Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Material

Nickel-Copper Supported on Carbon Black Hydrogen Oxidation Catalyst Integrated in Anion-Exchange Membrane Fuel Cell

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Section 1: Supplementary information related to the calculation of exchange current density.

The exchange current density (j_0), the reaction rate of the forward and reverse reactions at chemical equilibrium, is an important kinetic parameter which describes how the rate of an electrochemical reaction increases as a function of applied overpotential (η). The exchange current density is related to overpotential as described by the Tafel equation:

$$\ln\left(\frac{j}{j_0}\right) = \frac{\alpha n F}{RT}\eta$$

Equation S1

Where *j* is the measured current density, α is the transfer coefficient, F is the Faraday constant, n is the number of electrons transferred, T is the absolute temperature in K, and R is the universal gas constant. Rearranging Equation S1 gives:

$$j = j_0^{\frac{\alpha n F}{RT}\eta}$$

Equation S2

To approximate *j*(η) at values within the micropolarization region, where η≈0, a Taylor series expansion around η=0 can be used to derive an expression for the linear dependence on *η* of *j*:

$$\sum_{n=0}^{1} \frac{j'(0)}{n!}(\eta - 0)^n$$

Equation S3

Differentiation of *j*(η) and evaluation at η=0 gives the linear dependence of *η* in the micropolarization region:

$$j = j_0 + j_0\frac{\alpha n F}{RT}\eta$$

Equation S4

which is of the form y = b +mx. By definition, j_0 is not directly measured since the net Faradic current where η=0 is also zero. However, the second term of the Taylor series expansion gives the linear relationship between *j* and η in the micropolarization region. Additionally, α is a measure of the fraction of the interfacial potential used to overcome the Gibbs free energy barrier of the reaction, and in the micropolarization region where η≈0, α≈1. Therefore, a plot of *j* vs η in the micropolarization region can be fit to a linear expression and the slope can be used to calculate j_0:

$$j = j_0\frac{nF}{RT}\eta = m\eta$$

Equation S5

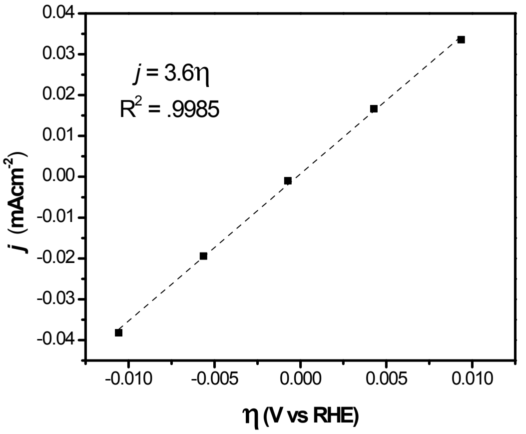

Figure S1. Plot of measured current density normalized to the geometric surface area of the working electrode versus overpotential in the microkinetic region (≈ -10 mV – 10 mV vs. RHE). Data was acquired using a scan rate of 5 mVs^{-1} with a rotation speed of 1600 RPM in hydrogen saturated 0.1 M KOH with a total catalyst loading of 100 μg.

Section 2: Supplementary information related to the effect of catalyst loading.

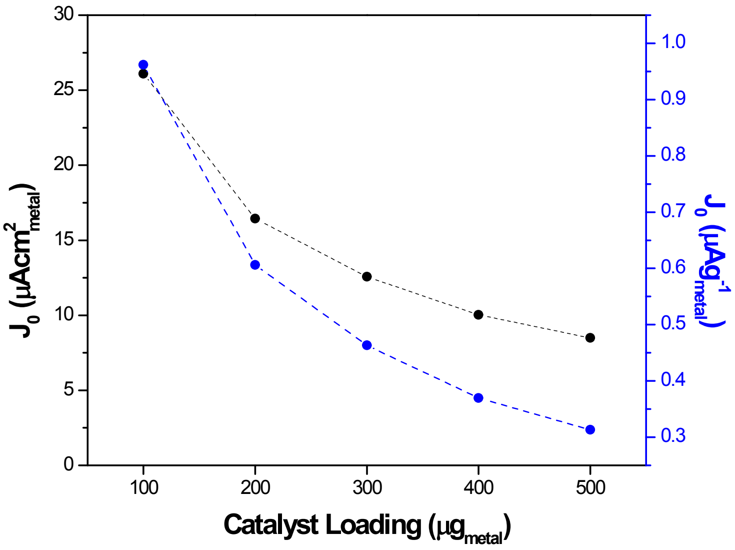

Figure S2. Specific activity and mass-weighted activity calculated from exchange current density for HOR on $Ni_{95}Cu_5$ catalysts as a function of catalyst loading on the working electrode. Exchange current densities were calculated from data obtained at a rotation rate of 1600 RPM.

Section 3: Supplementary information related to the crystal structure of β-NiOOH and β-Ni(OH)$_2$.

Based on first principles simulations, the structure of β-NiOOH is considered to be similar to that of β-Ni(OH)$_2$, Trigonal in the P3m1 space group. One key difference between the two phases are in the degree at which the (001) surface is terminated with hydrogen, which ranges from 100 % in β-Ni(OH)$_2$ to as low as 25 % in β-NiOOH as calculated in literature[1,2]. Figure S2 shows the case of 100 % termination in β-Ni(OH)$_2$ and 50 % termination in β-NiOOH of the (001) plane.

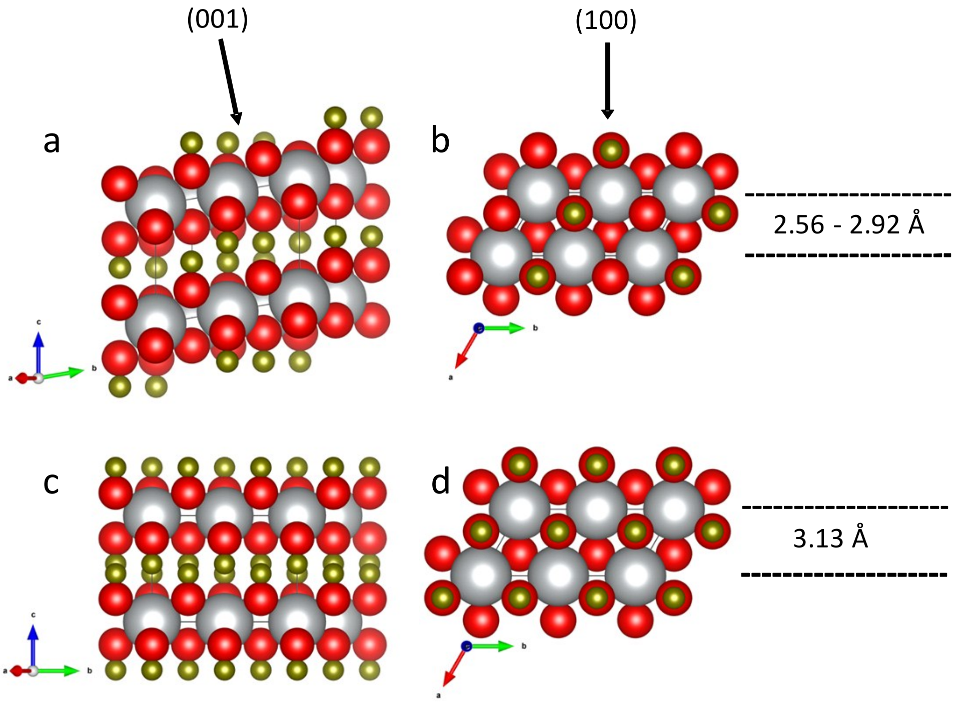

Figure S3. Unit cell representations for a) β-NiOOH projected perpendicular to the (001) direction, b) β-NiOOH projected along the (001) direction, c) β-Ni(OH)$_2$ projected perpendicular to the (001) direction, and d) β-Ni(OH)$_2$ projected along the (001) direction. Crystal structure visualizations were created using VESTA[3].

The result of hydrogen vacancies in the (001) plane of β-NiOOH is hydrophilicity due to the formation of hydrogen bonds from water with the hydrogen deficient surface of β-NiOOH. Similarly, the fully saturated (001) surface of β-Ni(OH)$_2$ leads to hydrophobicity[1]. In the present work, the observed hydrophobic nature of the Ni$_{95}$Cu$_5$ electrode suggests similar hydrophobicity to that which is exhibited by β-Ni(OH)$_2$. Therefore, it is likely that the hydroxylated surface of the Ni$_x$Cu$_{1-x}$ electrode is isostructural with β-Ni(OH)$_2$. The isostructural nature of Ni$_x$Cu$_{1-x}$ with β-Ni(OH)$_2$ can be rationalized by the lattice expansion along the (100) direction in β-Ni(OH)$_2$ compared to β-NiOOH (as shown in Figure S2). Cu, with a covalent radius approximately 5-8% larger than that of Ni, when alloyed with Ni will elicit a similar lattice expansion along the (100) direction.

References:

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2. A. J. Tkalych, K. Yu and E. A. Carter, *The Journal of Physical Chemistry C*, 2015, **119**, 24315–24322.
3. K. Momma and F. Izumi, *Journal of Applied Crystallography*, 2011, **44**, 1272–1276.