Fabrication of Fe-Metal Organic Framework-derived Fe₂O₃ Nanoparticle Li-ion Battery

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ABSTRACT

We, for the first time, fabricated an additive-free battery electrode composed of Fe-zeolitic imidazolate frameworks-derived Fe₂O₃ nanoparticles (NPs) incorporated in carbon shells (Fe₂O₃@C) through electrophoretic deposition (EPD). High specific capacity of Fe₂O₃@C without additives comparable to that of the theoretical capacity (1007 mAh/g) suggests that the electrochemical conversion reactions accompanied by lithiation and delithiation process are not significantly limited by the absence of the conductive agents and binders. The additive-free system paves the way for an efficient experimental probe to investigate the intrinsic electrochemical properties of the metal-organic framework-derived nanostructures.

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Keywords : Electrophoretic Deposition, Fe₂O₃, Cycle Performance, Metal-Organic Framework

1. Introduction

Fe₂O₃ has been explored as Li-ion battery anode materials due to their high theoretical specific capacity and low cost.^{1–5} Various nanostructures were formed using metal-organic frameworks (MOFs) as the main scaffold.^{6–10} High specific area and hollow structure of various Fe₂O₃ composites embedding carbonaceous materials have motivated extensive research even with challenging issues, including volume expansion, poor electrochemical stability and poor electronic conduction.^{8–11}

Despite significant enhancement in the cycle performance and the high rate capability with a variety of Fe₂O₃ nanostructured composites, the slurry-based battery electrodes incorporating the conductive agents and the binders complicate the analysis of electrochemical reaction associated with lithiation and delithiation process. Few studies of binder-free Fe₂O₃ nanostructured anodes have been reported.^{7–9} Surprisingly, Fe-zeolitic imidazolate frameworks (ZIF)-derived nanoparticle (NP) battery electrode without additives has not been studied despite its advantages over tunability of various nanostructure. Here, we, for the first time, fabricated an Fe-ZIF-derived additive-free Fe₂O₃ NP Li-ion battery electrode using the electrophoretic deposition (EPD) method which can be utilized as an experimental testbed through which fundamental understanding of the structure-property relation can be elaborated, eliminating complications arising from the interfacial reactions between the additives and the active layers.

2. Experimental

2.1 Fabrication of Fe-MOF-derived additive-free Li-ion battery electrodes

To synthesize the Fe-ZIF precursor, we prepared a ferrous sulfate (FeSO₄·7H₂O) solution in methanol (25 mL), followed by a slow injection of a 2-methylimidazole (328 mg) and PVP (0.3 g) in methanol. After stirring, we centrifuged the precipitates and dispersed the white-colored powders in 1-methyl-2-pyrrolidone solvent for the subsequent EPD process. To deposit the Fe-ZIF onto the stainless steel current collector, we applied a voltage of 90 V for 2 min between the two stainless steel electrodes spaced by 2 mm, as

seen in Fig. 1(a), forming a ~9 μm thick Fe-ZIF film. The details are described in the supporting information (Fig. S1). After EPD of the Fe-ZIF, high-temperature annealing for carbonization was carried out to transform the Fe-ZIF to Fe₂O₃@C at 620°C for 1 h. After calcination process at 620°C, we observed the nitrogen-doped carbon matrix as seen in the energy dispersive spectrometer (EDS) images in the supporting information (Fig. S2). For charging-discharging battery characterizations, we assembled the 2032 coin cells configuring a Li foil as a negative electrode in an electrolyte solution (1 M lithium hexafluorophosphate in ethylene carbonate/dimethyl carbonate (1:1, v/v)).

3. Results and Discussion

The EPD system is illustrated in Fig. 1(a) in which the stainless steel current collectors were attached to the stainless steel pads connected to a power supply. Figure 1(b) shows the x-ray diffraction (XRD) data which evidences the formation of the rhombohedra α-Fe₂O₃ (after annealing) from the amorphous Fe-ZIF film (before annealing). The scanning electron micrographs in Fig. 1(c) show that, during the calcination process, spherical-shaped particles emerge from the Fe-ZIF in which the Fe-ZIF nanoclusters formed islands as a result of three-dimensional growth. It is also noted that the broad carbon peak between 20–30° becomes sharp after annealing. In combination with the XRD data, we interpret that, after completion of the calcination process, the Fe-ZIF structure is transformed to the spherical-shaped α-Fe₂O₃ phase NPs embedded in carbon shells with decomposition of the organic ligands.

Cyclic voltammetry (CV) measurements in Fig. 2(a) show that significant difference between the 1st and the subsequent peaks during the conversion reactions, $Fe_2O_3 + 6Li^+ + 6e^- \leftrightarrow 2Fe + 3Li_2O$, exist for the additive-free Fe₂O₃@C electrodes. The cathodic peak at around 0.4 V in the 1st cycle is ascribed to the reduction reaction from Fe₂O₃ to Fe and the formation of solid electrolyte interface (SEI).^{6–8} Without additives, peaks associated with Li intercalation to Fe₂O₃ (~1.65 V) and the reduction of Fe³⁺ to Fe²⁺ (0.93 V) were not observed while, for the slurry-based conventional electrodes, those peaks appear in the 1st cycle the origin of which should be further investigated. For anodic scans, the peak at 1.67 V

Figure 1. (a) Schematics of an Fe-ZIF electrode preparation on a stainless current collector through the EPD process (90 V for 2 min). (b) Comparison of the XRD data between before and after annealing of the Fe-ZIF. (c) The SEM images of the Fe-ZIF and the Fe_2O_3 NP electrode after completion of calcination at 620°C for 1 h.

Figure 2. (a) CV plots of the electrophoretic-deposited Fe_2O_3 nanostructured electrode. The scan rate was 0.1 mV/s. (b) Discharge-charge curves at (c) 0.1C-rate and (d) 2C-rate. (d) Cycle performance and rate capability test curves at 0.1 and 2C rate.

arises from the oxidation of Fe to FeO .^{6–8} It is important to emphasize that, after the 1st scan, the peak intensity and the position remain the same, implying that the cycle performance is stabilized after the irreversible capacity loss due to the SEI formation.

Irreversible capacity loss after the 1st scan is more clearly observed in the battery charging/discharging curves in Figs. 2(b) and 2(c). In the 1st scan of Fig. 2(b), a prominent potential plateau at 0.8 V led to a far higher specific capacity (~ 1400 mAh/g) than that

in the subsequent cycles in which the potential plateaus are reproducibly observed close to 1 V. The deviation of the peak position between the CV and the potential profile plots may be attributed to the difference of the scan rate. From the observation, a significant irreversible capacity loss in the subsequent cycles after the 1st cycle results from the decomposition of the SEI film as well as reduction reaction from Fe_2O_3 to Fe, excluding the effect of additives on the electrochemical reactions. As the C-rate increases from 0.1C to 5C in Fig. 2(d), the stabilized specific capacity decrease was not significant compared with that of the slurry-based electrode systems containing additives. It is interesting to observe the fluctuation of the specific capacity with cycles. The fluctuation of the capacity was reproducibly observed in our binder-free battery system. From previous studies,¹² the increase in the capacity with cycles is attributed to addition of the interfacial charge storage and/or the formation/decomposition of the electrolyte-derived surface layer during charging/discharging. It is also important to emphasize that annealing process after the EPD process is critical in enhancing the cycle performance. With the annealing process, the specific capacity was, indeed, retained while the specific capacity dropped to 50% of the initial value after tens of cycles without annealing (Data not shown). We believe this is attributed to the difference in the interfacial contact properties between the current collector and the active layer resulting from the annealing process through which electrical contact can be enhanced.

In conclusion, we fabricated Fe-ZIF-derived additive-free electrophoretic-deposited Fe_2O_3 NP electrode embedding carbon shells and demonstrated a high specific capacity close to the theoretical capacity without additives, suggesting that the additive-free system is a promising testbed to optimize the electrochemical properties through structural tuning of the Fe-ZIF at various reaction conditions.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-00025>.

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