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Supporting Information

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Discovery of New Oxygen Evolution Reaction Electrocatalysts by Combinatorial Investigation of the Ni–La–Co–Ce Oxide Composition Space

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Table of Contents

Materials and Methods

Preparation of Pseudo-quaternary Library	p. 2
Preparation of $\text{Ni}_{0.1}\text{La}_{0.1}\text{Co}_{0.3}\text{Ce}_{0.5}\text{O}_x$ Catalyst on Glassy Carbon	p. 2
Electrochemical Characterization with Scanning Electrochemical Drop Cell	p. 3
Electrochemical Characterization with Glassy Carbon RDEs	p. 3
SEM and EDS Characterization of the Library and Glassy Carbon RDEs	p. 5
XPS Characterization of Catalyst film on Glassy Carbon	p. 5
Figure S1	p. 6
Figure S2	p. 7
Figure S3	p. 8

Materials and Methods

Sample Preparation (for 5.0 at% library). The discrete pseudo-quaternary (Ni-La-Co-Ce) O_x library was designed as an array with 5.0 at% composition steps for each of Ni, La, Co, and Ce. The complete array of 1771 samples was deposited by inkjet printing onto the FTO-coated side of a 10 cm x 15 cm glass plate at a resolution of 2880 x 1440 dpi (21, 22). Four separate metal inks, of the type previously described by Fan and Stuckey,[8] were prepared by mixing 5 nmoles of each of the Ni, La, Co, and Ce precursor with 0.80 g Pluronic F127 (Aldrich), 1.0 mL glacial acetic acid (T.J. Baker, Inc.) (≤ 0.2 ppm Fe), 0.40 mL of concentrated HNO_3 (EMD) (≤ 0.2 ppm Fe), and 30 mL of 200 proof Ethanol (Koptec). The metal precursors were $Ni(NO_3)_2 \cdot 6H_2O$ (1.56 g, $\geq 98.5\%$, ≤ 10 ppm Fe, Sigma Aldrich), $La(NO_3)_3 \cdot 6H_2O$ (2.19 g, 99.999%, ≤ 10 ppm Fe, Sigma Aldrich), $Co(NO_3)_2 \cdot 6H_2O$ (1.49 g, 99.999%, 2.1 ppm Fe, Sigma Aldrich), and $Ce(NO_3)_3 \cdot 6H_2O$ (2.47 g, 99.99%, ≤ 5 ppm Fe, Sigma Aldrich). After printing the library of compositions as a set of 1 mm x 1 mm spots on a 2 mm pitch, the inks were dried and the metal precursors converted to oxides by calcination in air at 40 °C for 18 h, then at 70 °C for 24 h, followed by a 5 h ramp and 10 h soak at 350 °C. The ink formulation and thermal processing protocol maintains intimate mixing of the precursors up to the final calcination step, during which the thermodynamics of the produced mixed metal oxides influences the final structure.

Preparation of Catalyst on Glassy Carbon. The selected composition ($Ni_{10}La_{10}Co_{30}Ce_{50}$) was printed onto glassy carbon rotating disk electrodes (GC RDEs, SIGRADUR G, HTW Hochtemperatur-Werkstoffe GmbH), which are cylinders 5 mm in diameter and 4 mm in height. Four separate metal inks were prepared as described above and printed at 2880 x 1440 dpi, at 7.5 nmoles of metal per mm^2 . After printing, the inks were dried and the metal precursors

converted to oxides using the same calcination and annealing process used for the combinatorial library.

Electrochemical Characterization

Scanning droplet photoelectrochemical cell.

The detailed geometry and operational performance of a scanning droplet cell were described by Gregoire, et. al.^[3b] Briefly, a drop of solution was formed on top of a 1 mm x 1 mm ink-jet printed sample. The shape of the droplet was directed and controlled by a solution inlet port and multiple solution outlet ports without the need for a sealing gasket. The scanning droplet cell (SDC) provided an individual 3-electrode cell for each sample, including a capillary Ag/AgCl reference electrode terminating within 1 mm of the sample surface and a platinum wire counter electrode placed in the solution influent. In this study, we continuously supplied an oxygen-saturated 1.0 M NaOH(aq) solution to form a drop contact to each catalyst sample, which in this SDC configuration produces an uncompensated resistance of approximately 15 Ω . After moving to a new sample location, a 2 second cell stabilization period preceded the electrochemical experiments, which included a 15 s CP measurement at current density $J = 10 \text{ mA cm}^{-2}$ followed by a CV at 100 mV s^{-1} from -60 mV to 480 mV overpotential for the OER reaction. The catalyst overpotential η was determined using the final measured potential of the CP measurement, creating the compositional maps of catalyst performance shown in Figures 1 and S1. Visual inspection of representative CP data confirmed that the overpotential stabilized within 5 mV by the end of the 15 s measurement.

Electrochemical analysis of catalysts on glassy carbon rotating disk electrodes. GC RDE electrodes coated with each composition were subjected to a series of electrochemical measurements in oxygen-saturated 1.0 M NaOH (prepared from millipure H₂O and NaOH

pellets, $\geq 98\%$, ≤ 5 ppm Fe, Sigma Aldrich Bio Ultra) blanketed under 1 atm $O_2(g)$. The working electrode was rotated at 1600 rpm and the counter and reference electrodes were a carbon rod (99.999%, Alfa Aesar), and a commercial saturated calomel electrode (SCE) (CH-Instruments), respectively.

All measurements were conducted in a modified two-chamber U-cell in which the first chamber held the working and reference electrodes in *ca.* 120 mL of solution, and the second chamber held the auxiliary electrode in *ca.* 25 mL. The two chambers were separated by a fine-porosity glass frit. The cell was purged for *ca.* 20 min with O_2 prior to each set of experiments. During static-voltammetry measurements, the solution in the first chamber was blanketed under O_2 . During rotating-disk electrode voltammetry measurements, the solution in the first chamber was continuously bubbled with O_2 . The uncompensated resistance of the cell was measured with a single-point high-frequency impedance measurement and IR drop was compensated at 85% through positive feedback using the Bio-Logic EC-Lab software. The typical electrochemical cell had uncompensated resistance of approximately 20Ω in 1 M NaOH. Each catalyst was investigated by a CV at 10 mV s^{-1} (forward and reverse sweep shown in Figure 2c), a series of 30 second controlled-current CP steps and a series of controlled-potential CA steps (shown in Figure 2a), and a 120 minute CP measurement at 10 mA/cm^2 current density (shown in Figure 2b).

The quasi-steady state CP and CA measurements in Figure 2 do not contain appreciable sample oxidation current and thus follow the Tafel trend. At high- η the data deviate from the exponential behavior, possibly due to bubble formation at the electrode surface and corresponding decrease in electrochemically accessible surface area.

SEM and EDS Characterization of the Library and Glassy Carbon RDEs. Select catalysts in the library were characterized using bulk composition measurements (energy dispersive x-ray spectroscopy, EDS), as reported in Table S1. The EDS analysis demonstrates reasonable fidelity between the measured and intended compositions; however, the measured concentration for La is somewhat lower than intended. The discrepancies are on the order of the general EDS accuracy of $\pm 10\%$ and we additionally note that the Ce-K and La-K peaks are strongly overlapped, creating the possibility of systematic quantification errors. Alternatively, the printed La concentrations could in fact be lower than intended due to poor control of the La concentration in the ink. The precursor $\text{La}(\text{NO}_3)_3$ salt is hygroscopic, confounding the measurement of precursor mass during ink preparation. The deviation from intended La concentration does not affect the discovery of new active composition regions. In this paper all compositions reported are the intended compositions, except where EDS measurements are noted. Pre- and post-stability test examination of the electrodes by SEM was performed and is summarized in Figure S2. The composition intended to be deposited on the GC RDEs was $\text{Ni}_{0.1}\text{La}_{0.1}\text{Co}_{0.3}\text{Ce}_{0.5}$. The measured EDS compositions of the corresponding RDE sample was $\text{Ni}_{0.12}\text{La}_{0.07}\text{Co}_{0.36}\text{Ce}_{0.45}$ as-prepared and $\text{Ni}_{0.12}\text{La}_{0.07}\text{Co}_{0.31}\text{Ce}_{0.50}$ after the extensive electrochemical testing. The decrease in Co concentration after the 2 h stability test may be related to selective dissolution or to the flaking of regions of catalyst film observed by SEM (see Figure S2). No Fe was detected by EDS in any samples examined.

XPS of Catalyst films on Glassy Carbon Disks. XPS survey scans were collected of the as-prepared films (before electrolysis) to check for Fe impurities. XPS data was collected using a Kratos Axis Nova with monochromatic Al $K\alpha$ excitation at 1486 eV and 150W power. Experiments were performed at the base pressure of 10^{-9} Torr. The data were collected at 160 eV

pass energy with an energy resolution of about 1.5 eV. No Fe was detected in these survey scans.

Table S1. Comparison of intended compositions with compositions measured by EDS for all 50:50 bimetallic composition samples.

Target compositions				Measured compositions			
Ni	La	Co	Ce	Ni	La	Co	Ce
0.5	0	0.5	0	0.48	0.01	0.49	0.03
0.5	0.5	0	0	0.54	0.4	0.05	0
0	0.5	0.5	0	0	0.38	0.61	0
0	0	0.5	0.5	0	0.02	0.46	0.52
0	0.5	0	0.5	0.02	0.4	0.01	0.57
0.5	0	0	0.5	0.51	0	0.02	0.47

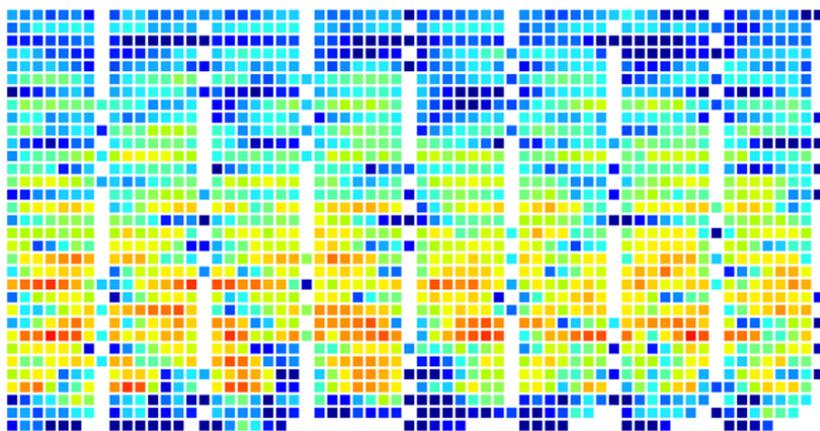


Figure S1. Performance map of (Ni-La-Co-Ce) O_x oxygen evolution catalysts. The overpotential required for performing oxygen evolution at 10 mA cm⁻² is shown as a function of physical position in the combinatorial library.

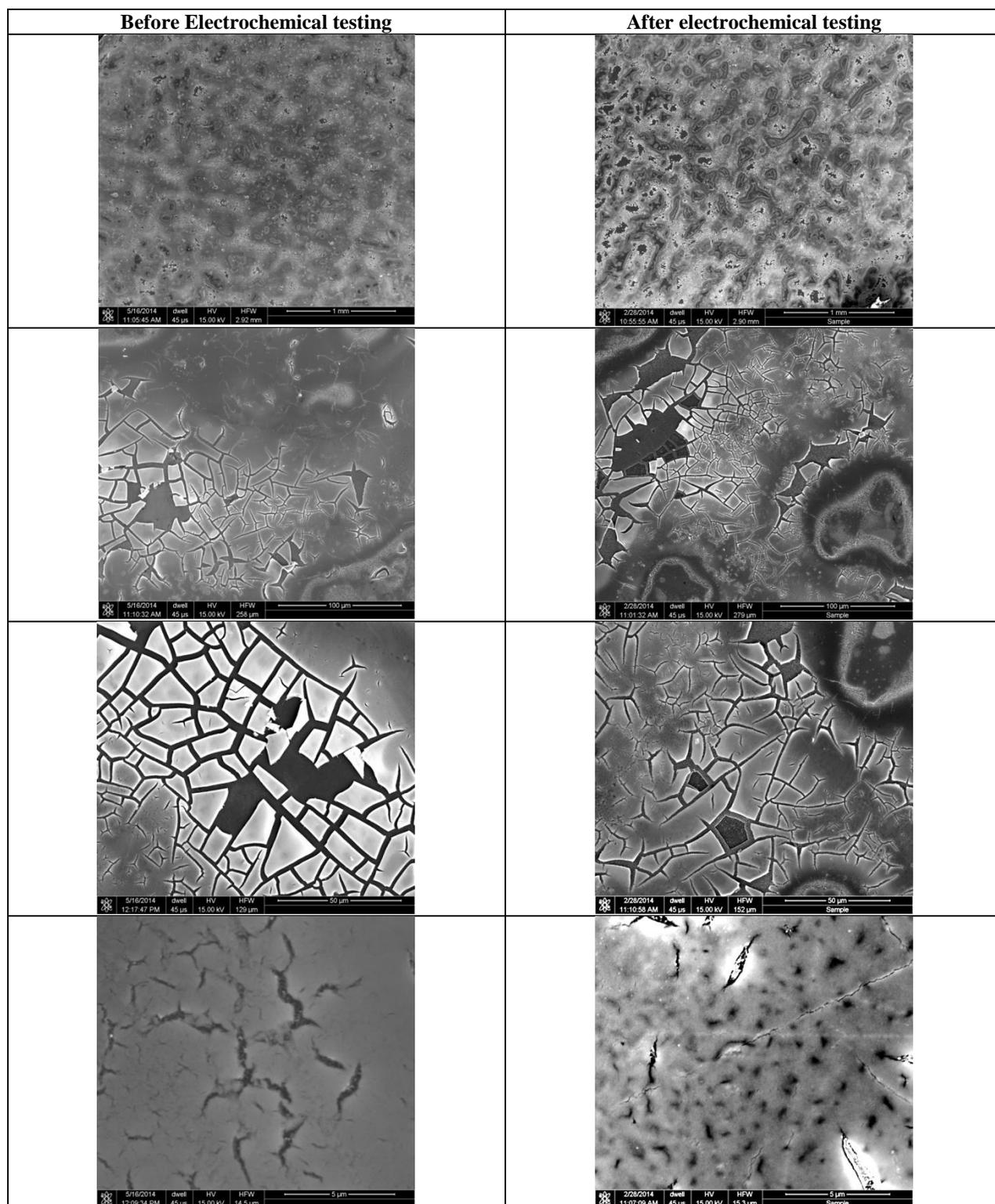


Figure S2. SEM/EDS characterization of the $\text{Ni}_{0.1}\text{La}_{0.1}\text{Co}_{0.3}\text{Ce}_{0.5}\text{O}_x$ catalyst on glassy carbon RDE electrodes before and after the standardized electrochemical testing protocol.

After calcination the catalyst film is cracked, with submicron gaps between film segments and with some regions of bare glassy carbon where the film flaked off. After the 2 h stability test, it is apparent that additional 10-20 micron diameter flakes of the cracked film have been removed, leaving dark black outlines on the glassy carbon surface. EDS confirms that only C, and no Ni, La, Co, or Ce were present on these dark regions. During the stability testing protocol the electrodes are rotated at 1600 rpm, and the associated hydrodynamic forces are apparently sufficient to delaminate some of the film flakes. After this initial mechanical failure, the remaining film is stable, as indicated by the stable CP trace in Figure 2b.

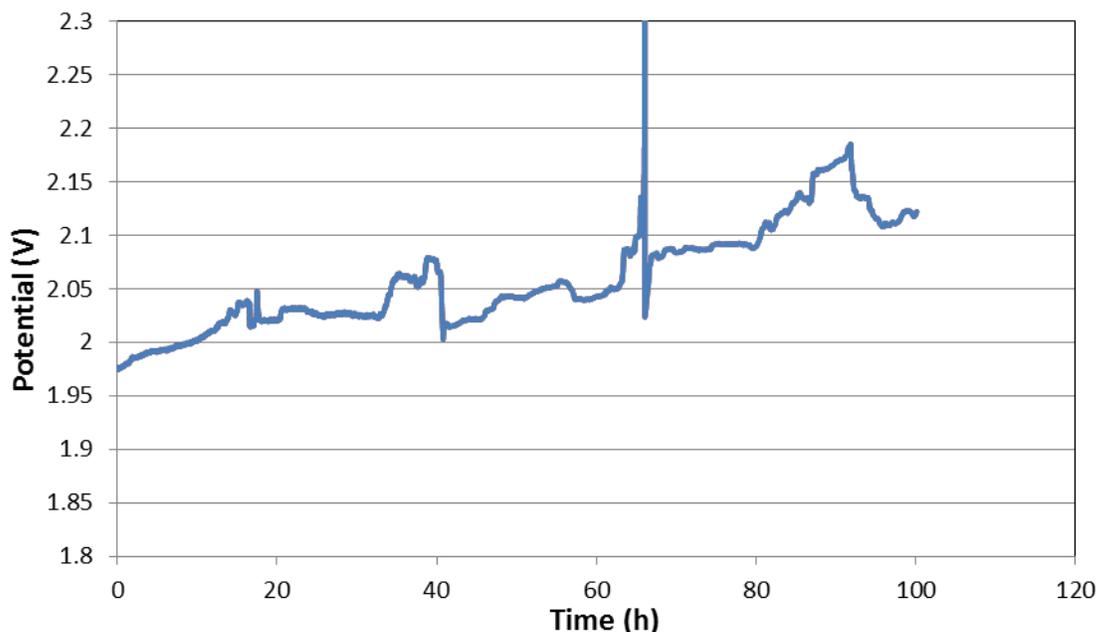


Figure S3. Voltage required to drive the electrolysis of water for 100 hours in a testbed two compartment electrolyzer at 20 mA ($4.0 - 4.5 \text{ mA/cm}^2$ current density). The broad peaks in potential result from changes in fill level of the 1 M NaOH(aq) electrolyte, when refilled the active surface area was increased and the potential dropped abruptly. The sharp peaks in voltage result from momentary loss of electrical contact to the electrolyzer.