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An active nanoporous Ni(Fe) OER electrocatalyst via selective dissolution of Cd in alkaline media

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ABSTRACT

Although there has been a significant progress regarding electrocatalysts for the electrochemical oxygen evolution reaction, further breakthroughs are still required due to its sluggish 4-electron transfer mechanism. Ni is considered as a potential candidate for the oxygen evolution reaction (OER) in alkaline media in lieu of noble metals, however, the utility of Ni has been limited by the required and relatively high overpotentials. In this study, we fabricated a nanoporous Ni structure by selective and partial dissolution of Cd from a NiCd composite (without using hazardous acids or bases). The formation of nanoporous Ni greatly enhanced OER performance because of the increased number of catalytic sites. Furthermore, there was a promotional electronic effect on the electrocatalyst induced by Cd atoms under the Ni surface tuning the catalytic reactivity could be tuned. Additionally, Fe deposition on the porous Ni-Cd structure significantly raised the OER activity via a reduction in the overpotential from a value of $\eta = 382$ mV (before Fe deposition) to $\eta = 290$ mV (after Fe deposition) to achieve 10 mA cm^{-2}.

1. Introduction

Hydrogen and oxygen obtained from water splitting are very important as a power source with regard to the growing demand for renewable energy [1–3]. However, the oxygen evolution reaction (OER) process is a four-electron transfer reaction ($4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ in an alkaline medium) limited by large overpotentials [4] and slow kinetics [5] so much research related to the OER regarding electrocatalysts, photocatalysts, or thermal decomposition pathways is currently underway. Among the various approaches for effective facilitation of the OER, employing electrocatalysts in alkaline electrolyte is considered one of the most viable solutions, especially considering the possibility of using alternative cheap earth-abundant catalysts [6] which can be applied as favorable oxygen electrocatalyts at the anode side [7]. Indeed, considering the cost of noble metals as OER electrocatalysts [8–11], there has been increasing interest in the application of non-noble metal based electrocatalysts (mostly 3d elements [7,12]). Among them, recent advances with Ni oxide have shown great improvement in OER activity and stability and nickel is abundant, cheap and has high stability in alkaline solution. There have been many Ni-based investigations from oxide [13,14] to mixed metal oxide (Ni-Fe [15–17], Ni-V [18], Ni-Co [19]) in recent years. However, since the utility of Ni-oxide electrocatalysts has still been limited by the required high overpotentials, there have been many studies aimed at effective strategies for activity improvement; one promising approach is the fabrication/synthesis of nanoporous electrocatalysts [20]. Because of their unique intermetallic connections and high surface area, nanoporous structures are exceptionally attractive as OER electrocatalysts. Thus, several attempts to synthesize nanoporous structures or 3D architectures have been made via templating [21,22], solvothermal [23], nanocasting [24], electrospinning [25], and nitridation reaction [26] techniques. Additionally, a common approach to obtain nanoporous sponge materials is an electrochemical dissolution method [27]. With this method, the porous structure can be fabricated with ease by selective dissolution of an unstable element from a composite [20] without hazardous acids or bases. Furthermore, it can lead to geometric effects as well as promotional electronic effects by forming a different elemental composition in the surface and sub-surface layers [28] which

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can alter the adsorption energy resulting in a tuning of the activity [29] since the OER consists of several elementary reaction steps involving adsorbates such as *O, *OH, and *OOH [30].

Here we describe our synthesis of a porous Ni structure with Cd (as a pore maker) which can be readily and effectively dissolved in an alkaline medium (pH 13–14) [31] for synergistic (geometry and electronic) electrocatalytic effects. Interestingly, nanoporous Ni electrocatalyst was clearly formed after Cd dissolution drastically enhancing OER performance compared to bulk Ni. Furthermore, a promotional electronic effect induced by Cd (at bulk) under Ni surface could promote the catalytic reactivity. Additionally, we readily deposited Fe on the porous Ni electrocatalyst using an electron-beam (e-beam). It basically proposes its empirical usage as a highly active nanoporous NiFe based electrocatalyst. The Fe evaporation boosted the OER activity from the overpotential of $\eta = 382$ mV (before Fe deposition) to $\eta = 290$ mV (at 10 mA cm^{-2}). Scanning electron microscopy (SEM), optical profilometry, X-ray diffraction (XRD), and electrochemical tests were conducted for the characterization of the nanoporous Ni electrocatalyst. X-ray photoemission spectroscopy (XPS) was employed to investigate potential electronic effects.

2. Experimental

2.1. Electrocatalyst fabrication

Polycrystalline titanium (1/4″ of diameter, 99.99% purity, and Kurt J. Lesker) was used as a substrate for the NiCd electrocatalyst. Details regarding preparations of the electrocatalyst can be found in reference [32] but a brief description of the synthetic procedure follows. Firstly, the Ti substrate was polished for ~30 min employing two different types of sandpaper (1500- and 2000-grit) and alumina powder having a particle size of 1 and 0.3 μm (CH instruments) in order to obtain a smooth surface. The polished Ti was then washed with distilled water three times while under sonication, and finally rinsed with distilled water in preparation for the deposition of Ni or NiCd.

The Ni or NiCd was electrodeposited on the prepared Ti under the modified conditions of Dougherty [33] at a constant cathodic current of 5 mA for 300 s without stirring. The solution for electrodeposition was prepared with water based mixing of $NiSO_4$ $6H_2O$ (9 mM) and $(NH_4)_2SO_4$ (25 mM) adjusting the pH to 3. For the NiCd electrocatalyst, the Cd precursor, $3CdSO_4$ $8H_2O$ (0.5 mM), was also added to the deposition electrolyte. Before the deposition process, the prepared solution was bubbled and fully saturated with Ar gas. The electrodeposition was carried out employing a hanging meniscus rotating disk electrode (RDE) configuration [34,35] for precise surface area determination. After the deposition, the prepared samples were rinsed with distilled water thoroughly. In order to conduct a systematic investigation, we prepared three samples each of NiCd with increasing Cd ratios including 100:3, 100:5, 100:10 and 100:20 (Ni:Cd) and named the samples with the following convention: NiCd(I) for the initial NiCd prior to any processing and NiCd(A) for the material after Cd dissolution from the NiCd(I).

For the preparation of the NiCd(A) electrocatalysts, the potential was swept in the range of 1.35–1.55 V (vs. RHE) with a scan rate of 50 mV s^{-1} for 500 cycles under rotating of 1600 rpm (experimental details in Fig. S1). An e-beam evaporator was used for deposition of Fe for the synthesis of both NiFe and NiCd(A)Fe electrocatalyst materials (characterization details in Figs. S2–S4). The e-beam deposition rates were controlled by adjustment of the emission current with a rate of 0.2 Å/s for a thickness of 3 nm as measured by a quartz crystal microbalance (QCM). The main chamber pressure was maintained at a pressure of 1×10^{-7} during the evaporation (TEM images of evaporated Fe on C-coated Cu grid and Ni film represent in Fig. S4).

The particle type NiCd catalyst with a molar ratio of 100:5 was prepared by a chemical reduction method. The stoichiometric amounts of $NiSO_4{\cdot}6H_2O$ and $CdSO_4{\cdot}8/3H_2O$ precursors were dissolved in 100 ml of D.I water followed by addition of 50 ml of 0.1 M $NaBH_4$ solution under vigorous stirring. After 1 h of stirring, the solution was filtered, washed with excess amount of water and dried at 80 °C for 12 h in an oven. The NiCd(A)_P was prepared in the above manner for the NiCd (A).

2.2. Characterization

All the samples were quantitatively analyzed for Ni, Cd, and Fe by using an inductively coupled plasma mass spectrometry (ICP-MS). A three-electrode system was used for the evaluation of the electrochemical behavior with a potentiostat (CHI660D, CH instruments) consisting of a working electrode (catalyst), reference electrode (Ag/AgCl in sat. KCl, converted to RHE scale as shown in Fig. S5) and an auxiliary electrode (Pt mesh). Cyclic voltammetry (CV) was conducted in the voltage range 1.0–1.1 V vs. RHE with a scan rate of 10, 20, 50, and 100 mV s^{-1} in Ar fully purged 0.1 M NaOH electrolyte in order to estimate the electrochemical surface area (ECSA). The water oxidation reaction was evaluated by measuring an anodic current sweep using linear sweep voltammetry (LSV) in the voltage range between 1.0–1.9 V with a scan rate of 5 mV s^{-1}. All electrochemical data have been corrected with an i-R compensation (27 Ω) and obtained at room temperature under ambient pressure. The total metal loading of catalysts was identical for electrochemical test as shown in Tables S1–S2 and S4. The NiCd(A)_P was dispersed on a glassy carbon electrode (1/4″ of diameter) with 89.6 ml of D.I water, 10 ml of isopropanol, and 0.4 ml of Nafion solution (5%). The 30 μl of ink was dropped on the working electrode with the same metal loading of the NiCd(A) catalyst. The surface of the thin film was observed using scanning electron microscopy (SEM, FEI Quanta 650 SEM) without a noble metal coating. The accelerating voltage was 15 kV with 2 nA of current and a 10 mm working distance. The surface profile was measured using a non-contact optical profilometer (Wyko NT 9100, FOV 2.0 X). XPS spectra were recorded on a Kratos Axis Ultra DLD spectrometer using monochromatic Al Kα radiation (1486.6 eV) with 400 μm spot sizes of X-ray monochromator under 1×10^{-10} Torr for information on elemental composition and chemical bonding states of samples. All XPS energy data were calibrated with the C 1s electron peak (284.6 eV). The samples were structurally characterized by X-ray diffraction (XRD, Rigaku Ultima IV) equipped with CuKα radiation ($\lambda = 1.54056$ Å) using a fixed glancing incidence angle $\alpha = 1^\circ$ at room temperature. Rietveld analyses were performed using the PANalytical X'pert highscore software (Philips, Netherlands). The microstructure of the catalytic film was investigated by using TEM (JEOL 2010F) with an electron gun operated at 200 KV.

3. Results and discussion

In order to identify the optimal compositions of Ni and Cd for creating active porous Ni electrocatalysts, the OER performance was measured with various ratio of Ni to Cd. Fig. 1 shows OER polarization curves for NiCd electrocatalysts as a function of Cd ratio (Ni:Cd = 100:3, 100:5, 100:10, and 100:20). The onset potential for OER shifted positively with an increasing ratio of Cd (Ni:Cd = 100:10 and 100:20). The Cd in the samples with the ratio of 100:10 and 100:20 may cover the active Ni sites while the samples with relatively low portion of Cd (100:3 and 100:5) required less overpotential and showed similar initial OER performance. All the samples have a significant activity enhancement after Cd dissolution, it is interesting to note that the electrocatalyst with Ni:Cd = 100:5 showed the best performance which could have optimal trade-off characteristics between pores and structural integrity. Thus, we decided to focus on the NiCd (100:5) material in this study of OER electrocatalysts.

Scanning electron microscopy (SEM) was used to examine the surface morphology of the samples. The microstructure of the NiCd(I) and NiCd(A) along with Ni films are shown via the SEM images shown in