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Short communication

Micro-sized organometallic compound of ferrocene as high-performance anode material for advanced lithium-ion batteries

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HIGHLIGHTS

- An organometallic compound of ferrocene as anode material was first investigated.
- The reversible conversion reaction occurred for the ferrocene anode.
- The ferrocene achieved great electrochemical performance.

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ABSTRACT

An organometallic compound of ferrocene is first investigated as a promising anode for lithium-ion batteries. The electrochemical properties of ferrocene are conducted by galvanostatic charge and discharge. The ferrocene anode exhibits a high reversible capacity and great cycling stability, as well as superior rate capability. The electrochemical reaction of ferrocene is semi-reversible and some metallic Fe remains in the electrode even after delithiation. The metallic Fe formed in electrode and the stable solid electrolyte interphase should be responsible for its excellent electrochemical performance.

1. Introduction

Applications of lithium-ion batteries (LIBs) are expanding rapidly from electronic devices to electric vehicles (EVs) and hybrid electric vehicles (HEVs), due to their high energy density, long lifespan, high voltage, low self-discharge and lack of memory effect [1]. Commercially available LIBs use graphitic carbons with a theoretical capacity of 372 mAh g⁻¹ as their anode materials. However, these anodes gradually impede the advanced technologies, which demand higher energy density and power sources [2]. Developing new anode material with high specific capacity is an effective way to increase the energy density of LIBs. A type of organometallic compound, ferrocene (consisting of two cyclopentadienyl rings bound on opposite sides of an iron atom), has ideal features of high thermal stability, chemical stability, electrochemical stability and excellent electrochemical response [3]. It has been reported that the ferrocene generally integrates into polymers and utilizes as cathode active materials in LIBs, which exhibit quickly chargeable, high power density and the stable voltage plateaus [4–6]. For example, Su et al. successfully synthesized a ferrocene-containing

polytriphenylamine derivative as the cathode material, which has higher discharge capacity and rate capability than polytriphenylamine electrodes [4]. Another application of ferrocene is used as anode buffer material in LIBs [7,8]. Li et al. reported ferrocene-encapsulated single-walled carbon nanotubes (Fc@SWNTs) as buffer material for SnO₂, which can enhance the reversible capacity of SnO₂ [8]. To the best of our knowledge, the ferrocene as active material has not been investigated for LIBs so far. Herein, we reported the electrochemical properties of ferrocene as a high-performance anode in LIBs for the first time. To achieve high specific capacity of ferrocene, lower charge-discharge voltages were adopted. Meanwhile, the structure evolution of ferrocene during the cycling was also studied in this work.

2. Experimental

Commercially available ferrocene particles (Aladdin) were utilized as the active material without further purification. The structure of ferrocene was characterized by ultraviolet absorption spectroscopy (UV) at the wave range of 250–600 nm, while its morphology was

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probed by scanning electron microscopy (SEM). The working electrodes were prepared by dispersing 60 wt% active material (ferrocene), 30 wt% conductive carbon, and 10 wt% binder (polyvinylidene fluoride) in 1-methyl-2-pyrrolidinone (NMP) to stir into a homogeneous slurry. The slurry was coated on copper foil, dried at 100 °C in a vacuum oven for 8 h. The active material loading of electrodes was in the range of 1–2 mg. The electrochemical properties were studied using coin cells (2032, R-type), which were assembled in the Ar-filled glove box. Lithium foils and polypropylene films were used as counter electrodes and separators, respectively. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The galvanostatic charge and discharge tests were performed at different constant current densities between 0.01 and 3.0 V using a LAND battery test system (Wuhan, China). Cyclic voltammetry (CV) was carried out on a CHI-660 workstation (Chenhua, Shanghai) within the range of 0.01–3.0 V at a scanning rate of 0.1 mV s⁻¹. Electrochemical impedance spectra (EIS) of the coin cells were collected by the CHI-660 workstation in the frequency range from 0.01 Hz to 100 KHz with an amplitude voltage of 5 mV. To analyze the structure evolution during cycling, the cycled electrodes at different states were explored by using a Bruker D8 Advance diffractometer (XRD) with Cu K α radiation, at 2 θ range of 10°–80° with 0.02 per step. For the XRD samples, the working electrodes were prepared by using the ferrocene, conductive carbon and PTFE-binder (60:30:10 wt%). The fabrication method and construction of cells were the same as described above.

3. Results and discussions

The structure and morphology of as-purchased ferrocene were characterized by UV and SEM. Fig. 1 shows UV spectrum and SEM image of as-purchased ferrocene particles. As shown in Fig. 1a, two strong peaks were observed at 325 nm⁻¹ and 450 nm⁻¹ in UV curve, which are the characteristic peaks of pure ferrocene [9]. The SEM observation (Fig. 1b) clearly shows that the ferrocene particles are irregularly shaped in large block with size more than 1 μ m and aggregated together.

The electrochemical properties of the as-purchased ferrocene anodes are shown in Fig. 2. Fig. 2a shows the first three charge/discharge cycles of ferrocene at current density of 100 mA g⁻¹. The initial discharge and charge capacities are 1127 and 562 mAh g⁻¹, respectively, which correspond to an initial Coulombic efficiency of ~50%. After the second cycle, the charge and discharge reactions proceed reversibly and the irreversible capacity is small. It can be clearly seen that the initial charge/discharge curves are different from that of the subsequent cycles. During the first discharge process, a slope plateau at around 1.6 V is observed, and the second plateau is found at about 1.3 V, followed by a long slope until cutoff voltage. However, these two plateaus disappear during the charge process. From the second cycle, no noticeable plateau is observed in the charge/discharge curves. To clarify the electrochemical reactions, cyclic voltammetry was performed at the scan rate of 0.1 mV s⁻¹ in the range of 0.01–3.0 V (vs. Li/Li⁺), as shown in

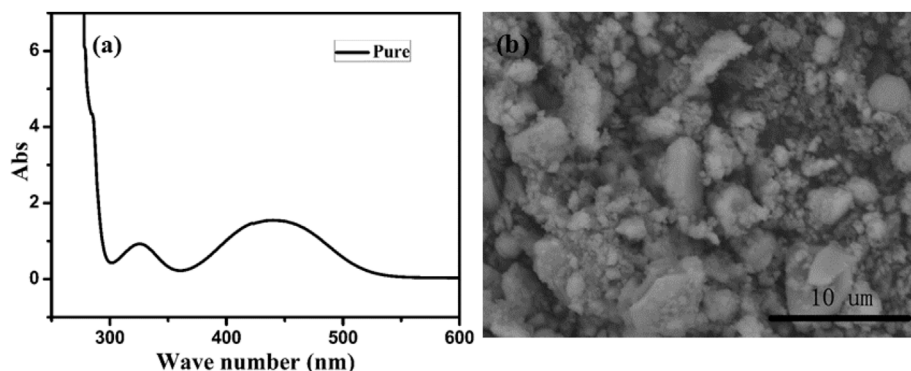


Fig. 1. (a) UV spectra and (b) SEM image of the ferrocene powders.

Fig. 2b. Consistent with the charge/discharge profile (Fig. 2a), the CV curves of the first cycle are quite different from that of the subsequent cycles, especially for the first lithiation process. During the first cathodic process, a remarkable cathodic peak at 1.3 V partly overlapped by a peak at 1.6 V is attributed to the formation of SEI film [10,11]. In addition, a large peak at 0.6 V is ascribed to the reduction/oxidation of Fe²⁺/Fe in the electrochemical reaction of Li⁺ with ferrocene [10,11]. However, these cathodic peaks significantly decrease in second cycle and then stabilize in subsequent cycles, which are agreed well with the charge/discharge curves.

Fig. 2c shows the cycling performance of ferrocene at the current density of 100 mA g⁻¹. The initial discharge capacity can achieve as high as 1127 mAh g⁻¹, and then stabilizes at ~560 mAh g⁻¹ with a small fluctuation up to 100 cycles. Moreover, the initial Coulombic efficiency of ferrocene is ~50%, which quickly increases to ~90% at the second cycle, and finally remains nearly 100% in subsequent cycles. In addition to high capacity and excellent cyclability, the ferrocene also exhibits a good rate capability (Fig. 2d). The rate capability of ferrocene was examined using the galvanostatic charge/discharge tests. When the current density increases from 100 to 5000 mA g⁻¹, seven cycles are recorded for each stepwise increment. The ferrocene electrode shows a reversible capacity of ~600 mAh g⁻¹ at a current density of 100 mA g⁻¹. When the current density increases to 5000 mA g⁻¹, the ferrocene electrode still has a capacity of ~100 mAh g⁻¹. Furthermore, the specific capacity could recover to 500 mAh g⁻¹, when the current rate returns to 100 mA g⁻¹. The great cyclability and high rate performance of ferrocene should be closely related to the advantages as following: (1) the improving conductivity of metallic Fe in electrode [12]; (2) the formation of a stable solid electrolyte interphase (SEI) film on the electrode after cycling [13].

To trace the structure evolution of ferrocene during the cycling, XRD was performed on the cycled electrodes. The cycled samples at different states in the first charge/discharge process were studied, as shown in Fig. 3. All the XRD patterns show a sharp diffraction signal at 18° in accordance with the peak of PTFE [14]. With the increase of the discharge depth, the peak is observed at around 43° and tends to be larger, indicating the formation of iron in the discharge process [14]. However, this peak is still found even after full charge, implying that some metallic Fe remains in the composite after delithiation. At the same time, a new peak appears at 38° during the lithiation, and then reduces in charge process, which may be a product of reaction between the cyclopentadienyl rings of ferrocene and Li⁺. All of the observed changes demonstrate that the lithiation of ferrocene is only semi-reversible and a part of ferrocene is not restored the original structure and some new substances are produced after the cycling, which is in accordance with the results of CV curves.

EIS was carried out to compare the ferrocene electrodes as the working electrode versus Li before and after cycling. Fig. 4 shows the Nyquist plots of the ferrocene electrodes before cycle and after 1, 5, 20 and 50 cycles, respectively, together with the corresponding equivalent circuit model. Obviously, all EIS spectra consist of a small intercept at

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