

## Research Article

# Sol–Gel Synthesized Nickel-Doped Ruthenium Oxide Aerogel for Highly Efficient Acidic Hydrogen Evolution Reaction

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Solar and wind energy for water electrolysis are gaining interest in contemporary times. In this context, platinum catalysts are commonly recognized as the standard for the hydrogen evolution reaction (HER), yet their effectiveness is constrained by their high cost and inadequate stability. Combining Ru and Ni lowers the material expense and greatly improves the electrocatalytic performance. Therefore, in the present study, a 3D nanostructured amorphous RuO<sub>2</sub> aerogel is doped with various concentrations of Ni for enhanced HER activity. The results indicate that the 4% Ni-RuO<sub>2</sub> aerogel exhibits a 0D colloidal network featuring interconnected mesopores, with a high specific surface area of 241.5 m<sup>2</sup>·g<sup>−1</sup>. In addition, the 4% Ni-RuO<sub>2</sub> aerogel catalyst exhibits the lowest overpotentials of 63 and 122 mV at current densities of 10 and 50 mA·cm<sup>−2</sup>, respectively, along with enhanced hydrogen adsorption activity for the HER due to the 3D porous structure of the aerogel. However, a further increase in Ni doping leads to a decrease in HER activity due to a reduction in the number of catalytic Ru sites. The study found that doping with the optimum amount of Ni causes a redistribution of charges on the sample surface, thereby uncovering more reaction sites and enhancing the electrocatalytic performance.

## 1. Introduction

There is presently an extensive discourse on the development of a clean hydrogen economy and the utilization of renewable sources for the production of high-energy-density hydrogen [1, 2, 3, 4]. This is a direct consequence of the rapid growth in the worldwide energy crisis and the continuous exhaustion of traditional fossil fuels [5, 6, 7, 8, 9]. The use of hydrogen as a carbon-free energy carrier has been widely acknowledged as a highly feasible choice for the future of energy [10, 11, 12, 13]. The application of solar and wind energy for the purpose of water electrolysis is a sustainable

and efficient method for generating highly purified hydrogen. This approach has attracted substantial attention in modern times. However, challenges exist in developing catalysts for the hydrogen evolution reaction (HER) under acidic conditions. This is because the Gibbs free energy of hydrogen adsorption ( $\Delta G_{H^*}$ ) of the catalyst is either too strong, thus causing a decrease in the hydrogen desorption rate during the Heyrovsky or Tafel stage of the reaction mechanism, or too weak, thereby limiting the rate in the Volmer step.

Currently, catalysts based on noble metals such as Pt, Pd, and Ru are chosen for their exceptional catalytic performance

in the HER. In particular, catalysts based on Pt have been widely accepted as the benchmark for the HER due to their favorable  $\Delta G_{H^*}$  of  $-0.09$  eV [14, 15, 16]. However, the low natural abundance and, hence, high cost of Pt have limited the widespread industrial use of such catalysts. Moreover, despite the value of precious metal catalysts in catalytic reactions, their synthesis usually requires extreme temperatures or pressures, and their stability under normal conditions restricts their potential uses. Meanwhile, catalysts based on non-noble metals exhibit lower catalytic efficiency and durability than those based on noble metals, thereby hindering their widespread use in practical applications. Hence, recent studies have extensively examined the capacity of relatively economical precious metals such as Ru, Ir, and Pd, to enhance the non-acidic HER performance via their favorable hydrogen bonding energy values. In particular, Ru is the most affordable precious metal in the platinum group [17, 18, 19] and has garnered significant interest for its capacity to operate effectively across a broad pH spectrum, along with its remarkable stability and comparable hydrogen bond strength (measured at  $65$  kcal·mol $^{-1}$ ) to that of Pt–H [20, 21]. Moreover, it has been noted that Ru exhibits a higher level of oxophilicity compared to Pt, thereby resulting in a greater ability to dissociate water molecules [22, 23, 24, 25]. Furthermore, Ru demonstrates strong corrosion resistance and chemisorption under catalytic conditions. Nevertheless, its performance is slightly inferior to that of the traditional Pt/C catalyst. Therefore, current efforts are focused on enhancing the performance of Ru-based catalysts to achieve improved and more stable HER performance, thereby bridging the gap between research and industrial application.

One approach to improve the HER performance of the Ru-based catalyst is to combine the Ru with another metal in order to take advantage of the correlation between the HER activity and the hydrogen–metal bond strength. For example, nickel (Ni) has a relatively feeble bond with hydrogen, while Ru demonstrates a considerably stronger attraction to hydrogen, as revealed by a so-called volcanic correlation diagram [26, 27, 28]. Therefore, the formation of covalent bonds between Ru and Ni can result in a reduction in the d-band center of the composite material, thereby moderately increasing the hydrogen–metal binding energy and, hence, improving the HER activity [29, 30, 31]. Furthermore, it has been noted that the existence of surface oxidized Ni can augment the separation of water into hydrogen atoms ( $H^*$ ) via a process referred to as the Volmer step, while the presence of Ru synergistically enhances the merging of  $H^*$  species into  $H_2$  [32, 33]. Therefore, the combination of Ru and Ni not only reduces material costs but also significantly enhances the electrocatalytic activity. The improvement can be ascribed to the modification of the charge distribution and the resulting alteration of the surface properties [34, 35].

In the present study, a ruthenium oxide electrocatalyst doped with various amounts of Ni is introduced for the highly efficient HER in acidic media. The Ni–RuO $_2$  aerogels are prepared via the conventional epoxide-initiated sol–gel method with the addition of an Ni precursor, followed by CO $_2$  supercritical drying. The doping with Ni is shown to enhance the specific surface area without altering its amorphous structure. The

optimal concentration of Ni doping increases the HER activity by enhancing both the surface area and intrinsic activity.

## 2. Experimental

**2.1. Chemicals.** Ruthenium (III) chloride hydrate (RuCl $_3$ ·xH $_2$ O, Sigma–Aldrich), nickel chloride hexahydrate (NiCl $_2$ ·6H $_2$ O, Duksan), and propylene oxide (C $_3$ H $_6$ O, Sigma–Aldrich) were used as received without further purification.

**2.2. The Synthesis of Ni-Doped Ruthenium-Based Aerogel.** A wet gel consisting of Ru was synthesized via an epoxide-initiated sol–gel technique using RuCl $_3$ ·xH $_2$ O as the precursor, with the addition of C $_3$ H $_6$ O to facilitate gelation. First, separate precursor solutions of RuCl $_3$ ·xH $_2$ O (2.99 g) and NiCl $_2$ ·6H $_2$ O (2.72 g) in ethanol were stirred in 25 mL volumetric flasks for 24 hr until the solids were completely dissolved. Next, 3 mL of the Ru precursor solution was transferred to a 10 mL vial, and various amounts (0, 2, 4, 6, 8, and 10 mol.%) of the Ni precursor solution were added. After that, C $_3$ H $_6$ O was added dropwise using a micropipette, leading to the formation of a dark brown wet gel within 4 hr. The wet gel was left to mature for 24 hr at ambient temperature, after which fresh ethanol (25 mL) was introduced and the wet gel was allowed to stand at room temperature for another 24 hr to remove any impurities. Then, the wet gel was dried in an autoclave using a supercritical CO $_2$  system (Ilsin Autoclave Co., Korea) at a pressure of 120 bar and a temperature of 60°C.

**2.3. Material Characterization.** The surface structures and elemental compositions of the as-synthesized aerogels were examined via field emission scanning electron microscopy (FESEM; JEOL JSM-7001F, Japan) with energy-dispersive X-ray spectroscopy (EDX). The microstructures and elemental compositions were further examined via transmission electron microscopy (TEM; JEOL, JEM-F200) and scanning transmission electron microscopy (STEM; Manufacturer, Model) with EDX at voltage of 200 kV. The selected area electron diffraction (SAED) patterns and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were also obtained. The crystal phases were analyzed via X-ray diffraction (XRD; Rigaku Ultima IV, Japan) using a copper (Cu) K $\alpha$  radiation source with a wavelength of 1.54 Å in the  $2\theta$  range of 10°–80°. The surface electronic states of the samples were analyzed via X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific, UK) with a monochromator (Al K $\alpha$  line: 1,486.6 eV, 3 mA, 12 kV). The amount of Ni doping in the RuO $_2$  aerogel was measured via inductively coupled plasma optical emission spectroscopy (ICP-OES; Thermo Fisher Scientific, iCAP Pro, UK). The Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore size distributions were calculated from the N $_2$  adsorption–desorption isotherms obtained by employing a multipoint BET and BJH surface analyzer (Quantachrome, Boynton Beach, USA) after preheating each sample to 100°C for 1 day.

**2.4. Electrochemical Analysis.** Electrochemical measurements were conducted using a multichannel electrochemical workstation (ZIVE MP2A, WonaTech, Korea) with a three-

electrode setup at room temperature (298 K). A graphite rod and a saturated calomel electrode were used as the counter and reference electrodes, respectively. The study used experimental methods such as linear sweep voltammetry (LSV) with iR correction, cyclic sweep voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometry (CP) at room temperature (298 K). To fabricate the working electrode, the catalyst powder (4 mg) was dispersed in 5% Nafion solution (50  $\mu$ L), ethanol (200  $\mu$ L), and deionized (DI) water (250  $\mu$ L) via sonication for 30 min to produce an homogenous catalyst ink. Then, 10  $\mu$ L of the catalyst ink was dispersed on a carbon paper via a micropipette. The HER activity was investigated in an acidic electrolyte (0.5 M H<sub>2</sub>SO<sub>4</sub>) saturated with nitrogen (N<sub>2</sub>), where the iR corrected LSV data were collected at a scan rate of 5 mV·s<sup>-1</sup> and converted to the reversible hydrogen electrode by the Equation (1):

$$E(\text{vs. RHE}) = E(\text{vs. Hg/Hg}_2\text{Cl}_2) + E^\circ(\text{Hg/Hg}_2\text{Cl}_2) + 0.0592 \times \text{pH}. \quad (1)$$

The Tafel slope was deduced and fitted in the linear region by using the Tafel Equation (2):

$$\eta = a + b \log(j). \quad (2)$$

EIS was executed in the frequency range of 1 Hz to 1 MHz at an overpotential of 150 mV. The nonfaradaic CV measurements were performed at scan rates of 10–100 mV·s<sup>-1</sup>. The specific capacitance (Cs) was selected as Cs = 0.035 mF·cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> based on previously reported values [36].

### 3. Results and Discussion

The electrocatalytic properties of the pristine RuO<sub>2</sub> and the RuO<sub>2</sub> doped with 2%, 4%, and 6% Ni are presented in Figure 1, while those of the 8% and 10% Ni-doped samples are indicated in Figure S1 of the Supplementary Material. Thus, the LSV results in Figure 1(a) clearly demonstrate that the addition of 2% and 4% Ni improves the HER activity, whereas the addition of 6% Ni is less effective. Moreover, the addition of even larger concentrations of Ni is found to compromise the HER activity, so that the 10% Ni-RuO<sub>2</sub> sample shows even less activity than the undoped RuO<sub>2</sub> aerogel (Figure S1). Consequently, as shown in Figure 1(b), the 4% Ni-RuO<sub>2</sub> aerogel catalyst has the lowest overpotentials of 63, 122, 157, and 207 mV at current densities of 10, 50, 100, and 200 mA·cm<sup>-2</sup>, respectively. These results indicate that the Ru atom is the catalytic center, so that higher Ni concentrations decrease the number of exposed catalytic Ru sites [37].

As shown in Figure 1(c), the Tafel slopes of the various catalysts exhibit a similar trend to that observed for the overpotential values, with the 2% and 4% Ni-RuO<sub>2</sub> samples having Tafel slopes of 40.2 and 62.1 mV·dec<sup>-1</sup>, respectively. Notably, the Tafel slope of 40.2 mV·dec<sup>-1</sup> indicates that electrochemical desorption is the rate-limiting step in the HER

catalyzed by the 4% Ni-RuO<sub>2</sub>, thereby suggesting the Volmer–Heyrovsky HER mechanism [38, 39]. Taken together, these results indicate that the HER activities decrease in the order 4% Ni-RuO<sub>2</sub> > 2% Ni-RuO<sub>2</sub> > 6% Ni-RuO<sub>2</sub> > RuO<sub>2</sub>. This is further supported by the EIS Nyquist plots in Figure 1(d), where the 4% Ni-RuO<sub>2</sub> exhibits a superior electron transfer rate, as demonstrated by the smallest semicircle, thereby indicating superior charge transfer at the electrode–electrolyte interface. Conversely, an increased Ni doping concentration hinders the HER activity and results in a larger semi-circle in the Nyquist plot. Additionally, Figure S2 displays the LVS curves prior to iR correction. The iR value was determined using a current interrupt potentiostatic iR measurement technique, and 85% of the iR value was adjusted for compensation.

The preparation of the Ni-doped catalyst is shown in Figure 2(a) and is described in the Experimental section. Here, the combination of the metal salt-based precursors with an epoxide enables the atomic doping of the aerogel material, as observed previously [40]. The addition of propylene oxide accelerates the gelation process and facilitates the formation of hydroxo and oxo bridges via ololation and oxolation reactions, as the strained epoxide ring of propylene oxide acts as a proton scavenger, speeding up the hydrolysis and condensation reactions by attacking protons.

The mesoporous structure of the as-fabricated 4% Ni-RuO<sub>2</sub> aerogel is revealed by the SEM and TEM images in Figures 2(b) and 2(c), while the microstructures of the other samples are shown in Figure S3. Thus, the 4% Ni-RuO<sub>2</sub> aerogel, which showed the most active HER property, exhibits a highly porous 3D colloidal aerogel network morphology, and an increase in Ni concentration does not significantly influence the microstructure of the aerogel. In addition, the TEM and HAADF-STEM images in Figures 2(c) and 2(d) reveal a distinct interconnected 3D network of mesopores, thereby bestowing a high specific surface area. Moreover, the inset SAED pattern in Figure 2(c) exhibits the typical halo ring of an amorphous material. In addition, high-resolution TEM (HRTEM) images were presented in Figure S4 indicating typical amorphous nature. Further, the EDX elemental mapping images in Figures 2(e), 2(f), 2(g), and 2(h) confirm the successful doping of Ni into the Ru-based aerogel. The weight and atomic percentage of Ni doping in the various RuO<sub>2</sub> aerogels, as measured via ICP-OES, are presented in Table S1. Here, the addition of 2 mol.% Ni precursor, for example, results in the doping with approximately 0.2 at.% Ni into the RuO<sub>2</sub> aerogel.

The XRD patterns of the various Ru-based catalysts in Figure 3(a) exhibit typical amorphous patterns, in agreement with previously reported results [41]. Moreover, no changes in the XRD patterns are observed even with the addition of high Ni concentrations (Figure S5(a)). Further, the N<sub>2</sub> adsorption–desorption isotherms in Figure 3(b) each exhibit IUPAC type II and H3 hysteresis, thereby indicating a narrow range of pore sizes with varying neck sizes. The 4% Ni-RuO<sub>2</sub> aerogel has a specific surface area of 241.5 m<sup>2</sup>·g<sup>-1</sup>, compared to 219.9 m<sup>2</sup>·g<sup>-1</sup> for the pristine RuO<sub>2</sub> aerogel (Table S2), with all samples exhibiting a pore size of approximately 4 nm (Figures S5(b) and S5(c)). Further, the specific

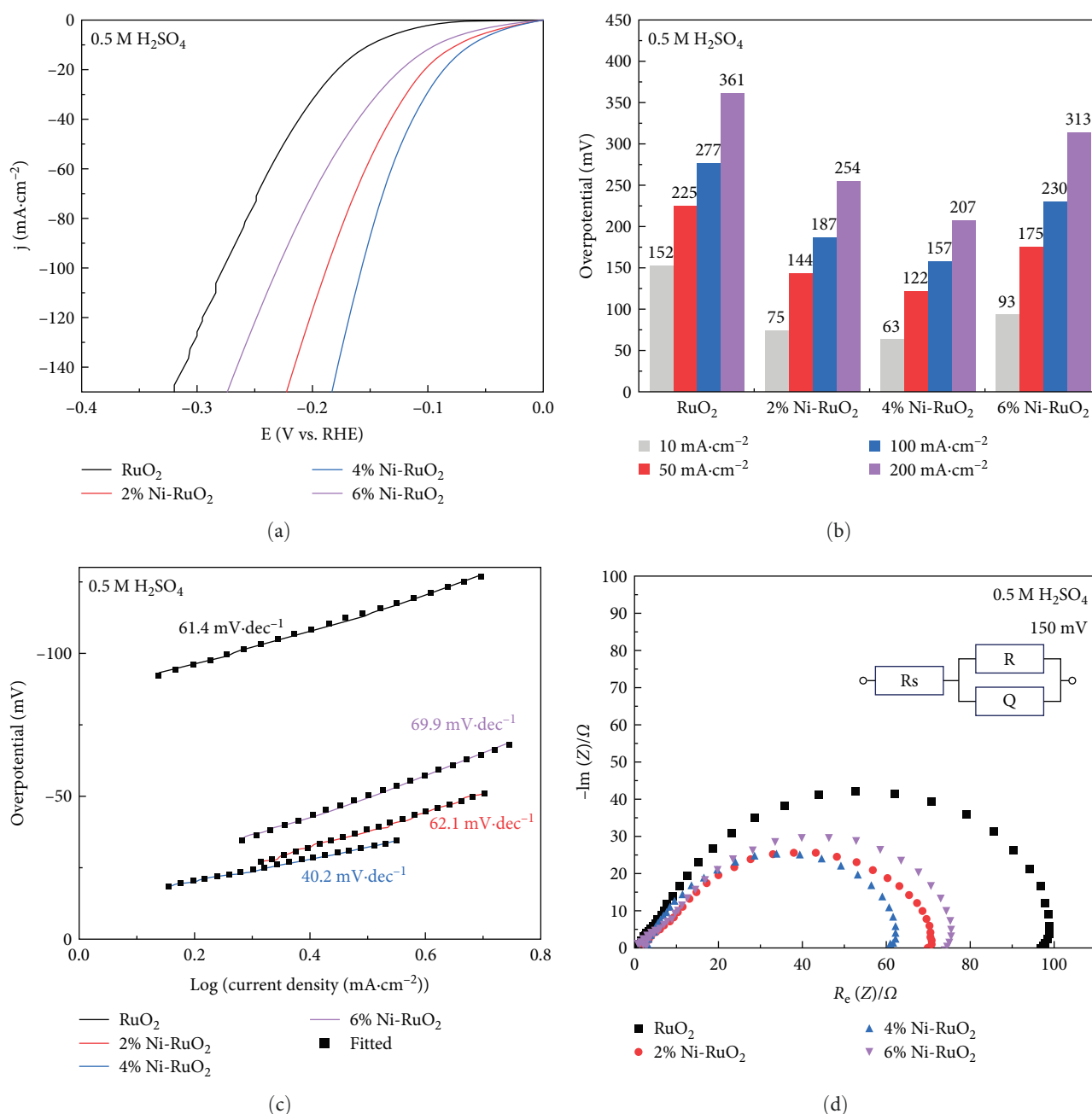


FIGURE 1: The electrochemical analyses of the RuO<sub>2</sub> aerogel catalyst with the addition of various concentrations of Ni: (a) the LSV curves providing a comparison of the electrochemical HER activities, (b) a bar chart providing a comparison of the overpotentials at current densities of 10, 50, 100, and 200 mA·cm<sup>-2</sup>, (c) the Tafel slopes (numerical values) obtained from the corresponding LSV curves, and (d) the EIS Nyquist plots obtained at 150 mV.

surface area increases slightly with the increase in Ni doping concentration. This is because the reaction between Ni chloride and the epoxide exhibits faster kinetics than the reaction with Ru chloride. Thus, when only Ni chloride was used to create a Ni(OH)<sub>2</sub> aerogel, the gelation process took around 30 min, and the resulting Ni(OH)<sub>2</sub> aerogel had a higher specific surface area of 413 m<sup>2</sup>·g<sup>-1</sup> [42, 43].

The surface chemical characteristics of the aerogel samples are further revealed by the XPS results in Figures 3(c) and 3 (d). Thus, in Figure 3(c), the main peaks of Ru 3p in

the RuO<sub>2</sub> aerogel are identified as Ru 3p<sub>3/2</sub> and Ru 3p<sub>1/2</sub> at 462.58 and 484.78 eV, respectively, corresponding to Ru<sup>4+</sup> [44]. Moreover, the Ru 3p peak positions exhibit various shifts to lower binding energy with the addition of Ni, thus signifying electron transfer from the Ni to RuO<sub>2</sub> [45] and enhanced electronic interactions between the Ni and RuO<sub>2</sub>. Meanwhile, a peak due to Ni appears in the Ni 2p spectrum upon the initial addition of Ni, and an extra peak develops with the increase in Ni concentration (Figure 3(d)). In addition, as shown in Figure S6, the presence of chlorine is also

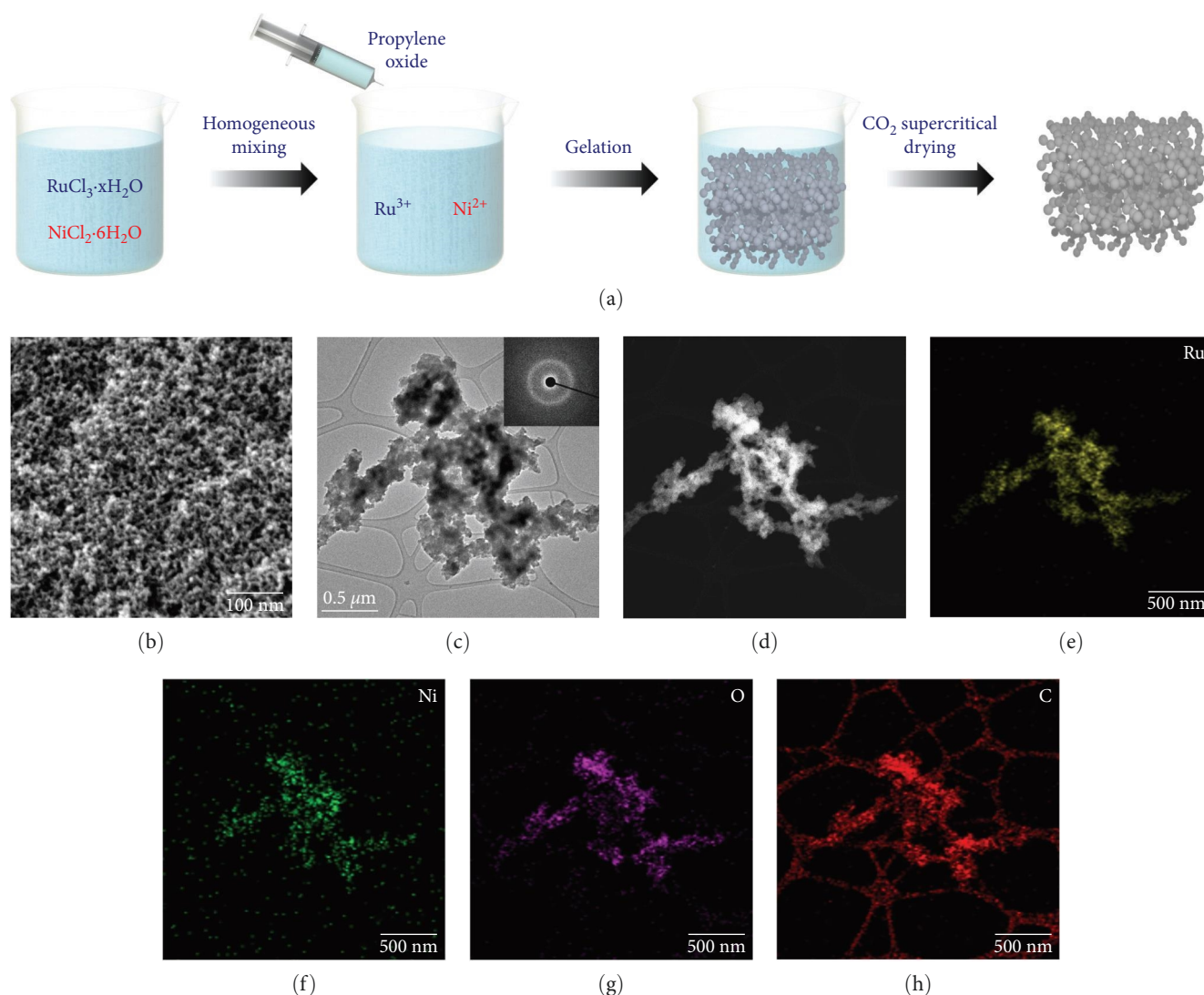


FIGURE 2: (a) A schematic diagram showing the synthetic procedure for the Ni-doped  $\text{RuO}_2$  aerogel. An SEM image (b), TEM image with inset SAED pattern (c), HAADF-STEM image (d), and EDX elemental mapping images of the 4% Ni- $\text{RuO}_2$  aerogel catalyst, including (e) Ru, (f) Ni, (g) O, and (h) C.

observed in the full survey spectra due to the use of chloride-based precursors during the synthesis.

The stability and durability of the 4% Ni- $\text{RuO}_2$  catalyst during 25 hr of continuous operation is demonstrated in Figures 4(a) and 4(b). Here, similar LSV curves are observed before and after the test, with a minimal decrease in the cathodic current. Figure S8 presents the results of the post-HER analyses conducted after subjecting the samples to long-term stability testing in acidic environments. The unique nanoporous structure of aerogel remained intact despite prolonged stability. Further, the CV curves of the pristine  $\text{RuO}_2$ , the 2% Ni- $\text{RuO}_2$ , the 4% Ni- $\text{RuO}_2$ , and the 6% Ni- $\text{RuO}_2$  catalysts at various scan rates are presented in Figure S7, and the corresponding electrochemical surface areas (ECSAs),

which are directly related to the double-layer capacitance of each catalyst [46, 47], are compared in in Figure 4(c). Here, the 4% Ni- $\text{RuO}_2$  catalyst exhibits the greatest ECSA, along with a high HER intrinsic activity, as indicated by the ECSA-normalized LSV curves in Figure 4(d).

Taken together, the above results demonstrate the advantages of the as-prepared catalyst, including (i) its aerogel architecture, (ii) its homogeneous doping, (iii) its amorphous structure, and (iv) its enhanced electrocatalytic activity, making it suitable for large-scale industrial use. Moreover, because the electrocatalytic reaction takes place on the surface of the composite material, its substantial specific surface area, high porosity, and extremely low density greatly influence its catalytic capability. In particular, the mesoporous 4% Ni-doped

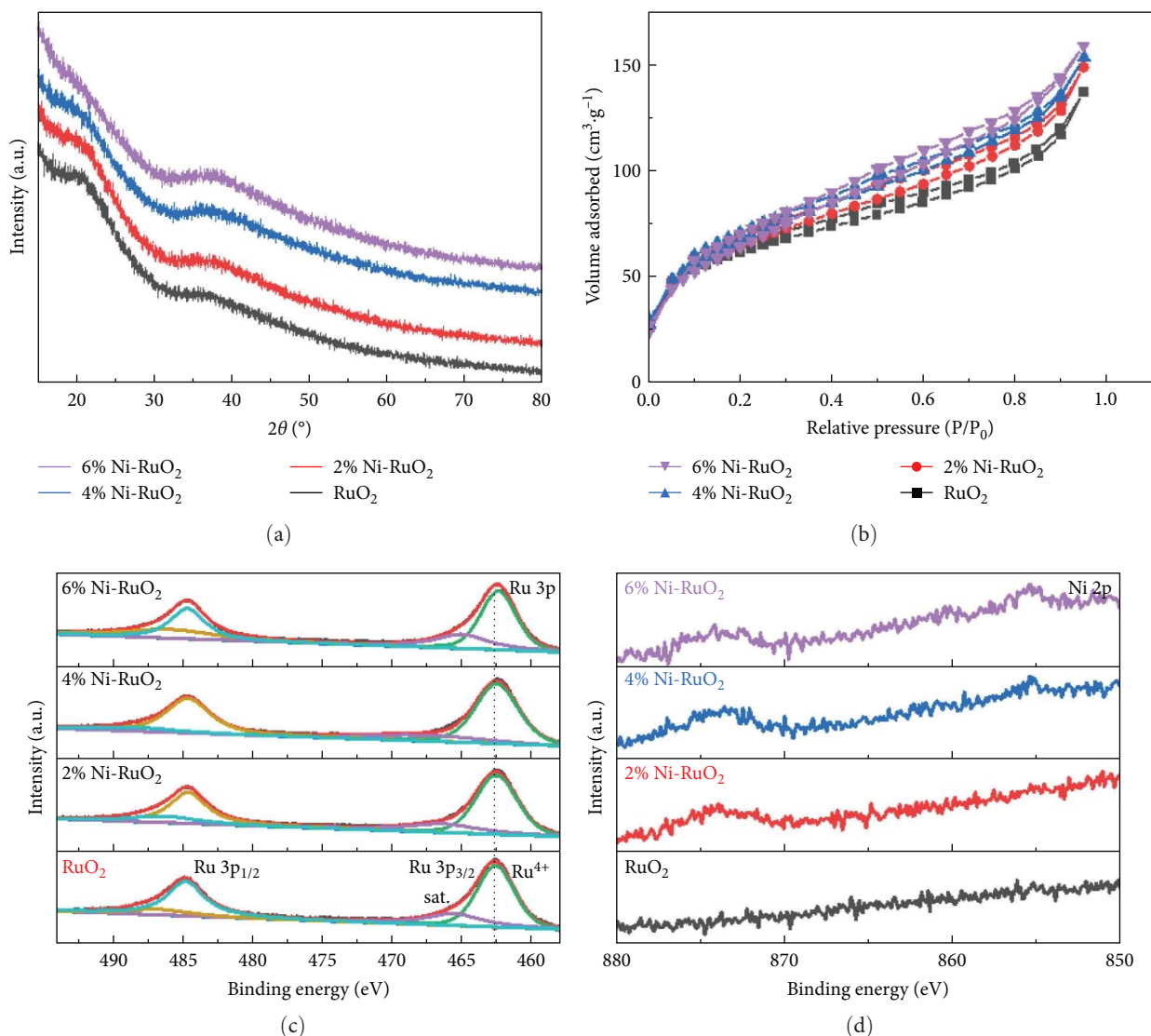


FIGURE 3: The XRD patterns (a), N<sub>2</sub> adsorption-desorption isotherms at 77 K (b), XPS Ru 3p spectra (c), and Ni 2p spectra (d), of the Ru-based aerogels with various Ni doping concentrations.

RuO<sub>2</sub> aerogel catalyst has a specific surface area of 241.5 m<sup>2</sup>·g<sup>-1</sup>, which is higher than that of many modern HER catalysts with high activity. In addition, the optimized doping concentration of Ni in the RuO<sub>2</sub> aerogel induces charge rearrangement on the sample surface, thereby leading to the exposure of additional reaction sites and ultimately improving the electrocatalytic activity. Furthermore, the 4% Ni-RuO<sub>2</sub> aerogel catalyst exhibits HER activities that are comparable to those of other Ru-based catalysts.

#### 4. Conclusions

Herein, a simple method was developed for the introduction of Ni into an RuO<sub>2</sub> aerogel to produce a catalytically active system. The nanoscaled network structure was shown to be highly porous, with the 4% Ni-doped RuO<sub>2</sub> exhibiting a

specific surface area of 241.5 m<sup>2</sup>·g<sup>-1</sup> due to its mesoporous structure. Notably, this is greater than that of numerous contemporary hydrogen evolution reaction (HER) catalysts known for their high activity. The improved HER performance was attributed to the optimal Ni doping, which provided a beneficial adsorption energy via charge redistribution on the sample surface, thereby uncovering extra reaction sites and enhancing the electrocatalytic performance. Moreover, the 4% Ni-doped RuO<sub>2</sub> aerogel showed good long-term stability in an acidic environment. In brief, the study presented a simple, novel, and flexible method for the Ni doping of RuO<sub>2</sub> aerogel electrocatalysts with great potential for extensive use in practical situations related to energy storage and conversion.

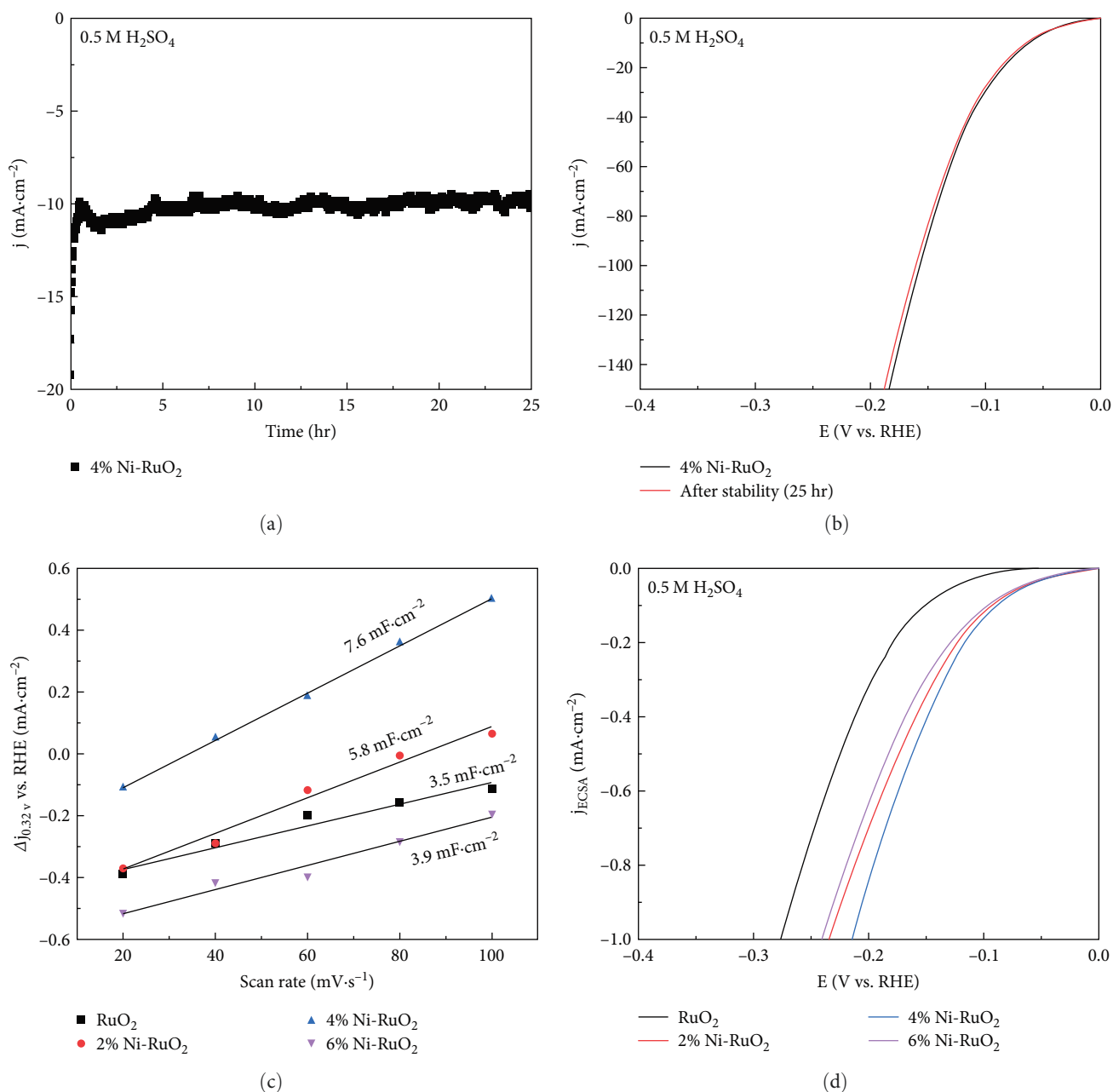


FIGURE 4: (a) The long-term (25-hr) stability test and (b) the LSV curves of the 4% Ni-RuO<sub>2</sub> before and after the stability test. (c) The electrochemical surface area (ECSA) values of the pristine RuO<sub>2</sub>, the 2% Ni-RuO<sub>2</sub>, the 4% Ni-RuO<sub>2</sub>, and the 6% Ni-RuO<sub>2</sub> calculated from the slope of the double layer capacitance at various scan rates. (d) The polarization curves of the various samples with the current normalized to the ECSA.

## Data Availability

Data will be made available on request.

## Conflicts of Interest

The authors declare that there are no known competing financial interests or personal relationships that could have influenced the work reported herein.

## Authors' Contributions

Taehee Kim was responsible for the conceptualization, formal analysis, and writing—original draft. Wonjun Lee was responsible for the methodology and formal analysis. Haryeong Choi and Vinayak G. Parale were responsible for the data curation. Umakant Patil was responsible for the writing—review and editing. Kazuyoshi Kanamori, Jeong Gil Seo, and Youn-Sang Bae were responsible for the writing—review

and editing. Sang-Woo Kim was responsible for the supervision and writing—review and editing. Hyung-Ho Park was responsible for the supervision, funding acquisition, and writing—review and editing.

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## Supplementary Materials

Figure S1: additional LSV, Tafel plots and EIS Nyquist plots. Figure S2: LSV curves without iR-correction. Figure S3: additional SEM images. Figure S4: HRTEM images. Figure S5: additional XRD and BET, BJH graphs. Figure S6: XPS survey scans. Figure S7: CV plots. Figure S8: post-analyses. Table S1: weight and atomic percentages of Ni doping. Table S2: pore properties. Table S3: comparison table. (*Supplementary Materials*)

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