

Hierarchical porous carbon toward effective cathode in advanced zinc-cerium redox flow battery

XIE Zhipeng (谢志鹏)^{1,2,*}, YANG Bin (杨斌)¹, CAI Dingjian (蔡定建)¹, YANG Liang (杨亮)¹

(1. College of Chemistry and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; 2. State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China)

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Abstract: Advanced zinc-cerium redox flow battery (ZCRFB) is a large-scale energy storage system which plays a significant role in the application of new energy sources. The requirement of superior cathode with high activity and fast ion diffusion is a hierarchical porous structure, which was synthesized in this work by a method in which both hard template and soft template were used. The structure and the performance of the cathode prepared here were characterized and evaluated by a variety of techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA). There were mainly three types of pore size within the hierarchical porous carbon: 2 μm , 80 nm, and 10 nm. The charge capacity of the cell using hierarchical porous carbon (HPC) as positive electrode was obviously larger than that using carbon felt; the former was 665.5 mAh with a coulombic efficiency of 89.0% and an energy efficiency of 79.0%, whereas the latter was 611.1 mAh with a coulombic efficiency of 81.5% and an energy efficiency of 68.6%. In addition, performance of the ZCRFB using HPC as positive electrode showed a good stability over 50 cycles. These results showed that the hierarchical porous carbon was superior over the carbon felt for application in ZCRFB.

Keywords: new energy; energy storage; redox flow battery; hierarchical porous carbon; cerium; carbon felt; electrode; electrolyte; rare earths

Energy crisis presents the most important challenges to the mankind nowadays^[1]. Looking into the future of energy source, we see a vista of combination of the reasonable utilization of fossil fuels (coal, oil, and natural gas) and the development of new energy sources (nuclear, solar, biomass, hydrogen, geothermal energy, ocean energy, and wind energy). Energy storage is the key technology for the application of new energy sources. There are many technologies currently available for energy storage such as pumped hydroelectric energy storage (PHES), compressed air energy storage (CAES), flywheels, superconducting magnetic energy storage (SMES), super capacitors^[2], and chemical batteries (lead-acid, nickel cadmium, nickel-metal hydride, lithium ion, sodium nickel-chloride, flow batteries, and metal-air batteries)^[3].

Rechargeable battery plays a significant role in the application of new energy source. Lead-acid battery is the most common rechargeable battery^[4] which has been a successful article of commerce for over a century. Lithium-ion battery is expected to be used as power supply for automobile due to its high energy density^[5,6]. The most notable feature of redox flow battery is that the active material of cell is soluble in the electrolyte^[7]. The separation of output power and capacity provides large

flexibility for system design. All-vanadium redox flow battery^[8] employs $\text{V}^{2+}/\text{V}^{3+}$, and $\text{VO}^{2+}/\text{VO}_2^+$ as negative- and positive-electrolyte, respectively; avoiding the loss of capacity caused by cross-contamination of electrolyte; one downside of this battery is that its cell voltage is relatively small (about 1.26 V). The zinc-cerium redox flow battery^[9] (ZCRFB) is known as the energy storage system with the maximum cell voltage, which uses aqueous electrolyte; its open circuit voltage can be up to 2.5 V or more. There is a great deal of current interest in the development of ZCRFB^[9–12]. Mixed-acid ($\text{CH}_3\text{SO}_3\text{H}$ and H_2SO_4) as the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple supporting media has the advantages such as larger solubility of cerium salt, and faster kinetics of electrode process^[13]; so energy density of the cell using mixed-acid electrolyte is expected to be higher. Leung et al. reported the performance of the zinc negative electrode as a function of Zn^{2+} ion concentration, methanesulfonic acid concentration, current density, electrolyte flow rate, operating temperature and the addition of electrolytic additives (potassium sodium tartrate, tetrabutylammonium hydroxide, and indium oxide)^[14]. An undivided zinc-cerium hybrid redox flow battery proposed by Leung et al. has high discharge cell voltage of *c.a.* 2.1 V at 20 mA/cm² and an

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* Corresponding author: XIE Zhipeng (E-mail: zhpxie_06@126.com; Tel.: +86-797-8312204)

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average energy efficiency of 75%^[15]. Eight two- and three-dimensional electrodes (platinised titanium, graphite, carbon polyvinylester, 30 ppi reticulated vitreous carbon, 100 ppi reticulated vitreous carbon, Alfa Aesar carbon felt, Sigratherm carbon felt, 4 platinised titanium mesh) were tested as positive electrode in ZCRFB under both constant current density and constant cell voltage discharge^[16]. Also, a number of investigations related to the application of cerium in other areas were easily found in literatures^[17,18].

Currently, the most widely used electrode in redox flow batteries is carbonaceous material such as carbon felt. Three-dimensional electrodes with larger surface area generally exhibit superior performance over the two-dimensional electrodes. In this work, hierarchical porous carbon electrode (HPCE) was designed and prepared with the aim of larger surface area and faster ion diffusion by a method in which hard- and soft-templates are used. Macropore is beneficial to the diffusion of ions within the electrode, while mesopore is beneficial to the increase of the surface area of electrode. Performance of ZCRFB using hierarchical porous carbon (HPC) as positive electrode was tested under constant current density. The results showed that HPC is superior over the carbon felt for use in advanced ZCRFB.

1 Methods

1.1 Chemicals and materials

Hierarchical porous carbon was prepared using the following method: briefly, 2.5 g phloroglucinol and 2.5 g polyethylene-oxide-b-polypropyleneoxide-b-polyethyleneoxide (Pluronic F127 EO₁₀₆PO₇₀EO₁₀₆) were dissolved in 18.0 g of a mixture of ethanol and water (5:4 in weight), then 0.2 g 37% HCl was added and the solution was stirred for 1 h. 2.6 g of 37% formaldehyde solution was then added to the mixture in one batch and stirred for 2 h. Then 1 mL of 25% NH₃, 0.5 g Ni(CH₃COO)₂, and 12 mL DMF (N, N-dimethylformamide) were added to the mixture and stirred for half an hour. The mixture was thermally treated at 80 °C for 2 h; then cured at 80 °C for 12 h. The cured mixture was carbonized under Ar in a tubular furnace via heating ramps of 1 °C/min from 50 to 400 °C and 5 °C/min from 400 to 850 °C and kept at 850 °C for 4 h. Then it was followed by an acid treatment (100 mL of 2 mol/L HCl) for three times in order to remove the Ni metal. After that it underwent thermal treatment at 450 °C for 6 h under air condition.

1.2 Materials characterization

Transmission electron microscopy (TEM) images were taken on a FEI Tacnai G2 electron microscope operated at 200 kV. The scanning electron microscopy (SEM) was performed using a field emission scanning

electron microscope (FE-SEM, HITACHI S-4800). The X-ray photoelectron spectroscopy (XPS) was collected using focused monochromatized Al K α radiation (1486.6 eV) (QUANTUM 2000, Physical Electronics, USA).

1.3 Electrochemical tests

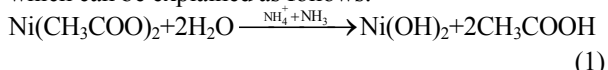
The cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA) tests of Ce³⁺/Ce⁴⁺ redox couple were carried out using a three-electrode cell which was controlled with a CHI660 workstation (CH Instruments, USA). A Pt mesh and SCE electrode were used as the counter and reference electrodes, respectively.

The cell performance was measured under a constant current using a self-designed flow cell that was connected with an eight-channel BTS-5V3A battery test system (Neware Ltd., China). Details of the flow cell setup were described in a previous paper^[12]. The composition of the electrolytes after cycling was determined by inductively coupled plasma/atomic emission spectrometry (ICP/AES, IRIS Intrepid II XSP, Thermo Electron Corporation) techniques after appropriate dilution.

2 Results and discussion

2.1 Morphology and structure

Porous carbon materials are used extensively as electrode materials for batteries^[19] due to their superior physical and chemical properties (electric conductivity, thermal conductivity, chemical stability, and low density) and wide availability. Porous carbon materials can be classified in accordance with their pore diameters as microporous (less than 2 nm), mesoporous (between 2 and 50 nm), and macroporous (more than 50 nm). Despite the wide applications of microporous materials, they suffer some limitations such as slow mass transport of ionics (because of small pore sizes), low conductivity, and collapse of porous structures (during high-temperature treatments). In this work, hierarchical porous carbon (with well-defined macroporous and mesoporous structures) was prepared by a method in which hard template was used along with soft template. As shown in Fig. 1(a) and (b), the macroporous structure (primarily including two kinds of pore sizes: 2 μ m and 80 nm) in the HPC was obtained using the hard-template synthesis method, which can be explained as follows:



In the construction of macroporous structure within HPC, Ni(OH)₂ is presynthesized as the hard template. At the same time, as shown in Fig. 1(c), the mesoporous

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