



Platinum-like oxidation of nickel surfaces by rapidly switching voltage to generate highly active bifunctional catalysts



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ABSTRACT

Recently the importance of catalyzing the water splitting step of the hydrogen evolution reaction (HER) was highlighted. We demonstrate here a treatment to modify a nickel surface into a highly effective bifunctional HER catalyst ($i_0 = 0.18 \text{ A/m}^2$, Tafel Slope = 106 mV/dec) that has a good distribution of both water splitting sites and H_{ads} combination sites. The resulting surface is characterized electrochemically, and with SEM, EDX, XPS and AFM. The data is found to be consistent with the treatment oxidizing the Ni surface in a novel way creating the hypothesized “ $\text{Ni}(\text{OH})_x$ ” structure (x between 0 and 2).

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1. Introduction

The world is expected to transition to a renewable energy economy in the future [1,2]. The Hydrogen Evolution Reaction (HER) is expected to play a role in this, but new materials are required for catalysts [1]. The most common type of electrolyzer for HER today is alkaline [3]. The accepted mechanism of the alkaline HER consist of two steps: the “Volmer” step (water splitting in alkaline media) resulting in adsorbed hydrogen H_{ads} ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^-$), followed by the combination step via either the “Heyrovsky” reaction, a second electron transfer reaction ($\text{H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$), or the “Tafel” reaction, a chemical recombination reaction ($2\text{H}_{\text{ads}} \rightarrow \text{H}_2$). The importance of the water splitting step in this reaction was recently highlighted, in addition to the previously-known H_{ads} combination step [4–6]. To achieve a high reaction rate both steps must be catalyzed [4].

With the knowledge that two different types of surface sites are important for catalyzing the HER, the challenge of developing HER electrodes is to maximize the triple phase boundary (TPB) between electrolyte, water splitting, and hydrogen recombination site. In previous work, $\text{Ni}(\text{OH})_2$ was used to catalyze the water splitting, and a bifunctional catalyst was synthesized by covering a metal with nano-sized islands of $\text{Ni}(\text{OH})_2$ [5,6]. To realize a better catalyst a larger TPB is desirable, which implies a more uniform mixture of sites is necessary. However, obtaining a good dispersion with $\text{Ni}(\text{OH})_2$ is challenging, because it forms via a Volmer–Weber nucleation and growth mechanism, resulting in the formation of islands [7,8].

In the present paper we propose a novel surface: $\text{Ni}(\text{OH})_x$, with x varying between 0 and 2, as an inherently bifunctional structure that sidesteps the nucleation and growth problem. Such a structure could be created by forcing a nickel surface to oxidize more like a platinum surface. Platinum oxidizes by incorporation of OH groups through place-exchange [7]. Place-exchange still occurs on nickel, but it is slow compared to nickel's other oxidation mechanisms. Nickel oxidation in weakly acidic solutions results in a $\text{Ni}/\text{NiO}/\text{Ni}(\text{OH})_2$ structure [8–10] but starts with the quick adsorption of OH groups. At the potentials where OH groups adsorb, there are two subsequent paths between a metallic nickel surface and the layered $\text{Ni}/\text{NiO}/\text{Ni}(\text{OH})_2$ structure [11]. The first is through continued oxidation of NiOH_{ads} groups, and the second is through the place-exchange process of $\text{Ni}/\text{NiOH}_{\text{ads}}^+ \rightarrow \text{Ni}/\text{OHNi}$, which is a slow reaction compared to the other pathways [11].

Application of a square wave potential is used in this work to oxidize a Ni surface. It is hypothesized this will cause it to progressively form the targeted $\text{Ni}(\text{OH})_x$ structure by exploiting the slow place exchange. During the anodic portion of each cycle a few OH groups will be buried in the electrode by place-exchange. Then, during the cathodic portion, all newly oxidized species will be reduced except the buried OHs. This is because the place-exchange is not electrochemical, so is slow in both directions. With each subsequent cycle more OH groups will be buried. With properly selected parameters, the end result could be the proposed $\text{Ni}(\text{OH})_x$ structure. This work explores the results of such a square wave treatment on Ni, especially for HER activity.

2. Materials and methods

Experiments were performed using an AMEL 7050 potentiostat, using a standard three electrode cell [12]. Potentials are with reference

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to the Hg/HgSO₄ electrode in saturated K₂SO₄. Solutions were prepared using ultrapure deionized water.

Nickel wire (99.98% purity, Alfa Aesar) of 0.5 mm diameter was used for the electrode preparation. Before each experiment an unused segment of wire was polished using 600 grit abrasive paper (Mastercraft), followed by rinsing with ultrapure deionized water (fresh polished wire avoids drift [13]). A 2 mm portion of the wire was exposed to the solution (remainder wrapped in Teflon tape). Unless otherwise noted, the pre-treatment surface area, measured by the method explained in [14], is used throughout as it is challenging to measure the surface area of Ni electrodes with high coverage of hydroxides [15]. Using the pre-treatment surface area is justified by the similar roughness before and after treatment.

The treatment was done by applying a square wave (frequency 8 Hz, high voltage of −125 mV and low voltage of −770 mV) for 40 min (longer times produce no further effects, shorter times produce proportionally less effect) in a 24 mM ascorbic acid and 0.2 M Na₂SO₄ solution. The counter electrode was a high surface area nickel wire coil.

The electrochemical characterization of the sample consists of cyclic voltammograms (CVs), chronoamperometry (two step polarizations, Tafel plots), and chronopotentiometry (stability test in the hydrogen region). Each point in the Tafel plot is from a 2 min polarization at a given potential. For the two step polarization, the initial potential was −1.7 V, the first step was to a varied potential, and the second step was back to −1.7 V. The electrode was held at each potential for five minutes. All electrochemical characterizations were done in a degassed (by nitrogen bubbling for 15 min prior to each experiment and throughout) solution of 1 M KOH (Fischer, ACS grade). The counter electrode was a high surface area platinum coil.

XPS spectra were taken on a Thermo Scientific Theta Probe instrument. The X-ray source was monochromatized Al K (1486.7 eV). The X-ray beam size was 400 μm and the energy resolution corresponds to Au3f7/2. XPS spectra were analyzed according to Biesinger [16] where only the Ni 2p3/2 region was fit, with the background line covering the entire Ni 2p region, and an offset added according to the iterative fitting method.

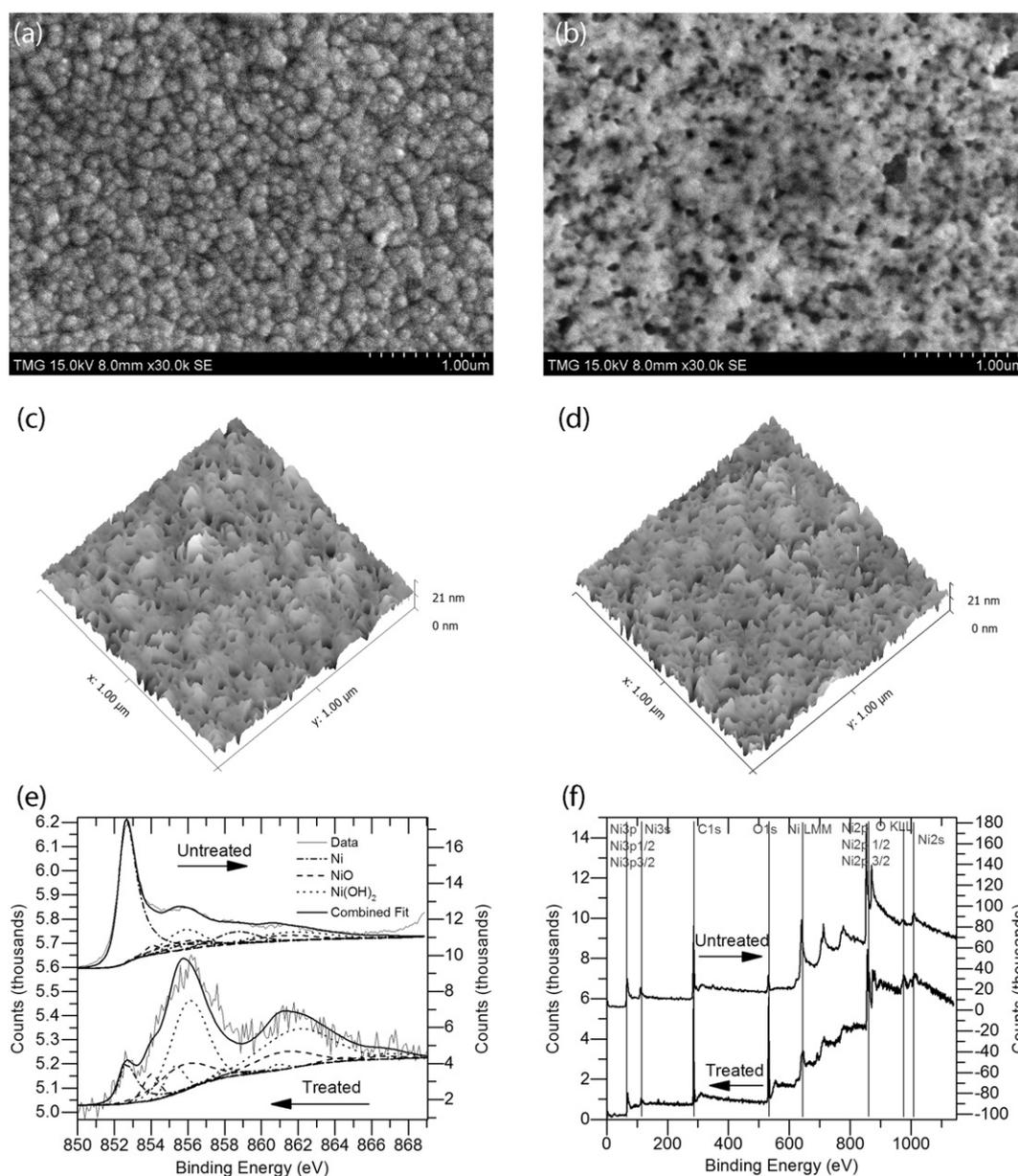


Fig. 1. Microscopy of samples. a) Untreated Ni SEM, b) treated Ni SEM, c) untreated Ni AFM (Ra 2.20 nm), d) Treated Ni AFM (Ra 2.17 nm). e) XPS 2p data fit to Ni/NiO/Ni(OH)₂ model [16]. f) Wide range XPS data.

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