



A highly permeable and enhanced surface area carbon-cloth electrode for vanadium redox flow batteries



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HIGHLIGHTS

- A high performance carbon cloth electrode is developed for flow batteries.
- The developed electrode offers good transport properties and high surface area.
- The battery with the carbon cloth electrode offers high performance.

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ABSTRACT

In this work, a high-performance porous electrode, made of KOH-activated carbon-cloth, is developed for vanadium redox flow batteries (VRFBs). The macro-scale porous structure in the carbon cloth formed by weaving the carbon fibers in an ordered manner offers a low tortuosity (~1.1) and a broad pore distribution from 5 μm to 100 μm , rendering the electrode a high hydraulic permeability and high effective ionic conductivity, which are beneficial for the electrolyte flow and ion transport through the porous electrode. The use of KOH activation method to create nano-scale pores on the carbon-fiber surfaces leads to a significant increase in the surface area for redox reactions from 2.39 $\text{m}^2 \text{g}^{-1}$ to 15.4 $\text{m}^2 \text{g}^{-1}$. The battery assembled with the present electrode delivers an energy efficiency of 80.1% and an electrolyte utilization of 74.6% at a current density of 400 mA cm^{-2} , as opposed to an electrolyte utilization of 61.1% achieved by using a conventional carbon-paper electrode. Such a high performance is mainly attributed to the combination of the excellent mass/ion transport properties and the high surface area rendered by the present electrode. It is suggested that the KOH-activated carbon-cloth electrode is a promising candidate in redox flow batteries.

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1. Introduction

Effective usage of the electricity harvested from the renewable energy sources that are intermittent in nature requires the deployment of reliable, efficient, and cost-effective large-scale energy storage systems [1–3]. Among large-scale energy storage systems, redox flow batteries (RFBs) have received extensive attentions because of its high efficiency, excellent scalability, flexible operation as well as long lifetime [4–6]. In particular, vanadium redox flow batteries (VRFBs), which employ the same element as redox active species in two half-cells and thus avoid the cross-contamination issue, have been identified as one of the most promising energy-storage systems [7–10].

Although the VRFB possesses attractive advantages, however, its widespread adoption is still significantly hindered by the high capital cost, resulting from the precious redox-active materials and low-performance power pack. For a flow battery system with given redox couples like the VRFB, maximizing the power density (operating current density) to reduce the stack size and increasing electrolyte utilization (charge-discharge depth) to enable effective usage of electrolyte should be the most direct and simple strategy to cut down the capital cost. Simultaneously maximizing these two parameters relies on minimizing the battery energy losses that come from activation loss, ohmic loss and concentration loss, respectively. In this sense, design over electrode structure and surface properties to manage the electrochemical reactions and electron/ion/species transport is critically important to achieve the optimal cell performance [11–14].

The first barrier that needs to be removed is the reaction kinetic

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issue. Conventional electrode materials, such as carbon felt and carbon paper, usually suffered from serious kinetic issue associated with poor catalytic activity for redox reactions and low specific surface area for the access of the active species, limiting the battery to be operated at current densities lower than 100 mA cm^{-2} [15–17]. To address this issue, various approaches have been proposed to increase the surface area and the catalytic activity. One of the common strategies is to thermally or chemically treat the electrode; hence the amount of functional groups on the surface is dramatically increased and thus the catalytic activity is correspondingly enhanced. Improvement on reaction kinetics was also found after introducing metal/metal oxide catalysts onto the electrode surfaces [18–24]. Similarly, the high surface area carbon materials, such as carbon nanotube, graphene, and nanofiber, were also coated onto the electrode surfaces, aiming at increasing the surface area and catalytic activity [25–31]. Recently, our group demonstrated [29] a simple method to increase the surface area of carbon paper electrode by using KOH treatment to form nanopores on the carbon fiber surfaces and 10 times improvement in surface area was found.

Apart from improving reaction kinetic, attentions should also be paid to managing the ion/mass transport through the porous electrodes, which are also critically important to the battery performance, especially at high current densities. The ion transport through the porous electrodes has a large contribution to the whole cell resistance while the mass transport through electrode will determine the concentration loss as well as the electrolyte utilization. Recently, the high current density operation has been considered to be an effective approach to reduce the stack size and thereby the cost. However, the electrolyte utilization is relatively low at high current density region. In our previous work, although the battery can work at high current densities ($>200 \text{ mA cm}^{-2}$) with a high energy efficiency (80%), the electrolyte utilization is often as low as 60%, which means the precious redox-active materials are not well utilized and results in an increased capital cost. Therefore, in order to further improve the battery performance (efficiency and electrolyte utilization), more attentions should be paid to the ion/mass transport properties of the electrode, which determines the ohmic and concentration losses.

In general, the reaction kinetics of an electrode mainly depends on surface morphology and surface activity while the ion/mass transport properties should be related to the macro-scale porous structure [32]. For the ion transport through the porous media, effective electrolyte conductivity was often used to characterize the ion conduction capability of a specific porous structure saturated with given electrolytes. It is known that the porosity and tortuosity are two key parameters that influence the effective electrolyte conductivity since porosity determines the effective transport area and tortuosity determines the length of the transport pathway. Typically, the porosity of the electrode of flow battery is around 80% (after compression) and cannot exceed 85% due to the electronic conductivity and surface area concerns. Therefore, the only effective way to increase the effective electrolyte conductivity should be tuning the tortuosity of the electrode. For the electrode made of carbon fibers, the tortuosity should be determined by the fiber arrangement pattern. Normally, the ordered arrangement pattern will produce a low tortuosity, and vice versa. Currently, the most widely used electrode is carbon paper/felt electrodes, which are formed from randomly laced carbon fibers. In this regard, a porous electrode with ordered fiber arrangement should be promoted to be used in VRFB systems. For flow batteries like VRFBs, the dominant mass-transport mechanism in the porous electrode should be convection as the intrinsic diffusivity of the metal ions and the operating temperature are relatively low [8]. Hence, the hydraulic permeability is the key parameter to evaluate the mass transport

properties. It is known that hydraulic permeability of the porous structure is closely related to the tortuosity, porosity, and pore sizes. In this sense, with a lower tortuosity and larger pore sizes, the permeability should be larger, and vice versa. Therefore, a porous structure has large pore sizes and lower tortuosity should be suitable for the VRFB applications.

With given fiber diameter and porosity, the pore size distribution and arrangement pattern of the carbon fibers should be the main contributor to tortuosity and hydraulic permeability [32–34]. As shown in Fig. 1, carbon cloth, which was previously used as gas diffusion layer in fuel cells and made by weaving the carbon fiber, has a relatively more ordered fiber arrangement pattern and a broad pore distribution from 5 to $100 \mu\text{m}$ [32] and thus lower tortuosity and higher permeability, as compared with carbon paper under the same fiber diameter and porosity [33,34], which may result in excellent transport properties. On the other hand, KOH treatment is found to be a simple method to increase the surface area of carbon paper electrode by forming nanopores on the carbon-fiber surfaces, leading to a significant improvement in reaction kinetics. In this work, we propose to develop a KOH-activated carbon-cloth electrode, which can combine the attributes of high surface area and excellent transport properties, for VRFBs. It is found that the low tortuosity combined with a broad pore distribution from 5 to $100 \mu\text{m}$ renders carbon cloth electrode desirable ion and mass transport properties (effective ionic conductivity and hydraulic permeability), which is particularly suitable for VRFB applications. We then apply the KOH-activation method to treat the carbon cloth electrode, increasing the surface area to as high as $15.4 \text{ m}^2 \text{ g}^{-1}$, which is six times higher than the pristine one. Finally, a VRFB assembled with as-fabricated electrodes was tested, demonstrating a high energy efficiency of 80.1% and electrolyte utilization of 74.6% at a current density of 400 mA cm^{-2} . The high performance of the present VRFB should be attributed to the excellent ion and mass transport properties as well as the high surface area.

2. Experimental

2.1. Fabrication and characterization of KOH activated carbon cloth

The pristine carbon cloth (ELAT[®] hydrophilic plain), provided by Fuel Cells Etc, was selected as the starting material. To introduce oxygen containing functional groups, the pristine carbon cloth was

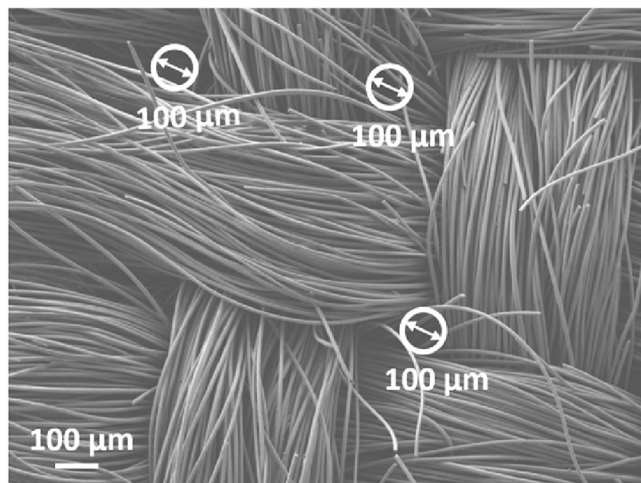


Fig. 1. SEM image of carbon cloth electrode.

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