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Stability and activity of cobalt antimonate for oxygen reduction in strong acid

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Abstract

Guided by computational Pourbaix screening and high throughput experiments aimed at development of precious-metal-free fuel cells, we investigate rutile CoSb_2O_6 as an electrocatalyst for oxygen reduction in 1 M sulfuric acid. Following 4 hours of catalyst conditioning at 0.7 V vs RHE, operation at this potential for 20 hours yielded an average current density of -0.17 mA cm^{-2} with corrosion at rate of $0.04 \text{ nm hour}^{-1}$ that is stoichiometric with catalyst composition. Surface Pourbaix analysis of the (111) surface identified partial H coverage under operating conditions. The Sb active site has a HO^* binding free energy of 0.49 eV, near the peak of the kinetic $4e^-$ ORR volcano for transition metal oxides in acidic conditions. The experimental demonstration of operational stability and computational identification of a reaction pathway with favorable energetics places rutile CoSb_2O_6 among the most promising precious-metal-free electrocatalysts for oxygen reduction in acidic media.

Main text

The development of active and stable catalysts for electrochemical reactions in harsh corrosive environments, such as strong acidic media under high electrochemical potentials, is a challenge at the forefront of electrochemistry for clean energy technologies. Platinum-based materials remain the state-of-the-art for catalyzing the oxygen reduction reaction (ORR), a half-cell cathode electrochemical reaction essential to energy conversion technologies such as fuel cells and metal-air batteries.¹⁻⁸ However, the limitations due to the inherent scarcity and expense of precious metals have been compounded by insufficient operational durability. Broad deployment of these technologies hinges upon development of active, corrosion-resistant, and earth-abundant electrocatalysts for the ORR, prompting the community's investigation of transition metal alloys and intermetallics; carbon-supported transition metal/nitrogen catalysts (Fe-, or Co-N/C); and transition metal oxides, nitrides, carbides, oxynitrides, carbonitrides, phosphides, and chalcogenides.^{3,6,9-28} Although some platinum-group-metal (PGM)-free Fe-N-C electrocatalysts have exhibited ORR activities approaching that of commercial Pt/C electrocatalysts,²⁹ to date these materials show limited stability and durability against chemical/electrochemical attack under the strong acidic conditions required for incorporation in proton exchange membrane fuel cells.

Using computational Pourbaix diagrams, a family of rutile transition-metal antimonate phases, MSb_2O_6 ($M = Mn, Fe, Co, Ni$), were among 68 oxide materials recently identified as Pourbaix-stable in potential ranges relevant for oxygen electrochemistry in strong acid electrolyte.^{22,30} Several transition-metal antimonates have been investigated experimentally as electrocatalysts for OER³¹⁻³⁴ and the chlorine evolution reaction (CER).^{33,35} Among them, $CoSb_2O_6$ exhibited a reasonable OER activity under acidic conditions as well as a high corrosion resistance under both OER and CER, in agreement with the theoretical results.^{22,30} Initial studies indicate that $CoSb_2O_6$ is stable and active for ORR in alkaline electrolytes,³⁶ and herein we explore Co-Sb oxides for ORR in 1 M H_2SO_4 .

Exploration of $MnSb_2O_6$ -based OER catalysts revealed that Ni substitution³¹ or Mn enrichment³² on the cation sub-lattice of the rutile structure greatly enhances activity. Given this precedent, catalyst screening in the present work commenced with combinatorial investigation of the phase behavior, activity, and stability of Co_xSb_{1-x} oxides, revealing that unlike $MnSb_2O_6$ for OER, the most promising catalyst for ORR is stoichiometric $CoSb_2O_6$ annealed at 700°C (see Supporting Information Figs. S1-S4). The activity and durability was evaluated with 24-hour electrolysis in recirculating electrolyte (Fig. 1a) from which aliquots at various time points were used to characterize the evolution of concentration of metals in electrolyte during operation (Figs. 1b-1c and S5). Cathodic current was observed throughout the 24-hour measurement (Fig. 1b), with a total cathodic charge density of 14.5 C cm^{-2} , for which ORR is the only plausible explanation. Characterization of the ORR onset potential is provided in Fig. S6, where

comparison of cyclic voltammograms with N_2 and O_2 -saturated electrolyte indicates that the ORR current is differentiated from the capacitive current at approximately 0.85 V vs RHE.

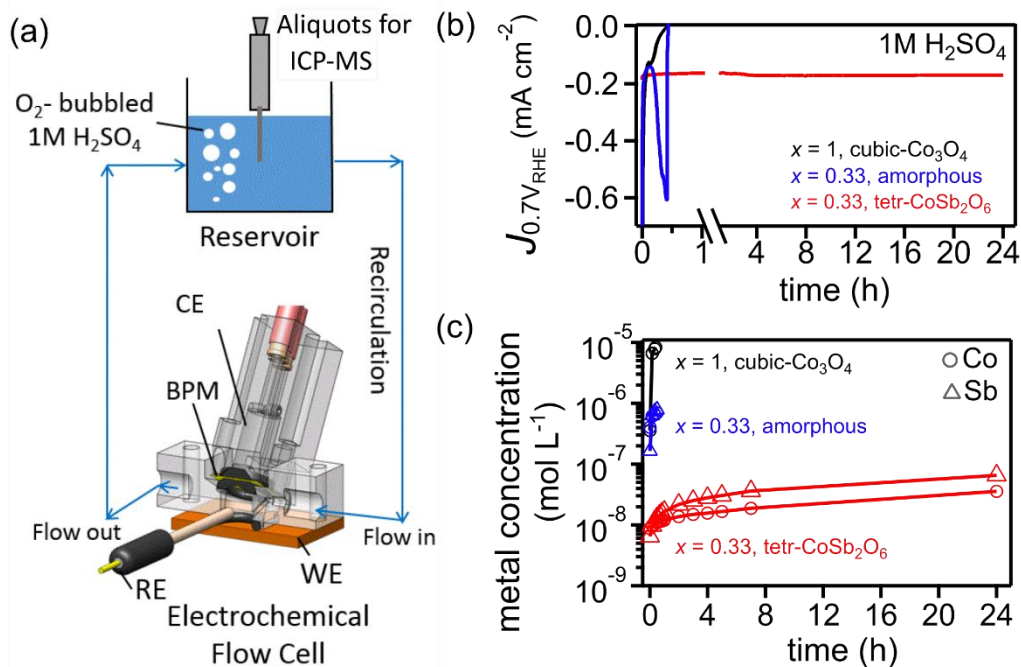
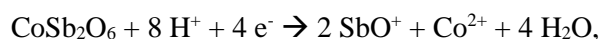


Figure 1: Electrochemical characterization of rutile $CoSb_2O_6$ ORR activity and stability in 1 atm O_2 -saturated 1 M H_2SO_4 electrolyte. (a) The electrochemical recirculation flow cell where a bipolar membrane (BPM) separates the counter electrode (CE) from the working electrode (WE) chamber that contains the Ag/AgCl reference electrode (RE). Recirculation of electrolyte enables equilibration of the operating catalyst with dissolved metals. Aliquots from the electrolyte reservoir are characterized by ICP-MS to measure the concentration of metals in electrolyte. (b) The current density at 0.7 V vs RHE over 24 hours is shown from the rutile $CoSb_2O_6$ electrode. The analogous result for a spinel- Co_3O_4 electrode is shown as a baseline with measurement terminated once the current density decayed to zero. (c) The measured metals concentration in electrolyte by ICP-MS over the course of the measurements in b).

The primary gradient in the dissolved metals concentrations occurs within 4 hours of electrolysis (Fig. 1c), at which time the concentrations of Sb and Co are approximately 3×10^{-8} and 1.5×10^{-8} mol L $^{-1}$, respectively. Each of these concentrations increases by approximately 2 \times over the next 20 hours, indicating a finite corrosion rate that is stoichiometric with the as-synthesized catalyst composition. Given the electrolyte volume (starting at 50 mL and decreasing by 2 mL for each aliquot), electrode area, and molar volume of $CoSb_2O_6$, the average corrosion rate over the first 4 hours and the final 20 hours of catalyst operation is 0.25 and 0.04 nm hour $^{-1}$, respectively. The average current density over this period is -0.17 mA cm $^{-2}$. To check for precious metal contamination of the electrochemical cell, measurements of

the dissolved Pt in the electrolyte were 4×10^{-11} mol L⁻¹ at the beginning of the measurement and 1×10^{-10} mol L⁻¹ at the end of 24 h electrolysis (Fig. S5), which are both within the noise level of the measurement. The Pt underlayer enabled electrical contact to mechanically-stable films, and further confirmation that it does not play a substantial role in the ORR catalysis is provided in Fig. S7 where comparable current densities are obtained with a Au underlayer.

The computational Pourbaix diagram^{22,37} for CoSb₂O₆ shows that near or below the operating potential of 0.7 V vs RHE at pH 0, the stable aqueous ionic species are SbO⁺ and Co²⁺, so assuming the corrosion reaction



the 4 e⁻ per CoSb₂O₆ formula unit (FU) of corrosion corresponds to an average corrosion current density of 6.9×10^{-6} mA cm⁻² over the final 20 hours of the measurement, which is a small fraction of the observed current density. Assuming the remainder of the current density results from 4 e⁻ ORR, the Faradaic efficiency toward ORR is approximately 99.99%, with each corroded FU supporting more than 6×10^4 ORR catalytic cycles. By these metrics, CoSb₂O₆ provides a remarkable combination of activity and stability for a PMG-free ORR electrocatalyst operating in strong acid. An initial characterization of the sensitivity of the catalytic activity with respect to dissolved metals concentrations is provided in Fig. S8.

For comparison, the electrolysis at 0.7 V vs RHE was performed on a reactive sputtered Co oxide film (Figs. 1b-1c) that formed a polycrystalline spinel Co₃O₄ with a domain size of 5 nm (Fig. S9). The cathodic current drops to zero and the Co concentration in electrolyte approaches 1×10^{-5} mol L⁻¹ within 20 minutes. Since the concentration of Co in electrolyte never appears to equilibrate with Co₃O₄ in this film, we can infer that the CoSb₂O₆ structure lowers the equilibrium concentration of Co²⁺ by more than 1000×. This observation is consistent with computational Pourbaix energetics at pH 0 and 0.7 V vs RHE, which indicate that rutile CoSb₂O₆ phase is stable at Co²⁺ concentration as low as 1×10^{-9} mol L⁻¹, which is comparable to the 10^{-8} mol L⁻¹ level observed in our experiments, while Co₃O₄ is predicted to dissolve as Co²⁺ even with concentrations as high as 1 mol L⁻¹.³⁸ To confirm the importance of crystallization into the rutile structure, a sputter-deposited thin film of the same compositions but without annealing was confirmed to be x-ray amorphous and tested at 0.7 V vs RHE where dissolved metals concentrations were 40× larger than the rutile CoSb₂O₆ catalyst, leading to loss of cathodic current after 26 mins (Figs. 1b-1c).

To compare CoSb₂O₆ with recent reports of non-precious metal electrocatalysts in terms of activity and stability (Table S1), we commence with consideration of molybdenum nitride and molybdenum oxynitride electrocatalysts that were studied for the acidic ORR with monitoring of metal dissolution by inductively coupled plasma optical emission spectrometry (ICP-OES).^{39,40} While MoN exhibits ORR

activity at 0.7 V vs RHE that is similar to CoSb_2O_6 in the present work, the dissolution rate is 100× higher.³⁹ Group 4 and 5 metal oxides/nitrides/oxynitrides (Ti, Zr, Ta, Nb, and Hf etc.) have been extensively studied as precious-metal-free ORR active catalysts due to the intrinsic Pourbaix stability of the surface oxides. For example, the solubility of dissolved metal was measured to be $3.5 \times 10^{-7} \text{ mol L}^{-1}$ for a TiO_x catalyst in 0.1 M H_2SO_4 at 50 °C⁴³ and $3.5 \times 10^{-6} \text{ mol L}^{-1}$ in 1 M H_2SO_4 at 70 °C for a ZrO_x catalyst.⁴⁴ These catalysts pose a challenge of simultaneously realizing activity and stability, as evidenced by the ZrO_x catalyst on glassy carbon exhibiting cathodic current density below $5 \mu\text{A cm}^{-2}$ at 0.7 V vs RHE.⁴⁴ Optimization of catalyst electrodes by using conductive graphitic carbon materials,^{42,45–47} controlling the nanoparticle size,⁴⁸ and/or increasing the oxygen vacancy density^{49–51} can increase the cathodic current density up to 0.2 mA cm^{-2} at 0.7 V vs RHE. The CoSb_2O_6 catalyst of the present work (at ambient temperature) exhibits 30× higher current density with 100× lower dissolved metals concentration compared to ZrO_x on glassy carbon, motivating further study of whether analogous optimization of electrode synthesis could elevate the current density of CoSb_2O_6 -based catalysts.

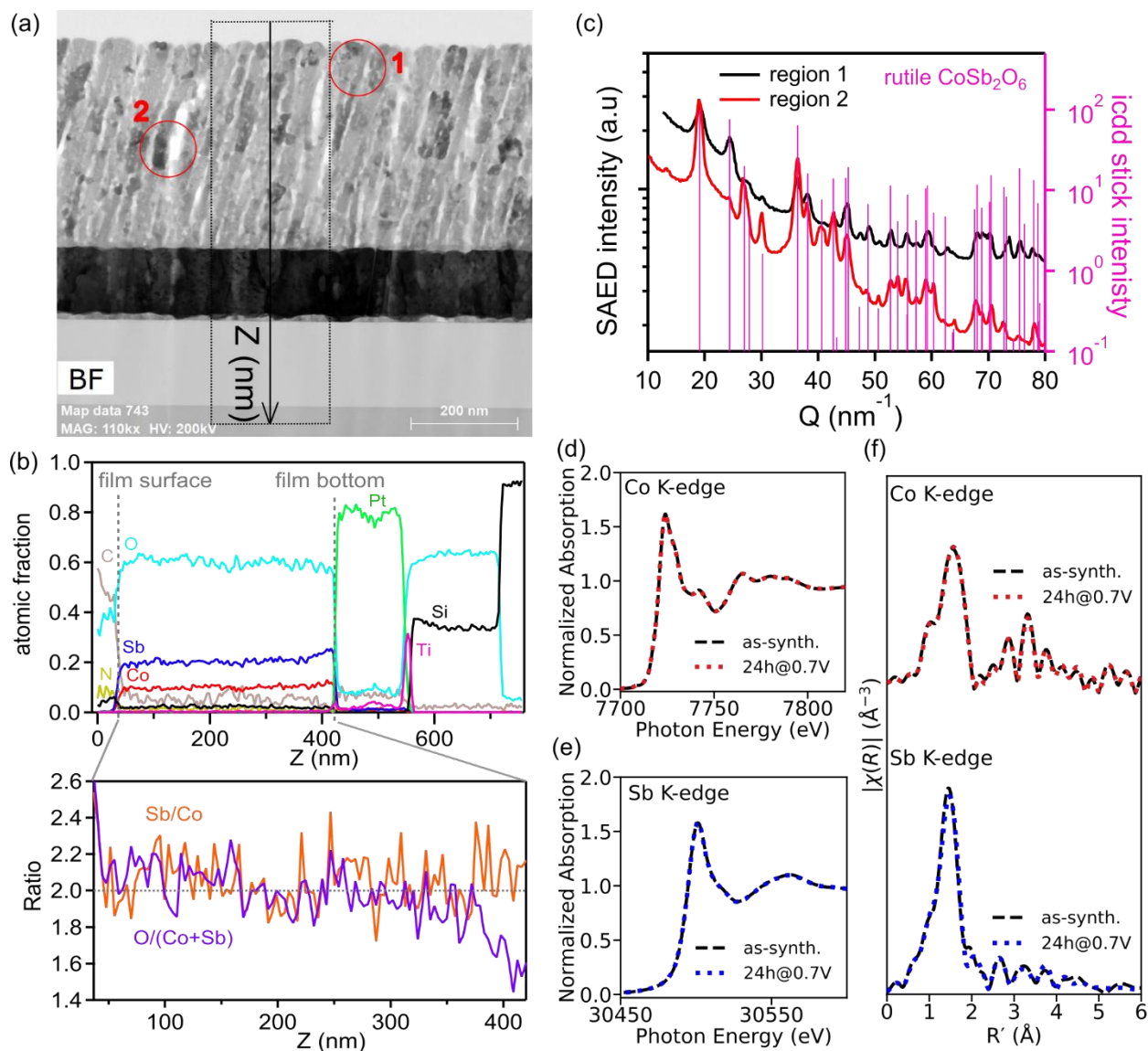


Figure 2: Transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS) characterization of the thin film CoSb_2O_6 electrocatalyst after 24 hours operation at 0.7 V vs RHE in 1 atm O_2 -saturated 1 M H_2SO_4 electrolyte. (a) The bright field image exhibits a columnar thin film with ca. 20 nm grains. (b) The depth profile of elemental concentrations demonstrates negligible interdiffusion with the metal contact layer, and the Sb/Co and O/(Co+Sb) remain within the uncertainty of the formula unit value throughout the ca. 400 nm thickness of the film. (c) The selected area electron diffractions (SAED) from 2 representative regions match the rutile CoSb_2O_6 structure with lattice constants $a = 4.654$ and $c = 3.094$ Å. (d) Co K-edge XANES, (e) Sb K-edge XANES, and (f) the respective EXAFS signals are compared for 2 CoSb_2O_6 electrodes, an as-synthesized electrode and the electrode from (a) that was operated for 24 h at 0.7 V vs RHE. The consistency of the XANES and EXAFS patterns highlights the chemical and structural stability of the catalyst.

Further characterization of the CoSb_2O_6 catalyst commenced with transmission electron microscopy (TEM) of the electrode after 24 hour electrolysis, revealing a film with low void density and low surface roughness (Fig. 2a). The elemental mapping indicates that Co and Sb are distributed uniformly in the thin film with no indication of phase segregation (Fig. S10). The measured depth profile of the composition matches the formula unit composition within uncertainty throughout the thickness of the film, corroborating the observation of stoichiometric dissolution of Sb and Co (Fig. 2b). The apparent crystal domain size of 20 nm is commensurate with the x-ray diffraction (XRD) analysis, as is the selected area electron diffraction (SAED images are shown in Fig. S11) from which more than 20 reflections can be indexed to the rutile structure. The integrated electron diffraction spectra in Fig. 2c suggest partial tri-rutile ordering, as evidenced by relatively low intensity (002) and (101) reflections at 13.5 and 15.09 nm^{-1} , respectively. The intensity of these tri-rutile-ordering peaks is below the detectability limit by XRD (Fig. S3), demonstrating that the majority of the crystalline grains are best characterized by the rutile structure with lattice constants $a = 4.654 \text{ \AA}$ and $c = 3.094 \text{ \AA}$. Comparison with an as-synthesized electrode demonstrates that the film morphology is unchanged by the 24 h electrolysis of Fig. 1 (Fig. S12). These results were further corroborated by x-ray fluorescence (XRF, Fig. S13) as well as X-ray absorption near edge structure (XANES, Fig. 2d-e) and extended X-ray absorption fine structure (EXAFS, Fig. 2f) characterization at both the Co K-edge and the Sb K-edge. These results indicate no change in bulk composition, oxidation state, or local structure from the 24-hour electrolysis. The XANES and EXAFS patterns are compared to binary oxide standards in Fig. S14.

X-ray photon spectroscopy (XPS) characterization (Fig. S15) of the same sample indicates that the near-surface region of the thin film catalyst (after exposure to air and XPS measurement at ultra-high-vacuum conditions) exhibits mixed-valency of both Co and Sb compared to the formal Sb^{+5} and Co^{+2} cations of the rutile structure. While these XPS measurements do not characterize the oxidation states of Sb and Co under ORR conditions, comparison of the XPS data with those of a duplicate film with no electrochemical operation reveals no noticeable difference (Fig. S15). The combined ICP-MS, TEM, XRF, and XPS characterizations thus indicate that the rutile CoSb_2O_6 film does not develop a passivation layer of different stoichiometry during ORR operation. The catalyst activity drops at the beginning of the measurement and then recovers as the concentrations in electrolyte equilibrate and reach the same Sb:Co stoichiometry as the catalyst (Fig. 1c). The demonstration of stoichiometric corrosion and stable current density is important for guiding investigation of the active site.

Motivated by the computational bulk thermodynamic stability²² and experimental demonstration of stable catalysis, spin-polarized density functional theory calculations with strong on-site Coulomb interaction of localized electrons (DFT+U) were performed to calculate the surface Pourbaix energetics of the surfaces

of rutile CoSb_2O_6 . The metal-terminated (111) facet was considered for calculations due to its relatively low surface energy ($0.068 \text{ eV}/\text{\AA}^2$, see Table S2). It can be seen in the surface Pourbaix diagram constructed at $\text{pH} = 0$ (Fig. 3a) that CoSb_2O_6 (111) is partly covered by H^* at the O-sites under acidic ORR conditions. The surface with H-coverage of 0.67 monolayer (ML), as illustrated in Figure 3b, is the most stable surface when the potential is at or below 0.7 V vs RHE, indicating that the operational catalyst surface is partially covered by HO^* under the acidic ORR conditions. Similar results can be found in facets such as CoSb_2O_6 (110), as shown in Fig. S16. The surface Pourbaix analysis of Fig. 3a also corroborates the bulk thermodynamic analysis that suggested operational stability of CoSb_2O_6 ; all surfaces involving lattice O removal exhibit relatively high energetics, demonstrating that several surface configurations are more favorable than those leading to corrosion.

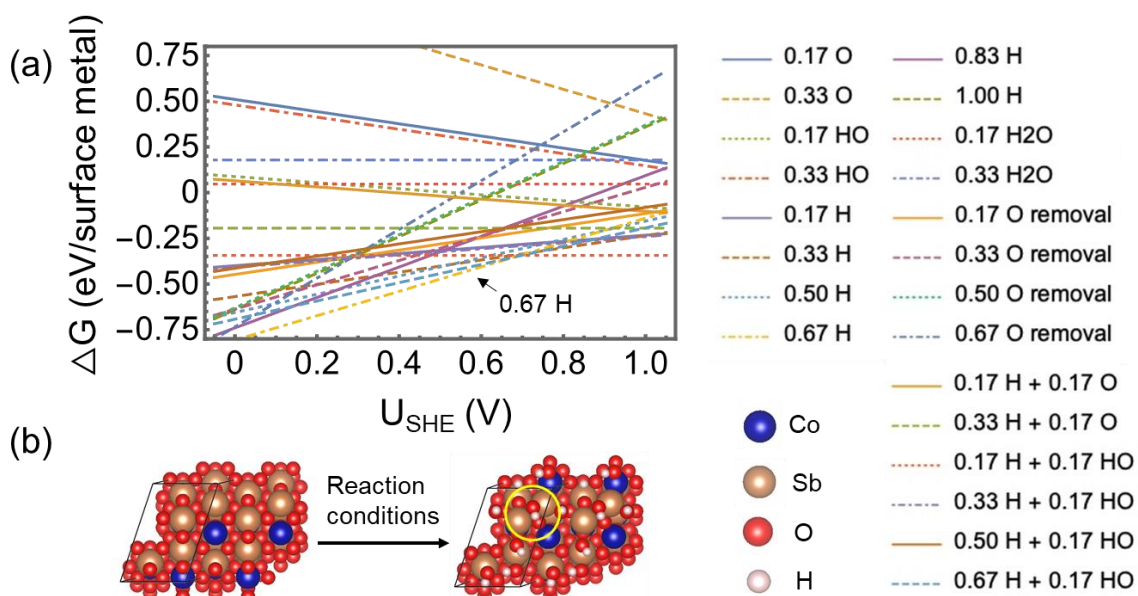


Figure 3: (a) Calculated surface Pourbaix energetics of CoSb_2O_6 (111) at $\text{pH}=0$. Each surface is labelled by the fractional monolayer coverage of the indicated species. (b) The metal-terminated CoSb_2O_6 (111) surface is shown, as well as the 0.67 H surface identified in a) to be the operational surface below 0.7 V vs RHE. Brown, blue, red, and pink spheres represent Sb, Co, O, and H, respectively. The yellow circle represents the identified active Sb-site for ORR.

Activity analysis based upon the Pourbaix-stable surface reveals that the Sb site of CoSb_2O_6 (111), which is circled in Fig. 3b, has favorable energetics for the acidic ORR. Fig. 4a compares the DFT-calculated free energy diagram for the $4 e^-$ ORR at this site to that of the state-of-art ORR catalyst, Pt, under applied potential of 0.7 V vs RHE (with estimated transition states using the method described in Refs. ^{21,52}). On Pt (111), the reaction proceeds with relatively facile energetics with the removal of HO^* as the rate-

limiting step. The rate-limiting step on $\text{CoSb}_2\text{O}_6(111)$ is the dissociation of the HO-O bond because of the relatively weak O-bonding at metal oxide surfaces.²¹

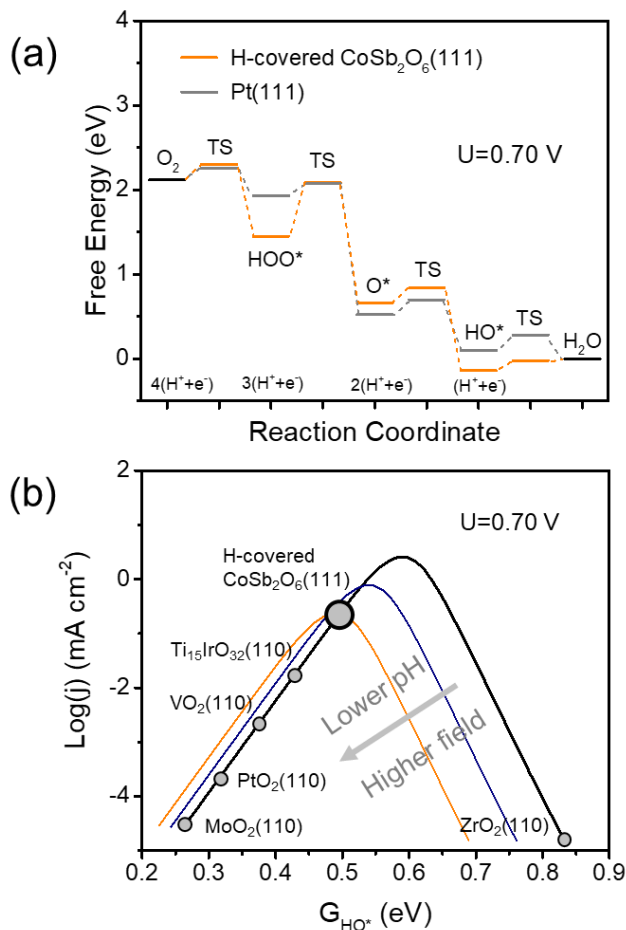


Figure 4: (a) Free-energy diagram for the four-electron ($4e^-$) ORR process on Pt and $\text{CoSb}_2\text{O}_6(111)$ surfaces under applied potential of 0.7 V vs RHE, where HOO^* , O^* , and HO^* are intermediates involved in $4e^-$ ORR path and TS indicates each transition state. (b) Kinetic volcano model for the $4e^-$ ORR at 0.7 V vs RHE. The black plot shows the model of rate vs HO^* binding free energy (G_{HO^*}) at the potential of zero charge where there are no electric field effects in the energies of transition states and intermediates.²¹ The colored curves show qualitatively the shift in the volcano for increasing electric field, which emulates the effect of decreasing pH. Among known catalysts, $\text{CoSb}_2\text{O}_6(111)$ has a unique G_{HO^*} that makes it especially well-suited for the acidic ORR.

Considering the Pourbaix-stable (0.67 ML H-covered) state of surface under reaction conditions, the calculated HO^* binding free energy (G_{HO^*}), which is the primary descriptor for ORR activity, of $\text{CoSb}_2\text{O}_6(111)$ is 0.49 eV. As illustrated in Fig. 4b, this value is near the peak of the kinetic $4e^-$ ORR volcano for transition metal oxides at acidic conditions.²¹ As we recently reported, the low pH leads to a left-and-

down shift of the ORR volcano for metal oxides, resulting in a theoretical maximum in activity at relatively strong HO-bonding. Detailed discussions related to pH and field effects on the shift of the ORR volcano can be found in our recent study.²¹ While further characterization of the operational catalyst and assessment of durability at longer time scales and higher temperatures remain important for further development of CoSb₂O₆-based catalysts for the acidic ORR, the seminal demonstration of CoSb₂O₆ operation with low dissolved metals concentration and low corrosion rate transforms the path toward precious metal-free fuel cells.

Experimental Methods

Co_xSb_{1-x}O_z composition libraries were fabricated atop 100-mm-diameter Pt/Ti/SiO₂/Si substrate by reactive co-sputtering of Co and Sb metal sources using 137 W and 55 W radio-frequency (RF) power supplies, respectively. The deposition proceeded in a mixed O₂ (0.9 mTorr) and Ar (5.1 mTorr) with 10⁻⁸ mTorr base pressure, followed by a post-deposition anneal in a box oven at 700 °C in air for 3 hours. In addition, a Co oxide library was deposited on a 100-mm-diameter FTO-coated glass (Tec-15) substrate using Co source at 140 W without additional post-deposition anneal.

Electrochemical characterization was performed in geometric working electrode area of 0.31 cm² defined by the o-ring in a customized fast flow cell.⁵⁴ Over the course of CA at 0.7 V vs RHE in 1 atm O₂-saturated 1 M H₂SO₄ aqueous electrolyte, aliquots of electrolyte (2 mL) at various time points were extracted to quantify the dissolved metal concentrations via inductively coupled plasma mass spectrometry (ICP-MS).

The metal oxide compositions were characterized by X-ray fluorescence (XRF) using an EDAX Orbis Micro-XRF system to obtain Co, Sb metal contents and values of $x = \text{Co}/(\text{Co}+\text{Sb})$ with ca. 1 at.% relative uncertainty. The oxygen signal and thus stoichiometry is not detectable by the XRF experiment.

The bulk crystal structure and phase distribution of composition libraries was determined by X-ray diffraction (XRD) using a Bruker DISCOVER D8 diffractometer with Cu K α radiation from a Bruker I μ s source. The X-ray spot size was limited to a 2 mm length scale, over which the composition is constant to within approximately 1-2 at.%.

X-ray photoelectron spectroscopy (XPS) spectra were measured to determine the near-surface chemistry using a Kratos Axis Ultra instrument with excitation from a monochromatized Al K α radiation at 150 W (10 mA at 15 kV). The collected spectra were calibrated to the carbon 1s peak of 284.8 eV.

To prepare a cross-sectional Transmission electron microscopy (TEM) specimen in the specific region tested for 24 hours electrolysis, a FEI DualBeam Focused Ion Beam/scanning electron microscope

(FIB/SEM) was used, and the sample was capped carbon/I-C prior to milling. TEM experiments were carried out in a FEI Tecnai Osiris FEG/TEM operated at 200 kV in bright-field (BF) and high-resolution (HR) TEM mode. Selected area electron diffraction (SAED) patterns were taken using the same machine. The energy-dispersive X-ray spectroscopy (EDX) elemental mapping was acquired using Bruker Quantax. This characterization was performed by Eurofins EAG Precision TEM in Santa Clara, California.

X-ray absorption spectra (XAS) at the Sb K-edge (30491 eV) were recorded at the Stanford Synchrotron Radiation Lightsource (SSRL, California, USA) at wiggler beamline 7-3, using a liquid-nitrogen-cooled Si(220) $\phi = 0^\circ$ double-crystal monochromator. The storage ring was operated at 3 GeV with a ring current of 494–500 mA in top-up mode. The incident X-rays were monochromatized using a Si (220) double crystal monochromator which was detuned to 20% of flux maximum at the Sb K-edge to minimize the higher harmonics. The intensity of the incident and transmitted X-rays was monitored using Ar-filled ion chambers. The CoSb₂O₆ samples were measured in fluorescence mode using a 30-element Ge detector (Canberra). An Sb reference (Sb foil) was scanned simultaneously with each sample for energy calibration. Monochromator energy calibration was done using Sb foil spectrum by setting the first inflection point at 30491.0 eV. The XAS measurements at the Co K-edge (7709 eV) spectra were performed at the SSRL at beamline 9-3. Beamline 9-3 is a 16-pole, 2-Tesla wiggler side station with a vertically collimating mirror for harmonic rejection and a cylindrically bent mirror for focusing. The photon energy was selected using a liquid-nitrogen-cooled, double-crystal Si (220) $\phi = 0^\circ$ monochromator. The XAS scans were performed in a continuous scan mode and recorded in fluorescence mode using N₂-filled ion chambers and a PIPS/Lytle detector. A Co reference (Co foil) was scanned simultaneously with each sample for energy calibration. Monochromator energy calibration was done using Co foil spectrum by setting the first inflection point at 7709.0 eV.

Inductively coupled plasma mass spectrometry (ICP-MS) by Thermo Fisher Scientific iCAP™ RQ instrument was used to determine the concentration of dissolved metals in electrolyte used for electrochemistry at different durations over the course of electrochemical measurements, including Co, Sb, and Pt.

Computational Methods

Spin-polarized DFT+U calculations were conducted using the VASP code, with the U_{eff} for Co acquired from the *Materials Project*.³⁷ The valence electrons were described by expanding the Kohn-Sham wave functions in a plane-wave basis set.⁵⁵ The kinetic energy cutoff was set to 400 eV. The core electrons were treated by the projector augmented-wave (PAW) method.⁵⁶ The electronic exchange and correlations were

described by the generalized gradient approximation (GGA) method and the revised functional of Perdew, Burke, and Ernzerhof (RPBE).⁵⁷ A (3×3×1) k-point mesh was used to sample the Brillouin zone. Convergence was defined after the forces of each atom fell below 0.05 eV/Å. The surface Pourbaix diagram calculations were described by our previous study.²¹ The HO* binding free energy was calculated using the total energies of H₂O and H₂ as the references. The zero-point energy, entropic, and solvation energy corrections were acquired from Refs.^{58,59}.

Supporting Information

High throughput experiments that provide the basis for the primary experiments; additional catalyst characterization data; additional computational results.

Acknowledgments

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