Long cycle life and high rate sodium-ion chemistry for hard carbon anodes

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ABSTRACT

As the most promising anode material for Na-ion batteries, hard carbons suffer both poor rate capability and cycling stability, which restrict its practical application. These challenges come not only from the carbonaceous electrode structure, but also from how to tailor-design an electrolyte that can support high sodium ion transport while simultaneously providing a protective solid-electrolyte-interphase (SEI). Here we develop a new strategy to decouple the "bulk ion transport" and "interphasial" requirements for electrolytes. By pre-engineering a "foreign SEI" from an ester-based electrolyte, we successfully stabilized the hard carbon anodes in ether-based electrolyte and realized significant improvement in electrochemical performance. At a high rate of 500 mA h g^{-1}, a capacity of 200 mA h g^{-1} was retained for over 1000 cycles without detectable capacity fading. Such an outstanding performance is attributed to the "foreign SEI" approach, which makes it possible for a synergistic cooperation between the rapid diffusion of sodium ions in ether-based electrolytes and a protective ester-originated interphase.

1. Introduction

Efficient harvest and utilization of clean energy for either automotive or grid-storage depend highly on the efficiency and rate capability of energy storage technology that must integrate merits of low cost, high energy density, high safety and long cycle life. The mature lithium-ion batteries (LIBs) have been considered as the most competitive candidate because of their high energy density and stable cycling performance. However, the rare and uneven distribution of lithium resource in the earth-crust has raised concerns on the affordability for next generation energy storage systems [1–3]. As an alternative, Na-ion batteries (NIBs) have attracted intensive attention due to the abundance and wide distribution of Na element and its electrochemical similarity to Li [4–7].

The transition from Li to Na systems, however, is by no means intuitive. Although a lower specific capacity is often observed, replacing Li with Na in some cathode materials doesn't induce significant impact on the cycling stability if material structures are carefully designed, and encouraging advances have been made, mainly including oxides [8–10] and polyanionic compounds [11–13]. The main challenge that NIBs are facing comes from the lack of suitable intercalation hosts to store

Na$^+$ ions. Graphite, a standard anode material in commercial LIBs, shows only fraction of Na storage capacity in traditional carbonate electrolytes due to thermodynamic instability of sodium-graphite intercalation compounds [14,15]. The use of ether-based electrolytes improved the sodium storage in graphite due to the co-intercalation of Na$^+$ solvated by ether molecules, and a highly reversible capacity of approximately 150 mA h g^{-1}, still inferior to LIBs, was reported [16–18]. Other proposed anode hosts for Na$^+$ ions include carbonaceous materials [19–24], oxides [25,26], alloys [27,28] and organic compounds [29,30], among which hard carbons (HCs) structured with random-oriented graphene layers and large fraction of micro-voids and defects have been the most promising, following the seminal work by Dahn and co-workers [22]. HCs accommodate Na$^+$-intercalation at a low average potential (~ 0.1 V vs Na$^+$/Na) and deliver a high reversible capacity (up to 300–400 mA h g^{-1}) [23,24,31–38], and its many allotropes including spheres [39–41], hollow wires [42], nanosheets [43,44], nanofibers [45–47], nanotubes [23], and three-dimensional porous framework [48,49] have been extensively investigated. However, HCs as NIB anode materials still suffer poor rate capability and insufficient lifespan, which prevent its practical applications. For example, several biomass-derived HCs in forms of microspherules,

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microtubes or irregular granules have been reported by Hu et al [23,31,40,50,51]. Despite high capacities of ~ 300 mA h g^{-1}, poor rate performance with capacity retentions of ~ 100 mA h g^{-1} at 600 mA g^{-1} and a limited cycle of 100 cycles were presented. Mitlin's group synthesized banana peel pseudographite, which delivered a moderate rate performance with a capacity of ~ 180 mA h g^{-1} at a high current of 1 A g^{-1} while a capacity degradation of 7% at 500 mA g^{-1} still occurred over 600 cycles [24]. HC fibers made via electrospinning improved the rate capability with a capacity retention of 200 mA h g^{-1} at 1 A g^{-1}. Although a longer cycle life was displayed, fast capacity degradation occurred, with a low capacity retention ratio of 71.5% after 1000 cycles at 500 mA g^{-1} [46].

The electrolytes as the key component bridging cathodes and anodes often dictate the reversibility and rate capability of the cell reactions in an electrochemical device, to which NIBs is no exception. In addition to the carbon structure, electrolyte and the accompanied interphase have been found to affect the electrochemical performance of hard carbon anode materials. Komaba et al. investigated the effects of electrolytes and concluded that a stable solid-electrolyte-interphase (SEI) layer is required to achieve a good stability for NIBs [52]. Ester-based electrolytes tend to form thick and stable SEI layers constructed on the reductive products from ester molecules, thus providing effective protection to the hard carbon anodes in NIBs [53–55]. The quality of SEI can be manipulated with fluoroethylene carbonate (FEC) as an additive in the electrolytes [56–59]. On the other hand, thin and compact SEI was originated from ether-based electrolytes on graphene NIB anodes, leading to markedly improved initial Coulombic efficiency and rate capability [60]. Similar results were reported on hard carbon anodes, where a diglyme electrolyte significantly enhanced the rate performance with a capacity of 142 mA h g^{-1} at a high rate of 3 A g^{-1} as a result of reduced electrochemical polarization [34]. However, a low capacity retention of 71 mA h g^{-1} was maintained after 2000 cycles at 2.1 A g^{-1}. Although the long-term cycling stability still awaits further improvement, these results did offer a valid approach to circumvent the origins of poor rate and insufficient capacity retention for HCs by optimizing electrolytes and related interphasial chemistries.

In this paper, we aim to integrate the merits of ester- and ether-based electrolytes to enable a highly reversible and high rate HC anode for NIBs. By pre-forming a stable SEI from ester-based electrolyte, we effectively stabilized HC surface, which operates with unprecedented reversibility in ether-based electrolyte. Excellent rate capability and cycling stability were demonstrated with HC anodes, which retain a record-high capacity of 200 mA h g^{-1} at a current density of 500 mA g^{-1} with no detectable degradation for over 1000 cycles. The origin of this performance enhancement in Na storage, which has never been achieved in literature to the best of our knowledge, is apparently the combination of fast kinetics of Na$^+$-transport in ether-based electrolyte and effective protection of the ester-originated SEI. The "foreign SEI" strategy described in this work should be of universal significance to other battery chemistries, as it decoupled the two most important property requirements of electrolytes, which are often difficult to satisfy in a single electrolyte.

2. Experimental section

2.1. Synthesis of the hard carbon

The hard carbon was prepared according to the previously reported method [61,62]. Typically, 20 g sucrose was dissolved in 6 M sulfuric acid to form 5% sucrose solution which was put in 1 L round bottom flask and refluxed at 120 °C for overnight. The obtained black suspension was filtered and washed with distilled water several times. Then after drying at 100 °C in oven for 24 h, the product was carbonized at 1000 °C for 3 h with heating rate of 5 °C min^{-1} under flowing Ar/5% H$_2$ atmosphere, to obtain the HC.

2.2. Materials characterization

Scanning electron microscope (SEM) measurements were performed using a S-4800 SEM (Hitachi, Japan). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) patterns were recorded by JEM-2100F transmission electron microscope (JEOL, Japan). X-ray diffraction (XRD) measurement was carried out using a D8 Advanced diffractometer (Bruker, Germany) with a Cu Kα radiation (V = 40 kV, I = 40 mA and λ = 1.5418 Å). Raman spectra (Thermo Fisher Scientific-DXR, USA) were collected with a 532 nm laser wavelength. The porous structure of the HC was analyzed using CO_2 (at 273 K) adsorption on a Micromeritics ASAP 2420-4 volumetric adsorption analyzer (USA). From the measured CO_2 isotherm, the micropore size distribution was calculated using non-local density functional theory (NLDFT) method and the micropore volume was calculated using the Horvath-Kawazoe method in the P/P$_0$ range from 0.01 to 0.03. X-ray photoelectron spectroscopy (XPS) was performed on an K-Alpha (Thermo Fisher) (UK) at room temperature with the mono Al Kα radiation at an ion energy of 200 eV and a high current. Atomic force microscope (AFM) observation was performed using Bruker Mutimode8 (Bruker, Germany) and the Young's Modulus was obtained based on Derjaguin-Muller-Toporov (DMT) model fitting the Force curves measured by PeakForce QNM (PFQNM) technique.

2.3. Electrode preparation and post treatment of electrodes for ex-situ characterization

Electrochemical experiments were performed with CR2032 coin cells. To make the working electrodes, as-obtained HC powder was homogeneously mixed with carbon black and sodium carboxymethyl cellulose (Na-CMC) (Sigma-Aldrich) binder at a weight ratio of 8:1:1 to form a slurry. The slurry was pasted uniformly onto an copper foil by a doctor blade and then dried in a vacuum oven at 80 °C overnight. The electrodes were cut into circular pieces with a diameter of 9 mm. The average loading mass of the hard carbon electrodes is ~ 1 mg cm^{-2}. The electrolytes were 0.8 M Sodium hexafluorophosphate (NaPF$_6$) (98.0%, Sigma-Aldrich, USA) dissolved in a mixture of ethylene carbonate (EC, 99.0%, Sigma-Aldrich, USA) and diethyl carbonate (DEC, ≥ 99.0%, Sigma-Aldrich, USA) (volume ratio:1:1) or 0.8 M NaPF$_6$ dissolved in Diethylene glycol dimethyl ether (DEGDME, 99.5%, Sigma-Aldrich, USA). With a pure sodium metal (Na, 99.5%, Sigma-Aldrich, USA) counter electrodes and Celgard®2400 (Celgard, LLC Corp., USA) separators, the coin cells were assembled in an argon-filled glovebox.

For all ex-situ characterization, the electrodes were disassembled, washed and dried in vacuum for 40 min to remove the residual electrolytes. For the replacement of electrolytes, the hard carbon electrodes were cycled in one electrolyte system firstly, and then were disassembled and dried in vacuum for 40 min before being assembled into a new cell.

2.4. Electrochemical characterization

The cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation CHI600E B 16436a (Shanghai, China) with a scan rate of 0.05 mV s^{-1} in the potential range of 0–2.5 V (vs Na$^+$/Na). Galvanostatic charge/discharge tests were performed on LAND CT-2001A instrument (Wuhan, China) in the voltage range of 0–2.5 V (vs Na$^+$/Na) at different current densities. The electrochemical impedance spectroscopy (EIS) measurements were conducted on PARSTAT MC 1000 with a frequency ranging from 0.01 Hz to 1 MHz and an ac amplitude of 5 mV.

3. Results and discussions

The HC structure was characterized using SEM, TEM, XRD and Raman spectroscopy and CO_2 adsorption/desorption (Fig. S1). The electrochemical Na$^+$-intercalation/de-intercalation behavior in the HC