



Electrocatalytic effect of the edge planes sites at graphite electrode on the vanadium redox couples



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ABSTRACT

Compared with the basal-planes of highly oriented pyrolytic graphite (HOPG), the edge-planes of HOPG exhibit a significantly enhanced electrochemical performance, indicating of the better electrocatalytic activity of the edge-planes at graphite electrode toward vanadium redox reactions, especially for the positive reaction. In order to further investigate the electrocatalytic activity of the edge plane sites, glass carbon (GC) modified by graphite powders (GP) with different particle sizes, which possess different content of the edge-planes, are used as electrodes and their physicochemical properties such as the morphology, microstructure, surface composition, and specific surface area, in addition to the corresponding electrochemical characteristics have been characterized systematically. The total electrochemical activity toward vanadium redox reaction increases greatly with the decrease of the particle sizes for GP, which mainly attributes to the increasing surface area and exposed edge plane sites. It is worth note that a large surface area often means abundant edge plane sites, and it is mainly in favor of the enhancement of the current response, while the proportion of the active area such as the edge-planes in total surface area to a large extent determines the electrocatalytic activity.

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1. Introduction

Vanadium redox flow battery (VRFB) has attracted lots of interests for the energy storage assorted with the intermittent renewable energy (such as solar and wind energy, etc.) in recent years due to its long cycle life, large capacities, flexible design and no cross-contamination [1,2]. As a typical electrode material, carbon felts (CF) are widely used in VRFB because of their large specific surface area, low electrical resistance, high porosity, wide operation potential range, and good stability in the concentrated acid solution [3,4]. However, the poor electrochemical activity of CF toward vanadium redox reaction results in a low energy efficiency (EE) for VRFB. Therefore, a great deal of work has been done to find out the factors that greatly affects the electrochemical activity of CF toward vanadium redox couples. Skyllas-Kazacos et al. firstly purposed the catalytic mechanism of oxygen functional groups toward $\text{VO}^{2+}/\text{VO}_2^+$ and $\text{V}^{2+}/\text{V}^{3+}$ redox couples [5,6]. Di Blasi et al. reported the carbon materials containing 4–5% atomic

content of oxygen functional groups possessed a good electrochemical activity [7]. Li et al. studied the electrochemical performance of vanadium redox couples on various carbon electrodes and found the electrochemical activity of oxygen functional groups should attributed to the carbon-oxygen double bond [8–10]. In addition, Shao et al. investigated the electrochemical activity of nitrogen functional groups toward $\text{VO}^{2+}/\text{VO}_2^+$ redox couple [11]. Jin et al. found the graphitic nitrogen was the active site among nitrogen functional groups for $\text{VO}^{2+}/\text{VO}_2^+$ redox reaction [12]. Taking a whole consideration of the previous researches, the carbon electrode possessing appropriate carbon-oxygen double bond or graphitic nitrogen exhibits excellent electrochemical activity toward vanadium redox couples.

However, the studies mentioned above just present the effect of the surface chemical characteristics just like the oxygen or nitrogen functional groups, while the overall structure-function relationship between the physicochemical properties such as the morphology, microstructure, composition, et al. and their electrochemical activity is in lack of investigation. Actually, compared with the basal-planes, the edge-planes of the carbon materials often exhibit more excellent electrochemical activity toward the redox reaction because of their distinct physicochemical properties [13–17]. Up to now, there are amounts of literature reported

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the strong electrocatalytic activity toward several redox couples for the edge planes of 2-dimensional graphitic lattice in the carbon materials [18,19]. For example, Yuan et al. found the graphene edge showed 4 orders of magnitude higher specific capacitance, much faster electron transfer rate and stronger electrocatalytic activity than those of graphene basal plane [17]. In addition, the influence of edge- and basal-plane sites on the vanadium redox kinetics for VRFB was investigated by Pour et al. and it was found that the edge carbon sites provide faster kinetics for $\text{VO}^{2+}/\text{VO}_2^+$ and $\text{V}^{2+}/\text{V}^{3+}$ redox couples than basal carbon, especially at low vanadium concentrations [20]. Park and his co-workers found the electrocatalytic activity of a selectively edge-functionalized graphene nanoplatelet catalyst towards vanadium redox couples is highly dependent on the selectively functionalized edge structure and the well-preserved basal plane with a high crystallinity [21]. In order to investigate the influences of the structural and surface characteristics of carbon fibres on the electrochemical activity toward vanadium redox couples, the polyacrylonitrile (PAN)-based electrospun carbon nanofibers (ECNF) were developed in our previous work and the coupling effect between the structure and surface characteristics of ECNF on the electrochemical activity towards $\text{VO}^{2+}/\text{VO}_2^+$ redox couple was studied systematically [22–26]. It was found that the electrochemical activity of ECNF toward vanadium redox couples not only closely related to the conversion of microstructure, but also depended on surface composition, especially for the quantity of edge planes in graphite layers, which might to a large extent determine the electrochemical activity of ECNF.

Even so, the detailed electrocatalytic interaction characteristics and corresponding mechanism of the edge plane sites on the vanadium redox reaction are still unclear, and it is hard to improve

the electrochemical performance of VRFB effectively. Therefore, the different types of the highly oriented pyrolytic graphite (HOPG) electrodes and graphite powders (GP) with different particle sizes were used as research object in this paper, and the important role of the edge-planes on graphite electrode in the electrochemical activity was studied.

2. Experimental

2.1. Pretreatment of the HOPG electrodes

Two types of HOPG electrodes, the edge plane pyrolytic graphite (EPPG) and basal plane pyrolytic graphite (BPPG), were obtained from Wuhan Gaossunion Tech Co. Ltd. The EPPG was polished with 0.05 μm alumina slurries and sonicated in deionized water and acetone for 1 min before use. The BPPG was pressed on the cello tape to remove the top layer of graphite and then cleaned in acetone. In addition, another BPPG sample was polished with 0.05 μm alumina slurries after the above-mentioned pre-treatment for comparison.

2.2. Preparation of the GC electrode modified by GP

GP with different particle sizes were obtained from Nanjing XFNANO Materials Tech Co. Ltd. The average dimensions of these GP in the direction parallel to the basal plane are 45, 25, 13, 4.5 μm , 400 and 30 nm, respectively. All of these samples were used as received.

Firstly, GP with different sizes (each for 4 mg) were added into the 1 mL DMF under ultrasonication, respectively. When GP were well dispersed and suspended in the solution, 20 μL suspension

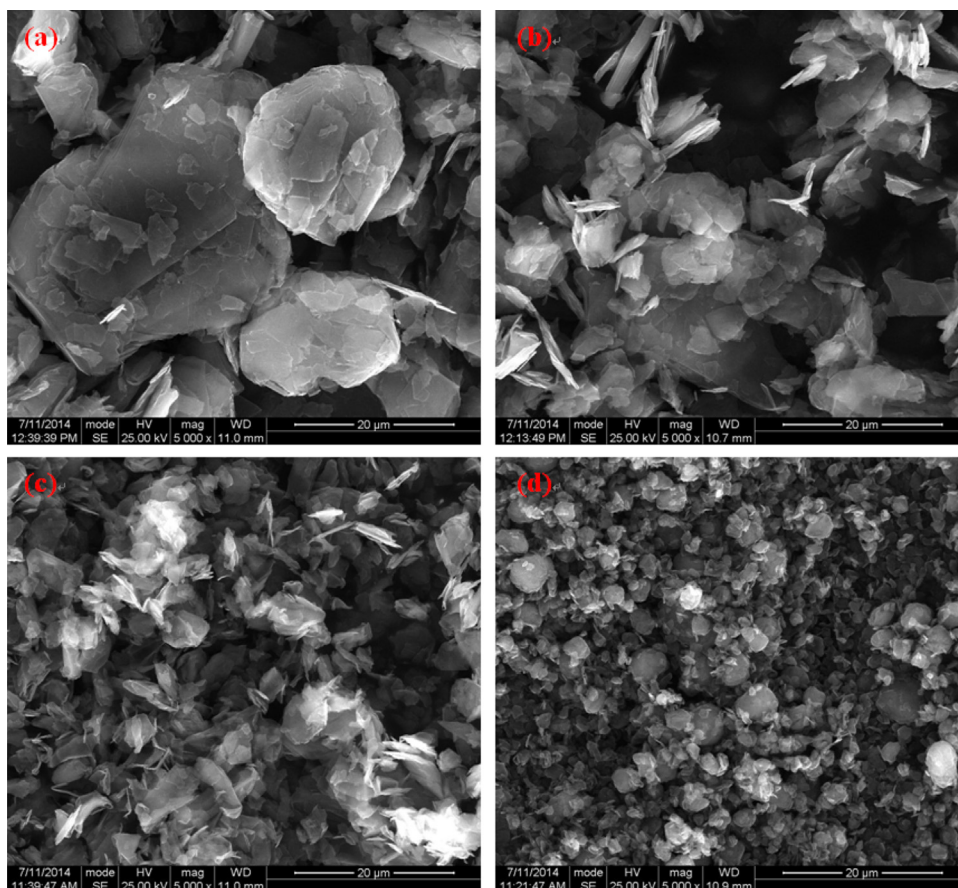


Fig. 1. Morphology of the GP with different particle sizes: (a) 45 μm , (b) 13 μm , (c) 4.3 μm , (d) 400 nm.

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