



# Modified carbon cloth as positive electrode with high electrochemical performance for vanadium redox flow batteries

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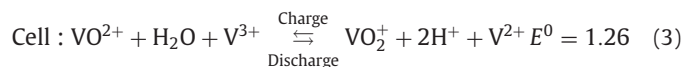
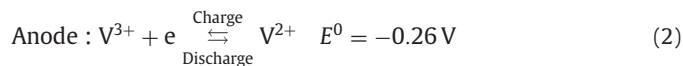
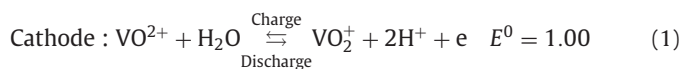
## ABSTRACT

Carbon cloth modified by hydrothermal treatment in ammonia water is developed as the positive electrode with high electrochemical performance for vanadium redox flow batteries. The SEM shows that the treatment has no obvious influence on the morphology of carbon cloth. XPS measurements indicate that the nitrogenous functional groups can be introduced on the surface of carbon cloth successfully. The electrochemical performance of V(IV)/V(V) redox couple on the prepared electrode is evaluated with cyclic voltammetry and linear sweep voltammetry measurements. The N-doped carbon cloth exhibits outstanding electrochemical activity and reversibility toward V(IV)/V(V) redox couple. The rate constant of V(IV)/V(V) redox reaction on carbon cloth can increase to  $2.27 \times 10^{-4}$  cm/s from  $1.47 \times 10^{-4}$  cm/s after nitrogen doping. The cell using N-doped carbon cloth as positive electrode has larger discharge capacity and higher energy efficiency compared with the cell using pristine carbon cloth. The average energy efficiency of the cell using N-doped carbon cloth for 50 cycles at 30 mA/cm<sup>2</sup> is 87.8%, 4.3% larger than that of the cell using pristine carbon cloth. It indicates that the N-doped carbon cloth has a promise application prospect in vanadium redox flow batteries.

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## 1. Introduction

Energy crisis and environmental pollution resulting from the exhaustion of fossil fuel have led to an increasing utilization of new energies generated from sources such as solar radiation and wind [1–4]. However, these new energies are difficult to integrate into electrical supply grids due to its intermittence and variation. Large-scale electrical energy storage (EES) is a good solution to solve this problem. Vanadium redox flow batteries (VRFB) have been considered as one of the most promising EES for new energies due to many advantages including high efficiency, long life, flexible design, and environmental friendliness [5–10]. In VRFB system, V(II)/V(III) and V(IV)/V(V) redox couples are utilized as the active species in negative and positive electrolytes respectively, separated by ion-exchange membrane. The same element in both half-cells for VRFB can avoid cross contamination of two electrolytes. A standard voltage of 1.26 V is produced by VRFB system through the following reactions:



The electrodes play very important role for VRFB since the redox reactions were carried out on the surface of electrode and the energy conversion efficiency was directly limited to the electrochemical activity of electrode. Currently, polyacrylonitrile (PAN)-based graphite felts are employed as the most widely used electrodes for VRFB. However, the poor electrochemical kinetics of PAN-graphite felts require modification for enhancing the electrochemical properties [11,12]. Many modification methods have been reported to improve their electrochemical activity, such as acid treatment, heat treatment, electrochemical oxidation and introducing catalytic materials [6,13–18]. Apart from graphite felt, many new materials were developed as electrode for VRFB, such as electrospun carbon nanofiber and carbon paper [19–22]. Electrospun carbon nanofibers with diameter of 100–200 nm were employed as electrode materials toward VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> redox couple for VRFB [19]. The relationship between the carbonization temperature and electrochemical activity of carbon nanofibers toward VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> redox

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couple was established, and the 1000 °C-carbonized nanofibers show excellent electrochemical performance. The good electrochemical behaviors of the carbonized nanofibers were attributed to the conversion of fibers inner-structure and the improvement of electrical conductivity. Liu [23,22] reported that the carbon paper was employed as electrode for VRFB and further investigated the effect of heat and acid treatment on electrochemical properties of carbon paper. The improved properties of modified carbon paper are ascribed to the introduced oxygen-containing functional group. However, the weak skeleton structure of electrospun carbon nanofibers and the plane structure of carbon paper limit their extensive application for VRFB.

Carbon cloth constituted by carbon fibers can be utilized as electrode for VRFB [24]. However, the poor hydrophilicity and electrochemical activity of original carbon cloth require modification to improve its properties. Nitrogen-doped carbon nanostructured materials demonstrate high electrocatalytic activity in many electrochemical fields such as flow batteries [17,13,25], biosensors [26] and fuel cells [27–32]. Shao et al. [17] reported that mesoporous carbon (MPC) prepared by soft-template method was doped with nitrogen by heat-treating MPC in  $\text{NH}_3$ . They found that nitrogen doping can facilitate the electron transfer on electrode/electrolyte interface for both oxidation and reduction process. The research work opens up a new direction for modification of electrode in VRFB system. Wu et al. [13] and Liu et al. [33] further modified the graphite felt electrode by hydrothermal method and heat treatment with liquid and gas ammonia as nitrogen sources respectively. The nitrogen doping for graphite felt can enhance the electrochemical performance of vanadium redox couples and improve energy storage efficiency. In this paper, we investigated the electrochemical performance of V(IV)/V(V) redox couple on nitrogen doped carbon cloth electrode treated by hydrothermal method with ammonia water as nitrogen sources. The electrochemical activity of V(IV)/V(V) redox couple have been enhanced and the cell using modified graphite felt electrode shows lower polarization.

## 2. Experimental

### 2.1. Preparation and characterization

N-doped carbon cloth (N-CC) was prepared by hydrothermal treatment in ammonia water. PAN-based carbon cloth (CC) and 25% ammonia water were placed into a 30 mL Teflon-lined stainless steel autoclave, and then treated at 200 °C for different time (5 h, 10 h, 15 h, 20 h). After treatment, the autoclave was cooled to room temperature. The treated carbon cloth was washed with distilled water until the pH of rinsed water was neutral, and then dried at 80 °C for 8 h.

The surface morphologies of samples were characterized with a field-emission scanning electron microscope (S-4800, Hitachi Limited, Japan) at an acceleration voltage of 25 kV. X-ray photoelectron spectroscopy measurements (XPS) were conducted on a K-Alpha 1063 (Thermo Fisher Scientific, UK) with Al  $K\alpha$  X-ray source generated at 12 kV and 6 mA in an ultra-high vacuum of about  $10^{-9}$  mbar.

The electrolyte was prepared by electrolytic dissolution and reduction of  $\text{V}_2\text{O}_5$  in  $\text{H}_2\text{SO}_4$  with appropriate concentration in a two-compartment electrolysis cell, in which  $\text{H}_2\text{SO}_4$  solution was employed as anolyte. The electrolytes in other valence were prepared by charge test in dynamic cell with  $\text{VO}^{2+}$  electrolyte as original electrolyte and diluted to specified concentration with 3 mol/L  $\text{H}_2\text{SO}_4$  solution.

### 2.2. Electrochemical measurements

Cyclic voltammetry and linear sweep voltammetry measurements were performed in a classical three-electrode system on CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). In a three-electrode system, a  $1 \times 1 \text{ cm}^2$  carbon cloth treated by above method was employed as the working electrode, a  $1 \times 2 \text{ cm}^2$  platinum net as the counter electrode, and saturated calomel electrode (SCE) along with a salt bridge filled with saturated potassium chloride solution as the reference electrode. Cyclic voltammetry tests were carried out with 1.0 mol/L  $\text{VO}^{2+} + 3.0 \text{ mol/L H}_2\text{SO}_4$  electrolyte between 0.2 V and 1.5 V vs. SCE at the scan rate of 10 mV/s. The linear sweep voltammetry tests were performed with 0.5 mol/L  $\text{VO}^{2+} + 0.5 \text{ mol/L VO}_2^+ + 3.0 \text{ mol/L H}_2\text{SO}_4$  electrolyte at the range of 0.8–1.0 V at the scan rate of 1 mV/s. The potassium chloride solution in salt bridge was replaced before measurements. Unless otherwise specified, the electrode potentials are reported relative to SCE electrode.

### 2.3. Charge–discharge test

Electrochemical performance of the cells using CC and N-CC electrode was evaluated in a single static cell. The PAN-based graphite felt ( $3 \times 3 \text{ cm}^2$ , Shenhe Carbon Fiber Materials Co. Ltd., China) was employed as negative electrode, and the CC and N-CC electrode ( $3 \times 3 \text{ cm}^2$ , Shenhe Carbon Fiber Materials Co. Ltd., China) were employed as positive electrode for comparison. The conductive plastics (Guangdong Foshan Plastics Factory, China) was used as current collector on both sides. The electrodes were encircled and fixed with polyurethane with thickness of 4 cm, and the polyurethane and conductive plastics were sealed with silicon rubber. The current was derived into the circuit by copper sheet between the conductive plastics and silicone rubber. Initial electrolytes include 1.2 mol/L  $\text{V}^{3+}$  in 3.0 mol/L  $\text{H}_2\text{SO}_4$  as negative electrolyte and 1.2 mol/L  $\text{VO}^{2+}$  in 3.0 mol/L  $\text{H}_2\text{SO}_4$  as positive electrolyte, respectively, which is separated by perfluorinated ion-exchange membrane (Nepem-1110, Best Industrial & Trade Co. Ltd., China). The charge–discharge tests were performed using CT2001C-10 V/2A (Wuhan Land Co. Ltd., China). The cells were galvanostatically charged and discharged between 0.7 V and 1.7 V. Prior to measurements, a charge–discharge test was carried out at the current density of  $10 \text{ mA/cm}^2$  for a cycle to activate the electrode.

## 3. Results and discussion

### 3.1. SEM analysis

The surface morphologies of carbon cloth untreated and treated in ammonia water at 200 °C for 15 h are shown in Fig. 1. It can be known that the diameter of carbon cloth fiber is about  $7 \mu\text{m}$ , smaller than that of the conventional graphite felt fiber (about  $17 \mu\text{m}$ ). This characteristic of carbon cloth is advantageous for mass transfer of vanadium ions on the surface of electrodes, compared with graphite felts. Hydrothermal treatment has no obvious influence on the morphology of carbon cloth fiber, without corrosion and collapsing. The relatively low temperature cannot change the arrangement and structure of inner atom of carbon cloth, so the modification cannot decrease its mechanical strength and stability, not affecting the service life of carbon cloth. Moreover, the treated carbon cloth fiber is cleaner than the pristine sample. The hydrothermal treatment with ammonia water at high temperatures can remove some contaminants which may be the remnant ingredient without carbonization in the production process of carbon cloth. In addition, the treatment can also bring the nitrogenous functional group, which is confirmed by XPS measurements.

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