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Parallel Electrochemical Treatment System and Application for Identifying Acid-Stable Oxygen Evolution Electrocatalysts

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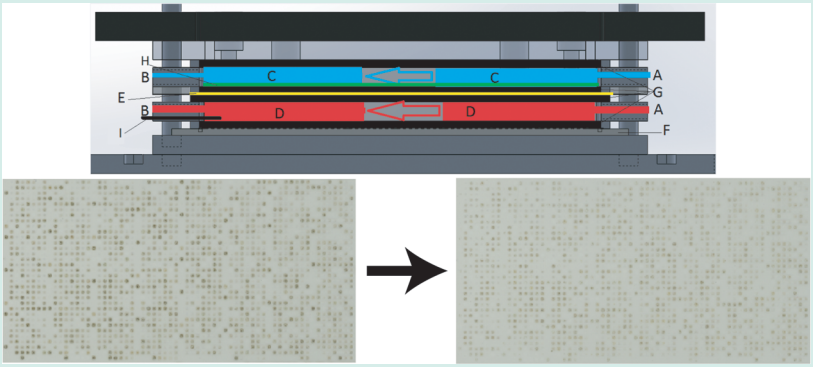

ABSTRACT: Many energy technologies require electrochemical stability or preactivation of functional materials. Due to the long experiment duration required for either electrochemical preactivation or evaluation of operational stability, parallel screening is required to enable high throughput experimentation. Imposing operational electrochemical conditions to a library of materials in parallel creates several opportunities for experimental artifacts. We discuss the electrochemical engineering principles and operational parameters that mitigate artifacts in the parallel electrochemical treatment system. We also demonstrate the effects of resistive losses within the planar working electrode through a combination of finite element modeling and illustrative experiments. Operation of the parallel-plate, membrane-separated electrochemical treatment system is demonstrated by exposing a composition library of mixed-metal oxides to oxygen evolution conditions in 1 M sulfuric acid for 2 h. This application is particularly important because the electrolysis and photoelectrolysis of water are promising future energy technologies inhibited by the lack of highly active, acid-stable catalysts containing only earth abundant elements.

KEYWORDS: *solar fuels, high throughput, oxygen evolution, electrochemical stability, combinatorial electrochemistry*

The efficient electrolysis and solar photoelectrolysis of water to hydrogen fuel are attractive clean energy technologies. Large-scale deployment of these technologies requires the discovery of improved electrocatalysts containing only earth-abundant elements.[1−3] In particular, the 4-electron oxygen evolution reaction (OER) is kinetically slow and improved catalysts are required to enable efficient H_2 production.[2] Operation in strong acid is desirable due to the availability of robust, efficient polymer exchange membranes[4] and hydrogen evolution catalysts.[1,5] The high operating potential of the OER catalyst in a strong acid electrolyte creates a highly corrosive environment in which only precious metal oxides have exhibited both catalysis and stability.[6] The nonprecious metal oxides that are known to be stable under these conditions are not highly active and vice versa, creating an opportunity for combinatorial experimentation to ascertain whether catalysis and stability can be simultaneously obtained with mixed-metal oxides. Screening composition libraries for these properties requires a high throughput instrument that can operate for long durations to assess stability, and which is able to mitigate a multitude of spatial inhomogeneities inherent to parallel experimentation.

Previous high-throughput searches for acid OER electrocatalysts have involved short electrochemical measurements of precious metal systems in mild acidic environments.[7−9] These high throughput screening techniques relied on parallel fluorescence imaging of a material library[10] immersed in an electrolyte with pH near or above 3. By polarizing the entire library at a chosen OER overpotential, active catalysts are identified by a pH-sensitive fluorescence method that responds to the local accumulation of protons, which are products of the OER. With a measurement time on the order of 10 s, the parallel imaging of pH alterations allows for rapid identification of the active compositions, but the technique cannot be

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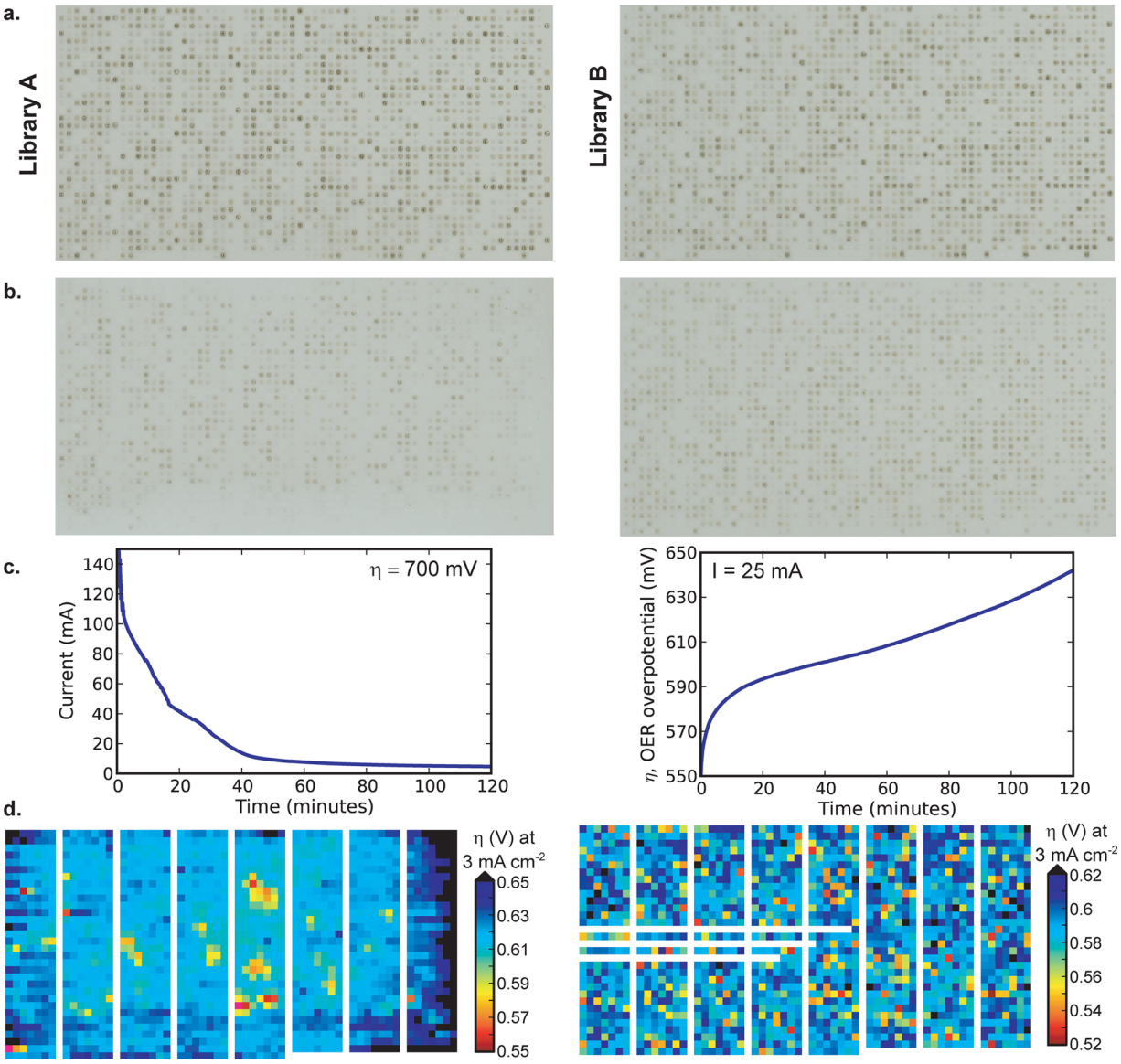

Figure 1. Two identically prepared libraries tested using different operating modes of the parallel electrochemical treatment system. Optical images of the libraries are shown before (a) and after (b) the stability experiment. (c) The electrochemical signal over the 2 h experiment showing the current from the chronoamperometry measurement of library A and the voltage from the chronopotentiometry measurement of library B. (d) The measured overpotential using the serial scanning droplet cell instrument after the respective 2 h stability experiment. The presence of spatial artifact for library A and lack of spatial artifact for library B can be seen in panels b and d.

employed at pH 0. The measurement requires that the catalysis-induced change in pH is localized to the catalyst region, limiting the experiments to short durations that preclude pH changes to the bulk solution. The intentional local pH decrease is also undesirable because it changes the thermodynamics of both the catalysis and material corrosion. The use of pH 0 electrolyte is not only technologically more relevant, but also limits significant changes to the local pH due to the high proton concentration. A new method is required to enable longer duration operation of the catalysts to test even moderate-duration stability.

While the desirable operating lifetime of an OER catalyst is on the order of years, initial high throughput screening can be performed on the order of hours, which is long enough to demonstrate initial stability. To meet these design requirements, we present a parallel electrochemical processing instrument that provides similar electrochemical history to each sample in a materials library. Large planar electrodes containing composition libraries have been employed for related electrochemical experiments,[10−12] with the associated instruments engineered to include auxiliary measurements such as imaging of evolved gases.[13] For the present purpose, electrochemical engineering is applied to optimize the uniformity of the electrochemical environment over a large-area electrode. Illustrative experiments are performed using composition libraries with compositions randomly distributed over a grid of library sample positions so that any spatial artifacts introduced by the parallel electrochemical treatment system would be apparent via spatial variations in the resulting changes to the performance or appearance of materials across the library plate. While spatial artifacts could be detected by measuring a "uniform" plate that contained an array of identical samples, demonstration with a mixed-metal oxide library was preferred due to the random distribution of stable and unstable

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materials across the plate. The newly implemented stability screening instrument was developed through extensive engineering and modeling to address the difficulties associated with parallel electrochemical experimentation: high, nonuniform concentration of leached metals; unknown or nonuniform solution potential; and nonuniform ohmic losses in the planar working electrode. The operation of the instrument is demonstrated using discrete combinatorial libraries containing mixtures of stable and unstable metal oxides.

To demonstrate the ability of this apparatus to minimize spatial variations in effective potential over the entire sample plate, and to demonstrate the impact of exposing samples to spatially nonuniform effective potentials, two duplicate libraries, A and B, were operated for 2 h in the parallel electrochemical treatment system under differing conditions. Library A was held at a constant potential of 503 mV vs the Ag/AgCl reference electrode, corresponding to an overpotential of η = 700 mV for the OER. Library B was held at a constant current of I = 25 mA. Photoscanned images of each library, shown in Figure 1a and b, before and after the experiment, reveal significant alterations to most of the samples. The electrical signals acquired during the stability experiments are shown in Figure 1c, and the catalytic performance of the poststability libraries is shown in Figure 1d. This serial scanning droplet cell (SDC) measurement of the OER overpotential at 3 mA cm^{-2} characterizes not only the catalytic activity, but also the 2 h stability of the material. Locations with completely corroded samples will produce the >650 mV overpotential of the SnO_2:F coating. Because of the randomized locations of the sample compositions, this performance metric is expected to vary significantly from one sample to the next, but be uniformly distributed over the entire library.

For library A, held at constant potential, the initial anodic current of approximately 150 mA decayed to approximately 10 mA over the first hour of operation, and remained relatively stable for the remainder of the experiment. The large total current experienced over the first 30 min induced substantial voltage losses for samples far from the working electrode contact, corresponding to significant spatial variation in the effective potential experienced by the samples. A lower voltage was experienced by the samples far from the contact, which generally corresponds to lower corrosion rates for metal oxides. The relative stability of these samples compared to the ones near the contact can be seen both visually in the left column of Figure 1b and in the SDC measurement of Figure 1d. The profile of this artifact is in excellent agreement with that of Figure 2. While the central samples experienced a lower potential at the beginning of the parallel electrochemical treatment system experiment, the low current at the end of the experiment indicates that they were still exposed to the intended 700 mV overpotential. These results indicate that the stability of these mixed-metal oxides is not only sensitive to applied potential but also to the potential-time profile. As noted above, limiting the current to 25 mA provides an acceptable voltage variation, and thus the corresponding results for library B show no evidence of a spatial artifact. In future work we will perform chemical and electrochemical characterization of composition libraries that have been processed in the parallel electrochemical system, building upon this demonstration of its performance and application to combinatorial libraries.

A new instrument for high-throughput, parallel electrochemistry was developed and applied to screen composition libraries for electrochemical stability under acidic OER conditions. Careful engineering of the electrochemical cell and simulation-guided design of experiments yielded a parallel electrochemical treatment system that provides uniform electrochemical exposure over a large-area working electrode. In particular, challenges arising from the parallel measurement scheme were addressed using continuous electrolyte recirculation, membrane-separated anolyte and catholyte chambers, and appropriate operating parameters. The parallel electrochemical treatment system can be used to provide a uniform electrochemical environment for a variety of experiments including corrosion stability experiments for other conditions and for parallel electrochemical materials processing.

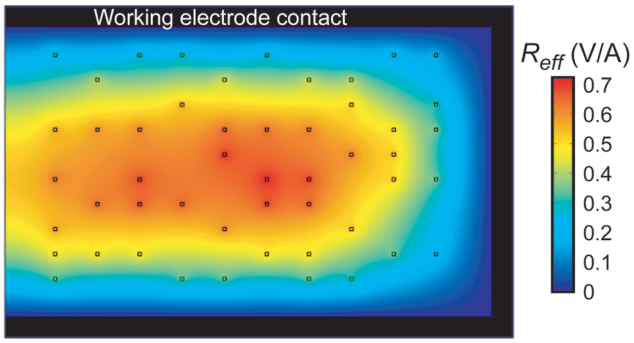

Figure 2. Spatial variation in the effective resistance (R_{eff}), which is independent of the total current, is mapped over the planar working electrode area using model simulations. Samples near the center experience a lower working electrode potential than those near the working electrode contact.

■ EXPERIMENTAL PROCEDURES

Two duplicate (Mn−Co−Ta−Sb)O_x composition libraries containing both stable (Ta, Sb) and unstable (Mn, Co) elemental oxides were each deposited as an array of 1771 discrete compositions, which covered the 4-element composition space with 5.0 at% composition steps.[14,15] Each library was fabricated by inkjet printing separate metal precursor inks containing $Mn(NO_3)_2$, $Co(NO_3)_2$, $TaCl_5$, and $SbCl_3$ onto a glass substrate with conductive SnO_2:F coating (Hartford Glass Company, Hartford, CT), which served as a common back contact. The ethanol-based inks contained 1% Pluronic F127 to influence ink rheology and drying. Each 1 mm × 1 mm composition sample contained a total loading of 3.8 nanomoles of metal, as described previously.[13,16] The inks were dried and the metal precursors converted to oxides by calcination in air at 450 °C. The composition library was imaged using a commercial photoscanner (Epson Perfection V600 PHOTO). The library plate served as the working electrode for electrochemical measurements, with electrical contact established by placing 0.25 in. wide copper tape (McMaster-Carr) around three of the four perimeter edges.

Parallel measurements were performed in the parallel electrochemical treatment system, described in detail below, which established simultaneous, uniform electrochemical exposure to each sample in the library. A potentiostat (Gamry Reference 600) was used to control 3-electrode measurements: a 2 h chronoamperometry (CA) measurement at 25 mA or a 2 h chronopotentiometry (CP) measurement at 700 mV overpotential for the OER. Considering the wetted substrate area (approximately 98 cm^2) and the 1771 composition samples, 25 mA total current corresponds to an average current density of 0.26 mA cm^{-2} for the wetted

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electrode area or 1.4 mA cm^{-2} for the composition samples. After the parallel electrochemical treatment system terminated operation, the library plate was immediately removed and excess electrolyte cleared from the surface.

While the instrument is compatible with a wide range of electrolytes, O_2-saturated 1.0 M H_2SO_4(aq) solution was used to evaluate catalyst stability at pH 0 under potentials applicable to the OER. After the stability screen experiment, the catalytic activity of the materials, which have reached quasi-equilibrium under operational conditions, must be evaluated by an auxiliary technique. For example, we have recently reported a bubble screening technique that could be used for parallel measurement of catalytic activity.[13] That technique provides parallel detection by imaging bubbles of both O_2 evolved at the working electrode and H_2 evolved at the counter electrode. However, it is generally not appropriate to use one parallel measurement to evaluate a new parallel measurement, due to inherent uncertainty as to the origin of any observed spatial artifacts. Therefore, after operation in the stability screen instrument, a previously reported serial measurement was used to establish catalytic activity of each composition in the library.[15] The scanning drop cell (SDC) was used to measure the activity of each catalyst composition with a 15 s chronopotentiometry (CP) measurement at 3 mA cm^{-2} in O_2-saturated 1.0 M H_2SO_4(aq).

Parallel Electrochemical Treatment System. The detailed schematic of the parallel electrochemical treatment system is illustrated in Figure 3. It consists of three

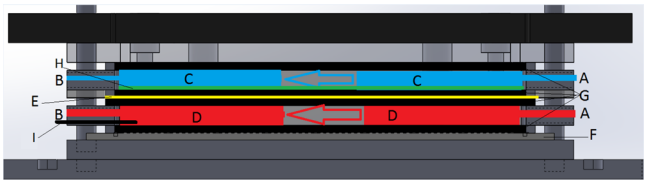

Figure 3. Schematic of the parallel electrochemical treatment system showing inlet (A) and outlet (B) ports for catholyte (C) and anolyte (D), Nafion membrane (E), working electrode (F), electrochemically inert gasket material (G), planar counter electrode (H), and reference electrode (I).

polymethyl-methacrylic (McMaster-Carr) pieces stacked on top of one another and separated by a Nafion (E) membrane (N117, IonPower Inc.). This stacked assembly is mechanically sealed to the library substrate via a pressure plate from the top. The stacked gasket geometry (G) provides solution contact to the inner area of the substrate containing the composition library, while avoiding solution contact to the outer perimeter of the substrate and the electrical contact (Cu tape). The aqueous electrolyte solution flows through the catholyte (C) and anolyte (D) chambers through ports (A and B) with constant solution flow of 10 mL min^{-1} maintained throughout the experiment. The library plate (F) serves as the working electrode, and a planar counter electrode (H) is suspended in the catholyte chamber so that it is parallel to the library plate.

Corrosion-Induced Artifacts. Long-duration polarization of unstable materials creates an opportunity for uncontrolled thermodynamics due to gradients in chemical potential that arise from variations in the concentration of each metal species. The driving force for corrosion of a given metal (oxide) decreases with increasing concentration of the product species in the electrolyte, which may increase during an experiment as some samples corrode. For example, complete dissolution of the material library in the described parallel electrochemical treatment system would produce dissolved metal concentrations in excess of 0.1 mM in the stagnant anolyte. Such high concentrations not only pose a risk of cross-contamination, but could significantly increase the chemical potential for metal ions in solution, possibly producing a false positive result for catalyst stability. Care must also be taken to avoid spatial inhomogeneities in ionic concentrations which could introduce artifacts into the stability screening results. Therefore, anolyte solution is continuously flowed over the working electrode to flush away dissolved species. For the experiments described below, the solution was recirculated from a 1 L reservoir, which limits the maximum metal ion concentration to 7 μM, even if the entire material library dissolved.

Electrode Geometry. Planar working and counter electrodes have been used for large area electrochemical characterization and in particular for combinatorial studies.[12,13] Ideally, the parallel planar geometry polarization of the working electrode with respect to the counter electrode yields uniform electric field lines perpendicular to the two electrode planes. This arrangement can be considered simultaneous establishment of a 2-electrode contact to each composition sample in the library. Electrochemical experiments characterize the aggregate electrochemistry of the entire, nonuniform working electrode. The addition of a reference electrode (Ag/AgCl, CH Instruments) provides measurement of the solution potential at a single point, enabling 3-electrode measurements under the uniform field approximation.

The planar mesh counter electrode provides distinct advantages over a single wire electrode placed at the edge of the library plate. In the latter scenario, solution resistance losses would create position-dependent working electrode potentials in 2-electrode operation and would violate the uniform electric field assumption in 3-electrode measurements. Exposure of the planar counter electrode to dissolved metals could similarly compromise experimental integrity. Many dissolved ions will be readily electroplated onto the counter electrode, which is operated at a substantially lower potential than the working electrode. Local electroplating near the source of dissolved ions will create variations in the counter electrode surface composition, which could significantly perturb an otherwise uniform electric field at the working electrode surface. This situation is avoided by isolating the catholyte with an ion exchange membrane.

Ohmic Losses. Chronoamperometry, in which a constant potential is applied for the duration of the measurement, is often desirable for stability experiments. At the beginning of a CA measurement with an as-prepared library, unstable materials rapidly corrode, producing a large current that slowly decreases as materials either completely etch or form passivation layers. A robust, parallel, combinatorial stability experiment requires each sample to experience the same potential-time profile. To facilitate the design of such experiments, and in particular to understand the effects of large currents, electrostatic modeling was performed via COMSOL Multi-Physics software using models of the parallel electrochemical treatment system generated in Solid Works. The position-dependence of the electrical potential in the planar working electrode was calculated using the following model.

Consider a total electrochemical current I entering the working electrode surface, which is transported to the electrical

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contact (Cu tape) through a sheet resistance, taken to be the SnO_2:F value of 7 Ω sq^{-1}. Each working electrode (sample) location experiences a unique ohmic loss that is determined not only by the electrical resistance from that location to the contact, but also by the spatial distribution of the current density, $J(x,y)$. To calculate $\delta V(x,y)$, the spatial distribution of working electrode potential with respect to the contact, $J(x,y)$ must be defined. We approximate that the total current I is introduced into the working electrode through 50 of the 1 mm^2 sample areas, distributed over the working electrode. This approximation is equivalent to an experiment in which most composition samples are electrochemically inactive and that the 50 composition samples are electrochemically equivalent. Finite element modeling provides a map of δV over the working electrode area, and it is important to note that the result can be made independent of the experimental current, I, by defining an effective resistance, $R_{eff} = \delta V/I$. The result is shown in Figure 2 with the locations of the 50 current sources indicated. Visual inspection reveals that the R_{eff} profile depends strongly on sample location with respect to the perimeter working electrode contact, and that the profile does not strongly depend on the number or exact locations of the current sources. The results indicate that at finite I, all samples experience a voltage deviation from the measured working electrode potential, and more importantly for combinatorial measurements, the voltage drop is larger for inner samples than for samples near the perimeter contact. By limiting the total current, I, delivered to the working electrode, spatial variations in $\delta V(x,y)$ can be minimized. In particular, Figure 2 shows that for I = 25 mA, the potential loss relative to the working electrode contact varies from approximately 4 to 18 mV. This variation of less than 15 mV in effective potential experienced by the samples is acceptable for most high throughput experiments.

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Notes

The authors declare no competing financial interest.

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