Non-noble electrocatalysts for alkaline hydrogen evolution and oxidation

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Intermittent renewable energy from wind and solar power requires cost-effective grid-scale energy storage technologies. Emerging alkaline-exchange-membrane unitized regenerative fuel cell (AEM-URFC) devices may provide scalable energy storage at acceptable costs.[1] When operating in electrolyzer mode, an AEM-URFC stores electricity from the grid by splitting water into hydrogen and oxygen. When energy is needed, the device runs in fuel-cell mode to convert hydrogen and oxygen into electricity and water. Integrating the functionalities of a fuel cell and electrolyzer reduces overall system costs, while the alkaline environment precludes the need for expensive platinum-based catalysts at the oxygen electrode. Increasing the round-trip efficiency and lifetime of AEM-URFCs requires improved catalysts for the hydrogen reaction at the negative electrode. In this work, we utilize a theory-guided approach to develop silver-nickel catalysts for hydrogen evolution and oxidation.

The binding energy of adsorbed hydrogen is a well-known descriptor for electrocatalytic hydrogen generation. Based on theoretical calculations of hydrogen binding energy, surface alloys of nickel and silver alloys are promising materials for hydrogen oxidation and evolution.[2] Incorporating more noble silver metal into nickel catalysts may also improve resistance to oxidation when in fuel-cell mode.

Because bulk silver and nickel are completely immiscible, we take two different approaches to form a metastable silver-nickel alloy. In the first approach, thin films are electrodeposited onto a glassy carbon substrate from a bath containing both nickel and silver salts. A scanning-electron microscopy (SEM) image of an electrodeposited silver-nickel alloy is shown in Fig. 1. The micrograph shows a uniform film composed of nanoparticles 50-100 nm in diameter. The standard reduction potentials of nickel and silver differ by approximately 1 V, but manipulating the bath concentration, electrode rotation speed, and deposition parameters permits control of the silver-to-nickel ratio.

In the second approach, electron-beam evaporation is used to codeposit nickel and silver. X-ray diffraction (XRD) patterns of Ni_xAg_{1-x} films, as deposited on glassy carbon substrates, are shown in Fig. 1. The broad peak at 44° corresponds to the glassy carbon substrate. The Ni (111) peak is located at $2\theta = 43.5^{\circ}$, while Ag(111) is located at 38.3° and Ag (200) at 43.3°. Fig. 2 shows that as x decreases, the Ag(111) peak shifts to higher values of 2θ because incorporating smaller nickel atoms into the lattice decreases the unit cell length. Correspondingly, the Ni(111) peak location decreases with increased Ag content, although scattering from the carbon substrate interferes with peak intensity.

Fig. 3 shows cyclic voltammagrams of electrodeposited nickel and electrodeposited silver-nickel alloys (Ag:Ni = 5:1) in H_2-saturated 0.1 M KOH at 900 rpm. Two samples

of each composition are shown. Curves were measured vs. a Hg/HgO electrode, but are reported with respect to the reversible hydrogen electrode (RHE). The hydrogen evolution current for the silver-nickel alloys is greater, suggesting that incorporating silver may improve the hydrogen binding energy, and thus the catalytic activity, over pure nickel. Future work will relate the superficial current density in Fig. 3 to the turnover frequency of the catalysts and discuss in more detail characterization and performance differences between the two synthesis methods.
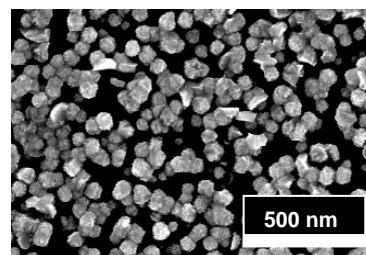

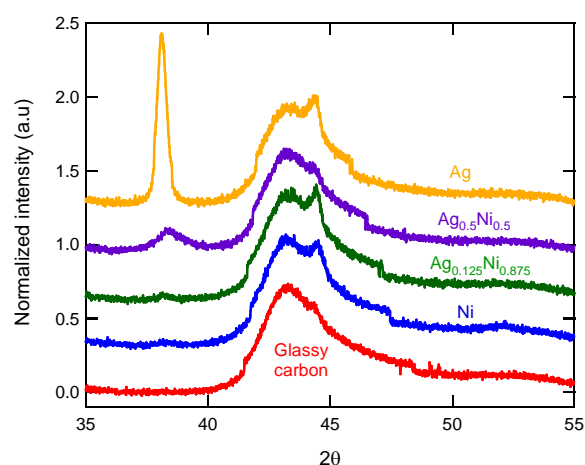Fig. 1: SEM image of electrodeposited AgNi.

Fig. 2: XRD patterns of electron-beam codeposited silver-nickel alloys on glassy carbon substrates. Alloying Ni and Ag changes the lattice spacing, shifting the Ag(111) and Ni (111) peaks.
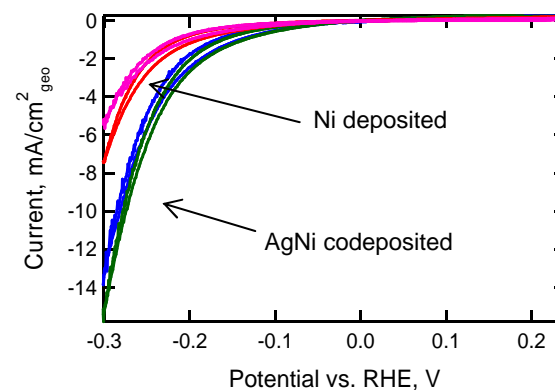

Fig. 3: Electrochemical performance of electrodeposited Ni and AgNi alloys. The AgNi demonstrates improved hydrogen evolution activity on a superficial area basis.

1. Ng, D., Gorlin,Y., and Jaramillo, T.F. (2013) *submitted*.
2. Greeley, J., & Nørskov, J. K. (2007). *Surf. Sci. 601*(6), 1590–1598.