



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

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ABSTRACT

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.

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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 (ϵ_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

* Corresponding author. Tel: +82-32-8500-287, Fax: +82-32-8500-230.

E-mail address: minhyung@kitech.re.kr (M.H. Lee).