

Electrodeposition of $\text{Co}(\text{OH})_2$ thin films for catalysis of the oxygen evolution reaction in alkaline solution

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We introduce a new method to electrodeposit $\text{Co}(\text{OH})_2$ films. Several other groups have shown that $\text{Co}(\text{OH})_2$ can be deposited using OH^- that is produced by reducing nitrate ions (1,2). The electrodeposited OH^- reacts with $\text{Co}(\text{II})$ in solution to produce $\text{Co}(\text{OH})_2$. In our electrochemical/chemical deposition scheme, $[\text{Co}(\text{en})_3]^{3+}$ (en = ethylenediamine) is electrochemically reduced in alkaline solution (pH ~ 14) to directly deposit crystalline $\text{Co}(\text{OH})_2$. We exploit the fact that the formation constants for $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{en})_3]^{2+}$ are $10^{48.69}$ and $10^{13.94}$, respectively. $[\text{Co}(\text{en})_3]^{3+}$ is nearly 35 orders of magnitude more stable than $[\text{Co}(\text{en})_3]^{2+}$. The $[\text{Co}(\text{en})_3]^{3+}$ is stable in alkaline solution, but the $[\text{Co}(\text{en})_3]^{2+}$ reacts with OH^- to produce $\text{Co}(\text{OH})_2$, as shown in equations 1 and 2 below.

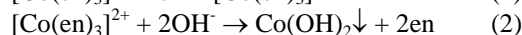
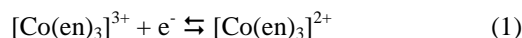


Fig. 1 shows a cyclic voltammogram at 5 mV/s and the corresponding Au-EQCM response in the deposition solution, which consists of 45 mM $[\text{Co}(\text{en})_3]^{3+}$ and 2 M NaOH at room temperature. The $\text{Co}(\text{OH})_2$ deposition occurs in the potential range of about -0.5 to -1.1 V vs. Ag/AgCl. At more negative potentials, Co is produced. The dashed line in Fig. 1 is of a pre-deposited $\text{Co}(\text{OH})_2$ in the 2 M NaOH solution. Fig. 2 shows the x-ray diffraction pattern of a film deposited onto a Ti electrode at -1.0 V at room temperature. The highly-crystalline film grows with a preferred (001) orientation. The morphologies of a thin film deposited for 15 min and a thicker film deposited for 1 hour are shown in Fig. 3. We are interested in using the electrodeposited $\text{Co}(\text{OH})_2$ as a catalyst for the oxygen evolution reaction (3,4). Linear sweep voltammograms at 1 mV/s of a Ti electrode and a $\text{Co}(\text{OH})_2$ -coated Ti electrode in unstirred 1 M KOH are shown in Fig. 4. The electrodeposited $\text{Co}(\text{OH})_2$ has essentially the same activity as the Co_3O_4 which we previously electrodeposited (4). $\text{Co}(\text{OH})_2$ has the advantages that it is deposited at room temperature instead of refluxing solution, and the pink $\text{Co}(\text{OH})_2$ films do not absorb light as strongly as the black Co_3O_4 films. Both of these advantages could be important if the material is used as an OER catalyst on n-type semiconductors in photoelectrochemical cells. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant DE-FG02-08ER46518.

References

1. W.-J. Zhou, J. Zhang, T. Xue, D.-D. Zhao, and H. L. Li, *J. Mater. Chem.* **18**, 905 (2008).
2. M. S. Yarger, E. M. P. Steinmiller, and K.-S. Choi, *Chem. Commun.* 159 (2007).
3. M. W. Kanan and D. G. Nocera, *Science* **321**, 1072 (2008).
4. J. A. Koza, Z. He, A. S. Miller, and J. A. Switzer, *Chem. Mater.* **24**, 3567 (2012).

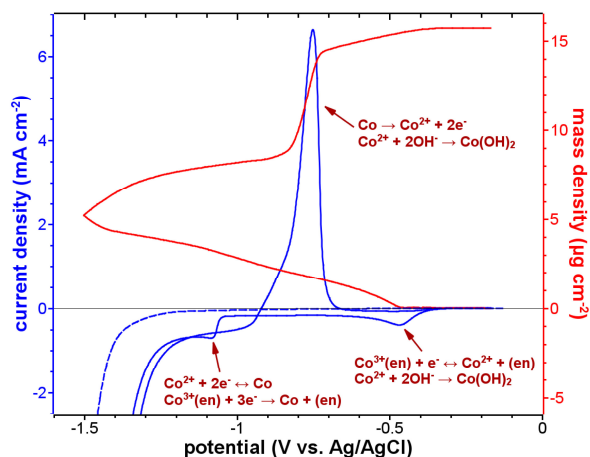


Fig 1. Cyclic voltammogram and EQCM at 5mV/s of a Au electrode in a solution of 45 mM $[\text{Co}(\text{en})_3]^{3+}$ in 2 M NaOH at room temperature.

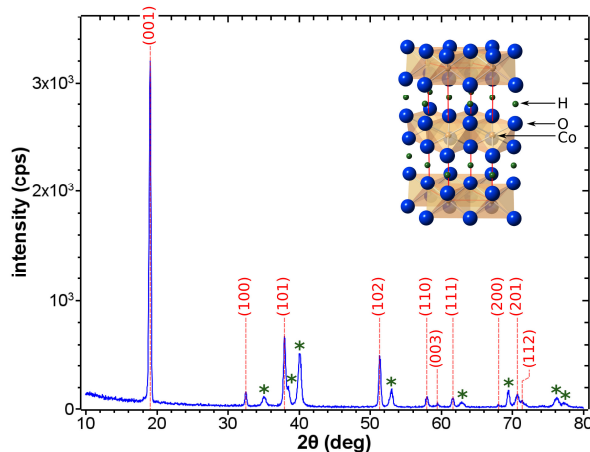


Fig. 2. XRD of electrodeposited $\text{Co}(\text{OH})_2$ on Ti.

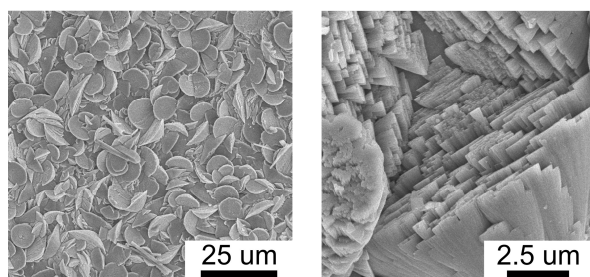


Fig. 3. SEM of thin (left) and thick (right) $\text{Co}(\text{OH})_2$ films.

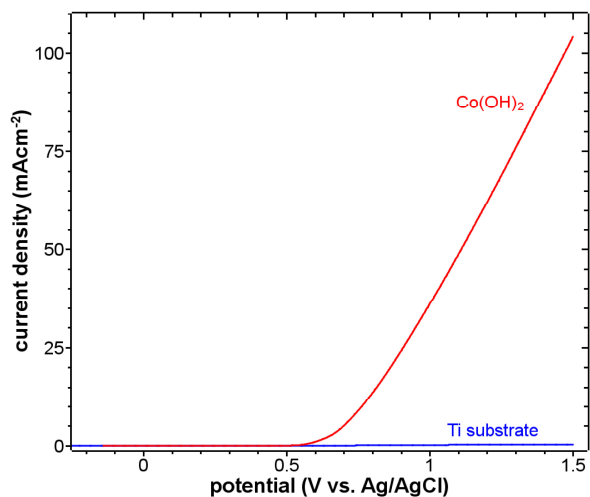


Fig. 4. Linear sweep voltammograms of a Ti electrode and a $\text{Co}(\text{OH})_2$ /Ti electrode in 1 M KOH (1 mV/s). The OER reaction is greatly enhanced when the Ti is coated with $\text{Co}(\text{OH})_2$. The Tafel slope was 39 mV/decade.