



# Achieving efficient and inexpensive vanadium flow battery by combining $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ electrocatalyst and hydrocarbon membrane



Lihong Yu<sup>a,\*</sup>, Feng Lin<sup>a</sup>, Wangdong Xiao<sup>a</sup>, Ling Xu<sup>a</sup>, Jingyu Xi<sup>b,\*</sup>

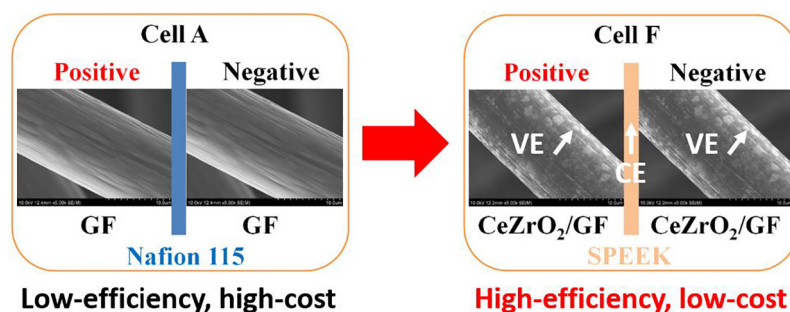
<sup>a</sup> School of Applied Chemistry and Biological Technology, Shenzhen Polytechnic, Shenzhen 518055, China

<sup>b</sup> Institute of Green Chemistry and Energy, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

## HIGHLIGHTS

- $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$  ( $x = 0.8, 0.5, \text{ or } 0.2$ ) composite electrodes are fabricated for VFB application.
- All  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$  show improved wettability and activity for  $\text{VO}^{2+}/\text{VO}_2^+$  and  $\text{V}^{2+}/\text{V}^{3+}$  couples.
- $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2/\text{GF}$  exhibits significantly enhanced voltage efficiency in Nafion membrane-based VFB.
- $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2/\text{GF}$  electrode combined with SPEEK membrane demonstrates superior VFB performance.
- An efficient and inexpensive VFB is achieved.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Vanadium flow battery (VFB) is one of the most promising technologies for grid scale energy storage because of its unlimited capacity and ultralong lifespan. Improving energy efficiency (EE) and reducing cost are critical to the practical application of VFB. The efficiency and cost of VFB mainly depend on its key materials such as electrode and proton-conducting membrane. Herein, we report the use of highly active ceria–zirconia mixed oxide decorated graphite felt ( $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$ ) electrodes in combination with a high proton-selective sulfonated poly(ether ether ketone) (SPEEK) membrane to achieve efficient and inexpensive VFB.  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  electrocatalysts can improve the electrolyte wettability and electrochemical activity of the GF electrode towards  $\text{VO}^{2+}/\text{VO}_2^+$  and  $\text{V}^{2+}/\text{V}^{3+}$  redox couples, leading to remarkably enhanced voltage efficiency (VE) of VFB. On the other hand, SPEEK membrane can effectively suppress the crossover of vanadium ions, resulting in greatly improved coulombic efficiency (CE) of VFB. As a result, the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$ -SPEEK combination demonstrates superior battery efficiencies (CE, VE and EE) and cycling stability to the traditional GF-Nafion combination. Meanwhile, since hydrocarbon-based SPEEK membrane is much cheaper than commercial Nafion membrane, the cost of VFB is also significantly reduced.

## 1. Introduction

Vanadium flow battery (VFB) is a promising electrochemical energy storage system because of unlimited capacity and ultralong lifespan [1].

Some MW class VFB demonstration programs have been established worldwide during past decade [2]. Currently, the main research direction of VFB is to improve high power-performance and reduce cost by optimizing key materials [3]. Vanadium electrolyte, proton-

\* Corresponding authors.

E-mail addresses: [yulihong@szpt.edu.cn](mailto:yulihong@szpt.edu.cn) (L. Yu), [xijy@tsinghua.edu.cn](mailto:xijy@tsinghua.edu.cn) (J. Xi).

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conducting membrane and carbon fabric electrode are three key components of the VFB [4]. Energy density of VFB is determined by the concentration of vanadium ions in the supporting electrolyte [5]. Although great efforts have been devoted to the development of high-concentration vanadium electrolytes, practical use concentration are still limited to 1.5–2.0 M [5–7]. Power density and rate performance of VFB depend on carbon fiber electrodes such as carbon felt (CF) and graphite felt (GF) [8,9]. Unfortunately, the pristine CF and GF show poor wettability and activity towards both positive  $\text{VO}^{2+}/\text{VO}_2^+$  and negative  $\text{V}^{2+}/\text{V}^{3+}$  electrolytes, resulting in low voltage efficiency (VE) and unstable cycling performance [10,11]. System cost and coulombic efficiency (CE) of VFB are determined by the proton-conducting membrane [3]. Currently, the perfluorosulfonic acid type Nafion membranes are still the widely used membrane in VFB due to its superior chemical/mechanical stability [12–14]. However, the expensive cost and fast vanadium crossover issues still remain great challenges [15,16]. Therefore, the development of high electrolyte accessibility and electrochemical active electrodes as well as low-cost and high proton permselectivity membranes are essential to promote the practical application of VFB.

Polyacrylonitrile-derived CF and GF are commonly used VFB electrodes due to their excellent electronic conductivity, chemical stability, 3D porous structure, and low cost [10,11]. The wettability and activity of GF (CF) on vanadium electrolyte are mainly affected by its surface morphology and functional groups [8]. In order to improve the wettability and activity of GF (CF), various strategies have been employed, such as bulk modification, heteroatom doping and electrocatalysts decorating [8,9]. Thermal treatment [17], acid activation [18], electrochemical oxidation [19], and chemical etching [20–22] are all efficient methods to enhance the performance of GF (CF). The improved performance can be attributed to the introduction of oxygen-containing functional groups, resulting defect sites and increased specific surface area. Heteroatom doping, including N [23,24], P [25], or B [26] doping, and N,P [27] and P,F dual-doping [28], can significantly improve GF (CF) performance by turning the surface electronic structure and generating catalytic sites [29]. To date, electrocatalyst modification has been the most effective way to boost the VFB performance of GF (CF) [8]. Carbon nanomaterials (e.g. carbon dots [30], carbon nanotubes [31,32] and Graphene [33]) and metal oxides (e.g.  $\text{WO}_3$  [34],  $\text{CeO}_2$  [35],  $\text{Nb}_2\text{O}_5$  [36],  $\text{TiO}_2$  [37] and  $\text{Mn}_3\text{O}_4$  [38]) are two main types of electrocatalysts that have been used. These electrocatalysts can simultaneously improve the electrolyte wettability and provide more reaction sites for  $\text{VO}^{2+}/\text{VO}_2^+$  and  $\text{V}^{2+}/\text{V}^{3+}$  redox couples, thus greatly increasing the operating current density of the VFB [8].

Although modified GF (CF) electrodes exhibit excellent VE and enhanced power density in VFB, the energy efficiency (EE) is still limited due to the low CE of commercial Nafion membrane resulting from severe vanadium ion crossover [13]. Thus the use of high proton selectivity membrane is essential to realize a high EE. Compared with Nafion membranes, hydrocarbon-based proton-conducting membranes have small ion clusters and therefore exhibit lower vanadium ion permeability [39,40]. In addition, the inexpensive hydrocarbon-based membranes are more suitable for large-scale VFB applications [15]. A large number of hydrocarbon-based membranes such as sulfonated poly(ether ether ketone) (SPEEK) [41,42], sulfonated polyimide (SPI) [43], polybenzimidazole (PBI) [44], and porous membrane [45] have been successfully used in VFB to achieve higher CE (> 98%). Among these alternative membranes, SPEEK may be the most promising candidate because of its high proton conductivity, low cost and scalable production [15].

Owing to abundant oxygen vacancy defects and high oxygen storage capacity, ceria–zirconia mixed oxides ( $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ) have been widely employed in energy and environmental fields as catalytically active species, promoter and support [46,47]. The unique properties of

$\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  inspired us to fabricate  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x = 0.8, 0.5, \text{ or } 0.2$ ) nanoparticles modified GF ( $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$ ) electrodes for VFB application, since it is generally believed that oxygen-containing functional groups participate in the electrode reaction of vanadium ions [8]. The electrochemical activity of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$  electrodes towards  $\text{VO}^{2+}/\text{VO}_2^+$  and  $\text{V}^{2+}/\text{V}^{3+}$  couples is evaluated and its possible reaction mechanism is discussed. The optimized  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2/\text{GF}$  electrode exhibits significantly enhanced rate performance in Nafion membrane-based VFB compared to the pristine GF. Unlike previous reports that only studied the effects of new electrodes or low-cost membranes, we attempt to combine high-activity electrodes with highly selective membranes to achieve efficient and inexpensive VFB. Therefore, VFB with  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2/\text{GF}$  electrode and SPEEK membrane is further assembled and investigated. As expected, the  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2/\text{GF}$ -SPEEK combination demonstrates superior rate performance and cycling stability to the  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2/\text{GF}$ -Nafion combination due to the excellent proton permselectivity of the SPEEK membrane [16].

## 2. Experimental section

### 2.1. Materials

PAN-based GF with 5 mm of thickness was purchased from Gansu HaoShi Carbon Fiber Co., Ltd.  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  were purchased from Tianjin Kermal Chemical Reagent Co., Ltd. Nafion 115 membrane (DuPont) was pretreated by the acid boiling procedure [48]. SPEEK membrane was prepared according to our previous report [41]. Other chemicals were of analytical reagent grade and were used without further purification.

### 2.2. Preparation of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$ electrodes

A series of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$  ( $x = 0.8, 0.5, \text{ or } 0.2$ ) electrodes were fabricated. Briefly, a stoichiometric ratio of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  were dissolved in deionized (DI) water to form 100 mL of 0.3 mM precursor solution. Then, the solution was transferred into a 200 mL PTFE-lined autoclave and a piece of GF (5 cm × 5 cm) was immersed into the solution. Afterward, the hydrothermal reaction was conducted at 200 °C for 8 h and cooled naturally. The modified GF was washed by DI water for several times and dried at 60 °C for 12 h. Finally, the modified GF was calcined in Ar gas at 800 °C for 4 h to obtain the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$ .

### 2.3. Characterization

Morphology and elements mapping of the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$  were characterized by scanning electron microscopy (SEM, S-4800, Hitachi) with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, Tecnai G2 F30, FEI). Surface composition of the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$  was analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM™). Electrochemical tests including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on a PARSTAT 2273 electrochemical workstation using a three-electrode cell [49]. A piece of GF or  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{GF}$  (1.5 cm × 1.5 cm) was used as working electrode. Pt plate and saturated calomel electrode (SCE) served as counter electrode and reference electrode, respectively. The positive CV and EIS tests were carried out in 0.1 M  $\text{VO}^{2+} + 2\text{ M H}_2\text{SO}_4$  solution while the negative tests in 0.1 M  $\text{V}^{3+} + 2\text{ M H}_2\text{SO}_4$  solution. CV was conducted with a scan rate of 1 mV s<sup>-1</sup>. EIS was measured with a 5 mV excitation signal in the frequency range of 10<sup>5</sup>–10<sup>-2</sup> Hz.

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