Electrodeposited Co_3O_4, $Co(OH)_2$, and CoOOH for Catalysis of the Oxygen Evolution Reaction

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We are interested in electrodepositing oxides and hydroxides of cobalt that are active catalysts for the oxygen evolution reaction (OER). We are particularly interested in depositing *crystalline* materials with well-characterized structures. Here, we present results on the electrodeposition of Co_3O_4 and $Co(OH)_2$. Because $Co(OH)_2$ can be electrochemically converted to CoOOH, and thermally converted to CoO and Co_3O_4, the material gives us the opportunity to directly compare the catalytic activity of several oxides, hydroxides, and oxyhydroxides. We are also able to deposit epitaxial films of these materials, so it may be possible to compare the catalytic activities of various surfaces of the materials. We further show that epitaxial films of $Co(OH)_2$ on Au can be converted to epitaxial films of CoOOH and Co_3O_4. The catalytic activity of these materials will be compared in this talk.

We have recently reported on the electrodeposition and OER activity of Co_3O_4.[1] The films were deposited by electrochemically oxidizing a tartrate complex of Co(II) in alkaline solution at reflux temperatures. The crystalline films deposit with the normal spinel structure with a lattice parameter of 0.8097 nm and a crystallite size of 26 nm.

In order to electrodeposit $Co(OH)_2$ films, we exploit the well-known coordination chemistry that Co(III) favors nitrogen ligands over oxygen ligands, whereas Co(II) favors oxygen ligands over nitrogen ligands. $[Co(en)_3]^{3+}$ is nearly 35 orders of magnitude more stable than $[Co(en)_3]^{2+}$(en = ethylenediamine). The formation constants for $[Co(en)_3]^{3+}$ and $[Co(en)_3]^{2+}$ are $10^{48.69}$ and $10^{13.94}$, respectively. Co(III) complexes are also substitutionally inert, whereas Co(II) complexes are substitutionally labile in aqueous solution. Hence, $[Co(en)_3]^{3+}$ is stable in an alkaline solution, but $[Co(en)_3]^{2+}$reacts with excess OH^- to produce $Co(OH)_2$. The formation constant of $Co(OH)_2$ is $10^{14.96}$. The $Co(OH)_2$ films were deposited according to equations 1 and 2. Films were deposited at room temperature at a potential of -1 V vs. Ag/AgCl in a solution of 45 mM $[Co(en)_3]^{3+}$ in 2 M NaOH.[2]

$$[Co(en)_3]^{3+} + e^- \leftrightarrows [Co(en)_3]^{2+} \qquad (1)$$
$$[Co(en)_3]^{2+} + 2OH^- \rightarrow Co(OH)_2\downarrow + 3en \qquad (2)$$

The $Co(OH)_2$ deposits with a dense microcone morphology (Fig. 1). It deposits with the brucite layered structure with measured lattice parameters of a = b = 0.3179 nm and c = 0.4658 nm in P-3m1 symmetry.

Electrodeposited $Co(OH)_2$ is a potent catalyst for the OER. Linear sweep voltammograms (LSVs) at a scan rate of 1 mVs^{-1} on a Ti electrode (blue) and a $Co(OH)_2$-coated Ti electrode (red) in unstirred 1 M KOH at room temperature are shown in Fig. 2. The LSV measured on electrodeposited, crystalline Co_3O_4 film, which is an active OER catalyst, is also shown (black) because the surface chemistry of both materials during OER is similar. The onset of OER on $Co(OH)_2$ is 0.51 $V_{Ag/AgCl}$ which is about 50 mV higher than that measured on Co_3O_4. However, current densities, based on the geometry of the electrodes, are much higher on the $Co(OH)_2$ film at more positive potentials.

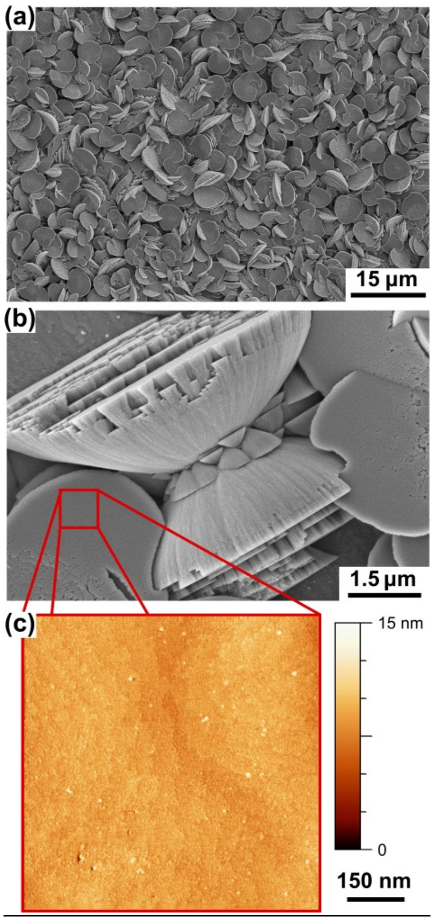

Figure 1. Morphology of electrodeposited $Co(OH)_2$ to a charge density of 0.6 Ccm^{-2}. (a) and (b) SEM images of the film. (c) AFM image of a flat disk surface.

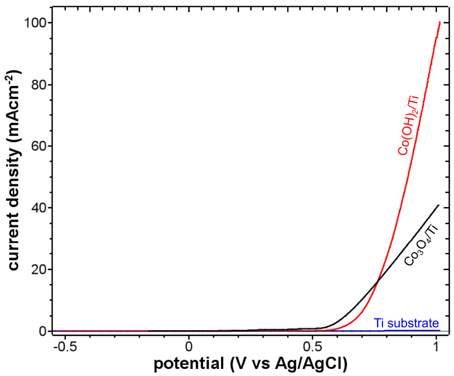

Figure 2. LSVs measured at 1 mVs^{-1} scan rate in 1 M KOH at electrodeposited $Co(OH)_2$ (red), crystalline Co_3O_4 (black) and uncoated Ti substrate (blue).

References

1. J. A. Koza, Z. He, A. S. Miller, and J. A. Switzer, "Electrodeposition of crystalline Co_3O_4 – A catalyst for the oxygen evolution reaction," *Chem. Mater.* **24**, 3567 (2012).
2. J. A. Koza, C. M. Hull, Y.-C. Liu, and J. A. Switzer, "Deposition of β-$Co(OH)_2$ films by electrochemical reduction of tris(ethylenediamine)cobalt(III) in alkaline solution," *Chem. Mater.* **25**, 1922 (2013).

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