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Research Paper

Facile synthesis of conjugated polymeric Schiff base as negative electrodes for lithium ion batteries



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The redox-active organic compounds show great potentials as anodes for high energy density Li-ion batteries (LIBs), comparing with the traditional transition metal-based inorganic compounds. However, the inevitable dissolution behaviors of these organics in organic electrolyte will arouse the recession in their cycling stabilities. To circumvent this problem, we successfully applied an electrochemically active imine group to connect the carbonyl compound to form conjugated polymer, where the occurrence of multi-electron reactions suppressed the dissolution of anthraquinone in the organic electrolyte with improved cycling stability and high capacity for LIBs. In detail, by virtue of a facile solid-phase reaction between 1, 4-diaminoanthraquinone (14DAAQ) and p-phthalaldehyde (PPD), a highly conjugated polymeric Schiff base (PSB) was synthesized. The obtained PSB exhibited a reversible specific capacity of 175 mAh g⁻¹ at a current density of 10 mA g⁻¹. In addition, after 100 cycles, a cycling stability with 90% capacity retention can be maintained, manifesting a promising application of the organic material in high performance anodes for LIBs.

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1. Introduction

With the rapid development of emerging electronic products, rechargeable lithium-ion batteries (LIBs) have attracted tremendous attention in our daily lives because they are lightweight and long-life span [1-4]. Nevertheless, the electrode materials of currently-used LIBs are composed of the transition-metal compounds, which are rooted in the limited non-renewable mineral resources with a great consumption in energy for exploitation. As promising candidates to the metal-based materials, organic materials with electrochemical activities have intrinsic merits of abundant source, structural flexibleness, and environmental friendliness [5–7]. Most importantly, the abundances in structural versatilities also enrich the exploration of these organic compounds in depth and length. Typically, among those organic materials based on conjugated carbonyl compounds, quinones have been proved as one of the most promising candidates for LIBs anodes with high theoretical capacities (up to 600 mAh g^{-1}), high redox reversibilities, and high resource availabilities [8]. However, it remains to be a great challenge to suppress the dissolution of the

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http://dx.doi.org/10.1016/j.electacta.2017.09.062 0013-4686/© 2017 Elsevier Ltd. All rights reserved. quinone derivatives in the organic electrolyte and improve their cycling stabilities. To conquer this problem, polymerizing those small molecules into polymers which are not soluble in organic electrolyte is an effective method among the feasible attempts. It was envisioned that their cycling stabilities would be boosted as well [9–14]. In general, traditional polymerization approaches are inclined to insert one or more inactive molecular linkers between active molecules, which will inevitably decrease the gravimetric capacities to a certain extent. It is expected that if the active molecular units are used as linkers for the formation of polymer chains, the objective polymers will present promising performances in energy storage without the sacrifice in electrochemical capacities [9–11,15].

Recently, $R_1HC=NR_2$, the basic functional group of the Schiff base, has shown great prospect as organic anode materials of LIBs [16]. In principle, during discharge process, the $R_1HC=NR_2$ can accept electrons that are donated from lithium metals to form radical anions. While during reversible charge process, the Schiff base become an electron donor and is oxidized in turn [17]. Hence, it is expected that the appearance of $R_1HC=NR_2$ in chain will endow the final product with an excellent electrochemical performance [16]. Alternatively, the condensation reaction between aldehydes and amines always occur with a high



product-yield, during which water (H₂O) is the sole by products [18]. On the other hand, the synthesis of Schiff bases is always via the wet chemistry route, in which a large amount of organic solvents and troublesome and time-consuming processes are involved. For example, M. Armand's group has synthesized various series of Schiff bases with reversible specific capacities for sodium ion batteries [16,19]. In their procedures, multi-steps such as the synthesis of oligomers and further solidification via anion exchange reactions are included. Similarly, a hyper-branched Schiff base polymer with large conjugated structure was synthesized by Cheng's group [17], where the complicated synthesis of the intermediate is also mentioned. All these achievements stimulated us to design a facile and simple process for the preparation of Schiff base, especially for those with excellent electrochemical performances in energy storage.

Taking the above issues together, we designed a highly conjugated polymeric Schiff base (PSB), which was synthesized via a facile solid-phase condensation reaction between 1, 4-diaminoanthraquinone (14DAAQ) and p-phthalaldehyde (PPD). With the cooperation of C=O and $R_1HC=NR_2$ groups, the asprepared PSB delivers a specific capacity of 175 mAh g⁻¹ at a current density of 10 mA g⁻¹. Moreover, the reversible capacity is higher than those of reported Schiff base anodes. Most importantly, a stable cycling with 90% capacity retention can be obtained after 100 cycles, due to the suppressed dissolution of these polymers into the organic electrolyte. Such success evidenced new avenues for designing more Schiff base polymers and developing more high-performance and promising organic anodes for LIBs.

2. Experimental sections

2.1. Materials and reagents

1, 4-diaminoanthraquinone and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received. Pphthalaldehyde was purchased from Aladdin Co., Ltd. and used without further purification.

2.2. Synthesis of the PSB

The PSB was synthesized via the condensation between 14DAAQ and PPD under the protection of argon. In a typical synthesis, equivalent molar ratio of 14DAAQ (5 mmol) and PPD (5 mmol) were ground in a mortar with a pestle until a homogeneous phase was formed. Subsequently, the mixture was transferred to a quartz boat and heated at 180 °C for 6 h in a tube furnace under the protection of argon. After cooling down to the room temperature, the product was purified by Soxhlet extracting

with ethanol and dried at $80 \,^{\circ}$ C under vacuum to obtain the final PSB (0.943 g, 58.9%).

2.3. Characterization of the PSB

The morphology of the sample was characterized by field emission scanning electron microscopy (FESEM, JSM-6701F) with an acceleration voltage of 5.0 kV. Fourier transform infrared spectroscopy (FTIR) was conducted on Thermo Nicolet (Nicolet 5700) in the wavenumber range of 4000–500 cm⁻¹ by KBr pellets. The thermogravimetric analysis (TGA) was carried out on PerkinElmer Diamond TGA-4000 apparatus from room temperature (30 °C) to 800 °C at a heating rate of 10 °C min⁻¹ in a N₂ flow.

2.4. Electrochemical measurements

The electrochemical tests were carried out with the configuration of half cells. To be specific, the working electrode was fabricated by homogeneously blending the as-prepared PSB, Super P, and PTFE in a mass ratio of 85:10:5 (the total weight was 9 mg). Then the obtained slurry was pasted on a piece of Cu grilling and dried in vacuum at 60°C for 12h. Metallic lithium foil was employed as counter and reference electrodes concurrently. Polypropylene membrane (Celgard 2400) was utilized as the separator. The electrolyte was made up of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 volume). The coin cells were discharged-charged at various current densities between 0.01 and 3.5 V on the Neware battery detecting system at room temperature. The cyclic voltammetry (CV) was implemented on a CHI630D electrochemical workstation within the voltage interval of 0.01-3.5V at a scanning rate of 0.1 mV s⁻¹. Electrochemical impedance spectra (EIS) were obtained with a Parstat 2273 electrochemical workstation with the frequency range of 100,000-0.1 Hz with an AC amplitude of 5 mV.

3. Results and discussion

The synthetic route of the PSB is presented in Fig. 1a. Typically, with the temperature gradually ascending to 180 °C, the polycondensation reaction between 14DAAQ and PPD begins under the protection of flowing argon, where the $-NH_2$ of 14DAAQ reacts with the -CHO of PPD without any catalysts, following the creation of vaporous H₂O. As recorded in Fig. S1, after the condensation reaction, the obtained PSB appears a black color, which is deeper than the color of the precursors respectively (mazarine for 14DAAQ and white for PPD), implying the successful formation of the large π conjugation structure in PSB. In addition, FESEM was adopted to observe the morphology of the synthesized PSB. As shown in



Fig. 1. (a) Synthesis route and (b) SEM image of the PSB.

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