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Synthesis and Evaluation of Nanostructured CoP Films as Bifunctional Electrocatalysts for Water Electrolysis

Maria Kelly, Julian A. Vigil, Timothy N. Lambert*

Department of Materials, Devices, and Energy Technologies
Sandia National Laboratories, P.O. Box 5800, MS 0734, Albuquerque, New Mexico 87185, USA.
*E-mail: tnlambe@sandia.gov

Introduction & Background

Efficient water splitting requires the use of catalysts to perform the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode. Renewable energy technologies such as electrolyzers, and also reversible fuel cells and solar fuel cells, could benefit from the identification of a single catalysts that can perform both the HER and the OER.

Water electrolysis, or water splitting, consists of two half-reactions: the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER).

HER $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$
OER $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$
OVERALL $2H_2O \longrightarrow 2H_2 + O_2$

Both the HER and the OER contribute to the overall efficiency of water electrolysis. While the thermodynamic potential difference between the HER and the OER is 1.23 V, high overpotentials are typically required due to inherently slow reaction kinetics as a result of electrical, transport, and electrochemical reaction resistances.[1]

Platinum group metals are known to be active and generally stable electrocatalysts, but their high cost and rarity limit their practicality in next-generation devices. Ru- and Ir-based catalysts are best for catalyzing the OER, while Pt-based catalysts are best for the HER. However, none of these metals are highly active for both of these reactions.

Emergent electrocatalysts intended to replace expensive platinum group metals are being assessed by the following criteria:

- overpotential
- bifunctionality
- mass activity
- stability

As a transition metal phosphide, CoP has been studied and identified as a highly active HER catalyst. However, its OER activity is not well documented and the first and only report of HER-OER bifunctionality for a cobalt phosphide was reported only recently.[2]

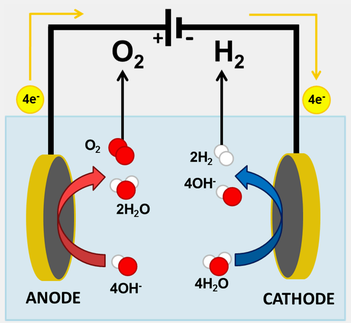

Figure 1 A schematic of an electrolyzer in basic conditions.

Herein we report on the preparation of high surface area, nanostructured CoP films prepared using a three-step electrodeposition-thermal annealing-phosphidation process. Films were synthesized on three different substrates to examine the effect of substrate on electrochemical activity. Electrochemical water splitting was then evaluated under low and high pH conditions using a rotating disk electrode apparatus. As a demonstration of their bifunctional nature, alkaline water electrolysis with CoP electrocatalysts at both the anode and cathode was demonstrated.

This versatile approach to CoP films has provided a simple way of preparing a new HER-OER bifunctional catalyst with high activity and an added insight of substrate selection for this class of materials.

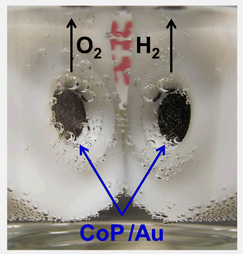

Figure 2 Image of electrolysis cell assembly using CoP/Au for both oxygen and hydrogen evolution electrodes.

CoP Film Synthesis and Characterization

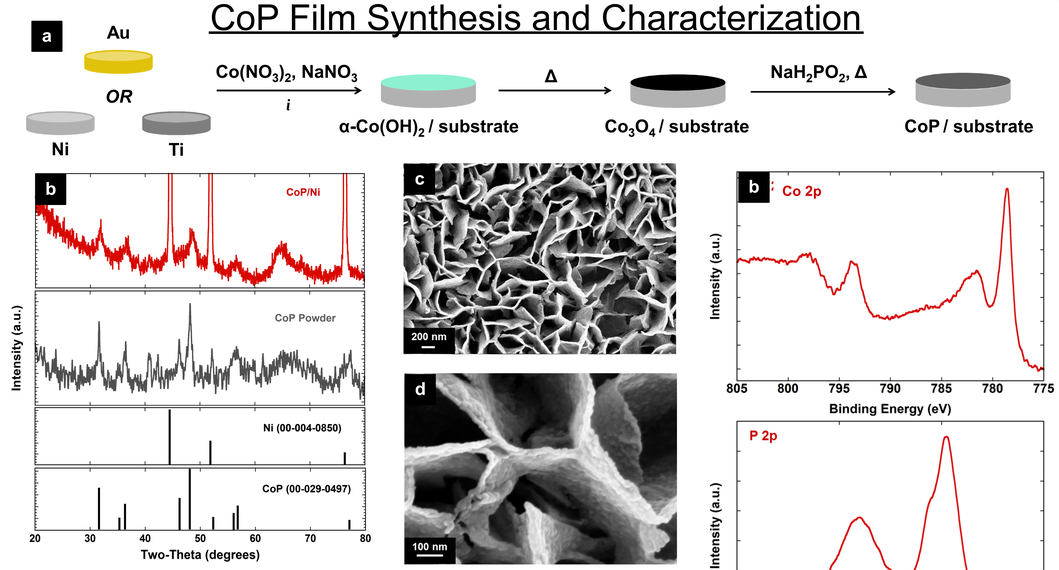

Figure 3 (a) Reaction schematic of electrodeposition-thermal annealing-phosphidation on Ni, Ti, and Au foil substrates; **(b)** XRD spectra of CoP/Ni and CoP powder indexed to Ni (PDF #004-0850) and CoP (PDF #029-0497); **(c),(d)** SEM images of CoP/Ni; **(e)** XPS spectra of CoP/Ni, in the Co 2p (top) and P 2p (bottom) regions.

CoP Film Electrocatalytic Results

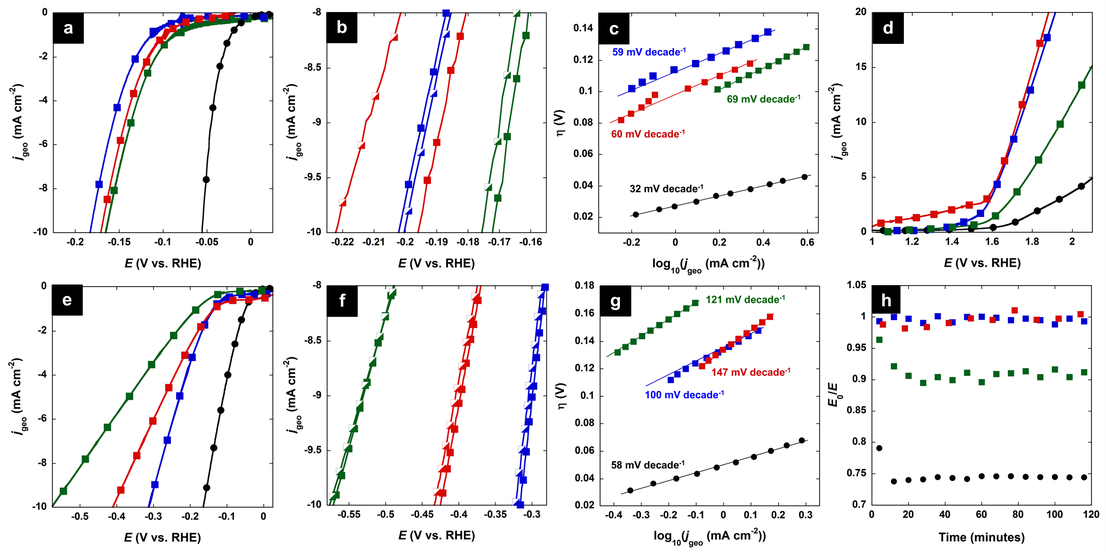

Figure 4 (a)-(c) HER experiments done in 0.5 M H_2SO_4, **(e)-(g)** HER experiments done in 0.1 M KOH, **(d),(h)** OER experiments done in 0.1 M KOH. **(a,e)** RDV scans of CoP/Ni (red, filled squares), CoP/Ti (green, filled squares), CoP/Au (blue, filled squares), and 20% Pt/C (black, filled circles); **(b,f)** RDV Stability of CoP/Ni, CoP/Ti, and CoP/Au, cycle 1 (filled squares) vs. cycle 100 (half-open squares); **(c,g)** Tafel plot and slopes of CoP/Ni, CoP/Ti, CoP/Au, and 20% Pt/C; **(d)** RDV scans of CoP/Ni, CoP/Ti, CoP/Au, and 20% Pt/C; **(h)** Galvanostatic stability of CoP/Ni, CoP/Ti, CoP/Au, and 20% Pt/C at j_{geo} = 10 mA cm^{-2} for 2 hours.

Discussion & Conclusion

Here we have reported the synthesis of nanostructured, high surface area CoP films on several conductive substrates. In summary:

- CoP films were synthesized via an electrodeposition-thermal annealing-phosphidation process. The resulting films exhibited highly textured nanostructured features.
- The CoP films performed well as electrocatalysts for the HER, in both acidic (η = 0.165 – 0.183 V @ -10 mA cm^{-2}) and alkaline (η = 0.196 – 0.577 V @ -10 mA cm^{-2}) electrolyte, and OER in alkaline electrolyte (η = 0.34 – 0.71 V @ 10 mA cm^{-2}).
- All substrates show excellent stability in 0.5 M H_2SO_4. CoP/Au and CoP/Ti are additionally stable in 0.1 M KOH.

The success of these films augurs for additional development of bifunctional HER-OER electrocatalysts.

Future Work

In addition to alkaline and acidic media, seawater electrolysis has gained attention. Seawater splitting has been shown to be useful for H_2 production and capturing carbon.[3]

In seawater, the OER presents the additional challenge of Cl_2 evolution at the anode.[4] Thus, the development of a catalyst that selectively evolves O_2 in seawater is one of the most pressing obstacles to seawater electrolysis. Catalysts that facilitate the HER in seawater are also of interest.

Preliminary results indicate that CoP films show electrochemical activity for the HER in seawater. Further study should be completed to determine the O_2 evolution selectivity of CoP films, their catalytic activity, and their stability for the OER and HER in seawater.

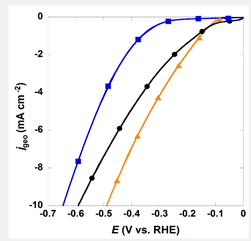

Figure 5 Preliminary HER results. RDV scans of Pt foil (orange triangles), 20% Pt/C (black circles), and CoP/Au (blue squares) in simulated seawater (pH=8.2).

References

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