Research Article

Preparation of a Nitrogen-Doped Reduced Graphene Oxide-Modified Graphite Felt Electrode for VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} Reaction by Freeze-Drying and Pyrolysis Method

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As one of the key factors that limit the development of vanadium redox flow battery (VRFB), the positive redox couple of VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} plays an important role on the overall performance of VRFB. To improve the kinetics of a positive reaction, a new designed nitrogen-doped reduced graphene oxide-modified graphite felt (N-rGO/GF) electrode was prepared by coupling the methods of freeze-drying and pyrolysis. The characteristics of the prepared electrode were measured by scanning electron microscope (SEM), Brunauer–Emmett–Teller (BET) analysis, Raman spectroscopy (Raman), X-ray diffraction (XRD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and charge-discharge tests. By coupling the methods of freeze-drying and pyrolysis, the N-rGO can be evenly dispersed on the surface of GF electrode, resulting in an excellent catalytic activity. The results demonstrate that the proposed N-rGO/GF electrode with pyrolysis temperature of 900°C shows excellent electrochemical performance and significantly improves the catalytic activity and electrochemical reversibility for the positive VO\textsuperscript{2+}/VO\textsubscript{2}\textsuperscript{+} reaction, indicating that the proposed composite electrode has potential applications in the improvement of VRFB performance.

1. Introduction

As one of the promising green energy sources for energy storage of intermittently renewable energy, such as wind and solar energy, vanadium redox flow battery (VRFB) has drawn increasing attention in recent years. VRFB has attractive features of high reliability, long cycle life, low cost, flexible design, and environmental friendliness. However, VRFB suffers from polarization when operated at high current density, which limits the realization of commercial applications [1, 2]. To improve the performance of VRFB, various efforts have been focused on the design of electrode materials. Most of the proposed electrodes are metallic and carbonaceous materials. Due to the disadvantages of low electrochemical reversibility and high cost, metallic materials have been rarely used [3, 4]. With the advantages of good stability, high specific surface area, high corrosion resistance, and high conductivity, polyacrylonitrile-based (PAN) graphite felt (GF) electrode has been widely used as the electrode material in VRFB.

However, GF electrode exists in the problems of poor wettability and low catalytic activity. Hence, various kinds of surface modification methods for GF electrode have been investigated. Surface modification methods for improving catalytic activity include metal or metal oxide treatment [5, 6], acid treatment [7, 8], hydrothermal ammoniation [9], plasma treatment [10], and radiation treatment [11]. Nitrogen-doped GF electrode has been widely investigated as electrodes for VRFB applications recently [12–17]. It has been proved that nitrogen doping into carbonaceous materials efficiently promotes the kinetics of vanadium redox reaction. The enhanced performance of VRFB is attributed to the introduction of nitrogen atoms, which facilitate the adsorption of vanadium ions on the active site and promote
the charge transfer process between electrode and vanadium ions, resulting in an improvement in catalytic activity [18–20]. The synergy of high catalytic active materials such as graphene oxide (GO) and graphene has also been reported recently [21–23]. As one of the carbonaceous materials, reduced graphene oxide (rGO) has exceptional electronic mobility and thermal and electrochemical stability, which is a benefit for the catalytic reaction during VRFB operation and long cycle life of the catalyst. Furthermore, it has been reported that nitrogen-doped reduced graphene oxide (N-rGO) shows higher catalytic activity. Fu et al. synthesized N-rGO/carbon nanotube composite as a new electrocatalyst to enhance the electrochemical kinetics of the $\text{VO}^{2+}/\text{VO}^{2+}$ couple reaction. Jin et al. [24] proposed that the nitrogen-doping level and doping type have significant influence on the catalytic activity of N-rGO. The enhanced catalytic activity of N-rGO is attributed to the introduction of defects by nitrogen doping. The introduced defects are more active and lead to the alteration of the chemisorption characteristics of vanadium ions [25, 26]. Shi et al. prepared nitrogen-doped graphene nanosheets with urea as the nitrogen source for the VRFB application [9]. During types of nitrogen species, quaternary-N in nitrogen-doped graphene nanosheets plays an important role for promoting the catalytic activity toward the $\text{VO}^{2+}/\text{VO}^{2+}$ couple reaction since the quaternary-N is more stable in the acidic environment [20, 27]. However, the direct modification of N-rGO on GF electrode is still limited. Furthermore, the preparation of N-rGO by a hydrothermal reaction in aqueous solution suffers from the problem of aggregation, leading to a decrease in the specific surface area and resulting in poor electrochemical performance. This problem can be solved by the freeze-drying method since the precursor of GO can be uniformly dispersed after freeze-drying.

In this study, the GO was evenly dispersed on the surface of GF electrode by the freeze-drying method. Then, the GO was transformed into rGO, and the nitrogen was doped into rGO during the pyrolysis process, resulting in the production of the N-rGO-modified GF electrode. With the strong synergy between N-rGO and GF electrode, the proposed composite electrode with the pyrolysis temperature of 900°C shows enhanced electrochemical performance.

2. Materials and Methods

2.1. Preparation of the Electrode. Hummers’ method was used for the preparation of graphene oxide. In brief, 1 g of graphite powder and 1.5 g of sodium nitrate (NaNO$_3$) were added into 60 mL of 98 wt.% H$_2$SO$_4$. The mixture was placed into an ice bath with magnetic agitation. Afterwards, 3 g of potassium permanganate was slowly added into the mixture. Then, the mixture was maintained at 35°C for 30 min in water bath. After that, 138 mL of deionized water was added into the mixture, causing a temperature rise to 98°C. Then, the temperature was maintained at 98°C for 15 min. Afterwards, the synthesis was proceeded by dropping 12 mL of 4% H$_2$O$_2$ solution into the mixture, resulting in a brown suspension. Finally, the product was obtained by centrifugation and repeatedly washed with 10% HCl solution to remove residual metal ions. Then, the product was further washed by deionized water and followed by centrifugation to remove. To remove any moisture, the prepared product was dried in a vacuum drying oven at 50°C for 48 h. The prepared graphite oxide was dispersed in water by ultrasonication for 1 h, resulting in a GO aqueous dispersion of 2 mg/L.

The procedure for the synthesis of N-rGO modified GF electrode is shown in Figure 1. Firstly, the GF electrodes were immersed in the suspension mixed of urea and GO solution (2 mg/mL) for 2 h, where the mass ratio of urea to GO was 10:1. Then, the treated GF electrodes were moved to a freeze-drying oven immediately and maintained at −50°C for 24 h. The samples were taken into a tube furnace under N$_2$ atmosphere after freeze-drying. Then, the samples were heat treated in the tube furnace at 500°C, 700°C, and 900°C for 5 h, respectively. The corresponding synthesized samples were named as N-rGO-500/GF, N-rGO-700/GF, and N-rGO-900/GF, respectively.

2.2. Material Characterization. The properties of rGO were characterized by XRD and Raman spectrum. The nitrogen doping level and doping type in the N-rGO modified composite electrode were evaluated by XPS. The surface morphology and the quality of the prepared composite electrode were measured by SEM and Raman spectrum, respectively.

2.3. Electrochemical Tests. The CV results were obtained by PARSTAT 4000+ workstation with a scan rate of 5 mV/s over the voltage range from 0 to 1.6 V. The EIS tests were operated by applying an alternating voltage of 5 mV over the frequency range of 0.01 Hz to 100 kHz. The evaluation of electrochemical performance was carried out by a three-electrode cell which composed of the N-rGO-modified GF electrode as a working electrode, a Pt electrode as a counter electrode, and an Ag/AgCl electrode as a reference electrode. The electrolyte used in the cell was 0.1 M VOSO$_4$ + 3 M H$_2$SO$_4$ aqueous solution.

The cell performance of VRFB equipped with different N-rGO-modified GF electrodes was assessed by charge-discharge tests operated at a constant current density of 80 mA/cm$^2$. The electrode area for the cell performance test was 10 mm $\times$ 10 mm. The cells were charged to an upper limit voltage of 1.6 V and discharged to a lower limit voltage of 1 V. The electrolytes used for charge-discharge tests were purchased from the Institute of metal research, Chinese Academy of Sciences. The electrolytes for the positive part and negative part were 1.5 M $\text{VO}^{2+}$ + 4.2 M H$_2$SO$_4$ and 1.5 M V$^{3+}$ + 4.2 M H$_2$SO$_4$, respectively.

3. Results and Discussion

3.1. Characteristics of rGO. Raman and XRD measurements were used to characterize the properties of the prepared rGO. Figure 2 shows the Raman spectra of graphite, GO, and rGO. G and D bands are associated with the vibrational stretching of sp$^2$ carbons and sp$^3$ defect site, respectively. The ratio of the intensity of the D band to that of the G band ($I_D/I_G$)
is used to indicate the disorder degree of carbonaceous materials. As can be seen from Figure 2, the G band for graphite is located at about 1582 cm\(^{-1}\), and no D band appears in the Raman spectrum of graphite, indicating an ordered crystal structure of graphite. After oxidation, a strong D band appears at about 1349 cm\(^{-1}\) in the spectrum of GO. The increase in disorder is due to the introduction of oxygen-containing groups during the oxidation process. The D band and G band for rGO are located at about 1350 cm\(^{-1}\) and 1589 cm\(^{-1}\), respectively. After reduction, the intensity ratio of \(I_D/I_G\) significantly increases, suggesting an increase in the disorder of rGO. This may owe to the disappearance of oxygen-containing groups (i.e., –OH and –COOH) after reduction, leading to more defects introduced in the structure of rGO. The Raman spectrum of rGO obtained by pyrolysis is similar to the Raman spectrum that prepared by the hydrothermal method reported in literature [28], indicating that the rGO can also be obtained by thermal reduction.

3.2. Characteristics of N-rGO-Modified GF Electrode. The surface morphology of the proposed composite electrode of N-rGO-500/GF is shown in Figure 4. The results show that the wrinkled N-rGO is successfully dispersed on GF electrode and no obvious aggregation of N-rGO is found. The specific surface area of electrodes under different pyrolysis temperatures was measured by the BET method (Micromeritics TriStar II 3020), as shown in Table 1. The BET surface area of the GF-modified electrode with N-rGO is higher than that of pristine GF. The results demonstrate that the adhesion of N-rGO on the surface of GF electrode leads to an increase in the specific surface area that may provide more active sites for redox reaction of vanadium ions. It should be noted that the N-rGO-900/GF shows high BET surface area of 0.84 m\(^2\)/g, which is about 8 times of pristine GF.

The main elemental compositions and nitrogen-bonding configurations on the surface of N-rGO-modified GF were investigated by XPS, as shown in Figure 5. It should be noted that an obvious peak corresponding to nitrogen element appears, suggesting that the nitrogen atoms are successfully doped into the rGO. According to Table 2, the contents of N, C, and O elements in N-rGO-900/GF are 3.32 at.%, 92.98 at.%, and 3.70 at.%, respectively. The results reveal that the content of the nitrogen element increases with an increase in pyrolysis temperature.

The N1s spectra of the N-rGO modified electrodes were performed in Figure 5. The N1s spectra could be deconvoluted into three different peaks, corresponding to pyridinic-N (397.8 eV), pyrrolic-N (398.5 eV), and graphitic-N (400.8 eV) [31, 32]. The relative content of each nitrogen specials is listed in Table 3. According to Table 3,
the main nitrogen-bonding configuration in N-rGO-modified GF electrode is pyridinic-N. Additionally, the content of graphitic-N in N-rGO-500/GF is 10.98%. While the content of graphitic-N in N-rGO-900/GF increases to 15.97%. The results confirm that the content of graphitic-N increases with the increasing pyrolysis temperature.

Raman spectra were conducted to further identify the microstructure of the composite electrode, as shown in Figure 3: XRD patterns of rGO (a), graphite oxide (b), and graphite (c).

Table 1: BET surface area of different types of N-rGO-modified electrodes.

| Samples               | Pristine GF | N-rGO-500/GF | N-rGO-700/GF | N-rGO-900/GF |
|-----------------------|-------------|--------------|--------------|--------------|
| Surface area          | 0.11 m²/g   | 1.45 m²/g    | 0.86 m²/g    | 0.84 m²/g    |

Figure 4: Surface morphology of N-rGO-modified GF electrode (a) and detailed view of the N-rGO absorbed on GF electrode. The red arrow in Figure 4 (b) points to the absorbed N-rGO.

Figure 3: XRD patterns of rGO (a), graphite oxide (b), and graphite (c).
Figure 5: XPS spectra and curve fit of N1s spectra from the prepared N-rGO-500/GF (a), N-rGO-700/GF (b), and N-rGO-900/GF (c).

Figure 6. By comparing the value of $I_D/I_G$ before and after electrode surface modification, no significant difference is found. However, the D band and the G band of the N-rGO-500/GF are broader than that of the pristine GF, suggesting that the disorder of GF electrode increases after modification. This may ascribe to the introduction of defects and the remarkable decrease of the size of the in-plane $sp^2$ domains by nitrogen doping [33].
3.3. Electrochemical Test. The electrochemical activity of the prepared composite electrode towards the positive redox reaction of $\text{VO}^{2+}/\text{VO}_2^+$ was tested by CV and EIS. The CV curves are shown in Figure 7. In comparison to the pristine GF, the N-rGO-900/GF shows the highest redox current. The oxidation peak and the reduction peak for the N-rGO-900/GF electrode are 0.15 A and 0.12 A, respectively. The oxidation peak and the reduction peak for the pristine electrode are 0.14 A and 0.07 A, respectively. It is clear that the peak currents of oxidation and reduction for the N-rGO-900/GF electrode are higher than that of the pristine electrode, demonstrating that the N-rGO-900 as a catalyst effectively improves the electrochemical kinetics of the $\text{VO}^{2+}/\text{VO}_2^+$ couple reaction. As seen in Table 4, the values of $\Delta E_{\text{sep}}$ for N-rGO-modified GF electrode are smaller than that of pristine GF. A smaller value of $\Delta E_{\text{sep}}$ indicates a better electrochemical reversibility. The smallest peak potential difference ($\Delta E_{\text{sep}}$) of 0.34 V is observed for the N-rGO-900/GF. Hence, both electrochemical activity and electrochemical reversibility are improved due to the modification of N-rGO-900. The enhanced electrochemical properties for the N-rGO-900/GF might be attributed to the introduction of defects and nitrogen-containing groups at the electrode surface, which accelerate the charge transfer rate across electrode/vanadium ions solution interface.

To further investigate the electrochemical performance of the proposed N-rGO/GF electrode, EIS measurement was conducted at the open-circuit potential. The obtained Nyquist plot is shown in Figure 8. It should be noted that the Nyquist curves of N-rGO-modified GF electrode with different pyrolysis temperatures are composed of a semicircle and a linear part in the frequency range from 0.01 Hz to 100 kHz. The semicircle part at high frequency represents the charge transfer process while the linear part represents the mass transfer process [34]. The Nyquist curves indicate that both charge transfer and mass diffusion play a main role in the positive $\text{VO}^{2+}/\text{VO}_2^+$ reaction [17]. However, the Nyquist curve of pristine GF is mainly composed of a semicircle part, indicating that the $\text{VO}^{2+}/\text{VO}_2^+$ reaction is mainly controlled by the charge transfer process when using pristine GF as electrode. The spectra can be fitted with an equivalent circuit, as shown in Figure 8. The $R_s$ in the equivalent circuit is the solution resistance, corresponding to the initial real part of impedance in the Nyquist plot. $R_{\text{ct}}$ is the charge transfer resistance across the electrode/solution interface. The value of $R_{\text{ct}}$ is equal to the diameter of the
semicircle in the Nyquist plot. \( Q_m \) represents the constant phase element associated with the vanadium ions transfer in the composite electrode. \( Q_t \) is the constant phase element, representing the capacitance of the electric double layer which exists at the electrode/solution interface [35].

The fitted values of the electrochemical parameters are listed in Table 5. According to Table 5, the \( R_{ct} \) of N-rGO-900/GF decreases to 1.14 \( \Omega \) while the \( R_{ct} \) of pristine GF is 12.21 \( \Omega \). This may be due to the fact that the lone-pair electron caused by doped nitrogen improves the electrical conductivity of the electrode and reduces the electrochemical polarization of the \( \text{VO}^{2+}/\text{VO}_2^+ \) reaction [20].

To evaluate the influence of N-rGO-modified GF electrode on VRFB performance, N-rGO-900/GF, N-rGO-700/GF, and air-heated GF were acted as the positive electrode in VRFB. The charge-discharge tests were conducted at a constant current density of 80 mA/cm\(^2\). The thickness of GF electrode is 5 mm, and the flow rate of the electrolyte is 15 ml/min. The charge and discharge curves are shown in Figure 9. According to Figure 9, the N-rGO-900/GF electrode shows the best cell performance. The charge voltage for the cell equipped with N-rGO-900/GF is significantly reduced, while the discharge voltage is significantly improved, resulting in a decrease in overvoltage. The charge capacity for the cell equipped with N-rGO-900/GF is 598 mAh, while the charge capacity for the cell with air-heated GF as an electrode is 568 mAh. The charge capacity for the cell equipped with N-rGO-500/GF shows the lowest value of 510 mAh. The current efficiency, voltage efficiency, and energy efficiency of the cell with different electrodes are in Table 6. Compared with the cell equipped with air-heated GF or N-rGO-700/GF, the cell with N-rGO-900/GF shows the highest energy efficiency of 76.08%, which is in accordance with the results of CV and EIS tests. The enhanced cell performance is attributed to the high specific areas and high nitrogen doping of N-rGO-900/GF, which provides more active sites and higher catalytic activity for the \( \text{VO}^{2+}/\text{VO}_2^+ \) reaction.

### Table 5: The fitted values of electrochemical parameters.

| Samples          | \( R_s (\Omega) \) | \( Q_t \) | \( n \) | \( R_{ct} (\Omega) \) | \( Q_m \) | \( n \) |
|------------------|---------------------|----------|--------|------------------------|----------|--------|
| Pristine GF      | 0.53                | 0.0016   | 0.97   | 12.21                  | 15.58    | 0.93   |
| Air-heated GF    | 0.62                | 0.0101   | 0.89   | 11.64                  | 0.79     | 0.85   |
| N-rGO-500/GF     | 0.54                | 0.0017   | 0.93   | 20.78                  | 0.12     | 0.49   |
| N-rGO-700/GF     | 0.43                | 0.0293   | 0.79   | 7.34                   | 0.32     | 0.67   |
| N-rGO-900/GF     | 0.47                | 0.0200   | 0.97   | 1.14                   | 0.32     | 0.54   |

### Table 6: Efficiency of cells equipped with different electrodes.

| Samples          | Coulombic efficiency (%) | Voltage efficiency (%) | Energy efficiency (%) |
|------------------|--------------------------|------------------------|-----------------------|
| Air-heated GF    | 92.62                    | 81.43                  | 75.42                 |
| N-rGO-500/GF     | 93.07                    | 80.98                  | 75.37                 |
| N-rGO-700/GF     | 91.90                    | 80.07                  | 73.59                 |
| N-rGO-900/GF     | 92.09                    | 82.62                  | 76.08                 |

### 4. Conclusions

This paper presents the preparation of N-rGO-modified GF electrode by coupling the methods of freeze-drying and pyrolysis. Owing to the large specific surface area and high catalytic activity of N-rGO, the prepared N-rGO-900/GF shows significant improvement in electrochemical performance. The \( R_{ct} \) of N-rGO-900/GF decreases to 1.14 \( \Omega \), and the energy efficiency for the N-rGO-900/GF equipped cell increases to 76.08%. With the advantages of cost efficiency, simple synthesis process, and high electrochemical performance, the designed N-rGO-900/GF electrode may provide potential application in the VRFB area.

### Data Availability

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

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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