Electronic Supplementary Material (ESI) for Energy & Environmental Science.
This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information

A survey of diverse earth abundant oxygen evolution electrocatalysts showing enhanced activity from Ni-Fe oxides containing a third metal

James B. Gerken, Sarah E. Shaner, Robert C. Massé, Nicholas J. Porubsky, and Shannon S. Stahl*
Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706

General Experimental Conditions and Apparatus.

Unless otherwise noted, all chemicals were obtained from Sigma-Aldrich and used without further purification. All solutions were prepared with purified water (ThermoScientific Nanopure, 18.2 MΩ cm^{-1}). All metal solutions were prepared from their respective nitrate salts except tungsten, molybdenum, titanium, and vanadium, which were prepared from $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $Ti(OC_2H_5)_4$, and NH_4VO_3, respectively. A 0.1 M titanium stock solution was prepared by dissolving $Ti(OC_2H_5)_4$ into 2.4 M HNO_3 to achieve a final acid concentration of ~2 M which prevented precipitation of TiO_2. Metal solutions were prepared from water with added 9 vol% glycerol to promote even evaporation of the precursor solutions. In the cases of iron, bismuth, cerium, gallium, vanadium, and titanium, nitric acid was included to stabilize the solutions against precipitation, and H_2O_2 was included in the tungsten solution. All metal solutions were 5 mM in metal.

"Binary Unicoat Pressure Sensitive Paint" was purchased from Innovative Science Solutions Inc. and used for O_2 sensing by painting it on 100 mesh stainless steel mesh as described previously.[1] A defocused diode laser array used to produce 400 nm illumination was produced by a local artificer. Fluorescence from the mesh was recorded with a Canon PowerShot G12 digital camera operated with manual exposure and white-balance control. A homemade remote shutter switch was used to minimize agitation of the camera during image acquisition. To prevent 400 nm light from reaching the camera, a 440 nm cut-off optical filter was constructed using a polystyrene culture flask with optically clear front and back surfaces filled with an aqueous solution of tartrazine (Betty Crocker brand yellow #5 food dye).[2] The dye concentration was adjusted until complete absorption at $\lambda < 440$ nm was achieved with good transmission through the rest of the visible spectrum.

All electrochemical experiments were performed with a 0.1 M NaOH electrolyte solution (pH 13) utilizing fluorine-doped tin oxide (FTO) coated electrodes (TEC-7, Hartford Glass) as the working electrode. Screening experiments were conducted with a constant-current two-electrode electrochemical cell and nickel wire counter electrode. Contact between the power supply lead and the FTO electrode was made with an alligator clip (see photograph in Figure S2 below). Because the screening experiments are performed at constant current, all points on the array are in series with any resistance resulting from the FTO contact, so a perfectly reproducible contact is not necessary under the present screening conditions. The circuit diagram for the constant-current power supply is shown in Figure S1. Tafel experiments were conducted using a Bioanalytical Systems EC Epsilon potentiostat with a three-component electrochemical cell, Ag/AgCl reference electrode, and platinum wire counter electrode.

---

[1] J. B. Gerken, J. Y. C. Chen, R. C. Massé, A. B. Powell, S. S. Stahl, *Angew. Chem.*, 2012, **124**, 6780 - 6784.

[2] R. B. Withrow, L. Price, *Plant Physiol.*, 1953, **28**, 105 - 114.

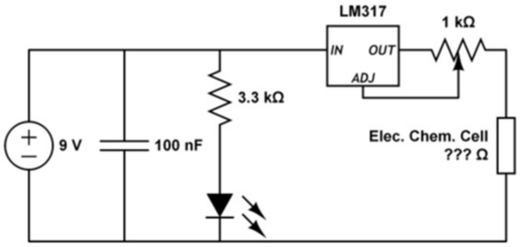

Figure S1 Circuit diagram of the constant-current power supply.

Electrochemical Cell

A custom electrochemical cell constructed from polycarbonate was used to position all of the electrochemical components as well as the O_2-sensing mesh (Figure S2). The FTO working electrode covered with the catalyst array was positioned between two pieces of polycarbonate and a seal was formed using an o-ring; one end of the FTO electrode protrudes from the cell to provide for easy attachment to the power supply. The cell was then be filled with electrolyte solution. The mesh was held about 2 mm above the catalyst array, and above that a spacer and nickel wire counter electrode were positioned. An optically transparent borosilicate glass cover with holes in the four corners for purging the electrolyte with Ar was secured to the top of the cell with electrical tape. The alligator clips from the red and black leads of the constant current power supply were clipped directly to the FTO electrode and nickel wire counter electrode, respectively (Figure S2).

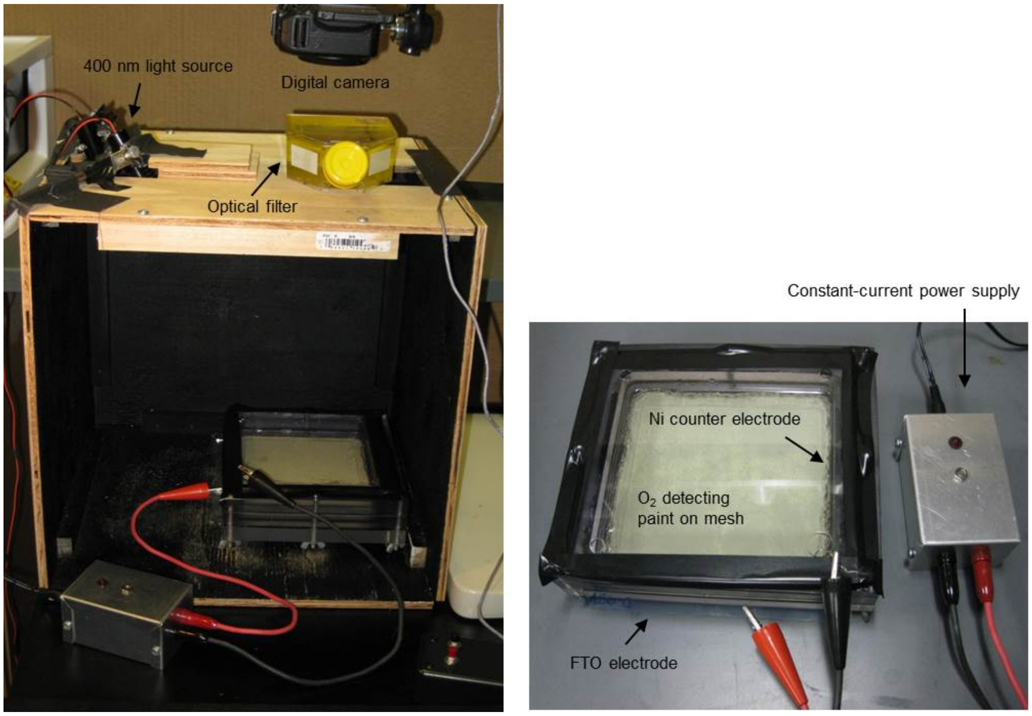

Figure S2 Photographs of the apparatus and close-up of the electrochemical cell. The 400 nm light source consists of an array of laser diodes with defocusing lenses to provide wide coverage. The camera is mounted via a tripod adaptor to a ring stand. At the lower right, the electronic shutter release for the camera can be seen.

Effect of screening conditions

Constant current vs. constant potential screening

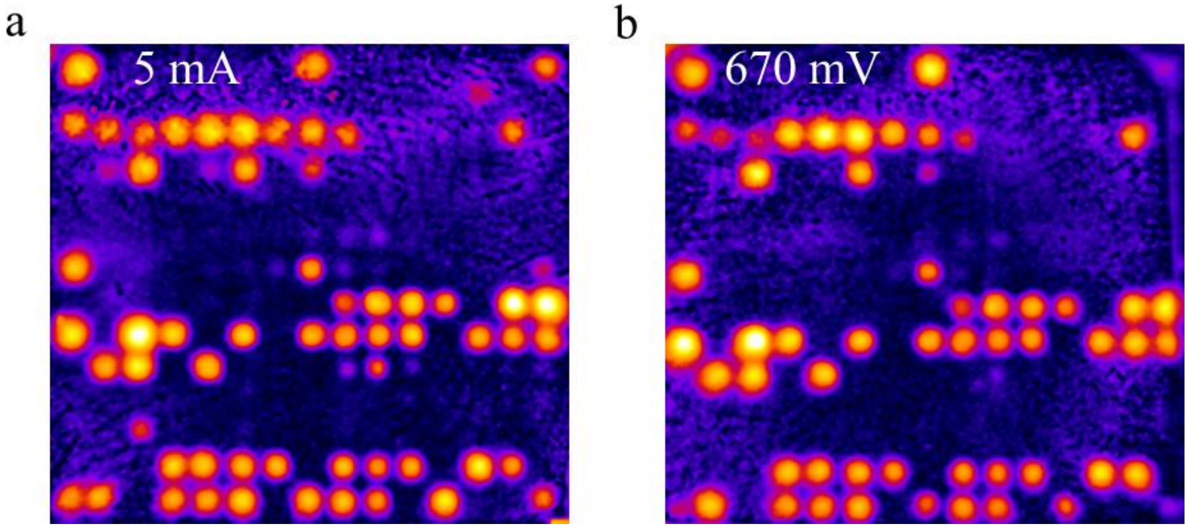

Figure S3 False-colour rendering of fluorescence data showing the effect of screening a catalyst array under constant current and constant potential conditions. Relative catalyst activities measured with a two-component electrochemical cell at a constant current of 5 mA (a) were qualitatively similar to those measured with a three-component electrochemical cell at a potential of 670 mV (vs. Ag/AgCl) (b). Both experiments utilized a nickel counter electrode. The constant-potential data was collected using a Bioanalytical Systems EC Epsilon potentiostat and an Ag/AgCl counter electrode.

Changing current

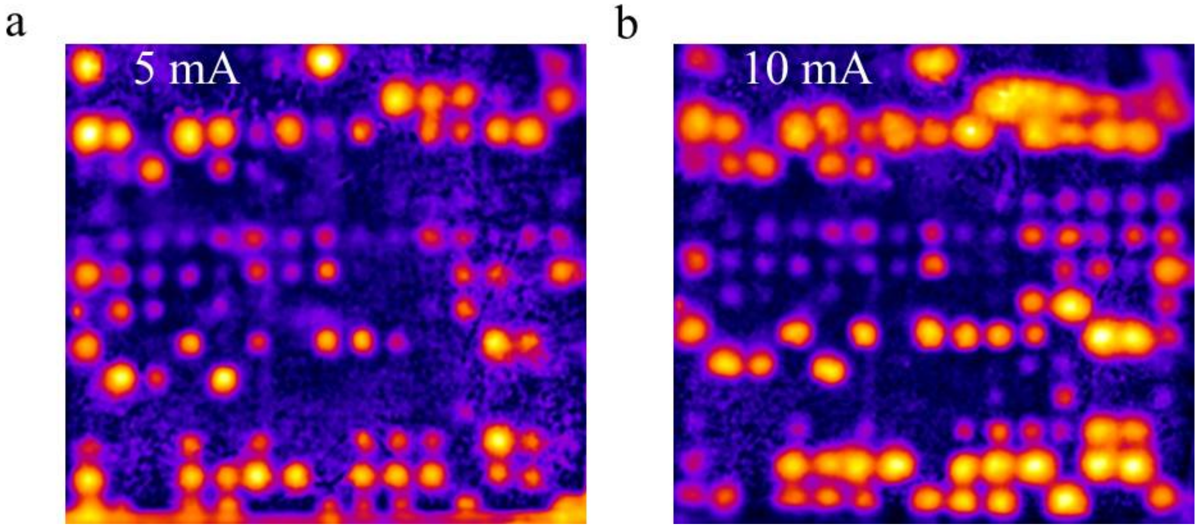

Figure S4 False-colour rendering of fluorescence data showing the effect of screening a catalyst array at 5 mA (a) and 10 mA (b). The two images are qualitatively similar, but at the higher current, the amount of O_2 produced by the most active compositions leads to loss of resolution between adjacent spots.

Pre- and post-electrolysis

The assay is typically performed on electrodes that have been subjected to electrolysis for one hour to drive the composition and structure of the catalysts towards steady-state. Measurements were performed on a catalyst array before and after electrolysis to study the changes in relative activity between different compositions during catalytic turnover. This comparison indicated most of the oxides retained similar activities before and after electrolysis, but that some compositions became more active towards water oxidation following this treatment. In contrast, a few oxides lost activity, presumably due to their instability under the highly oxidizing and alkaline experimental conditions (Figure S5).

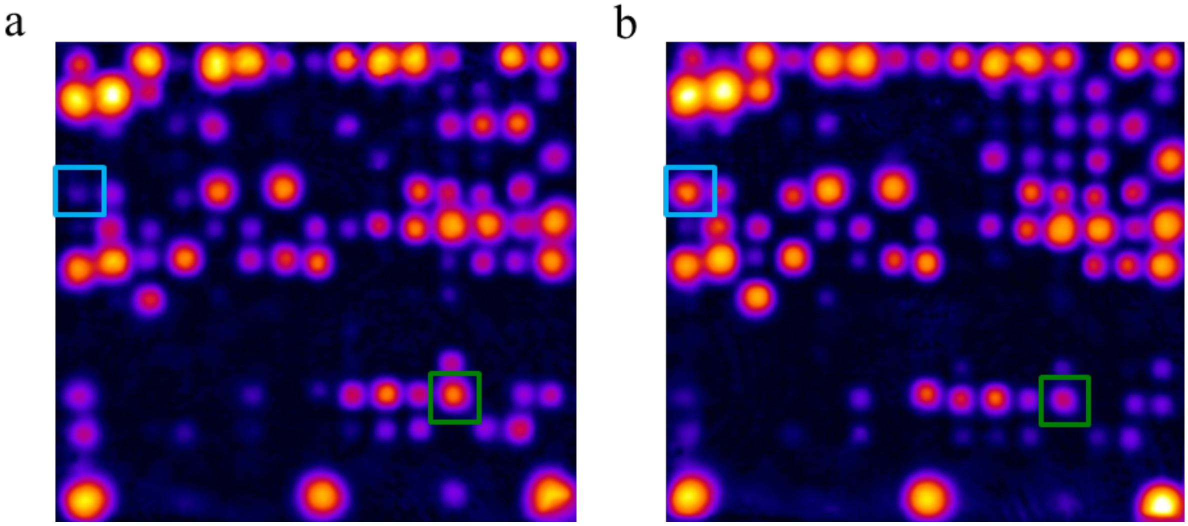

Figure S5 False-colour rendering of fluorescence data showing the effect of screening a catalyst array before (a) and after (b) electrolysis at 5 mA of current for 1 h. Some compositions require this electrolysis to reach steady state and become active catalysts. Other compositions that are not stable under the experimental conditions (highly oxidizing and alkaline) may become less active after electrolysis. The compositions indicated by the light blue (Ni-Ga-Ca 40:40:20) and green (Co-Ca 80:20) squares are the mixed-metal oxides in the array that exhibit the largest increase and decrease in activity, respectively, due to the 1 h electrolysis.

Preparation of catalyst arrays

An FTO-coated glass electrode (15 × 15 cm) was rinsed with water and dried, and the FTO-coated side was rinsed with methanol, which was allowed to evaporate prior to depositing the catalyst precursor solutions. A Gilson liquid handling robot (215 Synthesis Workstation) was used to mix metal solutions in the desired ratios and deposit 1 μL of each precursor solution onto the FTO electrode.[3] Eight different metals were incorporated onto each catalyst array to produce 201 catalyst compositions containing up to three metals each (Figure S6). Fourteen of these three-metal ternary mixtures ($A_{(100\,\%\,-\,p)}B_{(p\,-\,q)}C_qO_m$, where p and q are varied in steps of 20 % from 0 to 100 % and m freely varies to fit the oxidation states of the

---

[3] Although it allows for quasi-continuous composition gradients, the inkjet-based approach to array generation has some unsolved problems that we wished to avoid. These are related to difficulties with inkjet print-heads and printing in the infernal method, by corrosives. Cf. W. Blake, *The Marriage of Heaven and Hell*, (1793) p 14.

cations in the catalyst) were encompassed within the 201 compositions on an electrode. Nine reference compositions comprised of Co-Fe-Ni in a ratio of 40:40:20 were also included on each electrode (these compositions are shown as green circles labeled R in Figure S6c). Electrodes decorated with the metal salt precursor solutions were calcined in an electric kiln (Xpress-Q-11A, Paragon Industries) at 500 °C, using a ramp rate of 250 °C/h, for six hours to form the corresponding mixed-metal oxide catalysts.

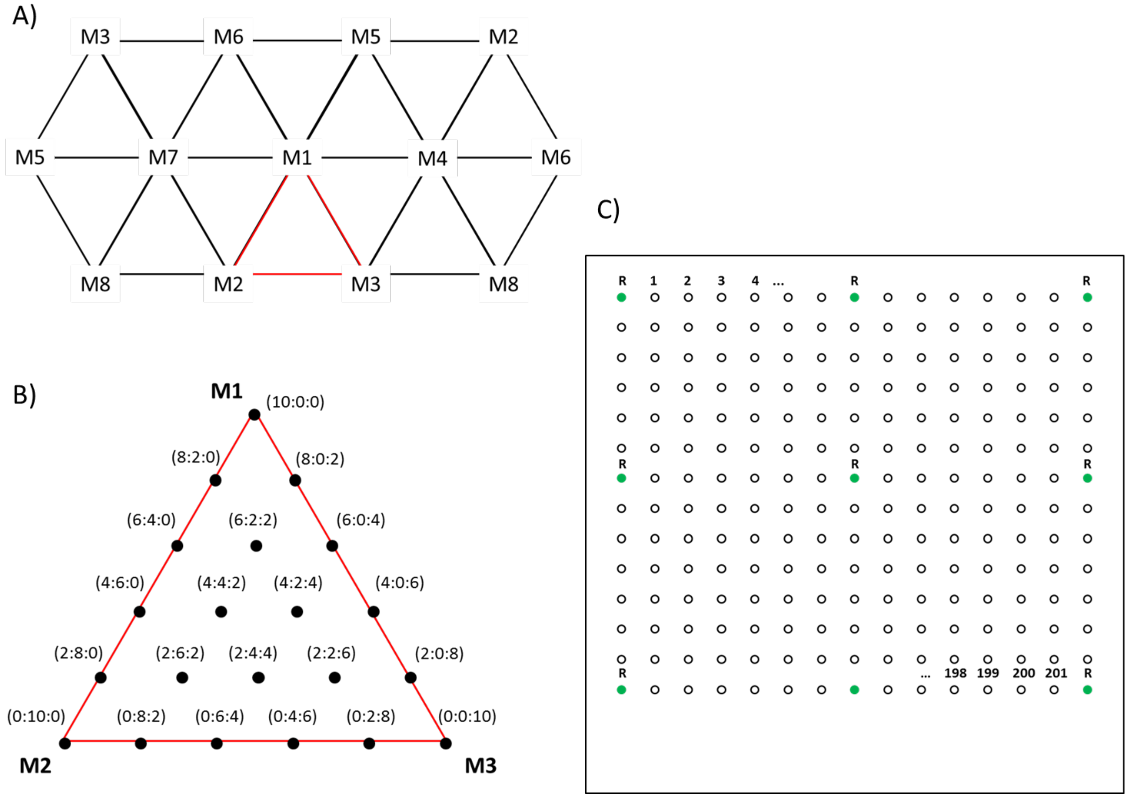

Figure S6 Mapping of catalyst compositions onto the FTO electrode to maximize screening composition space. A) Schematic indicating how fourteen ternary oxide compositions prepared from eight metal salt precursors can be consolidated to maximize shared edges. B) Representative composition space screened for each ternary mixed-metal oxide combination, $A_{(100\,\%\,-\,p)}B_{(p\,-\,q)}C_qO_m$. C) Layout of the catalyst compositions on the FTO-coated glass electrode showing the position of the 201 catalysts to be tested and nine reference spots (green circles labeled R).

Data Acquisition and Processing

Prior to image acquisition, the catalyst array was submitted to 1 h of pre-electrolysis driven at a current of 5 mA. A custom electrochemical cell held the O_2-sensing mesh 2 mm above the catalyst array. Electrolysis during image acquisition was performed for 10 minutes in a dark room following 1 h of purging the electrolyte with Ar. Images were taken at 30 s intervals during the electrolysis and processed using ImageJ and a spreadsheet as previously described.[1] Briefly, the initial steps in the data analysis are to separate the colour images into greyscale images of the red, green, and blue components and to produce a new greyscale image where each pixel's intensity is the quotient of the corresponding red and green pixels. The next step in the process is to background-correct the image to remove variations in background intensity. The greyscale red/green ratio images are summed to create a greyscale image of the integral of the images taken during the electrolysis. The maximal intensity of each spot is then determined and recorded. These steps were further automated using the ImageJ macro (Listing S1) and Java program (Listing S2) provided below for image processing and measuring integrated intensity, respectively.

Listing S1 Image processing macro for use with ImageJ.

```
	location = getDirectory("Choose a Directory");
	files = getFileList(location);

	for (i = 0; i<files.length; i++) {
		if (endsWith(files[i], ".jpg") || endsWith(files[i], ".JPG")) { //can 
change file extension based on camera output
			open(location + files[i]);
		}
	}
	run("Images to Stack", "name=Stack title=[] use");
	waitForUser("Done rotating and cropping?");
	run("Split Channels");
	selectWindow("Stack (blue)");
	close();
	selectWindow("Stack (green)");
	run("32-bit");
	run("Gaussian Blur...", "sigma=7 stack"); // 'sigma' value can be modified to 
improve blurring
	selectWindow("Stack (red)");
	run("32-bit");
	run("Gaussian Blur...", "sigma=7 stack"); // 'sigma' value can be modified to 
improve blurring
	imageCalculator("Divide create 32-bit stack", "Stack (red)","Stack (green)");
	selectWindow("Stack (red)");
	close();
	selectWindow("Stack (green)");
	close();
	selectWindow("Result of Stack (red)");
	run("Multiply...", "value=128 stack");
	run("Z Project...", "start=1 stop=21 projection=[Sum Slices]");
	run("Invert");
	selectWindow("Result of Stack (red)");
	close();
	selectWindow("SUM_Result of Stack (red)");
	run("Rotate... ", "angle=180 grid=1 interpolation=Bilinear"); // this command 
is only necessary if pictures are upside-down
	run("Subtract Background...", "rolling=150 sliding"); // 'rolling' value should 
be approximately 2*width of spot in pixels
	/*
	saveAs("Tiff", outputFilePath);
	*/
}
```

Listing S2 Java program for determining image intensity corresponding to O_2 produced at each catalyst position in ImageJ.

```
import ij.*;
import ij.process.*;
import ij.gui.*;
import java.awt.*;
import java.awt.geom.*;
import java.util.*;
import ij.plugin.*;
```

```
import ij.measure.*;

public class Grid_Autoprocessor implements PlugIn {
        static String[] colors =
{"Red","Green","Blue","Magenta","Cyan","Yellow","Orange","Black","White"};
        static String color = "Cyan";
        static float tileWidth=16, tileHeight=16, tileWidthOffset=0,
tileHeightOffset=0.0001f, threshold=10, border=10;



             int xstart, ystart;

        public void run(String arg) {
                if (IJ.versionLessThan("1.43u"))
                        return;
                ImagePlus imp = IJ.getImage();
                boolean notDone = true;
                        //next lines update tileWidth and tileHeight based on
imagesize, can use or not
                           if ((tileWidth == 16) & (tileHeight == 16)) {
                                 tileWidth = setWidth(imp, 15);
                                 tileHeight = setHeight(imp, 14);
                           }
                do {
                        if (showDialog())
                           drawGrid(imp);
                        else {
                           notDone = false;
             break;
                        }
                } while(!gridGood());
                    if(notDone) {
                           if (showDialog2())
                                 getSomePoints(imp);
                    }

        }

        void drawGrid(ImagePlus imp) {
                GeneralPath path = new GeneralPath();
                int width = imp.getWidth();
                int height = imp.getHeight();
                float xoff = tileWidthOffset;
                while (true) { // draw vertical lines
                        if (xoff>=width) break;
                        path.moveTo(xoff, 0f);
                        path.lineTo(xoff, height);
                        xoff += tileWidth;
                }
                float yoff = tileHeightOffset;
                while (true) { // draw horizonal lines
                        if (yoff>=height) break;
                        path.moveTo(0f, yoff);
                        path.lineTo(width, yoff);
                        yoff += tileHeight;
                }
                if (path==null)
                        imp.setOverlay(null);
                else
                        imp.setOverlay(path, getColor(), null);
        }
```

```
        void getSomePoints(ImagePlus imp) {
                int width = imp.getWidth();
                int height = imp.getHeight();
                float yoff = tileHeightOffset;
                while (true) { // move down
                        if (yoff>=(height - tileHeight)) break;
                        float xoff = tileWidthOffset;
                        while (true) { // move across
                                if (xoff>=(width - tileWidth)) break;
                                imp.setRoi((int) (xoff + border), (int) (yoff +
border), (int) (tileWidth - (2 * border)), (int) (tileHeight - (2 *border)));
                                //in progress
                           //threshold = optimizeThreshold(imp);
                           IJ.run(imp, "Find Maxima...", "noise=" + threshold + "
output=[Point Selection] exclude");
                                IJ.run(imp, "Measure", "");
                                xoff += tileWidth;
                        }
                        yoff += tileHeight;
                }
        }

       float optimizeThreshold(ImagePlus imp) {
             //IJ.run(imp, "Find Maxima...", "noise=10 output=Count");
             return 0;
       }

        boolean gridGood() {
                GenericDialog gd = new GenericDialog("Ok?");
                gd.showDialog();
                if (gd.wasCanceled()) return false;
                return true;
        }

        boolean showDialog() {
                GenericDialog gd = new GenericDialog("Grid");
                gd.addNumericField("Tile Width:", tileWidth, 0);
                gd.addNumericField("Tile Height:", tileHeight, 0);
                gd.addNumericField("X offset:", tileWidthOffset, 0);
                gd.addNumericField("Y offset:", tileHeightOffset, 0);
                gd.addChoice("Colour:", colors, color);
                gd.showDialog();
                if (gd.wasCanceled()) return false;
                tileWidth = (float)gd.getNextNumber();
                tileHeight = (float)gd.getNextNumber();
                tileWidthOffset = (float)gd.getNextNumber();
                tileHeightOffset = (float)gd.getNextNumber();
                color = gd.getNextChoice();
                return true;
        }

        boolean showDialog2() {
                GenericDialog gd = new GenericDialog("Parameters for peak finding");
                gd.addNumericField("Threshold:", threshold, 2);
                gd.addNumericField("Border:", border, 2);
                gd.showDialog();
                if (gd.wasCanceled()) return false;
                threshold = (float)gd.getNextNumber();
                border = (float)gd.getNextNumber();
                return true;
        }

        Color getColor() {
```

```
            Color c = Color.cyan;
            if (color.equals(colors[0])) c = Color.red;
            else if (color.equals(colors[1])) c = Color.green;
            else if (color.equals(colors[2])) c = Color.blue;
            else if (color.equals(colors[3])) c = Color.magenta;
            else if (color.equals(colors[4])) c = Color.cyan;
            else if (color.equals(colors[5])) c = Color.yellow;
            else if (color.equals(colors[6])) c = Color.orange;
            else if (color.equals(colors[7])) c = Color.black;
            else if (color.equals(colors[8])) c = Color.white;
            return c;
    }

          float setHeight(ImagePlus imp, int rows) {
               return imp.getHeight()/rows;
          }

          float setWidth(ImagePlus imp, int columns) {
               return imp.getWidth()/columns;
          }
}
```

Screening Activities and Tabulated Catalyst Screening Data To calculate screening activities, the integrated intensity of each catalyst spot on an electrode array was determined relative to the average integrated intensity of the nine reference spots (Co-Fe-Ni 40:40:20) on that electrode. For catalyst compositions that appear on more than one electrode, the activities from each experiment were averaged. See the database provided as part of the Supporting Information for the complete tabulated data. While catalyst activities in the database are reported relative to the Co-Fe-Ni reference oxide, in all other instances these raw activities have been normalized so that Ni 100 has a screening activity of 1.0.

Tafel Measurements on Selected Catalysts

Electrode Preparation.

Aliquots of 5 mM aqueous metal solutions (9 vol% glycerol) were mixed in the desired ratio. Two 1 μL drops were deposited onto a FTO electrode (2.5 cm × 1 cm, that had been rinsed with MeOH) and dried on a hotplate. The electrode is then calcined at 500 ºC for 6 h. The major and minor axes of the elliptically-shaped catalyst spots were measured to 0.1 mm using a microscope, and current densities are reported based on the geometric surface areas calculated from these measurements. Further normalization based on electrochemical surface area was also performed as described below.

Tafel Analysis.

Pre-electrolysis was performed at 700 mV (vs. Ag/AgCl) until the current stabilized. Subsequently, steady-state currents were monitored as the applied potential was varied starting from 1000 mV (vs. Ag/AgCl); the potential was reduced in 50 mV (1000 to 800 mV) or 25 mV steps (< 800 mV) until the recorded current was below 10^{-7} A. Potentials were iR corrected, and each curve is the average of three experiments performed on three separate electrodes. Tafel plots for all of the selected catalyst compositions are shown in Figure S7; the currents are normalized to the geometric surface area of the catalysts. Tafel slopes and other electrochemical parameters or these compositions are reported in Table S1.

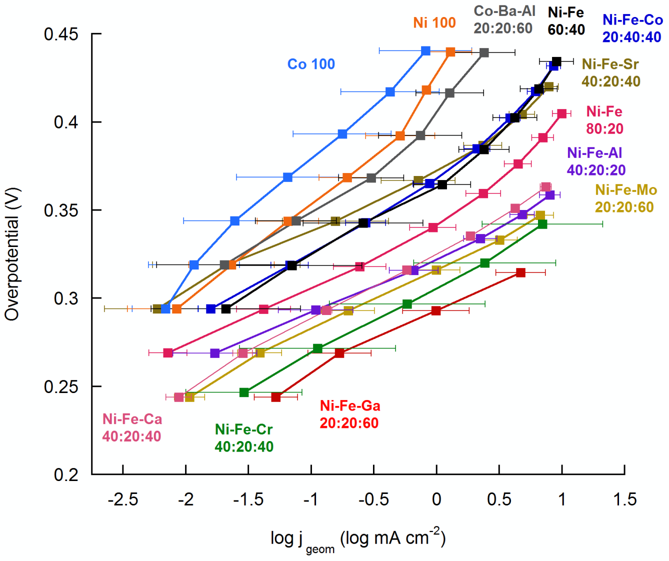

Figure S7 Tafel data for selected catalyst compositions from the combinatorial screening assay. X-axis error bars indicate one standard deviation based on multiple samples. Current densities are based on the geometric surface areas of the of the catalyst films.

Table S1 Tafel parameters and screening activities for selected compositions. Errors in activity represent 1 standard deviation, low activity catalysts (see database) have much lower errors which suggests a low false-positive rate for the assay.

Composition	Tafel slope (mV/log j)	Roughness factor	Log $j_{\eta=345mV}$ (log (mA·cm^{-2}))	ScreeningActivity (times screened)
Ni-Fe-Al 40:20:20	30	17	0.68	3.8 ± 1.2 (5)
Ni-Fe-Mo 20:20:60	36	17	0.83	2.4 ± 1.4 (2)
Ni-Fe-Cr 40:20:40	38	162	0.85	4.0 ± 1.3 (3)
Ni-Fe-Ga 20:20:60	35	52	1.40	3.8 ± 0.8 (3)
Ni-Fe-Sr 40:20:40	34	12	-0.81	4.4 ± 0.6 (3)
Ni-Fe-Ca 40:20:40	44	49	0.62	4.7 ± 1.1 (4)
Ni-Fe-Co 20:40:40	40	99	-0.57	2.0 (reference)
Co-Ba-Al 20:20:60	46	274	-1.12	1.6 ± 1.8 (3)
Ni-Fe 80:20	33	138	-0.59	2.4 ± 1.3 (30)
Ni-Fe 60:40	41	101	-0.03	2.4 ± 1.0 (30)
Ni 100	54	165	-1.19	1.0 ± 1.0 (88)
Co 100	75	160	-1.61	0.4 ± 0.6 (78)

The relative electrochemical surface area (roughness factor) for each catalyst was determined as described previously.[1] The Tafel data normalized to relative electrochemical surface areas are presented in Figure S8.

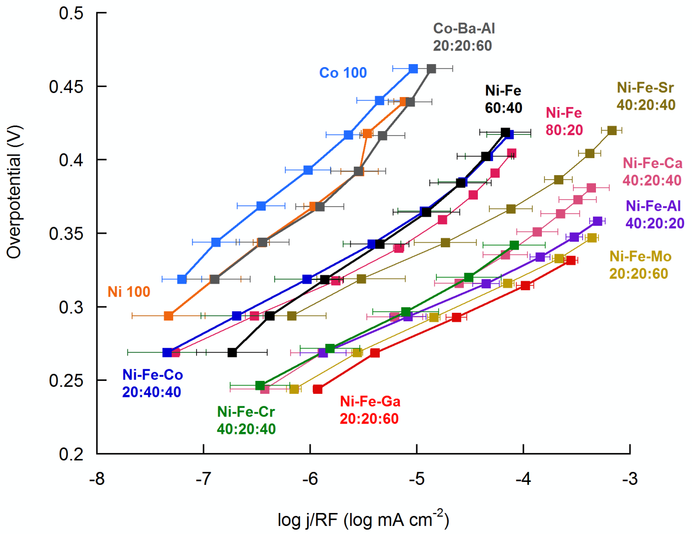

Figure S8 Tafel data for selected catalyst compositions from the combinatorial screening assay. X-axis error bars indicate one standard deviation based on multiple samples. Current densities are based on the relative electrochemical surface areas of the of the catalyst films determined by cyclic voltammetric capacitance measurements as described previously.