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A hybrid sodium-ion capacitor with polyimide as anode and polyimide-derived carbon as cathode

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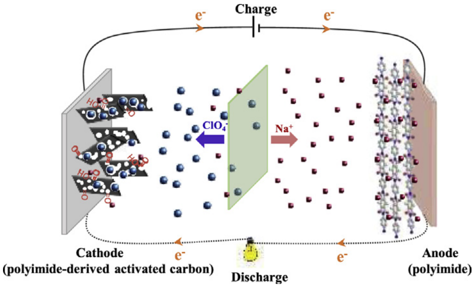
HIGHLIGHTS

- Both of anode and cathode came from the single polymer.
- Polyimide and polyimide-derived carbon were respectively used as anode and cathode.
- Battery-type anode and capacitor-type cathode made hybrid sodium-ion capacitor.
- Pore texture of polyimide-derived carbon with high surface area was adjusted.

GRAPHICAL ABSTRACT

A scheme showing the configuration of a hybrid sodium-ion capacitor.



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ABSTRACT

In this work, pyromellitic dianhydride-based polyimide was hydrothermally synthesised and further thermally treated to prepare porous carbon materials. The porous structure of the polyimide-derived carbon can be controlled by varying the reactant concentrations during the hydrothermal reaction and KOH activation to achieve a highly accessible specific surface area of 1302 $m^2 g^{-1}$. A hybrid sodium-ion capacitor fabricated with the polyimide as anode and the polyimide-derived carbon as cathode can be operated at a voltage of 4.2 V, delivering an energy density of 66 Wh kg^{-1} at power density of 196 W kg^{-1}, and an energy density of 13.3 Wh kg^{-1} at power density of 1200 W kg^{-1}.

1. Introduction

Sodium-ion storage systems including sodium-ion batteries (NIBs) and sodium-ion capacitors (NICs) are regarded as promising alternatives to lithium-ion storage systems, due to the high abundance and low cost of sodium resources (the cost of Na_2CO_3 is only 3% of that of Li_2CO_3), as well as the similar electrochemical properties to lithium (sodium is only 0.3 V more positive than lithium) [1–14]. Sodium-ion based batteries provide a high energy density but suffer from sluggish charge and discharge responses [15]. NICs are sodium-ion based hybrid ion capacitors consisting of a battery-type negative electrode (anode) and a capacitor-type positive electrode (cathode) [16]. Such a system works via two charge storage mechanisms: (i) for the anode, charge is stored by insertion/extraction of the cations, which can produce high energy density but sluggish kinetics; (ii) for the cathode, charge is stored by fast reversible adsorption/desorption of the anions, which can enhance the rate capability to offer higher power density.

One of the major challenges for sodium-ion storage systems is the lack of a suitable anode material [17–22]. The most commonly used anode in lithium-ion batteries (LIBs), graphite, is thermodynamically unfavourable for NIBs [23]. Many transition-metal oxides have been studied as anode materials for NIBs [24–28]. The insertion of sodium

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ions into these materials can cause multi-step phase transitions, leading to a low utilisation of capacity and/or a sluggish kinetics [29].

In recent years, organic materials have received increasing research attention because of their facile processability, compositional diversity and flexibility [30,31]. Such materials can be obtained from natural products and biomasses with minimum energy consumption by appropriate design and treatment, which may further lower the cost of devices [32–34]. Polyimides have high mechanical strength, excellent thermal stability and high density of electroactive functional groups [35,36], are cheap and easy to be scaled up in production [37], and hence are of particular importance to rechargeable batteries. Aromatic polyimides, containing a dianhydride core as the aromatic backbone, have been used as cathodes for NIBs [38–42]. Recently, it was found that when altering the aromatic core from perylene 3,4,9,10-tetracarboxylic dianhydride (PTCDA) to 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and further to pyromellitic dianhydride (PMDA), the average discharge voltage became progressively lowered [33]. And the average discharge voltage of the PMDA-based polyimides was about 1.73 V, suggesting its suitability as an anode for NIBs [23].

Polyimides have been used as a precursor to prepare porous carbon materials [43–45], which can be used as a capacitor-type cathode for NICs due to their excellent electrical conductivity, high surface area, good thermal and chemical stability, as well as low cost. In this study, a hybrid NIC was realized for the first time by employing a PMDA-based polyimide as the anode and a polyimide-derived porous carbon as the cathode. The NIC cell delivered a high energy density without significantly sacrificing power density.

2. Experimental section

2.1. Synthesis of polyimides

According to our previous work [46], 2.5 mmol *p*-phenylenediamine (PPD) was dissolved in 30.0 mL *N*,*N*-dimethylformamide (DMF) followed by addition of equimolar PMDA. Then, the mixture was transferred into a Teflon-lined autoclave and heated at 210 °C for 10 h in an oven. The precipitates were centrifuged, washed with DMF and ethanol, and dried under vacuum at 80 °C. The obtained polyimide samples are designated as PI-1.25, PI-2.5 and PI-5, where 1.25, 2.5 and 5 indicate the concentrations of PPD and PMDA added to the synthesis system in millimoles per litre.

2.2. Synthesis of polyimide-derived carbons

PI-1.25, PI-2.5 and PI-5 were further thermally treated at 650 °C for 3 h under N_2 to obtain carbon samples, designated as C(PI-1.25), C(PI-2.5) and C(PI-5). To further develop pores, KOH activation was used to activate the polyimide-derived carbons. Typically, 1 g C(PI-1.25), C(PI-2.5) or C(PI-5) was impregnated in a mixture of 40 mL of 0.1 g mL^{-1} KOH solution and 4 mL of 25% ethanol aqueous solution. After stirring for 1 h, the mixture was dried at 60 °C overnight to evaporate the solvent and heated at 650 °C for 1 h under N_2 at a heating rate of 5 °C min^{-1}. The activated carbons were then immersed in 1 mol L^{-1} HCl to remove the residue KOH and washed with distilled water until neutral pH. Samples thus obtained are designated as AC(PI-1.25), AC(PI-2.5) and AC(PI-5).

2.3. Characterization

Thermogravimetry (TG) analysis was conducted on a thermal analyser (DTG-60A, Shimadzu) under nitrogen at a heating rate of 5 °C min^{-1}. Field emission scanning electron microscope (FESEM) (JSM-7001 F, JEOL) was used to characterise the morphology of the samples. Transmission electron microscopy (TEM) images were recorded on a transmission electron microscope (JEM2100, JEOL). X-ray diffraction (XRD) measurements were collected on an X-ray diffractometer (Bruker D8 Advance, Bruker) with Cu Kα radiation (λ = 1.54056 Å). Raman spectra were performed using a Raman spectrometer (Renishaw) with a 514 nm laser. Argon adsorption-desorption measurements were carried out on a TriStar II 3020 (Micromeritics) at 87.3 K. The specific surface area (S_{BET}) and pore size distribution were analysed by using the Brunauer-Emmett-Teller (BET) and non-local density functional theory (NL-DFT) methods, respectively. The total pore volume (V_t) was estimated at a relative pressure of 0.99. The micropore volume (V_{mic}) was obtained from the t-plot method. The mesopore volume (V_{meso}) was calculated from the difference between V_t and V_{mic}. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos Axis Ultra photoelectron spectrometer.

2.4. Electrochemical measurements

For the preparation of polyimide electrodes, polyimide, carbon black and poly (vinylidene difluoride) (PVDF) at a mass ratio of 6:3:1 were dispersed in *N*-methyl pyrrolidone (NMP) to form a slurry, which was cast onto a copper foil current collector using a doctor blade. The electrode was dried at 60 °C under vacuum overnight. For the fabrication of polyimide-derived porous carbon electrodes, the same procedure was used except the mass ratio of porous carbon:carbon black:PVDF = 8:1:1 and the current collector was aluminium foil.

Half cells were assembled in an Ar-filled glovebox using the polyimide or polyimide-derived porous carbon as the working electrode, pure sodium foil as the counter electrode, glass fibre as the separator and 1 mol L^{-1} $NaClO_4$ in equal volumes of ethylene carbonate (EC) and propylene carbonate (PC) mixed with 0.3 wt % fluoroethylene carbonate (FEC) as the electrolyte. NIC cells were fabricated using the polyimide electrode as anode and polyimide-derived porous carbon electrode as cathode with the same separator and electrolyte.

Galvanostatic discharge and charge (GCD) cycling of the half cells and NICs were conducted on a battery tester (CT3008, Neware) and a potentiostat/galvanostat (PGSTAT302 N, Metrohm Autolab) at room temperature. Cyclic voltammetry (CV) was performed on an electrochemical workstation (CHI 660D, Chen Hua Instrument). The calculations for the NICs were based on the total mass of active materials in both anodes and cathodes. The energy and power densities were calculated according to the following equations:

$$E = P \times t \tag{1}$$

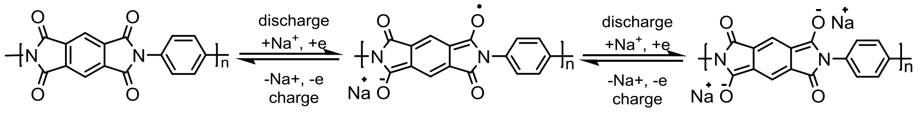
$$P = \frac{E}{t} = \Delta V \times \frac{I}{m} = (V_{max} - V_{min}) \times \frac{I}{m} \tag{2}$$

where t is the discharge time, I is the discharge current, m is the total mass of active materials in both electrodes, and V_{max} and V_{min} are the voltage at the beginning and end of discharge, respectively.

3. Results and discussion

3.1. Polyimide as anode material

PI-2.5 delivering a reversible discharge capacity of 125 mAh g^{-1} was employed as the anode material for the hybrid sodium-ion capacitor, the redox mechanism (Scheme 1) of which can be illustrated as a



Scheme 1. Discharge and charge mechanism for the polyimide electrode in half cell.