# Superaerophobic Polyethyleneimine Hydrogels for Improving Electrochemical Hydrogen Production by Promoting Bubble Detachment

Misol Bae, Yunseok Kang, Dong Woog Lee, Dasom Jeon,\* and Jungki Ryu\*

Removal of gas bubbles from the electrode surface is practically important to maintain the activity of electrochemical gas evolution reactions. Conventionally, most studies have focused on the development of electrocatalysts and paid less attention to the bubble removal issues. Recently, it has been reported that attached gas bubbles can be readily eliminated by imparting extremely gas-repellent properties (so-called superaerophobicity) to electrodes via controlling their nano/microstructure. However, this approach is material-specific and requires harsh and expensive synthetic conditions, causing difficulties in scaling up to large-area electrodes for commercialization. To address these issues, a universal method to impart superaerophobicity to various electrodes through simple coating with porous polymeric hydrogels without affecting the underlying target substrates is reported. The modification of electrodes with superaerophobic polymeric hydrogel substantially enhances the efficiency of the hydrogen evolution reaction because the hydrogel can facilitate the removal of as-generated gas bubbles and thereby minimize ohmic and concentration overpotentials. Particularly, electrodes modified with the superaerophobic hydrogel outperform those modified with electrocatalysts at high current densities where more gas bubbles are generated and adhered to. The results provide insights into the design of various electrochemical devices that are based on gas-involving reactions.

M. Bae, Y. Kang, D. W. Lee, D. Jeon, J. Ryu Department of Energy Engineering School of Energy and Chemical Engineering Ulsan National Institute of Science and Technology (UNIST) Ulsan 44919, Republic of Korea E-mail: dsjeon@unist.ac.kr; jryu@unist.ac.kr M. Bae, Y. Kang, D. Jeon, J. Ryu Emergent Hydrogen Technology R&D Center Ulsan National Institute of Science and Technology (UNIST) Ulsan 44919, Republic of Korea D. Jeon, J. Ryu Center for Wave Energy Materials Ulsan National Institute of Science and Technology (UNIST) Ulsan 44919, Republic of Korea

D The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aenm.202201452.

© 2022 The Authors. Advanced Energy Materials published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

#### DOI: 10.1002/aenm.202201452

1. Introduction

Water electrolysis is one of the key technologies for carbon-neutrality because it can allow the effective utilization of fluctuating renewable electricity and the decarbonization of diverse sectors, such as chemical industries, transportation, and power generation.<sup>[1–5]</sup> Accordingly, researchers have extensively studied the development of efficient and stable electrocatalysts by using abundant and relatively inexpensive elements (e.g., Fe, Co, and Ni)<sup>[6-12]</sup> or minimizing the use of expensive elements (e.g., Ru, Ir, and Pt).<sup>[13-18]</sup> However, the development of such watersplitting electrocatalysts is a highly challenging task due to the well-known trade-off relationship between the activity and stability of electrocatalysts.<sup>[19-21]</sup> Moreover, even transition metals can have sustainability issues (Table S1, Supporting Information). On the contrary, the adsorption and desorption of produced gas bubbles have been overlooked despite their practical importance in water electrolysis (Figure 1).<sup>[22–24]</sup> The gas bubbles grow

and remain attached to the solid surface until the buoyancy force overcomes the adhesion force that is proportional to the radius of the gas bubble (Figure 1a). And the attached bubbles have a detrimental effect on the performance and stability of electrodes/electrocatalysts (Figure 1b).<sup>[25–27]</sup> They block electrochemical active sites and impede efficient mass transport, leading to a substantial increase of ohmic and concentration overpotentials.<sup>[28]</sup> Moreover, the adsorption and desorption cycle of gas bubbles can continuously exert stretch force to the electrode/catalysts and cause exfoliation of the catalysts.<sup>[29]</sup>

To address these issues, researchers have developed strategies to efficiently remove gas bubbles for improving the performance of water electrolysis (Figure 1c). For example, researchers reported the fabrication of extremely gas bubble-repellent (socalled superaerophobic) electrodes/electrocatalysts by controlling the morphology of themselves.<sup>[30]</sup> Examples include the aligned MoS<sub>2</sub> nanoplatelets<sup>[31]</sup> and pine-shaped Pt nanoarrays<sup>[32]</sup> for hydrogen evolution reaction (HER) and woodpile-structured Ir<sup>[33]</sup> and Ni<sup>[34]</sup> for oxygen evolution reaction. However, such strategies are material-specific, often require complex and harsh processes, or necessitate additional apparatus, making them



MATERIALS



**Figure 1.** The scheme for a mechanism of bubble-detachment. a) Normal flat electrode, b) the problems of adhered bubbles, and c) various approaches for the removal of gas bubbles. In (a), R,  $\rho$ , g, and  $\lambda$  indicate the dimension of bubbles, the density of a solution, gravitational acceleration constant, and surface tension of a solution, respectively.

difficult to scale up for practical application. In this context, we recently reported a method to impart superaerophobicity to the underlying electrode by coating it with porous hydrophilic hydrogel.<sup>[35]</sup> Despite its simplicity and universal applicability, it was limited to a proof-of-concept demonstration using flat Pt film that cannot be utilized for practical application.

In this study, we report a simple strategy to enhance the efficiency of electrochemical hydrogen production by imparting superaerophobicity to an underlying electrode with porous polymeric hydrogels. Superaerophobic hydrogels were readily coated on target substrates by cross-linking polyethyleneimine (PEI) via Schiff-base condensation reactions followed by freeze-drying. We can readily control the pore size, porosity, and superaerophobicity of the hydrogel-coated electrodes by varying the concentrations of PEI upon crosslinking. The deposition of porous PEI hydrogel substantially improved both the aerophobicity and HER performance of the flat Pt and porous Ni foam (NF) electrodes without noticeable performance degradation for 20 h. Notably, the PEI hydrogelmodified NF exhibited a superior performance even without additional HER electrocatalysts especially at a current density higher than -500 mA cm<sup>-2</sup> due to a notable decrease of ohmic and concentration overpotentials. These results imply the feasibility of a practical electrolyzer through enhanced hydrogen evolution by controlling the wettability of electrodes with superaerophobic hydrogels without expensive electrocatalysts.

# 2. Results and Discussion

Polymeric hydrogels were readily coated on the desired substrates by cross-linking PEI (Figure 2). Note that in our previous study<sup>[36]</sup> for the proof-of-concept demonstration, we used M13 bacteriophage as a building block of hydrogels due to its inherent nanofibrillar structure beneficial for obtaining porous nanostructures as well as hydrophilicity. However, M13 bacteriophage is not only expensive but also difficult to culture and handle for those who do not have proper biotechnological knowledge and training. In this regard, we selected commercially available and inexpensive branched PEI (Mn = 10000) as a building framework that has inherent hydrophilicity and abundant amine groups for cross-linking. PEI was cross-linked via Schiff-base condensation reaction using glutaraldehyde and freeze-dried on the desired electrode (Figure 2a). For improved adhesion of PEI hydrogels, target electrodes were functionalized with amine groups-which can form covalent bonding with PEI using glutaraldehyde-via aminosilane treatment, and it had no significant effects on the wetting properties and electrocatalytic activity of the underlying electrodes (vide infra). We hypothesized that PEI hydrogel-coated electrodes without additional electrocatalysts can exhibit superaerophobicity and outperform those modified with electrocatalysts, especially at high current densities, because attached bubbles can significantly lower mass transport and active surface area for electrochemical reactions.

www.advancedsciencenews.com

ANCED

ADVANCED ENERGY MATERIALS www.advenergymat.de



Figure 2. a) The mechanism for cross-linking of PEI with GA. b) Photographs of the NF electrodes before and after the coating with PEI hydrogel. c-f) SEM images of various NF-based electrodes: c) Bare NF, d) PEI-0.5%, e) PEI-2.0%, and f) PEI-7.3%. g) Air contact angles of the NF-based electrodes.

To control the structure and aerophobicity of hydrogels, we tested cross-linking of PEI at various concentrations (hereafter, PEI-X.X%, X.X denotes the initial concentration of PEI) (Figure 2a,b). The concentration of PEI varied from 0.5% to 7.3% while maintaining the concentration of glutaraldehyde at a constant of 1 wt.%. For the deposition on the desired electrode, we employed two different methods: dip-coating for NF and spin-coating for flat Pt film. Scanning electron microscopy (SEM) and elemental mapping analysis confirmed the deposition of porous PEI hydrogel networks over the entire substrate, confirming that a large portion of the substrate was exposed to an electrolyte (Figure 2c–f; Figures S1–S3, Supporting Information). The morphology of PEI hydrogel is independent of the types of the underlying substrates and coating methods but highly dependent on the PEI concentration. We found that PEI can be gelated at concentrations higher than 0.5%. After freeze-drying, gelated PEI (i.e., PEI-2.0%, PEI-5.5%, and PEI-7.3%) exhibited a porous network structure (Figure 2e,f; Figure S2, Supporting Information), whereas PEI-0.5% formed aggregates without any porous structure (Figure 2d). According to image analysis using custom-made software (please see the experimental part for more information), the pore size and porosity of the PEI hydrogel were gradually decreased with the increase of PEI concentration (Figure S3, Supporting Information). However, uniform pore size was observed within each hydrogel prepared by a different concentration of PEI (Figure S3, Supporting Information). The average pore sizes of PEI-2.0%, PEI-5.5%, and PEI-7.3% were 20.18, 12.98, and

ADVANCED SCIENCE NEWS

11.15  $\mu m$  with the corresponding porosities of 10.94%, 5.01%, and 2.37%, respectively.

We found that the aerophobicity of substrates can be substantially increased by modifying them with porous PEI hydrogels (2g; Figure S4, Supporting Information). To exclude the effect of the morphology of substrates on their wetting behavior, we used a flat Pt-coated fluorine-doped tin oxide (FTO) and porous NF as model substrates to compare their air contact angles before and after the modification. The PEI-modification substantially increased the air contact angle, regardless of the underlying substrates and PEI concentration. In particular, the deposition of PEI-2.0% hydrogels imparted superaerophobicity with the air contact angle higher than 150° (153.7° for NF and 147.7° for Pt-FTO). Although PEI-5.5% and PEI-7.3% also exhibited significantly enhanced aerophobicity, they had a slightly lower air contact angle than PEI-2.0%. One can expect that sufficiently high concentration of PEI leads to the cross-linking of most amine groups and even agglomeration of PEI, resulting in the burial of hydrophilic amine groups. Indeed, SEM analysis showed that PEI-7.3% with a lower air contact angle have large agglomerations of PEI. PEI-0.5% did not form porous network structure and was less effective to increase an air contact angle from 134.5° to 141.8°. These results suggest that the hydrophilicity and porous structure of PEI play a critical role in implementing superaerophobicity to the substrates.

Then, we investigated the effect of aerophobicity imparted by modification with PEI on the HER performance of electrodes (Figure 3). We tested the HER activity of porous NF electrodes without any additional electrocatalysts and flat Pt electrodes under alkaline conditions (1 M KOH, pH 14). We found that APTES treatment had a negligible influence on the

performance of the electrode (Figure S5, Supporting Informtion). However, the modification with PEI hydrogel significantly improved the HER performance, regardless of electrodes (Figure 3a; Figure S6, Supporting Information). It is noteworthy that the performance improvement becomes larger at higher current densities probably due to the large amounts of attached gas bubbles. In particular, the electrodes modified with PEI-2.0% hydrogel exhibited the best performance. At a current density of -500 mA cm<sup>-2</sup>, for example, the bare NF, PEI-0.5%, PEI-2.0%, PEI-5.5%, and PEI-7.3% electrodes required a potential of 774.3, 656.6, 608.8, 660.3, and 718.7 mV versus reversible hydrogen electrode (RHE), respectively, without ohmic potential drop compensation (iR compensation). We found that PEI with both the highest aerophobicity and porosity had the best performance (Figure 3b). One can expect that both the aerophobicity and porosity of electrodes can have counter effects on their performance. This can also explain why PEI-0.5% with a lower aerophobicity and a higher porosity can have an HER performance comparable to PEI-5.5%.

To better understand the observed performance improvement by PEI hydrogel, we conducted electrochemical impedance spectroscopy (EIS) and the measurement of electrochemically active surface area (ECSA) before and after the modification with the hydrogel. EIS results at -0.25 V versus RHE showed that after the modification of NF with PEI-2.0% hydrogel, there was a decrease of both the series resistance ( $R_1$ ) related to the electronic and ionic conduction throughout the circuit and the charge transfer resistance ( $R_2$ ) related to the efficiency of electrochemical reactions (Figure 3c). The decrease of both  $R_1$  and  $R_2$  values indirectly suggests efficient removal of gas bubbles by the imparted superaerophobicity because the



Figure 3. a) The effect of hydrogels on the HER performance of NFs. b) The effect of the concentration of PEI on HER efficiency, aerophobicity, and porosity of the PEI hydrogels. c) EIS and d) ECSA of PEI-2.0% hydrogel-modified and bare NF electrode.



attached gas bubbles can lead to the reduction of surface area and increase both ohmic and concentration overpotentials.[37] More in-depth EIS analysis can be found in the following section. According to ECSA analysis, the modification led to only a slight decrease of the active surface area (Figure 3d; Figure S7, Supporting Information). For example, the bare and PEI-2.0% hydrogel-modified NF electrodes have ECSA values of 1.315 and  $1.072 \text{ mF cm}^{-2}$ , whereas their current densities at -0.6 V versus RHE were -265.7 and -488.6 mA cm<sup>-2</sup>, respectively. Despite a slight reduction of the active surface area, the hydrogel coating significantly enhanced the overall HER performance, implying a much greater beneficial effect of hydrogel on the bubble detachment than the negative effect (e.g., partial blocking of active sites). This also suggests that too small pore sizes can lead to performance degradation due to significant blocking of the active site.

To demonstrate our hypothesis that the PEI hydrogel-coated electrodes without additional electrocatalysts outperform those modified with electrocatalysts at high current densities, we prepared and tested NF electrodes modified with various electrocatalysts (**Figure 4**). For comparison, we deposited nickel hydroxide nanoparticle (Ni(OH)<sub>2</sub>),<sup>[38]</sup> iron and nickel double hydroxide (FeNi),<sup>[39]</sup> nickel nanotube array (NTA),<sup>[40]</sup> and metallic Ru layer<sup>[41]</sup> as representative HER catalysts (Figure S8, Supporting Information). Note that it is generally recommended to carry out the characterization of catalysts' performance after iR compensation for fair comparison of their intrinsic activity.<sup>[42]</sup> In this study, however, we intentionally did not apply iR compensation unless stated otherwise because the adhered gas

bubbles can extrinsically affect their performance by lowering the efficiencies of mass transport and catalytic charge transfer processes. As expected, at lower current densities, the NF electrode modified with PEI-2.0% hydrogel had a moderate HER activity: better than those with inexpensive transition metalbased catalysts (i.e., Ni(OH)2, FeNi, and NTA) but lower than that with expensive precious metal-based catalysts (i.e., Ru). However, at a current density higher than  $\approx$ -500 mA cm<sup>-2</sup>, the PEI-2.0% hydrogel-coated electrode outperformed Ru-modified electrode (Figure 4a; Figures S10,S11, Supporting Information) due to efficient removal of hydrogen bubbles. For example, NF electrodes modified with PEI-2.0% hydrogel and metallic Ru required applied potential of -0.608 and -0.617 mV versus RHE at 500 mA cm<sup>-2</sup>, respectively. The PEI-2.0% hydrogel electrode had a Tafel slope similar to that of the bare NF electrode, whereas NF electrodes modified with various electrocatalysts had a smaller Tafel slope than the latter (Figure S9, Supporting Information). These results suggest that PEI hydrogel had a negligible influence on the HER mechanism,<sup>[43-44]</sup> whereas electrocatalysts had a profound influence.

To more clearly demonstrate the role of superaerophobic PEI hydrogels in the observed outstanding performance, we examined the HER performance of various NF electrodes with and without iR corrections and conducted EIS analysis (Figure 4c; Table S2, Supporting Information). Since an iR drop is related to the solution resistance in the electrolyte, we speculated that the superaerophobic electrodes had relatively low ionic resistance and thus could reduce the discrepancy in the applied voltages between with and without iR correction



**Figure 4.** a) LSV curves of various electrodes for alkaline hydrogen production (without an iR correction). b) Comparison of HER performance with and without iR corrections. c) The EIS analysis of (a) systems. d) The corresponding bar graph to (c).

( $\Delta V$ ). The bubble-repellency led to a smaller  $\Delta V$  at high current densities. The bare and PEI hydrogel-modified electrodes had almost identical polarization curves after iR corrections, again confirming no or negligible catalytic activity of the hydrogel. EIS analysis showed that the hydrogel modification significantly lower both  $R_1$  and  $R_2$  values (Figure 4c,d). Although the electrodes modified with electrocatalysts also had much lower  $R_2$  values, they had higher  $R_1$  value than the bare counterpart. Of note,  $R_1$  is a series resistance related to the electrical conduction through an external circuit  $(R_{ext})$ , contact resistance between a support and a catalyst/overlayer ( $R_{contact}$ ), and a resistance about the ionic conduction through an electrolyte ( $R_{\text{ionic}}$ ):  $R_1 = R_{\text{ext}} + R_{\text{contact}} + R_{\text{ionic}}$ ). One can easily know that the bare and hydrogel-coated NF electrodes have the same Rext value and that the  $R_{\text{contact}}$  value of the bare should be 0 (because NF directly contacts with an electrolyte), smaller than that of the hydrogel-modified one. However, the hydrogel coated electrode had a lower  $R_1$  value than the bare one, suggesting that the former has a much smaller  $R_{\text{ionic}}$  than the latter. Since we utilized the same electrolyte throughout experiments, the different  $R_{\text{ionic}}$  values can be attributed to the different active surface area of electrodes. Considering that the hydrogel-coated one has a smaller ECSA than the bare one (Figure 3d), a smaller R<sub>1</sub> value and higher activity of the hydrogel-coated electrode can be attributed to its higher surface area during HER by facile removal of the attached gas bubbles. All the analysis results support that the superior performance of hydrogelmodified electrodes can be attributed to facile removal of gas bubbles by superaerophobicity.

DVANCED

SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

**Figure 5** shows the suggested mechanism for the performance enhancement by PEI hydrogel. Upon the application of cathodic potential, there would be the production of hydrogen and the nucleation of gas bubbles. Further generation of hydrogen leads to the growth of gas bubbles, resulting in the blocking of active surface area for HER. Once the buoyance



**Figure 5.** Suggested mechanism for the enhanced hydrogen evolution activity by superaerophobic hydrogel.

force overcomes the adhesion force, the adhered gas bubble can be detached from the electrode surface. Porous and hydrophilic nature of hydrogel can not only lower bubble's adhesion force but also prevent the blocking of active sites. In other words, we can physically separate catalytic active sites (i.e., electrode surface) and bubble repelling sites (hydrogel overlayer). Porous network structure may also provide a path for bubble removal. As a result, hydrogel-coated electrodes can maintain higher catalytically active surface area during water electrolysis and have higher activity than the bare electrode. Thus, in principle, our strategies can also be applied to various gas-evolving reactions, such as oxygen evolution and hydrazine oxidation reactions. However, the application of hydrogel in such oxidation reactions may require the exploration of stable hydrogels as well as further optimization since many organic and polymeric materials can be oxidized at highly anodic potentials.

To check the stability of superaerophobic polymeric hydrogels for practical application, we conducted two types of long-term stability tests: repeated CV cycles and chronopotentiometry (Figure 6). There was a negligible change in the shape of the polarization curves before and after repeated CV cycles for 1000 times with a scan rate of 100 mV s<sup>-1</sup> (Figure 6a). Also, Raman analysis showed the chemical stability of PEI hydrogelmodified electrode after 1000 cycles of CV test (Figure 6b). Chronopotentiometry was performed at current densities of -100, -300, and -500 mA cm<sup>-2</sup>, which is more relevant to practical water electrolysis conditions. The hydrogel-modified electrodes maintained stable potentials of  $\approx$ -0.5, -0.55, and -0.7 V versus RHE for 20 h, respectively, without any external convection (Figure 6c; Figure S12, Supporting Information). It is noteworthy here that as the applied current density increased, the difference between the required potential for the bare NF and PEI-2.0% electrodes increased more. Considering that more hydrogen bubbles are produced and attached to the electrodes at a higher current density, these results demonstrate significance of bubble detachment issue and validity of our approach to address this issue. Structural stability of hydrogel-modified electrodes was confirmed by SEM and air contact angle measurements before and after the stability tests by the repeated CV cycles and chronopotentiometry (Figure 6d). Regardless of the testing conditions, there were negligible changes of their morphology and air contact angles. Even after chronopotentiometry at -500 mA cm<sup>-2</sup> for 20 h, PEI-2.0% hydrogel maintained its superaerophobicity and inherent porous structure. However, one can expect that the performance of hydrogel-modified electrodes can be degraded by many factors: e.g., 1) structural collapse due to continuous mechanical stress caused by repeated bubble growth and departure cycles and 2) chemical degradation under more harsh conditions (e.g., hydrolysis of cross-linked PEI at extreme pHs).

## 3. Conclusion

In summary, we report that the performance of electrodes for alkaline HER can be significantly improve even without expensive electrocatalysts and complicated processes by modifying them with superaerophobic polymeric hydrogels. Briefly, the porosity, aerophobicity, HER activity of electrodes can be www.advancedsciencenews.com

DVANCED





**Figure 6.** Stability of superaerophobic PEI hydrogels. a) Measurement of LSV before and after CV 1000 times within the same sweep potential range. b) Raman spectroscopy to confirm the structural stability after 1000 cycles of CV test. c) Chronopotentiometry of the bare and hydrogel-modified NF electrodes at  $-500 \text{ mA cm}^{-2}$  for 20 h without any external convection. d) SEM images of the hydrogel-modified NF electrodes after the corresponding stability test. Inset shows air contact angles.

controlled by changing the concentration of building block polymers for cross-linking. Due to facile removal of as-generated hydrogen bubbles, the NF electrode modified with PEI hydrogel only outperformed those modified with expensive electrocatalysts especially at high current densities. We believe that our results can pave the way for the practical application of water electrolysis by providing insights into the design of electrodes and electrolyzers.

## 4. Experimental Section

*Materials*: NF (thickness: 1.6 mm) was purchased from MTI (Korea). Pt film with an average thickness of 500 nm was coated on FTO by an electron beam evaporator. PEI with a number average molecular weight of 10 000, KOH ( $\geq$ 85%), HCl (37%), NaCl, (3-aminopropyl) triethoxysilane (APTES, 99%), and ethanol were purchased from Sigma–Aldrich (USA). Glutaraldehyde (50 wt.% in H<sub>2</sub>O) was obtained from Alfa Aesar (USA).

Deposition of Cross-Linked PEI on Target Substrates: Before the deposition of cross-linked PEI, all substrates were functionalized with amine groups to improve the adhesion of PEI to the substrates using APTES according to literature.<sup>[45]</sup> PEI was dissolved at desired concentrations of 0.5%, 2%, 5.5%, and 7.3% (v/v) in 37.5 × 10<sup>-3</sup> M NaCl solution. The pH of the PEI solutions was adjusted to ≈6.0 using concentrated HCl. NF was coated with PEI hydrogel by dipping methods: 1) dipping in PEI solution under mild stirring for 1 h, 2) baking at 120 °C for 10 min for better adhesion of PEI and the substrate,<sup>[46–47]</sup> 3) cross-linking PEI with 1 wt.% glutaraldehyde (in H<sub>2</sub>O) for 1 min, and 4) freeze-drying. PEI hydrogel was deposited on flat Pt film by 1) spin-coating the 2% PEI solution at

1250 rpm for 2 min, 2) baking at 120  $^\circ C$  for 10 min, 3) cross-linking PEI with 1 wt.% glutaraldehyde for 5 min, and 4) freeze-drying.

Preparation of Alkaline HER Electrocatalysts: Ni(OH)<sub>2</sub> nanoparticles,<sup>[38]</sup> iron-nickel double hydroxide (FeNi),<sup>[39]</sup> nickel nanotube array (NTA),<sup>[40]</sup> and metallic Ru electrocatalysts<sup>[41]</sup> were prepared according to literature and deposited on NF. Ni(OH)<sub>2</sub> was electrodeposited on NF at a constant cathodic current density of 5 mA cm<sup>-2</sup> for 300 s, rinsed with deionized water and ethanol, and dried in air at 60 °C. For the synthesis of FeNi, NF was hydrothermally reacted with the aqueous solution (30 mL) containing Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O (0.3030 g), NH<sub>4</sub>F (0.1666 g), and urea (0.54 g) at 120 °C for 12 h and then with that containing Ni(NO)<sub>3</sub>•6H<sub>2</sub>O (0.0218 g), NH<sub>4</sub>F (0.0167 g), and urea (0.054 g) at 120 °C for 12 h. The resultant FeNi on NF was dried in vacuum at 60 °C. NTAs were prepared by electrodepositing NiCu alloy film on NF and etching at 0.5 V for 30 min in the same electrolyte under the following conditions: -0.8 V for 1 h in an aqueous electrolyte of 0.5 м NiSO<sub>4</sub>, 0.025 м CuSO<sub>4</sub>, and 0.25 м H<sub>3</sub>BO<sub>3</sub>. Surface oxide was removed by treating with 1 M HCl. Metallic Ru HER catalysts were hydrothermally synthesized on NF using  $1 \times 10^{-3}$  M RuCl<sub>3</sub> solution in the 1:1 mixture of ethylene glycol and deionized water at 90 °C for 2 h. The resulting product was repeatedly rinsed with deionized water and ethanol, and then dried at 60 °C.

*Characterization*: Spectroscopic analysis was conducted using a 670/620 Fourier-transform infrared (FT-IR) spectrometer (Agilent, USA) in an ATR mode and alpha300 S Raman spectrometer (WITec, Germany) upon excitation at 532 nm. Morphology of cross-linked PEI on target substrates was observed with an S-4800 scanning electron microscope (Hitachi, Japan). Average pore diameter and porosity of PEI-modified electrodes were calculated using custom-made software (http://39.122.59.86:3000/). Of note, custom-made porosity analyzer was based on an algorithm similar to freely-available ImageJ software—that counts the fraction of pore pixels based on contrast and bright differences—but can have higher accuracy than

SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

DVANCED

Image) because it allows more flexible control for image analysis. The air contact angles were measured by a DSA100 drop shape analyzer (KRÜSS GmbH, Germany).The air contact angle was also measured by using custom-made software (https://contact-angle.superclass.io/multiple).

*Electrochemical Measurements*: All electrochemical characterizations were conducted in 1 multiple KOH (pH 14). Polarization curves were measured using an SP-150 potentiostat/galvanostat (Bio-Logic Science Instruments, France) under the following conditions: a reference electrode, Ag/AgCl (1 multiple KCl); a counter electrode, Pt mesh; and scan rate, 10 mV s<sup>-1</sup>. Electrochemical impedance spectra were measured under the following conditions: a reference electrode, Ag/AgCl; a counter electrode, Ag/AgCl; a counter electrode, Pt mesh; applied potential, -0.25 V versus RHE; amplitude, 20 mV; and frequency scan range, 100 kHz to 0.1 Hz.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

#### Acknowledgements

This work was supported by the Basic Science Research Program (2021R1A2C2013684 and 2021R1A6A3A01088433) and the Technology Development Program to Solve Climate Changes (2019M1A2A2065614) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT of Korea. This research was also supported by "Regional Innovation Strategy (RIS)" through the NRF funded by the Ministry of Education (MOE) (2021RIS-003).

# **Conflict of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## **Keywords**

hydrogels, hydrogen evolution reaction, polyethyleneimine, superaerophobicity, three-phase interface

Received: April 28, 2022 Published online:

- J. A. Cracknell, K. A. Vincent, F. A. Armstrong, Chem. Rev. 2008, 108, 2439.
- [2] T. M. Gur, Energy Environ. Sci. 2018, 11, 3055.
- [3] J. R. Varcoe, P. Atanassov, D. R. Dekel, A. M. Herring, M. A. Hickner, P. A. Kohl, A. R. Kucernak, W. E. Mustain, K. Nijmeijer, K. Scott, T. W. Xu, L. Zhuang, *Energy Environ. Sci.* 2014, *7*, 3135.
- [4] J. T. S. Irvine, D. Neagu, M. C. Verbraeken, C. Chatzichristodoulou, C. R. Graves, M. B. Mogensen, *Nat. Energy* 2016, 1, 15014.
- [5] I. Vincent, D. Bessarabov, Renew. Sust. Energy Rev. 2018, 81, 1690.
- [6] W. J. He, L. L. Han, Q. Y. Hao, X. R. Zheng, Y. Li, J. Zhang, C. C. Liu, H. Liu, H. L. L. Xin, ACS Energy Lett. 2019, 4, 2905.

#### www.advenergymat.de

- [7] L. H. Zhuang, L. Ge, Y. S. Yang, M. R. Li, Y. Jia, X. D. Yao, Z. H. Zhu, Adv. Mater. 2017, 29, 1606793.
- [8] P. W. Du, R. Eisenberg, Energy Environ. Sci. 2012, 5, 6012.
- [9] M. Abu Sayeed, T. Herd, A. P. O'Mullane, J. Mater. Chem. A 2016, 4, 991.
- [10] D. Friebel, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M. J. Cheng, D. Sokaras, T. C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Norskov, A. Nilsson, A. T. Bell, J. Am. Chem. Soc. 2015, 137, 1305.
- [11] M. Gong, Y. G. Li, H. L. Wang, Y. Y. Liang, J. Z. Wu, J. G. Zhou, J. Wang, T. Regier, F. Wei, H. J. Dai, J. Am. Chem. Soc. 2013, 135, 8452.
- [12] B. H. Solis, S. Hammes-Schiffer, J. Am. Chem. Soc. 2012, 134, 15253.
- [13] T. Reier, M. Oezaslan, P. Strasser, ACS Catal. 2012, 2, 1765.
- [14] B. M. Tackett, W. C. Sheng, S. Kattel, S. Y. Yao, B. H. Yan, K. A. Kuttiyiel, Q. Y. Wu, J. G. G. Chen, ACS Catal. 2018, 8, 2615.
- [15] Y. J. Wang, N. N. Zhao, B. Z. Fang, H. Li, X. T. T. Bi, H. J. Wang, *Chem. Rev.* 2015, 115, 3433.
- [16] L. C. Seitz, T. J. P. Hersbach, D. Nordlund, T. F. Jaramillo, J. Phys. Chem. Lett. 2015, 6, 4178.
- [17] B. Jiang, Y. N. Guo, J. Kim, A. E. Whitten, K. Wood, K. Kani, A. E. Rowan, J. Henzie, Y. Yamauchi, J. Am. Chem. Soc. 2018, 140, 12434.
- [18] Y. C. Pi, N. Zhang, S. J. Guo, J. Guo, X. Q. Huang, Nano Lett. 2016, 16, 4424.
- [19] S. P. Chen, Z. Q. Niu, C. L. Xie, M. Y. Gao, M. L. Lai, M. F. Li, P. D. Yang, ACS Nano 2018, 12, 8697.
- [20] X. Liang, L. Shi, R. Cao, G. Wan, W. S. Yan, H. Chen, Y. P. Liu, X. X. Zou, Adv. Mater. 2020, 32, 2001430.
- [21] W. R. Zheng, L. Y. S. Lee, K. Y. Wong, Nanoscale 2021, 13, 15177.
- [22] A. R. Zeradjanin, P. Narangoda, I. Spanos, J. Masa, R. Schlogl, Curr. Opin. Electrochem. 2021, 30, 100797.
- [23] J. K. Lee, A. Bazylak, Joule 2021, 5, 19.
- [24] W. W. Xu, Z. Y. Lu, P. B. Wan, Y. Kuang, X. M. Sun, Small 2016, 12, 2492.
- [25] J. K. Zhang, F. Y. Dong, C. Q. Wang, J. M. Wang, L. Jiang, C. M. Yu, ACS Appl. Mater. Interfaces 2021, 13, 32435.
- [26] J. J. Shen, B. Li, Y. Zheng, Z. Y. Dai, J. L. Li, X. Z. Bao, J. P. Guo, X. Q. Yu, Y. Guo, M. Z. Ge, W. Lei, H. Y. Shao, *Chem. Eng. J.* **2021**, 133517.
- [27] Y. Yang, J. Li, W. Yang, Y. R. Yang, Q. Fu, L. Zhang, Q. Liao, X. Zhu, Chem. Eng. J. 2021, 407, 127159.
- [28] A. Angulo, P. van der Linde, H. Gardeniers, M. Modestino, D. F. Rivas, *Joule* 2020, 4, 555.
- [29] Q. Song, Z. J. Xue, C. Liu, X. Z. Qiao, L. Liu, C. H. Huang, K. Y. Liu, X. Li, Z. L. Lu, T. Wang, J. Am. Chem. Soc. 2020, 142, 1857.
- [30] X. J. Feng, L. Jiang, Adv. Mater. 2006, 18, 3063.
- [31] D. Seo, A. M. Schrader, S.-Y. Chen, Y. Kaufman, T. R. Cristiani, S. H. Page, P. H. Koenig, Y. Gizaw, D. W. Lee, J. N. Israelachvili, *Proc. Natl. Acad. Sci. USA* 2018, 115, 8070.
- [32] Z. Y. Lu, W. Zhu, X. Y. Yu, H. C. Zhang, Y. J. Li, X. M. Sun, X. W. Wang, H. Wang, J. M. Wang, J. Luo, X. D. Lei, L. Jiang, Adv. Mater. 2014, 26, 2683.
- [33] Y. J. Li, H. C. Zhang, T. H. Xu, Z. Y. Lu, X. C. Wu, P. B. Wan, X. M. Sun, L. Jiang, Adv. Funct. Mater. 2015, 25, 1737.
- [34] Y. J. Kim, A. Y. Lim, J. M. Kim, D. H. Lim, K. H. Chae, E. N. Cho, H. J. Han, K. U. Jeon, M. H. Kim, G. H. Lee, G. R. Lee, H. S. Ahn, H. S. Park, H. S. Kim, J. Y. Kim, Y. S. Jung, *Nat. Commun.* **2020**, *11*, 4921.
- [35] T. Y. Kou, S. W. Wang, R. P. Shi, T. Zhang, S. Chiovoloni, J. Q. Lu, W. Chen, M. A. Worsley, B. C. Wood, S. E. Baker, E. B. Duoss, R. Wu, C. Zhu, Y. Li, *Adv. Energy Mater.* **2020**, *10*, 2002955.

#### **ADVANCED** SCIENCE NEWS

www.advancedsciencenews.com



- [36] D. Jeon, J. Park, C. Shin, H. Kim, J. W. Jang, D. W. Lee, J. Ryu, Sci. Adv. 2020, 6, eaaz3944.
- [37] G. B. Darband, M. Aliofkhazraei, S. Shanmugam, Renew Sust Energ Rev 2019, 114, 109300.
- [38] B. Zhang, J. Liu, J. S. Wang, Y. J. Ruan, X. Ji, K. Xu, C. Chen, H. Z. Wan, L. Miao, J. J. Jiang, *Nano Energy* **2017**, *37*, 74.
- [39] K. F. Huang, R. H. Dong, C. Wang, W. Li, H. X. Sun, B. Y. Geng, ACS Sustainable Chem. Eng. 2019, 7, 15073.
- [40] D. D. Li, G. Y. Hao, W. J. Guo, G. Liu, J. P. Li, Q. Zhao, J. Power Sources 2020, 448, 227434.
- [41] J. W. Xia, M. Volokh, G. M. Peng, Y. S. Fu, X. Wang, M. Shalom, *ChemSusChem* **2019**, *12*, 2780.
- [42] L. Yu, Z. Ren, Mater. Today Phys. 2020, 14, 100253.
- [43] W. Gao, W. Y. Gou, X. M. Zhou, J. G. Ho, Y. Y. Ma, Y. Q. Qu, ACS Appl. Mater. Interfaces 2018, 10, 1728.
- [44] A. Lasia, Int. J. Hydrog. Energy 2019, 44, 19484.
- [45] H. Yuk, T. Zhang, S. T. Lin, G. A. Parada, X. H. Zhao, Nat. Mater. 2016, 15, 190.
- [46] T. Davidson-Hall, H. Aziz, Nanoscale 2018, 10, 2623.
- [47] S. Ohisa, D. Takashima, T. Chiba, J. Kido, J. Mater. Chem. C 2019, 7, 6759.