



Fabrication of $\text{CuCo}(\text{OH})_2$ /graphene paper electrode and their application for anion exchange membrane water electrolysis

In Tae Kim^{1,2} · Jeong-Mi Yeon³ · Sun-Yong Choi³ · Yoo Sei Park^{2,†}

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Abstract: In this study, we synthesized $\text{CuCo}(\text{OH})_2$ on graphene (Gr) paper via electrodeposition and explored its effectiveness as a hydrogen evolution reaction (HER) electrode for anion exchange membrane (AEM) electrolysis. The resulting $\text{CuCo}(\text{OH})_2$ exhibited a nanosheet morphology, increasing the surface area for electrochemical processes, thereby enhancing the extrinsic activity. Compared to the AEM electrolysis cell equipped with $\text{Co}(\text{OH})_2/\text{Gr}$, that equipped with $\text{CuCo}(\text{OH})_2/\text{Gr}$ exhibited superior efficiency, highlighting its potential for sustainable hydrogen production.

Keywords: Anion exchange membrane water electrolysis; Water splitting; Hydrogen energy; Electrocatalysis

1. Introduction

Hydrogen energy is an eco-friendly, sustainable energy source with a high energy density and does not emit greenhouse gases; it is attracting attention in the context of accelerating global warming [1]. Among the various hydrogen production technologies, water electrolysis, which entails the use of electricity to split water into hydrogen and oxygen, is considered the most environmentally friendly [2]. The water electrolysis reaction involves two distinct processes: the oxygen evolution reaction (OER), an oxidation reaction, and the hydrogen evolution reaction (HER), a reduction reaction [3]. Each of these reactions requires considerable overpotential. Therefore, efforts are necessary to minimize overpotential and achieve high-efficiency water electrolysis. In particular, because the HER is a key reaction that generates hydrogen during water electrolysis, reduction of its overpotential is important. This necessitates the development of highly active electrocatalysts for HER.

Cobalt, known for its activity as indicated by its HER volcano plot, is a prominent material used in the catalysts for HER. Copper also exhibits catalytic activity and excellent conductivity. Consequently, substitution with Cu can enhance the conductivity and

modify the electrical structure of Co, thereby promoting the HER.

Recently, there has been a growing interest in anion exchange membrane (AEM) water electrolysis (AEMWE) technology, which utilizes cost-effective non-precious metals (non-PGMs) and can afford high efficiencies at high current densities [4]. This next-generation water electrolysis technology combines the advantages of alkaline water electrolysis (AWE) and proton-exchange membrane (PEM) water electrolysis [5]. However, the commercialization of AEMWE has been hindered by its low efficiency, primarily because of the high overpotential of both the OER and HER due to insufficient catalytic activity [6].

In this study, we developed a highly active non-PGM-based HER electrocatalyst ($\text{CuCo}(\text{OH})_2$) for AEM electrolysis. $\text{CuCo}(\text{OH})_2$ was synthesized directly on graphene (Gr) paper via electrodeposition. The synthesized $\text{CuCo}(\text{OH})_2$ exhibits fine nanosheet shape and yields a large surface area for electrochemical reactions. The incorporation of Cu into $\text{Co}(\text{OH})_2$ modified the electronic structure of Co, resulting in enhanced HER activity. In addition, the AEM electrolysis cell equipped with $\text{CuCo}(\text{OH})_2/\text{Gr}$ exhibited a higher efficiency than that equipped with $\text{Co}(\text{OH})_2/\text{Gr}$.

† Corresponding Author (ORCID: <http://orcid.org/0000-0002-5154-2323>): Assistant Professor, Department of Urban, Energy, and Environmental Engineering, Chungbuk National University, Chungdae-ro 1, Seowon-Gu, Cheongju, Chungbuk, 28644, Republic of Korea, E-mail: yspark@chungbuk.ac.kr, Tel: 82-43-261-2418

1 M. S. Candidate, Department of Urban, Energy, and Environmental Engineering, Chungbuk National University, E-mail: dlsxowlwhs123@naver.com

2 Department of Advanced Material Engineering, Chungbuk National University

3 Nano Materials R&D Division, Cheorwon Plasma Research Institute

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2. Experimental

2.1 Preparation of Co(OH)₂/Gr and CuCo(OH)₂/Gr

CuCo(OH)₂/Gr was prepared via electrodeposition performed using a three-electrode system [7]. A saturated calomel electrode (SCE) and titanium felt were used as the reference and counter electrodes, respectively. The Gr paper, used as the working electrode, was prepared by grinding Gr powder by using a mortar. An aqueous solution of 10 mM Cu(NO₃)₂ and 50 mM Co(NO₃)₂ was used as the electrolyte for electrodeposition. A potential of -1 V_{SCE} was applied to the working electrode for 5 min. After electrodeposition, the samples were washed with deionized (DI) water and dried at room temperature. Co(OH)₂/Gr was prepared by applying a potential of -1 V_{SCE} to the working electrode for 5 min in a solution containing 50 mM Co(NO₃)₂.

2.2 Characterization of Physical Properties

The surface morphology was examined via field-emission scanning electron microscopy (FE-SEM; CZ/MIRAI LMH, TESCAN). The crystal structures of the samples were analyzed using X-ray diffraction spectroscopy (XRD, Ultimalv, Rigaku) in the scattering angle (2θ) range of 5°–80°.

2.3 Electrochemical Characterization

Electrochemical measurements were performed using a three-electrode system with a potentiostat (ZIVE MP1, WonATech). The prepared samples were used as working electrodes. A graphite rod and Hg/HgO (in 1 M KOH) were used as the counter and reference electrodes, respectively. A solution (1 M KOH) was used as the electrolyte and purged with N₂ gas for 30 min to eliminate the effect of the dissolved oxygen gas [8]. The performance of the prepared electrode for HER was assessed using linear sweep voltammetry (LSV) at a scan rate of 5 mV/s with iR correction. All potentials were converted to the reversible hydrogen electrode (RHE) potential by using the Nernst equation [9]. Electrochemical impedance spectroscopy (EIS) was conducted at -0.250 V_{RHE} over frequencies ranging from 100 kHz to 1 Hz, with a signal amplitude of 10 mV.

2.4 AEM Electrolyzer Testing

AEM electrolyzer comprised a flow channel (Ti and graphite at anode and cathode), a gold-plated current collector, an AEM (Sustainion®X37-50 Grade T, Dioxide Materials), and an end plate. The prepared CuCo(OH)₂/Gr and Co(OH)₂/Gr composites were used as cathodes. The anodes were prepared using a spraying method. An ink solution for spraying was prepared by mixing

NiFe layered double hydroxide (NiFe-LDH) powder (OER catalysts), DI water, isopropyl alcohol, and an ionomer (Fumion® FAA-3-solut-10). The NiFe-LDH was synthesized based on previous studies [10]. The loading mass of NiFe-LDH was 5 ± 10% mg/cm². The active area of AEM electrolyzer was 0.785 cm², and the operating temperature was approximately 55 °C. KOH solution (1 M) was supplied to the AEM electrolyzer at a flow rate of 50 mL/min. The cell voltage was measured as a function of the current density by using a DC power supply (MK-W102, MKPOWER) to obtain the polarization curves of the AEM electrolyzer. The durability of the AEMWE was tested at a current density of 0.5 A/cm² for 60 h. The cell efficiency was determined using the following equation:

$$\text{Cell efficiency (\%)} = \frac{\Delta H_{\text{H}_2, \text{LHV}} \times n_{\text{H}_2, \text{measured}}}{I \times V (\text{AEMWE power})} \times 100\% \quad (1)$$

where $\Delta H_{\text{H}_2, \text{LHV}}$ is the lower heating value reaction enthalpy for water electrolysis (241.8 kJ mol⁻¹), $n_{\text{H}_2, \text{measured}}$ is the hydrogen production (mol s⁻¹) measured using the DC power supply, I is the applied current (A), and V is the applied voltage (V) [11].

3. Results and Discussion

3.1 Catalyst Synthesis and Structure Characterization of Samples

CuCo(OH)₂/Gr were analyzed using scanning electron microscopy (SEM). The surface morphology of Co(OH)₂/Gr showed rough and large nanosheets. Conversely, CuCo(OH)₂/Gr showed a fine nanosheet, which provided a larger surface area to promote electrochemical reactions (Figure 1) [12].

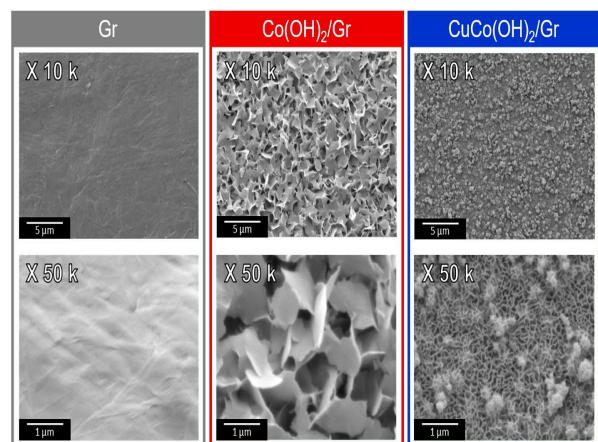


Figure 1: SEM images of Gr, Co(OH)₂/Gr, and CuCo(OH)₂/Gr

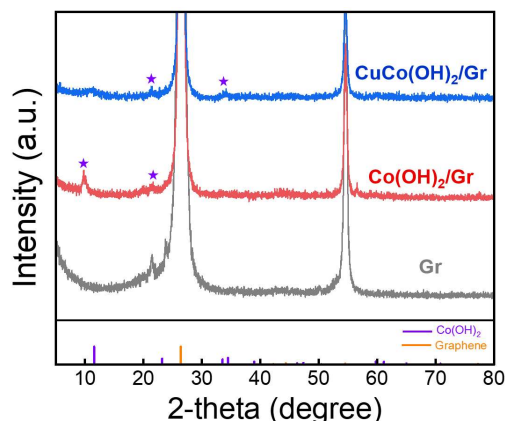


Figure 2: XRD patterns of Gr, Co(OH)₂/Gr, and CuCo(OH)₂/Gr

XRD patterns were obtained to confirm the crystal structures of Gr, Co(OH)₂/Gr, and CuCo(OH)₂/Gr (**Figure 2**). For Co(OH)₂/Gr and CuCo(OH)₂/Gr, distinct peaks corresponding to the (003) and (006) planes of Co(OH)₂ are observed at 11° and 22°, respectively [13]. Interestingly, the crystallinity of CuCo(OH)₂/Gr was lower than that of Co(OH)₂/Gr because it entailed the simultaneous nucleation of different metal ions to form hydroxides.

3.2 Electrochemical Analysis of Gr, Co(OH)₂/Gr, and CuCo(OH)₂/Gr

The electrode performances for HER were evaluated using a three-electrode system in 1 M KOH purged with N₂ gas. The overpotential at the current density of -10 mA/cm² of Gr, Co(OH)₂/Gr, and CuCo(OH)₂/Gr showed 440 mV, 328 mV, and 300 mV, respectively. These results indicate that CuCo(OH)₂/Gr is the best HER electrode (**Figure 3a**). The introduction of Cu into Co(OH)₂ modified the electronic structure of Co, leading to an improvement in the intrinsic HER activity. In addition, the fine

nanosheet improved the extrinsic HER activity. As a result of this synergistic effect, CuCo(OH)₂/Gr exhibited the best HER performance. The Tafel slope of CuCo(OH)₂/Gr is the lowest at 126 mV/dec, indicating that CuCo(OH)₂/Gr exhibits the fastest HER kinetics (**Figure 3b**). A Nyquist plot was used to investigate the polarization resistance of the HER. The radius of the semicircle in the Nyquist plot indicates the polarization resistance [14]. This was the smallest for CuCo(OH)₂/Gr; therefore, CuCo(OH)₂/Gr exhibited the best HER performance (**Figure 3c**).

3.3 Testing of AEM Electrolyzer

Polarization curves of the AEM electrolyzer were obtained to evaluate its performance. The AEM electrolyzer exhibited current densities of 0.3 A/cm² and 0.5 A/cm² at 2.0 V_{cell} when equipped with Co(OH)₂/Gr and CuCo(OH)₂/Gr, respectively (**figure 4a**). Given that all other conditions were identical except for the HER electrode, the difference in cell performance can be attributed to this electrode. Among the three voltage losses of the AEM electrolyzer (i.e., ohmic, activation, and mass transport losses), the activation loss has a direct correlation with the electrode performance. Therefore, the activation loss of the AEM electrolyzer at 0.5 A/cm² was investigated; the results are depicted in **Figure 4b**. The activation loss of CuCo(OH)₂/Gr was calculated at 0.73 V, which was 0.09 V lower than that of Co(OH)₂/Gr. The energy-conversion efficiency of the AEM electrolyzer was then calculated (**Figure 4b**). The AEM electrolyzer equipped with CuCo(OH)₂/Gr demonstrated approximately 3.2% higher efficiency compared to that equipped with Co(OH)₂/Gr. The durability test of the AEM electrolyzer equipped with CuCo(OH)₂/Gr was performed at 0.5 A/cm² for 60 h, and the cell efficiencies throughout the test were calculated (**Figure 4c**). The

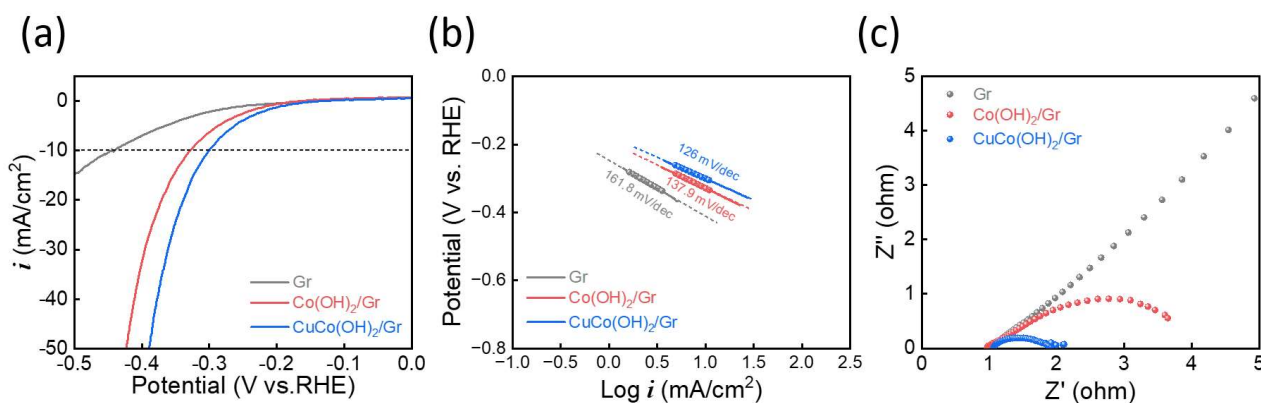


Figure 3: Electrochemical measurement results of Gr, Co(OH)₂/Gr and CuCo(OH)₂/Gr in 1M KOH

(a) Polarizations for HER. (b) Tafel plots. (c) Nyquist plots for HER

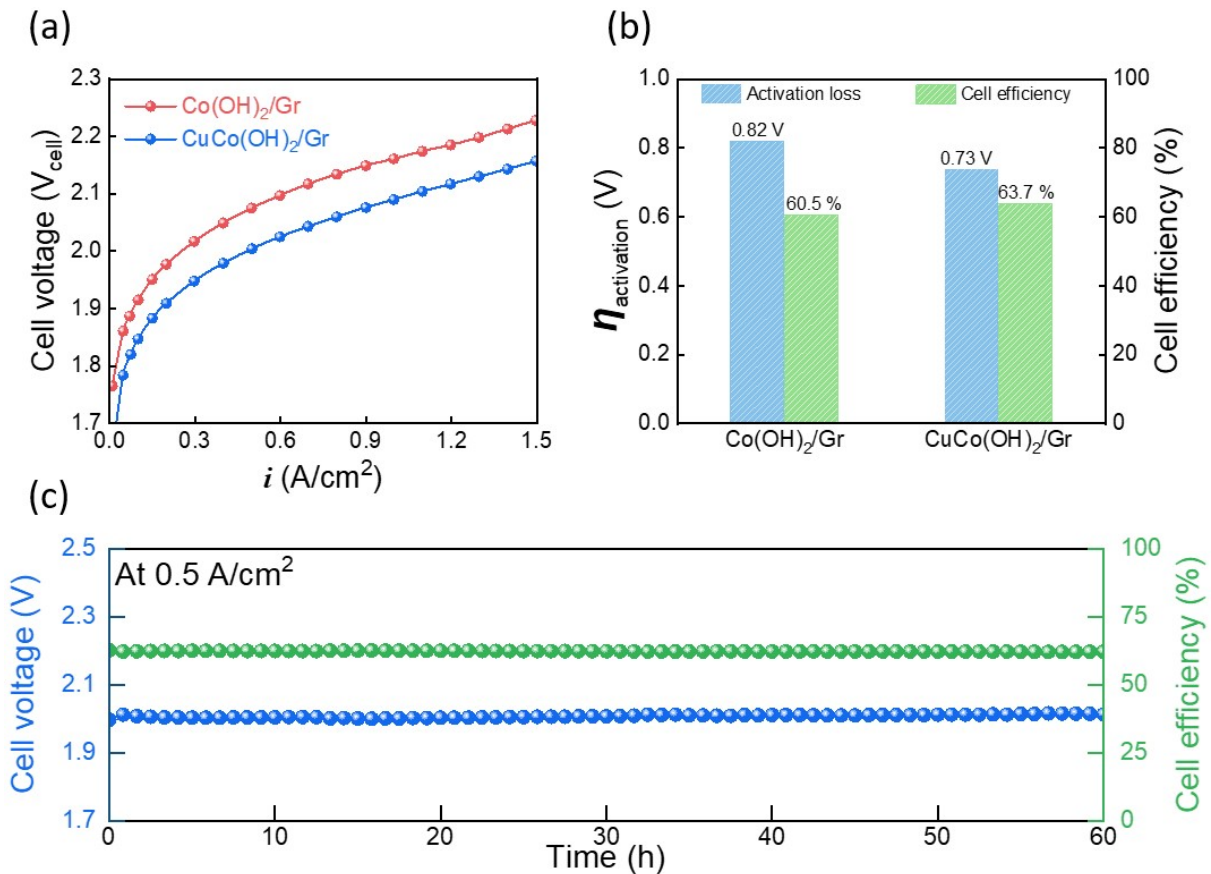


Figure 4: Test of AEM electrolyzer equipped with $\text{Co}(\text{OH})_2/\text{Gr}$ and $\text{CuCo}(\text{OH})_2/\text{Gr}$

(a) Polarization curves. (b) Activation loss ($\eta_{\text{activation}}$) and cell efficiency at $0.5 \text{ A}/\text{cm}^2$ current density. (c) Durability and cell efficiency at $0.5 \text{ A}/\text{cm}^2$ current density

cell voltage exhibits stable changes throughout the durability tests, with a degradation rate of $0.3 \text{ mV}/\text{h}$. In addition, the cell efficiency dropped only 1.49% , indicating that the AEM electrolyzer equipped with $\text{CuCo}(\text{OH})_2/\text{Gr}$ demonstrated good durability.

4. Conclusion

We prepared $\text{CuCo}(\text{OH})_2/\text{Gr}$ via electrodeposition and examined its utilization as an HER electrode for AEM electrolysis. The synthesized $\text{CuCo}(\text{OH})_2$ exhibits a fine nanosheet shape and yields a large surface area for electrochemical reactions, thereby attaining enhanced extrinsic activity. The incorporation of Cu into $\text{Co}(\text{OH})_2$ modifies the electronic structure of Co, enhancing its intrinsic activity. The AEM electrolysis cell equipped with $\text{CuCo}(\text{OH})_2/\text{Gr}$ demonstrated higher efficiency than that with $\text{Co}(\text{OH})_2/\text{Gr}$.

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Author Contributions

Conceptualization, Y. S. Park; Formal Analysis, I. T. Kim, J.-M. Yeon, Investigation, Y. S. Park, S. -Y. Choi; Resources, S. -Y. Choi, J. -M. Yeon; Data Curation I. T. Kim and Y. S. Park; Writing-Original Draft Preparation, I. T. Kim; Writing-Review & Editing, Y. S. Park; Supervision, Y. S. Park; Funding Acquisition, Y. S. Park.

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