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Phosphorus-doped graphite felt allowing stabilized electrochemical interface and hierarchical pore structure for redox flow battery

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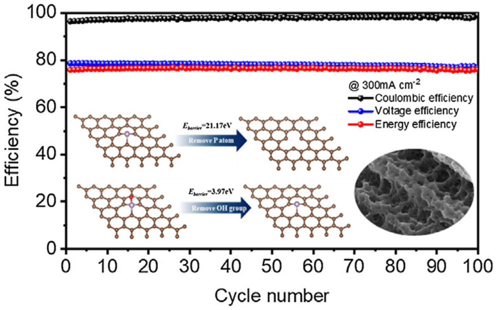
HIGHLIGHTS

- A phosphorus-doped graphite felt electrode for redox flow batteries is developed.
- Phosphorus-doped electrode yields an energy efficiency of 64% at 500 mA cm^{-2}.
- The electrode allows stabilized electrochemical interface for electrolyte reaction.
- The electrode allows hierarchical pore structure for electrolyte transport.

GRAPHICAL ABSTRACT



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ABSTRACT

The redox flow battery technology is of great potential for large-scale energy storage. However, its widespread application is suffering from the challenges of low energy efficiency and considerable performance degradation in the high-current cycles. Herein, we propose and develop a phosphorus-doped electrode with stabilized electrochemical interface and hierarchical pore structure for cost-effective flow batteries. Density functional theory calculation was first used to demonstrate the stability and activity of phosphorus-doped graphite surface. On basis of theoretical design, the phosphorus-doped graphite felt electrode was fabricated by a facial thermally treating method. Stabilized heteroatom-doped chemical surface with abundant phosphorus-containing functional groups (1.7%) was observed. Beyond that, the hierarchical pore structure from macro (~20 μm) to nanoscale (< 200 nm) was formed synchronously, suggesting the enhanced reaction activity, stability and mass transport. In charge-discharge test, flow battery assembled with phosphorus-doped electrodes yielded a prominent energy efficiency of 81% at 200 mA cm^{-2}, 46% higher than battery with traditional electrodes. Even current densities up to 500 mA cm^{-2}, battery with phosphorus-doped electrodes still exhibits a workable energy efficiency of 64% while batteries with other electrodes cannot operate properly. Moreover, the superior durability of battery with phosphorus-doped electrodes was verified after 100-cycle charge-discharge test with nearly no-decay energy efficiencies. This work offers a promising way to develop stable and efficient flow batteries for the energy storage systems.

1. Introduction

Increasingly striking issues of energy shortage and environmental pollution call for widely utilization of various renewable energy resources [1], like wind and solar [2]. However, fluctuant and intermittent of these energy sources restrict the large-scale applications [3],

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accelerating the development of cost-effective [4], fast-response [5] and high-durability [6] energy storage systems. The flow batteries, due to its superior reliability and long cycle life [7], are regarded as the promising technology for energy storage [8]. Particularly, all-vanadium redox flow batteries (VRFBs) draw the most attention [9], due to alleviating the crucial cross-contamination issue by cycling same element in negative and positive sides [6]. Even so, current VRFBs are still suffering from the challenge of high operating cost, hindering its large-scale commercial application [10]. The unfavorable operating cost mainly reflects the poor energy efficiency and adverse performance degradation in the high-current cycles [11]. Thus, developing cost-effective flow batteries with excellent energy efficiency and superior durability at high current densities is crucial for its commercialization.

As the pivotal component in flow batteries, electrodes directly determine the battery operating performance [12], because it doesn't merely provide pathways for electrolyte transfer, but also offers active interface for electrolyte redox reactions [13]. At present, the graphite felt, with the advantages of large corrosion resistance and excellent electrical conductivity [14], is applied as electrode material generally [15]. Unfortunately, pristine graphite felt (pristine GF) with smooth carbon fibers inside exhibits poor specific surface area and dreadful mass transfer, reducing energy efficiency in battery operation [16]. To remedy these problems, an effective approach is to create porous physical structure on the graphite fiber surface by various etching methods, such as K_2FeO_4 etching [16], KOH etching [17,18], $FeCl_3$ etching [19], $Zn(NO_3)_2$ etching [20] and FeOOH etching [21]. A FeOOH-etched electrode with nanosized pores was fabricated with the enlarged specific surface area up to 10.2 $m^2\ g^{-1}$, improving the energy efficiency to 57.3% at 300 mA cm^{-2} [21]. Furthermore, a hierarchical pore structure, that contains multiscale pores from nano to micro size, was built after a facial etching process, which could accelerate both mass transfer and redox reactions in VRFBs [16].

In addition, the chemical structure of graphite fiber surface, composed of inert and hydrophobic C-C bonds, subject to the high kinetic irreversibility and the sluggish electrochemical activity, seriously hindering the enhancement of battery performance [22]. Massive efforts have been put into modifying the chemical structure of graphite surface to improve battery performance [23], such as introducing oxygen [24], nitrogen [25], boron [26] or phosphorus [27] into graphite frameworks [28]. An army of researches have stated that introducing oxygen-containing functional groups of especially -OH group in connection with the formation of active sites for vanadium redox reactions [29,30]. A reduced graphene oxide coated electrode with abundant C-OH functional groups was confirmed that achieving an excellent energy efficiency of 72% at 200 mA cm^{-2} in battery test [31]. Although promising, a critical issue should be mentioned that oxygen-containing functional groups are unstable in repeated charge-discharge process [32], deteriorating the cycling performance [33]. Hence, to further enhance the efficiency and durability of flow batteries, an ideal electrode that holds both porous physical structure and stable heteroatom functional groups is required.

In order to achieve these objectives, in this work, a phosphorus doped graphite felt electrode (P-doped GF), which was designed by density functional theory calculations, fabricated by a facile one-step thermally treating method, analyzed by the chemical and physical characterization, and tested in the battery system, was proposed and developed for the cost-effective flow battery (Fig. 1). Density functional theory calculations demonstrate that P-doped graphite surface possesses active and stable C-P and P-OH functional groups, enhancing the activity and durability for redox reactions. The P-doped GF electrode was therefore fabricated and tested. It is found that the P-doped GF not only has active and stabilized electrochemical interface with heteroatom functional groups, but also has hierarchical pore structure with high surface area, thus greatly improving battery performance. In the charge-discharge test, the assembled battery with P-doped GF exhibits a superior energy efficiency of 81% at 200 mA cm^{-2} and still exhibits a workable energy efficiency of 64% at an ultra-high current densities of 500 mA cm^{-2}. Moreover, the battery exhibits remarkable stability with nearly no-decay efficiencies in long-cycle charge-discharge tests.

2. Methods

2.1. Computational methods

Density functional theory (DFT) calculations [34] were carried out by projector-augmented-wave (PAW) method [35] in the Abinit software package. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [36] was applied to deal with exchange-correlation interactions. The slab models were built for monolayer graphite (0001) and P-doped graphite (0001) surfaces in 4 × 4 × 1 supercells. The vacuum with a thickness of 20 Å was adopted to avert the interactions between two periodically repeated layers [37]. The convergence threshold for self-consistent loops was 10^{-5} eV. The conjugated gradient method was utilized to perform the geometric optimization and the force of every atom was relaxed to be smaller than 0.01 eV/Å.

The $E_{barrier}$ was defined to evaluate the energy barrier for removing the hydroxyl (OH) group or P atom.

$$E_{barrier} = E_{system} - E_{substrate} - E_{group} \quad (1)$$

where E_{system} and $E_{substrate}$ were the total energies of optimized ground state of the substrate with and without OH group or P atom, respectively. E_{group} is the total energy of OH group or P atom.

2.2. Experimental methods

The graphite felt (SGL carbon, GFA6 EA) was separated along the cross section to obtain three pieces of pristine graphite felt. After washing by deionized water and dried thoroughly, pristine GF was heated at 400 °C for 4 h in air atmosphere to fabricate thermally treated graphite felt (thermally treated GF). Then, thermally treated GF was soaked in 70% H_3PO_4 (Aladdin, 85%) solution and dried at 60 °C for overnight. Subsequently, the prepared samples were thermally treated at 800 °C for 2 h under argon flow. At last, after washing in 10% HCl (Honeywell, 37%) solution and deionized water and dried at 60 °C for 12 h, the P-doped GF was achieved. Furthermore, various concentrations of H_3PO_4 solution from 10% to 70% were adopted in electrode preparation process for comparison.

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were executed by an electrochemical workstation (CHI 760E, Chenhua) in a three-electrode system containing 0.1 M $VOSO_4$ + 3.0 M H_2SO_4 (VWR, 95%) solution. Prepared samples, Ag/AgCl electrode and graphite plate were adopted as the working electrode, reference electrode and counter electrode, respectively. In the CV measurements, potential ranges of −0.65 V to −0.25 V (vs. Ag/AgCl) and 0.6 V to 1.2 V (vs. Ag/AgCl) were adopted to both negative side and positive side redox reactions with IR-compensation. EIS measurements were executed in the frequency range from 10^{-2} to 10^5 Hz at the potentials of −0.45 V and 1.0 V for negative and positive reactions, respectively.

The charge–discharge curves were revealed in the battery test system (BT-G, Arbin) at current densities from 200 to 500 mA cm^{-2}. The prepared electrodes (2 × 2 cm) were assembled in a single cell for the charge–discharge tests. Nafion 212 (Dupont, USA) membrane (3 × 3 cm) was adopted as separator. The negative and positive electrolytes consisted of 20 mL 1.0 M V^{3+} + 3.0 M H_2SO_4 solution and 20 mL 1.0 M VO^{2+} + 3.0 M H_2SO_4 solution, respectively. In operation, electrolytes circular cycled at 46 mL min^{-1} using peristaltic pumps (WT600-2J, Longer). Nitrogen gas was flowed through electrolytes at 100 mL min^{-1} beforehand to displace air to prevent the side reactions. Morphologies of samples were examined by the scanning electron microscopy (SEM, MAIA3 LMH, Tescan). The Brunauer-Emmett-Teller