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Chemical Science

ARTICLE

Design of template-stabilized active and earth-abundant oxygen evolution catalysts in acid

Michael Huynh, Tuncay Ozel, Chong Liu, Eric C. Lau, Daniel G. Nocera

Oxygen evolution reaction (OER) catalysts that are earth-abundant and are active and stable in acid are unknown. Active catalysts derived from Co and Ni oxides dissolve at low pH, whereas acid stable systems such as Mn oxides (MnOx) display poor OER activity. We now demonstrate a rational approach for the design of earth-abundant catalysts that are stable and active in acid by treating activity and stability as decoupled elements of mixed metal oxides. Manganese serves as a stabilizing structural element for catalytically active Co centers in CoMnOx films. In acidic solutions (pH 2.5), CoMnOx exhibits the OER activity of electrodeposited Co oxide (CoOx) with a Tafel slope of 70–80 mV/decade while also retaining the long-term acid stability of MnOx films for OER at 0.1 mA/cm². Driving OER at greater current densities in this system is not viable because at high anodic potentials, Mn oxides convert to and dissolve as permanganate. However, by exploiting the decoupled design of the catalyst, the stabilizing structural element may be optimized independently of the Co active sites. By screening potential–pH diagrams, we replaced Mn with Pb to prepare CoFePbOx films that maintained the high OER activity of CoOx at pH 2.5 while exhibiting long-term acid stability at higher current densities (at 1 mA/cm² for over 50 h at pH 2.0). Under these acidic conditions, CoFePbOx exhibits OER activity that approaches noble metal oxides, thus establishing the viability of decoupling functionality in mixed metal catalysts for designing active, acid-stable, and earth-abundant OER catalysts.

Introduction

Adoption of solar energy is a desired low-risk climate pathway to meet growing global energy demand. Solar energy is the only renewable source scalable to the projected tens of terawatts of global energy consumption while remaining sustainable and cost-effective. Widespread solar implementation, however, requires inexpensive and high-density energy storage to manage the diurnal nature of the solar energy supply as well as to provide off-grid energy utilization. For large scale storage, batteries are ultimately limited by their energy density, thus providing an impetus for the solar-driven production of chemical fuels; central to this process is the splitting of water to oxygen and hydrogen. Of these two reactions, the oxygen evolution reaction (OER) is the more kinetically demanding half-reaction: the transfer of four protons is coupled to the loss of four electrons from two water molecules to produce a single oxygen molecule. We and others have sought to create catalysts that lower these kinetic barriers such that energy can be stored efficiently through water splitting. Inexpensive and active catalysts based on cobalt, nickel, and other earth-abundant metals for OER in neutral and alkaline pH have been developed, but these catalysts corrode in acidic solutions. Recent attempts to realize acid-stable systems from non-critical metals (such as Mn) suffer from low OER activity. Consequently, there are no acidic OER catalysts that are highly active, stable, and earth-abundant with only two out of the three criteria satisfied for known catalysts operating in acid.

The acidic pH regime is important for OER because of its applications in electrolysers and photoelectrochemical (PEC) devices as well as in fundamental mechanistic studies and catalyst design. Electrolysers based on acidic proton exchange membranes (PEM) are compact (sharing similar designs as PEM fuel cells), operate at high current and power densities, and achieve low gas crossover. However, their sulfonated Nafion membranes create an acidic local environment of pH ~0–3 in water which necessitates corrosion-resistant components such as noble metal catalysts comprising Ir and Ru oxides for OER. Similarly, certain PEC photoelectrodes employ photovoltaic materials (such as silicon) that are more stable in acidic pH. Moreover, studying OER in acidic solutions contributes to a mechanistic understanding of how protonation influences OER kinetics when the solution is a poor proton acceptor thus opening avenues for designing and assessing, for example, catalysts with internal proton relays. Finally, the knowledge gained from optimizing catalysts for acid stability may be applied to other reactions at low pH including hydrohalic acid splitting, oxygen reduction (the opposite of OER where good proton donors facilitate the reaction), and formic/phosphoric acid oxidation (for fuel cell applications).

We now demonstrate a pathway for the design of active, stable,
and earth-abundant acidic OER catalysts comprising oxides of mixed metals. The experimental design is based on electrodeposited manganese oxide (MnOx), which is stable in acid but poorly catalyzes oxygen evolution. \textsuperscript{23}\textsuperscript{,} Increased activity for MnOx catalysts may be achieved through potential cycling deposition (alternating between anodic and cathodic potentials). \textsuperscript{25}\textsuperscript{,} To advance beyond activated MnOx, we have turned to a design principle to incorporate different co-interacting metals to fulfill specific roles to achieve desired functionality. To this end, OER activity and stability have been decoupled such that each property could be furnished by separate metals and optimized independently. Mixed metal oxide films have been constructed with Co as the catalytic metal and Mn as the structural metal (denoted CoMnOx). These films exhibit similar catalytic OER activity as electrodeposited Co oxide (CoOx) with Tafel slopes of \textasciitilde 60 mV/decade in neutral pH and of \textasciitilde 83 mV/decade in acidic conditions. Whereas CoOx fully dissolves within 3 h when operated at 0.1 mA/cm\textsuperscript{2} for OER at pH 2.5, we show that CoMnOx remains intact and stable for over 12 h of continuous operation. For the latter, stability at high anodic potential is limited by transformation to permagmanate (MnO\textsubscript{2}O\textsubscript{7}). \textsuperscript{45}\textsuperscript{ Further, exploiting the ability to optimize the structural metal independently, Pb oxide was utilized to furnish high anodic stability at low pH. Mixed metal oxides were electrodeposited with Co as the catalytic component and Pb (with Fe dopant) as the structural element. These films exhibit similar Tafel behaviour as CoOx in neutral and acidic pH, yet they do not dissolve when operated at current densities of 1 mA/cm\textsuperscript{2} in acid continuously for over 12 h at pH 2.5 and over 50 h at pH 2.0. Under these conditions, the performance of these films begins to approach noble metal oxides, operating at \textasciitilde 220 mV higher overpotential than Ir oxide. These results demonstrate that catalysts may be designed by mapping their target properties onto individual components of mixed metal films and show that an approach of using a stable metal oxide as a scaffold for active OER metals provides a promising path for the development of active, stable, and earth-abundant OER catalysts.

**Results**

**Electrochemical deposition and Tafel analysis**

Unary metal oxide catalysts. Oxide films containing a single type of metal serve as benchmarks to mixed metal systems composed of Co as the catalytic metal and Mn, Fe, or Pb as the structural elements. Ni and Ir unary oxides are also included for comparison as acid unstable and stable oxides, respectively. For each case, thin metal oxide films (denoted MOx where M is the metal) were electrodeposited at constant anodic potential from aqueous solutions containing the metal salt and methylphosphonate (MeP\textsubscript{3}) buffer at pH 8, as is consistent with known procedures for these oxides. \textsuperscript{18,24,46,47} Exceptions to electrodeposition in MeP\textsubscript{3} include FeOx where the kinetics for anodic deposition were slow and thus required bufferless conditions (containing only KNO\textsubscript{3}) as supporting electrolyte at higher temperatures (75 °C) \textsuperscript{48} and IrOx that was electrodeposited from alkaline carbonate buffer. \textsuperscript{49}\textsuperscript{ To determine the anodic deposition potential for each metal oxide film, cyclic voltammograms (CV) were recorded for FTO electrodes in the quiescent precursor solutions (Figure S1). By applying potential at the anodic features in the CVs (some of which are described in literature), the following films were deposited: CoOx (at a constant anodic potential of 1.05 V), NiOx (1.25 V), FeOx (1.20 V), MnOx (0.54 V), PbOx (1.35 V), and IrOx (0.85 V). Mass loadings of the films were roughly matched for each sample to account for the different faradaic efficiencies and kinetics of deposition that are unique to each film composition.

The OER activity of the unary films was evaluated by measuring the steady-state current density as a function of applied potential in a Tafel analysis. Tafel plots for each film were collected in phosphate-buffered (P\textsubscript{2}O\textsubscript{5}) solutions at neutral (pH 7.0, Figure 1a) and acidic (pH 2.5, Figure 1b) conditions. The slope of these plots served as the primary descriptor for comparing activity because the slope reflects the intrinsic kinetics of the catalyst’s active site and is invariant to the amount of deposited catalyst. \textsuperscript{50}\textsuperscript{ At pH 7.0, the Tafel slopes are: 60 mV/decade for CoOx, 90 mV/decade for NiOx, 45 mV/decade for FeOx, 125 mV/decade for MnOx, 130 mV/decade for PbOx, and 41 mV/decade for IrOx. Tafel slopes at pH 2.5 are: 82 mV/decade for CoOx, 121 mV/decade for PbOx (increasing to “infinite” slope at higher current densities), and 32 mV/decade for IrOx. A reliable Tafel plot could not be constructed for NiOx in acid since the film dissolved rapidly in solution. These slopes are consistent with our previous work on Co, Ni, and Mn oxides as well as literature on Fe, Pb, and Ir oxides. \textsuperscript{14,18,23,47,51–53}

![Figure 1. Tafel plots of oxygen evolution for unary metal oxides in 0.10 M P\textsubscript{2}O\textsubscript{5} and 1.0 M KNO\textsubscript{3} at (a) pH 7.0 and (b) pH 2.5 of CoOx (red ■, 60 and 82 mV/decade Tafel slope at pH 7.0 and 2.5, respectively), NiOx (light magenta ▲, 90 mV/decade at pH 7.0), FeOx (orange ▼, 45 and 51 mV/decade at pH 7.0 and 2.5, respectively), MnOx (blue ◄, 125 and 650 mV/decade at pH 7.0 and 2.5), PbOx (brown ▶, 130 and 121 mV/decade at pH 7.0 and 2.5), and IrOx (purple ★, 41 and 32 mV/decade at pH 7.0 and 2.5).](image-url)
**Mixed metal oxide catalysts.** Having established deposition procedures and kinetic profiles of unary metal oxides, similar steps were taken for mixed metal films. Starting with Co as the catalytic metal and Mn as the structural metal, CVs were collected for solutions containing equal concentration of Co$^{2+}$ with Mn$^{2+}$ (Figure 2a). The CVs show anodic features similar to that of the individual metals. By comparison to CVs of the native metal ions, the anodic waves at approximately 0.70 and 0.95 V are assigned to MnOx and CoOx deposition, respectively. Mixed CoMnOx films were electrodeposited at three potentials: a light brown film similar to that of MnOx was produced near the onset of the MnOx deposition wave (0.65 V), a pale brown film formed near the onset of CoOx deposition (0.90 V), and a light olive-colored film similar to that of CoOx was created past both processes slightly into the catalytic OER wave (1.15 V). Tafel plots in neutral pH (Figure 3a) show that CoOx was created past both processes slightly into the catalytic OER electrodeposited at 0.90 (dark green ●, 65 and 81 mV/decade at pH 7.0 and 2.5), and 0.65 (light green ●, 85 mV/decade at pH 2.5), and 1.15 V (cyan ●, 83 mV/decade at pH 2.5). Unary metal oxides provided for comparison with slopes defined in Figure 1, CoOx (red ■), MnOx (blue ▲), and IrOx (purple ★).

![Figure 2](image1.png)

**Figure 2.** Cyclic voltammograms (CVs) of a 1 cm$^2$ FTO electrode at 50 mV/s in 50 mM MeP$i$ buffer at pH 8.0 with 0.25 mM of each metal: (a) Co$^{2+}$ and Mn$^{2+}$ (red ●); and (b) Co$^{2+}$ and Pb$^{2+}$ (light green ●) with addition of Fe$^{2+}$ (dark green ●). Background CV of metal-free MeP$i$ buffer (grey □) included for comparison.

![Figure 3](image2.png)

**Figure 3.** Tafel plots of oxygen evolution for CoMnOx in 0.10 M $\text{Pb}^{2+}$ and 1.0 M $\text{KNO}_3$ at (a) pH 7.0 and (b) pH 2.5 of: CoMnOx deposited at 0.90 (dark green ●, 65 and 81 mV/decade at pH 7.0 and 2.5), and 0.65 (light green ●, 85 mV/decade at pH 2.5), and 1.15 V (cyan ●, 83 mV/decade at pH 2.5). Unary metal oxides provided for comparison with slopes defined in Figure 1, CoOx (red ■), MnOx (blue ▲), and IrOx (purple ★).
and studies on similar NiFeOx systems. Although Fe deposition is not observable in the CV, a small percentage of Fe is trapped and incorporated into the mixed films during growth as supported by elemental analysis (a small percentage of Fe is trapped and incorporated into the mixed temperatures). Although Fe deposition is not observable in the CV, a small percentage of Fe is trapped and incorporated into the mixed films during growth as supported by elemental analysis (vide infra) and studies on similar NiFeOx systems.\(^{20,35}\) Tafel plots of the Fe-incorporated mixed films (CoFePbOx films, Figures 4a and 4b) at neutral and acidic pH exhibit similar slopes of \(\sim 70\) mV/decade as obtained for Fe-free films. The highly facile kinetics of CoFeOx in the alkaline regime with \(30\) mV/decade slope does not appear to persist in neutral and acidic solutions.

**Acid stability and faradaic efficiency**

The acid stability of unary and mixed metal films was evaluated by using long-term chronopotentiometry. Solution conditions were the same as that employed for Tafel analysis (i.e., phosphate buffer with nitrate supporting electrolyte at pH 2.5). Electrodeposited films were immersed in stirred solutions and initially held at a constant current density of 0.1 mA/cm\(^2\) where after a brief capacitance period, only OER is sustained (as confirmed by direct O\(_2\) measurement, vide infra). OER on blank FTO occurs at a steady potential of 2.3 V (shown for \(\sim 12\) h in Figure 5a). Whereas the substrate oxide is highly acid stable, it is an exceptionally poor OER catalyst. NiOx films dissolve quickly at pH 2.5. The applied potential required to maintain 0.1 mA/cm\(^2\) rises immediately and undergoes inflection at 40 min to correspond to the potential of that for blank FTO, indicating complete film dissolution. CoOx films have slightly longer stability than NiOx and catalyze OER at \(\sim 1.6\) V for almost 3 h before potential inflection, a sign of full dissolution. We note that dissolved Co\(^{2+}\) ions can still promote OER\(^{36}\) and thus the potential plateaus about 300 mV below that of blank FTO. Moving to the left on the periodic table, we have shown that MnOx can perform OER in acid with limited degradation by trading off activity for stability.\(^{23}\) Indeed whereas MnOx requires a high anodic potential of 2.0 V to maintain 0.1 mA/cm\(^2\), the current remains stable for over 12 h of testing. As a control, IrOx is included to represent a catalyst with both high activity and stability. OER from IrOx occurs at 1.4 V sustaining 0.1 mA/cm\(^2\) over the 12 h testing duration.

To investigate if a structural metal could stabilize unary metal oxides against dissolution, Co (the catalytic element) was co-deposited with Mn (the structural component) at three different potentials (0.65, 0.90, and 1.15 V) to create CoMnOx films with different Co:Mn ratios. Stability tests were repeated for these films under the same conditions as for unary catalysts (Figure 5b). For OER at 0.1 mA/cm\(^2\), CoMnOx electrodeposited at 0.90 V exhibited a low OER potential of 1.5 V (similar to that of CoOx before dissolution) while remaining intact over 12 h of operation. Similarly, for CoMnOx deposited at 0.65 V, the films remained stable but exhibited a slight increase of 100 mV in its potential to sustain OER.

**Figure 4.** Tafel plots of oxygen evolution in 0.10 M P\(_2\)O\(_5\) at (a) pH 7.0 and (b) pH 2.5 for CoPbOx (light green ●), PbOx (brown ▲), and IrOx (purple ▣). The inflection of potential in the plots indicates film dissolution.

**Figure 5.** Electrochemical stability for acidic OER measured by sustained chronoamperometry at: (a) 0.1 mA/cm\(^2\) in pH 2.5 P\(_2\)O\(_5\), for CoMnOx deposited at 0.65 (light green ●), 0.90 (dark green ▲), and 1.15 V (cyan ▣) along with CoOx (red ●), NiOx (light magenta ▲), MnOx (blue ▲), IrOx (purple ▣), and FTO (grey ●●●) for comparison; (b) 1.0 mA/cm\(^2\) in pH 2.5 P\(_2\)O\(_5\), for CoPbOx (light green ●), and CoFePbOx (dark green ▲) with CoFeOx (orange ▲), CoOx (red ●), and PbOx (brown ▲) for comparison; and (c) 1.0 mA/cm\(^2\) in pH 2.0 sulfate for CoFePbOx (dark green ▲). The inflection of potential in the alkaline regime with \(30\) mV/decade slope does not appear to persist in neutral and acidic solutions.
The dissolution of Mn at high anodic potentials (caused by operating at higher current densities) prompted its replacement by another structural metal that is not prone to molecular decomposition. Lead was selected as an alternative for manganese after evaluating the potential−pH properties of many corrosion-resistant elements (search process presented in the Discussion). As a control, acidic stability tests at 1 mA/cm² were performed on PbOx, which demonstrated long-term acidic stability over 12 h at 2.9 V (Figure 5b). Because Pb was a promising structural metal, mixed metal films incorporating Co and Pb were prepared and evaluated under similar conditions at higher current densities. Indeed, the presence of Pb in CoPbOx films extended the operation of “CoOx” from 20 min to 7 h at ~1.65 V before eventually dissolving (Figure 5b). Pb thus slowed the rate of corrosion in CoPbOx films significantly.

Incorporation of lead was also investigated in Co oxide films doped with Fe. As a control, CoFeOx degrades quickly during acidic OER at 1 mA/cm² as indicated by the rising potential around 1.7 V that inflects to indicate dissolution after 1 h (Figure 5b). The unary FeOx is also unstable at higher current densities, degrading after 2 h (Figure S2). However, the slight addition of Fe to CoPbOx produced CoFePbOx films that could sustain OER at ~1.65 V for over 12 h. Moreover, CoFePbOx operated at 1 mA/cm² in sulfate buffer at pH 2.0 (Figure 5c) remained stable at ~1.8 V for over 50 h of continuous electrolysis, demonstrating that these films are both active and exhibit superior stability under laboratory test conditions. Overall, Pb appears to fulfill its role as a structural element and confers acidic corrosion resistance when incorporated in mixed metal oxide films.

To confirm that acid-stable mixed metal films are performing OER, the evolved oxygen was directly measured by gas chromatography in a gas-tight electrochemical cell and compared to the charge passed to the electrode during electrolysis. Employing the same solution conditions as that used for stability tests, CoMnOx was operated at 0.1 mA/cm² and CoFePbOx at 1.0 mA/cm², and the O₂ concentration was measured every 20 min (Figure S3). The faradaic efficiency was calculated by dividing the moles of detected oxygen by the moles of transferred electrons. The average efficiency for CoMnOx is 91% and that for CoFePbOx is 97%. The slight decrease in efficiency of CoMnOx may result from the lower current densities of operation that correspond to a lower O₂ signal-to-noise ratio and consequently decreased accuracy. Overall, both systems demonstrate faradaic efficiencies near unity for long-term OER in acid.

Physical characterization

Elemental analysis. To determine how deposition protocols affect the composition of mixed metal oxide films, elemental analysis of the films were performed by energy dispersive X-ray spectrometry (EDS) and were confirmed on select samples with inductively coupled plasma mass spectrometry (ICP-MS). EDS was first explored for CoMnOx films deposited at 0.65 V (near the onset of the MnOx deposition but below that of CoOx deposition), 0.90 V (near the onset of CoOx deposition), and 1.15 V (past both processes and slightly into the catalytic OER wave). The EDS spectra were quantified using ZAF (atomic number, absorption, and fluorescence) correction factors to obtain the relative ratios of elements (Table S1). The composition for films deposited at 0.65 V is 40% Co and 60% Mn, 0.90 V is 50% each of Co and Mn, and 1.15 V is 83% Co and 17% Mn. EDS results for CoMnOx deposited at 0.90 V were examined by ICP-MS, a more rigorous technique for elemental analysis, and revealed a composition of 51% Co and 49% Mn, which is consistent with EDS reported values. These experiments demonstrate that the composition of CoMnOx films can be controlled by the deposition potential—as potential increases (to the direction of CoOx formation), more Co is incorporated in the mixed films.

For mixed films containing Pb, ICP-MS shows that CoPbOx comprises 18% Co and 82% Pb, while CoFePbOx contains 15% Co, 2% Fe, and 83% Pb (Table S1). In these films, the structural element (Pb) is the dominant component. Nevertheless, co-depositions include appreciable amounts of catalytic sites and sufficient Fe infiltrates the films during growth, despite the difficulty of directly electrodepositing FeOx at those same potentials. Overall, elemental analysis shows that anodic co-deposition is a viable approach for incorporating both catalytic and structural elements in the resulting mixed metal films.

Morphology and homogeneity. Scanning electron microscopy (SEM) was used to investigate homogeneity of mixed metal films (Figures 6 and 7); images of unary metal oxide catalyst are provided as reference. CoOx has a smooth surface with slight cracking from drying, MnOx exhibits thin filament-like petals, and PbOx has ~10 nm particles that combine into larger porous structures. For CoMnOx films (Figure 6), deposition at 0.65 V results in a smooth sheet, 0.90 V produces round grains that are aggregates of even smaller 100–200 nm diameter particles, and 1.15 V gives a mixture of sheet and ball features. Similarly, CoPbOx shows formation of 100–200 nm particles, and CoFePbOx resembles CoPbOx in that there are nanoparticles (slightly larger) that merge together to create a continuous coating (Figure 7). Elemental maps by SEM (EDS) were constructed for each case and show that CoMnOx and CoFePbOx films are homogeneously mixed on the 20 nm per pixel resolution (Figures 8 and S4). Because it is possible for mixed metals to form separate individual metal oxide domains that have smaller
than 20 nm diameter, scanning transmission electron microscopy (STEM) with EDS was employed for CoMnOx and CoFePbOx films on the angstrom-level resolution (Figure 9). The lack of coherent lattice fringes in the STEM images indicates that the catalyst is largely amorphous (Figure S5). Importantly, EDS maps on the 7.4 Å/pixel resolution further demonstrate homogeneous distribution of Co throughout the structural metals (Mn or FePb). Overall, high-resolution electron microscopy coupled with positional elemental mapping suggest that the electrodeposited mixed films incorporate catalytic and structural metals homogeneously on the length scale of these experiments.

**Powder x-ray diffraction.** To check if the mixed metal oxide films form crystalline phases that could lead to the identity of the film composition, Bragg–Brentano X-ray diffraction was performed on powders of CoMnOx and CoFePbOx. These powders were prepared by thin film electrodeposition on large FTO substrates. The films were then mechanically separated from the underlying FTO and ground into a powder. The advantage of this approach is that sufficient catalyst material may be accumulated to obtain better diffraction signal and that the strongly interfering FTO substrate may be eliminated. Both CoMnOx and CoFePbOx films exhibited no features over a wide range of 2θ, with only a strong baseline that is indicative of amorphous material (Figure S6). These results are consistent with STEM imaging where catalyst domains lack lattice

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**Figure 6.** FESEM images of CoMnOx electrodeposited at (a) 0.65, (b) 0.90, and (c) 1.15 V with (d) CoOx and (e) MnOx for comparison. All samples were prepared on FTO substrate, and scale bars are 200 nm.

**Figure 7.** FESEM images of (a) CoPbOx and (b) CoFePbOx with (c) PbOx and (d) FTO for comparison. All samples were electrodeposited on FTO, and scale bars are 100 nm.

**Figure 8.** EDS elemental maps recorded through SEM of (a) CoMnOx (deposited at 0.90 V) and (b) CoFePbOx. Individual elemental channels for Co (red), Mn (blue), Fe (orange), and Pb (green) were combined and overlaid on the respective SEM image. All samples were prepared on FTO substrate, and scale bars are 200 nm for CoMnOx and 100 nm for CoFePbOx.

**Figure 9.** High-resolution EDS elemental maps recorded through STEM of (a) CoMnOx (deposited at 0.90 V) and (b) CoFePbOx. Individual elemental channels for Co (red), Mn (blue), Fe (orange), and Pb (green) were combined and overlaid on the respective image. Scale bars are 15 nm for a resolution of 7.4 Å/px.
regions were compared to that of CoOx and MnOx, respectively. The Co 2p and Mn 2p (Figure 10). The Co 2p spectra were Co$_{3/2}$-like and analogous in peak positions and shape between both CoMnOx and CoOx samples. The Mn 2p spectra for both samples were also similar, but CoMnOx has a slightly broader 2p$_{3/2}$ peak than MnOx, which suggests a decrease of the peak at 642.2 eV with an increase at 643.5 eV. Since these features reflect populations of Mn in different chemical states, growth at the higher peak binding energy supports an average Mn oxidation state closer to +4.0 (or β-MnO$_2$), which is inactive for OER.\textsuperscript{15} CoPbOx and CoFePbOx films also demonstrate no change in the Co 2p positions or shape when compared to CoOx (Figure 11). However, the Pb 4f region exhibits an overall increase of ~0.6 eV in binding energy progressing from PbOx to CoPbOx to CoFePbOx. The presence of Co and additional doping of Fe appears to maintain a high average Pb oxidation state similar to that of PbO$_2$.\textsuperscript{59} The trace amount of Fe in CoFePbOx films (comprising 2% of the film by ICP-MS) was too low for detection by XPS, especially since the Fe 2p peaks overlap with the broad Sn 3p$_{3/2}$ feature that manifests from the FTO substrate (Figure S7). Overall, XPS suggests that there is no change in Co sites when co-deposited with Mn or Pb, which is consistent with results from Tafel analysis showing no difference in catalysis between unary and mixed metal systems.

**Discussion**

Heterogeneous OER catalysts based on metal oxides exhibit a propensity for corrosion in low pH solutions. Acids react with basic metal oxides to protonate the metal oxide framework, weakening metal–oxygen bonds and facilitating dissolution.\textsuperscript{60–62} For this reason, the only known viable acidic OER catalysts are based on platinum group metals, in particular, iridium and ruthenium.\textsuperscript{31,63,64} Consequently, performing OER in acid typically relies on using catalysts derived from Ir and Ru oxides with most studies focused on increasing the accessible active sites while decreasing the mass loading.\textsuperscript{65–69} Conversely, development of OER catalysts from earth-abundant metal oxides have targeted the alkaline regime, where stability is generally not a concern, with the use of multiple metals for the sole purpose of catalytic synergy (e.g. NiFe oxides) or for increasing the surface area of active catalyst material.\textsuperscript{70–74} OER in neutral solutions has been achieved through the development of self-healing unary catalysts,\textsuperscript{75,76} and in some cases, performance in acid may be achieved at low current density.\textsuperscript{71,75} Our interest to develop further design principles for active, stable, and earth-abundant acidic OER catalysts has led us to consider using mixed-
Figure 12. Progression of designing an active, stable, and earth-abundant acidic OER catalyst. The first generation system focused on demonstrating film stability at low pH with MnOx.\textsuperscript{23,24} The activity of MnOx was improved in the second generation by activating MnOx for OER.\textsuperscript{25} The catalyst was reformulated as a mixed metal oxide for the third generation, where functionality was separated into catalytic and structural elements comprising Co and Mn, respectively. Finally, the degradation of Mn oxides at high anodic potentials was solved by replacing it with a FePb oxide structural component to create the fourth-generation catalyst.

...metals as a framework for decoupling activity from stability by employing two different metals: one that acts as a catalytic element and the other that acts as a structural element. In assessing these mixed-metal catalysts, their performance is benchmarked against each other and to unary metal oxide films using techniques employed in our previous mechanistic studies\textsuperscript{14,19,25} as well as those outlined elsewhere.\textsuperscript{25,77–79} Benchmarking typically comprises measurements on elemental composition, surface area, faradaic efficiency, catalytic activity, and stability. Of these criteria, we exclude surface area because a rigorous measurement on porous thin films is unfeasible.\textsuperscript{80} Instead we rely on activity comparisons as defined by Tafel plots, where the slope is a measure of catalyst kinetics that is independent of catalyst loading or surface area.

The iterative design path employed for this study is shown in Figure 12. Metal oxide films increase in stability from NiOx to CoOx and to MnOx, a trend which is consistent with an increase in metal–oxygen bond strength traversing from late to early first-row transition metals as embodied by the principles of the "oxo wall".\textsuperscript{81} Indeed, the intrinsic strength of Mn–O bonds in MnOx results in resistance to corrosion of the oxide at low pH; this passive stability is augmented by the functional stability of the film derived from self-healing (the catalyst can re-form at the anodic potentials of 600 mV) while remaining stable for over 8 hr of continuous operation at 0.1 mA/cm\textsuperscript{2}. Spectroscopic and structural studies suggest that these phase changes trap catalytic Mn\textsuperscript{II} sites within a robust Mn\textsuperscript{III} oxidic matrix, and thus there are two types of Mn sites that allow both activity and stability to co-exist.\textsuperscript{25,85,86} However with structure and function embodied in the same metal, there is no clear path for independent optimization.

CoMnOx

Accordingly, we turned to using manganese as the structural element and Co as the catalytic element as we have extensively characterized CoOx, which is among the most active materials for OER in neutral pH.\textsuperscript{78} An advantage of a mixed metal Mn and Co system is that the oxides can be easily electrodeposited at modest potentials in buffered solutions (MeP\textsubscript{2} at pH 8) with known deposition kinetics.\textsuperscript{24,46} Furthermore, the ratio of Co to Mn in the films can be controlled by the deposition potential. In the CV of Co\textsuperscript{II} and Mn\textsuperscript{II} in MeP\textsubscript{2} buffer at pH 8 (Figure 2a), the deposition peak for MnOx occurs ~250 mV to lower anodic potential (i.e., less positive) than that of CoOx deposition. This separation in potentials can be exploited to regulate the kinetics of the two reactions. When the electrode potential is near that of MnOx deposition, more Mn than Co will be incorporated into the catalyst. As the potential is raised nearer to that of CoOx deposition, more Co is assimilated into the final film (Table S1). SEM and STEM elemental mapping, to resolution of ~7.4 Å, indicates no segregated domains of CoOx and MnOx (Figures 8a and 9a).

Whereas the application of CoMnOx as battery and supercapacitor material is well-known,\textsuperscript{88,89} and studies for seawater\textsuperscript{90} and alkaline\textsuperscript{91} electrolysis, their application towards acidic OER has only recently begun to be explored through screening.\textsuperscript{78} For the studies performed herein, the performance of CoMnOx for oxygen evolution in neutral and acidic pH was evaluated using Tafel analysis (i.e., log j vs. E plots). In general, better catalysts are positioned lower on the Tafel plots (i.e.,
Process for independently optimizing the structural component of mixed metal films to discover a metal oxide that is both stable at high anodic potentials and at acidic pH. Pourbaix diagrams of metals (shown as simplified representations of stability and corrosion, generated from the Materials Project and experimental data) were analyzed for stability in the top left region of the plots (corresponding to high anodic potentials and low pH). The candidates were then filtered by removing precious and rare metals; then further refined by excluding oxides that were incompatible with anodic electrodeposition in buffer. In this manner, Pb was identified as a promising replacement for Mn for stabilizing OER catalysts in acid.

Figure 13. Process for independently optimizing the structural component of mixed metal films to discover a metal oxide that is both stable at high anodic potentials and at acidic pH. Pourbaix diagrams of metals (shown as simplified representations of stability and corrosion, generated from the Materials Project and experimental data) were analyzed for stability in the top left region of the plots (corresponding to high anodic potentials and low pH). The candidates were then filtered by removing precious and rare metals; then further refined by excluding oxides that were incompatible with anodic electrodeposition in buffer. In this manner, Pb was identified as a promising replacement for Mn for stabilizing OER catalysts in acid.
catalytic/structural mixed-metal approach. On its own, PbOx electrodeposits under similar conditions as CoOx but with faster deposition kinetics (as evidenced by the steepness of the Pb$^{2+}$ oxidation wave in Figure S1e). PbOx exhibits ~120–130 mV/decade Tafel slopes for OER in neutral and acidic pH.\textsuperscript{100} When compared to CoOx under the same conditions, PbOx is a relatively poor catalyst and also suffers from a sudden increase to “infinite” slope near 1 mA/cm$^2$ for the acidic regime (Figure 1b), suggesting that additional driving force has no effect on the rate of the reaction. Disregarding its inferior OER properties, PbOx is an excellent structural metal for long-term acidic OER stability at higher current densities (of 1 mA/cm$^2$, Figure 5b), with over 12 h of continuous operation without degradation. We note stability measurement conditions are comparable to those made on acidic OER catalysts near pH 0 at ~3 mA/cm$^2$ for at least 2 h. Here a slightly less acidic pH is offset by better buffering conditions (sulfate and phosphate at pH 2 and 2.5, respectively).

Against this backdrop, Pb was employed as the structural element for Co as the catalytic component. Electrodeposition of CoPbOx was similar to that for CoMnOx with the precursor solution containing equal concentrations of Co$^{2+}$ and Pb$^{2+}$ in MeP$_2$ buffer at pH 8. However, the potentials for CoOx and PbOx deposition are similar (~1.15 V) unlike that for CoMnOx and MnOx deposition; thus, the composition of the mixed metal film could not be as easily controlled through varying the potential. Instead, the initial concentrations of Co$^{2+}$ and Pb$^{2+}$ can be relatively adjusted to change composition. For solutions containing equal concentrations of Co$^{2+}$ and Pb$^{2+}$, electrodeposited CoPbOx films contain 18% Co and 82% Pb (as measured by ICP-MS, Table S1) with homogeneous distribution of the two metals throughout the film (as observed from EDS elemental maps from SEM, Figure S4c). The use of CoPbOx as a stable electrode has precedence in the electrosynthesis of oxidants, decomposition of organics, as well as electrowinning of metals.\textsuperscript{101,103} Although the application of CoPbOx for acidic oxygen evolution has largely been unexplored, its prior history in corrosive environments suggested that it was a promising target.

Like CoMnOx, the OER performance of CoPbOx resembled that of CoOx with similar Tafel slope of ~72 mV/decade in neutral and acidic pH (Figure 4). While there is no catalytic synergism between Co and Pb, there is no discord either: the presence of Pb does not hinder the OER activity of Co sites. Interestingly, given that the mass loading of the films are comparable, the number of total Co active sites (i.e., 18% Co) in CoPbOx should be less than that of CoOx. However, Tafel plots of CoPbOx overlaid with those of CoOx, which indicates a similar level of activity. This effect could manifest from: first, the difference in morphology of the films where CoOx has a smooth surface that may limit the accessibility of active sites while CoPbOx is a rougher film comprised of small nanoparticles; and secondly, the high electrical conductivity of PbOx may enable a greater number of Co sites to be electrically addressed in CoPbOx with low internal resistance. Four-point probe electrical measurements of PbO$_{2}$ exhibit metallic-like bulk resistivity from $10^{-5}$ to $10^{-3}$ ohm cm.\textsuperscript{104,105} Conversely, early transition metal oxides generally behave as insulators or semiconductors with high resistivity (in units of ohm cm): CoO$_{2}$ on the order of $10^{3}$,\textsuperscript{106,107} MnO$_{2}$ from $10^{5}$ (electrolytic manganese dioxide, EMD) to $10^{3}$ (birnessite).\textsuperscript{108,109} and Fe$_{2}$O$_{3}$ and FeOOH from $10^{4}$ to $10^{8}$\textsuperscript{110,111} PbO$_{2}$ is orders of magnitude more conductive than CoO$_{2}$O$_{4}$ although its exact influence on CoOx when co-deposited as CoPbOx requires direct conductivity measurements by electrochemical impedance spectroscopy or via an interdigitated electrode array. Thus, Pb in the mixed metal film appears to act as a structural metal while Co plays the catalytic role.

The acidic OER stability of CoPbOx was evaluated at intermediate (1 mA/cm$^2$) current densities (Figure 5b) where the presence of Pb enhanced the corrosion resistance of the films. For OER at 1 mA/cm$^2$, both CoMnOx and CoOx films fully dissolve within 30 min while CoPbOx resists degradation to 7 h. While the addition of Pb does not confer long-term stability against acid corrosion, it does slow the rate of degradation. Thus, the role of Pb as an anodically stable metal in acid was promising and encouraged us to test variants of CoPbOx.

One such variant involved the use of Co and Fe as the catalytic metal components with Pb remaining as the structural element. The motivation for CoFe stemmed from recent studies demonstrating a synergetic effect that increases the kinetics for OER when Fe is doped into Co or Ni oxides.\textsuperscript{51,54,55,70} We were curious if the low Tafel slope of 30 mV/decade in alkaline pH could translate to neutral and acidic solutions with the aid of Pb for stabilization at lower pH. As a control, Tafel plots of CoFeOx$^{12}$ were recorded at neutral and acidic pH; here, Co and Fe did not show any catalytic synergy, as the Tafel plots (with 65–70 mV/decade slope) overlaid with those of CoOx (Figure 4). Stability tests of CoFeOx at higher current densities of 1 mA/cm$^2$ show improvement in stability with film dissolution at ~1.5 h instead of at ~0.5 h for CoOx (Figure 5b). This demonstrates that Fe has a minor structural role, which is consistent with a trend of trading off activity for stability when moving to earlier first-row transition metals. Next, Pb-stabilized CoFeOx was anodically electrodeposited in a solution containing equal concentrations of Co$^{2+}$, Fe$^{2+}$, and Pb$^{2+}$. The resulting film exhibited a composition of 15% Co, 2% Fe, and 83% Pb (by ICP-MS, Table S1) with homogeneous distribution of the three metals (as determined to ~7.4 Å resolution by EDS elemental maps from SEM and STEM, Figures 8 and 9). Tafel analysis of CoFePbOx in neutral and acidic solutions shows no difference from that of CoOx films (slopes of 65–70 mV/decade, Figure 4). However, unlike CoOx and CoFeOx catalyst films, CoFePbOx exhibits long-term stability in acid, even at higher current densities. While CoPbOx, CoFeOx, and CoOx dissolve in pH 2.5 buffer when performing OER at 1 mA/cm$^2$, CoFePbOx can maintain a steady ~1.65 V for over 12 h of operation (Figure 5b) with a faradaic efficiency near unity (Figure S3). To further demonstrate the robustness of these films, CoFePbOx was continuously operated at 1 mA/cm$^2$ for over 50 h in sulfate buffer at pH 2.0 (Figure 5c) and at only ~220 mV higher potential than IrOx operating in the same conditions (Figure 5b); little degradation was observed at OER operating voltages of ~1.8 V.

CoMnOx (at 0.1 mA/cm$^2$) and CoFePbOx (at 1 mA/cm$^2$) exhibit chemically stability when performing acidic OER near pH 2.5. There are two important considerations for their operation. First their stability depends on application of an anodic bias above ~1.3 V during operation to maintain its oxidic state. As known for CoOx and as apparent in the Pourbaix diagrams of Co and Pb (Figure S8), the CoO$_{2}$ and PbO$_{2}$ states are only maintained at high anodic
potentials. When voltage is switched off, there is a slow decay of the film back to its original Co$^{2+}$ and Pb$^{2+}$ ions in solution. Second, whereas these films are chemically stable, they are not indefinitely stable because they lack the ability to self-heal. Over long period of operation, mechanical stress on the film from the evolution of O$_2$ gas slowly removes catalyst material from the electrode. Because CoFePbO$_x$ and also CoMnO$_x$ cannot be electrodeposited in acidic conditions (their electroosynthesis occurs at near-neutral pH), mechanical losses cannot be repaired during operation. Discovering an OER catalyst that can be both electrodeposited and operate efficiently under acidic pH will furnish self-healing and allow mechanical challenges to be overcome, as is the case for native CoP$_x$ and NiB$_x$ catalysts.

Nature of stability

The foregoing results demonstrate that structural metals stabilize catalytic sites in mixed metal oxide films. Guidelines emerge for achieving stability while maintaining OER activity. First, mixed metal films should be composed of at least 50% structural metal to maintain an appreciable stability. For example, CoMnO$_x$ films prepared with ≥50% Mn do not dissolve in pH 2.5 solution (for OER at 0.1 mA/cm$^2$) while the film with only 17% Mn degraded quickly, similar to a CoO$_x$-only film (Figure 5a). Given the homogeneous distribution of metals in these catalysts, the requirement that at least half of the film is composed of structural metal suggests that stabilization of active sites requires sufficient scaffolding to exist around those sites. Second, Tafel analyses of mixed metal films show no improvement in OER kinetics when compared to the unary catalytic metal oxide films. This is consistent with XPS spectra indicating negligible differences in the electronic features of Co when comparing CoMnO$_x$ and CoFePbO$_x$ to CoO$_x$ (Figures 10a and 11a), suggesting that the Co catalytic sites are unchanged from the unary system and obey the same catalytic mechanism (i.e., same Tafel slope) in all three systems. As a corollary, the structural metals do not significantly participate in catalysis, as both MnO$_x$ and PbO$_x$ have poor OER kinetics and do not affect the Tafel slope of Co catalytic sites in the mixed metal films. However, the structural metal does appear to engage in internal transport of electrons (and possibly protons) inasmuch as even when the number of catalytic sites diminishes in mixed films, its absolute activity (i.e., position of the Tafel plot) remains similar, suggesting that the scaffolding provided by the structural element permeates throughout the film and provides an electronic pathway for addressing active sites.

These results are consistent with the contention that the structural metal provides an oxide that embeds the catalytic element and prevents it from dissolution. After OER, the metal–oxygen framework is disrupted with the elimination of O$_2$ and the formal oxidation state of the catalytic metal is reduced, resulting in a weakening of the metal–oxygen framework owing to population of metal-oxygen antibonding orbitals and an attendant decrease in the ligand field strength afforded by moving from oxo to hydroxyl/water. The presence of structural metals helps fortify the oxygen framework about the catalytic active site thus minimizing its degradation and leading to enhanced stability of the mixed-metal oxide. This fortification of the oxygen framework stems from the lack of catalysis at structural sites and thus preservation of the structural metal at a high formal charge, as indicated by XPS spectra on CoMnO$_x$ (Figure 10) and CoPbO$_x$/CoFePbO$_x$ (Figure 11). For the former, XPS spectra indicates a slight broadening of the Mn 2p peaks to incorporate features of higher binding energies relative to that of MnO$_x$ (Figure 10b). Given that as-deposited MnO$_x$ is birnessite-like ($\delta$-MnO$_x$), which has an average Mn oxidation state of +3.8, the shifting of Mn 2p peaks to higher binding energies suggests an increase in Mn oxidation state nearer to +4.0, which may reflect a pyrrhotite-like phase ($\beta$-MnO$_x$). Similarly, for CoPbO$_x$ and CoFePbO$_x$, the shift of the Pb 4f peaks to higher binding energies when compared to PbO$_x$ implies the stabilization of the PbO$_x$ phase. It is important to maintain this phase because the reduction of PbO$_x$ to Pb$^{2+}$ can occur readily at low pH (as governed by its Pourbaix diagram). Thus the increase in binding energy, especially from the doping of Fe, corresponds to a slightly higher average formal oxidation state of Pb, which provides additional anodic protection of PbO$_x$ against corrosion. We believe that while catalytic sites undergo redox state changes during OER that can momentarily weaken the metal–oxo bond, the oxidation state and bonding environment of the structural metal remains consistent and provides the electron and proton conductivity to facilitate re-oxidization of catalytic species before dissolution.

Conclusion

The current status of acidic OER catalyst properties can be summarized by picking any two properties from highly active, stable, and comprised of earth-abundant materials. Commercial catalysts use Ir or Ru oxides, which are expensive and not scalable, while the best earth-abundant catalysts (such as Co and Ni oxides) dissolve in acid. We demonstrate here that catalysts may be iteratively designed to fulfill the three properties for acidic OER. Unary metal oxides trade activity for acid stability. This trade-off may be circumvented by decoupling catalytic and structural sites as separate elements in mixed metal oxide films. Combining Co as the catalytic metal with Mn as the structural element engenders fast OER kinetics for CoMnO$_x$ in acid (≈82 mV/decade Tafel slope in pH 2.5) with sustained activity of 0.1 mA/cm$^2$ for over 12 h; this behavior contrasts CoO$_x$, which dissolves in minutes under the same conditions. To operate at higher current densities, Pb serves as the structural element in CoPbO$_x$ and CoFePbO$_x$ films, which maintain the OER activity of Co while displaying resistance to corrosion in pH 2.5 solution. Whereas CoO$_x$ dissolves within 30 min, CoPbO$_x$ is stable for 7 h and CoFePbO$_x$ does not degrade after 12 h. Furthermore, CoFePbO$_x$ can sustain OER current densities of 1 mA/cm$^2$ for 50 h at pH 2.0. This result is noteworthy in the context that the activity of CoFePbO$_x$ comprising earth-abundant elements occurs at ~220 mV higher overpotential than that of IrO$_x$ operating at 1 mA/cm$^2$ in pH 2.5 solution. In this regard, the principle of using different metals to fulfill independent functional components within extended lattices may be useful for designing catalysts that need to fulfill several different criteria simultaneously.

Acknowledgements

We thank Nancy Li and Zhongxing Chen for help with ICP-MS, Jules Gardener for assistance with STEM imaging, and Mircea Dincă for assistance with STEM imaging, and Mircea Dincă
for discussions. C. L. acknowledges Prof. X. Ling at Nanyang Technological University and financial support from Lee Kuan Yew Postdoctoral Fellowship. This material is based upon work supported under the Solar Photochemistry Program of the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences of the U. S. Department of Energy, SEM, TEM, and XPS were performed at Harvard University’s Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network (NNIN), which is supported by the National Science Foundation under ECS-0335765.

Experimental

General electrochemical details

Electrochemical experiments were conducted on a CH Instruments 760D potentiostat. A three-electrode configuration (working, reference, and auxiliary) in glass H-cells was employed where a porous glass frit separated the working and auxiliary compartments. Glassware was pre-cleaned by soaking in aqua regia followed by type I reagent water (EMD Millipore, 18 MO cm resistivity). The working electrode was fluoroine-doped, tin oxide-coated glass (FTO) with 7 Ω/sq. surface resistivity (TEC-7, precut 1 cm × 2.5 cm slides from Hartford Glass). Prior to use, FTO slides were cleaned by sonication in acetone and then rinsing with type I reagent water to remove any lingering trace metal ions and subsequent electrochemical characterization was performed immediately to prevent films from drying.

Electrodeposition conditions for unary metal oxide films employed previous literature procedures in the presence of 50 mM MeP, at pH 8.0: MnOx from 0.5 mM MnO42− (MnCl2·4H2O, 99.995% trace metal basis, Strem) at 0.54 V.46 cobalt oxide (CoOx) from 0.5 mM Co3O4 (using Co(NO3)2·6H2O, 99.999% trace metal basis, Strem) at 1.05 V.47 nickel oxide (NiOx) from 0.5 mM Ni3O4 (using Ni(NO3)2·6H2O, 99.9988% trace metal basis, Strem) at 1.25 V;18 and lead oxide (PbOx) from 0.5 mM Pb2+ (using Pb(NO3)2, 99.999% trace metal basis, Strem) at 1.35 V.47 Iron oxide (FeOx) was electrodeposited at 1.20 V in a solution of 0.5 mM Fe2+ (using (NH4)2Fe(SO4)2·6H2O, 99.997% trace metal basis, Aldrich) with 1.0 M KNO3 (99.0–100.5%, Macron) heated to 75 °C.48 For comparison, iridium oxide (IrOx) was prepared following literature procedures at 0.85 V in 2 mM Ir3+ (from K3IrCl6, Aldrich) with 15 mM oxalate (from oxalic acid, 98.9–101.0%, Aldrich) in 100 mM carbonate buffer (from K2CO3, >99.0%, Aldrich) at pH 10.5. Cobalt–iron oxide (CoFeOx) films were cathodically electrodeposited from 1 mM ea. Co2+ and Fe2+ at ~0.3 V, similar to literature procedures.34 Mixed metal oxide films were also anodically co-deposited in MeP, buffer at pH 8.0: CoMnOx at 0.65, 0.90, and 1.15 V in 0.25 mM ea. of Co2+ and Mn2+; CoPbOx at 1.15 V in 0.25 mM ea. Co2+ and Pb2+; and CoFePbOx at 1.15 V in 0.125 mM ea. Co2+ and Pb2+ with 0.25 mM Fe2+. All deposition protocols aimed to achieve roughly similar mass loading of films.

Tafel data collection

The oxygen evolution activity of catalyst films was evaluated by measuring the steady-state current density (j) as a function of applied potential (E) in buffered solutions of 100 mM phosphate (Pi, prepared from phosphoric acid, 99.99% trace metal basis, Aldrich) and 1.0 M KNO3 at neutral (pH 7.0) and acidic (pH 2.5) conditions. Steady-state conditions were achieved by holding films at each discrete potential for at least 30 s to allow the current to converge, and measurements were initiated at the highest potential (the first point in the series) for at least 100 s to further minimize any pseudocapacitance. Solutions were stirred at ~600 rpm with a teflon stir bar (sufficient to remove mass transport limitations) and applied potentials were post-corrected for uncompensated resistance by subtracting iR (measured on a blank FTO in same solution conditions) from each point where typical values of uncompensated resistance are ~17 Ω at pH 7 and 2.5. Further precautions were exercised by targeting Tafel data collection at current densities between 1 μA/cm2 and 1 mA/cm2 where these lower currents minimize the impact of any ohmic drop. The current–potential data were plotted as log j vs. E (or η, the overpotential) to construct Tafel plots, where the position and slope within ±5 mV/decade of independently prepared films under the same conditions were reproducible.

Acid stability during oxygen evolution

Catalyst degradation during oxygen evolution in acidic pH was assessed by long-term chronoamperometry. Similar conditions were employed as for Tafel measurements but with higher concentration of buffer to decrease local pH gradients in the H-cell during prolonged electrolysis: 0.5 M Pi at pH 2.5 and stirred at ~600 rpm. Chronoamperometry on catalyst films was performed at 0.1
mA/cm² and 1.0 mA/cm², and the potential was recorded over time until films were completely dissolved or until 12 h had passed. Dissolution was indicated visually (i.e., the FTO becomes transparent) and also by the inflection in potential that sharply increases to resemble the catalytic properties of blank FTO or catalysis by metal ions in solution. As a demonstration, CoFePbOx was also evaluated over longer time and at slightly lower pH in 0.5 M sulfate (from sulfuric acid, 99.99% trace metal basis, Aldrich) at pH 2.0 for over 50 h of continuous operation. Independently prepared samples following the same protocol were reproducible within 20 min of stability time.

**Faradaic efficiency of oxygen evolution**

The faradaic efficiency of oxygen evolution on CoMnOx and CoFePbOx was determined in 0.5 M P₅ in pH 2.5 using a gas chromatograph. The films were mounted in a custom-built two-compartment electrochemical cell where a cation-exchange membrane (Nafion 117, Sigma Aldrich) was used to separate the two chambers. A Ag/AgCl-based leak-free reference electrode (LF-1, Warner Instruments) was used as the reference electrode and a Pt wire was the counter electrode. A Viton O-ring was applied to define the area of working electrode and OER was sustained at constant current densities of 0.1 and 1 mA/cm² for CoMnOx and CoFePbOx, respectively. While stirring, a constant flow of Ar gas (20 sccm) was bubbled through the chamber of working/reference electrodes. The gas outlet was connected to a gas chromatograph equipped with a thermal conductivity detector (multiple gas analyzer #3, SRI Instruments). The amount of O₂ in the out-fluxing Ar gas was quantified, based on the calibration with known O₂ concentrations. Initial control experiments were performed to ensure that the O₂ in the air has no contribution to the measured O₂ signals. The detected O₂ concentrations were compared to the theoretical yield of O₂ (calculated by dividing the charge passed by 4Faradaic efficiency)

**Inductively coupled plasma mass spectrometry (ICP-MS)**

Trace elemental analysis on catalyst films was performed with a quadrupole ICP-MS (Thermo Electron, X-Series ICP-MS with CCT). Because these films are resistant to passive dissolution in acid, they were digested by voltage cycling (between 1.3 and –0.4 V) in 12 mL of 2% v/v nitric acid (TraceSELECT, Fluka). Co, Mn, Pb, and Fe calibration standards were prepared from corresponding ICP standard solutions (TraceCERT, Fluka), which enabled the construction of a calibration curve to convert the detected counts for ⁵⁹Co, ⁵⁷Mn, ²⁰⁸Pb, and ⁷⁷Fe to concentrations (in ppm).

**Electron microscopy**

The compositional morphology of catalyst films was observed by field emission scanning electron microscopy (SEM, Zeiss Supra 55VP) operated at a beam voltage of 15.0 kV, working distance of ~8.5 mm, a 30 µm aperture, and an InLens detector. Elemental quantification was determined at a beam voltage of 14 kV with an energy dispersive X-ray spectrometer (EDS from EDAX Inc.) using EDAX ZAF correction factors. Homogeneity on the 20 nm/px scale of mixed metal films were evaluated by EDS elemental maps using signals corresponding to K line energy values for cobalt, manganese, and iron; and L line energy values for lead.

**X-ray photoelectron spectroscopy (XPS)**

Comparison of oxidation state and chemical environment between unary and mixed metal catalyst films employed XPS (using a Thermo Scientific K-Alpha XPS system). Catalyst films were electrodeposited on FTO as described above for: CoFePbOx, CoPbOx, CoMnOx, CoOx, PbOx, and MnOx. All samples were illuminated using a monochromated Al Kα X-ray source (1486.6 eV energy and 0.85 eV line width) with a 400 µm spot size. Surface charging was compensated by a low-energy (0–14 eV) electron flood gun. The system was pre-calibrated with Au, Ag, and Cu standards built into the sample stage using an automated routine. High-resolution spectra for Co 2p, Mn 2p, Pb 4f, and Fe 2p were measured with a step size of 0.1 eV. All spectra were then calibrated to the C 1s peak at 284.8 eV.³²

**Powder X-ray diffraction (XRD)**

The crystallinity of CoMnOx and CoFePbOx samples were tested by XRD. To maximize the possibility of observing diffraction, powder samples of the catalysts were prepared by large-scale electrodeposition (using the same protocols described earlier) on multiple 20 × 8 cm² FTO plates. The thin films were briefly immersed in type I water to remove any residual solution, dried, carefully stripped from the FTO, and ground into a fine powder. The powders were loaded in a small cavity in a Si zero-diffraction plate (MTI Corporation) and inserted into a Bruker D2 Phaser powder diffractometer equipped with a Cu Ka X-ray source (generated at 20 kV and 20 mA; passed through a 1 mm slit) and LynxEye detector. A knife-edge attachment was used to reduce scattered signal, and the stage was rotated by 3°/min. Samples were examined in Bragg-Brentano mode from 29 = 10 to 75° in 0.02° increments with 0.5 s/pt scan rate.

**References**


