

## **Supporting Information**

13 October, 2014

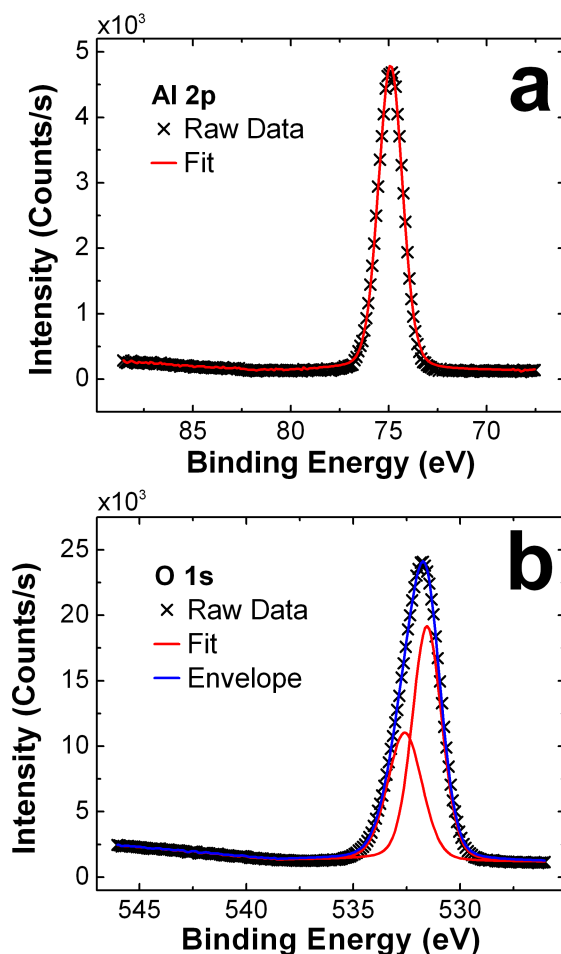
**Ms. ID: 1a-2014-03232m**

### **Electrochemical Properties of Metal-Oxide-Coated Carbon Electrodes Prepared by Atomic Layer Deposition**

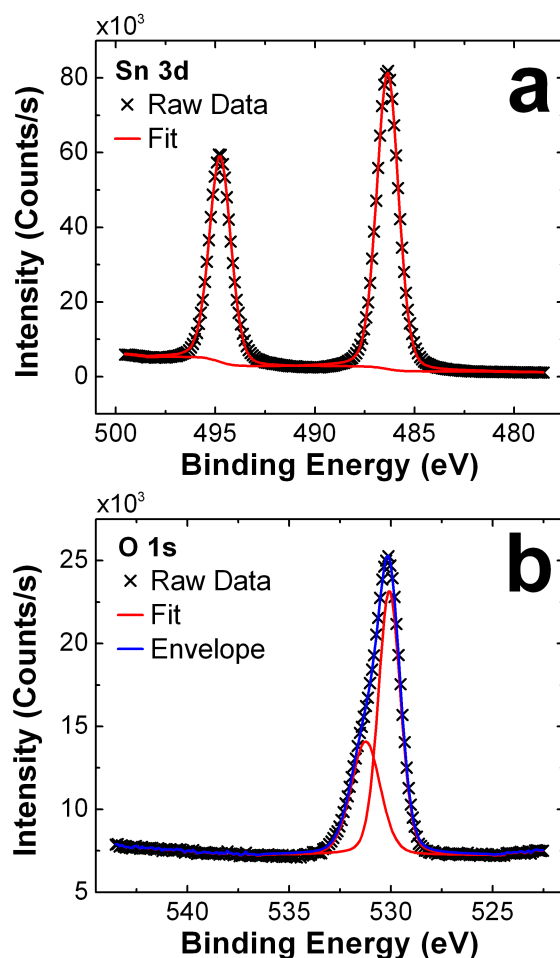
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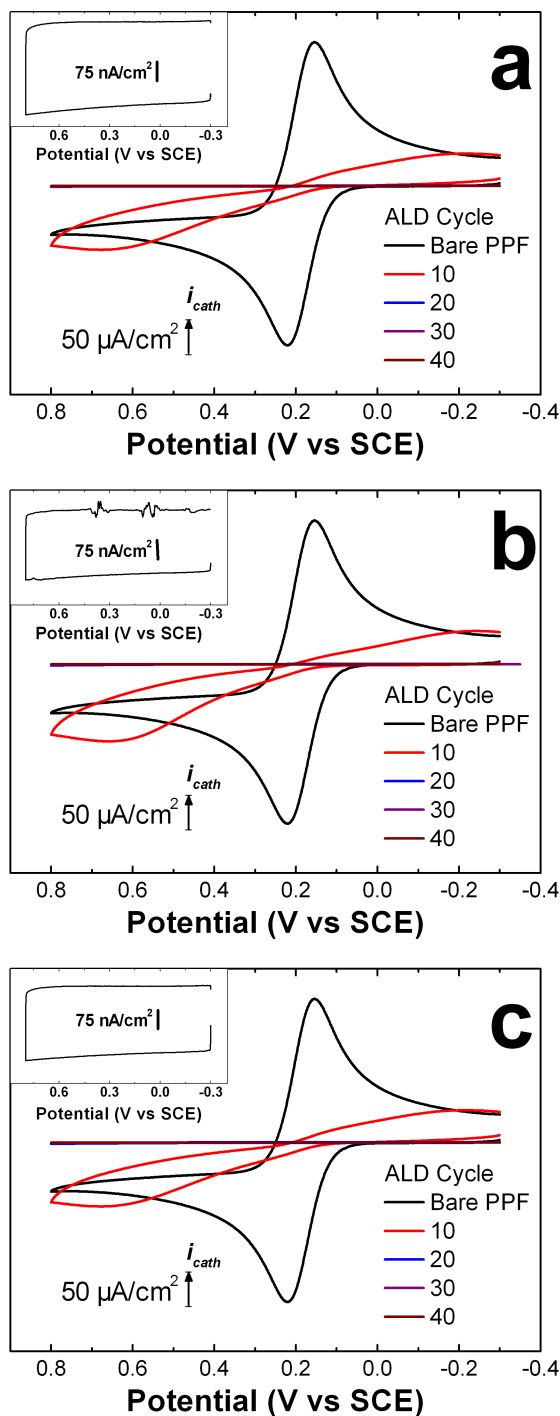


**Figure S1.** High-resolution XPS spectra after 100 ALD cycles of Al<sub>2</sub>O<sub>3</sub> deposition onto a PPF substrate pretreated with 15 s of air plasma for the (a) Al 2p and (b) O 1s regions. The Al 2p peak is centered at 75.0 eV. The separation between the Al 2p and O 1s envelope peaks is 456.8 eV, which is in agreement with previous reports.<sup>1-4</sup> The Al 2p and O 1s spectra exhibit one and two peaks, respectively, which is in agreement with previous reports.<sup>1-4</sup> These data are consistent with previously reports of fully oxidized and amorphous Al<sub>2</sub>O<sub>3</sub> films.<sup>1,2,4</sup>

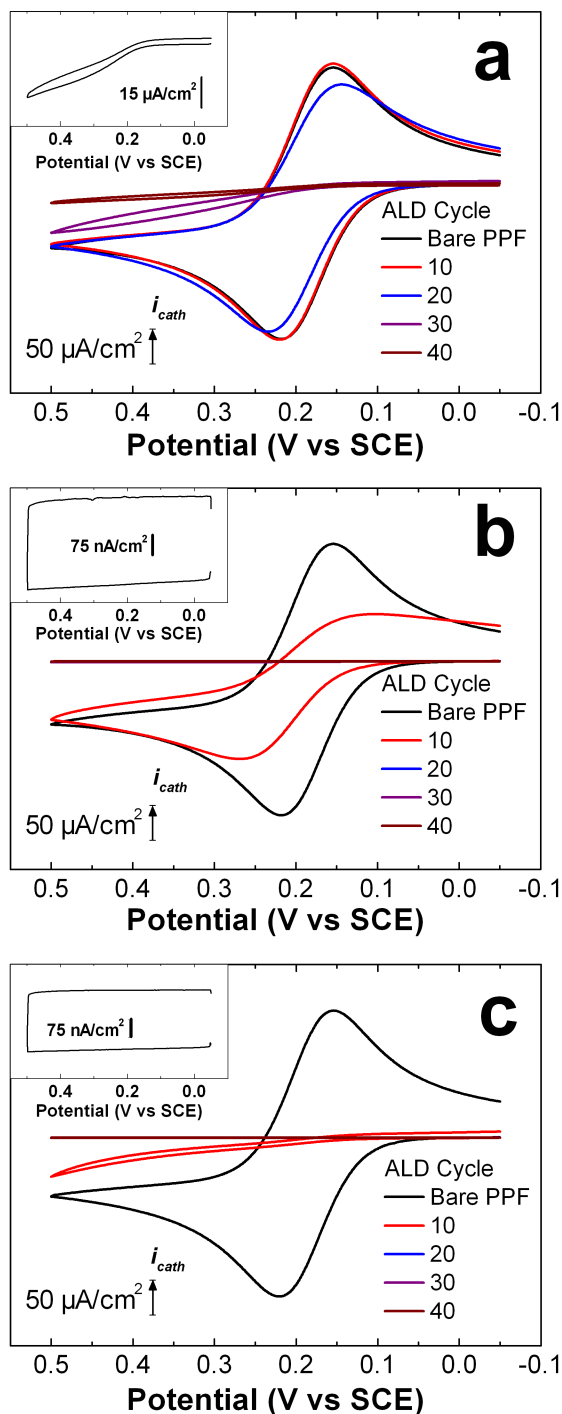


**Figure S2.** High-resolution XPS spectra after 90 ALD cycles of SnO<sub>2</sub> deposition onto a PPF substrate pretreated with 15 s of air plasma for the (a) Sn 3d and (b) O 1s regions. The Sn 3d<sub>5/2</sub> peak for the SnO<sub>2</sub> films is centered at 486.4 eV and the O 1s envelope peak is at 530.1 eV. The separation between the O 1s and Sn 3d<sub>5/2</sub> lines is 43.7 eV. The literature reports the separation between the Sn 3d<sub>5/2</sub> and O 1s peaks for SnO and SnO<sub>2</sub> to be 43.7 and 43.6 eV, respectively.<sup>5,6</sup> Due to the uncertainty in the measurements ( $\pm 0.1$  eV), it is difficult to assign an oxidation state for

the SnO<sub>x</sub> films. For the purposes of this paper, therefore, these films are denoted as SnO<sub>2</sub>.

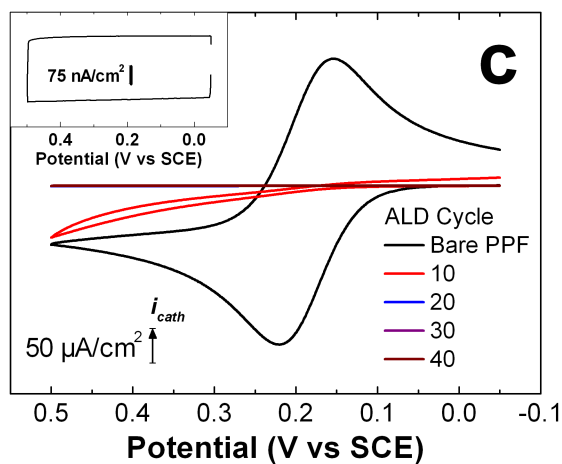
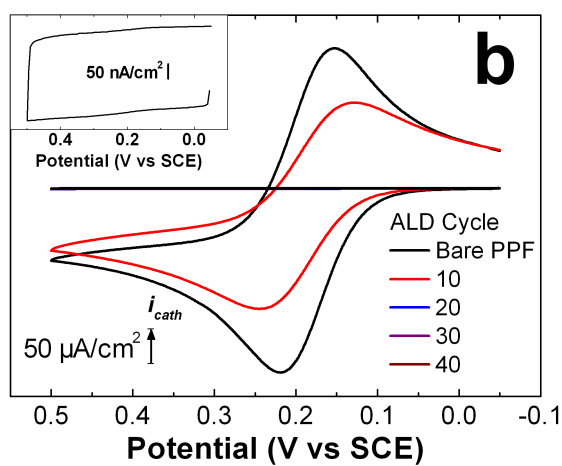
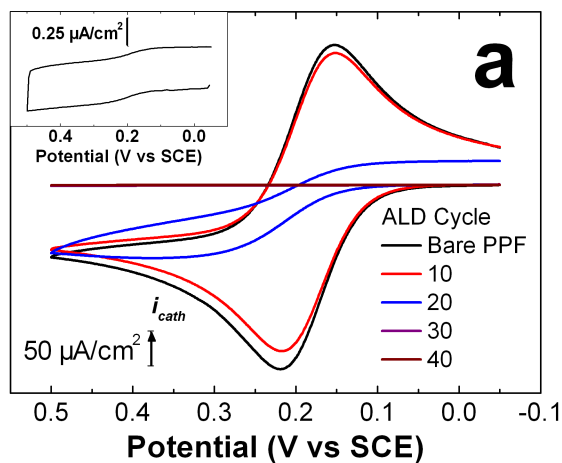


**Figure S3.** (a) The electrochemical response of the electrode used to obtain the data in Figure 3c (main text), but obtained over a larger potential range. The data shown in (b) and (c) are the electrochemical responses of the electrodes used to obtain the data shown in Figures S4c and S5c, respectively, over a larger potential range. The electrodes used to obtain the data in all three frames were prepared using nominally identical conditions. Specifically, the PPF electrodes were pretreated with 30 s of air plasma and then coated with  $\text{Al}_2\text{O}_3$  via ALD. The inset in the three frames is the expanded view for electrodes coated using 40  $\text{Al}_2\text{O}_3$  cycles. The electrolyte aqueous electrolyte solution contained 1.0 mM FcMeOH and 0.10 M  $\text{KNO}_3$ .

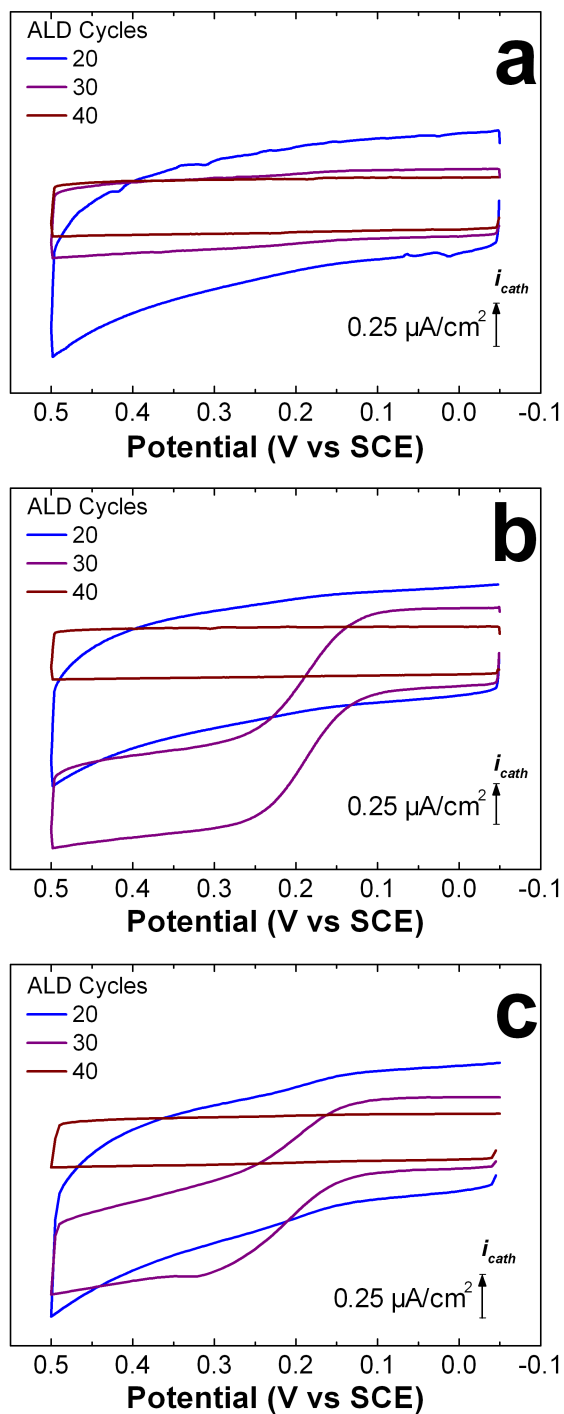


solution contained 1.0 mM FcMeOH and 0.10 M KNO<sub>3</sub>. The scan rate for all CVs was 100 mV/s and the geometric area of the electrodes was 0.0095 cm<sup>2</sup>.

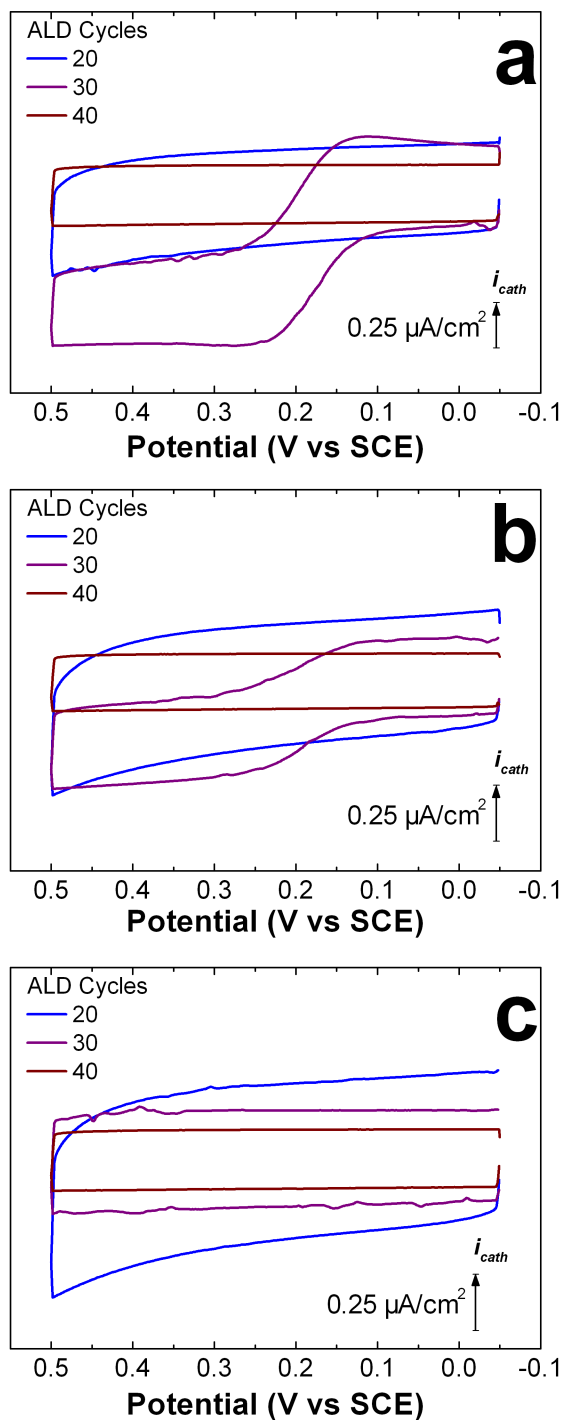
**Figure S4.** Replicate data sets corresponding to Figure 3 in the main text. The Al<sub>2</sub>O<sub>3</sub>-coated PPF electrodes were prepared under nominally identical conditions as those in Figure 3. (a) No plasma pretreatment of the PPF electrodes. The inset is the CV of the electrode modified with 40 Al<sub>2</sub>O<sub>3</sub> cycles. (b) PPF electrodes pretreated with 15 s of plasma and then coated with Al<sub>2</sub>O<sub>3</sub> ALD films. The inset is the CV of the electrode modified with 40 ALD cycles. (c) PPF electrodes pretreated with 30 s of plasma and then coated with Al<sub>2</sub>O<sub>3</sub> ALD films. The inset is the CV of the electrode modified with 40 ALD cycles. The results indicate that the electrochemical properties of Al<sub>2</sub>O<sub>3</sub>-coated PPF electrodes are reproducible (compare to Figure 3 in the main text and Figure S5). The aqueous electrolyte



**Figure S5.** A second set of replicate data corresponding to Figure 3 in the main text and Figure S4. Conditions for each frame in this figure are identical to those of Figure S4.

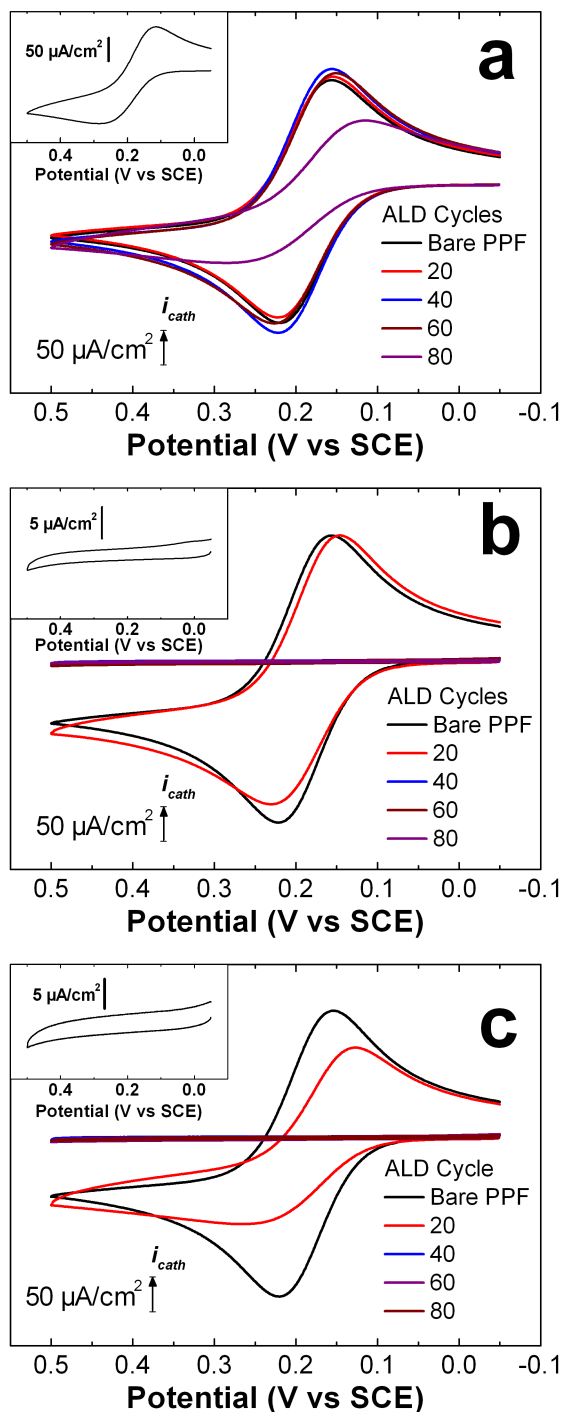


**Figure S6.** The electrochemical response of PPF electrodes pretreated with 15 s of air plasma and coated with the number of  $\text{Al}_2\text{O}_3$  ALD cycles indicated in the legends. Expanded views of the CVs corresponding to those shown in (a) Figure 3b, (b) Figure S4b, and (c) Figure S5b. The aqueous electrolyte solution contained 1.0 mM FcMeOH and 0.10 M  $\text{KNO}_3$ . The scan rate for all CVs was 100 mV/s and the geometric area of the electrodes was 0.0095  $\text{cm}^2$ .



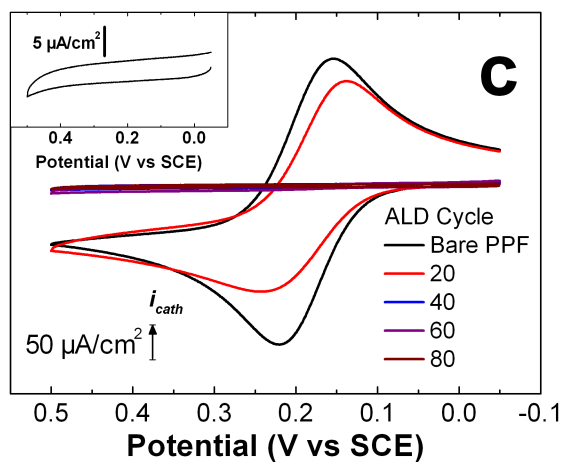
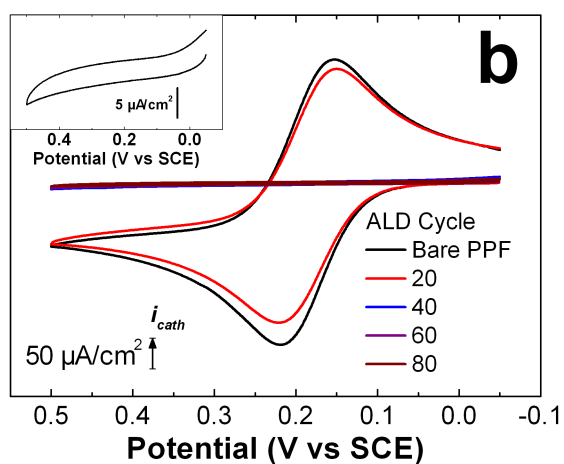
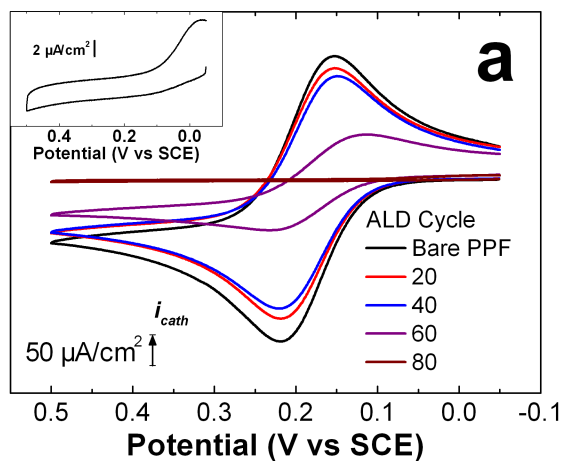
**Figure S7.** The electrochemical response of PPF electrodes pretreated with 30 s of air plasma and subject to the number of  $\text{Al}_2\text{O}_3$  ALD cycles indicated in the legends. Expanded views of the CVs corresponding those shown in (a) Figure 3c, (b) Figure S4c, and (c) Figure S5c. The aqueous electrolyte solution contained 1.0 mM FcMeOH and 0.10 M  $\text{KNO}_3$ . The scan rate for all CVs was 100 mV/s and the geometric area of the electrodes was  $0.0095 \text{ cm}^2$ .



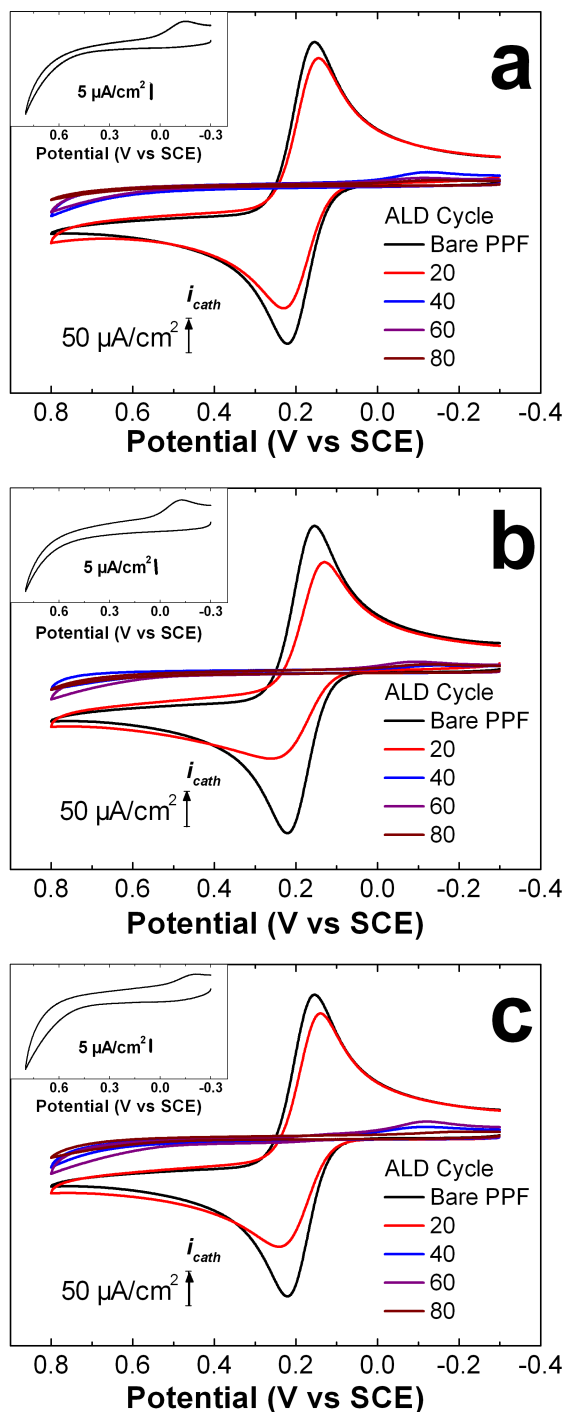


The aqueous electrolyte solution contained 1.0 mM FcMeOH and 0.10 M KNO<sub>3</sub>. The scan rate for all CVs was 100 mV/s and the geometric area of the electrode was 0.0095 cm<sup>2</sup>.

**Figure S8.** Replicate data sets corresponding to Figure 4 in the main text. The SnO<sub>2</sub>-coated PPF electrodes were prepared under nominally identical conditions as those in Figure 4. (a) No plasma pretreatment of the PPF electrode. The inset shows an expanded view of the CV generated using the electrode coated using 80 SnO<sub>2</sub> ALD cycles. (b) Same as (a), but the PPF electrodes were treated with 15 s of air plasma prior to coating with SnO<sub>2</sub>. The inset shows an expanded view of the CV generated using the electrode coated using 80 SnO<sub>2</sub> ALD cycles. (c) Same as (b), but the PPF electrodes were treated with 30 s of air plasma. The results indicate that the electrochemical properties of SnO<sub>2</sub>-coated PPF electrodes are reproducible (compare to Figure 4 in the main text and Figure S9). The

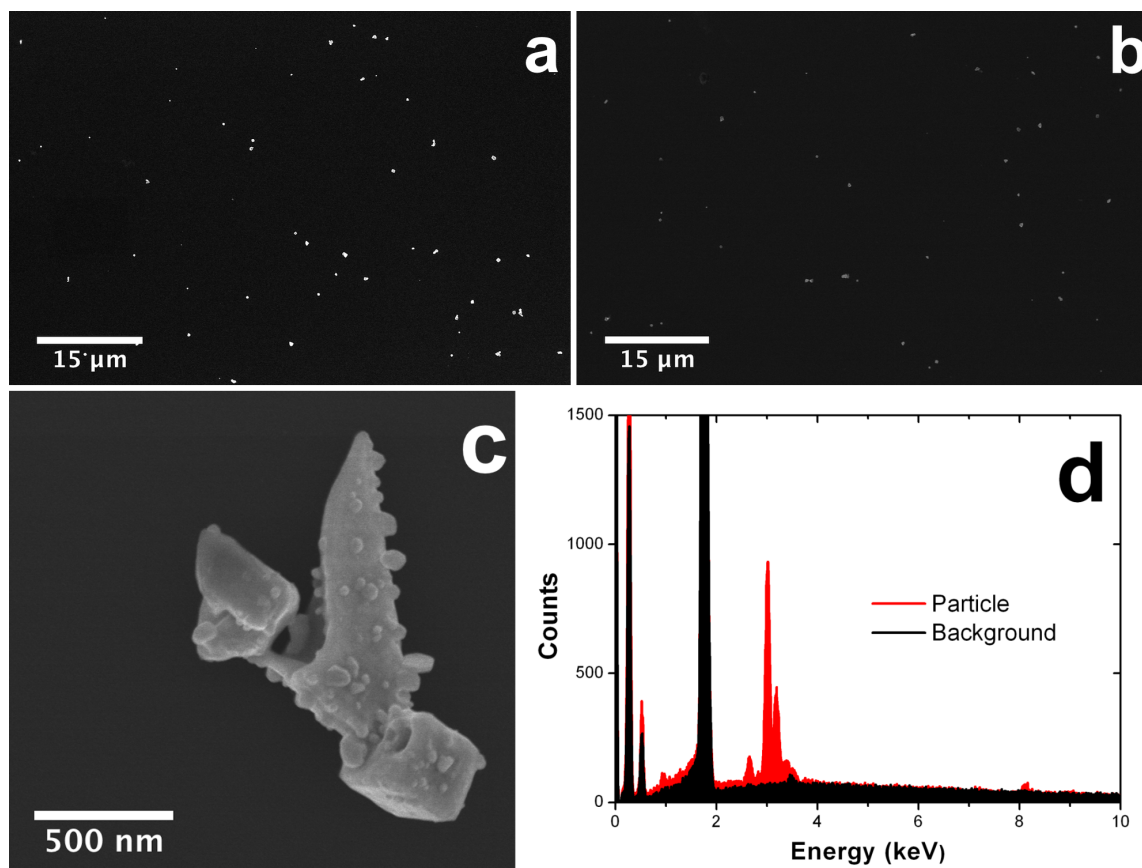


**Figure S9.** A second set of replicate data corresponding to Figure 4 in the main text and Figure S8. Conditions for each frame in this figure are identical to those of Figure S8.

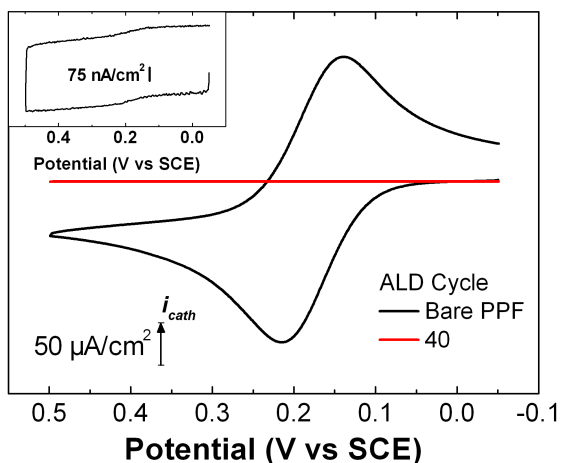


**Figure S10.** (a) The electrochemical response of the electrode from Figure 4c in the main text over a larger potential range. The electrodes from both (b) and (c) are the electrochemical response of the electrodes from Figures S6c and S7c over a larger potential range, respectively. The electrodes for the (a), (b), and (c) data sets were prepared under nominally identical conditions. These PPF electrodes were pretreated with 30 s of plasma and coated with  $\text{SnO}_2$  via ALD. The insets are the expanded view of CVs obtained after 80  $\text{SnO}_2$  cycles. The solution was 1.0 mM FcMeOH in a 0.10 M  $\text{KNO}_3$  electrolyte solution. For the electrodes with 40, 60, and 80 cycles of  $\text{SnO}_2$  there is a small cathodic peak varying in potential from -0.11 to -0.15 V (vs SCE) possibly due to FcMeOH

reduction. We attribute this to the semiconductor behavior of the  $\text{SnO}_2$  ALD films. Similar behavior has been previously shown for semiconducting metal oxide electrodes with tested to redox probes in solution.<sup>7</sup>

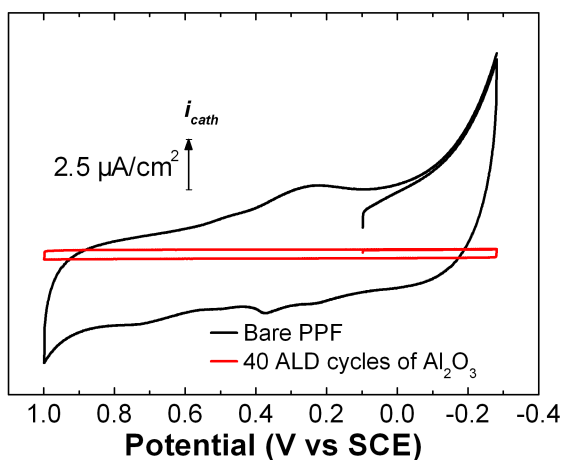


**Figure S11.** Representative SEM images and EDS of Ag electrodeposited onto PPF substrates modified using 20 ALD cycles of  $\text{SnO}_2$ . Ag was electrodeposited from a solution containing 0.50 mM  $\text{AgNO}_3$  and 0.10 M  $\text{KNO}_3$ . The electrodeposition was carried out at  $-0.25$  V vs. MSE for 50 s. (a) An SEM micrograph obtained from a PPF electrode that had been treated with air plasma for 15 s prior to  $\text{SnO}_2$  ALD. (b) Same as (a) except the PPF electrode was treated with plasma for 30 s. (c) A representative high-magnification image of a single Ag island. (d) The red EDS spectrum was obtained from the center of the particle in (c), and the black spectrum was obtained from a nearby dark section of the surface. The peaks at 0.27, 0.52, and 1.73 keV, present in the spectra for both the background and the particle, are assigned to the C, O, and Si bands of the substrate, respectively. The group of peaks beginning at 3.01 keV is assigned to Ag.<sup>8</sup>



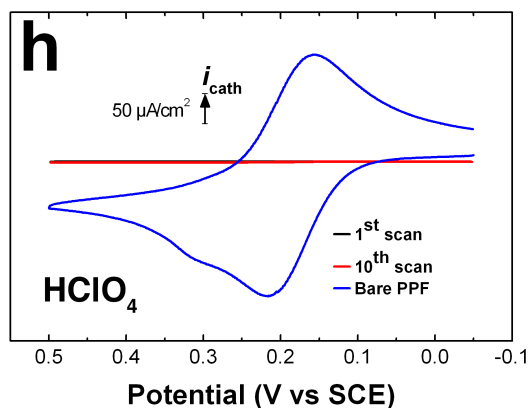
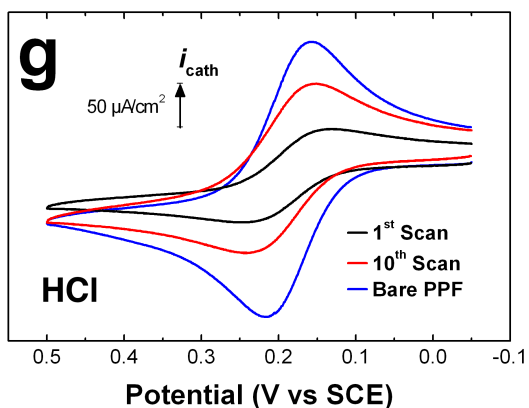
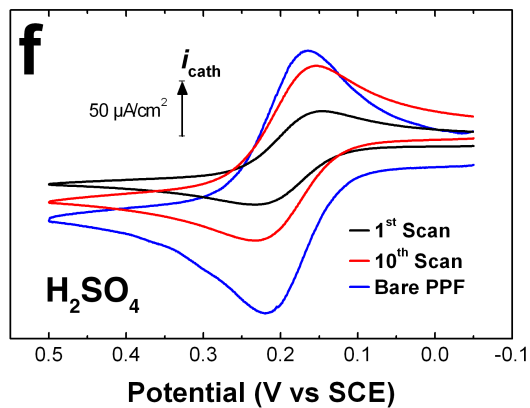
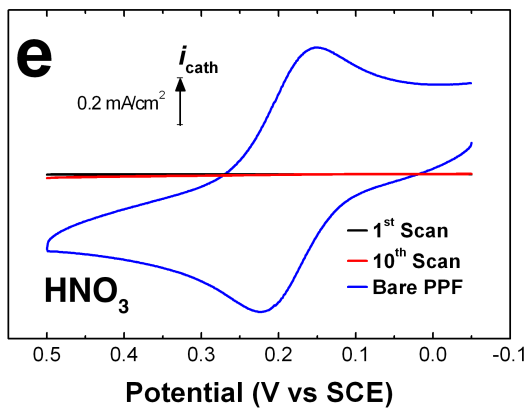
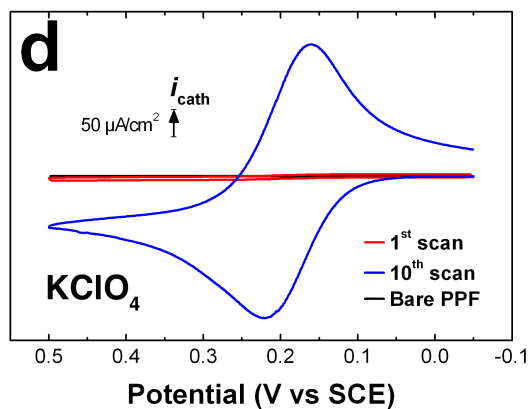
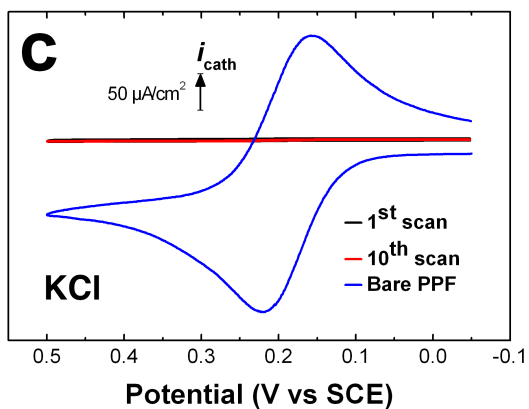
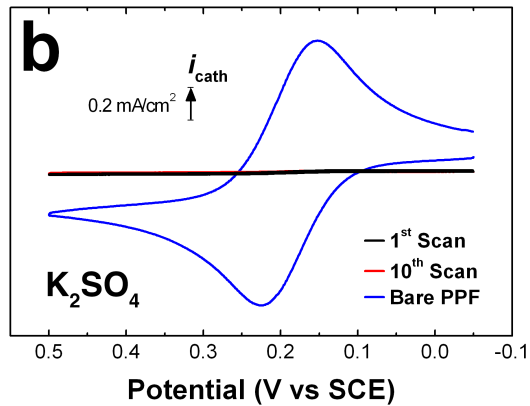
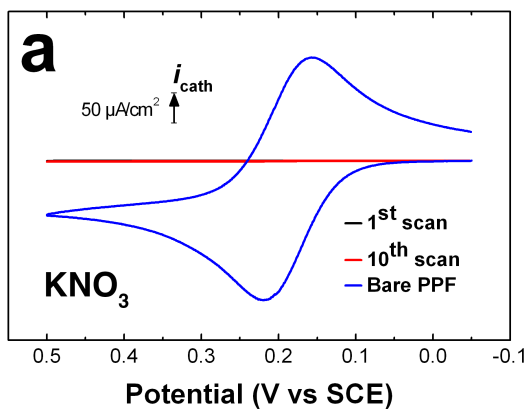
**Figure S12.** CVs obtained using a bare PPF electrode (black) and a PPF electrode pretreated with 30 s of plasma and 40 ALD cycles of  $\text{Al}_2\text{O}_3$  (red). The aqueous electrolyte solution contained 1.0 mM FcMeOH and 0.10 M  $\text{HClO}_4$ . The inset is an expanded view of the ALD-coated

electrode. The CVs correspond to the 17<sup>th</sup> voltammetric scan. The data were collected using an  $\text{Hg}/\text{HgSO}_4$  reference electrode (MSE, 0.64 V vs. NHE), but the potential scale has been corrected to SCE for consistency. The scan rate was 100 mV/s and the geometric area of the electrode was  $0.124 \text{ cm}^2$ .

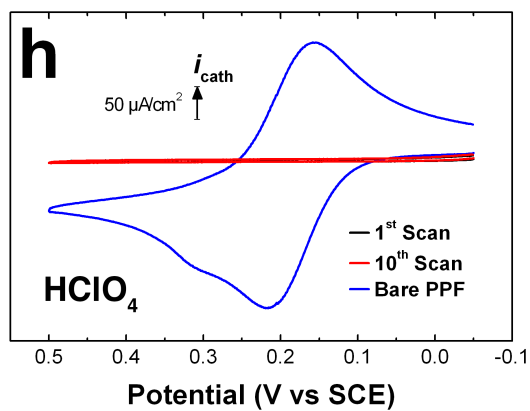
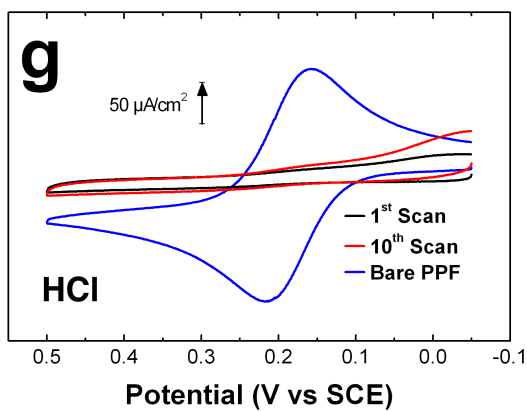
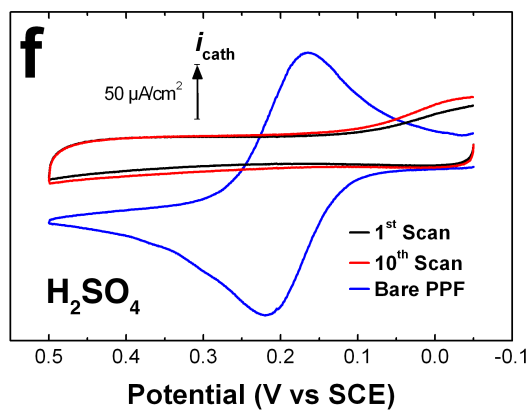
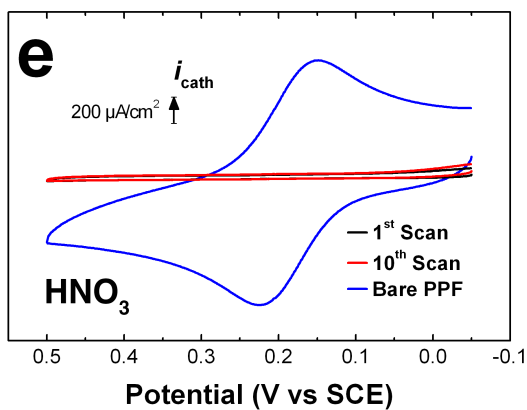
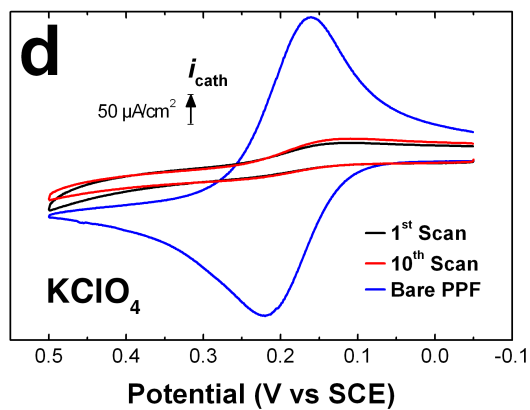
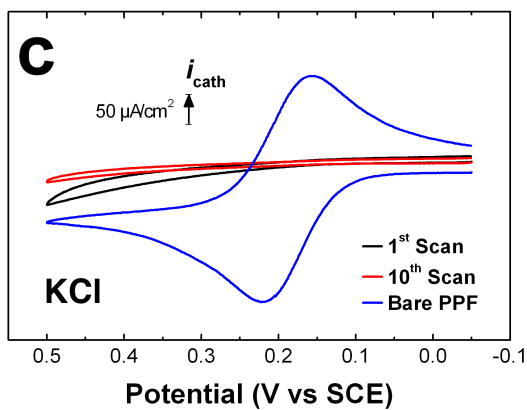
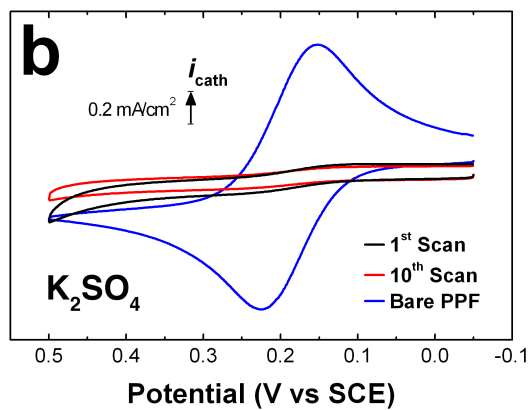
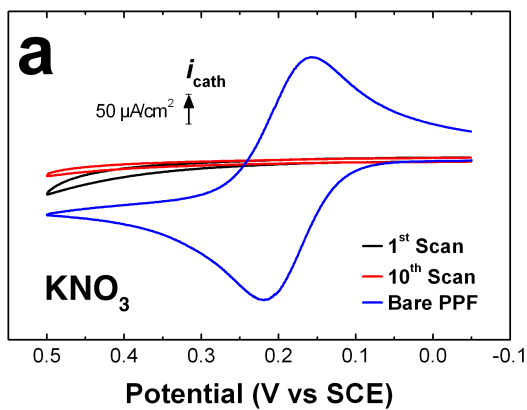


**Figure S13.** CVs obtained using a bare PPF electrode (black) and a PPF electrode pretreated with 30 s of plasma and 40 ALD cycles of  $\text{Al}_2\text{O}_3$  (red). The aqueous electrolyte solution contained only Ar-purged 0.10 M  $\text{HClO}_4$ . The CVs correspond to the 17<sup>th</sup> voltammetric scan. The

data were collected using a MSE reference electrode, but the potential scale has been corrected to SCE for consistency. The bare PPF electrode exhibits a large capacitive current relative to the ALD-treated electrode.<sup>9</sup> The scan rate was 100 mV/s and the geometric area of the electrode was  $0.124 \text{ cm}^2$ .



**Figure S14.** To determine the scope of the stability of the  $\text{Al}_2\text{O}_3$  ALD layers in the electrochemical environment, CVs were obtained in the 8 electrolytes indicated in the figure. The working electrodes were oxidized PPF (15 s air plasma) coated with 30 ALD cycles of  $\text{Al}_2\text{O}_3$ . A CV obtained using a bare PPF electrode is shown for comparison for each electrolyte solution. The redox probe was 1.0 mM FcMeOH and the concentration of the electrolyte was 0.10 M in all cases. The first scan was initiated immediately after the working electrode was introduced to solution. Each subsequent CV (2-10) was taken at 120 s intervals. By the 10<sup>th</sup> scan the working electrode had been exposed to solution for ~20 min. The reference electrode was an SCE, the counter electrode was a Pt wire, and the scan rate was 100 mV/s.





**Figure S15.** To determine the scope of the stability of the SnO<sub>2</sub> ALD layers in the electrochemical environment, CVs were obtained in the 8 electrolytes indicated in the figure. The working electrodes were oxidized PPF (15 s air plasma) coated with 100 ALD cycles of SnO<sub>2</sub>. A CV obtained using a bare PPF electrode is shown for comparison for each electrolyte solution. The redox probe was 1.0 mM FcMeOH and the concentration of the electrolyte was 0.10 M in all cases. The first scan was initiated immediately after the working electrode was introduced to solution. Each subsequent CV (2-10) was taken at 120 s intervals. By the 10<sup>th</sup> scan the working electrode had been exposed to solution for ~20 min. The reference electrode was an SCE, the counter electrode was a Pt wire, and the scan rate was 100 mV/s. It is important to note that the current density scale used for K<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> is higher than the others because these solutions consistently leaked under the silicone gasket that was used to define the electrode area, thereby increasing the effective geometric area exposed to the solution.

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