Fabrication of Ni–Mo-based Electrocatalysts by Modified Zn Phosphating for Hydrogen Evolution Reaction

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ABSTRACT

The preparation of low-cost, simple, and scalable electrodes is crucial for the commercialization of water electrolyzers for H₂ production. Herein, we demonstrate the fabrication of cathodes through Mo-modified Zn phosphating of Ni foam (NiF) for water electrolysis, which has been largely utilized in surface coating industry. In situ growth of electrocatalytically active layers in the hydrogen evolution reaction (HER) was occurred after 1 min of phosphating to form ZnNiMoP, and subsequent thermal treatment and electrochemical activation resulted in the formation of ZnNiMoPO₅ₓHᵧ. ZnNiMoPO₅ₓHᵧ exhibited superior HER performance than NiF, primarily because of the increased electrochemically active surface area of ZnNiMoPO₅ₓHᵧ compared to that of bare NiF. Although further investigations to improve the intrinsic electrochemical activity toward the HER and detailed mechanistic studies are required, these results suggest that phosphating is a promising coating method and will possibly advance the fabrication procedure of electrodes for water electrolyzers with better practical applications.

Keywords : Carbon-Neutrality, Water Splitting, Hydrogen Evolution Reaction, Ni-Mo, Zn Phosphating

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1. Introduction

Hydrogen (H₂) production by water (H₂O) electrolysis is an important future energy source because of its carbon neutrality (H₂O → H₂ + 1/2 O₂) [1-3]. To achieve this goal, which would ultimately aid in the commercialization of water electrolyzers, it is indispensable to develop electrocatalysts that exhibit high activity and physical/chemical stability toward the hydrogen evolution reaction (HER), while reducing the material and fabrication costs. Zn phosphating, which is widely used in the coating industry, has remarkable advantages in this regard; it involves the in situ growth of electrocatalytically active layers in a simple chemical bath at temperatures in the range of 50-80°C [4]. The nucleation and growth during Zn phosphating occur by balancing the corrosion of the metal substrate to increase the surface pH, resulting in the precipitation of Zn²⁺ and PO₄³⁻. Our previous reports suggest that the metal ions corroded from the substrate and the other ions in the chemical bath were also deposited in the film during the precipitation [5,6]. This allows elemental tunability of the catalytic layers for various target electrocatalytic reactions. Moreover, the direct growth of catalysts by phosphating renders the unhindered conductivity by polymeric binder, which is essential for the fabrication of electrodes with powdery catalysts [7].

Since the Sabatier principle and Trasatti volcano plot, which relate the chemisorptive bonding strength of intermediates in the rate-determining step and the overall heterogeneous electrocatalytic reactions, were reported [8], extensive efforts have been devoted to the development of cost-effective materials that can replace the Pt-group metals [9-11]. Based on the previous studies on the HER, noteworthy progress has been made with Ni-containing species such as intermetallic Ni–Mo catalysts, which show good electrocatalytic activity owing to the synergistic effects of Ni
and Mo [12,13]. Ni–Mo catalysts can be prepared simply by electrodeposition on a conductive substrate [14,15]. Following the development of Ni–Mo catalysts fabricated by electrodeposition, substantial efforts have been dedicated toward the further improvement of their electrocatalytic activity and stability in the HER. One of the representative strategies is to adopt additional elements or phases. Recently, Cao et al. reported Ni–Mo–O derived Ni–Mo/MoO$_3$$_x$$_2$ catalysts fabricated through hydrothermal reaction and annealing under a H$_2$ atmosphere by varying the H$_{ad}$–alloy binding strength [16]. Eladgham et al. synthesized homogeneous and heterogeneous Ni–Mo–P nanoparticles via chemical routes and thermal treatment [17]. Chang et al. fabricated Ni–Mo/Cu nanosheets using chemical and electrochemical methods [18]. Although the previously developed Ni-Mo-based electrocatalysts show excellent performance in HER [16–18], there are still plenty of opportunities to further optimize the catalytic performance using simpler fabrication procedures with scalability.

In this paper, we report a simple method for the fabrication of Ni–Mo-based cathodes for water electrolyzers to produce renewable molecular H$_2$ production after further optimization of catalytic activities owing to its simplicity and scalability.

2. Experimental

2.1 Electrode preparation

Phosphating on NiF was conducted following a previously reported procedure with a slight modification. The NiF substrate was cleaned by sequentially immersing it in 0.2 M NaOH for 10 min and 1% HCl for 5 min at 80°C and room temperature, respectively. After washing thoroughly with deionized water (18.2 MΩ cm$^2$), the catalytically active layers were simply deposited in a phosphating bath at 80°C for a designated time. The phosphating bath comprised 10 mM aqueous Zn(NO$_3$)$_2$·6H$_2$O and Na$_2$MoO$_4$·2H$_2$O solutions containing 150 mM H$_3$PO$_4$, 30 mM HNO$_3$, 0.5 mM NaF, 1.8 mM KNaC$_3$H$_5$O$_4$·4H$_2$O, and 25 mM KNO$_2$. The pH of the bath was adjusted to 2.5 using 2.0 M NaOH. The deposited ZnNiMoP$_x$/NiF was washed with deionized water and dried in an oven at 80°C. Following this, ZnNiMoP$_x$ was annealed by calcination at 300°C for 2 h. For converting ZnNiMoP$_x$ to ZnNiMoPO$_x$H$_y$, 150 rounds of consecutive potential cycling were conducted between 1.0 and 1.6 V vs. RHE ($V_{RHE}$) to activate the surface for HER.

2.2 Electrochemical characterization

All electrochemical experiments were performed with a three-electrode configuration consisting of Hg/HgO (1.0 M KOH as filling solution, Pine Research Instrumentation) and carbon cloth as the reference and counter electrodes, respectively. To prepare the working electrode, NiF-based electrodes were cut into 1.0 cm × 1.5 cm. The electrochemical cells were home-built quartz cells, and the compartments of the counter electrode were separated by glass frit. The electrolyte was 1.0 M KOH. To evaluate the HER performance, cyclic voltammograms (CVs) were acquired in a H$_2$-saturated electrolyte using a potentiostat (VSP, BioLogic). Electrochemical impedance spectroscopy (EIS) was performed under a constant potential of −0.25 V$_{RHE}$ with 10 mV amplitude from 100 kHz to 100 mHz. Pt/C was prepared by drop casting ink, composed of commercial Pt/C powders (20 wt.%, Johnson Matthey) and Nafion ionomer (5 wt.%) dispersed in DMF, onto the surface of a glassy
carbon rotating disk electrode (RDE) tip. The final Pt loading was 15 μg cm\(^{-2}\). The HER performance of Pt/C was evaluated using RDE assemblies (Pine Research Instrumentation) at 1600 rpm.

2.3 Physical characterization

Field emission scanning electron microscopy (FESEM) images were acquired using a SUPRA 55VP (Zeiss) instrument at an acceleration voltage of 2 kV at the National Instrumentation Center for Environmental Management of Seoul National University. XRD patterns were obtained on a SmartLab diffractometer (Rigaku) with a Cu X-ray source at the Yonsei Center for Research Facilities. XPS measurements were performed on a Kα X-ray photoelectron spectrometer with a monochromated Al source (Thermo Fisher Scientific).

3. Results and Discussion

Linear sweep voltammograms (LSVs) were obtained after five potential cycles by varying the immersion duration in the phosphating bath to evaluate the electrode performance toward the HER. Fig. 1a shows the voltammograms of ZnNiMoPO\(_{x}\)H\(_{y}\)/NiF prepared by phosphating and electrochemical activation, but without annealing at 300°C. ZnNiMoPO\(_{x}\)H\(_{y}\)/NiF fabricated by 1 min of phosphating (red line) showed the best HER performance in H\(_2\)-purged 1.0 M KOH. This was confirmed by EIS, studies, indicated that the ZnNiMoPO\(_{x}\)H\(_{y}\)/NiF phosphatized for 1 min (red dots) exhibited the smallest charge transfer resistance, as evident from the smallest diameter of the semicircle in the Nyquist plot (Fig. 1b). However, as shown in Fig. 1c, the current density steadily increased with increasing potential cycles. Fig. 1d shows the chronopotentiometric curve of ZnNiMoPO\(_{x}\)H\(_{y}\) deposited for 1 min obtained at 50 mA cm\(^{-2}\). H\(_2\)-saturated 1.0 M KOH electrolyte was used for evaluating the HER performance.
decreased during the first five potential cycles, which were performed to stabilize the catalytic surface. Moreover, the chronopotentiometric curve obtained at -50 mA cm\(^{-2}\) showed that the overpotential increased during the first 30 min of measurement, indicating poor stability (Fig. 1d). We assume that this instability originates from the physically weak adhesion of the catalytic layers formed due to phosphating.

To improve the stability, the deposited ZnNiMoP/ NiF electrodes were subjected to heat treatment at 300°C for 2 h in air before electrochemical activation. The ZnNiMoPO\(_x\)H\(_y\)/NiF electrodes exposed to heat showed better electrochemical stability. As shown in Fig. 2a, the current density for the HER stabilized within the first five potential cycles. Unlike the electrodes without heat treatment, a stable current density (red line) for the thermally treated ZnNiMoPO\(_x\)H\(_y\)/NiF was observed at a current density that was slightly higher than the initial current density (purple line). The LSV curve of the heat-treated ZnNiMoPO\(_x\)H\(_y\)/NiF indicated better HER performance compared to that without annealing, especially at an overpotential higher than 300 mV (Fig. 2b). However, the initial performance of the ZnNiMoPO\(_x\)H\(_y\)/NiF was poorer. According to the Nyquist plots, ZnNiMoPO\(_x\)H\(_y\)/NiF shows a comparable charge transfer resistance (R\(_{CT}\)) at of ~3 Ω cm\(^2\) at -0.25 V\(_{RHE}\), regardless of the thermal treatment. The R\(_{CT}\) value was calculated by numerical fitting using a simple Randles equivalent circuit. Based on our observations, we postulate that the improved performance, which is observed only at current densities higher than 50 mA.

Fig. 2. (a) Five consecutive CVs of ZnNiMoPO\(_x\)H\(_y\)/NiF obtained after depositing ZnNiMoP for 1 min and annealing at 300°C. (b) HER polarization curves and (c) Nyquist plots at ~0.25 V\(_{RHE}\) for the ZnNiMoPO\(_x\)H\(_y\)/NiF with and without heat treatment of ZnNiMoP. The electrolyte and potential sweep rate were 1.0 M KOH and 10 mV s\(^{-1}\), respectively.
cm$^{-2}$ after annealing, probably originates from the better physical adhesion of the catalytic layers and not from the chemical and/or structural changes.

Fig. 3a and b show the FESEM images of ZnNiMoP$_i$ and ZnNiMoPO$_x$H$_y$ on NiF, respectively. Upon heat treatment at 300°C, ZnNiMoP$_i$ exhibited a rough morphology with an inhomogeneous surface (Fig. 3a). Our previous reports suggest that the film deposited by Zn-based phosphating is composed of a crystalline mixture of phosphophyllite (Zn(M)(PO$_4$)$_2$·4H$_2$O and hopeite (Zn$_3$(PO$_4$)$_2$·4H$_2$O), resulting in decreased uniformity, as indicated by the varying brightness in the FESEM images [5]. After electrochemical activation by 150 rounds of potential cycles in 1.0 M KOH (ZnNiMoPO$_x$H$_y$), the uniformity of the catalyst surface improved. Moreover, the higher brightness in the FESEM images implies better conductivity than that of ZnNiMoP$_i$ (Fig. 3b) [19]. At a higher magnification (Fig. 3b, right panel), a rougher surface comprising both particulates and small layered structures was observed.

To investigate the elemental states of the surface catalytic layers, XPS analysis was conducted (Fig. 4). The overall shape of the Ni 2p spectrum of the phosphated ZnNiMoP$_i$ is similar to that of NiO [20]. After thermal treatment and electrochemical activation, the shape of the Ni 2p spectrum of ZnNiMoPO$_x$H$_y$ was similar to that of a typical Ni 2p spectrum in Ni(OH)$_2$ (Fig. 4a) [20]. In Fig. 4b, the peak positions of Mo 3d$_{5/2}$ in ZnNiMoP$_i$ and ZnNiMoPO$_x$H$_y$ indicate a characteristic of Mo$^{6+}$ [21]. The most prominent variation upon the post-treatment of ZnNiMoP$_i$ to form ZnNiMoPO$_x$H$_y$ is seen in the Zn 2p spectra (Fig. 4c). The peak height of Zn 2p in ZnNiMoP$_i$ significantly decreased after the formation of ZnNiMoPO$_x$H$_y$, while the Zn 2p$_{3/2}$ peak shifted.
toward negative binding energy from 1021.7 to 1021.2 eV. The reduced peak intensity after exposure to 1.0 M KOH electrolyte is in good agreement with that observed in our previous study, wherein the reduced peak intensity was attributed to the dissolution by forming [Zn(OH)]\(^{2-}\) [22]. However, the peak of P 2p spectrum at ~133 eV remained after the electrochemical activation, indicating the presence of residual phosphate groups in the catalytic layers of ZnNiMoPO\(_x\)H\(_y\) (Fig. 4d). As the exact chemical states of the catalysts surface related to the electrochemically active sites in the HER are not yet clear, further in-depth analysis and optimization of the HER performance using phosphatized Ni–Mo-based electrodes are underway in our laboratory.

The electrochemical performance toward HER is shown in Fig. 5. Fig. 5a shows the CVs during the electrochemical activation for the conversion of heat-treated ZnNiMoP\(_i\) into ZnNiMoPO\(_x\)H\(_y\) by 150 rounds of potential cycles in 1.0 M KOH. After the first CV, the redox peaks responsible for the electrochemical reaction Ni\(^{3+} + e^- \leftrightarrow Ni^{2+}\) slightly increased with increasing number of potential sweeps, indicating an enlarged electrochemically active surface area (ECSA) [23]. The 150\(^{th}\) CV curves of NiF, ZnNiPO\(_x\)H\(_y\), and ZnNiMoPO\(_x\)H\(_y\) were recorded to
compare the ECSA (Fig. 5b). ZnNiPO\(_x\)H\(_y\) was fabricated by the same procedure as that used to fabricate ZnNiMoPO\(_x\)H\(_y\), but without Mo\(^6+\) in the phosphating bath. The ECSAs of ZnNiPO\(_x\)H\(_y\) and ZnNiMoPO\(_x\)H\(_y\) increased by 4.5 and 5.4 times, respectively, compared to that of NiF. The relative ECSAs were compared by integrating the peak area related to the reduction of Ni\(^3+\) ions (Ni\(^3+\) + e\(^-\) \rightarrow Ni\(^2+\)), as shown in Fig 5b. The peak-to-peak separation corresponding to the Ni redox reaction (Ni\(^2+\) + e\(^-\) \leftrightarrow Ni\(^3+\)) was higher.
for ZnNiPO₃Hₓ (394 mV) than for NiF (142 mV). However, this peak-to-peak separation was slightly reduced when Mo was incorporated into the catalytic layers (293 mV). To evaluate the HER performance, the LSVs were acquired in H₂-saturated 1.0 M KOH at 10 mV s⁻¹ (Fig. 5c). Although commercial Pt/C shows the best HER performance (at overpotential < 350 mV), the ZnNiMoPO₄Hₓ/NiF electrodes exhibited reasonable activity at an overpotential of 346 mV for achieving a current density of 100 mA cm⁻². Overpotentials of 386, 328, and 378 mV are required for 100 mA cm⁻² in NiF, Pt/C, and ZnNiPO₃Hₓ, respectively. The remarkably better performance of ZnNiMoPO₄Hₓ than ZnNiPO₃Hₓ (without the incorporation of Mo) clearly revealed that elemental Mo is essential for achieving higher electrochemical activity in the HER. The LSV curve of ZnNiPO₃Hₓ was comparable to that of bare NiF, even though the ECSA of ZnNiPO₃Hₓ was higher than that of NiF. This also corroborates that Mo is the most important element for imparting a high HER activity to ZnNiMoPO₄Hₓ. The Tafel slopes in the potential range between 50 and 75 mV of overpotential for NiF, ZnNiPO₃Hₓ, and ZnNiMoPO₄Hₓ were all ~120 mV dec⁻¹, while the value for Pt/C was ~45 mV dec⁻¹ (Fig. 5d). However, the Tafel plots clearly indicated that NiF had a higher geometric current density than ZnNiMoPO₄Hₓ at an overpotential < ~200 mV, revealing that the improved HER performance of ZnNiMoPO₄Hₓ compared to NiF at a relatively high current density predominantly resulted from the increased ECSA due to Mo-modified Zn phosphating of NiF, rather than the enhanced intrinsic electrocatalytic activity toward HER. Indeed, the current density of ZnNiMoPO₄Hₓ at ~0.4 V increased by 1.5 times than the one of bare NiF, which is the lower extent than the increased ratio of ECSA in ZnNiMoPO₄Hₓ/NiF. According to the Nyquist plots, ZnNiMoPO₄Hₓ showed a smaller charge transfer resistance than NiF and ZnNiPO₃Hₓ, indicating a higher HER performance (Fig. 5e). As shown in Fig. 5f, the chronopotentiometric curve shows reasonable stability for ZnNiMoPO₄Hₓ at 50 mA cm⁻². Although the potential corresponding to 50 mA cm⁻² steadily retarded during the measurements, the performance slightly recovered after exchanging with a fresh 1.0 M KOH electrolyte. We shall verify the exact origin of this phenomenon by further investigation of the surface reconstruction under HER conditions.

4. Conclusions

We demonstrate the fabrication of cathodes for water electrolysers by Mo-modified Zn phosphating. The ZnNiMoPₓ layer is grown on NiF by phosphating at 80°C for 1 min, followed by heat treatment at 300°C under air and subjecting to 150 rounds of potential cycling for electrochemical activation. Thermal annealing is required to improve the stability. During the activation in 1.0 M KOH, ZnNiMoPₓ converts into ZnNiMoPO₄Hₓ by the exchange of phosphates with hydroxides [5,6], while the ECSA increases by 5.4 times, compared to that of bare NiF. XPS analysis before and after the activation reveals that the chemical state of Ni is transformed into Ni(OH)₂ from NiO, while the others, including Mo, Zn, and P, retain their qualitative states even after exposure to the KOH electrolyte in electrochemical environments. However, the peak intensity in the Zn 2p spectrum was largely reduced, indicating significant dissolution of Zn during activation. This might be the origin of the increased ECSA, while resulted in the formation of porous catalytic layers. The ZnNiMoPO₄Hₓ/NiF electrodes require 346 mV of overpotential for achieving a current density of 100 mA cm⁻² and good durability in the HER; this overpotential is lower than those required by bare NiF and ZnNiPO₃Hₓ/NiF. Tafel analysis indicates that the improved HER performance of ZnNiMoPO₄Hₓ/NiF compared to NiF might predominantly originate from the increased ECSA, although Mo is an essential element for the electrocatalytic activity toward HER, as suggested by the LSV curves and Nyquist plots. The phosphating method based on in situ growth of catalytic layers can be advantageous for water electrolyzers in terms of simplicity and scalability, although further optimization of the HER performance by variation of additional elements in the phosphating bath and detailed mechanistic studies on the electrochemical activation and the HER process are necessary.

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