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# Insights into the Impact of the Nafion Membrane Pretreatment Process on Vanadium Flow Battery Performance

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#### **Supporting Information**



**ABSTRACT:** Nafion membranes are now the most widely used membranes for long-life vanadium flow batteries (VFBs) because of their extremely high chemical stability. Today, the type of Nafion membrane that should be selected and how to pretreat these Nafion membranes have become critical issues, which directly affects the performance and cost of VFBs. In this work, we chose the Nafion 115 membrane to investigate the effect of the pretreatment process (as received, wet, boiled, and boiled and dried) on the performance of VFBs. The relationship between the nanostructure and transport properties of Nafion 115 membranes is elucidated by wide-angle X-ray diffraction and small-angle X-ray scattering techniques. The self-discharge process, battery efficiencies, electrolyte utilization, and long-term cycling stability of VFBs with differently pretreated Nafion membranes are presented comprehensively. An online monitoring system is used to monitor the electrolyte volume that varies during the long-term charge–discharge test of VFBs. The capacity fading mechanism and electrolyte imbalance of VFBs with these Nafion 115 membranes are also discussed in detail. The optimal pretreatment processes for the benchmark membrane and practical application are synthetically selected.

KEYWORDS: vanadium flow battery, Nafion membrane, pretreatment process, cycling performance, capacity fading

### 1. INTRODUCTION

Development of large-scale and highly efficient energy storage technology is significantly important for the protection of grid security and promotion of the use of renewable energy.<sup>1–3</sup> Vanadium flow batteries (VFBs) have become one of the fastest growing and most promising energy storage technologies because of advantages such as a long cycle life, easily implemented large-scale, flexible operation, and weak environmental impact.<sup>4–6</sup> The VFB system utilizes VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> and V<sup>3+</sup>/V<sup>2+</sup> redox couples as the catholyte and anolyte, respectively, an ion-exchange membrane (IEM) as the separator, and carbon fabric material as the electrode.<sup>7–10</sup>

The IEM is the core material of a VFB that directly determines the manufacturing costs, energy efficiency, and cycle stability of that VFB.<sup>11–14</sup> An ideal IEM for VFBs should possess high ion selectivity (the ratio of proton conductivity to vanadium ion permeability) and outstanding oxidation stability

and mechanical strength and should be affordable.<sup>11</sup> The stateof-the-art perfluorosulfonic Nafion membranes<sup>15</sup> have been widely employed as the benchmark in VFBs because of their high proton conductivity and remarkable chemical stability.<sup>16–21</sup> However, fast crossover of vanadium ions and the high cost limit its practical application in VFBs.<sup>11,12</sup> Over the past few decades, great achievements have been made in the search of alternative hydrocarbon skeleton polymer-based IEMs for proton-exchange membrane fuel cells and direct methanol fuel cells.<sup>22–24</sup> These well-developed and closely studied cationexchange membranes (CEM)<sup>14</sup> and anion-exchange membranes (AEM)<sup>25,26</sup> have been gradually used in VFB systems and exhibited excellent cell performance. Recently, non-fluoride

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porous membranes have also been successfully used in VFB systems.<sup>27,28</sup> Despite their lower price and higher efficiency compared to those of the Nafion membrane, these non-perfluorinated membranes display poor cycle stability because they are prone to degrading under the harsh acid and oxidation of vanadium electrolytes.<sup>29–31</sup> Therefore, the extremely stable Nafion membranes are by now still the best choice for most large-scale and long-life VFB energy storage systems.<sup>9,16,18–20</sup> Accordingly, what type of Nafion membranes should be selected and how to pretreat these Nafion membranes have become two critical issues, which directly affect the performance and cost of VFBs.

Since the invention of VFBs, Nafion series membranes of various thicknesses with different pretreatments have been reported in both lab-scale single cells and kW-class stacks.<sup>7,32</sup> The tested Nafion series include Nafion 211 (25  $\mu$ m),<sup>19</sup> Nafion 212 (50  $\mu$ m),<sup>33,34</sup> Nafion 112 (50  $\mu$ m),<sup>21,35</sup> Nafion 1135 (88  $\mu$ m),<sup>21,36</sup> Nafion 115 (125  $\mu$ m),<sup>28,37</sup> and Nafion 117 (175  $\mu$ m).<sup>17,38</sup> The pretreatment methods include immersion in water, boiling in acid, using as received, etc. Actually, both the thickness and the pretreatment method have a significant impact on the performance and cost of Nafion membranes.<sup>39-42</sup> For instance, a thinner Nafion membrane exhibits a smaller area resistance (higher voltage efficiency), higher vanadium ion permeability (lower Coulombic efficiency and faster capacity fading rate), and cheaper price compared with the values of the thicker membrane.<sup>11,15,39</sup> On the other hand, water and acid pretreatment would swell the micro micelle structure of the Nafion membrane,<sup>15,41,42</sup> resulting in higher proton conductivity (higher voltage efficiency), faster vanadium ion crossover (lower Coulombic efficiency), and larger membrane area (namely decreasing cost) compared to those of the as-received dry membrane. Consequently, to set a balance between price and performance, an optimized Nafion membrane thickness together with a rational pretreatment process should be chosen for VFB application. In our previous work,<sup>21</sup> we have studied the impact of the

In our previous work,<sup>21</sup> we have studied the impact of the thickness of the Nafion membrane on the performance of VFBs over a broad current density range from 40 to 320 mA cm<sup>-2</sup>. The self-discharge process, cell efficiencies, electrolyte utilization, and long-term cycling stability of VFBs based on Nafion 112, 1135, 115, and 117 membranes have been compared comprehensively. The results showed that the Nafion 115 membrane presents the highest energy efficiency and electrolyte utilization at current densities from 120 to 240 mA cm<sup>-2</sup>, because of the good balance between vanadium ion permeability and membrane resistance. These results inspire us to further uncover the impact of Nafion membrane pretreatment on VFB performance.

Through a literature survey, it is found that large deviations of VFB performance have been reported even upon assembly with the same type of Nafion membrane.<sup>11–14,33–38</sup> Besides the influence of the battery structure and effective area employed, the main reason should be the different membrane pretreatment methods before assembly of the battery. Recently, a few preliminary studies in terms of the impact of Nafion membrane pretreatment on VFB performance have been reported.<sup>43,44</sup> Hickner et al. investigated the effect of hydration treatment on the VO<sup>2+</sup> permeability of the Nafion 117 membrane. They found that the Nafion 117 membrane boiled in 0.5 M H<sub>2</sub>SO<sub>4</sub> showed faster vanadium ions crossover and a shorter self-discharge time compared to those of the Nafion 117 membrane immersed in water, which can be explained by the swolen ionic

nanostructure during the pretreatment process.<sup>43</sup> Xie et al. studied how manufacturing processes and pretreatments affected the proton conductivity and vanadium ion permeability of a series of Nafion membranes. They found that the proton conductivity and vanadium permeability of membranes boiled in 0.5 M  $H_2SO_4$  were higher than those of the as-received membrane and water-treated membrane for all types of Nafion membranes.<sup>44</sup> Unfortunately, until now, a comprehensive evaluation of the impact of pretreatment on the nanostructures of the Nafion membrane and its VFB performance such as battery efficiencies, electrolyte utilization, imbalance of the electrolyte, and capacity fading mechanism has not been published.

On the basis of our previous study of the influence of Nafion membrane thickness,<sup>21</sup> we chose the Nafion 115 membrane to further investigate the effect of the pretreatment process (see Table 1) on the performance of VFBs in this work. The

# Table 1. Nomenclature, Pretreatment Processes, andPhysicochemical Properties of Various Nafion 115Membranes

nomenclature	pretreatment process	thickness (µm)	area resistance $(\Omega \text{ cm}^2)$	$VO^{2+}$ permeability $(\times 10^{-7} \text{ cm}^2 \text{ min}^{-1})$
as received	used without any treatment	138	2.10	3.1
wet	soaked in deionized (DI) water for 24 h	150	1.02	7.3
boiled	boiled in 3 wt % H <sub>2</sub> O <sub>2</sub> , DI water, 1 M H <sub>2</sub> SO <sub>4</sub> , and DI water for 1 h	158	0.91	20.2
boiled and dried	vacuum dried at 90 °C for 24 h after the boiling treatment	135	2.64	1.3

relationship between the nanostructure and transport properties of Nafion 115 membranes is elucidated by wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) techniques. The self-discharge process, battery efficiencies, electrolyte utilization, and long-term cycling stability of VFBs with different membranes are presented comprehensively. An online monitoring system (OMS) is used to monitor the electrolyte volume that varies during the long-term charge– discharge test of VFBs. The capacity fading mechanism and electrolyte imbalance of VFBs with various Nafion 115 membranes are also discussed in detail.

#### 2. EXPERIMENTAL SECTION

**2.1. Membrane Pretreatment.** The Nafion 115 membrane was purchased from DuPont Co. Four types of Nafion 115 membranes were compared in this study. The nomenclature and a brief description of the pretreatment process are listed in Table 1. Other chemicals were of analytical grade and used without further purification. Regardless of the macro or micro view, the surfaces of various Nafion membranes are dense and smooth.

**2.2. Membrane Characterization.** *2.2.1. Physicochemical Properties.* The physicochemical properties of water uptake,<sup>21</sup> swelling ratio,<sup>21</sup> ion-exchange capacity (IEC),<sup>45</sup> area resistance,<sup>46</sup> and VO<sup>2+</sup> permeability<sup>47</sup> were measured as reported previously, and the experimental details are given in the Supporting Information. Three parallel measurements were conducted for each parameter, and the averages of three testing results were recorded.

2.2.2. WAXD and SAXS Characterization. WAXD spectra of the membranes were recorded on a Rigaku D/max-2500 PC diffractometer with Cu K $\alpha$  radiation. Angular scanning was performed

between 5° and 75° at a scan rate of 4° min<sup>-1</sup>. The nanostructure of the membranes was studied by SAXS using a Rigaku D/max2500v/Pc instrument (CuK 40 kV, 200 mV) at a rate of  $0.1^{\circ}$  cm<sup>-1</sup>.<sup>48</sup> All the measurements were performed at room temperature. The scattering vector q (inverse nanometers) was calculated according to the following equation:<sup>49</sup>

$$q = 4\pi \sin(\theta/2)/\lambda \tag{1}$$

where  $\theta$  is the scattering angle and the wavelength  $\lambda = 0.1542$  nm. The D-spacing, *d* (nanometers), was calculated by the following equation:

$$d = 2\pi/q \tag{2}$$

**2.3. Single-Cell Test and Online Monitoring.** The configuration of a VFB single cell and its testing method were the same as in our previous work,<sup>50,51</sup> as shown in the left part of Figure 1. A Nafion 115



Figure 1. Photograph of VFB single cells and OMS.

membrane (7 cm × 7 cm), two graphite felt electrodes (5 cm × 5 cm × 0.5 cm), and two 50 mL portions of electrolytes (1.5 M V<sup>3.5+</sup> in 2 M free H<sub>2</sub>SO<sub>4</sub>) were used.<sup>52</sup> An online monitoring system (OMS) was used to study the change in the volume of electrolytes during the long-term cycle life test.<sup>21</sup> The right part of Figure 1 shows the BTS control interface and OMS control interface, which is real-time monitoring the electrolyte tanks.

#### 3. RESULTS AND DISCUSSION

**3.1. Membrane Characterization.** Digital photos of Nafion 115 membranes with different pretreatment methods before and after a VFB single-cell test are shown in panels a and b of Figure 2, respectively. It can be seen that all the fresh membranes are smooth and transparent. The color change of the boiled and dried membrane is due to the reaction of residual organic species during the heating vacuum drying process (Table 1).<sup>15</sup> The four membranes have the same initial dimensions of 70 mm  $\times$  70 mm. As shown in Figure 2a, pretreatment can lead to significant changes in the size of the membrane. Specifically, as shown in Figure 2c, wet and boiled

pretreatment processes bring about 18 and 30% expansions of Nafion 115 membrane's area, respectively, because of the swelling of the ionic micelle nanostructure.<sup>15,41</sup> On the other hand, compared with the as-received membrane, the area of the boiled and dried membrane decreases slightly. From an economic point of view, the resulting increase in area through the wet and boiled treatments is beneficial for reducing the cost of the Nafion membrane. Of course, changes in the nanostructure and area will also lead to changes in other physicochemical and transport properties of the Nafion membrane, which will be discussed below. For the Nafion 115 membranes that were used, as shown in Figure 2b, the middle area (intermediate 50 mm × 50 mm region<sup>47</sup>) exhibits a light blue color and a wrinkled morphology, suggesting the swelling of membranes by vanadium electrolytes during the VFB testing process.

The physicochemical properties of four Nafion 115 membranes are compared in Table 1 and Figure 3. The



Figure 3. (a) Swelling ratio in there forms of various pretreated Nafion 115 membranes. (b) Water uptake and IEC of different Nafion 115 membranes.

thicknesses of as-received, wet, boiled, and boiled and dried membranes are 138, 150, 158, and 135  $\mu m$ , respectively. The



Figure 2. Digital photos of various pretreated Nafion 115 membranes (a) before and (b) after a single-cell test. (c) Relative areas of Nafion 115 membranes subject to different pretreatments.

boiled membrane possesses the highest swelling ratio (Figure 3a) and level of water uptake (Figure 3b) because the temperature of the boiled membrane was close to the glass transition temperature of the dry Nafion ionomer (110-120 °C).53 Boiling in sulfuric acid can effectively overwrite the thermal history of membranes and lead to the opening of large continuous hydrophilic pathways, which are previously isolated free volume voids connected by tiny channels.<sup>44,54</sup> The extremely high water uptake and swelling ratio of the boiled membrane result in high cation permeability, which is a disadvantage for VFB application.<sup>11,55</sup> Area resistance is an important parameter of the IEM that mainly determines the voltage efficiency (VE) of a VFB.<sup>11</sup> According to previous reports, area resistance of IEM is affected by IEC and water uptake.<sup>41,56</sup> Although subjected to different pretreatments, all Nafion 115 membranes have approximate IEC values (Figure 3b) because they have the same chemical structure, which is consistent with their theoretical value (0.91 mmol g<sup>-1</sup>).<sup>15</sup> Therefore, area resistance will decrease with an increase in the level of water uptake because a high level of water uptake can facilitate proton migration.<sup>23</sup> It can be seen from Table 1 that the area resistance of boiled and wet membranes is much lower than that of as-received and boiled and dried membranes.

In addition to the influence of physicochemical properties, the pretreatment method also strongly influences the permeation of the membrane by vanadium ions.  $VO^{2+}$ permeabilities of Nafion membranes were tested by the diffusion cell as shown in Figure 4. The obtained  $VO^{2+}$ 



Figure 4. Change in the concentration of  $VO^{2+}$  in a  $MgSO_4$  solution across different pretreated Nafion 115 membranes. The inset is a photograph of a diffusion cell.

permeabilities for different membranes are listed in Table 1. It can be seen from Figure 4 that the order of  $VO^{2+}$  crossover is as follows: boiled > wet > as received > boiled and dried [the same order observed for the water uptake level (Figure 3b)]. A high level of water uptake indicates a large fraction of free volume in the swollen Nafion matrix and, consequently, results in fast VO<sup>2+</sup> permeability through the membrane.<sup>11,44</sup> The  $VO^{2+}$  permeability of the boiled membrane (20.2 × 10<sup>-7</sup> cm<sup>2</sup>  $\min^{-1}$ ) is nearly 1 order of magnitude larger than that of the asreceived membrane  $(3.2 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1})$ , because of the substantially altered membrane free volume and nanostructure after boiling in sulfuric acid.44,57 The higher level of water uptake along with a lower area resistance of the membrane is beneficial for increasing the voltage efficiency (VE) of VFBs. On the other hand, greater vanadium ions crossover will decrease the Coulombic efficiency (CE) of VFBs. Therefore,

the optimized pretreatment protocols allow Nafion membranes with a good balance of vanadium ions crossover and area resistance, which would lead to better and more stable cycling performance of VFBs.

WAXD and SAXS are powerful techniques for studying the morphology of Nafion membranes.<sup>15,49</sup> Typical WAXD patterns of different pretreated Nafion 115 membranes are shown in Figure 5a. To assay for crystallinity, the deconvolution



Figure 5. (a) WAXD patterns and (b) corresponding peak deconvolution curves of various Nafion 115 membranes.

of the peak from the original WAXD curves by Gaussian functions is shown in Figure 5b.<sup>58</sup> According to previous reports, the broad peak at  $2\theta < 16.0^{\circ}$  and the distinct sharp peak at  $2\theta > 17.8^{\circ}$  can be attributed to the amorphous region and crystalline region, respectively.<sup>58</sup> The calculated crystallinities for as-received, wet, boiled, and boiled and dried membranes are 16.3, 15.8, 15.6, and 17.8%, respectively. These values are consistent with the previously reported crystallinity of the Nafion membrane, which is in the range of 12-23%.<sup>59</sup> It is worth noting that the crystallinity is strongly related to the water uptake of the membrane. Four Nafion 115 membranes present the same trend on water uptake and crystallinity, which is in accordance with the results by Gierke et al., who found that the crystallinity of a Nafion membrane would increase with a decrease in water content.<sup>60</sup>

To improve our understanding of how pretreatment methods affect the ion cluster and nanostructure of Nafion

115 membranes, various pretreated membranes were investigated by SAXS, and the results are shown in Figure 6. A broad



Figure 6. SAXS curves of various Nafion 115 membranes.

scattering peak is commonly observed if ion-containing polymer materials are irradiated with monochromatic Xrays.<sup>49,61</sup> Via calculation from the position of this peak  $(q_{\text{max}})^{48,61}$  the distances (d) between the hydrophilic and hydrophobic domains of as-received, wet, boiled, and boiled

and dried membranes are 3.0, 4.2, 4.8, and 2.7 nm, respectively, as shown in Figure 6. This reveals that the ionic cluster in the Nafion 115 membrane can be expanded when the membrane is immersed in DI water and boiled in the sulfuric acid solution. The larger size of the water channel for wet and boiled membranes will lead to a higher swelling ratio, a higher level of water uptake, a lower area resistance, and faster vanadium ions crossover, as discussed in Figures 2-4 and Table 1.11,55,62

3.2. VFB Performance Evaluation. All Nation 115 membranes were assembled in a VFB single cell to further investigate the impact of pretreatment method on battery performance. To eliminate the system error, all batteries were tested simultaneously, as shown in Figure 1. As discussed above, the area resistance of the Nafion 115 membrane is greatly influenced by the pretreatment method (Table 1). Hence, EIS was conducted first to verify the trend of membrane resistance. The EIS measurement was performed at different times after the electrolytes had been pumped into the battery. Nyquist plots of VFBs recorded at 10, 20, and 30 min are illustrated in Figure 7. All batteries present a similar impedance response. The low-frequency and high-frequency intercepts in the Nyquist plot can be assigned to the total resistance  $(R_t)$  and the ohmic resistance  $(R_b)$  of the VFB, respectively.<sup>63</sup> Then, the polarization resistance  $(R_p)$  of the VFB can be achieved by subtracting  $R_b$  from  $R_t$ ,  $R_p$  is mainly determined by the activity of the electrode.<sup>63</sup> Therefore, all batteries exhibit approximate  $R_{\rm p}$  values of ~2  $\Omega$  because of the same graphite felt electrode that was used. In a VFB, R<sub>b</sub> consists of electrode resistance, electrolyte resistance, membrane resistance, and contact resistance. It should be emphasized that in addition to the membrane, all the parameters of four batteries are exactly the



Figure 7. Nyquist plots of VFBs assembled with various membranes: (a) as received, (b) wet, (c) boiled, and (d) boiled and dried. Insets show the high-frequency regions of the Nyquist plots.

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same. Hence, the discrepancy in VFB's  $R_b$  is due to the difference in the membrane's area resistance. It can be seen from Figure 7 that the  $R_p$  and  $R_b$  (see the inset of Figure 7) of all VFBs decrease with time and remain stable after 20 min. The decrease in  $R_b$  can be attributed to the swelling of the membrane in a vanadium electrolyte, which results in a decrease in membrane resistance. The slight decrease in  $R_p$  is probably due to the improving accessibility of the electrolyte to the electrolyte has been pumped for ~30 min. The high-frequency regions of the Nyquist plots recorded at 30 min are shown in Figure S1 to carefully compare the  $R_b$  values of VFBs assembled with various membranes. It shows that the order of  $R_b$  is as follows: boiled < wet < as received < boiled and dried (which agrees well with the area resistance results).

After EIS measurements, all batteries were charged to the 50% state of charge (SOC) at a current density of 60 mA cm<sup>-2</sup> to conduct the self-discharge test.<sup>21</sup> Figure 8 displays the self-



Figure 8. Self-discharge curves of VFBs assembled with various membranes.

discharge curves of VFBs assembled with various membranes. The open circuit voltage (OCV) of all batteries gradually decreases first and then appears to undergo two sharp voltage drops. According to the literature,<sup>64</sup> the first sharp decline of the OCV to 0.8 V is due to the disappearance of  $VO_2^+$  ion in the positive electrolyte, while the second sharp decline of the OCV to 0.2 V is due to the disappearance of  $V^{2+}$  ion in the negative electrolyte. The self-discharge times to reach 0.8 V are 28, 65, 99, and 116 h for boiled, wet, as-received, and boiled and dried membranes, respectively. Following the same order, the times from 0.8 to 0.2 V are 41, 72, 201, and 444 h for boiled, wet, as-received, and boiled and dried membranes, respectively. The self-discharge rate of the different pretreated membranes is in accordance with the vanadium ion permeability results depicted in Figure 4.

The VFBs assembled with the four membranes were then subjected to a charge-discharge test over a wide current density range from 40 to 320 mA cm<sup>-2</sup>, corresponding to currents of 1-8 A. As mentioned in section 2.3, the charge cutoff voltage was set to 1.65 V to prevent the corrosion of the graphite felt electrode and the graphite plate current collector.9,10 It should be noted that only the VFB with the boiled membrane can run at the very high current density of 320 mA cm<sup>-2</sup> because it has the lowest membrane area resistance (Table 1) and battery internal resistance (Figure S1). The highest working current densities for the VFBs with asreceived, wet, and boiled and dried membranes are 240, 280, and 240 mA cm<sup>-2</sup>, respectively. Typical charge-discharge curves of VFBs with various membranes are compared in Figure S2. With the increase in current density, the efficiencies of all batteries show the typical change trend of VFBs.<sup>11</sup> As shown in Figure 9, Coulombic efficiency (CE) increases with an increase in current density, while voltage efficiency (VE) and



Figure 9. Cell performance of VFBs assembled with various membranes: (a) Coulombic efficiency, (b) voltage efficiency, (c) energy efficiency, and (d) discharge capacity.



Figure 10. Long-term cycling performance of VFBs with various membranes at 120 mA cm<sup>-2</sup>: (a) Coulombic efficiency, (b) energy efficiency, (c) discharge capacity, (d) discharge capacity retention, and (e) electrolyte volume change rate.

energy efficiency (EE) decrease with an increase in current density. The increase in CE with current density is caused by the shorter charge-discharge time at a higher current density, resulting in slower crossover of vanadium ions and capacity loss.<sup>11,17</sup> In a VFB, CE is mainly affected by vanadium ion permeation.<sup>12</sup> It can be seen from Figure 9a that the order of CE is as follows at all current densities: boiled and dried > as received > wet > boiled [as expected from the  $VO^{2+}$  permeation (Figure 4) and self-discharge results (Figure 8)]. It is worth noting that the wet membrane exhibits an only slightly lower CE compared to those of as-received and boiled and dried membranes. In addition, the CE of the wet membrane is >95% when the current density is >80 mA  $cm^{-2}$ , which is acceptable for the VFB system. The VE of a VFB is determined by the electrode activity and battery resistance.8,65 Because of the identical electrodes used in all batteries, the internal resistance becomes a major factor in determining the VE. As shown in Figure 9b, the VE decreases in the following order: boiled > wet > as received > boiled and dried (which is consistent with the EIS results depicted in Figure S1). The gradual decrease in VE with the increase in current density could be attributed to the increase in ohmic polarization.<sup>47</sup> Energy efficiency (EE), determined by CE and VE, is an important parameter for evaluating the energy loss in a charge-discharge process of VFBs.<sup>7</sup> The EE of the VFB with the boiled membrane is much lower than the others at a current density of 40 mA cm<sup>-2</sup> (Figure 9c), because of the lowest CE of the boiled membrane. All batteries present nearly the same EE of  $\sim$ 81% at a current density of 80 mA cm<sup>-2</sup>. At higher current densities from 120 to 320 mA cm<sup>-2</sup>, VFB with a boiled membrane demonstrates a

superior EE versus those of other VFBs because of the highest VE. These results reveal that VE becomes the decisive factor in EE at higher current densities. The discharge capacity of VFBs with various membranes is shown in Figure 9d. The capacities of all VFBs decline with an increase in current density, attributed to the increasing ohmic loss.<sup>21</sup> Moreover, the ratio of reduced discharge capacity decreases in the following order: boiled and dried > as received > wet > boiled (the same trend observed for membrane area resistance and battery internal resistance).

Electrolyte utilization (EU), the ratio of actual discharge capacity to theory capacity, is also a critical index of VFBs. High EU is beneficial for improving the energy density of VFB. In this work, the theory capacity is 2010 mAh according to 50 mL of 1.5 M vanadium electrolyte used. As shown in Figure S3, EU of all VFBs decreases with an increase in current density. The four batteries have similar EUs of ~90 and ~83% at current densities of 40 and 80 mA cm<sup>-2</sup>, respectively. At a current density of >80 mA  $cm^{-2}$ , the VFBs with boiled and wet membranes exhibit EU decline rates relatively slower than that of as-received and boiled and dried membranes. This phenomenon can be explained by the fact that the increase in current density leads to higher ohmic polarization for asreceived and boiled and dried membranes but lower vanadium ion crossover for boiled and wet membranes. The variation of EU that resulted from the compromise between ohmic polarization (VE) and vanadium ion crossover (CE) is in accordance with the EE results depicted in Figure 9c.

**3.3. VFB Cycling Stability Evaluation.** The long-term cycling stability, such as the stability of the battery efficiency,



Figure 11. Monitor images recorded at different cycle numbers for the VFBs with various membranes cycling at 120 mA cm<sup>-2</sup>.



Figure 12. Comprehensive analysis of electrolyte status at 50% capacity retention: (a) monitor images, (b) volumes and various vanadium ion concentrations in the positive and negative electrolyte, and (c) total species amounts and average valence status of vanadium ions.

the slow electrolyte imbalance and capacity decay rate, and the suppressed side reactions, is essential for the safe operation of VFBs.<sup>7–11</sup> To understand the impact of the Nafion membrane pretreatment method on the cycling stability of VFBs, four VFBs assembled with various membranes were run continuously at a relatively high current density of 120 mA cm<sup>-2</sup> until the discharge capacity retention decayed to 50%. The powerful OMS was utilized to record the electrolyte volume change simultaneously, as shown in Figure 1.

The cycling performances, including battery efficiencies, discharge capacities, discharge capacity retentions, and volume change rates, of all VFBs are shown in Figure 10. It can be seen that the CE (Figure 10a) and EE (Figure 10b) of all VFBs remain nearly stable during the whole cycle life test, indicating that there is no obvious nanostructure change happening in all membranes. It is well-known that fast capacity fading is one of the critical issues for the practical application of VFBs.<sup>32</sup> According to a previous study, the capacity decay of VFB is mainly caused by the crossover of vanadium ions through the membrane, which leads to the imbalance of volume and concentration between positive and negative electrolytes.<sup>66–69</sup>

As discussed in Figures 4 and 8, the boiled membrane suffers the highest vanadium ion permeability. Consequently, the VFB assembled with the boiled membrane presents the fastest capacity fading rate, as shown in Figure 10c. When the capacity retention decays to 50%, the VFBs with as-received, wet, boiled, and boiled and dried membranes were run for 724, 586, 342, and 597 cycles, respectively, as shown in Figure 10d. The capacity decay rate of the boiled and dried membrane is faster than that of the as-received membrane, which should be ascribed to the side reactions that resulted from the highest ohmic polarization (see Figure S1). To the best of our knowledge, these exciting results exceed all previous reports about Nafion-based VFB systems,11-14,28,66 which demonstrates that a reasonable pretreatment method can endow the Nafion membrane with a promising efficiency as well as a slow capacity fading rate. For instance, the wet treated (soaked in DI water for 24 h) Nafion 115 membrane exhibits an outstanding VFB performance, such as 96% of CE, 76% of EE, and 55% of capacity retention after 500 cycles, at a higher current density of  $120 \text{ mA cm}^{-2}$ .

The volume change is a direct indicator of the imbalance of electrolytes. The corresponding electrolyte volume change rate and the real-time monitor images of various VFBs obtained from the OMS are displayed in Figure 10e and Figure 11, respectively. Figure 11 directly shows the gradual electrolyte imbalance process of all four batteries. The severe imbalance of electrolytes of VFBs with boiled and wet membranes can be observed clearly, especially at the 300th and 500th cycle. The volume change rate decreases in the following order: boiled > wet > as received > boiled and dried (in agreement with the vanadium permeability and self-discharge results mentioned above). When the discharge capacity decays to 50%, the volume change rates of VFB with as-received, wet, boiled, and boiled and dried membranes are 21, 38, 53, and 11%, respectively.

To further investigate the capacity fading mechanism, a comprehensive analysis of the electrolyte status was conducted as soon as the VFB was stopped at 50% capacity retention. The results, including monitor images, volumes, and various vanadium ion concentrations in both half-cells and total vanadium species amounts and average valence status of vanadium ions, are shown in Figure 12. The concentrations of vanadium ions in different oxidation states were determined by potentiometric titration methods. To prevent  $V^{2+}$  and  $V^{3+}$  from being oxidized by the oxygen in air during the test, the potentiometric titration of the negative electrolyte was conducted under nitrogen protection. As shown in Figure 12c, the total vanadium species concentration of four batteries in the final state is very close to the initial value of 1.50 M, demonstrating the good reliability of our experiments. During the operation of the VFB, water transfer is mainly caused by the transfer of vanadium ions with bound water and the transfer of water driven by osmosis.<sup>67</sup> Hence, the faster vanadium permeability will result in a higher volume change rate of the electrolytes. In addition, the transfer rate of  $V^{2+}/V^{3+}$  is higher than that of  $VO_2^{+}/VO_2^{+}$ , thus bringing about the net transfer of vanadium species from the negative to the positive half-cell.<sup>67,</sup> Accordingly, the transfer of water and vanadium ions during the long-term charge-discharge cycling would result in a continuously increasing volume in the positive half-cell and a decreasing volume in the negative half-cell,<sup>66</sup> as confirmed by Figure 11. Besides, the side reactions occurring in positive (oxygen evolution reaction) and negative (hydrogen evolution reaction) half-cells also lead to capacity fading in the VFB system.<sup>64</sup> Along with the charging and discharging process, more and more VO<sub>2</sub><sup>+</sup> would accumulate at the positive half-cell because the side reaction on the negative electrode is faster than that on the positive electrode,<sup>64,69</sup> as confirmed by Figure 12b.

As shown in panels a and b of Figure 12, for all batteries, the volume and vanadium ion concentration of the electrolyte increase on the positive side and decrease on the negative side. The severe electrolyte imbalance of the boiled membrane is caused by its highest vanadium ion permeability. According to the results depicted in Figures 10e and 12b, the 50% capacity decay of the VFB with boiled membranes is basically the same as its electrolyte volume change ratio (53%), suggesting that the crossover of vanadium ions is the main reason for capacity fading.<sup>21</sup> However, VFBs with as-received, wet, and boiled and dried membranes present a faster capacity fading rate compared with their electrolyte volume change rate (Figure 10d,e). The inconsistent change speed between capacity and electrolyte volume could be attributed to the combined impact of vanadium ion crossover and undesirable side reaction. The

amount of accumulated  $VO_2^+$  in the positive electrolyte of VFBs decreases in the following order: boiled and dried > as received > wet > boiled (Figure 12b) [the same order as battery resistance (membrane area resistance)]. The average valence state and total vanadium species of both half-cells are listed in Figure 12c. The slight change in total vanadium species after the test is due to the titration error and volumetric reading error. The average valence states of vanadium ions in VFBs with as-received, wet, boiled, and boiled and dried are 4.16, 4.09, 3.89, and 4.07, respectively. The higher of the average vanadium valence states means the more serious charge imbalance. The vanadium amount imbalance (both volume and concentration) can be solved by remixing and redistributing the positive and negative electrolytes.<sup>10,32</sup> However, the charge imbalance (that resulted from side reaction) can be recovered only by the relatively complicated process such as the electrolysis method.<sup>32</sup> Therefore, the charge imbalance should be avoided as much as possible.

In summary, the boiled Nafion membrane has the lowest area resistance and can serve as a benchmark in VFBs for evaluating other materials, like a non-fluoride porous membrane,<sup>28</sup> a novel electrode,<sup>65</sup> electrolyte stabilty,<sup>63</sup> etc. However, considering the practical application of VFBs, the wet treated (just soaked in DI water) Nafion membrane may be the best choice because of its comprehensive merits, such as ease of operation, relatively low cost, proper physicochemical properties, acceptable vanadium ion permeability, excellent battery performance, and outstanding cycling stability.

#### 4. CONCLUSIONS

Nafion 115 membranes subjected to different pretreatment processes have been studied comprehensively for VFB application. Our work demonstrates the following. (1) The area resistance, battery resistance, self-discharge time, CE of the membranes (or VFBs) follow the order of boiled < wet < as received < boiled and dried while the VO<sup>2+</sup> permeability, VE, and electrolyte volume imbalance rate of the membranes (or VFBs) present the opposite trend. (2) The as-received and boiled and dried membranes are more suitable for working at current densities of <120 mA cm<sup>-2</sup>, while the boiled and wet membranes present better energy efficiency and electrolyte utilization at higher current densities of 120-320 mA cm<sup>-2</sup>. (3) Capacity fading of VFBs could be attributed to the combined impact of vanadium ion crossover and undesirable side reaction. (4) The boiled membrane can serve as a benchmark in VFBs for fundamental research. (5) The wet treated Nafion membrane may be the best choice for practical VFB application because of its comprehensive merits in terms of cost, efficiency, and cycling stability.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b03529.

Additional information, including experimental details, Nyquist plots, charge–discharge curves, and electrolyte utilization (PDF)

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Notes

The authors declare no competing financial interest.

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