Research paper

Non-precious metal electrocatalysts for hydrogen production in proton exchange membrane water electrolyzer

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ABSTRACT

Electrodeposited Cu_xMo_{100-x} catalysts were prepared on a Ti substrate for the hydrogen evolution reaction (HER) in acidic medium. By varying the electrolyte composition for electrodeposition, the atomic concentration of the Cu_xMo_{100-x} electrocatalysts could be controlled, and the Mo content ranged between 0.8 and 6.9%. In the first cyclic voltammetry scan in a $0.5\,M\,H_2SO_4$ electrolyte, the recorded HER current densities of the Cu_xMo_{100-x} electrocatalysts at $-0.50\,V_{RHE}$ increased on increasing the Mo content to 3.8%; then, a further increase in Mo to 6.9% led to a saturation in the HER activity. The maximum value of the normalized current density with respect to the electrochemical surface area and the loading mass was found for the $Cu_{99.2}Mo_{0.8}$ electrocatalyst. Characterization of the prepared catalysts revealed that the enhancement of catalytic activity originates from changes in the grain size and electronic structure. To operate a single cell of the proton exchange membrane water electrolyzer (PEMWE), we electrodeposited CuMo catalyst on carbon paper, and this was used as the cathode, while IrO_2 electrodeposited on carbon paper was used as the anode. The cell performance was normalized with respect to the metal mass loading and was found to be $3.4\,A/mg_{metal}$ at 1.9 V, a 2.2–10.8 times better catalyst cost-activity relationship compared to that of currently reported PEMWEs using Pt-based cathodes. Consequently, the results presented here show that non-noble metal cathodes can be used for PEMWE operation.

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1. Introduction

Hydrogen is a clean and efficient fuel with various applications in electrochemical energy conversion, especially in fuel cells for vehicle and power generation [1,2]. Water electrolysis is one means of producing pure hydrogen, and electrolysis powered by electricity generated from renewable sources (e.g., sunlight, wind, etc.) is environmentally friendly [3,4]. Recent investigations have used solid polymer electrolyte water electrolyzers (SPEWEs), which have many advantages over alkaline diaphragm water electrolyzers, for example, simple construction/maintenance, generation of high purity hydrogen, low ohmic resistance, and prevention of gas crossover [5]. There are two types of SPEWEs, and these are classified by the type of conducting ions in the solid polymer electrolytes: proton exchange membrane water electrolyzer (PEMWE) [6–11] and anion exchange membrane water electrolyzer (AEMWE) [12–17]. However, PEMWEs are more efficient and produce more hydrogen faster than AEMWEs [6–17].

Nevertheless, practical applications of PEMWEs have been limited by their high cost, which arises in part owing to their use of large amounts of noble metals [6,18]. In addition, the oxygen evolution reaction (OER) at the anode is known to be a kinetic bottleneck [19–22], and noble metals and their oxide catalysts for OER (e.g., RuO_2 and IrO_2) undergo severe corrosion under acidic conditions when operating at highly positive overpotentials [23–25]. These disadvantages have led to extensive research into the development of noble metal alloy OER catalysts [26,27] or noble metals overlaid [28,29] with other elements to obtain reasonable activity and stability. Concerning the cathodic reactions, Pt metal is the best HER catalyst [30,31], although platinum group metals (PGMs) are also highly active and stable catalysts for acidic HER [32]. Consequently, modified PGM catalysts have been heavily investigated over the last few decades [33]. During operation of PEMWEs, HER catalysts suffer fewer kinetic and stability problems because of the relatively facile reduction of protons in acidic media and the negative poten-

tial window for operation, respectively. This opens the possibility of using non-noble metals as HER catalysts for PEMWE.

For many years, HER electrocatalysis on various metals has been investigated theoretically and experimentally [33–37]. Using density functional theory and electrochemical measurements, Nørskov et al. demonstrated that there are strong correlations between the hydrogen binding energy and HER activity for various PGMs and non-noble metals [37]. The calculated free energy of hydrogen adsorption (ΔG_H) on PGMs (e.g., Pt, Pd, Rh, and Ir) range from −1.4 to 0.02 eV, and the HER exchange current densities range from $10^{-3.7}$ to $10^{-3.0}$ A/cm^2 [37]. The HER exchange current densities of non-noble metals (e.g., Ni, Co, Cu and W) are 2–3 orders lower than those of PGMs and have ΔG_H values far from zero [37]. Despite their low activities for acidic HER, non-noble metals are still attractive catalysts because of their low cost.

Consequently, various non-noble metals have been studied for acidic HER; [19] in particular, Ni is known to be an effective HER catalyst [30]. Strategies to increase the activity and stability of non-noble metal catalysts have mainly focused on the alloying or overlaying of other elements to improve electronic effects and increase the electrochemically active surface area (ECSA) [38–52]. However, Ni and Ni-based catalysts (e.g., Ni metal alloy, NiS$_x$, NiP$_x$, etc.) can undergo dissolution during HER because the standard reduction potential of Ni (Ni^{2+} + 2e$^-$ → Ni) is −0.280 V vs. the normal hydrogen electrode (NHE); [53] furthermore, this problem also limits the acidic HER catalysis on other non-noble metals such as Co (−0.277 V$_{NHE}$), Fe (−0.440 V$_{NHE}$), and Mo (−0.200 V$_{NHE}$) [53]. Regarding the standard reduction potential, Cu (0.339 V$_{NHE}$) is an attractive non-noble metal for stable HER catalyst in an acidic environment [53]. However, Cu catalysts have not been significantly studied because Cu is not highly active for the acidic HER, as has been shown by theoretical and experimental investigations [35–37].

In this study, we prepared and characterized nanocrystalline Cu$_x$Mo$_{100-x}$ catalysts for acidic HER and found that they have high catalytic activity for HER catalysis. The nanocrystalline Cu$_x$Mo$_{100-x}$ catalysts were prepared by electrodeposition. The morphologies were observed by field emission scanning electron microscope (FESEM) and compositional analysis was conducted by energy dispersive spectroscopy (EDS). The crystal and electronic structures were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The catalytic activities were examined by repeated cyclic voltammetry (CV) in H$_2$SO$_4$ electrolyte. Furthermore, the performance of PEMWE single cells using the developed CuMo HER catalysts as the cathode were examined and their performance was discussed. We would like to emphasize that PEMWE operation with a non-noble metal cathode is not common.

2. Experimental

Electrodeposition was used to prepare the Cu$_x$Mo$_{100-x}$ catalysts, and a conventional three-electrode cell was used. For electrodeposition, Ti foil (Sejin, 2 × 2 cm^2, thickness: 0.1 mm) was used as a working electrode and sealed by a home-made Teflon holder with an area exposed to the electrolyte of 1.13 cm^2. A Pt wire and saturated calomel electrode (SCE) were employed as counter and reference electrodes, respectively. Prior to electrodeposition, the organic residues on the Ti foil surface were removed by sonication in a 20% ethanol solution for 10 min. Then, the native oxide on the Ti foil surface was eliminated by using a 6 M HCl solution at 70 °C for 30 min [27].

To prepare the electrolyte, 0.05 M CuSO$_4$·7H$_2$O (Daejung, 2588-4400) and 0.25 M Na$_3$C$_6$H$_5$O$_7$ (Sigma-Aldrich, C3474) were

dissolved in 18.2 MΩ deionized water; then, Na$_2$MoO$_4$·2H$_2$O (Sigma-Aldrich, 331058) was added to the electrolyte at concentrations from 0.01 to 0.60 M. The prepared electrolytes were purged by N$_2$ bubbling for 30 min. The electrodeposition was carried out at constant potential (−1.0 V$_{SCE}$ for 600 s), controlled by a potentiostat (Autolab, PGSTAT302F, Metrohm). All experimental conditions for electrodeposition are summarized in the Supporting Information (Table S1).

To characterize the electrodeposited Cu$_x$Mo$_{100-x}$ catalysts, we used several analytical techniques. Morphological and compositional observation of the electrodeposits were conducted by FESEM (Sigma, Carl Zeiss) and EDS (Thermo, Noran System 7), respectively. The crystal structures and grain size were analyzed by XRD (New D-8 Advance, Bruker-AXS) with the rate of 5°/min in the range of 30–80°. The change of electronic structure after addition of Mo to Cu was investigated by XPS (Kratos, AXIS-His). The ECSA was measured by linear sweep voltammetry (LSV) with the potential range of −1.2 to 0.5 V$_{SCE}$ at a scan rate of 10 mV/s in 0.5 M NaOH electrolyte [54,55].

The catalytic activities and stabilities of the electrodeposited Cu$_x$Mo$_{100-x}$ catalysts were examined by repeated CV scans within the potential range of −0.2 to −0.8 V$_{SCE}$ at a scan rate of 50 mV/s in 0.5 M H$_2$SO$_4$ electrolyte under atmospheric conditions. Two types of electrochemical cells such as a non-divided batch cell and an H-type cell with Nafion membrane to divide the cathodic and anodic parts were used; the non-divided batch cell was used in the initial activity test while both cells were used in the stability test to confirm the effect of dissolution of Pt anode during the repeated cycles. The pH of the 0.5 M H$_2$SO$_4$ electrolyte was measured by pH meter (UB-7, Denver Instrument), and all potentials are expressed with respect to the reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy (EIS, Iviumstat, Ivium Technology) was used to determine the electrolyte resistance between the working and reference electrodes at constant potential of −0.4 V$_{SCE}$ and a frequency scan of 10^{-2}–10^5 Hz. The averages of electrolyte resistances for the non-divided batch cell and the H-type cell were 1.79 ± 0.03 and 0.93 ± 0.01 Ω, respectively. The obtained values were used for *iR*-correction of the voltammetry results.

To prepare a PEMWE single cell test, we electrodeposited Cu$_{93.7}$Mo$_{6.3}$ and IrO$_2$ catalysts onto carbon paper (CP, TGPH-090, Toray) for use as cathode and anode, respectively. The membrane electrode assembly (MEA) was fabricated by sandwiching the IrO$_2$/CP anode [7] and Cu$_{93.7}$Mo$_{6.3}$/CP cathodes on both sides of the Nafion membrane (212, Dupont Co.). The active area of the MEA was 4 cm^2. After cell assembly, the temperature of the cell was maintained at 90 °C. Pre-heated deionized water (50 °C) was injected into the PEMWE as a reactant with a flow rate of 15 mL/min. For single-cell operation, the potentiostatic method was adopted with the potential window from 1.35 to 2.00 V$_{cell}$, and the stabilized currents after 5 min for each potential were recorded with an interval of 0.05 V.

3. Results and discussion

Fig. 1 shows the morphologies of Cu$_{100}$ and Cu$_x$Mo$_{100-x}$ deposits and their elemental compositions obtained by EDS analysis (see Fig. S1 in Supporting Information). The Cu$_{100}$ deposit contains polygonal aggregates with sizes ranging from 100 to 200 nm (Fig. 1a). When the Mo content of the alloy was 0.8%, the size of the aggregates relative to those of pure copper changed little; however, the angles between the faces of the aggregates became sharper and the surfaces rougher (Fig. 1b). On increasing the Mo content to 2.4%, the morphology drastically changed, becoming dendritic with sharp edges (Fig. 1c). On increasing the Mo content from 3.8 to 6.9%, the particles became more rounded (Fig. 1d–f). The