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A high-performance carbon nanoparticle-decorated graphite felt electrode for vanadium redox flow batteries

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HIGHLIGHTS

- Propose a carbon nanoparticle-decorated graphite felt electrode for VRFBs.
- The energy efficiency is up to 84.8% at 100 mA cm^{-2}.
- The new electrode allows the peak power density to reach 508 mW cm^{-2}.

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ABSTRACT

Increasing the performance of vanadium redox flow batteries (VRFBs), especially the energy efficiency and power density, is critically important to reduce the system cost to a level for widespread commercialization. Unlike conventional VRFBs with flow-through structure, in this work we create a VRFB featuring a flow-field structure with a carbon nanoparticle-decorated graphite felt electrode for the battery. This novel structure, exhibiting a significantly reduced ohmic loss through reducing electrode thickness, an increased surface area and improved electrocatalytic activity by coating carbon nanoparticles, allows the energy efficiency up to 84.8% at a current density of as high as 100 mA cm^{-2} and the peak power density to reach a value of 508 mW cm^{-2}. In addition, it is demonstrated that the battery with this proposed structure exhibits a substantially improved rate capability and capacity retention as opposed to conventional flow-through structured battery with thick graphite felt electrodes.

1. Introduction

Vanadium redox flow batteries (VRFBs) have been considered as one of the most promising power sources for large-scale electrical energy storage systems [1–3], due to their independence of capacity and power, the elimination of crossover contamination in electrolytes, short response time and long cycle life [4,5]. Despite these compelling advantages, the commercialization of the VRFB is still hindered by its relatively low energy density and consequent high cost [6–8]. On this occasion, VRFBs capable of achieving enhanced energy efficiency under high operating current density, best expressed as high power density, are always desired. At the cell level, the improved power density is tantamount to decreasing stack size, including the total area of electrodes and membranes which represents a significant cost of the system [9,10].

As one critical component of VRFBs, an electrode contributes to the system polarization through not only the ohmic resistance, but also the charge transfer polarization [11,12]. Thus, the performance of the VRFBs, including power density and energy efficiency, is highly dependent upon the electrodes which provide electroactive surfaces and conduct electrons for redox reactions [13]. Among the electrodes to choose from, millimeter level graphite felt possessing satisfactory chemical stability, low cost and high electric conductivity, have been commonly utilized in VRFBs [14–16]. However, poor kinetic reversibility and electrochemical activity toward vanadium redox reactions has been a long-standing barrier to improve the battery performance. In an effort to improve the surface activity of carbon material, enhancements to the electrochemical properties of VRFB electrodes have been previously investigated. Such pre-treating approaches include acid treatment [17–19], thermal treatment [14,20], nitrogenization treatment [21–23]. In addition, a variety of metal and carbon-based nanomaterials were tested to decorate the surface of graphite felt [24]. However, the previous work mainly focused on enhancing the electrochemical activity rather than addressing the high ohmic resistance induced by the use of thick graphite felt. As a result, energy efficiency drops quickly with an increase in

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current density, even when high electroactive materials are applied [25].

Conventionally, the VRFB adopts a flow-through structure, as shown in Fig. 1a, in which the electrolyte is pumped through the porous electrode with a flow-frame. This type of cell structure is simple and straightforward to fabricate. However, to circumvent the high flow resistance and pump loss, traditional graphite felt electrode has to be relatively thick (3–6 mm), bringing a high ohmic resistance of 3–5 $\Omega\,cm^2$ [26], which often limits the flow battery system to an operating current density lower than 100 $mA\,cm^{-2}$ [27]. In this regard, some researchers replaced graphite felt electrodes to a thinner carbon paper cooperating with the flow-by mode as shown in Fig. 1b. This novel cell configuration, exhibiting a much smaller ohmic loss, enables the battery to achieve a significantly improved power density compared with conventional design [9,28,29]. Nevertheless, inadequate wettability owing to its hydrophobic surface and poor electrochemical property toward the vanadium redox reactions, as well as low surface area for redox reactions, lead to a significant decline of the charge and discharge performance. Moreover, unlike flexible graphite felt, electrodes made of brittle and expensive carbon paper are not suitable for stack installation and cost reduction.

In this work, we propose a VRFB featuring a flow-field structure with a carbon nanoparticle-decorated graphite felt electrode. This novel structure plays a key role in decreasing the ohmic resistance by reducing the electrode thickness and features improved electroactive surface areas by coating nitric acid treated carbon nanoparticles. The energy efficiency of the present battery can reach 84.8% and 72.7% at a current density of 100 and 200 $mA\,cm^{-2}$. Furthermore, it is also demonstrated that the battery with the new electrode exhibits a substantially improved rate capability and capacity retention compared with that of conventionally structured battery.

2. Experimental

2.1. Electrode fabrication

The electrode was fabricated through a four-step process: (i) commercial graphite felt GFA5 (SGL, uncompressed thickness: 6 mm) was cross-sectioned and divided into four pieces, washed with deionized (DI) water and dried in a vacuum oven; (ii) carbon nanoparticles were activated in 68 wt.% nitric acid (Aldrich) at 110 °C for 8 h. Subsequently, the treated nanoparticles were washed with DI water and dried at 80 °C for 12 h; (iii) the treated carbon nanoparticles and 5 wt.% Nafion solutions were dispersed in ethanol and sonicated for 40 min; (iv) the graphite felt was dipped in the suspension and dried in air. The aforementioned dip-withdraw-dry process was repeated until an anticipated loading amount of carbon nanoparticles was achieved. The as-prepared graphite felt was dried in the vacuum oven at 60 °C overnight.

2.2. Performance tests and characterizations

Fig. 1a presents the battery without flow fields, which is known as a typical flow-through structure. It consists of two PMMA frames, in which the positive and negative electrodes are placed. Fig. 1b illustrates the battery of flow-by structure with a single serpentine flow field (1.5 mm in width, 1 mm in depth, and 2 mm in rib width). The geometric area of electrodes in both configurations was 18 mm × 26 mm, and Nafion® 115 was employed as the membrane. 20 mL of a solution containing 1 M VO^{2+} + 3 M H_2SO_4 and 20 mL of a solution containing 1 M V^{3+} + 3 M H_2SO_4 were used as the positive and negative electrolytes, respectively. The electrolytes in the batteries maintained a constant flow rate of 0.5 $mL\,s^{-1}$ with two pumps. Before each measurement, nitrogen gas (high purity) was bubbled to exhaust any entrapped air in

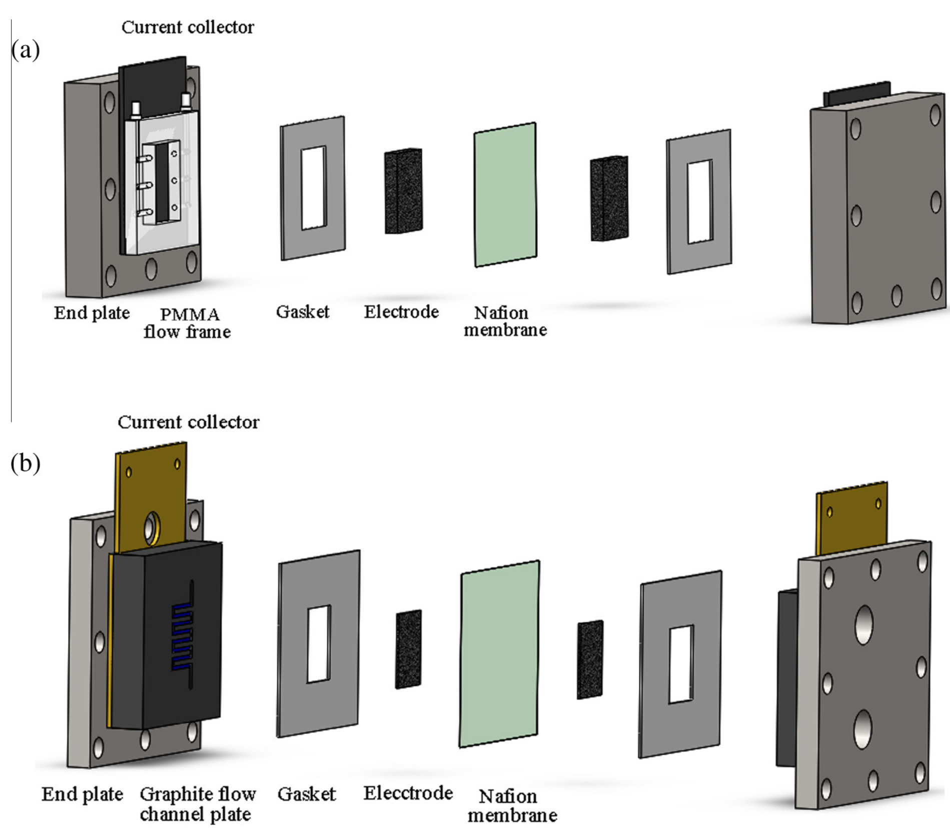

Fig. 1. Schematic of the components of a VRFB (a) flow-through structure without flow fields; (b) flow-by structure with single serpentine flow field.