Combined Catalysis and Optical Screening for High Throughput Discovery of Solar Fuels Catalysts

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Considerable research and development efforts are being devoted to the efficient generation of solar fuels. A solar fuels device couples a solar photoabsorber with catalysts to convert solar energy to chemical energy via reactions such as oxygen evolution (water splitting). Widespread deployment of this technology hinges upon discovery of new materials through efforts such as the high throughput screening of oxygen evolution catalysts, as discussed in this manuscript. We derive an expression for the efficiency of the oxygen evolution catalyst that combines catalytic and optical properties. Using this hybrid efficiency, we screen 5456 samples in a (Fe-Co-Ni-Ti)Ox pseudo-quaternary catalyst library using automated, high throughput electrochemical and optical experiments. The observed compositional trends in this catalyst efficiency lead to the discovery of a new high performance composition region.

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Solar fuel technology offers the formidable capability to convert solar energy and store it in chemical bonds. Given the easy storage and transport of liquid fuel, solar fuel generation is an attractive technology for the renewable energy landscape.1−12 The widespread deployment of this technology requires a device fabricated with high-performance, robust materials made from earth-abundant elements.3 The realization of this device relies on the discovery of new materials, prompting an aggressive high-throughput materials discovery effort within the Joint Center for Artificial Photosynthesis (JCAP, http://solarfuelshub.org/).

This effort includes searches for new photoanodes, photocathodes, and catalysts for several solar fuels reactions, of which the oxygen evolution catalyst is discussed in this manuscript.

One established solar fuel generator concept combines a solar photoabsorber with an optically inactive heterogeneous catalyst to evolve oxygen (water splitting).1−14 That is, the oxygen evolution reaction (OER) is mediated by a “dark” catalyst that is coupled to a photoabsorber, which provides the required potential and current for the electrocatalytic reaction through the photovoltaic effect. This anodic reaction balances a fuel-producing cathodic reaction such as hydrogen evolution or CO2 reduction. Variations within this solar fuel design concept include the use of a tandem absorber containing a coupled photoanode and photocathode instead of a single photoabsorber3−7 or the use of a homogeneous OER catalyst instead of the heterogeneous catalyst.3,8−11 Homogeneous catalysts are not considered in this manuscript, and the general discussion of optimizing the OER catalyst is applicable to any photoabsorber device. Our primary assumptions concerning device architecture are that the OER catalyst coats the photoanode and this anode is exposed to solar illumination. These assumptions are based upon a tandem photoabsorber system in which the photoanode is the top cell and has a larger bandgap than the photocathode.

While heterogeneous catalysts are used in a variety of technologies, the OER catalyst in this solar application has a special optical performance requirement. Since the solar radiation impinges the catalyst before reaching the photoabsorber, the catalyst layer must be sufficiently transparent. Since the optical properties of the electrocatalyst could play an important role in the overall solar-to-fuel conversion efficiency, the evaluation of these properties should be incorporated into a high-throughput search for new solar fuels OER catalysts.

While the ultimate development of a solar fuels device requires careful integration of the device components, high-throughput discovery and optimization is most practically performed on each component individually.3,14,12−14 Such studies require a heuristic figure of merit to evaluate the performance of the independent material. We derive such a figure of merit (FOM) for the oxygen evolution catalyst by combining the electrocatalytic performance and optical transparency under solar air mass 1.5 irradiance. The resulting FOM for the overall catalyst efficiency is evaluated for 5456 (Fe-Co-Ni-Ti)Ox catalysts using automated, high-throughput electrochemical and optical experiments. These catalysts cover the quaternary metal space with 3.33 at.% interval and the optimal composition region for the overall catalyst efficiency is markedly different than the optimal composition region for electrocatalytic activity.

The combination of techniques and application of the efficiency model described in this manuscript comprise a new high-throughput technique for evaluating OER catalysts. Previous combinatorial studies of OER electrocatalysis and photoelectrocatalysis systems12−14 do not provide the necessary information to identify an optimal catalyst for the device architecture described above. The electrochemical and optical measurements employed in this study provide archived data of catalytic current as a function of overpotential and transmission as a function of wavelength, which may be used to assess a catalyst’s performance for any photoabsorber system. This capability will be quite useful since new photoabsorbers are being discovered and developed in parallel with the catalyst research. This tailoring of material characterization techniques for solar fuels applications and the deployment of high-throughput realizations of these techniques will streamline the catalyst discovery process by ensuring that the high-throughput screening criteria are directly applicable to operational devices.

Figures of Merit for Solar Fuel OER Catalysts

Exploration of composition trends in multi-dimensional parameter space, such as quaternary composition space, is most effectively performed by mapping a scalar figure of merit over the parameter space. For the purposes of screening OER catalysts for solar fuels applications, we describe figures of merit for catalytic activity, solar transparency and overall catalyst efficiency.

Catalytic activity figure of merit.— The performance of an OER electrocatalyst is most explicitly characterized by the molar oxygen production rate at a given overpotential, VOER. In electrochemical characterization, one instead measures the anodic current density JVoER (V0ER) as a function of the overpotential and carries out additional experiments to access the Faradic efficiency for O2 production. A figure of merit for the electrochemical characterization can be defined as either the minimum VOER required to obtain a desired current density, or as the maximum Jc attained at a given overpotential.

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Using the latter definition, we employ high throughput methods to map $J_C(450 \text{ mV})$ across our catalyst library.

**Optical transparency figure of merit.**— During incorporation of the OER catalyst and the photoabsorber, the catalyst transmittance must be considered for proper light management and optimal use of the incident solar power. Using the ASTM 6173-03 standard for global tilt air mass 1.5 (AM1.5) spectral irradiance, $E_{\text{AM1.5}}$, the electrical power density generated by the photoabsorber system is given by

$$P = \int E Q E_{\text{PA}}(\lambda) T_{C}(\lambda) E_{\text{AM1.5}}(\lambda) \, \text{d}\lambda,$$

where $E Q E_{\text{PA}}$ is the spectral external quantum yield of the photoabsorber and $T_{C}$ is the spectral transmittance of the catalyst. In the development of a catalyst for a given photoabsorber, catalyst optimization can be performed using the known $E Q E_{\text{PA}}$ spectrum. In the development of OER catalysts for a generic photoabsorber, a corresponding figure of merit is the transmission efficiency of the solar irradiance over a wavelength range of interest:

$$\eta_{C,T} = \frac{\int_{\lambda_1}^{\lambda_2} T_{C}(\lambda) E_{\text{AM1.5}}(\lambda) \, \text{d}\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\text{AM1.5}}(\lambda) \, \text{d}\lambda}. $$

This normalized efficiency approaches zero for opaque catalysts and unity for transparent catalysts. The numerator integral is essentially the same as Eq. 1 with $E Q E_{\text{PA}}$ equal to 1 between $\lambda_1$ and $\lambda_2$ and 0 elsewhere. A practical value for the high wavelength limit $\lambda_2$ is that of the anticipated (lowest energy) bandgap of the photoabsorber and $\lambda_1$ for transparent catalysts. The spectral irradiance is relatively small beyond this limit.

**Combined figure of merit.**— To combine catalytic activity and optical transparency performance, further knowledge of the photoabsorber and cathode catalyst system is required. A photoabsorber is most traditionally characterized by $J_{PA}(V_{ph})$ performance, the standard photovoltaic current-voltage relationship. For solar water splitting the current density $J_{PA}$ must match the catalytic current for both the anodic and cathodic reactions, with respective overpotentials provided by the photovoltage $V_{ph}$.

The mathematical expression for the efficiency of a water splitting device is a recursive function of the performance metrics of the individual components. For the present purpose of high throughput electrocatalyst screening, we require an expression for catalytic efficiency that is independent of the detailed device physics of the absorber materials. This efficiency can be succinctly stated in terms of two photoabsorber parameters: $V_{PA,\text{OER}}$ and $J_{PA,\text{max}}$. At its operating photovoltage $V_{ph}$, the photoabsorber supplies an OER overpotential to the OER catalyst, which we define as $V_{PA,\text{OER}}$. During the photoabsorber’s independent operation at this voltage, the photocurrent is given by the $J_{PA}(V_{ph})$ characteristic. Due to the current-matching constraint for the photoabsorber and catalyst, this is the maximum operating current of the integrated device and is defined as $J_{PA,\text{max}}$. Since the catalyst needs to provide an OER catalytic current no greater than $J_{PA,\text{max}}$, the catalytic efficiency is given by

$$\eta_{C,OER} = \text{Min}[J_{C}(V_{PA,\text{OER}}), J_{PA,\text{max}}]/J_{PA,\text{max}}. $$

In essence, this expression gives the catalytic efficiency of O$_2$ production compared to the maximum attainable with a given photoabsorber.

The photoabsorber will only be able to operate at this limit if the catalyst is perfectly transparent. Precise modeling of the device efficiency as a function of catalyst transparency requires knowledge of the irradiance-dependence of $J_{PA}(V_{ph})$. For the present purpose, we assume the device efficiency varies linearly with the irradiance transmittance of the catalyst (Eq. 2). Thus, the overall efficiency of the catalyst can thus be approximated by combining the catalytic and optical efficiencies:

$$\eta_C = \eta_{C,T} \eta_{C,OER}.$$
yielded a throughput of 3 s per sample. As shown in Fig. 1, the array with a 2 s integration time, which combined with 1 s translation time transmission measurement. Each transmission spectra was acquired off a translation stage such that each sample could be positioned in the on a regular grid on the FTO coated glass plates.

0.8 s translation between samples, yielded a sample throughput of 5.5 s per sample.

High throughput optical screening.— The optical transparency of each catalyst was measured after the electrochemical experiments using a fiber-coupled mercury arc lamp (Newport 66921, 450W-1000W) and an integrating sphere (Ocean Optics ISP.50-8-R-GT) coupled to a UV-visible spectrometer (Ocean Optics USB4000). The end of the 0.1 mm fiber was positioned 1.6 mm from the sample such that the divergent beam generated a circular footprint on the sample with diameter of approximately 1 mm. Transmitted and low-angle scattered light was collected by the integrating sphere after transmission through the FTO coating, the 2.2 mm glass plate and a 2 mm air gap. The 8 mm-diameter aperture of the integrating sphere and its 5.8 mm separation from the fiber termination provided a collection angle of 35° with respect to the fiber and 44° with respect to the sample. The sample plate was mounted on a frame, which was cantilevered off a translation stage such that each sample could be positioned in the transmission measurement. Each transmission spectra was acquired with a 2 s integration time, which combined with 1 s translation time yielded a throughput of 3 s per sample. As shown in Fig. 1, the array samples were arranged on each plate such that every eighth column in the array did not contain samples. These bare positions were used as spectral reference sites, where a reference transmission measurement was made after every set of 7 measurements of catalyst samples. Using a computer-actuated shutter, dark spectra were also collected at these sites so that the a corrected, normalized spectral transmission was calculated for each sample as

\[
T_C(\lambda) = \frac{S_C(\lambda) - S_{dark}}{S_{ref} - S_{dark}},
\]

where \(S_C\) and \(S_{ref}\) are the measured spectra at the catalyst sample location and bare reference location, respectively, and \(S_{dark}\) is the measured dark spectrum.

This spectral transmission was used in data interpretation, as described by Eq. 2, and the wavelength range of the transmission measurement constrained the integration range in this equation. While photoabsorbers with bandgap energy down to approximately 1 eV are of interest for solar fuel generation, in this work we use a \(\lambda_c\) value of 925 nm (1.35 eV), for \(\lambda_c\) we use 400 nm (3.1 eV), below which lies less than 5% of the energy content of the AM1.5 spectrum. This wavelength range contains over 65% of the AM1.5 energy content and is a prime range of interest for solar photoanodes.

Results and Discussion

Images of the 3 library plates acquired with a flatbed scanner (Epson V600 Photo) containing the 5456 samples in the (Fe-Co-Ni-Ti)Ox library. The thin film samples are each 1 mm square and are arranged on a regular grid on the FTO coated glass plates.

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catalytically active surface area. The porous samples are believed to have appreciable specific area compared with the 1 mm² footprint, but the characterizations of this area and of the porous structure of the films are beyond the scope of the present manuscript.

Each sample’s spectral transmission was used to calculate the transmission efficiency of the AM1.5 solar irradiance using Eq. 2. The irradiance used in the experiments is shown along with the AM1.5 spectrum in Fig. 3, which also contains transmission spectra from select samples. In addition to the mesostructure imposed by the structure directing agent, the samples were visibly rough with non-uniform thickness. Every sample appeared to have similar roughness, but the compositional uniformity of the sample morphology is under further investigation.

The FTO coated glass has near perfect transmission over this entire wavelength range and the spectrometer has a flat, low-intensity dark noise spectrum. The processing function of Eq. 5 thus provides a high wavelength range and the spectrometer has a flat, low-intensity dark noise spectrum. The processing function of Eq. 5 thus provides a high fidelity transmission spectrum for each sample, which could be used for modeling each sample’s optical bandgap. This type of information is important for development of not only photoabsorbers but also photocatalysts, which perform both optical absorption and catalytic functions. While these functional materials are of great interest to ICAP, the focus of the present manuscript is the evaluation of so-called “dark” catalysts.

Given these electrochemical and optical characterizations for each sample, the catalytic efficiency $\eta_{C\text{-OER}}$ and overall efficiency $\eta_C$ can be readily evaluated given the photoabsorber parameters of Eq. 3. The choice of these parameters strongly dictates the resulting calculated efficiencies and composition trends, which highlights the importance of archiving the electrochemical and optical data so that catalysts can be vetted for new photoabsorbers. For the present purposes, we choose an overpotential of 450 mV vs. O$_2$/H$_2$O and a photocurrent density of 23 mA cm$^{-2}$ under AM1.5 irradiation, which is optimal for water-splitting reactions under certain assumptions.\textsuperscript{11} These conditions correspond to Eq. 3 parameter choices of $V_{PA\text{-OER}} = 450$ mV and $J_{PA\text{,max}} = 23$ mA cm$^{-2}$.

Performance maps in composition space.—The figures of merit for catalysis, $J_C$ (450 mV), and those described by Eqs. 2 and 4 were analyzed for each library sample. The metal composition of each sample was taken to be that of the precursor printing design. The composition fidelity of the precursor printing has been verified for similar libraries with identical drying and calcination treatments (data not shown). Such studies have also demonstrated the efficient removal of the precursor ligands and block copolymers during the calcination. The oxygen stoichiometry of the samples was not measured, but the compositional map of the catalyst performance is evaluated using the metal stoichiometry, as shown in Fig. 4.

The quaternary composition map of OER current shows non-monotonic trends with respect to each of the elements. The optimal composition region extends to the Fe-Ni binary line with $J_C$ (450 mV) in excess of 70 mA cm$^{-2}$ from Fe$_{0.23}$Ni$_{0.13}$O$_x$ to Fe$_{0.1}$Ni$_{0.9}$O$_x$. This result is in strong agreement with previous reports of catalysis in this pseudo-binary system.\textsuperscript{18} The catalytic current map also shows a local maximum near the Fe-Co-Ti plane. This composition region exhibits improved catalysis compared to the pure metal oxides, and the active region is bounded by Ti concentrations of 30 and 70 at.%. The existence of a finite optimal Ti concentration is interesting given the marked inactivity of TiO$_x$.

The compositional variation of $\eta_{C\text{-T}}$ is relatively straightforward, and the most significant trends in the optical transmission are the decrease with respect to Co concentration and increase with respect to Ti concentration. The visible appearance of the pure element oxides are translucent red FeO$_x$, black CoO$_x$, transparent-white NiO$_x$, and transparent TiO$_x$, and the measured variation in optical transparency is consistent with a monotonic interpolation of these end-member properties.

The two composition regions noted above, which are locally maximal in the measured catalytic current, are also locally maximal in the map of $\eta_C$. However, the globally maximum composition region for catalytic current is not the globally maximum region in the map of $\eta_C$. Figs. 2 and 3 contain data for a representative sample from each of these regions (Fe$_{0.23}$Co$_{0.13}$Ni$_{0.07}$Ti$_{0.57}$O$_x$ and Fe$_{0.3}$Ni$_{0.7}$O$_x$). Fig. 2 shows that both samples provide the target 23 mA cm$^{-2}$ at 450 mV and thus in these regions, $\eta_C$ is determined by the transmission efficiency. The transmission spectra in Fig. 3 show that the Fe$_{0.3}$Ni$_{0.7}$O$_x$ sample is less transparent in the UV, most likely due to absorption at wavelengths below an optical gap. Due to the very high transparency of the catalysts with composition near Fe$_{0.23}$Co$_{0.13}$Ni$_{0.07}$Ti$_{0.57}$O$_x$, this region exhibits the highest $\eta_C$ values in this library. That is, by considering both catalytic and optical efficiency, optimal catalysts are discovered in this surprising composition region. We note that this result is particular to catalysts prepared in this format, and that the excessive catalytic current in the Fe$_{0.3}$Ni$_{0.7}$O$_x$ region suggests that the target current may be attained with thinner (or lower areal density) catalysts. Such catalysts could compete with the Fe$_{0.23}$Co$_{0.13}$Ni$_{0.07}$Ti$_{0.57}$O$_x$ catalysts for optimal performance, but an increase in $\eta_C$ upon thinning the catalyst is not guaranteed as the resultant material properties cannot be ascertained from the data at hand. For example, the transparency of thinned Fe$_{0.3}$Ni$_{0.7}$O$_x$ may remain unchanged if this catalyst suffers from reflective losses. In general such proposed catalysts must be synthesized and screened by the methods described above.

In this study, a mesoporous OER catalyst structure was chosen due to its relevance for incorporation into a solar fuels device. Porous films with thickness on the order of 100 nm have a significant technological advantage over dense films due to their increased catalytic surface area, which relieves the requirement on catalyst turnover frequency. To evaluate materials with this technologically relevant format, we constructed performance metrics that conform to the requirements of an operational solar fuels device. As shown in Figs. 3-4, films with this structure can be highly transparent and yield high catalyst efficiency, and the noted composition regions should be further explored for solar fuels applications. New OER catalysts must still be developed for further optimization of solar fuel generation, especially with respect to the required OER overpotential.

We note that the performance metrics described in this manuscript are extrinsic material properties, as opposed to the intrinsic properties typically mapped in a combinatorial materials study (for example, geometric current instead of specific current density). In the discovery and optimization of materials for a specific application, the most...
Figure 4. Performance as a function of library composition is shown for the OER catalytic current (top), transparency efficiency (middle) and overall catalyst efficiency (bottom). Each performance metric is mapped onto a stacked-ternary (middle) and tetrahedron (right) representation of the quaternary composition space using a false color scale (left). The tetrahedron plot contains horizontal planes of data points corresponding to 3.3 at. % intervals of Ti concentration. Sets of 3 planes are plotted together in each of 10 ternary composition plots in the stacked-ternary representation.

**Conclusion**

To evaluate OER catalysts for solar fuel applications, a catalyst efficiency is derived using parameters of the photoabsorber to which the catalyst would be coupled in an operating device. The efficiency includes OER catalytic current as well as the catalyst’s transmission of the solar irradiance. This expression for efficiency is applicable to dark catalysts, which must transmit the solar energy to be converted by the photoabsorber. To enable high-throughput mapping of this catalyst efficiency, both electrochemical and optical screenings are performed on a quaternary metal oxide library at a throughput of 5.5 s and 3 s per sample, respectively. Of the 5456 samples in the (Fe-Co-Ni-Ti)Ox library, two composition regions of interest are identified. The optimal OER catalytic activity is observed near Fe0.3Ni0.7Ox, and the optimal catalyst efficiency is observed near Fe0.23Co0.13Ni0.07Ti0.57Ox. The identification of optimal performance in this composition region highlights the utility of high-throughput experimentation for the discovery of new materials in unexpected composition spaces. The appreciable Ti concentration in this optimal region prompts future characterization of these catalysts and exploration of related composition spaces.

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