Graphitization of carbon-based catalyst for improving the performance of negative electrode in vanadium redox flow battery

Bingxue Hou, Rui Tang, Qi Zhang, Xumei Cui and Yungui Chen

Abstract
Carbon-based materials were prepared to catalyze the $V^{3+}/V^{2+}$ couple of vanadium redox flow battery using chitosan as the preliminary material and FeCl$_3$ as activating agent. Graphite microcrystals were the main structures of the obtained catalyst (CTS-Fe-900) activated by FeCl$_3$, and they contained a large number of curled and overlapped carbon nanosheets. Compared with CTS-D-900 (without FeCl$_3$ as an activating agent), CTS-Fe-900 exhibits a better structure, higher graphitization degree, stronger current response, and smaller charge transfer resistance. The charge/discharge measurements indicates that the performances of the cell are improved by using the CTS-Fe-900-modified negative electrode in terms of increased discharge capacity and energy efficiency. Compared with pristine cell, the capacity retention for the CTS-Fe-900 modified cell maintains 82.2% at 50 mA cm$^{-2}$ after 50 cycles, increased by 5.2%, and the corresponding energy efficiency reaches 81.3%, enhanced by 5.1%. This work reveals that CTS-Fe-900 catalyst can improve the comprehensive energy storage performance. The excellent electrocatalytic properties are mainly attribute to the effect of the FeCl$_3$ template and the increase in the degree of graphitization.

1. Introduction

With the impoverishment of resources and the extensive utilization of new energy (wind energy, solar energy, etc.), the technology of energy storage has been extensively developed to resolve the discontinuity and geographical distribution of new energy [1–5]. Vanadium redox flow battery (VRFB), which was first proposed by Skyllas-Kazacos et al in 1985 [6], has been investigated extensively because of its many advantages such as long life, high efficiency and environmental friendliness [7–9]. VRFB uses $V^{3+}/V^{2+}$ and $VO^{2+}/VO_2^+$ redox couples in sulfuric acid as the negative and positive half-cell electrolytes, respectively, and it exhibits an open circuit voltage of approximately 1.26 V produced from the potential separation of two couples [10–12]. Two reactions take place on the electrode surface; however, the electrode does not participate in the reaction [13]. Hence, the electrochemical activity of the electrode is crucial for the performance of the cell. VRFB mainly employs carbon-based fiber such as graphite, graphite felt, carbon cloth, and carbon paper, etc as electrode [14]. Nevertheless, the electrochemical activity of these raw electrodes is not perfect enough. Thus, various methods for enhancing the electrochemical properties of the carbon electrodes, such as acid treatment, electrochemical oxidation, and heating treatment, have been reported [15–17]. Moreover, the catalyst introduced onto the surface of the electrode is a research hotspot for enhancing the electrochemical activity of the electrode. The catalysts used in VRFB include carbon-based materials (graphene [18], carbon nanotubes (CNTs) [19], and carbon fibers [20] etc), metals (Pt [21], Ir [22], and Sb [23], etc), and metal oxides (ZrO$_2$ [24], Mn$_3$O$_4$ [25], and Nb$_2$O$_5$ [26] etc). Although metals exhibit excellent catalytic properties for the VRFB, they are susceptible to gas evolution and are
expensive. Consequently, more researchers have focused on designing many low-price metal oxides and nitrides catalysts to replace the noble metal catalysts. However, some metal oxides and nitrides demonstrate relatively poor conductivity and stability on the electrode surface. Carbon-based catalysts demonstrates excellent electrochemical catalytic activity for $\text{V}^{3+}/\text{V}^{2+}$ redox couples because of their high conductivity, high specific surface areas, and excellent corrosion resistance. Nevertheless, graphene and carbon nanotubes are limited in commercial applications due to their tedious preparation and high cost.

Recent research has mainly focused on improving the electrochemical performance of positive electrodes [22, 25, 27, 28]. However, improving the performance of the negative electrode is crucial for improving the performance of the battery. This is because the negative reaction takes larger proportion of the voltage loss of the cell [29]. In this work, chitosan was used as the preliminary material and FeCl$_3$ as the activating agent to obtain carbon-based catalysts for VRFB. The carbon-based catalyst was acted the as electrocatalyst for the $\text{V}^{3+}/\text{V}^{2+}$ couple of VRFB. Notably, the obtained carbon-based catalyst shows excellent electrocatalytic performances for $\text{V}^{3+}/\text{V}^{2+}$ couple of VRFB.

2. Experimental

2.1. Preparation of materials

Chitosan (1.5 g) and FeCl$_3$ (3 g) were soaked in 10 ml of deionized water and sufficiently stirred, the resulting mixture was then dried at 80 °C. The solid materials were calcined at 900 °C (5 °C min$^{-1}$) for 2 h in argon. Thereafter, the resultant product was soak in 1 mol l$^{-1}$ HCL solution for 24 h, washed with deionized water to pH 7, and dried at 80 °C before use (named as CTS-Fe-900). The chitosan (without FeCl$_3$) was calcined directly at 900 °C (5 °C min$^{-1}$) for 2 h in argon for comparison (named as CTS-D-900).

2.2. Characterizations of materials

The morphology of the samples was studied through scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The degree of surface defects in the samples was investigated by Raman spectroscopy (DXR, Thermo Fisher Scientific). The phase of the as-prepared sample was verified via x-ray diffraction (XRD, DX-2700, Dandong Haoyuan, China). Hydrophilicity performance was evaluated using water contact angle measurement (JC2001, Dong guan saite testing equipment co. LTD).

2.3. Electrochemical measurements

The as-prepared samples (each 10 mg) was dissolved into the 5 ml N,N-dimethylformamide (DMF) via ultrasonication for 3 h to ensure that the samples was well dispersed in the solution, and 20 μl of dispersed solution was dropped onto the surface of glass carbon electrode and dried at 80 °C for 4 h.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments were performed on CHI660E electrochemical workstation (Shanghai Chenhua, China) in 1.6 mol l$^{-1}$ $\text{V}^{3+} + 3.0$ mol l$^{-1}$ $\text{H}_2\text{SO}_4$ electrolyte. Electrochemical measurements were conducted using typical three-electrode system, GCE coated...
with samples as the working electrodes, Pt sheet (1 × 1 cm²) as the counter electrodes, and a saturated calomel electrode (SCE) as the reference electrodes.

2.4. Single cell tests
CTS-Fe-900 (6 mg) was ultrasonically dispersed in 15 ml DMF, and the pristine graphite felt (4 cm × 4 cm) was immersed in the solution until it was completely drained by the graphite felt (GF). The modified GF was dried in an oven at 80 °C for 8 h. Using the CTS-Fe-900 modified GF as the negative electrode, the performance of the VRFB was evaluated in a static cell. The pristine GF and CTS-Fe-900 modified GF were employed as positive and negative electrodes, respectively. Two half cells were separated by ion-exchange membrane. 1.6 mol l⁻¹ V¹O²⁺ + 3 mol l⁻¹ H₂SO₄ and 1.6 mol l⁻¹ V³⁺ + 3 mol l⁻¹ H₂SO₄ were stored in corresponding positive and negative electrode. Galvanostatic charge/discharge measurement was conducted on CT2001A testing system (Land, Wuhan). The upper and lower limits of the charge and discharge voltage was 1.7 and 0.7 V. The charge/discharge performance was evaluated at a series of current density of 50–90 mA cm⁻² and 50 mA cm⁻² for 50 cycles. Additionally, the pristine GFs were also used as positive and negative electrodes for comparison.

3. Results and discussion
The XRD patterns of CTS-D-900, CTS-Fe-900 and CTS-Fe-900 precursor (the sample was not washed with deionized water) are shown in figure 1. There are two diffraction peaks at 23° and 44° of 2θ for CTS-D-900, and the diffraction peaks at 23° are formed by the superposition of the amorphous carbon diffraction peak at 22° and
the crystallographic planes diffraction peak at 26°. Compared with CTS-D-900, CTS-Fe-900 has a sharp and intense diffraction peak at 26° and no diffraction peaks of other substances, which indicates a higher organized crystal than CTS-D-900. The diffraction peaks at 2θ = 26° for CTS-Fe-900 precursor is also attributed to crystallographic planes, and other peaks for CTS-Fe-900 precursor are attributed to Fe and oxides (FeO, Fe₂O₃, and Fe₃O₄). Fe is a good graphitization-reinforcing catalyst that converts the amorphous carbon into graphite carbon; therefore, the electronic conductivity of carbon materials can be improved by improving the graphitization degree of carbon materials. The increase in electron conductivity can accelerate the electron transfer during electrochemical reaction, and thus accelerate electrode reaction process.

SEM images of CTS-D-900 and CTS-Fe-900 samples at different magnifications are shown in figure 2. The CTS-D-900 sample is an irregular carbon block, some of which are up to 10 μm in size (figures 2(a), (b)). The CTS-Fe-900 sample is composed of a large number of curled and overlapped carbon nanosheets (figures 2(c), (d)). As can be seen, the size of the carbon sheet of the CTS-Fe-900 sample is significantly smaller than that of the CTS-D-900 sample. Moreover, the CTS-Fe-900 sample exhibits a better porous structure. Evidently, the CTS-Fe-900 sample has a larger specific surface area than the CTS-D-900 sample. The carbon nanosheets are formed because FeCl₃ not only acts as an oxidant at high temperatures and a template, but also facilitates redox reactions with biomass materials. FeCl₃ is embedded into the chitosan during the high temperature reaction, however, FeCl₃ and its intermediate products can be removed by pickling after the high-temperature reaction, leaving behind a porous lamellar structure.

The graphitization of the carbon materials of CTS-D-900 and CTS-Fe-900 was studied through Raman spectroscopy, and the results are shown in figure 3. Figure 3 shows that the Raman spectra of the two samples are similar, with two strong peaks at 1350 and 1580 cm⁻¹ representing disordered amorphous carbon (D band) and crystalline graphitic carbon (G band), respectively [30]. In general, a smaller ratio of the D to G peak intensity (I_D/I_G) can reveal more crystalline graphitic carbon [31]. Notably, I_D/I_G for CTS-Fe-900 is 0.62, which is smaller than that for CTS-D-900 with I_D/I_G of 0.97. This indicates that the CTS-Fe-900 sample has a higher degree of graphitization than the CTS-D-900 sample. This is consistent with the XRD results.

A test of water contact angle was conducted to examine the wetting performance of the two samples, and the results are shown in figure 4. A larger water contact angle indicates worse hydrophilicity; the worse hydrophilicity reflects a higher degree of graphitization. As seen, the water contact angle of CTS-Fe-900 is 139.4°, which is larger than that for CTS-D-900 (99.1°). It indicates that CTS-D-900 has a higher degree of
graphitization. This is because the FeCl₃ generates Fe at high temperatures. Fe can improve the graphitization degree of the material, and the increase in the degree of graphitization causes a decline in hydrophilicity.

The electrocatalytic activity of the two samples were compared via CV measurements with scanning rate of 5 mV s⁻¹ in 1.6 mol l⁻¹ V³⁺ + 3.0 mol l⁻¹ H₂SO₄. The cyclic voltammograms of the two samples are presented in figure 5. As seen, CTS-D-900 displays a pair of relatively poor redox peaks for the V³⁺/V²⁺ couple. Compared with CTS-D-900, CTS-Fe-900 presents a clear peak shape, showing a higher peak current density and better symmetry for the redox peak of V³⁺/V²⁺ couple. The reduction peak currents of the CTS-D-900 and CTS-Fe-900 are 1.235 and 3.165 mA, respectively. The oxidation peak currents of the CTS-D-900 and CTS-Fe-900 are 0.377 and 1.532 mA, respectively. Evidently, CTS-Fe-900 exhibits better electrocatalytic performance than CTS-D-900. The peak potential gap is a crucial parameter for evaluating the electrochemical reversibility of the V³⁺/V²⁺ reaction [18]. In general, a smaller peak potential gap corresponds to better electrochemical reversibility. The peak potential gap for CTS-Fe-900 is 265 mV, which is smaller than that of CTS-D-900, implying that the electrochemical reversibility of the V³⁺/V²⁺ reaction on CTS-Fe-900 is better than that on CTS-D-900. The superior electrocatalytic performance of CTS-Fe-900 can be attributed to two reasons. First, CTS-Fe-900 has a larger specific surface area, which can provide a larger reaction site for the electrode reaction. Second, improving the graphitization degree of carbon materials improves the electronic conductivity of the materials.

To investigate the electrochemical kinetics of the V³⁺/V²⁺ couple, EIS measurements were carried out for the CTS-D-900 and CTS-Fe-900 electrodes. Nyquist plots of the two samples and the corresponding equivalent electrical circuit are shown in figure 6. Nyquist plots are made of two parts for each sample, including a semicircle ascribed to the charge transfer process in the high frequency range and a sloped line reflecting the diffusion process of vanadium ions in the low frequency range, respectively [32]. It implies that the V³⁺/V²⁺ couple is conjointly dominated by the diffusion process of active species and charge transfer processes. In the electric equivalent circuit, Rₛ is the ohmic resistance composed of the solution, electrode, and contact resistance,
Rct is the charge transfer resistance, Qt and Qm are constant-phase elements, where Qt is the diffusion capacitance of vanadium ions, and Qm is the electric double-layer capacitance between the electrode/electrolyte surface. The electrochemical parameters are listed in Table 1. It can be seen that Rct of CTS-Fe-900 is 7.84 Ω, which is smaller than that for CTS-D-900 (8.19 Ω). This is because the higher graphitization degree of CTS-Fe-900 reduces the ohmic resistance of the GCE/CTS-Fe-900 electrode. Meanwhile, Rct for CTS-Fe-900 (7.57 Ω) is significantly smaller than that for CTS-D-900 (199.30 Ω), demonstrating quicker charge transfer for redox reaction on CTS-Fe-900, which is because of larger surface area and higher graphitization. In addition, Qm and Qt for CTS-Fe-900 increased significantly compared with those of CTS-D-900, which indicates that the increase in the specific surface area and graphitization degree of the material could improve the diffusion process of vanadium ions and the electrochemical reaction of the V\textsuperscript{3+}/V\textsuperscript{2+} redox couple.

The adhesion of CTS-Fe-900 to graphite felt was studied by SEM. Figure 7 shows the blank graphite felt and CTS-Fe-900 modified graphite felt. The surface of the blank graphite felt is relatively clean, and there is no obvious impurity (Figure 7(a)). As displayed in figure 7(b), a large number of nanoscale sheets of CTS-Fe-900 electrocatalyst attached to the surface of blank graphite felt evenly, which can greatly improve the surface area of the graphite felt. The thickness of the electricity catalyst is nanosized, therefore, it did not affect the flow of the electrolyte on the electrode surface.

| Current density (mA cm\textsuperscript{-2}) | Pristine (V) | Using CTS-Fe-900 (V) |
|------------------------------------------|-------------|---------------------|
| 50                                       | 1.265       | 1.283               |
| 60                                       | 1.227       | 1.254               |
| 70                                       | 1.192       | 1.222               |
| 80                                       | 1.158       | 1.192               |
| 90                                       | 1.127       | 1.162               |

Figure 8. Charge and discharge curves of pristine cell and the cell using CTS-Fe-900 as negative electrocatalyst at different current density.

Figure 9. Discharge capacity (a) and energy efficiency (b) of pristine cell and the cell using CTS-Fe-900 as negative electrocatalyst for 50 cycles at current density of 50 mA cm\textsuperscript{-2}.
Charge-discharge tests were carried out to study the effect of CTS-Fe-900 on the rate performance of the cell. Figure 8 displays the charge-discharge voltage profiles of the pristine cell and CTS-Fe-900 modified cells at different current densities. As can be seen, the related voltage separation of the two cells increases with increasing current density, but the cell using CTS-Fe-900 exhibits a lower charge plateau and higher discharge plateau at 50–90 mA cm$^{-2}$ due to lower overpotential. The mean discharge voltages at different current densities are listed in table 2. The mean discharge voltage of the two cells decreased with increasing current density because of the electrochemical polarization. The mean discharge voltage for the CTS-Fe-900-modified cell was higher than that of the pristine cell at 50–90 mA cm$^{-2}$. In particular, the mean discharge voltage for the CTS-Fe-900-modified cell was 1.162 V at 90 mA cm$^{-2}$, with an increase of 0.035 V compared with that of the pristine cell (1.127 V). Evidently, CTS-Fe-900 reduced the overpotential and enhanced the mean discharge voltage owing to its larger surface area and higher graphitization, and it can weaken the electrochemical polarization and improve the energy density of the cell.

To study the cycling performance of the pristine- and CTS-Fe-900-modified cells, charge-discharge tests were performed at 50 mA cm$^{-2}$ for 50 cycles, as shown in figure 9. As shown in figure 9(a), the discharge capacity of both cells gradually decreased with an increasing number of cycles. This is because the charging and discharging processes weaken the electrode activity, and some vanadium ions in the electrolyte penetrate the membrane with an increasing number of cycles, resulting in a decline in the discharge capacity. However, the CTS-Fe-900-modified cell demonstrated a higher discharge capacity than the pristine cell. The original discharge capacity of the CTS-Fe-900-modified cell is 220.0 mA h, which is 15.5 mA h higher than that of the pristine cell. Moreover, the capacity retention of the CTS-Fe-900-modified cell maintains 82.2% after 50 cycles, 5.2% larger than that of the pristine cell. The energy efficiency of two cells are compared in figure 9(b). Energy efficiency of the CTS-Fe-900 modified cell is 81.3% at 50 mA cm$^{-2}$, which is 5.1% higher than that of the pristine cell (76.2%). The above results demonstrate that the CTS-Fe-900 modified cell has more excellent cycling stability than the pristine cell during the charge and discharge processes.

4. Conclusions

In summary, carbon-based materials were prepared to catalyze $V^{3+}/V^{2+}$ using chitosan as the preliminary material and FeCl$_3$ as the activating agent. The main structure of CTS-D-900 without FeCl$_3$ as an activating agent was amorphous carbon with a lower degree of graphitization and irregular micron carbon particles. The main structure of the obtained catalyst (CTS-Fe-900) activated by FeCl$_3$ was graphite microcrystals and it contained a large number of curled and overlapped carbon nanosheet materials, there, it had a better structure and higher graphitization degree. Compared with those of CTS-D-900, the current response of CTS-Fe-900 was stronger and the charge transfer resistance was smaller; therefore, it had stronger electrocatalytic activity than CTS-D-900. As a result, the CTS-Fe-900 modified cell demonstrates higher discharge capacity and energy efficiency than the pristine cell at 50 mA cm$^{-2}$ for 50 cycles. The capacity retention of the CTS-Fe-900 modified cell maintains 82.2% after 50 cycles, 5.2% larger than that of the pristine cell. The energy efficiency of the CTS-Fe-900 modified cell is 81.3% at 50 mA cm$^{-2}$, which is 5.1% higher than that of the pristine cell. This indicates that using CTS-Fe-900 catalyst can improve the performance of comprehensive energy storage. The excellent electrocatalytic properties mainly come from the effect of the FeCl$_3$ template and the increase in the degree of graphitization.

Acknowledgments

The authors acknowledge the support of the project of Civil Aviation Flight University of China (J2020-045) and Sichuan science and technology program project (2020YJ0501).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Bingxue Hou https://orcid.org/0000-0003-1650-8813
Yungui Chen https://orcid.org/0000-0001-8403-7289
References

[1] Liu J, Wang Z A, Wu X W, Yuan X H, Hu J P, Zhou Q M, Liu Z H and Wu Y P 2015 Porous carbon derived from disposable shaddock peel as an excellent catalyst toward VO$_2^+$/VO$_2$ couple for vanadium redox battery J. Power Sources 299 301–8

[2] Li Y, Zhang X, Bao J and Skyllas-Kazacos M 2017 Studies on optimal charging conditions for vanadium redox flow batteries J. Energy Storage 11 191–9

[3] Kim J and Park H 2017 Experimental analysis of discharge characteristics in vanadium redox flow battery Appl. Energy 206 651–7

[4] Zhang C, Nagasaki Y, Miyi D, Touda M, Komagome T, Tsukada K, Hamajima T, Ayakawa H, Ishid V and Yonekura D 2019 Stored energy control for long-term continuous operation of an electric and hydrogen hybrid energy storage system for emergency power supply and solar power fluctuation compensation Int. J. Hydrogen Energy 44 8403–14

[5] Li C, Xie B, Chen J, He Z, Chen Z and Long Y 2019 Emerging mineral-coupled composite phase change materials for thermal energy storage Energy Convers. Manage. 183 633–44

[6] Skyllas-Kazacos M, Rychich M, Robins R G, Fane A G and Green M A 1986 New all-vanadium redox flow cell J. Electrochem. Soc. 133 1057–8

[7] Atto P, Guarneri M and Moro F 2014 Redox flow batteries for the storage of renewable energy: a review Renew. Sustain. Energy Rev. 29 325–35

[8] Skyllas-Kazacos M, Chakrabarti M H, Hajimolana S A, Mjalli F S and Saleem M 2011 Progress in flow battery Research and development J. Electrochem. Soc. 158 R35–79

[9] Mehboob S, Ali G, Shin H J, Hwang J, Abbas S, Chung K Y and Ha H Y 2018 Enhancing the performance of all-vanadium redox flow batteries by decorating carbon feltedelectrodes with SnO$_2$ nanoparticles Appl. Energy 229 910–21

[10] Baye A W, Khabatama D M, Chang Y C, Chen G C, Chen H Y, Lin G Y, Liu T R, Wondimu T H, Wang K C and Wang C H 2018 Ta$_2$O$_5$-nanoparticle-modified graphite felt as a high-performance electrode for a vanadium redox flow battery, ACS Sustain. Chem. Eng. 6 3019–28

[11] Jung H Y, Cho M S, Sadhasivam T, Kim J Y, Roh S H and Kwon Y 2018 High ionic selectivity of low permeable organic composite membrane with amphilphilic polymer for vanadium redox flow batteries Solid State Ionics 324 69–76

[12] He Z X, Dai I, Liu S Q, Wang L and Li C C 2015 Mn$_3$O$_4$ anchored on carbon nanotubes as an electrode reaction catalyst of V(IV)/V(V) couple for vanadium redox flow batteries, Electrochem. Acta 176 1434–40

[13] Huang P, Liang W, Sheng H, Zhou Y, Wu X, Zeng X X, Wu X and Guo Y G 2018 Heteroatom-doped electrodes for all-vanadium redox flow batteries with ultrafragile lifespan J. Mater. Chem. A 6 41–4

[14] Kabir H, Gyan I O and Cheng I F 2017 Electrochemical testing of a pyrolytic graphite sheet for improved negative electrode performance in the vanadium redox flow battery J. Power Sources 342 1–7

[15] Sun B and Skyllas-Kazacos M 1992 Chemical modification of graphite electrode materials for vanadium redox flow battery application: I. Acid treatments Electrochem. Acta 37 2459–65

[16] Sun B and Skyllas-Kazacos M 1992 Modification of graphite electrode materials for vanadium redox flow battery application: I. Thermal treatment Electrochem. Acta 37 1253–60

[17] Wu T, Huang K, Liu S, Zhuang S, Fang D, Li S, Lu D and Su A 2012 Hydrothermal ammoniated treatment of PAN-graphite felt for vanadium redox flow battery J. Solid State Electrochem. 16 579–85

[18] Di Blasi O, Briguglio N, Busacca C, Ferraro M, Antonucci V and Di Blasi A 2015 Electrochemical investigation of thermically treated graphene oxides as electrode materials for vanadium redox flow battery Appl. Energy 147 74–81

[19] Noil C, Moon S, Chung Y and Kwon Y 2017 Chelating functional group attached to carbon nanotubes prepared for performance enhancement of vanadium redox flow battery J. Mater. Chem. A 5 23334–42

[20] Feytan A, Deri I, Kayarkatte M K, Langner J, Bernsmeier D, Kraehnert R and Roth C 2015 Electrospun carbon nanofibers as alternative electrode materials for vanadium redox flow batteries Chem. Electro. Chem. 2 2055–60

[21] Jeong S, Kim S and Kwon Y 2013 Performance enhancement in vanadium redox flow battery using platinum-based electrocatalyst synthesized by poloyl process Electrochem. Acta 114 439–47

[22] Wang W H and Wang X D 2007 Investigation of Ir-modified carbon felt as the positive electrode of an all-vanadium redox flow battery Electrochem. Acta 52 6735–62

[23] Shen J, Liu S, He Z and Shi L 2015 Influence of anion exchange effect on the electrochemical performance of vanadium redox flow batteries Electrochem. Acta 151 297–305

[24] Zhou H, Shen Y, Xu J, Qiu X and Chen L 2016 ZrO$_2$-nanoparticle-modified graphite felt: bifunctional effects on vanadium flow batteries ACS Appl. Mater. Inter. 8 15369–78

[25] Kim K J, Park M S, Kim J H, Wang U H, Lee N J, Jeong G and Kim Y J 2012 Novel catalytic effects of Mn$_3$O$_4$ for all vanadium redox flow batteries Chem. Commun. 48 5455–7

[26] Li B, Gu M, Nie Z M, Wei X L, Wang C M, Sprenkle V and Wang W 2014 Nanorod niobium oxide as powerful catalysts for an all-vanadium redox flow battery Nano Lett. 14 1358–65

[27] Lv Z Q, Zhang J, Lv Y, Cheng Y, Jiang S P, Yang L and Lu S F 2018 The electrochemical characterization and mechanism of carbon nanotubes with different numbers of walls for the VO$_2^+$/VO$_2$ redox couple Phys. Chem. Chem. Phys. 20 7791–7

[28] Lv Y R, Zhang L, Cheng G, Wang P F, Zhang T Z, Li C C, Jiang Y Q, He Z X, Dai L and Wang L 2019 Preparation of carbon nanosheets by molten salt route and its application in catalyzing VO$_2^+$/VO$_2$ redox reaction J. Electrochem. Soc. 166 A935–9

[29] Sun C N, Delnick F M, Aaron D S, Papandrew A B, Mench M M and Zawodzinski T A 2013 Probing electrode losses in all-vanadium redox flow batteries with impedance spectroscopy ECS Electrochem. Lett. 2 A43–5

[30] Sun D, Tang Y, He K, Ren Y, Liu S and Wang H 2015 Long-lived aqueous rechargeable lithium batteries using mesoporous LiTi$_2$(PO$_4$)$_3$ cathodes Nature Chem. 7 17452–9

[31] Sun D, Xue X, Tang Y, Jia Y, Huang B, Ren Y, Yao Y, Wang H and Cao G 2015 High-rate LiTi$_2$(PO$_4$)$_3$@N–C composite via bi-nitrogen sources doping ACS Appl. Mater. Inter. 7 28337–45

[32] Yun N, Park J J, Park O O, Lee K B and Yang J H 2018 Electrocatalytic effect of NiO nanoparticles evenly distributed on graphite felt electrode for vanadium redox flow batteries Electrochim. Acta 278 226–35