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Novel hyper-crosslinked polymer anode for lithium-ion batteries with highly reversible capacity and long cycling stability

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ABSTRACT

Organic materials with high natural abundance, low price as well as environmental friendliness have been considered as proper alternatives to replace inorganic electrodes. However, it is still challengeable for exploiting novel organic materials incorporating highly stable framework in electrolyte, optimized nanostructure and large lithium storage capacity. In the present work, hyper-crosslinked polystyrene (HPS) nanospheres are fabricated by combination of emulsion polymerization and subsequent Friedel-Crafts reaction. The obtained HPS has abundant oxygen-containing functional groups for reversible lithium ions storage reactions, uniform spherical morphology along with well-developed porous structure to minimize transfer distance of lithium ions, rigid macromolecular frameworks to resist the dissolution of electrolyte. Therefore, HPS presents promising potential as electrode in lithium ion battery. The initial discharge and charge capacities of HPS can reach 533 and 262 mAh g^{-1}, respectively, and a stable capacity of 356 mAh g^{-1} is delivered after repeated charge-discharge for 100 times at 0.2 A g^{-1}. Even cycled for 1000 times at 2 A g^{-1}, the capacity remains 222 mAh g^{-1}.

1. Introduction

As one of the most outstanding representives of secondary energy storage devices, lithium ion batteries have found critical and irreplaceable application in portable electronics, mobile communications and hybrid electric vehicles, due to their high output voltage, superior energy and power density and good long-term cycling stability. [1–8]. In the past decades, inorganic electrodes with high specific Li storage capacities are dominated in scientific research and practical exploration. [9–16]. Nevertheless, the further application of metal-based inorganic electrodes is hampered by environment and resource concerned issues. [17–20].

As a proper alternative to inorganic electrodes, organic materials with high natural abundance, low price as well as environmental friendliness have stimulated lots of research enthusiasm. [21–23]. Normally, organic compounds storage energy by reversible lithiation/delithiation reactions between Li^+ and heteroatom-containing functional groups of carbonyl [24,25], carboxyl [26], amino group [27,28], imide [29–31] *etc*. For example, it has been extensively proved that Li^+ can react with carbon oxygen double bond via addition reaction, and carbonyl has long been considered as one of the most potential organic functional groups. [24,32,33]. Accordingly, a serial of carbonyl-based organic materials were fabricated and presented attractive electrochemical energy storage performance. [34,35]. Similarly, other oxygen-containing chemicals, such as conjugated dicarboxylate anodes and polymethyl methacrylate (PMMA, involves ester groups −COO−), also have been developed as electrode materials in lithium ion batteries. [22,26,36]. These organic materials show completely different redox potential with carbonyl compounds, and reveal specific application merits. Except above-mentioned oxygen-containing compounds, many other organic materials, including phenazines (−C═N) [27], aromatic diimide dilithium carboxylates [30], nitrogen-rich graphene-like holey conjugated polymers (−C═N, $-NH_2$ and −C═O) [35] and so on, also have been exploited as high-performance organic electrodes. Very recently, with the aim of further improving the lithium storage behavior, carbon materials were utilized as substrate of redox organic compounds based composites to endow organic materials with flexible macroscopic morphology, stable microscopic framework, and enhanced electrical conductivity. [37,38].

Despite distinct improvements have been achieved, until now, the organic electrodes suffer from some inevitable drawbacks. First

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of all, in most cases, organic electrodes show low structural stability in electrolyte, leading to a fast capacity loss with increasing the cycling numbers. Long π-conjugated and polymeric organic frameworks have been proposed to be good solutions to resist the erosion of electrolyte, but the effects are still limited. [19,25,39]. Second, current organic electrodes prepared through single chemical reactions without nanoengineering are usually lack of nanostructure to optimize the ion diffusion and storage, which might be the significant reason that causes inferior electrochemical reaction efficiency along with low capacity. Therefore, it is still urgent for exploiting novel organic materials incorporating highly stable framework in electrolyte, optimized nanostructure and large lithium storage capacity.

Hyper-crosslinked polymers (HCPs) are novel porous materials with high surface area, low bulk density and abundant surface functional groups. [40–44]. More importantly, HCPs have extremely high molecular structural rigidity, and can tolerate the attack of various organic solvents and high-temperature heat-treatment. In some cases, HCPs even can keep nanostructure during tough carbonization process (>800 °C). [45–48]. Owing to so many structural features, in recent years, a large amount of HCPs have been synthesized, including solid/hollow nanospheres [47,49,50], three-dimensional nanonetworks [51], nanofibers [46,52] and ordered arrays [53]. Also, in very recent years, a few publications have reported the exploitation of HCPs as electrode in energy concerned applications, such as lithium ion battery [54,55], Li-S battery [56] and supercapacitor [57]. Without doubt, HCPs have huge potential as the organic electrode in lithium ion batteries: the functional groups supply active sites for redox lithium storage reactions, controllable nanomorphology and pore structure increases accessible surface area of electrode, and the rigid and powerful molecular skeleton gives HCPs superior cycling stability.

Based on above consideration, in the present paper, hyper-crosslinked polystyrene (HPS) nanospheres with rigid molecular framework, well-defined micropores as well as anchored −C═O/−COOH are developed as anode in lithium ion battery. First, HPS has regular nanospherical morphology with well-developed micropores, which can increase accessible surface area of electrode and shorten transfer distance of Li^+. Second, the reversible redox reactions between the functional groups of −C═O/−COOH and Li^+ endow HPS with high capacity of 533 mAh g^{-1}. Moreover, hyper-crosslinked molecular framework gives the HPS high structural stability to resist the dissolution of electrolyte, accompanying with remarkable cycling capability. After 100 cycles at 200 mA g^{-1}, a stable capacity of 356 mAh g^{-1} can be reached, and even after a long-term cycle for 1000 times at 2 A g^{-1}, the capacity remains 222 mAh g^{-1}.

2. Experimental

2.1. Materials preparation

HPS was fabricated by combining emulsion polymerization and Friedel-Crafts hyper-crosslinking according to a previously reported method [49]. First, emulsion polymerization was employed to synthesize divinylbenzene (DVB) pre-crosslinked polystyrene nanospheres (PPS). In a typical process, 10 mL styrene, 1.2 mL DVB, 80 mg sodium dodecyl sulfate (SDS) and 400 mL H_2O were added in a four-neck flask under room temperature with a mechanical stirring of 250 rpm. After removing the air by Ar for 30 min, 0.4 g initiator potassium peroxydisulfate (KPS) was added quickly. Subsequently, the temperature was raised to 75 °C and the polymerization reaction started. Three hours later, another 1.2 mL DVB was added and the reaction was kept for 24 h. After centrifugation, washing with deionized water for three times and drying at 70 °C, PPS was collected.

Then, Friedel-Crafts hyper-crosslinking was carried out to prepare HPS nanospheres. First, 1 g PPS nanospheres were swelled in 100 mL CCl_4 at 70 °C for 12 h under mild magnetic stirring. Then, 2 g anhydrous $AlCl_3$ was added in above dispersion to start the crosslinking reaction. The reaction was stopped after 8 h by pouring the reactants into cold ethanol-water solution (ethanol/water = 80 mL/20 mL). After filtering off, washing with ethanol and water for several times, followed by drying at 70 °C for 8 h, the HPS nanospheres were obtained.

2.2. Structural characterization

A Hitachi SU8010 scanning electron microscope (SEM) and a JEM-2100F transmission electron microscope (TEM) were used to characterize the morphologies of the as-obtained samples. The Nicolet 380 FTIR spectroscopy was adopted to record the fourier transform infrared (FTIR) spectra. The thermal decomposition behavior was measured by using a TA SDT 2960 thermogravimetric analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out with an Thermo Scientific ESCALAB250Xi instrument. Surface area and pore size distribution were investigated in a Micromeritics ASAP 2460 surface area and porosity analyzer, and BET surface area (S_{BET}) and pore size distribution were analyzed by Brunauer-Emmett-Teller (BET) theory and no-local density functional theory (NLDFT) respectively.

2.3. Electrochemical measurements

The lithium ion storage performances of obtained samples were measured using 2032-type coin cells assembled in an argon-filled glove box (H_2O, $O_2 < 1$ ppm). The working electrode was prepared by mixing active material, conducted carbon black and polyvinylidene fluoride (PVDF) binder with a weight ratio of 50:40:10 in N-methyl-2-pyrrolidone (NMP) solvent, and pasting onto a Cu foil. Before use, the electrode was dried in a vacuum oven at 100 °C for 12 h. Metallic Li sheets and 1 M $LiPF_6$ in propylene carbonate (PC) were adopted as counter electrode and electrolyte respectively. Celgard 2500 was used as separator. Cyclic voltammograms (0.01–3.0 V, 0.2 mV/s) and electrochemical impedance spectroscopy (0.01–10, 000 Hz) were executed using a Chenhua CHI660E electrochemical workstation. Galvanostatic charge-discharge measurements in a voltage range of 0.01–3.0 V were performed in a LAND-CT2001A instrument. Specifically, the capacity of HPS (C_{HPS}, mAh/g) is obtained by the following equation: $C_{HPS} = (C_{total} - C_{carbon} \times m_{carbon})/m_{HPS}$, where C_{total} is the tested capacity of composite electrode (mAh, not mass specific capacity), C_{carbon} is the tested mass specific capacity of carbon black (mAh/g), m_{carbon} and m_{HPS} are the weights of carbon black and HPS in the composite electrode.

3. Results and discussion

As illustrated in Fig. 1, HPS was prepared by combination of emulsion polymerization and subsequent Friedel-Crafts crosslink.

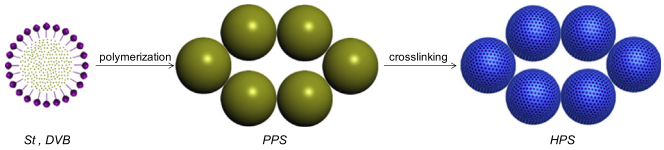

Fig. 1. Schematic illustration for the preparation of HPS by emulsion polymerization and hyper-crosslinking.