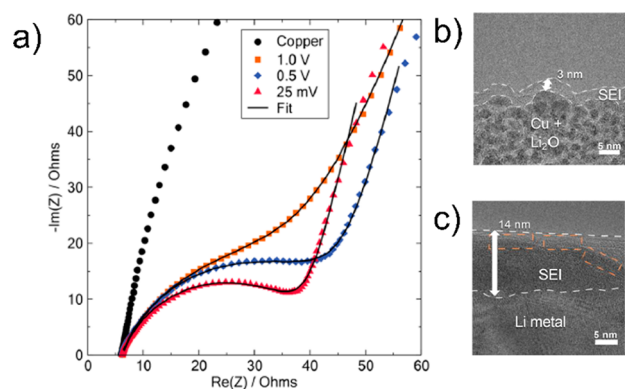


Figure 22. (a) Nyquist plots before the growth of SEI (copper) in addition to SEI formation at 1.0, 0.5, and 0.025 V vs Li^+/Li . Transmission electron micrographs of electrode surfaces following an applied potential of (b) 1.0 V and (c) <0.0 V showing the formation of the SEI layer. Reproduced with permission from ref 235. Copyright 2019 American Chemical Society.

formation of the SEI layer can be observed as a function of the applied potential vs Li^+/Li . At potentials greater than 1.0 V, the impedance response was capacitive from charge accumulation on the CuO electrode. However, once a potential of 1.0 V was applied, CuO was reduced to Cu and Li_2O and a depressed semicircle was observed, characteristic for the formation of an SEI layer. As the potential was lowered from 1.0 to 0.025 V, the semicircle became more well-defined. It was determined that, as the potential begins to approach 0 V, the ionic resistance for Li^+ migration through the SEI layer decreased; however, the thickness of the layer increased. This was determined by transmission electron microscopy collected for samples after each applied potential. The thickness of the SEI layer grew from 3 nm at 1.0 V vs Li^+/Li to 14 nm upon deposition of Li metal. The decrease in ionic resistance was proposed to be the result of a dense, ionically conductive amorphous layer at lower potentials and highlighted the importance of the structure of the SEI layer and not just its thickness.

TiO_2 has also been an interesting material studied for anode applications in Li-ion batteries, but as the direct anode and as a coating material for the anode to enhance overall stability and performance.^{267–270} Qiu et al. used EIS to study TiO_2 reduced graphite nanocomposites as the active anode material in Li-ion batteries. The conductivity of the reduced graphene oxide nanosheets was found to facilitate the charge transfer process in Li-ion batteries.²⁷⁰ As an anode material, the structural and morphological characteristics of oxygen-deficient anatase TiO_2 using EIS has been reported.^{271–276} Liu et al. studied TiO_2 electrodes in an aqueous Li-ion battery and the decomposition of inorganic compounds (LiF , Li_2CO_3 , and Li_2O) on the surface of TiO_2 using EIS in conjunction with scanning

electron microscopy.²⁷⁶ Balogun et al. studied the capacity and long-term cycling capabilities of oxygen-deficient $\text{TiO}_2/\text{Li}_4\text{Ti}_5\text{O}_{12}$ (TiO_2/LTO) where $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a chemically lithiated phase grown from TiO_2 .²⁷⁴ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is of interest because of its well-defined potential for Li^+ intercalation at 1.55 V vs Li^+/Li . A comparison of TiO_2 nanosheets and TiO_2/LTO nanosheet electrodes with and without annealing under a H_2 environment ($\text{H-TiO}_2/\text{LTO}$) revealed the lowest charge transfer resistance for $\text{H-TiO}_2/\text{LTO}$ electrodes and the highest R_{ct} for TiO_2 electrodes. This was attributed to a higher concentration of oxygen vacancies in the $\text{H-TiO}_2/\text{LTO}$ electrode, as measured by XPS and TGA experiments.

4d. Na-Ion and Zn-Ion Batteries. Various monovalent and divalent ions in addition to Li^+ have been explored in metal oxide ion battery research. In particular, Na^+ has been frequently used as a monovalent ion in studying electrochemical performance of battery materials via EIS.²⁷⁷ Huang et al. explored silver-containing $\alpha\text{-MnO}_2$ cathode derivatives, $\text{Ag}_x\text{Mn}_8\text{O}_{16}$, where $x = 1.22$ or 1.66, as a host material for intercalation of Li^+ and Na^+ .²⁵³ These oxides possess a 2×2 tunnel structure where cations can intercalate. The use of Ag^+ further controls tunnel size and helps stabilize the structure. EIS studies showed that a significant decrease was observed in R_{ct} associated with charge transfer to the oxide when Na^+ intercalated in and out of the structure (Figure 23). R_{ct}

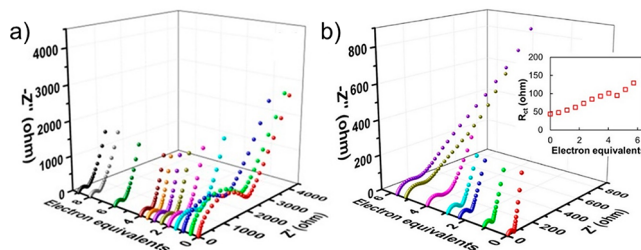


Figure 23. Comparison of Nyquist plots obtained from (a) Na^+ intercalation and (b) Li^+ intercalation into $\text{Ag}_{1.22}\text{Mn}_8\text{O}_{16}$ cathodes. Intercalation of Na^+ resulted in decreased charge transfer resistance, and intercalation of Li^+ resulted in increased charge transfer resistance. Reproduced with permission from ref 253. Copyright 2017 American Chemical Society.

stabilized at a consistent value once 4 electron equivalents of Na^+ were intercalated into the structure of $\text{Ag}_{1.22}\text{Mn}_8\text{O}_{16}$ and 1 electron equivalent for $\text{Ag}_{1.66}\text{Mn}_8\text{O}_{16}$, showing that stable structures were obtained at these conditions. This data was contrasted with results for Li^+ intercalation where a gradual increase in R_{ct} was observed as more Li^+ ions were incorporated. This result was explained on the basis of the similar ionic radii of Na^+ and Ag^+ , which led to very little structure displacement upon intercalation.

Wang et al. have used EIS to compare NaCrO_2 (NCO) powders synthesized via a decomposition reaction, followed by calcination (Ig-NCO) and a solid-state reaction (s-NCO), as cathode materials for Na-ion batteries.²²⁵ These synthetic conditions produce different morphologies which impact the capacity and long-term cycling capabilities of the materials. Studies using TEM and HRTEM reveal that Ig-NCO is made of large particles layered in multiple stacking sheets, whereas the s-NCO product is within the submicron range and has a flakelike particle morphology with distinct edges and an affinity to aggregate. Figure 24 shows EIS curves of Ig-NCO and s-NCO cathodes in the charged state of 3.6 V after different

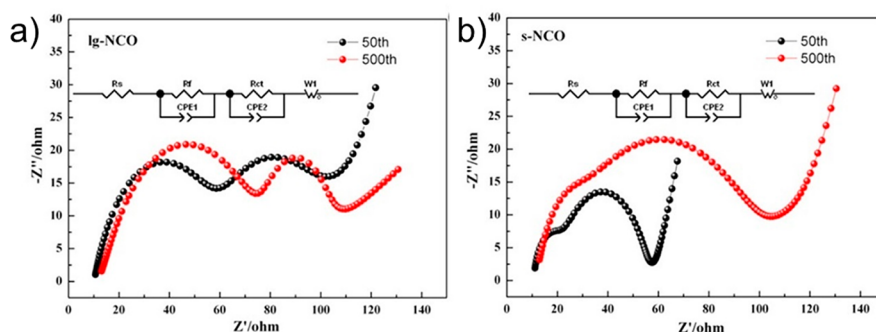


Figure 24. Nyquist plots and their respective equivalent circuits for (a) Ig-NCO electrodes and (b) s-NCO electrodes measured in the charged state of 3.6 V after a different number of cycles. Reproduced with permission from ref 225. Copyright 2019 American Chemical Society.

cycles at 0.1 C (charge rate). The Nyquist plots reveal two semicircles and a linear feature which represent the resistance of the surface film R_f , the charge transfer resistance R_{ct} , and the Warburg impedance Z_w , respectively, as discussed previously for Li-ion battery EIS studies. As the cycling number increased from 50 to 500, R_f for both oxides increased as the surface layer grew; however, R_{ct} decreased for Ig-NCO and increased for s-NCO. The smaller charge transfer resistance observed in Ig-NCO was attributed to suppression of side reactions due to its small specific surface area and highly (110)-oriented morphology, allowing improved intercalation and deintercalation of Na^+ during cycling.²²⁵

Metal oxide anodes such as CuO have also been studied as anode materials for Na-ion batteries with a reactivity similar to that described for lithium (i.e., $\text{CuO} + 2\text{Na}^+ + 2\text{e}^- \rightarrow \text{Cu} + \text{Na}_2\text{O}$). Nanoflake, nanoellipsoid, and nanorod structures were compared by Rath et al. using EIS to determine the diffusion coefficients of Na^+ for each structure.²²⁹ R_{ct} at the electrode/electrolyte interface of the nanorods was significantly lower than what was observed in the other nanostructures; therefore, the Warburg diffusion feature could be clearly resolved. In this case, Z_{Re} can be plotted directly versus $\omega^{-1/2}$ and the diffusion coefficient obtained from the slope based on eqs 17 and 18. Figure 25 shows Z_{Re} vs $\omega^{-1/2}$ along with determined diffusion

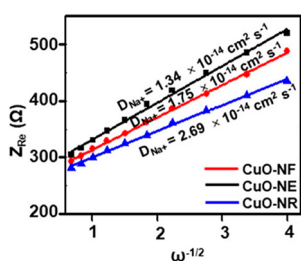


Figure 25. Z_{Re} vs $\omega^{-1/2}$ plot in the low-frequency region for CuO nanorod, nanoellipsoid, and nanoflake electrodes used as anodes in Na-ion batteries. Reproduced with permission from ref 229. Copyright 2018 American Chemical Society.

coefficients for each nanostructure. The larger diffusion coefficient determined for the nanorod morphology was attributed to a more favorable diffusion path along the length of the rod compared with the other nanostructures.

$$Z_{Re} = R_e + R_{ct} + \sigma\omega^{-1/2} \quad (17)$$

$$D_{\text{Na}^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C_0 \sigma^2} \quad (18)$$

Exploration of divalent ion batteries using EIS have mostly focused on Zn^{2+} ,^{244,254,256,278} however, some studies have appeared for Mg^{2+} .^{279–281} In the case of ZnMnO_2 batteries, correlations have been deduced using EIS between applied strain and the ionic conductivities of polyacrylamide hydrogel electrolytes.²⁵⁵ When compressional strain was increased to 22.2%, a dramatic decrease in resistance was observed, which was attributed to a shortened ionic transport distance as the compressional strain increases, thereby improving the efficiency of ionic migration. $\text{Zn}/\delta\text{-MnO}_2$ cells have also been studied using EIS to compare different cycling points, with equivalent circuit models provided for fitting as seen in Figure 26 to ultimately analyze the voltage and capacity of the material after long-term cycling.²⁴⁵ The additional circuit component seen in equivalent circuit 2 represents the growth of an additional passivation layer which is likely due to electrolyte decomposition. During cycling, small changes were seen in the resistance due to the electrolyte and the capacitance for the passivation layer. R_{ct} decreased and CPE_{ct}

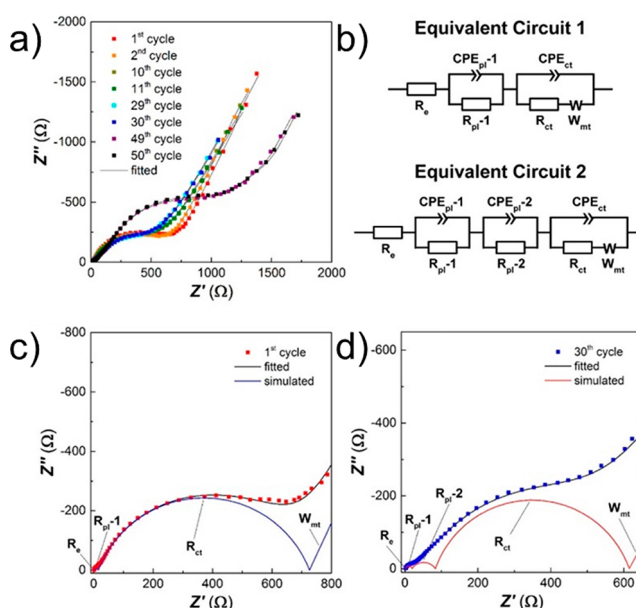


Figure 26. (a) Nyquist plots of $\text{Zn}/\delta\text{-MnO}_2$ cells at different cycle numbers. (b) Equivalent circuits. (c) Nyquist plots zoomed in for the first cycle showing minimal contribution for surface layers. (d) Nyquist plots zoomed in for the 30th cycle showing larger contributions from surface layers. Reproduced with permission from ref 245. Copyright 2017 American Chemical Society.

increased up to 30 cycles which could be explained by an increase in the surface area of the active materials.

5. CATALYSIS

5a. Overview. Electrocatalysis and photocatalysis of energy relevant chemical reactions using metal oxide electrodes has been investigated by a wide range of electrochemical techniques. In most cases, cyclic or linear sweep voltammetry in combination with chronoamperometry is used for catalysis studies; however, EIS has also been used to study the specific impact of the metal oxide interface on reactivity. Reactions which have been investigated using EIS include the oxygen evolution reaction (OER; $2\text{H}_2\text{O} \rightarrow 4\text{e}^- + 4\text{H}^+ + \text{O}_2$),^{282–313,2,314,315,33,316,5,317–319,37,320–328,31,32,329} the oxygen reduction reaction (ORR; $4\text{e}^- + 4\text{H}^+ + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$),^{291,330–338} the hydrogen evolution reaction (HER; $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$),^{339–345} as well as various forms of carbon dioxide reduction. These reactions are important for energy applications as they represent the conversion between electrical/solar energy into chemical energy and vice versa. For example, overall water splitting combines OER and HER catalysis to store 4.36 eV of energy per H_2 molecule generated. This reaction is important for the development of efficient electrochemical fuel cells as well as photoelectrochemical cells which convert solar energy directly to chemical energy.^{323,333,346,347} In the context of fuel cells and metal–air batteries, ORR is equally important as it represents the thermodynamic reversal of OER and allows for electrical energy to be extracted from O_2 .^{334,338,348,349} Development of metal oxide catalysts which can do both OER and ORR has indeed been an active area of research.^{336,337}

Electro/photocatalytic studies with metal oxides have focused on understanding the impact of morphology, surface defects states, and the purposeful addition of surface layers to enhance reactivity. Morphological changes have largely been modeled using simple Randle circuits (model A in Table 2) where decreased charge transfer resistance is attributed to better catalytic activity. Importantly, R_{ct} is inversely proportional to the exchange current at each applied potential. Therefore, Tafel plots may be constructed by plotting $\log(1/R_{\text{ct}})$ vs E_{app} and examining the slope.^{350,351} This method is particularly useful because it is automatically corrected for any series resistance in the electrical circuit. This resistance is known to greatly affect Tafel measurements from other techniques such as linear sweep voltammetry.

Defect states and surface layers have been studied using derivatives of models B and C (Table 2), where surface dependent features are modeled with a second RLC circuit either positioned in series with or imbedded within a primary RLC circuit intended to model the bulk properties of the metal oxide electrode. Particular attention has been paid to the capacitance of defects and surface layers to understand their energy level distribution.^{2,31–33,37,319} Diffusional resistance of electroactive reactants in solution (H_2O , H^+ , OH^- , O_2 , etc.) is not typically observed in these studies due to the inherently complex, multielectron reactions which must occur during charge transfer with the metal oxide.

In the following sections we discuss specific examples of EIS studies used to understand electrocatalysis and photocatalysis with metal oxide electrodes. We focus this discussion on examples related to OER and ORR catalysis given that these reactions are the most studied in the field of metal oxide electrodes across all electrochemical methods. It should be

noted, however, that a small number of HER and CO_2 reduction studies with EIS have been reported.^{341–345,349,352}

5b. OER/ORR Electrocatalysis. The goal of many electrocatalysis studies with metal oxides is to understand the specific role of surface termination on catalysis. Morphological changes inherently result in different exposed crystal faces and therefore different activation energies for catalysis at each distinct metal oxide surface. EIS has been an effective tool to study the influence of morphology and surface termination on ORR.^{291,296,330–332} and OER electrocatalysis.^{282–284,287,288,290–301,303} Morphologies such as core–shell nanoparticles,³⁵³ nanosheets,³⁵⁴ nanowires/nanorods,³⁵⁶ and nanocubes³⁵⁵ for various metal oxides have been studied by EIS. In these examples, clear changes in the charge transfer resistance of the metal oxide/electrolyte interface were assigned to differences in surface termination based on morphology. For example, Co_3O_4 nanorods terminated in (110) surfaces along their length were found to exhibit better OER electrocatalysis (i.e., lower R_{ct}) than Co_3O_4 nanocubes terminated in (100) facets.³⁵⁵ However, in many of these examples, metal oxide catalysts were synthesized using solution methods and then deposited onto conductive substrates for EIS measurements. Therefore, knowledge of the specific orientation of the metal oxide surface once deposited is often difficult to have or predict. Precise preparation of metal oxides grown on a single crystalline surface is required to ensure surface termination of a particular facet.

Poulain et al. synthesized electrocatalytic NiO thin films with (100)-, (110)-, and (111)-oriented facets grown on single crystalline MgO substrates.³⁵⁶ EIS experiments were performed over a range of applied potentials for the three NiO faceted samples where it was observed that the order of R_{ct} measured for OER was $\text{NiO}(100) < \text{NiO}(111) < \text{NiO}(110)$. This ordering indicated that the (110) surface was the most catalytically active, on the basis of the idea that β -NiOOH formation on the surface resulted in improved catalysis. The authors noted that NiO(111) surfaces observed similarly low R_{ct} values with NiO(110); however, these surfaces prefer to form a γ -NiOOH phase which is less stable. The much larger R_{ct} values observed for NiO(100) surfaces were attributed to its lower concentration of hydroxide sites and therefore lower catalytic activity. Cyclic voltammetry and chronoamperometry measurements observed the same ordering in terms of catalytic current.

Other studies of precise metal oxide termination have been reported for LaSrCoO_3 .^{334,338} These oxides have been shown to be great catalysts for ORR in the context of solid oxide fuel cells. In these devices, catalysis occurs at the interface between the metal oxide and a gas phase environment, as opposed to a liquid phase electrolyte which has been discussed throughout this review. Reduction of O_2 at these metal oxide catalysts results in an uptake of oxygen atoms into the lattice, which diffuse through a solid-state electrolyte such as yttria stabilized zirconia (YSZ) to the anode catalyst where they form H_2O upon oxidation of H_2 .

Lee et al. studied $\text{La}_2\text{NiO}_{4+\delta}$ thin films oriented on the (100) facet grown via pulsed layer deposition on YSZ substrates for ORR.³³⁸ EIS measurements were used to show a dramatic dependence of electrocatalysis on film thickness and the partial pressure of oxygen. Figure 27 shows Nyquist plots obtained at 550 °C for both variables where R_{ct} decreased for thinner films and higher partial pressures. These results suggested that thinner films were able to incorporate oxygen into their lattice

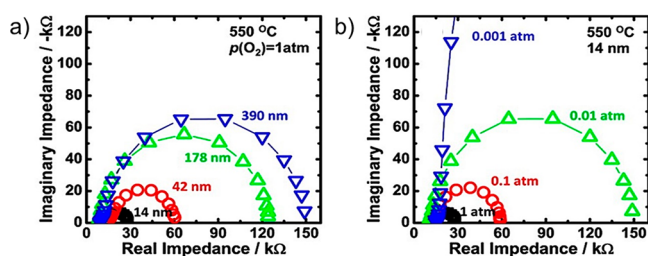


Figure 27. EIS results of microelectrodes for (100)-oriented epitaxial $\text{La}_2\text{NiO}_{4+\delta}$ thin films with varied (a) thickness and (b) oxygen partial pressure. The oxygen dependent data is shown for a 14 nm thick film. Reproduced with permission from ref 338. Copyright 2013 the American Chemical Society.

via surface oxygen exchange with a larger rate constant. High-resolution X-ray diffraction showed that thinner films were highly strained along the *c*-axis due to lattice mismatch with the substrate. The strained lattice was therefore believed to be responsible for the larger rate constant of surface oxygen exchange. Similar results have been observed by Lee et al. for (001)-oriented $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ where larger in-plane tensile strain observed for thinner metal oxide films resulted in smaller charge transfer resistance due to oxygen exchange.³³⁴ Additionally, these studies showed improved ORR kinetics due to a Sr-rich layer near the film surface.

5c. OER Photocatalysis. EIS studies coupled with steady-state photoexcitation of semiconductor metal oxides have been reported for investigating OER photocatalysis. Much of this work has focused on $\alpha\text{-Fe}_2\text{O}_3$ ^{2,5,31,32,37,314,315,317,318,320,321,324,325,328} and BiVO_4 ^{33,285,286,297,302,316,319,326,357} due to their narrow band gaps and visible light absorption; however, UV photocatalysis with TiO_2 ,^{358–361} ZnO ,^{339,362} IrO_2 ,^{340,353,363} and copper delafossites^{323,327} have also been reported. Here we focus on EIS studies that have been particularly important in understanding the role of surface defect states and cocatalysts in $\alpha\text{-Fe}_2\text{O}_3$ and BiVO_4 photoelectrodes.

The role of surface defect states in $\alpha\text{-Fe}_2\text{O}_3$ for photocatalytic OER has recently been reviewed by Tang and Arbuiol.³⁶⁴ These states naturally occur due to the contact of the metal oxide with the oxygen-rich aqueous solution. Klahr et al. reported a detailed EIS study that showed the significance of these states in the OER mechanism.² Figure 28 shows a Nyquist plot of EIS data collected at 0.65 and 0.70 V vs Ag/AgCl under 1 sun illumination by a white light source. The equivalent circuit used to model these data is shown in Figure 28 where $R_{\text{ct,trap}}$ and C_{trap} refer to the charge transfer and capacitance associated with defect (trap) states at the metal oxide/electrolyte interface. The terms $R_{\text{ct,bulk}}$ and C_{bulk} refer to the charge transfer and capacitance of bulk valence band states, and R_{trapping} describes the impedance associated with transferring holes between the bulk and surface defects. Theoretical justification for this model has been provided by Bisquet,³⁶⁵ and this model is commonly used to describe surface defects in metal oxide semiconductors.^{20,366–368} Modeling of the data revealed that $R_{\text{ct,bulk}} = 0$ under illumination, and all charge transfer through the metal oxide/electrolyte interface occurred through defect states described by the larger, low-frequency semicircle arc. The smaller, high-frequency arc was assigned to the parallel combination of $R_{\text{trapping}}||C_{\text{bulk}}$. In the absence of illumination, only a single semicircle arc was observed, and therefore, $R_{\text{ct,trap}} = 0$. This was an important result because it

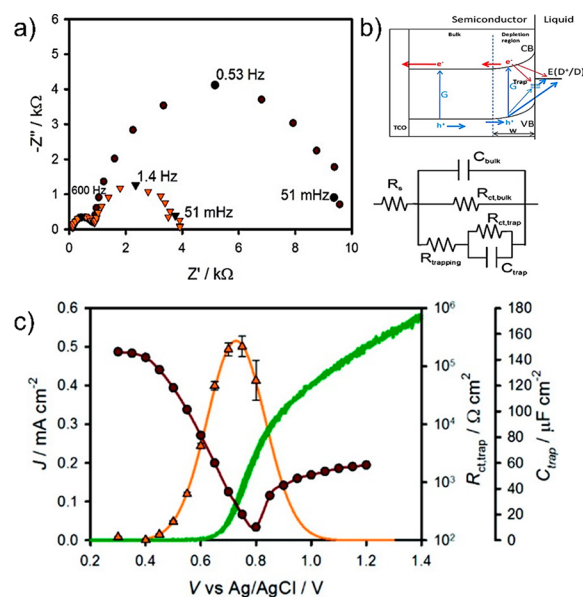


Figure 28. (a) Nyquist plots measured at pH 6.9 with applied potentials of 0.65 V (red circles) and 0.70 V vs Ag/AgCl (orange triangles) under 1 sun illumination. (b) Band diagram showing trap states relative to the conduction and valence bands of $\alpha\text{-Fe}_2\text{O}_3$ along with the equivalent circuit used to model EIS data. (c) Gaussian distribution of C_{trap} (orange triangles) and $R_{\text{ct,trap}}$ (red circles) measured by EIS overlaid with photocurrent measured by linear sweep voltammetry (green line). Reproduced with permission from ref 2. Copyright 2012 American Chemical Society.

indicated that defect states were only able to participate in OER if they were populated by holes under illumination. The capacitance associated with these defect states could be measured as a function of applied potential where a Gaussian distribution of states was observed just above the valence band edge. Other characteristic results such as a 59 mV shift in their energy levels with pH and an increase in their capacitance with illumination intensity further corroborated their existence. Importantly, the energetic distribution of these states was shown to occur directly at the onset of photocurrent measured by linear sweep voltammetry, indicating their importance in OER photocatalysis (Figure 28).

In a series of follow-up studies, Klahr et al. used similar EIS methods to study $\alpha\text{-Fe}_2\text{O}_3$ photocatalysis of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ on bare electrodes² and of H_2O with the addition of a Co-Pi (cobalt phosphate) cocatalysts.⁵ The $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ allowed them to observe the maximum photocatalytic properties of the metal oxide including contributions for surface defect states. The addition of Co-Pi to the surface of $\alpha\text{-Fe}_2\text{O}_3$ resulted in larger photocurrent and a lower onset potential for OER. Similar studies had previously been reported,^{5,37} but Klahr et al. were able to show the dependence of OER photocatalysis on the density and distribution of Co-Pi electronic states using EIS. Figure 29 shows the capacitance of these states measured under illumination as a function of Co-Pi thickness deposited via photoelectrodeposition and expressed as the quantity of charge passed in mC cm^{-2} . Data were obtained on the basis of an equivalent circuit similar to that shown in Figure 28 above. The capacitance data clearly showed an increase in the density of Co-Pi states above those for the surface defect states (SS) of the underlying $\alpha\text{-Fe}_2\text{O}_3$. As the thickness of Co-Pi grew, the entire $\alpha\text{-Fe}_2\text{O}_3$ surface became coated and the surface capacitance was only reflective of Co-Pi. Concomitant with

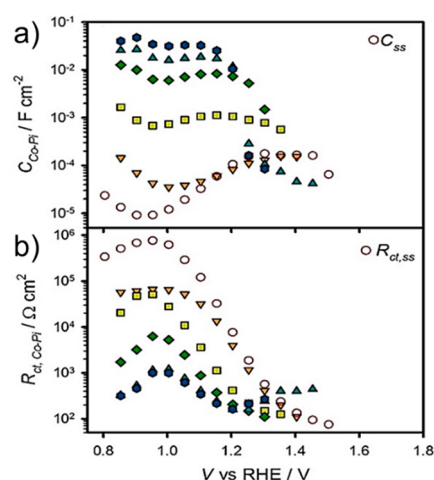


Figure 29. (a) Capacitance and (b) resistance values measured for the Co-Pi catalyst deposited on the surface of α -Fe₂O₃ photoelectrodes. Colored symbols represent different amounts of deposited catalyst: 0 (red open circles), 1 (orange triangles), 2 (yellow squares), 15 (green diamonds), 45 (teal triangles), and 90 mC cm⁻² (blue hexagons). Reproduced with permission from ref 5. Copyright 2012 American Chemical Society.

the growth of Co-Pi capacitance was a decrease in $R_{ct,Co-Pi}$ as these states became the active sites for OER catalysis. A more recent study by Carroll and Gamelin deposited Co-Pi onto a mesoporous α -Fe₂O₃ photoelectrode and observed similar EIS behavior in terms of capacitance and resistance associated with OER catalysis by Co-Pi surface states.³⁷ The mesoporous structure of α -Fe₂O₃, however, resulted in a $\sim 1.5\times$ increase in photocurrent at 1.6 V vs RHE due to the higher surface area of the photoelectrode.

In addition to α -Fe₂O₃, BiVO₄ has also been extensively studied for OER photocatalysis.^{33,285,286,297,302,316,319,357} Jeong et al. studied BiVO₄ photoelectrodes modified by hexavalent dopants (Cr⁶⁺, W⁶⁺, and Mo⁶⁺), heterojunction formation with WO₃, and deposition of Co-Pi as a cocatalyst.²⁸⁶ EIS data revealed lower charge transfer resistances for OER for WO₃/BiVO₄ heterojunctions due to an increase in light absorption and the incorporation of the Co-Pi cocatalyst. Doping with W⁶⁺ and Mo⁶⁺ was also found to slightly decrease R_{ct} ; however, Cr⁶⁺ resulted in a larger R_{ct} . In-depth analysis of surface state contributions was not performed in this particular study. However, Shi et al. recently presented a detailed EIS study on W-doped BiVO₄ photoelectrodes where the %W was varied from 0 to 5%.³³ Photocurrent as a result of OER was found to increase dramatically from 0 to 2% doping and then decrease for 5%. EIS data collected under illumination and fit to an equivalent circuit similar to that shown in Figure 30 revealed that surface states were induced by W-dopants and maximized in their capacitance at the 2% level. A decrease in surface state capacitance for 5% W⁶⁺ was consistent with photocurrent data. The maximized benefit of W-doping was reasoned on the basis of a balance in the density of surface states which controlled catalysis at the metal oxide surface and the density of dopant donors in the bulk which contributed to conductivity and extraction of electrons.

Further studies of BiVO₄ photoelectrodes with EIS have shown that continuous illumination under basic pH conditions can also result in a high concentration of surface states without the need for dopants. Trześniewski et al. synthesized BiVO₄

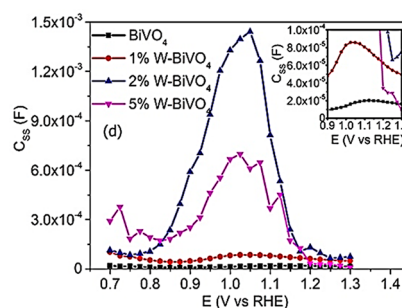


Figure 30. Surface state capacitance obtained from fitting photo-induced EIS data for BiVO₄ and 1%, 2%, and 5% doped W-BiVO₄ photoelectrodes. Reproduced with permission from ref 33. Copyright 2018 American Chemical Society.

thin films of 50, 100, 200, and 300 nm thicknesses by spray pyrolysis and exposed them to 10 h of continuous solar simulated illumination.³¹⁹ The EIS measurements and subsequent modeling with the same equivalent circuit shown in Figure 30 showed the existence of a broad distribution of surface states as opposed to the monoenergetic distribution observed for W-doped BiVO₄ and α -Fe₂O₃ discussed above. The mechanism of formation of these states was proposed to be due to trapping of photoexcited electrons via reduction of V⁵⁺ $\rightarrow$ V⁴⁺ in the bulk and subsequent migration of holes to the surface to form an adsorbed layer of oxyl/hydroxyl species. Importantly, the phototreatment of BiVO₄ electrodes resulted in greatly improved photocatalysis for OER where the internal quantum efficiency increased from $\sim 20\%$ for untreated electrodes to $\sim 100\%$ following phototreatment at pH 10.

6. CONCLUSIONS AND OUTLOOK

In conclusion, EIS is a highly versatile technique that can be used to study metal oxide electrodes in a wide variety of energy applications. The key feature of this electrochemical method is the frequency dependence exhibited by fundamental circuit elements used to describe the flow of current through the metal oxide interface. Modeling EIS data to well-supported equivalent circuits is a critical aspect toward gaining physically relevant information. Detailed studies as a function of modulation frequency and applied potential can reveal significant information about the capacitance of electronic states and their resistance for electron transfer.

Data such as this is important to wide band gap metal oxide semiconductors used in heterojunction solar cells. Understanding the energy distribution of electronic defects states within the band gap can lead to improvements in performance by controlling the prevalence for these states. By far, the largest amount of work has been focused on n-type metal oxide semiconductors such as TiO₂, ZnO, and SnO₂. A similar level of detailed studies on p-type metal oxides such as NiO and CuGaO₂ is warranted. In particular, charge transport through these metal oxides is uniquely complex given the mixed metal/oxygen valence band. Fundamental EIS studies could lead to great improvement in our understanding of these materials.

In terms of ion batteries, understanding the role of surface passivation layers that occurs at anodes and cathodes is of great importance for energy storage. Extended battery cycling has shown a continuous increase in these layers which contributes to higher overall resistance for electrical energy storage and thus degraded battery performance. EIS has proven to be important in this regard and will continue to be used to analyze

new metal oxide electrodes as they are discovered. While metal oxides are commercially used for Li-ion batteries, a push to develop metal oxide battery electrodes for application in alternative ion batteries is of great interest. Low-toxicity battery components that are environmentally friendly and composed of earth abundant metals are ideal for future advancements in energy storage devices. Candidates include both alternative monovalent ion batteries such as Na⁺ and K⁺ as well as multivalent ion batteries such as Zn²⁺ and Ca²⁺. As metal oxides are investigated to be implemented in alternative ion batteries, EIS will prove to be a useful analytical technique to measure their performance capabilities for these relatively new and scarcely studied applications.

The use of metal oxide electrodes as electrocatalysts and photocatalysts for energy relevant chemical reactions such as oxygen evolution/reduction and proton reduction will continue to be an important area of research due to the need to convert renewable forms of energy into chemical fuels. EIS has been applied rather sparingly in this area, likely due to the fact that other techniques such as linear sweep voltammetry are more easily applied, yet the opportunity for further studies is enormous. Studies highlighted here show the impact EIS can have on developing an intimate understanding of defect states at the metal oxide interface and the influence of these states on catalysis. Further EIS studies in the areas of metal oxide degradation in aqueous media and the use of metal oxide surface layers to protect crystalline semiconductor surfaces could provide useful knowledge about long-term stability of metal oxide interfaces.

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Notes

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