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Boosting vanadium flow battery performance by Nitrogen-doped carbon nanospheres electrocatalyst

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ABSTRACT

Fabricating cost effective and high-performance electrodes is essential to the development of vanadium flow battery (VFB). Moreover, improving the stability of electrodes in acidic electrolyte remains key issues. In this work, we describe a simple method to prepare novel electrodes composed of N-doped carbon nanospheres (NCS) grown on graphite felt (GF) fibers. Dopamine monomers are used as both carbon and nitrogen source. Physical and electrochemical results reveal that the as-prepared NCS/GF electrode exhibits excellent electrocatalytic activity as well as wettability for vanadium ion redox reactions. The single cell tests at current densities of 50–300 mA cm^{-2} demonstrate superior battery performance in terms of energy efficiency and capacity retention. Exceptional durability of the NCS catalyst is confirmed by long-term cycles at a higher current density of 150 mA cm^{-2}. NCS/GF electrode also shows excellent temperature adaptability from −15 °C to 50 °C. The facile approach reported in this study can pave a new route to fabricate high-performance electrodes for VFB.

1. Introduction

Nowadays, the all-vanadium flow battery (VFB) is one of the most promising batteries for large-scale energy storage because of its unlimited capacity and long cycle life [1–6]. VFB is clearly different from other redox flow batteries (RFB) with VO^{2+}/VO_2^{+} in positive electrolyte and V^{2+}/V^{3+} in negative electrolyte, which means only vanadium ions with different valence states involved in electrode reactions [7–10]. Thus, it is convenient to recover capacity by adjusting the valence of vanadium ions to the initial state.

The redox reactions of vanadium ion couples mainly occur on electrode surface. Thus electrode materials play an important role for battery application. Currently, graphite felt (GF) is widely used as electrode material, because of its high conductivity, good corrosion resistance and three-dimensional (3D) porous structure [11]. However, the pristine GF has several disadvantages such as low electrochemical activity and poor hydrophilicity. In order to enhance the performance of GF, various treatments have been used [12–14], including acid treatment [15], thermal activation [16], electrochemical oxidation [17,18] and modification with metals (Bi [19], Ir [20] etc.) or metal oxides (Mn_3O_4 [21], PbO_2 [22], CeO_2 [23], WO_3 [24], Nb_2O_5 [25], ZrO_2 [26] etc.). These methods can introduce oxygen-containing functional groups or other high electrocatalytic activity metal elements to provide active sites for catalytic reaction of vanadium ions during charge-discharge process. However, the above approaches have either quite limited improvement or high cost by the use of precious metals.

Moreover, the carbon-based nanomaterials (i.e., graphene and carbon nanotube) are also widely used as electrocatalyst in VFB system [27–31]. Recently, much attention has been paid on heteroatoms doped carbon-based nanomaterials [32–34], especially nitrogen-doped carbon nanomaterials [35–39], which have been used as electrocatalyst for VFB and showed enhanced performance of battery. For the pristine GF electrodes used in VFB, the carbon fibers are composed of C–C bonds in the microstructure with chemical inertness and poor wettability. After modified by N-doped carbon catalysts, the composite GF electrode not only has high specific surface area owing to the introduced carbon-based nanocatalysts, but also has excellent electrochemical activity and wettability due to the formed C–N polar bonds [32]. It is considered that the introduction of N atoms into carbon framework can introduce defects and vacancy into the carbon matrix and

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change the charge distribution between C and N atoms, which can promote the vanadium ions mobility and improve electronic conductivity [40,41]. Besides, the N atoms with electronegativity doped into carbon framework can be ionized out free electrons, which can contribute to the ion exchange and promote vanadium ion redox reaction as new active sites [14,39].

In this work, we report a simple method to prepare N-doped carbon nanospheres modified graphite felt (NCS/GF), using dopamine as carbon and nitrogen sources simultaneously. It has been demonstrated that dopamine monomers can be oxidized with the presence of oxygen and self-polymerize under alkaline environment [42]. Lu et al. reported that dopamine monomers can be self-polymerized immediately when achieving reaction conditions, and then form different size polydopamine (PDA) carbon spheres or uniform PDA coating by controlling the concentration of dopamine and reaction time [43]. This self-polymerization reaction require neither complex instruments nor harmful chemicals, thus it is convenient and environment-friendly. The products of the polymerization reaction can directly be immobilized on GF fiber surface, followed by carbonization in N_2 atmosphere, and then the resulted NCS/GF was used as high reaction activity electrodes for VFB. Furthermore, the catalytic mechanism and electrochemical performance of NCS catalyst towards both VO^{2+}/VO_2^{+} and V^{2+}/V^{3+} redox reactions were investigated and compared to pristine GF through physical and electrochemical analysis.

2. Experimental section

2.1. Preparation of NCS/GF

The NCS/GF was synthesized by a facile carbonization process after the self-polymerization of dopamine on GF (Gansu Haoshi carbon Fiber Co., Ltd.) directly. The details of experimental procedures are as follows: 200 mg of dopamine was dissolved into 100 mL of distilled water by magnetic stirring for 30 min to form a solution at room temperature. Then a piece of GF ($50 \times 50 \times 5$ mm) was immersed into the resulting solution. To facilitate the penetration of dopamine monomers into the GF monolith, the solution was hold in a vacuum chamber for 3 h. Afterwards, 75 μL of Tris-buffer was added to the solution to initiate the self-polymerization of dopamine. The reaction was conducted at room temperature with varying times including 4, 8, 12, 16 and 20 h, and the solution was stirred at a constant speed in the air at the same time. Subsequently, the resulting product was thoroughly washed with deionized water, dried at 50 °C for 12 h and carbonized using a tube furnace at a certain temperature (600, 700, 800 and 900 °C) for 2 h under N_2 atmosphere. According to various analysis shown in the Supporting Information (see Fig. S1–S3 and corresponding discussion), the sample obtained after 8 h self-polymerization was denoted as PDA/GF, and then the NCS/GF electrode with highest electrochemical activity is acquired at carbonization temperature of 900 °C.

2.2. Physical and electrochemical characterization

The surface morphology and elemental composition of the samples were observed via scanning electron microscopy (SEM, ZEISS SUPRA® 55) and the energy dispersive X-ray spectroscopy (EDX) equipped into the SEM, respectively. The surface composition of samples was analyzed using X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM™).

Cyclic voltammograms (CV) was performed on PARSTST 2273 electrochemical workstation (Princeton Applied Research) using a three-electrode system. A graphite plate and a saturated calomel electrode (SCE) were utilized as counter electrode and reference electrode, respectively. Electrochemical impedance spectroscopy (EIS) measurements were conducted on PARSTST 2273 electrochemical workstation in the frequency range from 100 kHz to 10 mHz with an excitation signal of 5 mV. The positive tests were carried out in a solution of 0.1 M VO^{2+} + 2 M H_2SO_4 while the negative tests were performed in a solution of 0.1 M V^{3+} + 2 M H_2SO_4. All the potentials reported in this work were referenced to SCE.

The configuration of VFB single cell (Fig. S4) was the same as reported formerly [44,45]. Two pieces of NCS/GF ($50 \times 50 \times 5$ mm) and a Nafion 115 membrane (70×70 mm) [46] were used as electrode and separator, respectively. The initial electrolyte in both positive and negative half-cells was a solution of 0.75 M VO^{2+} + 0.75 M V^{3+} + 2 M free H_2SO_4 [47], and the volume of electrolyte

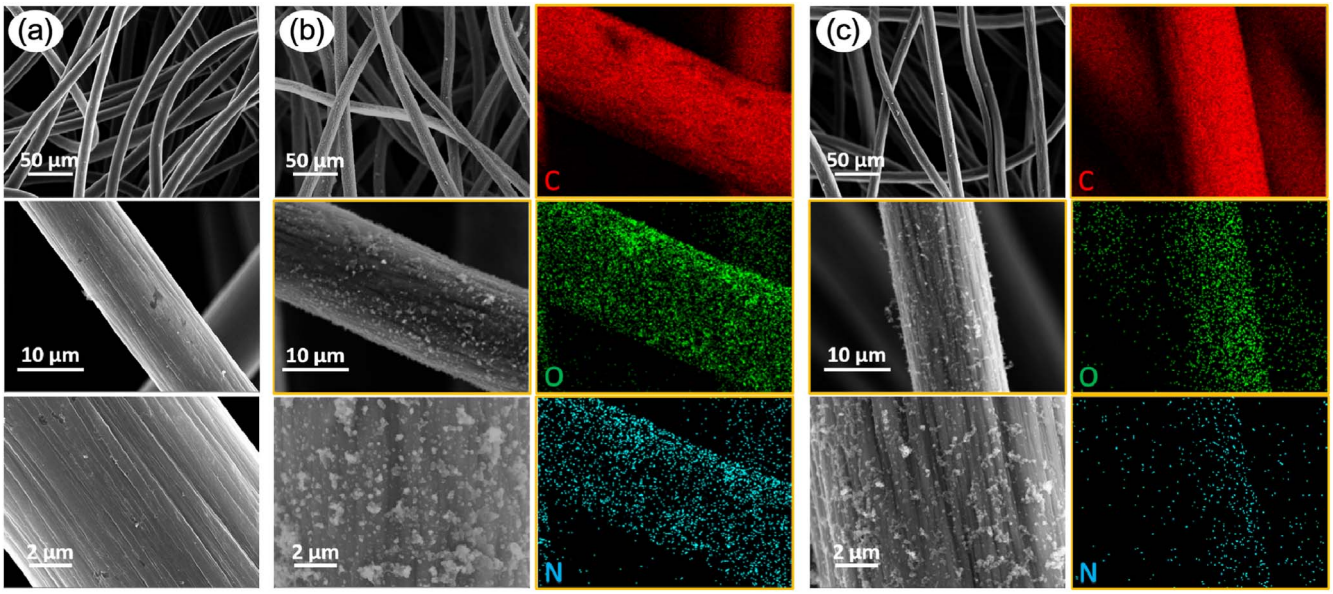

Fig. 1. (a)SEM images of GF. SEM images and EDX elemental mapping of (b) PDA/GF; (c) NCS/GF.