Research Article

Crosslinked Polyethyleneimine Gel Polymer Interface to Improve Cycling Stability of RFBs

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Redox flow batteries are considered a promising technology for grid energy storage. However, capacity decay caused by crossover of active materials is a universal challenge for many flow battery systems, which are based on various chemistries. In this paper, using the vanadium redox flow battery as an example, we demonstrate a new gel polymer interface (GPI) consisting of crosslinked polyethyleneimine with a large amount of amino and carboxylic acid groups introduced between the positive electrode and the membrane. The GPI functions as a key component to prevent vanadium ions from crossing the membrane, thus supporting stable long-term cycling. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted to investigate the effect of GPI on the electrochemical properties of graphitic carbon electrodes (GCEs) and redox reaction of catholyte. X-ray photoelectron spectroscopy (XPS) and ¹H nuclear magnetic resonance (NMR) spectra demonstrated that the crosslinked GPI is chemically stable for 100 cycles without dissolution of polymers and swelling in the strong acidic electrolytes. Results from inductively coupled plasma mass spectrometry (ICP-MS), Fourier-transform infrared (FTIR) spectroscopy, and energy-dispersive X-ray (EDX) spectroscopy proved that the GPI is effective in maintaining the concentration of vanadium species in their respective half-cells, resulting in improved cycling stability because of it prevents active species from crossing the membrane and stabilizes the oxidation states of active species.

1. Introduction

Because of their ability to store and release large amounts of energy in a controlled manner, stationary energy storage systems have become increasingly important for renewable energy integration and grid modernization. Among various technologies, redox flow batteries (RFBs) have received much attention as one of the most promising candidates for stationary energy storage because of their inherent safety, decoupled power/energy, and long service life [1–3]. However, a universal challenge for RFB technologies is the substantial capacity fading caused by crossover of active species from one half-cell to the other through the membrane, especially over long-term operations [4–6]. Constant capacity decay requires the system to be overdesigned to deliver the rated power/

energy, as well as implementation of extra system and operational measures to ensure stable cycling.

Material degradation and side reactions obviously can lead to capacity decay [7]. Another major contribution however is crossover of active materials [2, 8, 9]. For example, one of the most highly developed RFB technologies is the vanadium redox flow battery (VRB) [6], which traditionally uses a proton-conductive membrane such as Nafion™ to separate the two half-cells. More detailed mechanistic study suggests that the main reasons for capacity decay in a VRB during cycling are imbalanced crossover of vanadium active species and asymmetrical valence of vanadium ions in the electrolytes caused by self-discharge reactions after crossover [10]. Many research efforts have been devoted to the development of new membranes or modification of Nafion™ to

SCHEME 1: Schematic illustration of the multifunctional effects of a PEIAA GPI introduced on the GCF to prevent crossover of vanadium ions in the VRB.

achieve better selectivity [11–14] (i.e., reducing crossover). For example, amine polymer-based membranes have been studied for VRBs because of their surface chemistry with positively charged groups to repel vanadium ions via Donnan exclusion in strong acid conditions [15–18]. Even though some of those membranes improved cycling performance by reducing permeability rates of vanadium ions, their complicated fabrication or modification processes may result in high cost. The cationic-charged polymer films or surface coating on a membrane acting as an electrical repulsion barrier also disturbs proton permeation, thus leading to higher area resistance [19]. Most current efforts to overcome the capacity decay issue are almost exclusively focused on membrane development and modification [20–22]. New approaches are rarely reported and discussed. Nevertheless, capacity decay remains a key challenge.

In its role of separating the positive and negative electrolytes, a membrane must provide both high conductivity towards charge transfer ions and high selectivity towards energy-bearing active species. These two competing requirements mean the structure and morphology of the membrane must be designed to achieve two opposing functionalities. Improvement of one function often is achieved at the sacrifice of the other. In light of this inherent challenge, we postulate a new component that can be introduced into the traditional RFB structure to prevent crossover of active species, thus providing more latitude for material selection and system design for both the membrane and the flow cell.

Using a VRB as an example, we created a gel polymer interface (GPI) consisting of crosslinked polyethyleneimine (PEI) with amino and the oxygen functional groups such as carboxylic acid and carbonyl and hydroxyl groups between the electrode and membrane to effectively prevent electrolyte crossover. We found that the as-synthesized GPI also increases the surface wettability of a carbon felt electrode because of its hydrophilicity. The PEI with amino and carboxylic acids (PEIAAs) in acidic conditions acts to not only repulse vanadium ion with expended polymer networks but to consequently stabilize the oxidation state of vanadium ions with positively charged amines. The PEIAA GPI with abundant amounts of primary, secondary, and tertiary amines and also oxygen-containing groups that are mainly carboxylic acid groups preserves almost the same concentration of negative and positive electrolytes even after 100 cycles and resulted in five times higher cycling stability in capacity retention (86.46% at the 100th cycle, a capacity fading rate 0.16%/cycle) with higher Coulombic efficiency (CE) (98.37% at the 100th cycle) than a pristine graphitic carbon felt (GCF) cell (17.65% at the 100th cycle with a CE of 96.73%, capacity fading rate of 0.81%/cycle). A schematic illustration of a novel GPI system in a VRB is presented in Scheme 1.

2. Results and Discussion

The chemical reaction that yields the PEIAA is shown in Figure 1.

FIGURE 1: Chemical structures of PEI and GA and their chemical reaction to form crosslinked regions and amino and carboxylic acid groups.

FIGURE 2: FTIR spectra of (black) pristine GCF and (red) PEIAA-GCF samples.

GA played two roles in this study. Uncrosslinked (linear) PEI is not stable in aqueous solutions because thermodynamically compatible water molecules easily diffuse into the PEI phase and disentangle them (see Fig. S1). Thus, GA was used as a crosslinker to stabilize the PEI under strong acidic conditions [23] because it readily reacts with amine-containing molecules such as PEI through the formation of Schiff bases. Thus, a GPI with a swellable three dimensionally crosslinked structure is obtained. GA molecules in aqueous solutions also form aldehyde polymers. In the drying step for the GCF samples treated in PEI and

GA solutions at 70°C in air, aldehydes are readily oxidized via the following reaction to form carboxylic acid groups:

FTIR spectra of pristine GCF and PEIAA-GCF samples reveal that the PEIAA-GCF sample had amino and carboxylic acid groups (amines and carboxylic acids). In the case of the pristine GCF, Figure 2 shows oxygen-containing groups in the PEIAA-GCF over a very broad band in the 3300–2500 cm⁻¹ region for hydroxyl (O-H) stretching,

FIGURE 3: SEM images of (a, b) pristine GCF and (c, d) PEIAA-GCF samples with different magnifications (1,000x and 10,000x). SEM-EDX (e) spectrum and element maps ((f) carbon, (g) oxygen, and (h) nitrogen) of a part of PEIAA-GCF sample. Contact angles of (i) the pristine GCF and (j) the PEIAA-GCF samples.

intense bands from 1760 to 1690 cm^{-1} and 1320 – 1200 cm^{-1} corresponding to C=O (polymeric aldehyde segment with carboxylic acids) [24, 25]. C-OH vibration comprised of a mixture of C-O stretch and C-O-H bend with the appearance of typical N-H and C-N stretching vibrations corresponding to amine groups and PEI backbone. Therefore, the amino and carboxylic acid groups were successfully introduced into PEI backbones.

Figure 3 shows scanning electron microscopy (SEM) images of (a and b) pristine GCF and (c and d) PEIAA-GCF electrodes under different magnifications.

After PEIAA modification using the immersion method and followed by oxidation in air, the string surface of the GCF became smooth with very thin polymer films around the carbon strings. Rapid reaction of aldehydes and primary amines of PEI dissolved in aqueous solutions by formation of Schiff bases makes the polymers partially hydrophobic so they have an affinity for the hydrophobic surface of the carbon strings [23]. After the formation of crosslinked PEI with GA, we dried the samples in air at 70°C for 12 hours in an oven to oxidize the aldehyde groups to carboxylic acid groups on the polymer backbone. The SEM images show that the uneven surface of the pristine GCF fibers changed to a smooth surface with a spider web-like polymer phase, thus demonstrating our approach to be a simple and effective way to coat graphite fibers in the widely used GCF electrode. Figures 3(e)–3(h) show a SEM-EDX spectrum (in Figure 3(e)) and element maps of the PEIAA-GCF sample. The polymer phase in the PEIAA-GCF sample consists of 90.2% (atomic) carbon, 4.5% oxygen existing in aldehyde polymer regions and carboxylic acids, and 5.1% of nitrogen

in the PEI regions, while pristine GCF is mostly carbon itself as shown in Fig. S2. Basically, the crosslinked PEI with GA does not have oxygen because the oxygens of aldehydes are removed by formation of Schiff bases with primary amines of PEI [21]. In this study, however, because GA caused aldehyde polymers to form with large amount of aldehyde groups, and after samples were dried at 70°C in air, aldehydes were oxidized to carboxylic acids to improve the surface hydrophilic property for better wettability of the GCF electrode, as explained above [26]. Therefore, the oxygen in the aldehyde and carboxylic acid groups was detected by EDX and FTIR. Figures 3(i) and 3(j) show the contact angles with water drops for the comparison of surface characteristics of GCF electrodes before and after PEIAA modification. The contact angle of pristine GCF was significantly reduced from 112° to 45° after PEIAA modification because of the large amount of oxygen-contained functional groups that improve the GCF surface. The polymer content introduced in PEIAA-GCF is $\sim 1.8\text{ wt\%}$, as measured by thermogravimetric analysis and presented in Fig. S3. The weight loss of PEIAA happens below 400°C , which is similar to neat PEI and indicates that the crosslinking density of the PEIAA phase is not too high because of the formation of aldehyde polymer regions [27]. We performed Brunauer–Emmett–Teller and Barrett–Joyner–Halenda analyses for pristine GCF and PEIAA-GCF samples to identify the graphite fiber surface physical property change induced by polymer modification. Fig. S4 and Table S1 demonstrate that the surface area and average pore size of the GCF became smaller and the pore volume also decreased after PEIAA modification. These results are consistent with the surface changes of the

FIGURE 4: (a, empty square) Discharge capacity, (a, solid circle) Coulombic efficiency, and (a, empty circle) energy efficiency; (b) voltage-time profiles of 1st, 50th, and 100th cycles of cells with (blue) pristine GCF and (pink) PEIAA-GCF electrodes under constant current charge at 50 mA cm⁻².

samples before and after PEIAA modification as shown in the SEM images discussed above.

We observed the swelling response of PEIAA by immersing the sample in 0.9 M H₂SO₄ solution for 5 hours. Fig. S5 shows that large volumetric swelling of the PEIAA sample occurs in the strong acidic environment. The swelling was caused by the considerable number of water molecules that were absorbed in PEIAA phase. To verify the electrostatic repulsion of PEIAA, colloidal PEIAA solutions were prepared with PEIAA particles (Fig. S6a) in DI water and 0.9 M H₂SO₄ solution, respectively, and then, zeta potential was measured. The digital photographs of PEIAA colloidal solutions shown in Fig. S6b clearly show that the strongly acidic condition leads to particle swelling, which leads to murky solutions as indicated by the large proportion of the light scattered by swollen particle phase while the PEIAA solution with DI water is relatively clear. Fig. S6c shows that zeta potential of the PEIAA solution with H₂SO₄ became much higher (47.2 ± 5.4 mV) than the one with just DI water (5.2 ± 0.22 mV). This result suggests that PEIAA particles are more stable in acidic conditions because of the strong electrostatic interactions of particle surfaces that lead to a distribution of charged polymer branches in the system.

We tested the electrochemical performances of PEIAA-GCF and pristine GCF electrodes in a flow cell with a traditional sulfuric vanadium electrolyte (1.5 M VOSO₄ in 3.5 M H₂SO₄). Testing was conducted within the voltage range of 0.8 V–1.6 V at a constant current density of 50 mA cm⁻². Results from flow battery cycling tests of two flow cells with a pristine GCF and a PEIAA-GCF electrode are presented in Figure 4. We conducted cycling tests to evaluate the effect of PEIAA modification on the cycling performance. Compared with the baseline GCF cell, the PEIAA-GCF cell exhibits better cell performance with much higher CE (~2% higher throughout 100 cycles) and most notably the significantly improved capacity retention (86.46% vs. 17.65% at 100th cycle) shown in Figures 4(a) and 4(b). To investigate the electrochemical properties of the different GCF electrodes, the cyclic voltammetry (CV) curves were analyzed and displayed in Fig. S7. Both two different electrodes exhibit an

anodic peak representing the oxidation of VO²⁺ to VO₂⁺ and a cathodic peak representing the reduction of VO₂⁺ to VO²⁺. The current density of the PEIAA-GCF in the CV test is close to that of pristine GCF at both two different scan rates, which means the PEIAA modification does not interrupt the electron transferring. In addition, the smaller peak-to-peak separation of PEIAA-GCF electrode means that PEIAA modification gives rise to better chemical and electrochemical reversibility due to its better wettability leading to continuous stable reduction and reoxidation of analyte. Thus, PEIAA-GCF has no issue of electrochemical reversibility with a low barrier to electron transfer.

The energy efficiency of the flow cell with the PEIAA-GCF is ~2% lower than that of the baseline cell, possibly due to an increased internal resistance of the cell from reduced electrode conductivity, which is a result from the PEIAA on the GCF coating with its smaller pore volume and surface area. The effect of electrode modified with PEIAA interface on the positive VO²⁺/VO₂⁺ reaction was investigated by EIS measurement, as seen in Fig. S8. For the fresh cells, one more semicircle (R_{sf} , surface film resistance) appears for PEIAA-GCF cell with a larger charge transfer resistance (R_{ct}) while the pristine GCF shows only one semicircle due to the new interface in the PEIAA-GCF cell from the electrode modification. At low frequency, PEIAA-GCF fresh cell results in a decrease in mass transfer resistance (W) due to the oxygen containing groups on PEIAA phase. The Nyquist plot of PEIAA-GCF cell at a SOC of 50% shows the lower charge transfer resistance due to the better wettability. However, the smaller surface area and the decreased pore volume resulting from smaller pore size and reduced electrical conductivity as mentioned earlier might cause a larger charge transfer resistance at a SOC of 100% and consequently, the lower charge-discharge capacities with a larger cell overpotential at the initial cycle. Figure 4(b) shows voltage-time profiles of the GCF baseline and PEIAA-GCF cells at the 1st, 50th, and 100th cycles. The capacity decrease of pristine GCF cell is observed with increasing overpotential and decreasing charge-discharge time as cycling proceeds while cycling ability of the

PEIAA-GCF cell is much more stable as seen in Figure 4(b). The poor cycling stability of the baseline cell could be attributed to both active species crossover and the subsequent increase of concentration polarization as cycling proceeds as previously reported [28]. In addition, the cycle performance tests prove that PEIAA is much more stable in vanadium electrolytes over 100 cycles.

To understand the mechanism of the GCF electrode modified with PEIAA on mitigation of the crossover-induced capacity decay, we performed ICP-MS analysis of the cycled electrolytes. The results revealed that the pristine GCF cell has an asymmetric valence of redox-active species in the anolyte (V^{3+}) and decreasing concentration of VO_2^{2+} (0.3 M/L, ~22% remained at the 100th cycle after discharge) in the catholyte during cycling. The imbalanced accumulation of VO_2^{2+} in the positive side contributes to capacity fading. As a result, the amount of redox-active species VO_2^{2+} (V(IV)) in the positive side was significantly reduced and replaced with a high concentration of VO_2^{2+} (V(V)) indicating the reaction became irreversible because of crossover of vanadium ions by possible diffusion, migration, electroosmotic convection, and subsequent side reactions in both electrolytes. Some of the potential reactions are listed in the below equations (2)–(5) [15]. Diffusion of vanadium ions through the membrane happens in the same direction regardless of charging and discharging. On the other hand, the direction of migration and electroosmotic convection is affected by charging or discharging. Different diffusion rates of vanadium ions can cause capacity fading due to a disparity between the state of charge of the anolyte and catholyte. Consequently, there is an accumulation of VO_2^{2+} in the catholyte as cycling proceeds. In comparison, the PEIAA-GCF cell retains almost the same concentration of VO_2^{2+} (1.45 M/L; ~99.4% remained at the 100th cycle) in the catholyte, leading to symmetric valence of redox-active species with a negligible amount of VO_2^{2+} even after the 100th discharge compared to the pristine cell. Because large amounts of amino groups in an abundance of PEI branches are protonated in strongly acidic conditions, strong positive charges prevent vanadium ion permeation by electrocharge repulsion. Besides, the significant expansion of PEIAA films with carboxylic acids helps limit undesired transport of vanadium ions and enhance electrochemical performance. To verify the effect of the PEIAA interface on reducing vanadium crossover, the 3.5 M H_2SO_4 solution was coupled with the catholyte (1.5 M V^{4+} in 3.5 M H_2SO_4 solution) and pumped through the cell where they are separated by Nafion 115 with pristine GCF or PEIAA-GCF electrodes for 5 days. UV-vis spectra were recorded for the concentrations of V^{4+} ions in H_2SO_4 solutions. The absorbance spectra at 765 nm of two samples revealed that the PEIAA interface led to ~25% lower V^{4+} crossover, as displayed in Fig. S9b. Under no externally applied electric field, the results confirmed that the PEIAA interface on GCF slows crossover of VO_2^{2+} ions via diffusion and convection. Along with the PEIAA-GCF electrode's ability to delay crossover, good wettability with aqueous electrolytes containing hydrated cationic vanadium ions with water molecules also is helpful to maintain good cycling stability. During charge and discharge processes, it is possi-

ble that vanadium ions coordinate with water molecules, with one oxygen atom coming from sulfate and one carboxyl oxygen atom coming from amino and carboxylic acid in the PEIAA as previous studies suggest [29, 30].

Therefore, hyperbranched PEIAA networks with carboxylic acids present in GPI between the surfaces of the positive electrode and the Nafion membrane are effective in preventing vanadium ion crossover through the mechanisms of electrical repulsion from the protonated amines in acidic condition, physical hindrance from swollen PEIAA films in strong acidic electrolytes to prevent undesired vanadium crossover, and improved wettability with possible coordination chemistry of the amino and carboxylic acid functionality of PEIAA to stabilize the oxidation state of VO_2^{2+} and VO_2^{+} species.

We further analyzed the cycled electrodes and electrolytes using SEM, EDX, XPS, and 1H -NMR. Fig. S10 and S11 show the smooth surface of carbon strings and the surviving polymer films detected with a EDX-nitrogen map after 100 cycles in vanadium electrolyte. Based on wide-scan XPS spectra, it is notable that N 1s spectra appear only in PEIAA-GCF samples due to the tertiary amino groups of PEI while pristine GCF has no N 1s signal, as shown in Figure 5 and Fig. S12.

XPS spectra of the PEIAA-GCF samples before and after 100 cycles also provide evidence that the crosslinked PEIAA is chemically stable in the strong acidic solution and oxidative environment of the VO_2^{2+} ions in the charged catholyte. The nitrogen binding energies for the primary, secondary and tertiary amine peaks detected between 399 eV and 401.7 eV [31] are retained after 100 cycles, as shown in Figures 5(a) and 5(b). Since PEI chains are crosslinked with GA and the aldehyde groups are oxidized to carboxylic acid groups, C=N and COOH bondings are also detected at 285.7 eV and 288.5 eV, respectively. In the case of the pristine GCF sample before the cell test, there also are several peaks of C 1s binding energies corresponding to C-OH, C-O-C, C=O, and COOH frequencies at 286.11, 286.72, 287.32, and 288.14, respectively. However, the intensities of these peaks were reduced significantly after 100 cycles, as shown in Figure 5(c). Thus, organics containing oxygen atoms on the GCF surface were removed or decomposed in the strong acidic electrolytes during long-term cycling. This result may correspond to the surface change from rough to relatively smooth after cycling, as shown in Fig. S13. In contrast, all C 1s binding energy peaks for PEIAA-GCF that underwent the same testing conditions, as shown in Figure 5(d), also show that no polymer (PEIAA) dissolution occurs in the catholytes over 100 cycles, as shown in Fig. S14. Thus, the chemical robustness of GPI consisting of the

FIGURE 5: Wide scan XPS and inserted N 1s spectra of PEIAA-GCF electrodes (a) before and (b) after 100 cycles under constant current charge at 50 mA cm^{-2} . High-resolution XPS C 1s spectra of (c) pristine GCF and (d) PEIAA-GCF electrodes before and after 100 cycles.

crosslinked PEIAA with carboxylic acids contributes to the long-term stability of vanadium redox flow battery cells.

3. Conclusions

We used a simple modification method to introduce a GPI to a chemically stable crosslinked PEIAA to the surface of a GCF acting as the positive electrode in a VRB. The PEIAA-GPI electrode demonstrated a significant blocking effect in preventing active vanadium species from crossover, thus providing more stable cycling performance. In contrast, serious imbalanced crossover and asymmetrical valence of active-species vanadium ions were observed in a cell using pristine GCF electrodes. The positive effect of the PEIAA GPI on cell cycling is attributed to the multifunctional mechanisms of electrorepulsion, physical hindrance from swollen PEIAA films to limit the vanadium crossover, and coordination chemistry of the chemically stable polymer interface with good wettability in strong acidic condition to maintain the concentrations of the vanadium active species stable in their respective half-cell reservoirs.

4. Experimental Section

4.1. Materials. Vanadium (IV) oxide sulfate ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, 99.5%, pure crystal) was purchased from Noah Technologies. The membrane (Nafion™ 115) was purchased from DuPont and pretreated in deionized (DI) water before use. The GCF (4 mm thick), and gasket (EPDM rubber sheet, $1/32$ in. thick) were purchased from the FuelCellStore. The PEI (branched, average Mw $\sim 25,000$) and glutaraldehyde (GA) (50% in H_2O) were purchased at Sigma-Aldrich.

4.2. PEIAA Modification on GCF Electrodes. The crosslinked PEIAA was introduced to the surface of the GCF by sequential immersion in two different DI waters containing hyper-branched PEI (25,000 Mw) and GA (50% in solution), respectively. To get carboxylic acid groups in the PEI backbone, we used GA (1 wt%). In this step, only one-fifth of a pristine GCF electrode ($5 \times 6 \text{ cm}^2$, 4 mm thickness) was immersed in each solution one-by-one two times. The samples were stored at 70°C for 12 hours in an oven. During this time, the samples dried and the aldehyde groups oxidized to carboxylic acid groups on the polymer backbone. Then, we washed the samples in DI water several times to remove

residual molecules. The dried PEIAA-GCF was cut into two pieces ($2 \times 5 \text{ cm}^2$) for use as electrodes. Scheme S1 shows the schematic illustration of bare GCF and PEIAA-GCF samples.

4.3. Swelling Behavior and Zeta Potential Measurement. The PEI polymeric solution was mixed with GA solution in a weight ratio of 10:1. After it was washed and dried using the same procedures used for the PEIAA modification on GCF, a PEIAA sample was prepared to observe its swelling behavior in acidic conditions. The PEIAA sample was fully immersed in 0.9 M H_2SO_4 solution for 5 hours. To investigate the electrostatic force of PEIAA in acidic condition, a zeta potential measurement was conducted by Malvern Zetasizer Nano ZS with the Smoluchowski model. While the diluted PEI solution (0.5 wt%) with 200 mL of DI water was stirred at 800 rpm in a round bottom flask using a magnetic spin bar, the diluted GA solution (1 wt%) with 100 mL of DI water was slowly added over a 2-hour period using a dropping funnel. To remove the entangled particles, we used centrifugation at 3000 rpm. After drying and washing using the same procedure described previously, the PEIAA particles were dispersed in DI water and 0.9 M H_2SO_4 solution by ultrasonication for 1 hour. The colloidal solutions were directly used for the zeta potential measurement.

4.4. Electrochemical Measurement. The cyclic voltammetry (CV) was carried out in 1.5 M VO_2^+ in 3.5 M H_2SO_4 catholyte from 0.4 to 1.7 V at 25°C. The pristine GCF and PEIAA-GCF samples were used as working electrodes attached with graphite electrode. The effective area of CF electrodes exposed to the catholyte is $6 \text{ mm} \times 6 \text{ mm}$. The glassy carbon and Ag/AgCl were used as the counter and reference electrodes, respectively. The three-electrode system was purged with N_2 gas for 10 min before the CV test. Electrochemical impedance spectroscopy (EIS) test was also operated over the frequency range of 0.1 Hz to 100 kHz with an amplitude of 5 mV.

4.5. Ultraviolet-Visible (UV-vis) Spectroscopy Analysis. The concentration of V^{4+} in the 3.5 M H_2SO_4 solutions was analyzed using a UV-vis spectrophotometer (UXL-360, HI2608) by monitoring the maximum absorbance wavelength located at 765 nm (Figure S9) [32]. First, we performed a standard calibration analysis based on a series of known concentrations of V(IV)OSO_4 solutions ranging from 0.01 M to 0.2 M. Then, the concentration of V^{4+} samples was determined by comparison with the standard calibration curve (Figure S9a).

4.6. Redox Flow Battery Test. Electrochemical performances of PEIAA-GCF and pristine GCF electrodes were tested in a homemade flow cell with a 10 cm^2 active area, which is controlled by an Arbin BT-2000 instrument for galvanic charge/discharge cycles within a 0.8 V–1.6 V voltage range at a constant current density of 50 mA cm^{-2} . The flow rate of the electrolytes was 30 mL min^{-1} (the pump was a Cole Parmer, easy-load 2, 77202-60). Vanadium 3^+ and 4^+ (VO^{2+}) solutions were prepared and used as the anolyte and catholyte (1.5 M VO_2^+ in 3.5 M H_2SO_4), respectively. N115 membranes were used for the cell test. Pristine GCF

and PEIAA-GCF were used as the electrodes. Detailed descriptions of the cell design and testing procedures are described in previous publications [28, 33–35].

Data Availability

The data and materials used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflict of interest regarding the publication of this article.

Authors' Contributions

The work was supervised by W. Wang. H.-S. Lim and W. Wang conceived the idea. H.-S. Lim designed detailed experimental procedures, performed the material preparation, redox flow battery test, and data analysis, and wrote the paper. S. Chae made contribution on the BET study and drawing schematic illustration. L. Yan provided technical support for battery test. G. Li made contributions on the SEM and EDX studies. R. Feng performed CV and EIS. Y. Shin performed and analyzed FTIR of GCF electrodes. Z. Nie and Y. Liang provided technical support for electrolyte preparation. V. Murugesan managed XPS and ^1H NMR studies. B. Modachur Sivakumar and V. Shutthanandan performed and analyzed XPS. J. D. Bazak performed and analyzed ^1H NMR. X. Zhang performed and analyzed UV-vis. S. Kim made contribution on the diffusion test. All data are available in the main text or the supplementary materials.

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Supplementary Materials

Scheme S1 Schematic illustration of the bare GCF and PEIAA-GCF electrodes. Figure S1: dissolution test of PEI and PEIAA films in DI water at 70°C. Figure S2: SEM images of (a) pristine GCF and (b) PEIAA-GCF samples. SEM-EDX (c) spectrum and element maps ((d) carbon, (e) oxygen, and (f) nitrogen) of a part of pristine GCF sample. Figure S3: thermogravimetric analysis curves of (a) pristine GCF and (b) PEIAA-GCF samples, performed in nitrogen gas. Figure S4: BJH adsorption pore size distribution based on the adsorption isotherm of (a) pristine GCF and (b) PEIAA-

GCF samples. Figure S5: digital photographs of PEIAA chunk sample before (left) and after (right) immersing in 0.9 M H_2SO_4 solution for 5 h. Figure S6: digital photographs of (a) PEIAA particles and (b) PEIAA colloidal solutions prepared with DI water and 0.9 M H_2SO_4 , respectively, and their (c) zeta potentials. Figure S7: (a) the three-electrode system for cyclic voltammetry (CV) test. (b) CV curves of pristine GCF and PEIAA-GCF electrodes under different scan rates (0.5 and 2.5 mV s^{-1}) in 1.5 M VOSO_4 in 3.5 M H_2SO_4 . Figure S8: EIS spectra of vanadium redox flow cells with a pristine (a) GCF and (b) PEIAA-GCF electrodes and equivalent circuit. (c) Fitted parameters measured from the equivalent circuit models. Figure S9: (a) UV-vis spectra of the V(IV)OSO_4 solutions ranging from 0.01 M to 0.2 M with a standard calibration curve and (b) UV-vis spectra of the 3.5 M sulfuric acid solutions with (black) pristine GCF or (red) PEIAA-GCF electrode after 5 days with a flow rate of 30 mL min^{-1} for crossover test. Figure S10: SEM images of (a) fresh PEIAA-GCF positive electrode and (b) after 100 cycles carried out at a current density of 50 mA cm^{-2} . Figure S11: (a) SEM image and SEM-EDX maps ((b) carbon, (c) oxygen, and (d) vanadium (e) nitrogen) of a part of PEIAA-GCF positive electrode after 100 cycles carried out at a current density of 50 mA cm^{-2} . Figure S12: wide scan XPS spectra of pristine GCF electrodes (a) before and (b) after 100 cycles under constant current charge at 50 mA cm^{-2} . Figure S13: SEM images of (a) fresh pristine GCF positive electrode and (b) after 100 cycles carried out at a current density of 50 mA cm^{-2} . Figure S14: comparison of ^1H NMR spectra of catholytes in (blue and green) pristine GCF and (orange and red) PEIAA-GCF cells before and after 100 cycles carried out at a current density of 50 mA cm^{-2} . Table S1: porous and surface properties of pristine GCF and PEIAA-GCF samples. (*Supplementary Materials*)

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