

Well-Defined NiFeAlO₄ Inverse Spinel as Efficient Alkaline Water Oxidation Catalyst

Jamie Chen, Shannon Stahl

Department of Chemistry,

University of Wisconsin - Madison, Madison, WI 53706

Alexey Serov, Plamen Atanasov

Department of Chemical and Nuclear Engineering and

Center for Emerging Energy Technologies,

University of New Mexico, Albuquerque, NM 87131

Photoelectrochemical (PEC) cells that convert solar energy into chemical fuels are an important component of energy policy and research efforts to reduce worldwide dependence on fossil fuels. Various chemical fuels that can be produced in such cells include hydrogen, methanol and formic acid, but all require a complementary anodic half-reaction to supply the necessary electrons and protons. Oxidation of water to O₂ is the ideal anodic reaction, but is currently limited by catalyst efficiency and cost. Our group has observed that the incorporation of redox-inert metals, particularly Al, into redox-active metal oxides often enhanced the oxygen evolution activity (OER), with Ni-Fe-Al admixtures showing the highest activity.¹ This result prompted us to examine the activity of well-defined oxides composed of Ni-Fe-Al and led us to identify the ternary inverse spinel NiFeAlO₄. Structural characterization of this oxide indicated that Al has substituted for the Fe-sites of NiFe₂O₄, which is also a known OER catalyst.² In an effort to elucidate the role of Al, we proceeded to investigate the activity of NiFeAlO₄ against compositionally and structurally relevant oxides (NiO, NiFe 9:1, NiFe₂O₄, NiAl₂O₄), including known catalysts (NiO,³ NiFe 9:1,⁴ NiFe₂O₄²), and established NiFeAlO₄ as superior electrocatalyst with high intrinsic activity (Fig. 1).

All oxide catalysts examined in this work were prepared with initial nitrate combustion followed by calcination. Appropriate ratio of 1 M aqueous metal nitrate solutions were mixed, followed by the addition of glycine (0.5 M), and combustion was allowed to take place on a hot plate. Post-combustion materials were subsequently calcined at 1100°C for 1 hour. The resulting oxide powders were prepared as conductive inks by mixing with acetylene black and 0.5 wt% Nafion, and deposited onto a glassy carbon rotating disk electrode.

The oxides were characterized by BET, SEM, XRD, and XAS. BET measured surface areas were low, which correlated well with the large particle size as indicated by SEM images. XRD patterns matched that of the expected oxide phases, which were further confirmed by XAS analysis. The evaluation of oxygen evolution activity was performed in a standard three-component electrochemical cell in 0.1 M NaOH electrolyte. Catalytic activity was examined via cyclic voltammetry and steady-state Tafel analysis (Fig. 1). Notably, the E_{1/2} of Ni(II)/Ni(III) is clearly related to the bulk structure of the oxide material, where the oxidation of Ni(II) neighboring M(III) requires more anodic potential. Additionally, the observation that neither of the bimetallic spinels oxides outperformed NiFeAlO₄ suggested that a unique synergistic effect exist between all three metal sites.

Another challenge in realizing an efficient PEC is the integration of catalysts with the working electrodes. Most commonly carbon-based conductive materials are added

to inks containing metal oxide catalysts, however, these systems tend to suffer from carbon degradation due to the highly alkaline and oxidizing conditions. More recently, nano-ITO powder has begun to receive attention as an alternative to carbon-based conductive additives.⁵ This study also provided an assessment of OER activity and system stability of NiFeAlO₄ using both carbon and metal oxide based conductive additives.

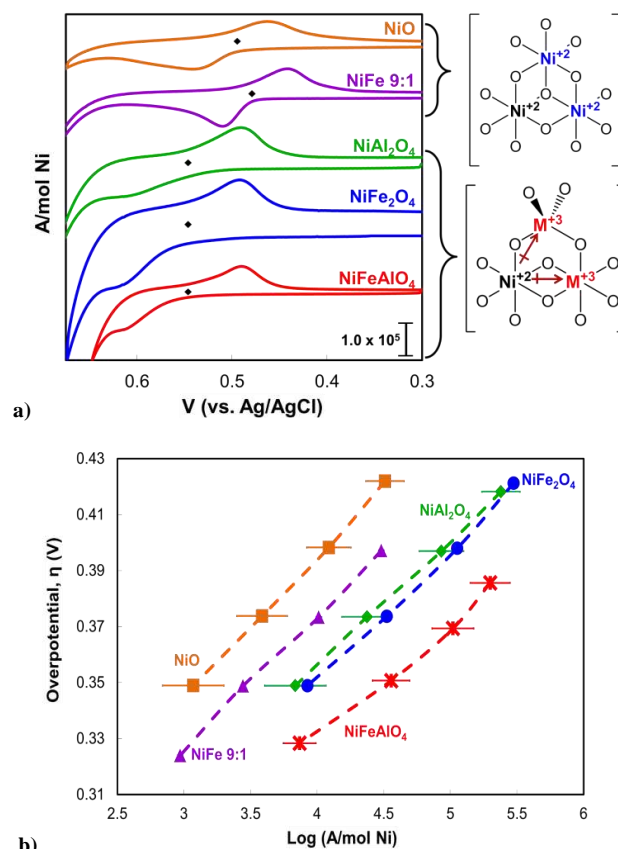


Figure 1. a) Cyclic voltammograms, of oxides recorded at the end of Tafel experiments. Black diamonds indicate the E_{1/2} of the Ni(II)/Ni(III). Representations on the right correspond to the bulk structure of the individual oxide. b) Steady-state Tafel plot of the oxides in the low current density linear regime, where NiFeAlO₄ clearly outperforms other compositionally and structurally relevant oxide catalysts. Dotted lines are there to guide the eyes only

Acknowledgement: This project is a collaborative effort between UW-Madison and UNM. Research done at UW-Madison is supported by the NSF under CCI Powering the Planet grant CHE-0802907. Research performed at UNM is supported by DOE-EPSCoR Implementation Award: Materials for Energy Conversion.

References:

1. J. B. Gerken, J. Y. C. Chen, R. C. Massé, A. B. Powell, S. S. Stahl, *Angew. Chem. Int. Ed.* 51 (2012), 6676-6680
2. C. Iwakura, M. Nishioka, H. Tamura, *Nippon Kagaku Kaishi* 7 (1982), 1136-1140.; N. K. Singh, R. N. Singh, *Indian J. Chem., Sect A* 38 (1999), 491-495.; J. R. Scheffe, J. Li, A. W. Weimer, *Int. J. Hydrogen Energy* 35 (2010), 3333-3340.
3. Y. W. D. Chen, R. N. Noufi, *J. Electrochem. Soc.* 131 (1984), 1447-1451.; M. Dinca, Y. Surendranath, D. G. Nocera, *Proc. Nat. Acad. Sci. USA* 107 (2010), 10337-10341.
4. D. A. Corrigan, *J. Electrochem. Soc.* 134 (1987), 377-384.; J. Landon, E. Demeter, N. İnoğlu, C. Keturakis, I. E. Wachs, R. Vasić, A. I. Frenkel, J. R. Kitchin, *ACS Catal.* 2 (2012), 1793-1801.; L. Trotochaud, J. K. Ranney, K. N. Williams, S. W. Boettcher, *J. Am. Chem. Soc.* 134 (2012), 17253-17261.
5. P. G. Hoertz, Z. Chen, C. A. Kent, T. J. Meyer, *Inorg. Chem.* 49 (2010), 8179-8181.