Supporting Information

Role of electrolyte composition on the acid stability of mixedmetal oxygen evolution catalysts

Nancy Li, Thomas P. Keane, Samuel S. Veroneau and Daniel G. Nocera*

Department of Chemistry and Chemical Biology, Cambridge, MA 02138 *Email: dnocera@fas.harvard.edu

Table of Contents

Index		Page
Experimental methods		
Figure S1.	SEM/EDS elemental maps	S7
Figure S2.	Average film stability for CoFePbOx films in different electrolytes	S8
Figure S3.	Chronopotentiometry (CPE) curves and average film stabilities for various films in KS _i and KP _i electrolytes	S9
Figure S4.	Extended CPE curves for CoFePbOx films in $\ensuremath{KS}\xspace_i$ and $\ensuremath{KP}\xspace_i$	S10
Table S1.	Elemental composition of films before and after electrolysis	S11
References		S12

Experimental Methods

Materials

Co(NO₃)₂•6H₂O (99.999%) was used as received from Strem. Pb(NO₃)₂ (99.999%), (NH₄)₂Fe(SO₄)₂•6H₂O (99.997%), H₃PO₄ (99.999%), and H₂SO₄ (99.999%) were used as received from Sigma Aldrich. KNO₃ (99.9%) was used as received from Macron. KOH (<0.001% Ni, Fe, and other heavy metals) was used as received from EMD Millipore. TraceSELECT Ultra nitric acid and TraceSELECT standards for ICP were used as received from Fluka Analytical. CH₃P(O)(OH)₂ (MeP_i) was purchased from Sigma Aldrich and then recrystallized twice from acetonitrile (HPLC grade, Sigma Aldrich). All electrolyte solutions were prepared with type I water (EMD Millipore, 18.2 MΩ cm resistivity). Fluorine-doped tin-oxide coated glass (FTO; TEC-7) was purchased as pre-cut 1 cm × 2.5 cm glass pieces from Hartford Glass with 7 Ω/sq surface resistivity.

General Electrochemical Methods

All electrochemical experiments were conducted on a CH Instruments 760D bipotentiostat, using an Ag/AgCl reference electrode (BASi, filled with saturated KCl), and a Pt-mesh (99.9% Alfa Aesar) counter electrode in a three-electrode electrochemical cell with a porous glass frit separating the working and auxiliary compartments.

All glassware was acid cleaned by soaking in aqua regia followed by copious rinsing with type I water (EMD Milipore, 18.2 M Ω cm resistivity). Prior to use, FTO slides were cleaned by sonication in acetone and then rinsed with type I water. A 1 cm² geometric electrode area was created by masking the FTO with Scotch tape. An Ag/AgCl reference electrode was positioned close to the FTO in the working compartment, and a Pt mesh electrode in the auxiliary side of the H-cell was used to complete the circuit.

Electrode potentials were converted to the NHE scale using E(NHE) = E(Ag/AgCl) + 0.197 V. Overpotentials for the oxygen evolution reaction from water were computed using $\eta = E(NHE) - (1.23 V - 0.059 V \times pH)$. All measurements were performed at room temperature (23 ± 1 °C).

Electrodeposition of Films

As-deposited films were prepared by applying a constant anodic potential to 1 cm² FTO for a specified amount of time in a 50 mM methylphosphonate (MeP_i) solution buffered at pH 8.0 containing a total of 0.5 mM metal solution. Electrodeposition conditions are based on previously published methods [1]: CoFePbO_x at 1.15 V for 1 h from solutions of 0.25 mM Fe²⁺, 0.125 mM Co²⁺, and 0.125 mM Pb²⁺; FePbO_x at 1.2 V for 1.5 h from solutions of 0.25 mM Fe²⁺ and 0.25 mM Pb²⁺; PbO_x at 1.35 V for 40 min from solutions of 0.5 mM Pb²⁺. To minimize precipitation of metal hydroxides from these solutions, 25 mL of 0.1 M MeP_i was added to 25 mL of 1 mM total metal solution. All deposition protocols furnished roughly similar mass loading of films. After deposition, films were briefly immersed in type I water to remove any lingering metal ions and subsequent electrochemical characterization was performed immediately unless otherwise noted.

Acid Stability During Oxygen Evolution

The stability of catalyst films for oxygen evolution in acid buffers was assessed by longterm chronopotentiometry. A 50 mL, two compartment H-cell was used and the electrolyte was stirred at 400 rpm in the working and reference electrode compartment to decrease local pH gradients during prolonged electrolysis. Chronopotentiometry was performed on freshly prepared catalyst films (after a quick gentle rinsed in type I water) at 1 mA cm⁻² and the potential was recorded over time until film dissolution was noted by a sudden jump in potential. Independently prepared films were made and tested for acid stability three times to ensure reproducibility.

Faradaic Efficiency of Oxygen Evolution

The faradaic efficiency of oxygen evolution on $CoFePbO_x$ films was determined in 0.1 M KS_i at pH 2.15 using a gas chromatograph as previously published [1]. The film was mounted into a custom-built two-compartment electrochemical cell where a cation-exchange membrane (Nafion 117, Sigma Aldrich) was used to separate the two chambers. An 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 density of 1 mA cm⁻². While stirring, a constant flow of Ar gas (20 sccm) was bubbled through the chamber containing the 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 O₂ in the air has no contribution to the measured O₂ signals. The detected O₂ concentrations were compared to the theoretical yield of O₂, which was calculated by dividing the charge passed by 4 Faraday to obtain the faradaic efficiency.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Trace elemental analysis was carried out with quadrupole ICP-MS (Thermo Electron, X-Series ICP-MS with collision cell technology). All pipettes and polypropylene tubes were soaked in ~5% TraceSELECT nitric acid overnight and rinsed with type I water. All pipette tips were pre-rinsed with 2% double-distilled trace nitric acid prior to use. Films were digested by soaking in 20% double distilled trace nitric acid over two days. FTO substrates were then scanned by cyclic voltammetry after soaking in 20% nitric acid to ensure complete film digestion. ICP samples were then scanned twice for 60 s each for 56 Fe,

⁵⁹Co, ⁶⁰Ni, and ²⁰⁸Pb. Internal standards and controls dispersed throughout the samples were run to confirm no signal drift.

Calculation of Buffer Capacity

For Sulfuric Acid

Calculations were conducted following previously published approach [2],

$$\begin{split} H_{2}SO_{4} + H_{2}O &\leftrightarrows H^{+} + HSO_{4}^{-} & K_{a1} = 1.0 \times 10^{3} \\ HSO_{4}^{-} + H_{2}O &\leftrightarrows H^{+} + SO_{4}^{2-} & K_{a2} = 1.0 \times 10^{-2} \\ v &= \frac{[H_{2}SO_{4}]}{[H^{+}]^{2}} \\ \frac{[H_{2}SO_{4}]}{v} &= [H^{+}]^{2} \\ \frac{[HSO_{4}^{-}]}{v} &= K_{a1}[H^{+}] \\ \frac{[SO_{4}^{2-}]}{v} &= K_{a1}K_{a2} \\ \frac{TM}{v} &= [H^{+}]^{2} + K_{a1}[H^{+}] + K_{a1}K_{a2} \\ \alpha_{o} &= \frac{[H_{2}SO_{4}]}{v} \frac{v}{TM} = \frac{[H^{+}]^{2}}{[H^{+}]^{2} + K_{a1}[H^{+}] + K_{a1}K_{a2}} \\ \alpha_{1} &= \frac{[HSO_{4}^{-}]}{v} \frac{v}{TM} = \frac{K_{a1}[H^{+}]}{[H^{+}]^{2} + K_{a1}[H^{+}] + K_{a1}K_{a2}} \\ \alpha_{2} &= \frac{[SO_{4}^{2-}]}{v} \frac{v}{TM} = \frac{K_{a1}K_{a2}}{[H^{+}]^{2} + K_{a1}[H^{+}] + K_{a1}K_{a2}} \\ \beta &= 2.303 \left\{ [H^{+}] + \frac{K_{W}}{[H^{+}]} + TM(\alpha_{0}\alpha_{1} + 4\alpha_{0}\alpha_{2} + \alpha_{1}\alpha_{2}) \right\} \end{split}$$

For Phosphate Buffer

$$\begin{split} \text{HPO}_4^{2-} + \text{H}_2\text{O} &\leftrightarrows \text{H}^+ + \text{PO}_4^{3-} \\ & v = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}^+]^3} \\ & \frac{[\text{H}_3\text{PO}_4]}{v} = [\text{H}^+]^3 \\ & \frac{[\text{H}_2\text{PO}_4^-]}{v} = K_{a1}[\text{H}^+]^2 \\ & \frac{[\text{HPO}_4^{2-}]}{v} = K_{a1}K_{a2}[\text{H}^+] \\ & \frac{[\text{PO}_4^{3-}]}{v} = K_{a2}K_{a3}[\text{H}^+] \\ & \frac{[\text{PO}_4^{3-}]}{v} = K_{a2}K_{a3}[\text{H}^+] \\ & \frac{TM}{v} = [\text{H}^+]^3 + K_{a1}[\text{H}^+]^2 + K_{a1}K_{a2}[\text{H}^+] + K_{a2}K_{a3}[\text{H}^+] \\ & \alpha_o = \frac{[\text{H}_3\text{PO}_4]}{v} \frac{v}{TM} = \frac{[\text{H}^+]^3}{[\text{H}^+]^3 + K_{a1}[\text{H}^+]^2 + K_{a1}K_{a2}[\text{H}^+] + K_{a2}K_{a3}[\text{H}^+]} \\ & \alpha_1 = \frac{[\text{H}_2\text{PO}_4^-]}{v} \frac{v}{TM} = \frac{K_{a1}[\text{H}^+]^2}{[\text{H}^+]^3 + K_{a1}[\text{H}^+]^2 + K_{a1}K_{a2}[\text{H}^+] + K_{a2}K_{a3}[\text{H}^+]} \\ & \alpha_2 = \frac{[\text{HPO}_4^{2-}]}{v} \frac{v}{TM} = \frac{K_{a1}K_{a2}[\text{H}^+]}{[\text{H}^+]^3 + K_{a1}[\text{H}^+]^2 + K_{a1}K_{a2}[\text{H}^+] + K_{a2}K_{a3}[\text{H}^+]} \\ & \alpha_3 = \frac{[\text{PO}_4^{3-}]}{v} \frac{v}{TM} = \frac{K_{a2}K_{a3}[\text{H}^+]}{[\text{H}^+]^3 + K_{a1}[\text{H}^+]^2 + K_{a1}K_{a2}[\text{H}^+] + K_{a2}K_{a3}[\text{H}^+]} \\ & \beta = 2.303 \left\{ [\text{H}^+] + \frac{K_W}{[\text{H}^+]} + TM(\alpha_0\alpha_1 + \alpha_1\alpha_2 + 4\alpha_1\alpha_3 + 4\alpha_0\alpha_2 + \alpha_2\alpha_3 + 9\alpha_0\alpha_3) \right\} \end{split}$$



Figure S1. EDS elemental maps recorded through SEM of (a) PbO_x, (b) PbFeO_x, (c) CoPbO_x and (d) CoPbFeO_x. Individual elemental channels for Sn, Pb, O, Co and Fe were taken on the same sample spot. All samples were prepared on FTO substrate, and scale bars are 600 nm.



Figure S2. Average stability of CoFePbO_x films performing OER at 1 mA/cm^2 in solutions buffered with either KP_i (a), or KS_i (b) using different buffer concentration and ionic strengths. All solutions were buffered to pH 2.15.



Figure S3. Representative chronopotentiometry curves (a) and average potential required to maintain 1 mA/cm² of current (b) for bare FTO in 0.1 M KS_i at pH 2.15 (orange), a PbO_x film in 0.1 M KS_i at pH 2.15 (red), a FePbO_x film in 0.1 M KS_i at pH 2.15 (green), and bare FTO in 0.1 M KP_i at pH 2.15 (blue).



Figure S4. Representative chronopotentiometry curves for $CoFePbO_x$ films held at a constant current of 1 mA/cm² in 0.1 M KS_i at pH 2.15 (green), and 0.1 M KP_i at pH 2.15 (red). Inset: Operating potentials for both conditions in the first 4 h of operation.

Condition	Total metal mol	Pb mol %	Co mol%	Fe mol%
As-deposited	256.2 ± 7.2	47.2 ± 1.6	41.8 ± 0.9	11.0 ± 1.8
10 min OER in 0.1 KP _i pH 2.15	221 ± 9.2	44.1 ± 2.1	39.9 ± 0.6	16.0 ± 1.4
10 min OER in 0.1 M KP _i + 1.0 M KNO ₃ pH 2.15	223.9 ± 8.3	45.6 ± 2.9	41.0 ± 4.3	13.4 ± 2.5
10 min OER in 0.1 H2SO4 pH 2.15	227.3 ± 6.9	46.9 ± 1.1	40.1 ± 2.9	13.0 ± 2.1
40 h OER in 0.1 KP _i pH 2.15	89.0 ± 8.9	62.8 ± 3.2	23.3 ± 1.1	13.9 ± 3.1
40 h OER in 0.25 KP _i pH 2.15	100.2 ± 12.1	57.0 ± 5.8	23.9 ± 7.5	19.1 ± 2.9
40 h OER in 0.1 M KP _i + 1.0 M KNO ₃ pH 2.15	108.1 ± 17.1	61.6 ± 3.9	25.3 ± 5.2	13.1 ± 3.3
40 h OER in 0.1 H ₂ SO ₄ pH 2.15	169.4 ± 16.1	62.7 ± 2.4	8.0 ± 2.2	29.3 ± 4.2

Table S1. Elemental composition of 1 cm^2 CoFePbOx as-deposited films and after operatingOER at 1 mA cm^{-2} for 10 min and 40 h in specific buffers at pH 2.15.

References

- 1. M. Huynh, T. Ozel, C. Liu, E. C. Lau and D. G. Nocera, *Chem. Sci.*, 2017, **8**, 4779–4794.
- 2. D. W. King and D. R. Kester, *J. Chem. Educ.* 1990, **67**, 932–933.