

A novel nickel-based mixed rare-earth oxide/activated carbon supercapacitor using room temperature ionic liquid electrolyte

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Abstract

Mesopore nickel-based mixed rare-earth oxide (NMRO) and activated carbon (AC) with rich oxygen-contained groups were prepared as electrode materials in a supercapacitor using room temperature ionic liquid (RTIL) electrolyte. These electrode materials were characterized by XPS, XRD, N₂ adsorption, SEM as well as various electrochemical techniques, and showed good properties and operated well with RTIL electrolyte. A 3 V asymmetrical supercapacitor was fabricated, which delivered a real power density of 458 W kg⁻¹ as well as a real energy density of 50 Wh kg⁻¹, and during a 500-cycle galvanostatic charge/discharge measurement, no capacity decay was visible. Such promising energy-storage performance was to a large extent ascribed to nonvolatile RTIL electrolyte with wide electrochemical windows and high stable abilities worked with both electrode materials.

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1. Introduction

There is a growing demand for more efficient and cleaner ways of producing energy and delivering power. Viable alternatives include battery and fuel cells, which readily provide large amounts of energy for proposed automotive, portable and power utility applications. The major disadvantage of these systems is low power capability caused by thermodynamic or electrode polarization problems. Supercapacitors solve the power issue when placed in parallel. Two basic types of supercapacitors can be realized using different charge-storage mechanisms [1,2]: (i) electrical double-layer capacitors (EDLCs), mainly focusing on carbon materials [3–6], which utilize the capacitance arising from charge separation at an electrode/electrolyte interface, and (ii) redox supercapacitors, materials, such as ruthenium oxide [7–9],

iridium composite oxide [10,11], cobalt oxide [12], nickel oxide [13], manganese oxide [14,15], vanadium oxide [16], which utilize the charge-transfer pseudocapacitance arising from reversible faradic reactions occurring at the electrode surface.

Asymmetrical supercapacitor can be fabricated with one electrode being of a double-layer carbon material and the other electrode being of a pseudocapacitance material. The energy density of asymmetrical supercapacitor can be significantly higher than that of EDLCs. Most supercapacitors used aqueous solution electrolytes for good conductivity. However, an obvious demerit for these devices was their inherently narrow electrochemical window (less than 1.23 V), which largely restricted both power and energy capability of these supercapacitors.

Room temperature ionic liquids are either organic salts or mixtures of salts that are fluid at room or near-room temperature. Due to their ionic nature, ionic liquids are highly polar, and they influence a course of ionic reactions [17,18].

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Because of zero vapor pressure, wide electrochemical window (commonly larger than 3.0 V), good electrolytic conductivity (10^{-1} to 10^{-2} S m $^{-1}$), high ionic mobility, they may serve as promising electrolytes for electrochemical processes [19–21].

In this work, an innovative asymmetrical supercapacitor composed of NMRO cathode and AC anode using solvent-free 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF $_6$) RTIL electrolyte was fabricated. The aim of replacement of aqueous phase electrolyte with RTIL was to achieve higher both power and energy capability. BMIM-PF $_6$ itself is not soluble to water and here plays a dual role, i.e. non-aqueous solvent and conductive ions. Nickel-based rare-earth alloys [22,23], such as LaNi $_5$ and MmNi $_5$, are commonly used as good hydrogen storage alternatives for their reversible adsorptive–desorptive properties under the electrical induction, and their oxides [24] are promising oxygen-storage materials originated from the special adsorptive–desorptive framework structures, which was thus considered as a feasible active material for the cathode of a supercapacitor. Meanwhile the KOH-treated activated carbon with high specific surface areas and special surface functional groups could be a suitable anodic material. The two electrodes coupled with nonvolatile BMIM-PF $_6$ RTIL electrolyte were expected to constitute a promising 3 V electrochemical energy-storage device.

2. Experimental

2.1. Chemicals and materials

1-Butyl-3-methylimidazolium hexafluorophosphate ($\geq 98\%$, solvent innovation) was further purified before use. The purchased BMIM-PF $_6$ was fully washed with double-deionized water under vigorous agitation. After repeated wash the separated lower-layer organic phase became pale-yellow, while the pH of the settled upper-layer aqueous phase was ca. 7. The organic phase was then decanted and dried by vacuum evaporation at 80 °C for 36 h. The treated dried BMIM-PF $_6$ was in airtight store for later use.

Activated carbon powders (Darco[®] KB-B, $< 2 \mu\text{m}$) from Aldrich were soaked into 9 mol L $^{-1}$ potassium hydroxide solutions for 24 h, and then dried at 120 °C for 6 h. The partly dried powders were transferred into a furnace and heat-treated at 600 °C for 4 h under nitrogen atmosphere. After that, the powders were repeatedly washed with deionized water until the pH of the solutions was ca. 7. The completely dried KOH-treated AC powders were used as active materials.

Nickel-based mischmetal (Mm: La 35%, Ce 55%, Pr 5%, Nd 5%) alloys (NMA) prepared in nitrogen atmosphere by high-energy mechanical milling [25] with the atom ratio of Ni:Mm = 5:1 were chosen as starting materials for fabricating active NMRO powders. The silvery-gray alloy powders were fully oxidized in a furnace at 600 °C in air for 10 h. The

annealed deep-black NMRO powders were sieved through 400-mesh and used as active materials.

2.2. Assembly of supercapacitors

The electrodes were prepared by mixing the active materials with conducting graphite, acetylene black and BMIM-PF $_6$ RTIL in a mortar at the ratio of 70:10:10:10 for the active NMRO electrode and 85:5:0:10 for the AC electrode. The mixtures were then rolled out on foam nickels, pressed at 2 MPa cm $^{-2}$ to form slices with the thickness of 0.05–0.1 mm for the active NMRO electrode and 0.1–0.3 mm for the AC electrode, respectively. The prepared electrodes were tightly laminated on stainless steel (SS) plate collectors and separated by a polypropylene separator fully wetted with BMIM-PF $_6$ RTIL electrolyte. This Sandwich-type structure inserted between two pieces of PTFE boards was compactly assembled by inward forces from a SS clamp.

2.3. Characterizations and measurements

The surface composition and structure of the KOH-treated AC was examined by X-ray photoelectron spectroscopy (XPS) with an ESCA LAB MK II spectrometer (VG Scientific, UK) employing a monochromatic Mg K α X-ray source (1253.6 eV) under a vacuum pressure $< 10^{-6}$ Pa at room temperature. The data were calibrated using the C 1s peak (284.6 eV).

The crystallographic structure of the NMRO powders was investigated by X-ray diffraction (XRD), recorded on RIGAKU D/max-IIB X-ray Diffractometer using Cu K α radiation (0.15406 nm) of 40 kV and 20 mA.

The specific surface areas and pore volumes of the KOH-treated AC and NMRO powders were determined by N $_2$ gas adsorption at 77 K on a Quantachrome NOVA 1000 (Version 6.11) system. The Barrett–Joyner–Halenda (BJH) average pore diameter was calculated by using a NOVA Enhanced Data Reduction Software (Version 2.13).

The surface morphology of active substances at the electrodes was observed through scanning electron microscopy (SEM) performed on a JEOL-JSM5310 at an accelerating voltage of 20 kV.

A three-electrode system was adopted to investigate well-prepared single-electrode. A large area of Ni gauze and a Ag/Ag $^+$ (10 mM AgNO $_3$ in CH $_3$ CN) pair were used as counter electrode and reference electrode, respectively. The cyclic voltammetric measurements were carried out with a CHI 630 electrochemical work-station (CH Instruments, USA). The typical scan rates were chosen as 100 and 10 mV s $^{-1}$ to present distinctive electrochemical reaction characteristics. The electrochemical impedance measurements were conducted with a Solartron 1255B frequency response analyzer (FRA) in conjunction with a Solartron Electrochemical Interface under Zplot program (Scribner Associates Inc.). The perturbation amplitude used was 10 mV, and the frequency range was from 10 5 to 10 $^{-2}$ Hz under open

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