



Carbon layer-confined sphere/fiber hierarchical electrodes for efficient and durable vanadium flow batteries



Yang Zhao^a, Lihong Yu^b, Xiping Qiu^{a,c}, Jingyu Xi^{a,*}

^a Institute of Green Chemistry and Energy, Graduate School at Shenzhen, Tsinghua University, Shenzhen, 518055, China

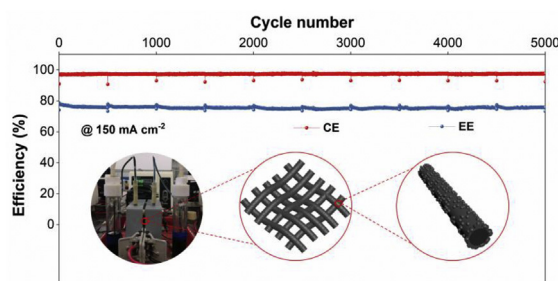
^b School of Applied Chemistry and Biological Technology, Shenzhen Polytechnic, Shenzhen, 518055, China

^c Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing, 100084, China

HIGHLIGHTS

- A carbon layer-coated sphere/fiber hierarchical electrode (CS/GF) is prepared.
- The carbon layer-confined structure endows superior durability of CS/GF in VFB.
- CS/GF displays enhanced electrolyte wettability and electrochemical activity.
- The VFB with CS/GF exhibits outstanding rate performance at 50–300 mA cm⁻².
- The VFB with CS/GF shows stable performance over 5000 cycles at 150 mA cm⁻².

GRAPHICAL ABSTRACT



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ABSTRACT

It is essential to boost the catalytic activity and cycling stability of the electrode for the ultra-long-term operation of vanadium flow battery (VFB). Herein, we report a novel hierarchical electrode by coating carbon spheres on the graphite felt (CS/GF) employing silicon dioxide nanospheres as templates and phenol formaldehyde resin as carbon sources. CS/GF possess larger surface areas and more defects than the thermally activated graphite felt, leading to better wettability and more active sites. As a result, the electrochemical activity and kinetic reversibility of the CS/GF electrode toward the $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox couples are promoted. Meanwhile, the novel carbon layer-confined structure ensures the superior durability of the CS/GF electrode during the ultra-long-term cycling test. The VFB assembled with CS/GF electrode exhibits outstanding rate performance at current densities of 50–300 mA cm⁻² as well as excellent stability over 5000 charge-discharge cycles at a high current density of 150 mA cm⁻². The facile method in this work provides a new idea for developing efficient and durable VFB electrodes.

1. Introduction

Nowadays, the redox flow battery (RFB) is considered as a very promising candidate of the large-scale energy storage systems owing to

its flexible modular design, controllable capacity and high safety [1,2]. In particularly, the vanadium flow battery (VFB) invented by M. Skyllas-Kazacos and co-workers [3] stands out from all RFBs resulting from not only common merits of high efficiencies, long cycle life, and

* Corresponding author.

E-mail address: xijy@tsinghua.edu.cn (J. Xi).

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environmental friendliness, but also the avoidance of the inevitable ion crossover [4–6].

However, the commercialization of VFB is still hindered by some technical and economic barriers, related to the electrode, the separator and the electrolyte [7]. Among them, the electrode that provides active sites for the redox reactions of $\text{VO}^{2+}/\text{VO}_2^+$ redox couple and $\text{V}^{3+}/\text{V}^{2+}$ redox couple plays a crucial role in the VFB [8]. Great efforts have been devoted to finding the proper materials as the electrode in the past decades. To date, graphite felt (GF) and carbon felt (CF) are typical electrode materials widely used in VFB because of their high electron conduction, excellent cycle stability, good corrosion resistance, three-dimensional porous structures and low cost [9,10]. Despite that, some drawbacks of the GF (CF) electrodes such as small surface area, low kinetic reversibility and poor hydrophilicity still limit the energy efficiency and power density of the VFB [11]. Hence, various strategies have been taken to enhance the performance of GF (CF), such as bulk modification and electrocatalysts modification. For bulk modification, the reported methods contain thermal activation [12], acid treatment [13,14], electrochemical oxidation [15], doping heteroatom [16,17] and etching surface [18–21]. These methods significantly improve the performances of the electrode through introducing more oxygen-containing functional groups on graphite (carbon) fibers surface and providing more active sites for the redox reaction. However, the VFBs with these modified GF (CF) electrodes are still far from achieving desirable energy efficiency and power density. Furthermore, the etched graphite (carbon) fiber surface of the electrode cannot withstand the tough treatment in the long-term cycling process. The above problems demonstrate that the bulk modification still needs further optimization. For electrocatalysts modification, many researchers have deposited metals or metal oxides on the surface of GF (CF) to facilitate their catalytic activity. Whereas, these metals (Bi [22], Ir [23], etc.) and metal oxides (Mn_3O_4 [24], WO_3 [25], Nb_2O_5 [26], CeO_2 [27], ZrO_2 [28], TiO_2 [29], etc.) can't meet the expectation as they may fall from the GF during long-term operation.

In order to avert the shortcomings of the above catalysts, some carbon-based nanomaterials, including carbon nanoparticles [30], carbon dots [31], carbon nanotubes [32,33], graphene [34] and heteroatom-doped carbon catalysts [35,36], have been introduced on the GF (CF) as catalysts in VFBs. Especially, zero-dimensional carbon-based materials like carbon nanoparticles and carbon dots attract the attentions. These materials not only have low cost but also possess high electron conduction and catalytic activity due to their large specific surface area and abundant surface defects. Thus, the modified electrode can effectively enhance the rate performance as well as electrolyte utilization and power density in the VFB. Nevertheless, a potential drawback still exists that the active materials might fall off the electrodes during the long-term cycling process (Fig. S1).

In this work, we report a novel nano-micro hierarchical electrode by coating carbon nanospheres (CS) on the GF (CS/GF) employing SiO_2 nanospheres (Fig. S2) as templates and phenol formaldehyde resin (PF) as carbon sources, as shown in Scheme 1. Firstly, SiO_2 nanospheres are strongly adsorbed and evenly dispersed on the graphite fibers surface

after modifying with poly(dimethyldiallylammonium chloride) (PDDA) to become positively chargeable. Then the PF coats the SiO_2 modified graphite fibers via simple polymerization reaction and hydrothermal reaction, followed by carbonization process of PF in Ar gas atmosphere to obtain CS/GF. The forming carbon layer remains the shape of both SiO_2 and graphite fibers, thus increasing the surface area of the graphite fibers. The carbon layer not only provides more active sites, but also is able to withstand the corrosion and washout of the electrolyte (Fig. S1). Therefore, CS/GF shows the highly enhanced electrochemical activity and reversibility of redox reaction during the VFB cycling test at different current densities as well as outstanding durability at a high current density during ultra-long-term charge-discharge cycles.

2. Experimental

2.1. Materials

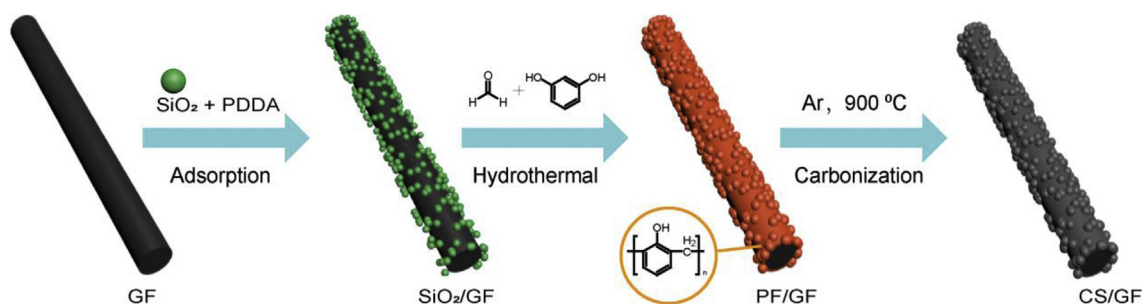
GF (Gansu HaoShi Carbon Fiber Co., Ltd.) was ultrasonically washed with ethanol and deionized water, and then thermally treated in air at 420 °C for 10 h. Thus, the thermally activated GF (TGF) was prepared. The other reagents were purchased in Aladdin Co., Ltd.

2.2. Preparation of CS/GF

The preparation process of CS/GF in Scheme 1 is as follow: firstly, the uniform SiO_2 nanospheres with a diameter of about 200 nm (Fig. S2) were produced using a classical Stöber process [37]. Then SiO_2 nanospheres (150 mg) was dispersed in PDDA solution (40 mM, 150 mL) through sonication for 30 min, followed by centrifuge and drying treatment to get the PDDA/ SiO_2 [38]. Subsequently, a piece of GF (50 mm × 50 mm × 5 mm) was immersed into the deionized water (150 mL) dispersed with PDDA/ SiO_2 (40 mg). The mixture was treated by sonication for 30 min, then set aside for 12 h at room temperature to form SiO_2 /GF. Next, a piece of dry SiO_2 /GF was soaked in the solution which consisted of ethanol (100 mL), deionized water (12 mL), ammonium hydroxide (8 mL), resorcin (0.8 g) and formaldehyde (37 wt%, 1.2 mL) at room temperature for 24 h, followed by the reaction in the hydrothermal reactor at 100 °C for 24 h. After cooled down to the room temperature, the felt was washed several times with deionized water and dried at 70 °C to obtain PF/GF [39]. Next, PF/GF was carbonized by annealing in Ar gas at 900 °C for 2 h with a heating rate of 3 °C min⁻¹. Finally, the CS/GF was obtained by thermally activating in air at 420 °C for 10 h.

2.3. Characterization

The morphology and elements distribution of the samples were characterized via transmission electron microscopy (TEM, Tecnai G2 T12, FEI) and scanning electron microscopy (SEM, ZEISS SUPRA® 55) with energy dispersive X-ray spectroscopy (EDX). The surface defects analysis was conducted by a Raman spectrometer (iHR320, Horiba) with a 532 nm laser excitation. Brunauer-Emmett-Teller (BET) surface



Scheme 1. Fabrication procedure of the CS/GF hierarchical electrode.

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