Research Paper

# Design of Nickel Electrodes by Electrodeposition: Effect of Internal Stress on Hydrogen Evolution Reaction in Alkaline Solutions

Sung-Min Kim[a], Sang-Hoon Jin[a,b], Yu-Jin Lee[a,c], Min Hyung Lee[a,*]

[a] Surface R&D Group, Korea Institute of Industrial Technology, Incheon-si, 406-840, Republic of Korea
[b] Department of Materials Engineering, Korea Aerospace University, Gyeonggi-do, 412-791, Republic of Korea
[c] Department of Materials Science & Engineering, Yonsei University, Yonsei-ro 50, Seodaemun-Gu, Seoul, 120-749, Republic of Korea

A B S T R A C T

Here we report the fabrication of Ni electrodes with induced internal stress, electrodeposited in the presence of coumarin (COU) or 1,3,6-naphthalenetrisulfonic acid trisodium salt (NTS), to enhance the hydrogen evolution reaction. The crystallographic structure and morphology of the Ni electrodeposits prepared from a plating bath containing COU showed large columnar structures with a [100] preferred orientation, whereas the electrodeposits with NTS grew fine columnar structures along the [111] and [100] direction. The tensile or compressive stress in the Ni lattice was controlled by additive concentration, which led to the incorporation of hydrogen or sulfur in the Ni matrix. The Ni electrode with induced compressive stress exhibited a higher exchange current density and lower Tafel slopes than those with induced tensile stress, which can be attributed to modification of the hydrogen adsorption energy, as evidenced by a downshift in the $d$-band center.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Hydrogen is one of the most promising clean energy candidates for replacing fossil fuels [1,2]. Among various strategies to produce hydrogen, alkaline water electrolysis has been gaining interest because of its stable output, high product purity and unlimited availability [3,4]. However, several barriers to the commercial viability of alkaline water electrolysis still remain. First, the cost of hydrogen production via alkaline water electrolysis is more expensive than that of conventional carbon based methods such as hydrocarbon reforming, coal gasification, and biomass pyrolysis [5,6]. Another problem is that the hydrogen evolution reaction (HER) at the cathode must be started with a large overpotential because of the lack of a proton source in the alkaline electrolyte [4]. To overcome these obstacles, many efforts have focused on the development of electrode materials with high catalytic activity, which is one method of realizing commercial scale hydrogen production via alkaline water electrolysis.

Pt is the most active cathode material presently known for HER [7–9]. Although Pt and Pt-based materials show excellent performance with high current density and nearly zero HER overpotential [10], they are too expensive to be used for the large scale production of hydrogen in industry. As an alternative to Pt, one common strategy has been to develop earth-abundant transition metals (Fe, Ni, Co, and Mn) as highly efficient HER electrocatalysts. Among these materials, Ni is a particularly attractive candidate due to its low cost, its high chemical stability in a basic solution, and low HER overpotential compared to other transition metals [8,11,12]. However, Ni is still not entirely effective at promoting HER activity, because the strong Ni-H$_{ad}$ bond strength blocks available reaction sites [7,9,13]. To improve its performance and enhance HER activity, it will be necessary to design the electronic structure of the Ni electrodes, and downshift the $d$-band center ($\varepsilon_d$, normally defined as the central position of the $d$-orbitals). This will facilitate relatively weaker hydrogen adsorption.

There are a number of synthesis methods which can be employed to optimize the Ni electrodes. In particular, electrodeposition is a versatile and scalable industrial process that only requires an ion source and simple equipment. Moreover, the electrodeposition technique allows precise control of the nucleation and growth processes, leading to the formation of desirable structures and morphologies in the Ni electrodeposits. In recent studies, Ni electrodes composed of various morphologies (particles, dendrites, films) have been electrodeposited using different potentials, and it was reported that their HER activities were enhanced, in the order of dendrite > particle > film > foil, due to the highly (111)-populated Ni dendrite structures, compared to

polycrystalline Ni particles and film [13]. Further, Xie and co-workers have reported the fabrication of several Ni electrodes by electrodeposition in the presence of ammonia, and found that enhanced HER activity was obtained, due to the small grain size and enlarged surface roughness induced by the complexation between the ammonia and Ni ions [14]. Although it is known that the stress-induced modification of electronic structures is directly correlated with the electrochemical activity of catalysts, most studies on Ni electrodes for HER activity have only focused on the morphology and crystallographic structure and their relationship to the electrochemically active surface area [15–18]. A rational design of the electronic structure tuned by compressive or tensile stress has not yet been reported for improving the intrinsic catalytic properties of Ni electrodes.

Herein, we experimentally demonstrate the correlation between stress-induced Ni electrodeposits and HER activity. To tailor the electronic structure of the Ni electrodeposits, the internal stress of the Ni electrodes was controlled in the presence of two kinds of additives. It was found that the compressive-stress-induced Ni electrodes increased the number of electron states far from the Fermi level ($\varepsilon_F$), and consequently enhanced the electrochemical activity toward the HER, as evidenced by spectroscopy and voltammetry. The combined study of crystallographic and morphologic characteristics and their correlation with HER activities were investigated using microscopy, and reported here. This study highlights a strategic approach to the fabrication of Ni electrodes with highly active HER via electrodeposition, which may provide a significant benefit for scientific and practical advancement in the energy conversion and storage fields.

## 2. Experimental Section

### 2.1. Chemicals

Nickel (II) sulfamate tetrahydrate (Ni(SO$_3$NH$_2$)$_2$·4H$_2$O), nickel (II) chloride hexahydrate (NiCl$_2$·6H$_2$O), boric acid (H$_3$BO$_3$), coumarin (denoted as COU, C$_9$H$_6$O$_2$) and 1,3,6-naphthalenetrisulfonic acid trisodium salt hydrate (denoted as NTS, C$_{10}$H$_5$(SO$_3$Na)$_3$·xH$_2$O) were purchased from Sigma Aldrich. Deionized (DI) water (18.2 M$\Omega$ cm) from Milli-Q system were used for all experiments.

### 2.2. The preparation of electrodeposited Ni electrodes

AISI 304L stainless steel plates with 9 cm$^2$ area and 0.5 mm thickness were used as the substrate material for deposition of the Ni films. Prior to Ni electrodeposition, the substrates were cleaned ultrasonically in acetone for 20 min, and then activated in 10% H$_2$SO$_4$ solution at room temperature for 15 sec. After washing with DI water, the substrates were promptly placed in the electrodeposition bath composed of 374 g L$^{-1}$ Ni(SO$_3$NH$_2$)$_2$, 30 g L$^{-1}$ H$_3$BO$_3$ and 8.55 g L$^{-1}$ NiCl$_2$ without additives (hereafter, the virgin make-up solution, VMS). The pH value of the bath was fixed at 4.0. The composition of the second electrolyte was the same as that of the VMS bath except for the addition of 200, 500 and 1000 mg L$^{-1}$ COU. The composition of the third electrolyte was also the same as that of the VMS bath except for the addition of 200 and 1000 mg L$^{-1}$ NTS. The resulting Ni electrodes were designated ED-VMS, ED-COU200, ED-COU500, ED-COU1000, ED-NTS200, ED-NTS500 and ED-NTS1000, respectively.

The substrate was connected to the cathode in the potentiostat (Versastat 4, Princeton Applied Research) and nickel sulfide (NiS) crowns in a titanium (Ti) basket were used as the anode. A plating current density of 20 mA cm$^{-2}$ was applied at 50 °C for 225−275 sec to attain a Ni thickness of *ca.* 1.5 μm for the electrodes. For the cathodic current efficiency, the current efficiency ratio was determined by weighing the electrodeposits, and the result was compared to the ideal mass calculated from Faraday's law. In addition, the potential was recorded *in situ* during deposition at a constant current density of 20 mA cm$^{-2}$. At that time, the Ag/AgCl reference electrode was employed and the potentials were converted to reversible hydrogen electrode (RHE).

### 2.3. Characterization of the electrodeposited Ni electrodes

The crystal structure was examined by high resolution X-ray diffraction (HR-XRD, Rigaku, Smartlab) with monochromatic Cu Kα radiation (0.15412 nm) at 45 kV and 200 mA. From the diffraction intensities of the (hkl) plane, used to estimate the preferred orientation of the Ni crystallites quantitatively, the texture coefficient TC$_{(hkl)}$ was calculated using the following equation [19].

$$TC_{(hkl)} = \frac{I_{(hkl)}}{I_{o(hkl)}} / \frac{1}{n} \sum \frac{I_{(hkl)}}{I_{o(hkl)}} \qquad (1)$$

where $I_{(hkl)}$ is the measured relative intensity, $I_{0(hkl)}$ is the relative intensity from a standard powder diffraction given by the JCPDS data, and $n$ is the total number of reflections.

In order to assess the effects of additives on the textures, the TCs were calculated by comparing the relative peak intensities $I_{0(hkl)}$ of the Ni electrodes electrodeposited with and without the additives. The TC of the Ni electrode electrodeposited in the absence of additives have, by definition, TC$_{(hkl)}$ = 1.

The morphology of the Ni electrodes was examined with an atomic force microscope (AFM, XE-100, Park System). Cross-section transmission electron microscopy (XTEM) and high-resolution transmission electron microscopy (HR-TEM) images were obtained using a JEOL JEM-ARM 200F microscope working at a 200-kV accelerating voltage. The internal stress can provide clues correlated to the hydrogen adsorption on catalyst surface because the XRD stress measurement for internal stress is confined to the surface of samples. Thus, the internal stress of the as-deposited Ni electrodes was determined by the XRD sin$^2\psi$ method, which used the lattice spacing d$_{(hkl)}$ of (hkl) planes as a strain gauge [20,21]. The strain in the crystal lattice was measured for at least four precisely known orientations relative to the sample surface, and subsequently, the internal stress was estimated from the slope of the sin$^2\psi$ vs. 2$\theta$ curves, using the following equation.

$$\sigma = \left(\frac{E}{1+\nu}\right)\frac{1}{d_0}\left(\frac{\partial d_\psi}{\partial sin^2\psi}\right) \qquad (2)$$

where E, $\nu$, $d_0$ and $d$ are the Young's modulus, Poisson's ratio, and the stress-free and measured inter-planar distances, respectively.

X-ray photoelectron spectroscopy (XPS, K-ALPHA, Thermo Fisher Scientific) measurements for the valence band and electronic structures were carried out using monochromatic Al Kα radiation ($h\nu$ = 1486.6 eV). For each XPS measurement, the Shirley background was subtracted from the measured spectra. To accurately compare all of the valence-band spectra, the upper level of the integration of the background subtraction was fixed at the 15.0 eV bonding energy position for all valence-band spectra.

### 2.4. Electrochemical measurements

Electrochemical measurements were carried out in a standard three electrode system controlled by a potentiostat. An electrodeposited Ni electrode with an area of 0.64 cm$^2$ served as the working electrode. A Pt mesh and a Hg/HgO electrode were used as the counter and reference electrodes, respectively. All potentials were without *IR* correction and referenced to the RHE potential according to the Nernst equation ($V_{RHE} = V_{Hg/HgO}$ + 0.0591 pH +