Tuning the Polarity of a Fibrous Poly(vinylidene fluoride-co-hexafluoropropylene)-Based Support for Efficient Water Electrolysis

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ABSTRACT: Water electrolysis under alkaline conditions is of interest due to the applicability of non-precious metal-based materials for electrocatalysts. However, the successful design and synthesis of earth-abundant and efficient catalysts for the oxygen evolution reaction (OER) remain a significant challenge. This work presents cost-effective and straightforward ways to improve the OER activity under alkaline conditions by activating the catalyst–support and reactant–support interaction. Micro/nano-sized fibrous poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) was synthesized via simple and scalable electrospinning and subsequently coated with Cu by electroless deposition to obtain the electrocatalyst with a large specific surface area, enhanced mass transport, and high catalyst utilization. Scanning electron microscopy, infrared spectroscopy, and X-ray diffraction confirmed the successful synthesis of the series of Cu/PVdF-HFP fibrous catalysts with varied ferroelectric polarizability of the PVdF-HFP support in the order of stretch-anneal > anneal > stretch > without pre-treatment of the catalyst. The best OER activity was confirmed for the Cu/PVdF-HFP catalyst with stretch and annealed treatment among the catalysts tested, suggesting that both the reaction kinetics and energetics of stretch-annealed Cu/PVdF-HFP catalysts were optimal for the OER. The electron delocalization between Cu and PVdF-HFP substrates (electron transfer from Cu to the negatively charged (δ−eff) PVdF-HFP region at the Cu/PVdF-HFP interface) and the enhanced transport of reactive hydroxide species and/or the increase in the local pH by positively charged (δ′eff) PVdF-HFP region concertedly accelerate the OER activity. The overall activity for the prototype water electrolyzer increased 10-fold with stretch-anneal treatment compared to the one without pre-treatment, highlighting the effect of tuning the catalyst–support and reactant–support interaction on improving the efficiency of the water electrolysis.

1. INTRODUCTION

Water electrolysis is one of the efficient and sustainable means to produce hydrogen, which is considered as a promising alternative to fossil-fuel-based energy sources, utilizing electricity generated from renewable sources, e.g., wind and solar.1–4 The overall efficiency and cost of the water electrolyzer are critical in achieving mass production of hydrogen via water electrolysis. Typical water electrolyzers operate under acidic or alkaline conditions at temperatures up to 80 °C.5,6 However, most non-precious metal-based catalysts gradually degrade in an acidic medium, and only precious metal-based catalysts can exhibit substantial stability.7–9 Therefore, the study under an alkaline condition is essential to develop water electrolyzers with cost-effective, non-precious metal-based catalysts.

In water electrolyzers operated under alkaline conditions,10,11 the hydrogen evolution reaction (HER, 2H2O + 2e− ⇌ H2 + 2OH−) and the oxygen evolution reaction (OER, 4OH− ⇌ O2 + 2H2O + 4e−) proceed at the cathode and anode, respectively. Although the HER has minimal energy losses,12,13 the OER is a more complicated process with multiple-electron transfer, which requires a large overpotential and leads to a substantial energy loss,14–16 even for the state-of-the-art OER catalyst (e.g., IrO217,18 and RuO217–19). Furthermore, these electrocatalysts commonly contain precious metals such as Ir and Ru, and their high cost and scarcity impede the large-scale application. Design-efficient and durable OER electrocatalysts based on earth-abundant elements, e.g., 3d transition metals,20,21 are thus crucial and have been investigated for more than decades.22–23 Among the 3d transition metals, Cu can be a potential candidate for the practical OER electrocatalysts due to its rich redox properties,24,25 low cost,26,25 and non-toxicity.25 Recent studies successfully developed Cu-based OER catalysts with OER activity comparable to well-optimized Ni/Co-based catalysts27–31 by tuning the energetics of the reaction intermediates via controlling sulfur content in Cu sulfide32 or alloying with other 3d metals33–35 or by adjusting the Cu...
oxidation state under the OER potential with $\text{H}_2\text{O}_2$,
and annealing treatment of the Cu surface. Furthermore, for composite catalysts, such as nanoparticles deposited on a conductive support, successful control of the micro/macrostructure effectively increased the OER activity of Cu-based catalysts by enhancing both mass transport and catalyst utilization.

In addition to active site engineering, designing the interactions between the catalyst atoms and support (catalyst-support interaction) plays a significant role in determining the stability and activity of catalysts. The support provides a platform where the catalytic reaction occurs and defines the electronic structure of the catalyst atoms. In this regard, to maximize the catalytic activity of Cu, optimizing the catalyst-support interaction is essential for the rational design of highly active Cu-based OER catalysts. Although the impact of the catalyst-support interaction on the OER activity has also been suggested for Cu-based catalysts, insights into tuning the catalyst-support interaction to optimize the electronic structure are still insufficient and are further explored.

We present a simple pre-treatment of the catalyst, e.g., stretch and anneal treatment, which can effectively activate the catalyst-support and reactant-support interaction and improve the OER activity under alkaline conditions. The best OER activity was confirmed for highly polarized Cu/PVDF-HFP catalysts with stretch and anneal treatment among the catalysts tested, suggesting that the reaction kinetics and energetics of the OER was optimized by the simple stretch and annealing treatment. We propose that the positively charged ($\delta^+_{\text{ad}}$) PVDF-HFP region facilitates the transport of reactive hydroxide species, while the electron transfer from Cu to the negatively charged ($\delta^-_{\text{ad}}$) PVDF-HFP region at the Cu/pPVdF-HFP interface accelerates the rate-determining step of the OER. A more than 10-fold increase in the overall performance was confirmed for a prototype water electrolyzer consisting of the bi-functional membrane electrode assembly with stretch-anneal treatment compared to the one without pre-treatment, further validating the effect of tuning the catalyst-support and reactant-support interaction on increasing the OER performance. Our findings provide a new design strategy for a highly active OER catalyst, whereby the OER activity can be increased by designing the active metal site and tuning the catalyst-support and reactant-support interaction.

2. EXPERIMENTAL SECTION

2.1. Electrocatalyst Preparation. The Cu-deposited fibrous electrode was prepared by the electrospinning method reported elsewhere. The electrospinning solution consisted of a THF and DMF mixture (7:3 by vol) containing 10 mg of PdCl$_2$ (Wako Pure Chemical) with 12 wt % of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, average molecular weight = 400,000). Electrospinning was performed using electrospinning equipment (NANON-03, MECC Co. Ltd.) at an applied voltage of 28 kV with a feeding rate of 1 mL h$^{-1}$ while rotating a drum-shaped collector along the rotating axis at 3000 rpm. The distance between the injector and the collector was set to 10 cm. The resultant fibers were dried at room temperature for 24 h under reduced pressure ($ca. 400\text{ Pa}$) to remove the organic residue. In order to vary the ferroelectric polarizability of PVDF-HFP/PdCl$_2$ fibers, the obtained fibers were mechanically stretched and/or annealed. PVDF-HFP/PdCl$_2$ fibers were mechanically stretched up to 150% along with the fiber at room temperature (denoted as PVDF-HFP$\text{stretch}$). Both pristine and stretched PVDF-HFP/PdCl$_2$ fibers were annealed at 140 °C for ca. 2 h under an atmosphere (denoted as PVDF-HFP/PdCl$_2\text{anneal}$ and PVDF-HFP/PdCl$_2\text{stretch-anneal}$, respectively). Subsequently, Cu electroless deposition was performed by immersing the resultant electrodes into the Cu plating solution, consisting of CuSO$_4$·5H$_2$O (0.80 g, Wako Pure Chemical), ethylenediaminetetraacetic acid (1.46 g, Nacalai Tesque), NaOH (2.0 g, Wako Pure Chemical), HCHO (0.5 mL, Wako Pure Chemical), and ultrapure water, at 40 °C for ca. 15 min. The Cu-deposited PVdF-HFP, Cu-deposited PVdF-HFP$\text{stretch}$, Cu-deposited PVdF-HFP$\text{anneal}$, and Cu-deposited PVdF-HFP$\text{stretch-anneal}$ fibers are represented as Cu/PVdF-HFP, Cu/PVdF-HFP$\text{stretch}$, Cu/PVdF-HFP$\text{anneal}$, and Cu/PVdF-HFP$\text{stretch-anneal}$, respectively.

2.2. Fabrication of Bi-functional Membrane Electrode Assembly. A multilayered fiber (PVdF-HFP/PdCl$_2$/PVdF-HFP/PVdF-HFP/PdCl$_2$) was synthesized using the setup mentioned above with multiple electrospinning of different electrospinning solutions. First, PVdF-HFP/PdCl$_2$ was synthesized using the electrospinning solution with the same composition described in Section 2.1. The PVdF-HFP was then synthesized over the PVdF-HFP/PdCl$_2$ fiber using the electrospinning solution without the PdCl$_2$ additive. Finally, the multilayered fiber of PVdF-HFP/PdCl$_2$/PVdF-HFP/PVdF-HFP/PdCl$_2$ was obtained by the electrospinning using the electrospinning solution with the PdCl$_2$ additive over the PVdF-HFP/PdCl$_2$/PVdF-HFP fiber. The obtained multilayered fiber was dried at room temperature for 24 h under a reduced pressure ($ca. 400\text{ Pa}$) followed by Cu electroless deposition in the same manner described in Section 2.1.

2.3. Characterization. The microstructure of all Cu/PVdF-HFP catalysts was analyzed by a scanning electron microscope (SEM, JSM-7600F, JEOL Ltd. with an accelerating voltage of 20 kV) equipped with an energy-dispersive X-ray spectrometer (EDS, JMS-7600F, JEOL Ltd.). The X-ray diffraction (XRD) patterns of Cu/PVdF-HFP catalysts were obtained by an X-ray diffractometer (Rigaku Ultima IV) with Cu K$\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) was performed on the K-Alpha spectrometer (Thermo Fischer Scientific). XPS spectra were calibrated by adventitious carbon at 284.8 eV (C 1s spectra). After subtraction of a Shirley-type background, the photoemission lines were fitted using combined Gaussian–Lorentzian functions. Electrochemical cleaning of the electrode was performed in a standard three-electrode cell and by cycling the potential between −0.9 and 1.8 V vs reversible hydrogen electrode (potential cycling was terminated at 1.8 V after 10 cycles). The infrared spectra of the materials were obtained on a Nicolet iS50 (Thermo Fischer Scientific) equipped with a deuterated triglycerine sulfate (DTGS) detector. A single reflection attenuated total reflection (ATR) accessory (Smart iTX, Thermo Fischer Scientific) with a ZnSe prism was used to obtain the spectra. The ATR measurements were performed at an incident angle of 45° with a 4 cm$^{-1}$ resolution. The spectra were collected in the wavenumber range 4000–500 cm$^{-1}$ with a cumulative number of 64. All spectra are shown in the absorbance units defined as $\log(I_0/I)$, where $I_0$ and $I$ represent the background spectra and sample spectra, respectively. The background spectrum $I_0$ was measured without any sample.

2.4. Electrochemical Measurements. Electrochemical measurements were carried out on an HZ-5000 potentiostat.
The successful synthesis of a series of Cu/PVdF-HFP fibrous catalysts was confirmed by scanning electron microscopy (SEM), infrared (IR) spectroscopy, and XRD, suggesting uniform Cu nanoparticle deposition for all the catalysts as well as diverse ferroelectric polarizability of PVdF-HFP substrates by annealing and/or stretching treatment (Figure 1).

The SEM images confirm that all the pristine PVdF-HFP/PdCl2 fibers, prepared by the electrospinning method with and without annealing and/or stretching treatment, possess a similar morphology with a fiber diameter of ca. 0.47 μm (Figure 1a–d, inset). After electroless deposition of Cu, the smooth surface of the PVdF-HFP substrate was covered by a particle-like deposit, in line with the increase in the average diameter of ca. 0.66 μm (Figure 1a–d). The energy-dispersive X-ray spectroscopy (EDS) identified the deposit as a Cu particle, which confirms the successful synthesis of the series of Cu/PVdF-HFP fibrous catalysts (Figure S2). Note that the Cu deposit (a light gray area in the SEM) did not fully cover the fiber surface, and the PVdF-HFP substrate was partially exposed (a dark gray area in the SEM). However, the obtained Cu/PVdF-HFP fibrous catalysts showed good electrical conductivity, suggesting that the Cu particle connected well enough to create the electron-conducting path. The high void volume observed for all the Cu/PVdF-HFP fibers contributes to the efficient mass transfer of reactant and product molecules.57

Infrared spectra of pristine PVdF-HFP/PdCl2 fibers showed distinctive features corresponding to β-phase PVdF-HFP at ca. 1275 cm⁻¹,53,54 suggesting the increased β-phase PVdF-HFP population in the following order: stretch-anneal > anneal > stretch > pristine (Figure 1e). The ferroelectric polarizability is in line with the amount of β-phase PVdF-HFP due to the following reasons: The β-phase PVdF-HFP has an orthorhombic structure and an all-trans molecule conformation, leading to alignment of the dipoles (−CH₂CF₂−) perpendicular to the chain axis (Figure S3).55,56 Therefore, the β-phase PVdF-HFP possesses a large spontaneous polarization, which evokes the characteristic ferroelectricity of PVDF and its copolymers. We thus conclude that the ferroelectric polarizability of PVdF-HFP can be tuned by the simple annealing

**Figure 1.** Characterization of the Cu/PVdF-HFP catalysts with various pre-treatments. SEM images of (a) pristine, (b) stretched, (c) annealed, and (d) stretch-annealed PVdF-HFP/PdCl2 fibers after Cu electroless deposition. The inset shows the corresponding SEM images before Cu electroless deposition. (e) Infrared spectra for pristine, stretched, annealed, and stretch-annealed PVdF-HFP/PdCl2 fibers before Cu electroless deposition. The peaks were normalized by the intensity of the CF2 stretching peak at 1176 cm⁻¹ shown in the inset. (f) XRD patterns of Cu/PVdF-HFP, Cu/PVdF-HFPanneal, Cu/PVdF-HFPstretch, Cu/PVdF-HFPstretch-anneal, and Cu/PVdF-HFPanneal fibers. XRD patterns of the Cu plate and standard Cu (PDF #00-004-0836) are shown for comparison.
and/or stretching treatment, resulting in the ferroelectric polarizability in the following order: Cu/PVdF-HFP < Cu/PVdF-HFPanneal < Cu/PVdF-HFPstretch < Cu/PVdF-HFPanneal < Cu/PVdF-HFPstretch. XRD patterns of the series of Cu/PVdF-HFP catalysts further supports the varied ferroelectric polarizability and deposition of Cu particles (Figure 1f). The characteristic XRD peak corresponds to the β-phase PVdF-HFP appeared at ca. 21° (200/110), 52,57 which gradually increased its intensity and shifted to a higher degree after annealing and/or stretching treatment, indicating the formation of a metastable β-phase by those simple treatments (XRD patterns of the pre-treated PVdF-HFP support without Cu deposition are shown in Figure S4). The XRD patterns also showed diffraction peaks corresponding to Cu, confirming the successful deposition of Cu on all Cu/PVdF-HFP catalysts. Note that Cu/PVdF-HFP catalysts are in the form of thin films, and the flexibility of the pristine PVdF-HFP/PdCl2 fiber is still maintained after Cu deposition.

The electrocatalytic activity toward the oxygen evolution reaction (OER) was clearly improved by the annealing and/or stretching treatment, while the hydrogen evolution reaction (HER) activity only showed slight improvement by the pre-treatment of the catalysts (Figure 2). The linear sweep voltammogram showed the similar HER current of ca. −500 μA cm⁻² at −0.45 V RHE for the catalysts with pre-treatment (Cu/PVdF-HFPstretch, Cu/PVdF-HFPanneal, and Cu/PVdF-HFPstretch-anneal), which was slightly larger than that of pristine Cu/PVdF-HFP (ca. −300 μA cm⁻² at −0.45 V RHE) (Figure 2a). The onset potential of the HER also showed a similar trend, where the catalysts with pre-treatment required slightly smaller (<0.1 V) overpotential to initiate HER compared to the pristine catalyst. The Tafel slope value was ca. 120 mV dec⁻¹ regardless of the pre-treatment (Figure 2b), indicating that the initial Volmer step (water dissociation: H₂O + e⁻ → H₂Oad + OH⁻) 58,59 could be the rate-determining step of the HER for the catalysts used in this study. From the above observations, we concluded that the change in the ferroelectric polarizability of the PVdF-HFP support slightly improved the HER activity. We here propose that the increased ferroelectric polarizability of the PVdF-HFP support lowers the water dissociation energy barrier (responsible for the rate-determining step for the HER in alkaline electrolytes) 60 by stabilizing the metal-OH-water (M-OHad-H₂Oad) complex due to the increased hydrophilicity 61 (discussed further in the later paragraph).

The specific OER current of Cu/PVdF-HFPstretch-anneal, Cu/PVdF-HFPanneal, and Cu/PVdF-HFPstretch catalysts at 1.65 V RHE showed ca. 6.9, 5.4, and a 1.6-fold increase compared to that of pristine Cu/PVdF-HFP catalyst, respectively (Figure 2c). Furthermore, the OER current at a relatively large overpotential region (>1.7 V RHE) observed for Cu/PVdF-HFPanneal and Cu/PVdF-HFPstretch-anneal showed a steeper slope compared to that of Cu/PVdF-HFPstretch and pristine Cu/PVdF-HFP. The result indicates the enhanced diffusion of the reactant and/or the product for catalysts with stretch-anneal and anneal treatments. Although the high void volume of the fibrous structure improves the mass transfer of reactant and product molecules and partial exposure of hydrophobic PVdF-HFP substrate assists the removal of the reaction product (oxygen gas) from the surface, 17 both of which cannot be the reason for the steep slope of the LSV at the large overpotential region for catalysts with stretch-anneal and anneal treatments. We here propose that the ferroelectric polarizability of PVdF-
HFP effectively anchors negatively charged OH$^-$ at the vicinity of the electrode, accelerating the OH supply to the Cu active sites. This hypothesis is supported by the fact that the OER activation by stretch-anneal treatment was not observed for the comparable fibrous Cu/polystyrene (Cu/PS) catalyst without ferroelectricity (Figure S5). Although the polarized PVdF-HFP surface possesses both positive and negative charges depending on the CH$_2$/CF$_2$ orientation, negatively charged PVdF-HFP (surface with CF$_2$ dipoles ($\delta_{eff}$)) might preferentially be covered by Cu since it attracts Cu$^{2+}$ during the electroless deposition process. The electrostatic interaction between the positively charged PVdF-HFP surface by CH$_3$ dipoles ($\delta_{eff}$) and negatively charged OH$^-$ anchors the OH$^-$ close to the electrode surface. Linear sweep voltammograms in various KOH concentrations further support our hypothesis (Figure S6). The OER current became more extensive along with the increase in the KOH concentration (from 1 to 2 M KOH) for pristine electrodes, suggesting the enhancement of OER by the increased amount of OH$^-$ active sites. The OER current for the catalyst with stretch-anneal treatment obtained in 1 M KOH was notably more significant than that for the pristine electrode in 2 M KOH, suggesting the high local concentration of OH$^-$ achieved by the enhanced ferroelectric polarizability of the PVdF-HFP support.

All the pre-treated Cu/PVdF-HFP catalysts exhibit superior specific OER activity compared to that of the pristine catalyst, with an overpotential ($\eta$) of 370 mV (stretch-anneal) < 380 mV (anneal) < 440 mV (stretch) < 490 mV (pristine) to reach 50 $\mu$A cm$^{-2}$ ECSA (Figure 2d). In addition, the Nyquist plot of the Cu/PVdF-HFP$_{stretch-anneal}$ catalyst shows a smaller charge transfer resistance than that of pristine Cu/PVdF-HFP, demonstrating the enhanced charge transfer kinetics (Figure S7). Tafel analysis further confirms the activation of OER for the Cu/PVdF-HFP$_{stretch-anneal}$ catalyst, showing the smallest Tafel slope value of 31 mV dec$^{-1}$ followed by Cu/PVdF-HFP$_{anneal}$ (32 mV dec$^{-1}$), Cu/PVdF-HFP$_{stretch}$ (52 mV dec$^{-1}$), and pristine (84 mV dec$^{-1}$) catalysts. The Tafel slope value slightly decreased from ca. 84 mV dec$^{-1}$ (1 M KOH) to 58 mV dec$^{-1}$ (2 M KOH) with increasing the KOH concentration for the pristine catalyst (Figure S8), suggesting that the enhanced OH$^-$ supply to the Cu active sites and/or the increase in pH at the vicinity of the electrode surface can be part of the reasons for the improved specific OER activity. However, a significant decrease in the Tafel slope value, as well as the overpotential observed for the catalyst with stretch-anneal treatment, cannot be explained only by the increase in the OH$^-$ concentration. We propose that the synergetic effect between Cu and PVdF-HFP (electron transfer from Cu to PVdF-HFP) at the CuPdVdF-HFP interface varies with the pre-treatment and optimizes reaction energetics for OER.

Attenuated total reflection infrared (ATR-IR) spectroscopy and ex situ XPS revealed that the electron delocalization between Cu and PVdF-HFP substrates was promoted for the catalyst with increased ferroelectric polarizability of the PVdF-HFP support. The electron transfer from Cu to PVdF-HFP alters the electronic states of Cu active sites, boosting OH binding on the Cu, especially for the Cu/PVdF-HFP$_{stretch-anneal}$ (Figure 3). A clear redshift of the $\nu_4$(CF$_2$) band was observed for Cu-deposited PVDF-HFP catalysts with respect to the corresponding PVDF-HFP/PdCl$_2$ fibers (before Cu deposition) confirms the existence of the electrostatic interaction between Cu and PVDF-HFP (Figure 3a). The amount of wavenumber shift depends on the pre-treatment; Cu/PVdF-HFP$_{stretch-anneal}$ ($\Delta$$\nu$) > Cu/PVdF-HFP$_{anneal}$ ($\Delta$$\nu$) > Cu/PVdF-HFP$_{stretch}$ ($\Delta$$\nu$) = pristine Cu/PVdF-HFP ($\Delta$$\nu$).
cm⁻¹), indicating the degree of electrostatic interaction between CF₂ dipoles (δ⁻eff) with Cu varies with ferroelectric polarizability of the PVdF-HFP support. We propose that well-aligned CF₂ dipoles (δ⁻eff) within β-phase PVdF-HFP interact with Cu and its large δ⁻eff strongly withdraws electron from Cu. Furthermore, the negatively charged PVdF-HFP region (surface with CF₂ dipoles (δ⁻eff)) can effectively interact with Cu since the negatively charged region is mostly covered by Cu owing to the preferential attraction of the positively charged Cu⁺ during the electroless deposition process.

The electron transfer from Cu to the PVdF-HFP substrate can also be suggested from Cu 2p spectra of the electrochemically cleaned Cu/PVdF-HFP catalysts (Figure 3b). The Cu 2p XPS spectra showed two asymmetric bands, which could be deconvoluted into two pairs of doublets assigned to Cu²⁺ (932.6−933.6 and 952.5−954.3 eV) and Cu²⁺ (934.8−935.7 and 954.6−956.2 eV). The contribution from Cu²⁺ (934.8−935.7 and 954.6−956.2 eV) was dominant for all the catalysts tested, indicating that the Cu mainly exists as Cu²⁺ in the Cu/PVdF-HFP fiber surfaces after electrochemical cleaning. CuO formation was also confirmed by comparing the XRD patterns before and after the OER, further emphasizing the importance of Cu²⁺ on the OER (Figure S10). The Cu²⁺ peaks shifted to a higher binding energy in line with the increase in the ferroelectric polarizability of the PVdF-HFP support: Cu/PVdF-HFP_stretch-anneal (935.7, 956.2 eV) > Cu/PVdF-HFP_stretch (935.4, 955.8 eV) > Cu/PVdF-HFP (935.0, 954.8 eV) = pristine Cu/PVdF-HFP (934.8, 954.6 eV). The positive shift in binding energies of Cu²⁺ peaks implies the electron deficiency of the Cu sites, which supports the existence of the electron transfer from Cu to PVdF-HFP. Furthermore, the trend in the binding energy of the Cu²⁺ peak coincides with the wavenumber shift of the ν(CF₂) band, strongly indicating that the electron transfer from Cu to PVdF-HFP can be accelerated by increasing the ferroelectric polarizability of PVdF-HFP.

The electron transfer from Cu to PVdF-HFP affects the binding energetics of the O/OH adsorbates, which can be confirmed by comparing the onset potential of the O/OH adsorption (Figure 3c). Cyclic voltammograms showed butterfly features at ca. 0.35 V_RHE corresponding to the O/OH adsorption/desorption on the Cu(100) face. The onset potential of the O/OH adsorption shifted to a lower potential by increasing the ferroelectric polarizability of the PVdF-HFP support: pristine Cu/PVdF-HFP (0.348 V_RHE) = Cu/PVdF-HFP_stretch (0.348 V_RHE) > Cu/PVdF-HFP_stretch-anneal (0.345 V_RHE) > Cu/PVdF-HFP (0.344 V_RHE). The trend suggests the strong O/H binding for the Cu on the highly polarized PVdF-HFP support, which is in accordance with the degree of the electron transfer from Cu to the PVdF-HFP substrate (Figure 3b).

The Cu/PVdF-HFP catalyst with stretch-anneal treatment showed the best OER activity among the catalysts tested, suggesting that both the reaction kinetics and energetics of the Cu/PVdF-HFP_stretch-anneal catalysts were optimal for OER. The positively charged (δ⁻eff) PVDF-HFP region facilitates the transport of reactive hydroxide species, while the electron transfer from Cu to the negatively charged (δ⁻eff) PVDF-HFP region at the Cu/PVdF-HFP interface accelerates the rate-determining step of the OER (Figure 4).

The highly polarized PVDF-HFP substrate with stretch-anneal treatment possesses both positive and negative charges depending on the CH₂/CF₂ orientation. Negatively charged PVDF-HFP (surface with CF₂ dipoles (δ⁻eff)) mostly covered by Cu owing to the electrostatic attraction between δ⁻eff and positively charged Cu⁺ during the electroless deposition process. The large electronegativity of the F atom effectively withdraws the electron from Cu to PVDF-HFP, creating a slightly electron-deficient Cu site. Stronger O/OH binding on the slightly electron-deficient Cu site than the normal Cu site promotes the initial hydroxide adsorption and the subsequent deprotonation of OH⁻ to form OOH₃ which agrees with the CVs in Figure 3c. Furthermore, the electrophilicity of the oxygen adsorbates (O_ads) on the slightly electron-deficient Cu site can be increased, promoting the formation of the OOH₃ via nucleophilic attack from OH⁻ within the electrolyte. The fourth electron transfer reaction of the OER (deprotonation of OOH₃ to form O₂) can also be facilitated through the electron-withdrawing inductive effect, which accelerates the overall OER activity (Figure 4). Tafel analysis of the stretch-annealed Cu-deposited PVDF-HFP catalyst further supports our hypothesis (Figure 2d). The Tafel slope (β) can be expressed as eq 1, where η is the overpotential, i is the current density, R is the universal gas constant, T denotes the absolute temperature, F is the Faraday constant, and α is the transfer coefficient.

\[
b = \frac{\partial \eta}{\partial \log(i)} = \frac{2.303RT}{\alpha F}
\]  

(1)

The transfer coefficient (α) for a multiple-electron reaction is shown in eq 2, where nᵣ is the number of electrons that transfer back to the electrode before the rate-determining step, ν is the number of rate-determining steps that have taken place in the overall reaction, nᵣ is the number of electrons that participate in the rate-determining step, and β is the symmetry factor (β = 0.5 in this study, assuming that overpotential is much smaller than the reorganization energy).

\[
\alpha = \frac{nᵣ}{\nu} + nᵣ\beta
\]  

(2)
A Tafel slope value of 31 mV dec⁻¹ for stretch-annealed catalysts thus suggests \( n_b = 3 \) and \( \nu = 2 \), which translated into the fact that the second (deprotonation of \( \text{OH}^\text{ad} \) to form \( \text{O}^\text{ad} \)) and fourth (deprotonation of \( \text{OOH}^\text{ad} \) to form \( \text{OO}^\text{ad} \)) electron transfer reactions can be the sluggish (energetically unfavorable) process (\( \nu = 2 \)), and the fourth reaction acts as a major rate-determining step \( (n_b = 3) \). The proposed rate-determining step agrees with the proposed OER energetics on \( \text{Cu} \), further validating our Tafel analysis. The Tafel slope value varies between 31 and 84 depending on the pre-treatment of the PVdF-HFP substrate, probably due to the change in the OER energetics and/or the existence of the mixed rate-determining step.

On the other hand, positively charged PVdF-HFP (surface with \( \text{CH}_2 \) dipoles \( (\delta^+_{\text{eff}}) \)) was preferably exposed to the electrolyte due to the electrostatic repulsion, which prevents the reduction of \( \text{Cu}^{2+} \) during the electroless deposition process. The electrostatic attraction between \( \delta^+_{\text{eff}} \) of the exposed PVdF-HFP surface and negatively charged \( \text{OH}^- \) in the electrolyte may promote (1) the diffusion of the \( \text{OH}^- \) toward the electrode and/or (2) increase the local pH at the vicinity of the surface. The former facilitates the diffusion kinetics of the reactant (\( \text{OH}^- \)) together with the unique fibrous structure of the substrate, while the latter improves the reaction energetics of the OER.

The unique interaction between \( \text{Cu} \) and PVdF-HFP with stretch-anneal treatment may strongly influence its activity for overall water electrolysis. The overall performance of the water electrolyzer consisting of the bi-functional membrane electrode assembly (MEA), Cu/PVdF-HFP/PVdF-HFP/Cu/PVdF-HFP, with stretch-anneal treatment was significantly improved in comparison with a pristine bi-functional MEA, together with the high (electro)chemical stability for more than 24 h (Figure 5).

The bi-functional membrane electrode assembly (MEA) was synthesized by a simple two-step process, electrospinning, and subsequent \( \text{Cu} \) electrodeposition, without slurry synthesis and/or screen printing of the catalyst, which was involved in the conventional MEA manufacturing process. The resultant bi-functional MEA is a single flexible sheet with a thickness of ca. 0.5 mm (Figure 5a,b). The cross-sectional image confirms that the top and bottom \( \text{Cu} \)-deposited layers (Cu/PVdF-HFP) are tightly attached to the PVdF-HFP layer (middle layer), and it is electrically separated from each other (Figure 5c,d). To evaluate the effect of pre-treatment on the stability and activity of the Bi-functional MEA, a water electrolyzer consisting of bi-functional MEA with and without stretch-anneal treatment was operated under a potentiostatic mode at an applied voltage of 2.5 V in 1 M KOH. As plotted in Figure 5e, both bi-functional MEAs exhibit a slight activity decay in the first 16 h of operation, subsequently representing a stable horizontal line up to 28 h. The cycling stability test suggests that the initial activity decay can be due to the partial aggregation of the \( \text{Cu} \) particles, which was confirmed by XRD, XPS, and SEM analyses (Figure S11). A more than 10-fold increase in the current was observed for the bi-functional MEAs with stretch-anneal treatment (9.63 mA cm⁻² at 28 h) compared to that without pre-treatment (0.63 mA cm⁻² at 28 h), demonstrating the outstanding improvement in the overall performance for the water electrolysis by the simple stretch and anneal treatment.

4. CONCLUSIONS

In this work, the oxygen evolution reaction activity on \( \text{Cu} \) in alkaline environments was significantly increased by activating the catalyst–support and reactant–support interaction via simple pre-treatment of the \( \text{Cu} \)-deposited fibrous PVdF-HFP catalysts. The ferroelectric polarizability of the PVdF-HFP support is successfully tuned by simple pre-treatment, leading to the increased population of the highly polarized \( \beta \)-PVdF-HFP in the following order: stretch, anneal, and stretch-anneal treatment. The electron transfer from \( \text{Cu} \) to PVdF-HFP was accelerated in line with the polarizability of the PVdF-HFP support, which was supported by the redshift of the \( \nu(C\equiv O) \) band and the positive shift in binding energies of \( \text{Cu}^{2+} \) peaks of the ATR-IR and XPS spectra, respectively. The Cu/PVdF-HFP catalyst with stretch and anneal treatment showed the best OER activity among the catalyst tested, suggesting that both the reaction kinetics and energetics of Cu/PVdF-HFP/stretch-anneal catalysts were optimal for the OER. The increased OER activity for the Cu/PVdF-HFP/stretch-anneal catalyst can be attributed to the (1) facile transport of reactive hydroxide species and increased local pH by the electrostatic interaction between the positively charged \( (\delta^+_{\text{eff}}) \) PVdF-HFP region and hydroxide ions and (2) the acceleration of the rate-
determining step of the OER (deprotonation of OOH₄ to form O₂) by the electron transfer from Cu to the negatively charged (δ⁻) PVdF-HFP region at the Cu/PVdF-HFP interface. The performance of the prototype water electrolyzer consisting of bi-functional membrane electrode assembly was significantly increased by stretch-anneal treatment, further validating the impact of tuning the catalyst–support interface and reactant-support interaction on the performance of the water electrolysis. The abovementioned interactions can be adjusted by simple pre-treatment with stretch and anneal, leading to aligning the molecular structure and increasing the polarity of the polymer substrate. Furthermore, the proposed pre-treatment, as well as the synthesis procedures for the flexible and durable membrane electrode assembly, is simple and scalable, which not only expands the applicability of the water electrolyzer but also opens up a new avenue to fabricate the membrane electrode assembly required for various electrochemical energy conversion/storage devices.

Author Contributions
The manuscript was written with contributions from all authors. All authors have approved the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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