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A porous ceramic membrane tailored high-temperature supercapacitor

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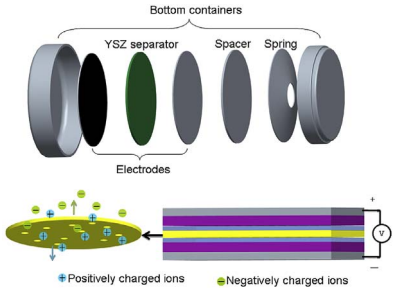
HIGHLIGHTS

- HTSCs tailored with porous ceramic separator are fabricated by YSZ and NiO.
- The HTSC with NiO/YSZ membrane has a high specific capacitance of 272 F g^{-1} at 90 °C.
- The resultant HTSC displays remarkable long-term stability over 1000 cycles at 90 °C.
- The NiO/YSZ membrane tailored HTSCs are promising in advanced energy storage devices.

GRAPHICAL ABSTRACT



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ABSTRACT

The supercapacitor that can operate at high-temperature are promising for markedly increase in capacitance because of accelerated charge movement. However, the state-of-the-art polymer-based membranes will decompose at high temperature. Inspired by solid oxide fuel cells, we present here the experimental realization of high-temperature supercapacitors (HTSCs) tailored with porous ceramic separator fabricated by yttria-stabilized zirconia (YSZ) and nickel oxide (NiO). Using activated carbon electrode and supporting electrolyte from potassium hydroxide (KOH) aqueous solution, a category of symmetrical HTSCs are built in comparison with a conventional polymer membrane based device. The dependence of capacitance performance on temperature is carefully studied, yielding a maximized specific capacitance of 272 F g^{-1} at 90 °C for the optimized HTSC tailored by NiO/YSZ membrane. Moreover, the resultant HTSC has relatively high durability when suffer repeated measurement over 1000 cycles at 90 °C, while the polymer membrane based supercapacitor shows significant reduction in capacitance at 60 °C. The high capacitance along with durability demonstrates NiO/YSZ membrane tailored HTSCs are promising in future advanced energy storage devices.

1. Introduction

Renewable energies accompanied with high-performance supercapacitors are considered as a promising solution to energy crisis and environmental pollution [1–7]. Supercapacitor, which is also called ultracapacitor or electric double-layer capacitor, is a high-capacity energy storage device bridging dielectric capacitor and the battery or fuel cell [8,9]. In recent years, supercapacitors have attracted growing attention due to their high power density, long cycle life, fast charge-discharge and zero emissions. And therefore supercapacitors are promising in hybrid electric vehicles, electrical communication equipment, consumer electronics and industries *etc* [10,11]. According to charge storage principle, supercapacitors are divided into two categories: (i) The electric double-layer capacitors using charge separation at electrode/electrolyte interface for energy storage; (ii) The pseudo-capacitors in which energy is reserved by fast and reversible redox reactions [12–14]. A classic supercapacitor is a sandwiched structure comprising of a permeable non-conductive separator between two current

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collectors to prevent direct contact and electron transfer between two electrodes [15]. Electrolyte in liquid, quasi-solid or full solid state is always filled in the space for charge diffusion.

In the last decades, the study on supercapacitors is focusing on increasing power storage capacity by persistent material and technology innovations at room temperature [16–18]. However, the application-specific requirements for advanced supercapacitors include high-temperature, rapid charge transportation and long-term stability for oil drilling, military and space utilizations [19]. One of the main problems to limit the high-temperature supercapacitors (HTSCs) is the use of state-of-the-art polymer-based separators such as polypropylene (PP) [20], polyethylene (PE) [21], polyoxyethylene (PEO) [22] and polyacrylonitrile (PAN) [23]. In general, the commonly used polymer-based separators always have shrinkage and deformation behaviors at temperatures higher than 80 °C, therefore leading to limited electrolyte diffusion and device structure damage. A solution to this impasse is to create a nano/microporous membrane [24,25] that has excellent chemical and electrochemical stabilities in the electrolyte and good thermal stability at elevated temperatures. Inspired by high-temperature solid-state fuel cells [26–29], in which thermally stable cermet anodes are always applied for high-temperature operation, it may also be applicable as separators in HTSCs highlighted by their high porosity, negligible electronic conductivity as well as especially good thermal and chemical stability.

In the current work, we present here the experimental realization of HTSCs tailored with porous NiO/YSZ ceramic separators made by yttria-stabilized zirconia (YSZ) and nickel oxide (NiO). It is known that ceramic membranes are electrically insulating and relatively stable in both chemical and thermal aspects even at hundreds of degrees. By combing two identical carbonaceous electrodes and potassium hydroxide (KOH) aqueous electrolyte, a coin-structured HTSC can be successfully made. Moreover, a traditional supercapacitor from polymer membrane is also fabricated as a reference. The focuses of current work are placed on comparison of specific capacitance and cyclic stability of NiO/YSZ membrane and polymer membrane tailored supercapacitors. By tuning operation temperatures from 20 to 90 °C, the electrochemical performances are detailedly studied to highlight the significances of HTSCs.

2. Experimental section

2.1. Preparation of NiO/YSZ ceramic membranes

NiO and YSZ were utilized as raw materials and graphite powders were pore-forming agents for ceramic membranes. In details, 4 g of NiO, 4 g of YSZ powders, 0.8 g of graphite powders and 5 mL of 6% polyvinyl butyral (PVB) ethanol solution were thoroughly grinded in an agate mortar to form a homogeneous colloid. And being dried by an infrared lamp, a 13 mm-diameter mould was applied to make disks under a pressure of 20 MPa. Finally, the round ceramic disks were air-sintered at 1200 °C for 2 h in a muffle furnace. The average diameter, thickness and weight of ceramic membranes were 12.3 mm, 0.30 mm and 0.2 g, respectively.

2.2. Fabrication of HTSCs

Each HTSC device was built by sandwiching a NiO/YSZ separator between two identical electrodes and filling with electrolyte. In details, activated carbon, carbon black and polytetrafluoroethylene (PTFE) in a mass ratio of 8: 1: 1 were thoroughly blended, and 6 mL of ethyl alcohol was added to make a mixture paste, which was incorporated into nickel foams to fabricate an electrode. After being pressed and dried, the active material mass of each electrode was 1.6 mg. Finally, two identical electrodes and a NiO/YSZ membrane were both soaked in 6 M KOH aqueous electrolyte for 1 h to fabricate a button HTSC device. Notably, a stainless steel spacer (CR 2032/CR2016-304, Φ15.5 mm × 0.5 mm), a spring (CR2032) and two bottom containers (CR2032) were also required for final device, as shown in Fig. 2a. The traditional supercapacitor with PE membrane was also build using the same method.

2.3. Electrochemical measurements

All the electrochemical measurements were performed on the button HTSCs at temperatures ranging from 20 to 90 °C using a CHI660E electrochemical workstation. Cyclic voltammetry (CV) curves were scanned in a potential range of 0–1 V at a scan rate of 10 mV s^{-1}, galvanostatic charge-discharge (GCD) was measured in the voltage window of 0–1 V at a current density of 1 A g^{-1}. The electrochemical impedance spectra (EIS) were recorded at 0 V in a frequency range from 1×10^5 to 0.01 Hz and at an ac amplitude of 5 mV. All the electrochemical parameters were obtained by fitting EIS spectra with the Zview modeling software. The specific capacitance of the button supercapacitor was calculated from the GCD curves according to following formula:

$$C = \frac{2i_m \int V dt}{V^2 |_{Vi}^{Vf}}$$

where C (F g^{-1}) represented the GCD specific capacitance, $i_m = I/m$ (A g^{-1}) was current density, I was current and m was active mass of an electrode, Vdt was the integral current area, V referred to the potential values at initial (V_i) or final state (V_f).

2.4. Other characterizations

The morphology of the NiO/YSZ membrane was observed by a SU8020 mode scanning electron microscope (SEM), while the crystalline structure of this NiO/YSZ membrane was conducted by an X-ray diffraction (XRD) pattern on an X-ray powder diffractometer (X'pert MPD Pro, Philips, Netherlands). The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of the NiO/YSZ membrane were performed in air atmosphere at a heating rate of 10 °C min^{-1}. The contact angels of two separators were tested on a contact angel tester (JC2000D3) by dipping 6 M KOH aqueous solution. The porosities were calculated using the following equation:

$$Porosity\ (\%) = \frac{W_f - W_i}{\rho V_i} \times 100\%$$

where W_i (g) and W_f (g) referred to the masses of membranes before and after immersion in n-butanol, respectively. ρ (g cm^{-3}) was the density of n-butanol, and V_i (cm^3) was the volume of separator.

3. Results and discussion

The microstructure of the as-obtained NiO/YSZ membrane with a glossy surface is shown in Fig. 1a. At first glance, the NiO/YSZ membrane surface is smooth without any aggregations or phase separations. The high-resolution SEM photograph in Fig. 1b indicates that the NiO/YSZ particles having average size of 50 nm are uniformly interconnected, producing a highly porous topology and mechanical strength. These porous channels provide sufficient pathways for liquid electrolyte diffusion through the separator. No attempt was made to optimize the pore size distribution and percentage by controlling graphite dosages. As a reference, the traditional polymer-based membrane has roughly granular surface with randomly distributed particle aggregations, as shown in Fig. 1c. The random micropores and incompact microparticles in Fig. 1d can block the channels for charge diffusion across the separator.

The NiO/YSZ tailored HTSC device has a typical sandwiched structure, as shown in Fig. 2a, in which a NiO/YSZ separator is sandwiched between two identical electrodes. A stainless steel spacer and a spring are also successively applied on an electrode, and two bottom