# CHAPTER 1 Computational Modeling of Photocatalytic Cells

### STEVEN J. KONEZNY AND VICTOR S. BATISTA\*

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107, USA \*Email: victor.batista@yale.edu

# 1.1 Introduction

Solar energy conversion into chemical fuels is one of the "holy grails" of the 21st century. Significant research efforts are currently underway toward understanding natural photosynthesis and artificial biomimetic systems. Photocatalytic cells absorb solar energy and use it to drive catalytic water oxidation at photoanodes:<sup>1,2</sup>

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2(g)$$
 (1.1)

effectively extracting reducing equivalents from water (*i.e.*, protons and electrons) that can be used to generate fuel, for example  $H_2(g)$  by proton reduction:

$$4H^+ + 4e^- \to 2H_2(g)$$
 (1.2)

The water oxidation half-reaction, introduced by Equation (1.1), is the most challenging obstacle for solar hydrogen production,<sup>3–6</sup> since it requires a fourelectron transfer process coupled to the removal of four protons from water molecules to form the oxygen–oxygen bond. In Nature, this process is driven by solar light captured by chlorophyll pigments embedded in the protein antennas

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of photosystem II and the energy harvested is used to oxidize water in the oxygen-evolving complex.<sup>3,7</sup> The development of photocatalytic solar cells made of earth-abundant materials that mimic these mechanisms and photocatalyze water oxidation has been a long-standing challenge in photoelectrochemistry research, dating back to before the discovery of ultraviolet water oxidation on n-TiO<sub>2</sub> electrodes by Fujishima and Honda 40 years ago.<sup>8</sup> However, progress in the field has been hindered by a lack of fundamental understanding of the underlying elementary processes and the lack of reliable theoretical methods to model the photoconversion mechanisms.

The landscape of research in solar photocatalysis has been rapidly changing in recent years, with a flurry of activity in the development and analysis of catalysts for water oxidation<sup>9–23</sup> and fundamental studies of photocatalysis based on semiconductor surfaces.<sup>24,25</sup> Significant effort is currently focused on the development of more efficient catalysts based on earth-abundant materials and various strategies for the design of molecular assemblies that efficiently couple multielectron photoanodic processes to fuel production. The outstanding challenge is to identify robust materials that could catalyze the necessary multielectron transformations at energies and rates consistent with solar irradiance.

A promising approach for photocatalytic water oxidation involves designing high potential photoanodes based on surface-bound molecular complexes and coupling the anodic multielectron reactions to fuel production at the cathode with long-range free energy gradients. Such a design problem requires fundamental understanding of the factors affecting photoabsorption, interfacial electron transfer to the photoanode, charge transport, storage of oxidizing equivalents for catalysis at low overpotentials and irreversible carrier collection by fuel-forming reactions at the cathode. The characterization of these processes by computational techniques clearly requires methods for modeling the complete photocatalytic mechanism as well as methods for understanding and characterizing the elementary steps at the detailed molecular level, including visible light sensitization of semiconductor surfaces by molecular adsorbates, charge transport and redox catalytic processes. This chapter reviews recent advances in the field, with emphasis on computational research focused on modeling photocatalytic cells and the elementary processes involved at the molecular level. The reviewed studies are part of an interdisciplinary research program including synthesis, electrochemistry and spectroscopy in a joint theoretical and experimental effort to advance our understanding of structure/function relations in high potential photoanodes based on functionalization of nanoporous TiO<sub>2</sub> thin films with transition metal catalysts.

The chapter is organized as follows. Section 1.2 reviews recent computational efforts focused on modeling current–voltage characteristics of functional dyesensitized solar cells (DSSCs) under operational conditions, with emphasis on the effect of the nature of the molecular adsorbates and redox couple on the overall efficiency of photoconversion. Section 1.3 reviews recent developments of methods for inverse design of molecular adsorbers with suitable solar-light photoabsorption. Section 1.4 reviews the development of theoretical models of

charge transport in nanoporous metal oxide thin films, with emphasis on the fluctuation-induced tunneling conduction (FITC) model as applied to the description of the temperature dependence of dc and ac conductivities and direct comparisons to experimental data. Section 1.5 is focused on reliable methods for modeling the redox properties of molecular adsorbates, with emphasis on the reduction of systematic errors introduced by either the level of theory (*i.e.*, the choice of density functional theory (DFT) functional, basis set and solvation model) or the electrochemical measurement conditions, including the nature of the solvent, electrolyte and working electrode. Section 1.6 presents a summary of the conclusions and outlook.

# 1.2 Photoelectrochemical Device Modeling

Modeling can provide a fundamental insight into the effects of individual system components on the overall device functionality.<sup>26</sup> A parameter-space analysis by systematic variation in device composition can lead to the discovery of assemblies with optimum performance. Insight into observed trends can be extracted from the parameters of equivalent-circuit current–voltage simulations. Here, we illustrate this systematic approach by analyzing of a series of high-potential porphyrin photoanodes, metal oxides and redox couples, suitable for photocatalytic cells. We show that DSSCs based on porphyrin dyes demonstrate superior performance owing to increased open-circuit voltage and the short-circuit current when using the relatively high-potential bromide–tribromide redox couple as a regenerative electron mediator rather than the standard iodide–triiodide couple. The resulting potentials progress toward sufficiently positive values suitable for water oxidation chemistry.

### 1.2.1 Modeling Current-Voltage Characteristics

The current–voltage characteristics, that is the current density J as a function of the applied voltage V, of photoelectrochemical cells are used to extract important parameters related to device performance. In the case of a DSSC, parameters of interest include the short-circuit current  $J_{SC} \equiv J(V=0)$ , open circuit voltage  $V_{OC} \equiv V(J=0)$  and the power conversion efficiency. However, owing to the complex nature of DSSC operation, these data alone offer a limited understanding of the underlying physical/electrochemical processes. Device modeling of current–voltage characteristics is needed in order to develop this understanding and establish property–performance relationships. This kind of an analysis is useful not only to DSSCs but to photoelectrochemical cells in general since they share common system components.

The equivalent circuit diagram used to model solar cell current-voltage characteristics is shown at the top of Figure 1.1. The schematic energy level diagram of a DSSC at the bottom of Figure 1.1 shows the various charge transfer processes that occur in photoelectrochemical cells and relates these processes to current pathways *via* components of the model circuit. An illumination current density  $J_{\rm L}$  is induced upon photoexcitation of the



Figure 1.1 Simple equivalent circuit (top) for modeling solar cell current–voltage characteristics and energy level diagram (bottom) mapping the various charge transfer processes in a DSSC to the current pathways of the model circuit. The dominant mechanisms are described by a current density  $J_L$  induced upon photoexcitation and electron injection into the conduction band of the metal oxide semiconductor surface MO, linear ( $J_{SH}$ ) and non-linear ( $J_D$ ) reverse current densities in parallel with photocurrent source and a series resistance  $R_S$  to account for electrode and ionic resistances. In Section 1.2.2: MO = TiO<sub>2</sub>, SnO<sub>2</sub>, X = Br, I.

adsorbed dye molecule, followed by interfacial electron injection into the conduction band of the metal oxide semiconductor. Direct recombination of the photoinjected carriers with redox species in the electrolyte solution and the dark current along the edges of the cell contribute to the shunt resistance  $R_{\rm SH}$  of the cell. Under applied bias, the cell can be modeled as a diode with a current density  $J_{\rm D}$  that runs parallel to  $J_{\rm L}$  and shunt current density  $J_{\rm SH}$  that opposes  $J_{\rm L}$ . The cell also has a net series resistance  $R_{\rm S}$ , which includes the resistance of the metal oxide and the ionic resistance of the redox pair in the electrolyte.

The output current density J of the solar cell as a function of applied bias voltage in the equivalent circuit model is:<sup>26,27</sup>

$$J = J_{\rm L} - J_0 \left\{ \exp\left[\frac{q(V + JAR_{\rm S})}{fkT}\right] - 1 \right\} - \frac{V + JAR_{\rm S}}{AR_{\rm SH}},\tag{1.3}$$

where  $J_0$  is the reverse saturation current, k is the Boltzmann constant, T is the absolute temperature, q is the electronic charge, A is the device area and f is the

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ideality factor. Equation (1.3), which was originally developed to describe the non-ideal diode behavior of inorganic semiconductor p-n junctions, has been applied to a wide range of solar cell technologies including hydrogenated amorphous silicon p-i-n cells, Cu(In,Ga)Se<sub>2</sub> cells, organic bulk heterojunction cells and DSSCs.<sup>26-29</sup> In the case of photoelectrochemical cells,  $J_0$  is related to the energy level alignment between the bottom of the conduction band of the metal oxide and the excited state donor level of the dye D\*. This differs from  $J_L$ , which is related to the coupling between D\* and states in the metal oxide that are closer in energy and therefore typically deeper in the conduction band. This means that a clear strategy for improving device performance is to adjust the energetic position of D\* relative to the metal oxide density of states to achieve maximum  $J_L$  and minimum  $J_0$ . The benefits of this approach are apparent in Equation (1.3), which gives an estimate of the open circuit voltage of the cell in the regime of high shunt resistance:

$$V_{\rm OC} \approx \frac{fkT}{q} \ln\left(\frac{J_{\rm L}}{J_0} + 1\right) \tag{1.4}$$

We note that this model could be extended to incorporate electrochemical processes. For example, the electrochemical kinetics at the electrodes is more appropriately described by the Butler–Volmer equation with non-linear J-V characteristics rather than an ohmic resistor. However, as shown in Section 1.2.2, much insight can be gained when using the equivalent circuit model of Figure 1.1 and Equation (1.3) to do a comparative analysis of a series of device architectures in which the relevant energy levels are systematically varied.

### **1.2.2 Bioinspired High-Potential Porphyrin Photoanodes**

Table 1.1 compares the equivalent circuit parameters that characterize the performance of solar cells based on sensitizers 1, 2 and 3 (Figure 1.2) and N719. The analysis includes solar cells with either  $I_3^-/I^-$  or  $Br_3^-/Br^-$  redox couples as regenerative electron mediators and TiO<sub>2</sub> or SnO<sub>2</sub> nanocrystalline substrates. It is shown that the series resistance increases when the TiO<sub>2</sub> photoanode is replaced by  $SnO_2$ , for a given dye and electrolyte, consistent with lower in vacuo room temperature nanoporous-film dark conductivities in TiO<sub>2</sub>  $(\sim 10^{-10} \Omega^{-1} \text{ cm}^{-1}; \text{ Figure 1.7})$  compared to  $\text{SnO}_2$   $(\sim 10^{-6} \Omega^{-1} \text{ cm}^{-1};$ Figure 1.10). In addition, the series resistance  $R_S$  decreases for iodide relative to bromide for dyes 1-3, consistent with the higher conductivity of iodide when compared to bromide at low concentrations.<sup>30</sup> In addition to changes caused by the intrinsic properties of the ions, the substitution of I<sup>-</sup> by Br<sup>-</sup> leads to a reduction in the saturation recombination current  $J_0$  and an increase in the open circuit voltage  $V_{\rm OC}$ , as observed for solar cells based on sensitizers 1–3. These changes in the current–voltage characteristics are due to a tighter binding of bromide to the porphyrin adsorbates, as shown by the analysis of the electrostatic potentials.

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Dye	Oxide	Electrolyte	$J_{\rm L}~({\rm mA/cm^2})$	$J_0 (\mathrm{mA/cm}^2)$	$AR_{\rm S}~(\Omega {\rm cm}^2)$	$AR_{\rm SH}~({\rm k}\Omega{\rm cm}^2)$	f	$J_{\rm SC}~({\rm mA/cm^2})$	$V_{OC}(\mathbf{V})$	FF	η (%)
1	TiO <sub>2</sub>	$I_{3}^{-}/I^{-}$	0.15	$3.81 \times 10^{-6}$	4.60	2.74	1.72	0.14	0.37	0.31	0.02
		$Br_3^-/Br^-$	0.13	$1.59 \times 10^{-7}$	19.5	4.64	2.23	0.13	0.62	0.26	0.02
	$SnO_2$	$I_{3}^{-}/I^{-}$	0.97	$1.47 \times 10^{-2}$	4.72	1.23	3.18	1.01	0.31	0.32	0.10
	-	$Br_3^-/Br^-$	2.58	$3.35 \times 10^{-4}$	77.8	9.79	2.81	2.53	0.64	0.47	0.76
2	TiO <sub>2</sub>	$I_{3}^{-}/I^{-}$	0.93	$4.20 \times 10^{-6}$	5.65	1.12	1.84	0.90	0.55	0.51	0.25
	-	$Br_3^-/Br^-$	0.17	$9.47 \times 10^{-7}$	27.9	4.15	2.43	0.21	0.69	0.42	0.06
	$SnO_2$	$I_{3}^{-}/I^{-}$	2.83	$4.82 \times 10^{-6}$	9.31	0.16	1.34	2.51	0.37	0.41	0.39
	-	$\dot{Br}_{3}^{-}/Br^{-}$	1.35	$1.16 \times 10^{-6}$	138	24.7	1.62	1.32	0.59	0.51	0.40
3	TiO <sub>2</sub>	$I_{3}^{-}/I^{-}$	0.26	$2.15 \times 10^{-3}$	2.69	0.22	3.18	0.25	0.37	0.26	0.02
	-	$Br_3^-/Br^-$	0.17	$5.46 \times 10^{-9}$	30.4	3.81	1.76	0.16	0.62	0.30	0.03
	$SnO_2$	$I_{3}^{-}/I^{-}$	0.76	$1.85 \times 10^{-2}$	4.85	11.3	3.46	0.81	0.31	0.37	0.09
	-	$Br_3^-/Br^-$	3.48	$3.13 \times 10^{-5}$	69.4	2.47	2.20	3.37	0.66	0.45	1.00
N719	TiO <sub>2</sub>	$I_{2}^{-}/I^{-}$	9.62	$5.53 \times 10^{-3}$	3.96	45.9	3.97	9.59	0.77	0.61	4.48
	-	$Br_3^-/Br^-$	0.16	$7.09 \times 10^{-5}$	9.58	7.95	3.63	0.15	0.67	0.45	0.05
	$SnO_2$	$I_{2}^{-}/I^{-}$	11.1	$3.26 \times 10^{-2}$	16.3	0.30	2.92	10.33	0.46	0.38	1.82
	2	$Br_3^-/Br^-$	0.25	$6.95 \times 10^{-5}$	9.97	5.03	3.46	0.04	0.08	0.71	0.00

**Table 1.1** Solar cell performance parameters including the parameters of the equivalent-circuit model, short-circuit current density  $J_{SC}$ , open-circuit voltage  $V_{OC}$ , fill factor *FF* and solar-to-electrical energy conversion efficiency  $\eta$  at 100 mW cm<sup>-2</sup> illumination (AM 1.5).



Figure 1.2 Compounds 1, 2 and 3.



Figure 1.3 Energy level diagrams illustrating reduction potentials of relevant half reactions. Ground state and excited state potentials of porphyrins 1 (red), 2 (green) and 3 (blue) were determined by cyclic voltammetry measurements together with absorption and emission spectra. Approximate potentials for the TiO<sub>2</sub> and SnO<sub>2</sub> conduction bands<sup>31,32</sup> and the  $I_3^-/I^-$  and  $Br_3^-/Br^-$  couples<sup>33,34</sup> are also shown. The O<sub>2</sub>/H<sub>2</sub>O couple is 0.82 V at pH = 7. All potentials are reported in V vs. the normal hydrogen electrode (NHE).

The analysis of electrostatic potentials suggest that  $Br^-$  ions interact more strongly than I<sup>-</sup> and bind more closely to the aromatic rings owing to their smaller ionic radius (Br<sup>-</sup>: 1.82 Å, I<sup>-</sup>: 2.06 Å). The resulting stabilization includes anion  $\pi$  interactions with the permanent quadrupole moments of the aromatic rings.<sup>35,36</sup> Up to 4 Br<sup>-</sup> anions per porphyrin are predicted to bind to 1 and 3 with binding energies in the -5 to -13 kcal mol<sup>-1</sup> range. Two Br<sup>-</sup> ions

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bind to the pentafluorophenyl groups while the other two bind to the carbomethoxyphenyl groups (Figure 1.4). In addition,  $Br^-$  can bind to Zn in 2, with a binding energy of -12.5 kcal mol<sup>-1</sup>. However, metal-anion interactions for Zn - I<sup>-</sup> and Pd - Br<sup>-</sup> are much weaker (*i.e.*, comparable to thermal fluctuations).<sup>26</sup> In contrast to bromide, iodide ions show much weaker specific interactions with 1-3 probably due to the larger ionic radius.

The analysis of adsorbate ions interactions provided fundamental understanding of the origin of changes in the I–V characteristics induced by changes in the nature of the redox couple. The larger concentration of smaller ions shifts the electron donor and acceptor states and the edge of the conduction band to more negative potentials, preventing recombination and reducing  $J_0$ (Figure 1.4). Therefore, the open circuit voltage  $V_{\rm OC}$  is increased and the slope of the characteristic curve is reduced as  $V \rightarrow 0$ . The illumination current density increases (or decreases) when the donor state is poised where the conduction band has a larger (or smaller) density of states.

The comparative analysis of porphyrin-based photoanodes suggests that new high-potential sensitizers and device architectures can significantly expand the available parameter space of DSSC current-voltage simulation methods. In particular, a suitable choice of electron-withdrawing substitution groups, or transition metal, can shift the porphyrin redox potential and make it sufficiently positive to activate water oxidation catalysts.<sup>26,34</sup> However, the porphyrin excited state which injects the photoexcited electrons into the metal oxide conduction band typically experiences a similar stabilization when changing the metal center or the substitution groups, giving similar vertical excitation bands as seen in the absorption spectra (Figure 1.3). Therefore, it is natural to expect that adsorbates that generate deep positive holes by excitation with visible light would photoinject electrons only into metal oxides with conduction bands that are more positive than the NHE (e.g., SnO<sub>2</sub>). Achieving efficient water oxidation and proton reduction by visible light photocatalysis on sensitized metal oxide surfaces thus might require two-photon schemes.<sup>37</sup> A simple example is shown in Figure 1.5 where red photons inject electrons into the photocathode at potentials more negative than the NHE, while blue photons generate holes in

Figure 1.4 Top: Illustration of photoinduced electron transfer into the semiconductor conduction band. Middle: Bromide binding to the bis-pentafluorophenyl free-baseporphyrin sensitizer bearing linkers for attachment to metal oxide surfaces: two equivalent low-energy positions at 3.9 Å from the pentafluorophenyl groups, stabilized by  $\pi$ -anion interactions with a stabilization energy of -7.9 kcal mol<sup>-1</sup> and two similar positions at 4.9 Å from the carbomethoxyphenyl groups stabilized by -4.9 kcal mol<sup>-1</sup>. Bottom: Shift of the edge of the conduction band upon substitution of  $I_3^-/I^-$ (dotted lines) by  $Br_3^-/Br^-$  (solid lines) in solar cells based on 1, 2, or 3, using  $TiO_2$  or  $SnO_2$  nanocrystalline substrates. Such shift leads to a reduction of  $J_0$  since the barrier for back electron transfer, from the bottom of the metal oxide conduction band to the donor state, is increased. The illumination current density  $J_{\rm L}$  is smaller (left) or larger (right) in  $Br_3^{-}/Br^{-}$ , according to the smaller or larger amplitude of the DOS at the energy of the donor state.





**Figure 1.5** Energy diagram (left) and schematic representation (right) of a photocatalytic cell based on a 2-photon tandem Z-scheme with high potential porphyrins covalently attached to SnO<sub>2</sub>.

porphyrins adsorbed on the photoanode, sufficiently positive as to activate water oxidation catalysts.

# **1.3** Inverse Design of Photoabsorbers

The search for molecular adsorbates for high potential photoanodes with high photoconversion efficiency is challenging. Most of the work reported to date has been based on direct molecular design using empirical strategies, where typical "guess-and-check" procedures face the challenge of selecting suitable candidates from an immense number of accessible stable molecules. Therefore, there is significant interest in the development of inverse design methods that bypass the combinatorial problem in the development of materials for solar energy conversion.

In recent work, a systematic inverse design methodology suitable to assist the synthesis and optimization of molecular sensitizers for dye sensitized solar cells has been proposed.<sup>38</sup> The method searches for molecular adsorbates with suitable photoabsorption properties through continuous optimization of "alchemical" structures in the vicinity of a reference molecular framework, avoiding the exponential scaling problem of high throughput screening techniques. It has been as applied to the design and optimization of linker chromophores for TiO<sub>2</sub> sensitization using the recently developed phenylace-tylacetonate (*i.e.*, phenylacac) anchor<sup>39</sup> as a reference framework. A novel anchor (3-acac-pyran-2-one) was found to be a local optimum, with improved sensitization properties compared to phenyl-acac. Its molecular structure is related to known coumarin dyes which could be used as lead chromophore anchors for practical applications in DSSCs. The findings are particularly relevant to the



Figure 1.6 Right: Density of states (DOS) of a bare  $TiO_2$  anatase nanostructure (a) and functionalized with phenyl-acac (b) and 3-acac-pyran-2-one (c). The solid-black areas in (b) and (c) are the projected DOS of the adsorbate molecules. Red and blue arrows point to electronic states with a predominant contributions to the absorption. Left: Solar spectrum model based on a black body at 5523 K.<sup>38</sup>

design of sensitizers for DSSCs because of the wide variety of structures that are possible and they should be equally useful for other applications such as ligand design for catalytic nanocrystalline structures (Figure 1.6).

The proposed methods use linear combination of atomic potential Hamiltonians

$$H_{i,j} = \sum_{A=1}^{N_{type}} \sum_{A'=1}^{N_{type}} b_i^{(A)} b_j^{(A')} h_{i,j}^{(A,A')},$$

defined in terms of tight-binding model Hamiltonians  $h_{i,j}^{(A,A')}$  and participation coefficients  $b_i^{(A)}$  that give the probability weight for the various possible atom types A at atomic sites i in the molecule. While for real molecules these coefficients  $b_i^{(A)}$  are either 1 or 0, since they must define pure atom types, they can change continuously *in silico* (between 0 and 1) while the molecule undergoes transformations in the "alchemist" space of intermediate states. The evolution is typically steered by gradients that optimize the expectation value of the molecular properties of interest. Upon convergence, optimum structures typically have atomic sites with fractional  $b_i^{(A)}$  that are readily rounded off to obtain the closest possible real molecule with optimized properties, assessed by using high-level quantum chemistry methods.

Photoanodes are designed for optimum activation with solar light, quantifying the photoabsorption intensity,  $f_{sum} = \sum_{pq} = f_{pq} \times P(\lambda_{pq})$ , as the sum of products of the solar power spectrum  $P(\lambda_{pq})$  and the oscillator strengths  $f_{pq} = 8\pi^2 v_{pq} m_w c |\mu_{pq}|^2 / (3he^2)$  associated with electronic state transitions  $q \leftarrow p$ with wavelengths  $\lambda_{pq}$ . The photoabsorption properties are computed as generalized expectation values,

$$ar{O} = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{A=1}^{N_{type}^{i}} \sum_{B=1}^{N_{type}^{j}} Q_{i}^{*(A)} Q_{j}^{(B)} O_{i,j}^{(A,B)}$$

in the basis of states obtained by solving the Schrödinger equation:  $\mathbf{H} \mathbf{Q} = \mathbf{E} \mathbf{S} \mathbf{Q}$ , where  $\mathbf{Q}$  is typically the matrix of eigenvectors in the basis of Slater-type atomic orbitals (STO),  $\mathbf{E}$  is the diagonal matrix of energy eigenvalues and  $\mathbf{S}$  is the overlap matrix

$$S_{i\alpha,j\beta} = \sum_{A=1}^{N_{type}^{i}} \sum_{B=1}^{N_{type}^{i}} b_{i}^{*(A)} b_{j}^{(B)} S_{i\alpha,j\beta}^{(A,B)}$$

While computationally demanding, these methods can be parallelized and scale only as  $(NN_{type})^2$ , with N and  $N_{type}$  the number of atoms and atom types, respectively. In contrast, assessing all possible  $N_{type}^N$  structures by brute force screening would obviously scale exponentially with  $N_{type}$ . Therefore, it is natural to anticipate that this kind of systematic methodology will provide powerful computational methods as well as guidelines for design of new materials for efficient solar energy conversion.

# 1.4 Charge Transport in Nanoporous Metal Oxides

The electronic mechanisms responsible for dark conductivity in nanoporous metal oxide materials control the efficiency of energy photoconversion in a wide range of applications, including photovoltaic devices,<sup>40–42</sup> photocatalysis and remediation of hazardous waste,<sup>41–44</sup> electrochromic windows and displays,<sup>42,45,46</sup> and chemical sensors.<sup>42,47</sup> Measurements in the 78–335 K temperature range show dc conductivity values spanning over four orders of magnitude, with a high-temperature Arrhenius dependence that gradually changes into a temperature-independent plateau at low temperatures. It has recently been shown that a FITC mechanism is fully consistent with TiO<sub>2</sub> and SnO<sub>2</sub> conductivity measurements over this entire temperature range.<sup>48,49</sup> These findings suggest that charge transport in nanoporous metal oxide films depends strongly on the properties of the junctions linking the constituent nanoparticles.

In recent years, there have been significant contributions towards understanding charge transport in nanoporous titania thin films.<sup>50–60</sup> The most popular models include variable range hopping (VRH) and/or multiple trap and release (MTR) of electrons in an electrically homogeneous medium containing a distribution of traps. These models have been particularly successful when applied to the conductivity of photogenerated electrons at temperatures experimentally accessible in a native device environment. However, they predict a temperature (*T*) dependence of the dark DC conductivity of the form ln  $\sigma \propto T^{-\alpha}$ , where  $\alpha = 1$  in the MTR model<sup>61</sup> and a = 1/4 for VRH.<sup>62</sup> As shown in Figure 1.7, this dependence does not account for the observed saturation of dark conductivity at low temperature, as reported here and elsewhere.<sup>63–66</sup> In contrast, the FITC model offers a quantitative description of conductivity over



Figure 1.7 Comparison of the dark DC conductivities of nanoporous  $TiO_2$  films, made by sintering Sigma-Aldrich (Sample A, filled circles) and Ishihara (Sample B, open squares) nanoparticles, as a function of inverse temperature (temperatures in K are shown on the top axis). Experimental data (solid circles and red boxes) are fitted by using the fluctuation-induced tunneling conduction (FITC) model (solid line), the variable-range hopping model (VRH, short-dashed line) and the multiple-trap-and-release model (MTR, long-dashed line).

the entire temperature range with a single set of structural parameters, predicting not only the Arrhenius high-temperature behavior but also the tunneling regime at low temperature. Since the model can be closely tied to the nanoporous film microstructure, it should provide valuable insight in the development of high performance electrode materials.

Most conductivity measurements reported to date have been limited to the high-temperature regime since the low-temperature conductivity is typically very small ( $\sigma \approx 10^{-13} \Omega^{-1} \text{cm}^{-1}$ ) and, therefore, difficult to measure. In the limit, the Arrhenius-type behavior predicted by the FITC model is indistinguishable from models based solely on thermally activated processes. Thus, it is not surprising that, until recently, the FITC mechanism has been largely overlooked.<sup>48,49</sup> Recent work, however, has been focused on high sensitivity measurements that allow for reliable measurements at very low temperatures and on the characterization of the samples by scanning electron microscope (SEM) images, powder X-ray diffraction (XRD) measurements and atomistic modeling. The combined experimental and theoretical analysis provided insight into the nature of conductivity in sintered TiO<sub>2</sub> thin films, as characterized by the FITC mechanism, with rate-limiting processes determined by the barriers for electron transport through the nanoparticle contact junctions.<sup>67</sup>

### 1.4.1 Fluctuation-Induced Tunneling Conductivity

The FITC model for dc conductivity is described in our previous work<sup>48,49,68,69</sup> and in other studies that apply a FITC model to systems with a comparable



**Figure 1.8** (a) Contact junction of two noncrystalline  $\text{TiO}_2$  nanoparticles (blue) sintered by disordered  $\text{TiO}_2$  (green). (b) Energy diagram for electron transport through the junction, showing the potential energy barrier under a bias  $V + V_T$ , where V is the applied voltage and  $V_T$  is the voltage fluctuation caused by thermal fluctuations in the density of free electrons at the junction. (c) Equivalent *RC* circuit of the contact junction.

microstructure.<sup>70–73</sup> A nanoporous metal oxide film can be modeled as a network of junctions that form where the nanoparticles come into contact [Figure 1.8(a)]. An important component of the FITC mechanism is that the junction is electrically inhomogeneous. Molecular dynamics simulation results for sintered TiO<sub>2</sub> nanoparticles show that anatase TiO<sub>2</sub> nanoparticles have a non-crystalline TiO<sub>2</sub> shell surrounding a crystalline core (Figure 1.9), which is consistent with reports of TiO<sub>2</sub> nanoparticle sizes, obtained from microscopy data, being larger than the size of the crystalline centers of the nanoparticles size, determined by XRD.<sup>48,74</sup> The conduction band offset between the crystalline and non-crystalline TiO<sub>2</sub> phases creates a barrier for electron transport. The fact that our data are consistent with the FITC model suggests that this



**Figure 1.9** (a) Molecular dynamics simulation results of two 4-nm particles sintered at 450 °C. (b) Cylindrical sample cut from (a) showing the crystalline anatase core and noncrystalline shell of the nanoparticles. (c) Average atomic root-mean-squared deviation (RMSD) relative to bulk anatase.

core shell structure applies to  $SnO_2$  nanoparticles and, by extension, other nanoporous metal oxides as well.

The FITC model describes the nanoparticle contact junction as an effective potential energy barrier for the transferring electron, owing to the intrinsic disorder of the semiconductor material between the nanocrystalline particles [Figure 1.8(b)].<sup>48</sup> At a given temperature, the electron transmission probability depends on the zero-field barrier height  $\varphi_0$ , effective width w and junction area A. In addition, fluctuations in the free-electron density on either side of the junction give rise to large voltage fluctuations that modulate the effective tunneling barrier. Typical parameters for TiO<sub>2</sub> nanoparticle junctions are given in Table 1.2. For a static dielectric constant of  $\varepsilon_r \approx 20$  inside the junction, the effective junction capacitance  $C = \varepsilon_r \varepsilon_0 A/w$  [Figure 1.8(c)] is on the order 10<sup>-6</sup> pF. Therefore, small thermal fluctuations in the density of free electrons near the junction give rise to significant voltage fluctuations with  $\langle V_T^2 \rangle = k_B T/C$ .

As a function of the electric field  $\mathscr{E}$ , the dark dc conductivity can be expressed as:

$$\sigma_{dc}(\mathscr{E}) = \frac{\gamma \langle j_{dc}(\mathscr{E}) \rangle A}{tV}$$
(1.5)

where V is the voltage across the junction, t is the thickness of the sample,  $\langle j_{dc}(\mathscr{E}) \rangle$  is the thermal average of the net dc current density and  $\gamma$  is a factor that relates the conductance of a single junction to the sheet conductance of the film.

**Table 1.2** FITC model parameters used for samples A and B in Figure 1.7, including the effective area A, width w, zero-field barrier height  $\varphi_0$  of the junction and the effective junction diameter given by  $d_j \equiv 2\sqrt{A/\pi}$  compared to the nanocrystallite diameter  $d_{nc}$  measured by XRD.<sup>48</sup>

	$d_{nc}$ (nm)	$\varphi_0 \text{ (meV)}$	<i>w</i> (nm)	$A (nm^2)$	$d_j$ (nm)
А	17.0	421	3.45	71.6	9.54
В	15.9	388	3.73	22.5	5.35

The tunneling current density is determined by the density of electrons per unit time incident on the junction and the transmission probability as a function of energy. Integrating over all electron energies one obtains:<sup>48,68</sup>

$$j_{dc}(\mathscr{E}) = \frac{mqk_B^2 T^2}{2\pi^2 \hbar^3} \left( \left\{ \frac{e^{-2\chi w\xi}}{T'^2} (1 - e^{-T'q\mathscr{E}w/k_B T}) \right\} + \left\{ \frac{e^{-2\chi w\xi}}{1 + T'} (1 - e^{-T'q\mathscr{E}w/k_B T}) \right\} \right) + \left\{ e^{-\varphi_m/k_B T} (1 - e^{-q\mathscr{E}w/k_B T}) \right\} + \left\{ \frac{e^{-2\chi w\xi}}{1 + T'} [(1 - e^{-(1 - T')\varphi_m/k_B T}) - (1 - e^{-(1 - T')(\varphi_m + q\mathscr{E}w)/k_B T}) e^{-T'q\mathscr{E}w/k_B T}] \right\},$$

$$(1.6)$$

where *m* is the charge carrier mass,  $\hbar$  is the reduced Planck constant,  $\chi = (2m\varphi_0/\hbar)^{1/2}$  is the tunneling constant, *q* is the electron charge, the dimensionless temperature-dependent parameter *T'* is given by  $2\chi w\eta k_B T/\varphi_0$  and  $\varphi_m$  is the maximum in the potential barrier.  $\xi$  and  $\eta$  are field-dependent dimensionless parameters that originate from the first two terms in a power series expansion of the exponent of the transmission coefficient under the WKB approximation.<sup>75</sup> Equations (1.5) and (1.6) provide a more explicit form of the dc conductivity than the approximation  $\sigma \approx \sigma_0 \exp[-T/(T_0 + T)]$ , where  $\sigma_0$ ,  $T_0$  and  $T_1$  are temperature-independent parameters. The simplified expression has a limited range of validity and can lead to inaccurate estimations of the contact junction parameters.

Equation (1.6) accounts for both the Arrhenius regime and the temperatureindependent low-temperature behavior, as described by the fluctuation-induced tunneling conductivity model. Each of the terms in curly brackets include a description of the forward current density component, in the direction of the applied electric field and a backflow current density in the opposite direction. The first term corresponds to the net current in the low-temperature limit, with an abrupt change in the density of states at the Fermi energy, while the other terms are corrections caused by expansion of the Fermi–Dirac distribution to first order in temperature.

Figure 1.7 compares the DC conductivity of nanoporous TiO<sub>2</sub> thin films and the corresponding conductivity curves obtained according to the FITC model

with structural parameters given in Table 1.2. Note that the FITC model describes the conductivity data over the entire temperature range, including both the thermally activated high-temperature regime (T > 250 K) and the temperature-independent regime (T < 150 K) in quantitative agreement with experiments. In contrast, the VRH and MTR models can only account for one of the two regimes with a unique set of parameters. The high-temperature conductivity for sample B gives an activation energy of 439 meV and a pre-exponential factor of  $7.4 \times 10^{-4} \ \Omega^{-1} \text{cm}^{-1}$ , assuming a thermally activated process (MTR model), while the VRH model gives  $\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}]$  with  $\sigma_0 = 1.3 \times 10^{20} \ \Omega^{-1} \text{cm}^{-1}$  and  $T_0 = 7.4 \times 10^9$  K. The effective zero-field barrier heights of 420 and 390 mV predicted by the FITC model for samples A and B, respectively, are similar to the activation energies  $E_a$  measured for the high-temperature data in various studies.<sup>63-66</sup> The slope of  $\ln \sigma vs. 1/T$  in the high-temperature regime is largely determined by  $\varphi_0$  and therefore  $\varphi_0 \approx E_a$ .

The value of  $\varphi_0$  depends on the distribution of traps below the conduction band, typically attributed to oxygen vacancies, Ti<sub>3</sub><sup>+</sup> states and interface states.<sup>63–66,76</sup> Therefore,  $\varphi_0$  depends on measurement and fabrication conditions such as the sintering time and exposure to ambient oxygen and Ndoping.<sup>64–66,76</sup> In fact, the experimental data show that the low-temperature plateau in the conductivity of sample A is nearly an order of magnitude lower than that of sample B, reflecting both a larger barrier height and a wider tunneling width (see Table 1.3). Increasing  $\varphi_0$  typically decreases the lowtemperature plateau conductivity and increases the slope of  $\ln \sigma vs. 1/T$  in the high-temperature region. Increasing the tunneling width w only reduces the former,  $^{69}$  while increasing the effective junction area A increases the conductivity for the entire temperature range, with a negligible effect on the hightemperature slope. Therefore, it is clear that the parameters A and  $\varphi_0$  determine the dark dc conductivity and can be tuned to optimize performance. The challenge ahead is thus to find materials that generate lower conduction band offsets, or fabrication conditions that optimize the defect distributions at the contact junctions.

**Table 1.3** Power law exponent *s* for the frequency-dependent component of the ac conductivity measured on different days and the FITC model parameters extracted from the dc component for the sintered SnO<sub>2</sub> nanoparticle film. *A*, *w* and  $\varphi_0$  are the effective area, width and zero-field barrier height of the junction, respectively and  $d_j$  is the effective junction diameter given by  $d_j \equiv 2\sqrt{A/\pi}$ .

Day	S	$\varphi_0 \; (meV)$	w (nm)	$A (nm^2)$	$d_j$ (nm)
1	1.23	166	3.13	5.58	2.67
9	1.13	137	3.68	44.2	7.50
11	1.09	113	3.49	11.6	3.83
20	$\sigma_{dc}$ only	102	3.43	29.7	6.14

The FITC model parameters have been compared to atomistic models of the contact junctions, obtained by sintering anatase nanoparticles using annealing molecular dynamics simulations, after thermalization of the system at 450 °C. Typical simulations of the sintering process were performed by using the LAMMPS package<sup>77</sup> in the NVT ensemble and the force field by Matsui and Akaogi<sup>78</sup> to describe the interactions between the atoms of the nanoparticle as in previous work.<sup>79</sup> The temperature was maintained at 450 °C using a Nose-Hoover thermostat with a damping time of 10 fs. The atomic positions and velocities were updated using the velocity-Verlet algorithm with a time step of 1 fs and a total run time of 250 ps. Atomic root mean square deviations (RMSD) were quantified to characterize the extension of the contact junctions by alignment of the anatase crystal structure to the crystalline core of each nanoparticle. Figure 1.9(a) shows a representative configuration of two sintered TiO<sub>2</sub> nanoparticles, obtained by annealing molecular dynamics simulations at 450 °C. A cylindrical sample extracted from these two nanoparticles, shown in Figure 1.9(b) reveals the internal atomic structure with non-crystalline TiO<sub>2</sub> at the contact junction and nanoparticle surface. The analysis of atomic RMSDs relative to the anatase crystal structure shown in [Figure 1.9(c)] quantifies the disorder observed in the non-crystalline phase at the junction and extremities of the cylindrical core. These RMSDs clearly indicate that the TiO<sub>2</sub> nanoparticles have a noncrystalline shell surrounding the crystalline core. This core shell structure is consistent with reports of the overall TiO<sub>2</sub> nanoparticle size, obtained from microscopy data, being larger than the nanocrystallite size, determined by XRD.<sup>48,74</sup> These results also agree with conductivity measurements of unsintered, spin-coated nanoparticle thin films that display both thermally activated and temperature-independent conductivity regimes,<sup>63</sup> suggesting fluctuation-induced carrier tunneling between crystalline cores through noncrystalline shells.

SEM and XRD data, as well as computational structural models, show that tunneling junctions are formed upon sintering TiO<sub>2</sub> nanoparticles, owing to the resulting multiphase composition at the contact.<sup>48</sup> The tunneling barrier height is determined by the energy difference between the conduction band of crystalline anatase and the electronic states of disordered  $TiO_2$  at contact (see Figure 1.8). This picture is consistent with optical pump/THz probe measurements providing evidence that the AC conductivity is within a factor of 2 to 4 of the single crystal DC value, although the DC conductivity of photoexcited nanocrystalline TiO<sub>2</sub> and ZnO is suppressed relative to bulk values.<sup>52, 80</sup> These results are therefore consistent with conductivity limited by transport through disordered  $TiO_2$  at the contact junctions, while carriers are relatively free within the crystalline nanoparticles. These observations are limited to vacuum conditions, while the presence of impurities, gas, or an electrolyte at the junctions might have a significant influence on the shape of the barriers and therefore on the overall conductivity through the nanoparticle network. It is therefore imperative to explore these effects since they are of great technological relevance.

#### **1.4.2** Power Law Dependence of the Dark AC Conductivity

The total measured ac conductivity can often be separated into frequencydependent and dc components and expressed as:

$$\sigma(\omega) = \sigma_{dc} + \sigma'(\omega) \tag{1.7}$$

where  $\sigma'(\omega)$  is the frequency-dependent component of the total conductivity  $\sigma$ . In a wide variety of disordered materials, including the systems studied in this work, Equation (1.7) is valid and  $\sigma'(\omega)$  has a power law form:<sup>81–83</sup>

$$\sigma'(\omega) = c\omega^s \tag{1.8}$$

where both the power law coefficient c and exponent s have temperature and frequency dependences that are indicative of the underlying charge transport mechanism. The functional forms of these parameters have been derived for many different models based on quantum mechanical tunneling or hopping. For example, the VRH model predicts a temperature-independent though frequency-dependent s, with a value of 0.8 for a typical characteristic relaxation time of  $10^{-13}$  s<sup>-1</sup> and a frequency-dependent s, though its value tends toward s = 1 as  $T \rightarrow 0$  K.<sup>83</sup> Current efforts are focused on deriving functional forms of c and s based on FITC. The present study focuses on extractions of the dc component, which was discussed in the previous section.

Figure 1.10 shows the temperature dependence of the dc conductivity on several measurement days spanning a 20-day period. The conductivity of the sample steadily grows with time and saturates after 20–25 days.<sup>49</sup> Such aging of the sintered  $\text{SnO}_2$  film is not surprising, as it is well known that the nanoporous semiconductor films are highly sensitive to the environment owing to their large

**Figure 1.10** Temperature dependence of the dc conductivity of the SnO<sub>2</sub> sample. Solid lines illustrate the FITC model fitting. The corresponding fitting parameters are listed in Table 1.3.



surface areas, a fact widely exploited in chemical sensor applications.<sup>42,47</sup> We ascribe the aging to changes (under ambient conditions) in the concentration of trap states, which have been attributed to oxygen vacancies,  $Ti_3^+$  states and interface states.<sup>76</sup> In the FITC model,  $\varphi_0$  is affected by defect states since they can reduce the effective barrier height for tunneling, though it is important to note that the defect states at the contact junction are relevant.

The measured conductivity is well described by the model at all stages of sample aging. The results of FITC model fitting are shown by solid lines in Figure 1.10 and the contact junction parameters are listed in Table 1.3. The junction width w did not change appreciably as the sample aged and no systematic change in the junction area A was observed. This suggests that physical rearrangement of the nanoparticles was not the primary cause of the increased conductivity over time. The large spread in the obtained values of A is likely to be due to a low sensitivity of the FITC fitting procedure to this parameter compared to w and  $\varphi_0$  for the range of junction parameters involved. There was, however, a systematic lowering of the tunneling barrier  $\varphi_0$  with sample aging (Table 1.3), which is consistent with continuous contaminant adsorption to  $SnO_2$  at the nanoparticle contact junctions. Contaminant adsorption can result in mid-barrier electronic states in the necking region that effectively lower  $\varphi_0$ . Learning how to design materials and fabrication conditions to minimize  $\varphi_0$ is of particular interest for designing materials for solar energy conversion applications because the conductivity is most sensitive to this parameter for the entire range of temperatures studied, including room temperature.

### **1.4.3 Experimental Methods**

Anatase nanoparticles were obtained from Sigma-Aldrich Corporation and Ishihara Corporation with diameters of < 25 nm and 7 nm, respectively. 1.5 g of TiO<sub>2</sub> was added to 1.3 mL of water, followed by sonication for 15 minutes. For the conductivity measurements, the nanoparticle slurry was spread onto a bottom electrode between two fiberglass spacers, which were  $200 \pm 4 \,\mu\text{m}$  thick with measured resistance > 200 T $\Omega$ . Immediately thereafter, the top electrode was applied, the excess slurry was removed and the sample was dried for 24 h at  $\sim$  70 °C. Dried samples were annealed at 450 °C for 1 h, the typical sintering conditions used for DSSCs. The sample electrodes were high chromium content stainless steel (grade 309). Samples for electrical measurements were lightly clamped with grade 309 bolts to maintain constant sample-to-electrode contact during the measurement and eliminate the effects of thermal expansion. The samples were loaded in a cryostat (Janis ST-100) and kept in the dark under vacuum (< 20 mTorr) for more than 24 h prior to measurement. A Stanford Research Systems SR570 low-noise current preamplifier was used to supply a 4 V bias and measure the current in a two-terminal measurement. To quantify the contact resistance in our devices, we varied the thickness of the  $TiO_2$ nanoparticle films. We found that the use of chromium-rich stainless steel as the contact surface minimizes both the oxide layer formed on the electrode during sintering and the corresponding contact resistance, which is negligible compared to the resistance of the  $TiO_2$  film.

SnO<sub>2</sub> nanoparticles with diameters of 22–43 nm where purchased from Alfa Aesar (tin (IV) oxide, NanoArc) for ac impedance and dc resistance measurements on sintered nanoparticle films. Nanoparticle slurry was made from 1.1 g of nanoparticle powder and 1 ml of distilled water by mixing with pestle and mortar. The sample was prepared with electrodes as described above for anatase samples, dried for 1 week at room temperature and then annealed in air at 450 °C for 40 minutes, the typical sintering conditions used for SnO<sub>2</sub> in DSSCs.<sup>84</sup> The applied bias voltage for the SnO<sub>2</sub> sample was 0.2 V and the sample displayed a linear *I–V* curve at room temperature at bias voltages up to 1 V. AC impedance was measured in the 0.3–30 000 Hz range using a Stanford Research Systems SR830 digital lock-in amplifier with ac biases of 0.25 and 1 V.

# 1.5 Calculations of Redox Potentials: Reduction of Systematic Error

We recently presented a practical, yet rigorous, methodology for quantitative predictions of redox potentials of transition metal complexes.<sup>85</sup> This is a particularly powerful tool in the context of solar energy conversion since it can give valuable insight into catalytic mechanisms and provide guidelines for the design of new electrocatalysts. In Section 1.2, we emphasized the importance of the potential of the regenerative electron mediators (e.g.,  $I_3^-/I^-$  vs.  $Br_3^-/Br^-$  redox couples), the position of the donor excited state level relative to the DOS of the metal oxide conduction band and the general investigation and optimization of the energy level alignment between of the redox active species in photoelectrochemical cells (Figure 1.1). Just as the ground and excited states can be estimated experimentally using cyclic voltammetry together with absorption and emission spectra, these data can be predicted using calculations of the ground state redox potential in parallel with the absorption spectra simulation methodologies discussed in Section 1.3. These predictive abilities enable the rational design of system components (e.g., sensitizer, redox mediator, photocatalyst) with optimal energetics.

The method reduces systematic errors that result from the theoretical approach (*i.e.*, the choice of DFT functional, basis set and solvation model) as well as the electrochemical measurement conditions, including the nature of the solvent, electrolyte and working electrode. Therefore, this method is particularly reliable in correlating experimental and theoretical data, even for secondand third-row transition metal complexes for which larger deviations have been previously reported. Standard methods for computation of redox potentials are commonly applied in electrochemical studies,<sup>86–101</sup> although methodologies that could account for systematic uncertainties about experimental or computational origin had yet to be established. Earlier reports typically documented deviations between experimental and theoretical values of redox 150–540 mV range for most of the available potentials in the

methodologies.<sup>86–94</sup> While these deviations continue to stimulate the development of more sophisticated DFT functionals, basis sets and solvation models, we note that deviations in the documented experimental data can often be a major factor in accounting for discrepancies of comparable magnitude. This is largely due to the fact that redox properties are typically quite sensitive to the particular choice of solvent, electrode, or electrolyte conditions. Therefore, identifying and reducing these sources of error is critical in establishing the capabilities and limitations of existing methods as well as for the design of new computational approaches.

In this section we outline a systematic methodology for removing uncertainties that are commonly included in comparisons between experimental and theoretical redox potentials, which are frequently reported relative to external reference couples, or reference electrodes. We study benchmark redox couples, including complexes that span three transition metal rows in various non-aqueous solvents. It is shown that the use of appropriate references, measured under the same conditions and calculated by using compatible computational frameworks, allows quantitative correlations between experimental and theoretical data. This approach leads to DFT redox potentials with standard deviations comparable to the experimental errors of cyclic voltammetry measurements, even at a rather modest level of theory (64 mV standard deviation for DFT/UB3LYP/LACVP/6-311G\* level; see Figure 1.11).



**Figure 1.11** Top: Correlation between measured  $E_{exp}^0$  and calculated  $E_{calc}^0$  redox potentials in V vs. RC, where RC =  $[FeCp_2]^{0/+}$ ,  $[Ru(bpy)_3]^{2+/3+}$  and  $[Ir(acac)_3]^{0/+}$  for first-, second-, and third-row transition-metal complexes, respectively, at the DFT/UB3LYP/LACVP/6-311G\* level of theory. Bottom: Distribution in  $E_{calc}^0 - E_{exp}^0$  (- 2 mV mean and 64 mV standard deviation).



Other Benchmark Redox Couples

Figure 1.12 Benchmark redox couples.

This is shown for a series of benchmark redox couples (Figures 1.12 and 1.13), including  $([MCp_2]^{0/+}(Cp = \eta^5 - cyclopentadienyl), [MCp^*_2]^{0/+}(Cp^* = \eta^5 - 1,2,3,4,5-pentamethylcyclopentadienyl), [M(bpy)_3]^{2+/3+}$  (bpy = 2,2'-bipyridine) and [Ir(a-cac)\_3]^{0/+} (acac = acetylacetonate), with M = Fe, Co, Ni, Ru, Os, or Ir) in various non-aqueous solvents [acetonitrile (MeCN), dimethyl sulfoxide (DMSO) and dichloromethane (DCM)].

#### 1.5.1 Methodology and Benchmark Results

The Gibbs free energy change  $\Delta G(\text{soln})$ , associated with the redox transition illustrated in Scheme 1.1, gives the absolute potential of a redox couple R/P, as follows:

$$E_{\text{calc}}^{\text{abs}} = \frac{\Delta G(\text{soln})}{nF} \tag{1.9}$$

where *n* is the number of moles of electrons involved in the redox reaction, *F* is the Faraday constant and  $\Delta G(\text{soln}) = \Delta G(g) + \Delta G_{\text{solv}}^{\text{P}} - \Delta G_{\text{solv}}^{\text{R}}$ . The resulting values are usually reported relative to a reference electrode (RE), such as the standard hydrogen electrode (SHE), or the silver-silver chloride saturated calomel electrode (SCE):

$$E_{\text{calc}}^{0}(\mathbf{V} \text{ vs. } \mathbf{RE}) = E_{\text{calc}}^{\text{abs}}(\mathbf{V}) - E_{\text{exp},\text{RE}}^{\text{abs}}(\mathbf{V})$$
(1.10)



**Figure 1.13** Cyclic voltammograms of  $[CoCp_2]^{0/+}$  (blue),  $[CoCp_2]^{0/+}$  (red),  $[FeCp_2]^{0/+}$  (green),  $[FeCp_2]^{0/+}$  (black),  $[Ir(acac)_3]^{0/+}$  (grey) and  $[Ru(bpy)_3]^{2+/3+}$  (purple) couples in 0.1 M [NBu<sub>4</sub>][BF<sub>4</sub>] in acetonitrile (100 mV s<sup>-1</sup> scan rate, T=25 °C, current density of  $[Ir(acac)_3]^{0/+}$  is reduced by a factor of 3).



Scheme 1.1 Thermodynamic cycle used for the calculation of changes in free energy in solution  $\Delta G(\text{soln})$  from states R to P based on gas-phase minimumenergy geometries and solvation free energies  $\Delta G_{\text{solv}}$ .

Experimental redox potentials are typically reported with respect to a reference redox couple (RC), such as ferrocene/ferrocenium ( $[FeCp_2]^{0/+}$ ):

$$E^{0}_{\exp}(\mathbf{V} \text{ vs. } \mathbf{RC}) = E^{0}_{\exp}(\mathbf{V} \text{ vs. } \mathbf{RE}) - E^{0}_{\exp,\mathrm{RC}}(\mathbf{V} \text{ vs. } \mathbf{RE})$$
(1.11)

Therefore, comparisons between calculated  $E_{calc}^{0}(V vs. RE)$  and experimental  $E_{exp}^{0}(V vs. RE)$  values require accurate potentials of the redox couples relative to the reference electrodes. However, the experimental values of both the redox couples and reference electrodes vary by hundreds of millivolts from solvent to solvent, or from experiment to experiment with the same solvent but different electrolytes (Table 1.4). Furthermore, the SCE typically generates a liquid junction potential that may not be reproducible in a given experiment

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Solvent	$E^{\rm abs}_{\rm exp,SHE}({\rm V})$
Water	4.24-4.44
Acetonitrile	4.56-4.66
Dimethylsulfoxide	3.83-4.04
Ethanol	4.20-4.24

 
 Table 1.4
 Experimental redox potentials reported
 for the SHE in various solvents.<sup>102–105</sup>

**Table 1.5** Redox potentials for the  $[FeCp_2]^{0/+}$  couple (in V vs. SCE) in various solvents and electrolyte solutions.<sup>107–110</sup>

Solvent	$Li[ClO_4]^a$	$[NBu_4][ClO_4]^{108}$	$[NEt_4][PF_6]^{109}$	$[NBu_4][PF_6]^{110}$
MeCN	0.31	0.40	0.38	0.40
DMSO		0.45	0.43	
DCM		0.48		0.46
DMF		0.47	0.46	0.45

<sup>a</sup>Kuwana *et al.*,<sup>107</sup> quarter-wave potential.

and non-aqueous reference electrodes are prone to issues of reproducibility caused by electrode surface chemistry.<sup>106</sup> In addition, the reference redox couple (such as the ferrocene/ferrocenium pair) can change by tens to hundreds of mV with solvent or electrolyte (see Table 1.5 and Section 1.5.3).<sup>107-110</sup> All of these aspects therefore introduce systematic errors into the correlation between experimental and theoretical data. Removing this uncertainty requires comparison of experimental and calculated redox potentials relative to a redox couple measured under the same solvent and electrolyte conditions, rather than relative to a reference electrode.

An outstanding challenge is to identify a set of redox couples that could be used as internal references for a wide range of electrolytes, solvents and working electrode conditions. Calculated redox potentials would then be reported as follows:

$$E_{\text{calc}}^{0}(V \text{ vs. } \mathbf{RC}) = E_{\text{calc}}^{\text{abs}}(V) - E_{\text{calc},\text{RC}}^{\text{abs}}(V)$$
(1.12)

where both  $E_{calc}^{abs}$  and  $E_{calc,RC}^{abs}$  are computed according to Equation (1.9). Analogous internal reference methodologies are common practice in other fields (e.g., reports of NMR chemical shifts) and reduce the systematic uncertainties caused by the sensitivity of the measurements to experimental conditions. Recent studies have shown that errors are significantly reduced when  $E_{exp}^{0}(V vs. RC)$ , obtained via Equation (1.11), is compared to  $E_{\text{calc}}^{0}(\text{V vs. RC})$  calculated *via* Equation (1.12) and the following criteria are met:<sup>85</sup> (*i*)  $E_{\text{calc}}^{\text{abs}}$  and  $E_{\text{calc,RC}}^{\text{abs}}$  in Equation (1.12) are calculated using identical conditions (e.g., same level of theory and solvent parameters); (ii)  $E_{exp}^0$  and

 $E_{\exp,RC}^0$  in Equation (1.11) are measured under identical conditions, for example, the same solvent, electrolyte and working electrode; (*iii*) A reference transition metal complex is chosen for  $E_{\exp,RC}^0$  in Equation (1.11) and the calculation of  $E_{calc,RC}^{abs}$  in Equation (1.12) is such that the metal lies in the same row of the periodic table as the complex used to calculate  $E_{calc}^0$ . These criteria are discussed in more detail in Sections 1.5.3 to 1.5.5.

### **1.5.2 Density Functional Theory Computational Methods**

DFT calculations were performed using the B3LYP exchange correlation functional with unrestricted Kohn-Sham wave functions (UB3LYP) as implemented in the Jaguar electronic structure program.<sup>111</sup> Minimum energy configurations were obtained by using a mixed basis in which the metal centers are described by the non-relativistic effective core potentials (ECPs) of the LACVP basis set. Different levels of theory were used in an effort to compare the effect of the ligand basis set on the resulting correlation between calculated and experimental data. In order of increasing computational cost, the ligand basis sets investigated were 6-31G, 6-311G\* and Dunning's correlation-consistent triple- $\zeta$  basis set<sup>112-114</sup> cc-pVTZ(-f), which includes a double set of polarization functions. In addition, the geometry optimizations based on 6-31G and 6-311G\* basis sets were followed by UB3LYP single point energy calculations with the cc-pVTZ(-f) basis. The resulting correlations with experimental data were analyzed to assess the minimum computational effort necessary for quantitative prediction of redox potentials and the validity of the single-point approximation method, a commonly used method to save on computational cost, as it applies to calculations of redox potentials.

All reduction potentials were computed, according to Equation (1.9), by calculating the free energy changes  $\Delta G(\text{soln})$  associated with reduction of the complexes in solution, as follows:

$$\Delta G(\text{soln}) = \Delta G(g) + \Delta G_{\text{solv}}^{\text{P}} - \Delta G_{\text{solv}}^{\text{R}}$$
(1.13)

where  $\Delta G(g) = \Delta H(g) - T\Delta S(g)$  is the free energy change for the reduction reaction in the gas phase. Solvation free energies for reactants and products,  $\Delta G_{solv}^R$  and  $\Delta G_{solv}^P$ , respectively, were computed using the standard self-consistent reaction field approach for the gas phase minimum energy configurations with dielectric constants of  $\varepsilon = 8.93$ , 37.5 and 47.24 and solvent radii of 2.33, 2.19 and 2.41 Å for DCM, MeCN and DMSO, respectively.<sup>111,112</sup>

### 1.5.3 Method Benchmark Results

The correlation between the computational and experiment data vs. RC, where  $RC = [FeCp_2]^{0/+}$ ,  $[Ru(bpy)_3]^{2+/3+}$  and  $[Ir(acac)_3]^{0/+}$  for first- (red), second-(navy) and third-row (green) metal complexes, respectively, is shown in

Figure 1.11 for the DFT/UB3LYP/LACVP/6-311G\* level of theory. This level of theory, though not the most computationally expensive, is the best performing in terms of standard deviation with respect to the experimental data. This level gives a standard deviation of 56 mV for 12 of 18 couples that lie in the first row, compared to 150 and 90 mV when using 6-31G and cc-pVTZ(-f) basis sets, respectively. When the same  $[FeCp_2]^{0/+}$  RC is used and extended to all couples, the standard deviation using 6-311G\* rises to 148 mV. Although this standard deviation is an improvement over previous reports of method performance, which we attribute to reductions in systematic error in the experimental data, it still marks a sharp decrease in performance compared to the first-row couples alone. However, when a RC with a similar ECP is used, the values are comparable to the first-row statistics. The DFT/UB3LYP/LACVP/ 6-311G\* level of theory yields a standard deviation of 64 mV and a mean of -2 mV for all 18 couples.

# 1.5.4 Choice of Reference Redox Couple

Internal reference redox couples can provide results that are consistent over a wide range of experimental conditions since they bypass problems common to reference electrodes Like SCE or SHE that might generate liquid junction potentials. Even non-aqueous reference electrodes are prone to issues of reproducibility owing to electrode surface chemistry.<sup>106</sup> These factors can contribute to discrepancies on the order of tens to hundreds of millivolts, even when comparing measurements reported under the same electrolyte and solvent conditions. Internal reference redox couples can remove these systematic uncertainties.

Earlier computational studies have been focused on finding appropriate functionals and basis sets to obtain accurate estimates of *absolute* redox potentials.<sup>86–94</sup> However, removing systematic errors caused by variations in the experimental conditions requires referencing the calculated potentials to redox couples calculated with the same functional and basis set, as in Equation (1.12). These systematic errors are partially canceled when the reference is calculated directly (*e.g.*, see Table 1.4). This is important since the accuracy of  $E_{calc}^0$  (Vvs.RC) is equally as dependent on the reference value as it is on the calculated absolute potential of the couple being studied [Equations (1.10) and (1.12)].

The results of Section 1.5.3 show that a suitable choice of a reference redox couple is period dependent.<sup>85</sup> For example, the  $[FeCp_2]^{0/+}$  redox couple is a valuable reference for transition metal complexes of the first period in non-aqueous solutions and has been extensively used in a host of electrochemical studies under a wide variety of experimental conditions.<sup>85,108,110,115–119</sup> In addition, several studies have explored first principle methods for calculating redox potentials with  $[FeCp_2]^{0/+}$  as a reference RC.<sup>87,98</sup> While comparisons for transition metal complexes of the first period have been successful, comparisons for second- and third-row transition metal complexes have proven to be more challenging. These discrepancies are likely to be due to systematic errors

introduced by the choice of basis sets, pseudopotentials, or solvation models that are expected to be comparable for transition metals of the same period. Therefore, reference couples based on transition metals of the same period as the system of interest should partially cancel the resulting systematic deviations and provide satisfactory results.

 $[FeCp_2]^{0/+}$  is the most common choice of RC. References for the second and third row, however, are a bit more challenging and have yet to be established. Electrochemical data is scarce and for most complexes (*e.g.*, the metallocene analogs) the measurements are reproducible only under limited experimental conditions. For example, it has been shown that ruthenocene and osmocene exhibit single, quasi-reversible oxidation waves in solutions of DCM and  $[NBu_4][B(Ar^F)_4]$  ( $Ar^F = 3,5$ -bistrifluoromethylphenyl).<sup>119</sup> However, in MeCN, oxidation of these metallocenes involves irreversible processes.<sup>115</sup> In addition, the  $[RhCp_2]^{0/+}$  couple can be highly reversible while the lifetime of rhodocene is on the order of seconds and is unstable at room temperature on the cyclic voltammetry timescale.<sup>120</sup> Therefore, instead of the metallocene analogs, reference couples for the second and third period have been based on  $[Ru(bpy)_3]^{2+/3+}$ , which is of interest in photoredox catalysis and artificial photosynthesis, <sup>121–123</sup> and  $[Ir(acac)_3]^{0/+}$ , which is often used as a precursor for complexes relevant to organic light-emitting diodes.<sup>124–126</sup> Both of these complexes show reversible or quasi-reversible peaks in both DCM and MeCN.

## 1.5.5 Accounting for Solvent Polarity and Supporting Electrolyte

The solvent and supporting electrolyte can significantly influence both the reference and the couple being studied. As an example, Figure 1.14 shows cyclic voltammograms of  $[FeCp_2]^{0/+}$  measured in 0.1 M  $[NBu_4][BF_4]$  in MeCN, DMSO and DCM solvents. The redox potential of such a couple is 84 (MeCN), 33 (DMSO) and 210 (DCM) mV *vs.* Ag/AgNO<sub>3</sub>, with a significant shift as large as 177 mV when comparing the oxidation potential in DCM relative to DMSO (see Figure 1.14). Similarly, calculations predict a shift of 179 mV in the calculated absolute redox potential of the  $[FeCp_2]^{0/+}$  couple in DMSO and DCM using the DFT/UB3LYP/LACVP/6-311G\* level of theory. These results illustrate the capabilities of self-consistent reaction field methods to account for solvent effects in electrochemistry calculations which are essential for comparison to experimental data.

The supporting electrolyte also affects the values for the redox potentials obtained by cyclic voltammetry and should be accounted for when comparing calculated and experimental data. The electrolyte affects the ionic strength, the conductivity and reactivity as well as the effective dielectric constant of the medium.<sup>127</sup> In addition, ion pairing with the supporting electrolyte counterions can become favorable in low dielectric solvents or when the complex is highly charged, as in the case of the [Ru(bpy)<sub>3</sub>]<sup>2+/3+</sup> couple. All of these effects can be partially removed by referring the measured potentials relative to an internal



**Figure 1.14** Cyclic voltammograms of the  $[FeCp_2]^{0/+}$  couple in 0.1 M  $[NBu_4][BF_4]$  in acetonitrile (red), dimethylsulfoxide (blue) and dichloromethane (green) solvents (100 mV s<sup>-1</sup> scan rate, T=25 °C).

reference to analogous electrolyte interactions. As an example, we consider the redox potential of the  $[Ru(bpy)_3]^{2+/3+}$  couple which is higher in DCM than in MeCN by 174 mV vs. Ag/AgNO<sub>3</sub>. However, when explicit  $[BF_4]^-$  counterions are included in DCM, the calculated difference in absolute potential is 102 mV at the DFT/UB3LYP/LACVP/6-311G\* level of theory. In contrast, a shift of 574 mV is obtained when ion pairing is neglected. Therefore, it is clear that ion pairing can account for significant shifts (*e.g.*, 472 mV in low-polar DCM,  $\varepsilon = 8.93$ ). These results emphasize the importance of including explicit counterions for highly charged species in low-polarity solvents.

# **1.6 Conclusions and Outlook**

Photocatalytic solar cells based on semiconductor materials functionalized with earth-abundant transition metal complexes are promising developments that should allow the sustainable production of chemical fuel from renewable resources (*e.g.*, water). In this chapter we have reviewed recent advances in computational modeling of fundamental aspects and mechanisms that affect the overall efficiency of solar light photoconversion, as determined by photoabsorption, charge transport and redox properties of systems with molecular adsorbates on metal oxide surfaces. While powerful on its own, when combined with structural and mechanistic characterization based on high-resolution spectroscopy and electrochemistry, the resulting computational methods are powerful tools for the design and characterization of new photocatalytic materials. These emerging methods are thus expected to continue to make significant contributions to the development of novel semiconductor materials for photocatalytic solar cell applications.

The chapter has focused on computational methods for analyzing complete solar cell assemblies using equivalent circuit modeling. A photoelectrochemical device model can be used to study current–voltage characteristics to provide a deeper understanding of the physical and electrochemical processes important to device performance. When used in conjunction with the methodologies discussed in order to calculate redox potentials, absorption spectra and the other relevant device parameters, these predictive abilities enable the rational design of photocatalytic solar cells, including tandem two-photon Z-schemes based on high potential photoanodes. Therefore, the computational methods discussed represent valuable tools for accurate prediction of redox potentials, photoabsorption and conductivity at the photoanode surface, which are necessary for optimizing the energetics of fundamental processes that determine the performance of photoelectrocatalytic devices.

The analysis of redox potentials in transition metal complexes shows that calculated and experimental data can be correlated with a standard deviation of 64 mV for 18 benchmark redox potentials and seven reference potentials calculated at the DFT/UB3LYP level of theory with LACVP and 6-311G\* basis sets. This correlation is within the experimental error of cyclic voltammetry measurements and is achieved when using three important guidelines for reducing systematic error: (i) using an experimental reference redox couple measured under the same experimental conditions as the system of interest: (ii) using a computational reference redox couple calculated at the same level of theory (which serves the dual purpose of removing computational systematic error while preventing the use of an external measurement of the absolute potential of a reference electrode that can introduce additional experimental systematic error); (iii) using references with metal centers of the same row of the periodic table as the electrochemically active complex. The choice of reference is essential to ensure a reduction of computational systematic error since elements in the same row share a common set of core electrons and there is therefore better agreement of the pseudopotentials of the metal basis set. The resulting methodology leads to accurate calculations of redox potentials at a relatively low computational cost, even for transition metal complexes in the second and third rows for which poor performance was previously reported and assigned to deficiencies in the DFT functionals.

Charge carrier collection and series resistance can have a significant impact on the efficiency of photoelectrocatalytic devices. It is therefore important to understand the mechanisms of electrical conductivity in photoanodes and photocathodes. It has been shown that the FITC model can describe electron transport in nanoporous metal oxide thin films in quantitative agreement with experimental data over the entire range of temperature accessible to reliable measurements. The structural parameters extracted from the conductivity data are consistent with the characterization of sintered TiO<sub>2</sub> nanoparticle films by SEM, XRD and annealing molecular dynamics simulations. The analysis reveals that the sintering process forms disordered TiO<sub>2</sub>, surrounding the crystalline core of nanoparticles and at the points of contact between the nanoparticle cores. The contact junctions determine rate-limiting energy barriers for electron transport from nanoparticle to nanoparticle that are significantly affected by the preparative procedures and by thermal fluctuations in the density of free carriers. Therefore, improvements in emerging technologies based on nanoporous  $TiO_2$  electrodes could be focused on ways of optimizing the nanoparticle interconnectivity and on sintering conditions that would provide optimum particle size and shape, choice of electrolyte, ambient conditions that affect the level of doping and therefore the alignment of electronic energy levels at the interparticle contact junctions. AC conductivity measurements of sintered  $SnO_2$  nanoparticle films exhibit a power law behavior with a dc component that is in quantitative agreement with the FITC description of electronic transport. This, coupled with the results for nanoporous  $TiO_2$  films and other systems that share a similar inhomogeneous microstructure, suggests that the FITC mechanism may have broad applicability for the wide variety of materials used for solar energy conversion.

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