Interplay of oxygen-evolution kinetics and photovoltaic power curves on the construction of artificial leaves

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Interplay of oxygen-evolution kinetics and photovoltaic power curves on the construction of artificial leaves

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Water splitting is the central chemistry that underlies the storage of solar energy in the form of chemical fuels because it delivers hydrogen from a renewable source (1–3). Direct solar-to-fuels conversion can be achieved by interfacing suitable catalysts that carry out two separate half-reactions of water splitting—the four electron-four proton oxidation of water to O2 and the two electron two-proton reduction of the produced protons to H2—to a photovoltaic (PV) material. Numerous device configurations have been proposed for photoelectrochemical (PEC) water splitting (4–10), and they can be broadly categorized into those devices wherein the photovoltaic material makes a rectifying junction with solution as opposed to those in which the rectifying junctions are protected from solution or “buried.” Fig. 1 schematically depicts the latter with a double-junction configuration of absorber materials with progressively larger band gaps that are connected in series using thin-film ohmic contacts to generate open circuit voltages (∆V oc) that are large enough to drive water splitting. Thin-film ohmic contacts at the termini of this stack serve both to protect the semiconductor from the chemistries occurring in solution and to enable efficient charge transfer to catalyst overlays, which execute the oxygen-evolution reaction (OER) and hydrogen-evolution reaction (HER). Whereas water-splitting catalysis is combined with charge separation, current rectification, and photovoltage generation in a solution junction PEC device, in a buried junction device, catalysis is separated from the current rectification, charge separation, and photovoltaic generation, which occur at the internal junction. The photovoltages produced at buried junctions are not fixed relative to a material-specific flatband potential (∆F). Unlike a solution junction, therefore, there is no requirement for the buried junction device that the flatband potentials of the semiconductors result in band edges that straddle the thermodynamic potentials of the OER and HER under the conditions of operation. This advantage of a buried junction dramatically expands the number of light-absorbing materials and catalysts that are available for constructing water-splitting devices. Additionally, as the buried junction device represents a photovoltaic power source in series with an electrochemical load, the OER and HER catalysts may be optimized independently such that maximum power transfer occurs to drive water splitting. We elaborate here on this latter issue and show that the kinetic profile of the catalyst is a key determinant of the overall solar-to-fuels efficiency (SFE).

A key bottleneck in the construction of buried junction PEC devices is the development of catalysts that can perform the multiple proton-coupled electron transfer chemistry of water splitting. Added benefits are realized if the catalyst is composed of inexpensive, highly manufacturable materials that are easily integrated with the photovoltaic substrate, and is able to operate under benign conditions so as to engender better stability of the semiconductor substrates. To this end, we have recently described the self-assembly of a highly active cobalt-based oxygen-evolving catalyst that forms as a thin film when aqueous solutions of Co2+ salts are electrolyzed in the presence of phosphate (Co-Pi), borate (Co-Bi), or methylphosphonate (Co-MePi) (collectively termed Co-OEC) (11, 12). More recently, we have used a similar strategy to prepare a Ni-Bi catalyst (13). These catalysts model the oxygen-evolving complex of Photosystem II (14) because they: (i) self-assemble under mild conditions (11–13, 15); (ii) exhibit high activity in pH 7–9 water at room temperature (11, 12); (iii) are functional in a variety of water sources (12, 15); (iv) are comprised of inexpensive, terrestrially abundant materials (11, 12); and (v) self-heal by reversing catalyst corrosion at open circuit upon application of a potential (16, 17). Their ability to be interfaced easily with light-absorbing and charge-separating materials (18–24) has permitted the construction of a buried junction PEC device (25, 26). In the wireless configuration, the buried junction device captures many of the functional elements of the water-splitting chemistry of a leaf (27, 28). In this artificial leaf, the Co-OEC catalyst is interfaced through a thin-film transparent conductor oxide ohmic contact to a triple-junction Si PV cell to allow for the direct splitting of water under illumination with 1-sun AM 1.5 simulated sunlight.

We interrogate here the interplay of OER catalysis and photovoltaic performance in defining SFE of the artificial leaves based

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on Ni-Bi and Co-Bi catalysts. Building on the theoretical work of Hanna and Nozik (9) and adapting the engineering loss analysis model of Rocheleau and Miller (10), we use Ni-Bi and Co-Bi electrokinetic data as a basis for modeling the electrochemical load of water splitting in a PEC cell. We show that Ni-Bi and Co-Bi exhibit markedly different Tafel slopes, pointing to different mechanisms of oxygen evolution that translate into disparate electrochemical loads for water splitting. By assembling the electrochemical profiles of Ni-Bi and Co-Bi systems with multijunction PV components of similar power-conversion efficiency but disparate open-circuit voltages, \( V_{oc} \), we show that OER-catalyst kinetics are a key determinant of SFE when water splitting is performed near its thermodynamic limit (i.e., low \( V_{oc} \)). This observation has not been broadly appreciated previously because most PEC cells have employed semiconducting materials with kinetic PV components of similar power-conversion efficiency but far removed from the thermodynamic limit of water splitting.

### Results and Discussion

Water-splitting catalysts are deposited as thin films by controlled potential electrolysis of Co\(^{2+} \) and Ni\(^{2+} \) solutions in 0.1-M potassium bismuthate electrolyte, pH 9.2 (Bi), at a potential of 0.92 and 1.15 V (vs. the normal hydrogen electrode, NHE), respectively (12, 13). Following electrodeposition, Co-Bi films may be rinsed and placed in electrolyte containing no additional Co\(^{3+} \) and Ni\(^{2+} \) ions to yield steady-state current densities that are high and remain unchanged over time (13, 30). The logarithm of the steady-state current density of Co-Bi films versus potential electrolysis of Co\(^{3+} \) and Ni\(^{2+} \) ions in 0.1-M Bi, pH 9.2 (blue triangles), and a Co-Bi-catalyst film operated in 1-M Bi, pH 9.2 (green squares). \( E^0 \) is the thermodynamic potential of water splitting under the conditions of the experiment, \( \eta \) is the overpotential, and \( iR \) accounts for the uncompensated cell resistance. The slopes of the linear fits to the data are approximately 60 mV/decade and 29 mV/decade for Co-Bi and Ni-Bi, respectively.

The disparate Tafel behaviors of Ni-Bi and Co-Bi films are paramount to determining the anodic electrochemical load in an artificial leaf. Specifically, the electrochemical load of water splitting is described by the following equation (10):

\[
V_{\text{op}}(j, A) = V^0 + \eta_{\text{OER}}(j) + \eta_{\text{HER}}(j) + \eta_{\text{oc}}(j, A),
\]

where \( V_{\text{op}} \) is the overall operational voltage necessary for water splitting at a given current density \( j \) over area \( A \), \( V^0 \) is the thermodynamic potential stored in water splitting (1.23 V under standard conditions), and \( \eta_{\text{oc}} \) represents the voltage required to overcome resistive losses in the device, including contact resistance between the components and ion transport resistance arising from the electrolyte solution. Typically these resistances are ohmic and therefore can be represented by the simple product of the net current \( (j/A) \) and an aggregate cell resistance, \( R \). The \( \eta_{\text{OER}} \) and \( \eta_{\text{HER}} \) terms represent the overpotential losses accompanying the oxygen-evolution and hydrogen-evolution half-reactions, respectively, and they are illustrated in Fig. 1. Both overpotential terms are functions of the current density as given by the Tafel law,

\[
\eta = b \log \left( \frac{j}{j_0} \right),
\]

in which \( b \) is the Tafel slope and \( j_0 \) is the exchange current density, representing the extrapolated rate at which the forward and back reactions occur under conditions of zero driving force, \( \eta = 0 \). Combining Eqs. 1 and 2 with consideration of the ohmic nature of the cell-resistance term engenders the following expression for the electrochemical load of water splitting,

\[
V_{\text{op}}(j, A) = 1.23 + b_{\text{OER}} \log \left( \frac{j}{j_{0,\text{OER}}} \right) + b_{\text{HER}} \log \left( \frac{j}{j_{0,\text{HER}}} \right) + jAR.
\]

In this expression, \( b_{\text{OER}}, j_{0,\text{OER}}, b_{\text{HER}}, \) and \( j_{0,\text{HER}} \) represent the Tafel slopes and exchange current densities of the OER and HER catalysts, respectively. In order to isolate the impact...
of disparate OER-catalyst kinetics, we chose to model the hydro-
gen-evolution catalyst using values both typical of the HER on high-surface area Ni electrodes (32, 33) and similar to those used in the artificial leaf (27). \( j_{\text{HER}} = 10 \mu\text{A cm}^{-2} \) and \( b_{\text{HER}} = 30 \text{ mV decade}^{-1} \), and we also assume a conservative value of \( R = 10 \Omega \left( A = 1 \text{ cm}^{2} \right) \) and note that resistive losses are highly dependent on cell geometry. Extrapolation of the Tafel data in Fig. 2 yields exchange current densities for Co-Bi and Ni-Bi of 2.1 ⋅ 10^{-12} and 5.0 ⋅ 10^{-18} A cm^{-2}, respectively. These values, taken together with the Tafel slopes of the two catalysts, yield the exchange current density for Co-Bi, the onset of appreciable water splitting occurs at a lower potential relative to Ni-Bi. However, the lower Tafel slope of Ni-Bi causes its \( j-V \) curve to rise far more steeply, requiring a lower voltage at high current density. In this treatment, we assume that the Tafel behavior shown in Fig. 2 is retained over the entire overpotential range and acknowledge that mass transport limitations and/or changes in OER mechanism at high overpotential may perturb the theoretical \( j-V \) behavior in Fig. 3. As further points of comparison, published Tafel data for RuO\(_2\) (34) and LaMnO\(_3\) (35) in 1 M NaOH are also overlaid on the graph to model the electrochemical load of water splitting using these catalysts. The reported Tafel data for RuO\(_2\) and LaMnO\(_3\) correspond to materials prepared by high-temperature calcination of metal salt precursors at >350°C. As such, these materials may not be suitable for integration into PV-PEC architectures, and we therefore include them in Fig. 3 as exemplars of high- and low-performance OER catalysts. Thus, they provide a benchmark for the impact of catalyst performance on SFE.

In the artificial leaf, the operating current density is given by the intersection of the \( j-V \) curve for the PV and the \( j-V \) curve representing the electrochemical load for water splitting. This operating current density multiplied by the thermodynamic potential of water splitting (1.23 V) defines the power stored in water splitting, and the ratio of this power to the incident power of the solar flux, 100 mW cm^{-2}, defines the SFE. For the purposes of illustration, we model in Fig. 3 the idealized PV behavior of a triple-junction amorphous Si (a-Si) | nanocrystalline Si (nc-Si) | nc-Si triple-junction cell stack (36) exhibiting \( V_{\text{oc}} = 1.94 \text{ V} \) and \( j_{\text{sc}} = 8.96 \text{ mA cm}^{-2} \), and a hypothetical multijunction cell with \( V_{\text{oc}} = 2.13 \text{ V} \) and \( j_{\text{sc}} = 8.15 \text{ mA cm}^{-2} \). Idealized behavior of the PV is modeled by ignoring efficiency losses caused by high series or low shunt resistances and assuming a diode ideality factor of 1 (details of PV modeling provided in Experimental Methods). Both idealized cells exhibit a power-conversion efficiency of 16%, but display dramatically different SFEs when paired with the various OER catalysts. For the cell possessing the lower \( V_{\text{oc}} \), the electrochemical load curves for water splitting using Ni-Bi and Co-Bi intersect the \( j-V \) curve of the PV at 1.85 and 1.89 V (Fig. 3), respectively, which is beyond the maximum power point \( (V_{\text{mp}} = 1.83 \text{ V}) \) of the PV. As the PV current density declines sharply beyond \( V_{\text{mp}} \), an artificial leaf utilizing Co-Bi is expected to exhibit a lower hydrogen production current density (7.6 mA cm^{-2}) than one utilizing Ni-Bi (8.7 mA cm^{-2}). Water splitting stores 1.23 V and, thus, these current densities translate to SFE = 9.3% and 10.7% for Co-Bi and Ni-Bi, respectively. The SFE declines further for the case of LaMnO\(_3\), which displays an overall water-splitting current density of 4.4 mA cm^{-2} and SFE = 5.4%. In contrast, RuO\(_2\), despite displaying greater OER-catalytic activity than thin-film Co-Bi and Ni-Bi, exhibits only a marginally larger SFE = 11.1%. The artificial leaf becomes even more insensitive to OER-catalytic activity if the \( V_{\text{oc}} \) of the PV is increased (Fig. 3). For the higher \( V_{\text{oc}} \) cell, all of the catalysts exhibit SFE = 10.0%, highlighting the fact that good catalyst performance and high SFE are only mandated if a suitable PV with a \( V_{\text{mp}} \) matched to the electrochemical load can be designed near the thermodynamic potential of water splitting. The foregoing analysis assumes that the PV exhibits ideal diode behavior with minimal series and maximal shunt resistances. In practice, multi-junction Si devices suffer from poor fill factors symptomatic of nonideal diode behavior and parasitic-resistance losses (36). Thus, we stress that the trends observed here are purely theoretical and that a more rigorous analysis performed on a specific PV/catalyst pairing would be necessary for device optimization. We do note, however, in a practical artificial leaf with minimized ohmic losses, an overall SFE = 5.2% has been observed for a PV cell of 7.7% efficiency (27).

In summary, we illustrate here that a key determinant of high SFE for artificial leaves, and more generally, photoelectrochemical cells, is the OER kinetic profile. In particular, thin Ni-Bi catalyst films exhibit a 29 mV decade^{-1} Tafel slope as compared to the 52 mV decade^{-1} slope observed for Co-Bi under similar electrolyte conditions. The disparate kinetics of Co-Bi and Ni-Bi translate into improved SFE of an artificial leaf utilizing the latter, suggesting that Ni-Bi is particularly well-suited to direct solar-to-fuels generation. We note that the critical role of catalysis in SFE has generally been underappreciated because PEC cells to date have generally relied on semiconducting materials with large band gaps (e.g., SrTiO\(_3\), TiO\(_2\), and WO\(_3\) display band gaps, \( E_g > 2.5 \text{ V} \)) that supply very high voltages to drive water splitting (37). These materials have typically been used as components of solution junction PEC devices rather than buried junction devices, complicating their analysis using the simple power matching model presented here (38). Notwithstanding, extremely poor catalytic activity of semiconducting oxides such as SrTiO\(_3\), TiO\(_2\), and WO\(_3\) can be masked by the large voltages they deliver to drive water splitting via high overpotential pathways (e.g., hydroxyl radical formation) (37, 39). As illustrated in Fig. 4, qualitatively, large band gap oxide PEC devices can be viewed as exaggerated cases of the high \( V_{\text{oc}} \) PV we model in Fig. 3, wherein load curves for poor catalysts still intersect the \( j-V \) curve of the semiconductor at or below the \( V_{\text{mp}} \). The maximum SFE of such cells, however, is intrinsically limited because of inefficient utilization of the solar spectrum. High SFEs can only be achieved for PVs operating near the thermodynamic potential of water splitting so that the absorption of the solar spectrum can be maximized. In this case, as illustrated in Figs. 3 and 4, the overall SFE becomes extremely sensitive to catalyst performance. These results show that the construction of efficient PEC devices such as the artificial leaf reduces to a problem of catalyst design. To this end, Co-Bi and Ni-Bi are ideal water-splitting catalysts when...
Electrolysis was carried out at 1.15 V without R compensation and with passage of 1 mC cm^{-2}. A typical deposition lasted 70 s. Following deposition, films were rinsed with 0.1-M Bi and subsequently anodized in 1-M Bi electrolyte by passage of 3.5-mA cm^{-2} for 1 h with stirring.

Current-potential data were obtained by conducting controlled-potential electrolysis in 0.5-M Bi 1.75 M KNO₃ electrolyte at a variety of applied potentials. Prior to film deposition and anodization, the solution resistance of the electrolyte to be used for Tafel data collection was measured using the R test function. The electrolysis solution was exchanged for Ni-Bi electrolyte without disturbing the relative positions of the working and reference electrodes. The film was prepared by controlled-potential electrolysis and anodized as described above. Following film preparation, the working electrode was rinsed in fresh Ni-free Bi electrolyte and transferred, without drying, to the same electrolysis bath in which the solution resistance was measured. The electrode was allowed to equilibrate with the electrolysis solution for 5 min while being held at the open circuit potential. The solution was stirred and steady-state currents were then measured at applied potentials that descended from 1.17 V to 0.96 V in 10- to 30-mV steps. For currents greater than 10 μA cm^{-2}, a steady-state was reached at a particular potential in 400-600 s. For currents lower than 10 μA cm^{-2}, longer electrolysis times (15–20 min) were utilized to ensure that steady-state conditions had been achieved. The solution resistance measured prior to the data collection was used to correct the Tafel plot for ohmic potential losses.

Current Density-Voltage Curve Modeling. The j-V curve representing idealized power output from a triple-junction Si photovoltaic stack was modeled using reported data for an a-Si/nc-Si/nc-Si cell (36), which exhibits \( V_{oc} = 1.94 \) V and \( j_{sc} = 8.96 \) mA cm^{-2} (Fig. 3). These two experimental

![Fig. 4. Low-SFE (dashed red with solid green line) and high-SFE PEC cells (solid red with solid blue or solid purple line). The j-V curves of a PV (dashed red line) of a typical metal oxide semiconductor operating at \( V_{oc} > 3.0 \) V and a PV (solid red line) operating near the region of thermodynamic potential for water splitting (gray bar) at arbitrary current density \( i \) overlaid with Tafel curves of catalysts exhibiting increasing performance (solid green to solid blue to solid purple lines). Note the sensitivity of the overall SFE to catalyst performance for PVS operating near the thermodynamic potential of water splitting.](image-url)
parameters were used to calculate the dark saturation current of an idealized cell, \( j_0 \), using the following equation:

\[
j_0 = \frac{j_s}{\exp\left(\frac{qV}{nknT}\right) - 1},
\]

where \( q \) is the fundamental charge of an electron, \( k \) is the Boltzmann factor, \( T \) is the temperature (taken as 300 K), and \( n \) is the diode ideality factor, taken as 1. Using the calculated value of \( j_0 \), the ideal \( j-V \) curve was calculated using

\[
j = j_s \exp\left(\frac{qV}{nknT}\right) - 1.
\]

The same analysis was applied to a hypothetical idealized cell with a 10% increase in \( V \), and a concomitant 10% decrease in \( j_s \) so as to preserve the same overall power-conversion efficiency of 16%. We note that the above equations produce upper-limit ideal behavior because they do not account for parasitic resistances that may exist within or between the individual \( p-n \) junction components of the triple-junction stack.

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