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High capacity Li-ion battery anodes: Impact of crystallite size, surface chemistry and PEG-coating

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ABSTRACT

Battery electrodes are complex mesoscale systems comprised of an active material, conductive agent, current collector, and polymeric binder. Previous work showed that introduction of poly [3-(potassium-4-butanoate) thiophene] (PPBT) as a binder component coupled with a polyethylene glycol (PEG) surface coating on magnetite (Fe_3O_4) nanoparticles enhanced electron and ion transport in the high capacity anode system. Here, the impact of Fe_3O_4 crystallite size (10 nm vs. 20 nm) and surface chemistry were explored to evaluate their effects on interfacial interactions within the composite PEG/PPBT based electrodes and resultant battery performance. The Fe_3O_4 synthesis methods inevitably lead to differences in surface chemistry. For instance, the Fe_3O_4 particles synthesized using ammonium hydroxide appeared more dispersed, and afforded improved rate capability performance. Notably, chemical interactions between the active nanoparticles and PPBT binder were only seen with particles synthesized using triethylamine. Capacity retention and cycling performance were unaffected. This study provides fundamental insights into the significant impact of active material synthesis on the design and fabrication of composite battery electrodes.

1. Introduction

Lithium-ion batteries are one of the most important energy storage devices used for a wide range of applications; however, to accommodate future demands for high density energy storage, significant performance enhancements are a necessity [1–3]. Graphite, the current anode material used in lithium-ion batteries, suffers from limited theoretical capacity (~372 mAh g^{-1}) [4]. Transition metal oxides, when fully reduced, have a high theoretical capacity (~500–1000 mAh g^{-1}) and are a promising alternative [5–8]. Magnetite (Fe_3O_4) is particularly attractive due to a high theoretical capacity (~925 mAh g^{-1}) [9], high electronic conductivity [9–11], low cost and low environmental impact. However, as with most other transition metal oxides, capacity retention with cycling can be challenging due to large volume changes that take place during repetitive charging-discharging [12–15]. Thus, if the active material is to become commercially viable, further research is needed to understand the electrochemistry of Fe_3O_4 anodes.

Recently, a poly [3-(potassium-4-butanoate)thiophene] (PPBT) binder component and a polyethylene glycol (PEG) surface coating for the active material augmented both electron and ion transport in magnetite based anodes [16]. Electron pathway enhancement, such as through carbon coatings [16–20] is often considered in the design of battery anodes, but attention is rarely given to ion transport even though these characteristics are important in the selection of polymer binders for electrode preparation. For instance, the most widely used polymeric binder, poly (vinylidene

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difluoride) (PVDF), is insulating and furthermore, PVDF requires the use of toxic organic solvents [21]. Alternatively, conjugated polythiophenes have relatively high electronic conductivity (10^{-2}-10^{-4} S cm^{-1}, i.e., poly (3-hexylthiophene)) [22]. PPBT is a water soluble, carboxylate substituted polythiophene that supports pore formation for ion transport in addition to electron transport via its conjugated backbone. As an aqueous soluble binder, PPBT also allows for more environmentally friendly electrode processing. Incorporation of poly (ethylene glycol) (PEG) as a coating on the active material reduces aggregate formation and improves materials dispersion in PPBT, leading to electron/ion transport enhancement [23]. The PEG/PPBT system is investigated in this study as a facile approach to advance the reversible electrochemistry of Fe_3O_4 anodes in battery applications.

A preliminary investigation of the PEG/PPBT system demonstrated improved Fe_3O_4 capacity and rate capability [16] warranting further exploration into this system for the design and development of robust Li-ion anode materials. A prerequisite is to elucidate the impact of active material surface chemistry and crystallite size on transport pathways. For instance, the synthesis method used for magnetite particle formation affects crystallite size, size distribution, agglomeration and surface chemistry [24]. Several synthetic methods have been described that are largely associated with efforts to control crystallite size [25–30]; however, few studies attempt to explore the impact of changes in synthetic method on electrode performance, vis à vis electron and ion transport [24]. Studies suggest that the electrochemical activity of Fe_3O_4 depends on crystallite size [29,30], but conclusions as to whether smaller or larger crystallites are optimal remain elusive. Here, we explore how crystallite size and surface chemistry work in concert to impact Li-ion battery anode electrochemistry, thereby demonstrating the critical role of interfaces, coupled with electron and ion transport mechanisms, in the design of robust, high capacity electrode materials for battery applications.

2. Experimental

2.1. Materials

Fe_3O_4 nanoparticles (~10 nm and ~20 nm) were synthesized by previously reported coprecipitation processes, involving triethylamine base [29,30] or ammonium hydroxide base [31]. All 20 nm samples were synthesized using ammonium hydroxide, whereas 10 nm samples were synthesized with either triethylamine or ammonium hydroxide. For preparation of Fe_3O_4 particles coated with PEG (PEG-Fe_3O_4), 0.5 g of Fe_3O_4 powders in 5 g DI water were sonicated for 1.5 min at room temperature with an ultrasonic probe (3 pulses of 30 s each, operated at 50 W, Qsonica Q700 sonicator). PEG 1500 solution (2 mL; 50% w/v, Sigma-Aldrich) was added with sonication for 30 s, and this process was repeated four times until the total amount of PEG 1500 added to the aqueous dispersion was 8 mL. The PEG-Fe_3O_4 powders were washed with acetone and extracted by centrifuge separation (VWR Clinical 200) with a speed of 6000 rpm for 5 min; this process was repeated 3 times. PPBT (M_w: 21 kDa, polydispersity: 2.2, head-to-tail regioregularity: 89%) was purchased from Rieke Metals Inc.

2.2. Electrode fabrication

The slurries for the PPBT-based electrode were prepared by mixing Fe_3O_4 (or PEG-Fe_3O_4) (0.214 g), carbon additives (0.043 g), and PPBT in DI water (10 wt % solution, 0.43 g), and in the case of the PVDF-based electrode, N-methyl-2-pyrrolidone (NMP) solvent was used (weight ratio of Fe_3O_4:carbon:polymer = 71.4:14.3:14.3). The electrodes for field-emission scanning electron microscopy (FE-SEM, Zeiss Ultra-60) measurement, energy dispersive x-ray spectroscopy (EDS, Oxford Aztec software) measurement, electrochemical evaluation, and spectroscopy characterization were produced by blade coating (doctor blade, MTI corp). The PPBT-based electrodes were first allowed to dry at room temperature for 2 h, followed by 110 °C for 12 h in a vacuum oven. In the case of the PVDF-based electrodes, the NMP solvent was first removed at 70 °C for 1 h, and the other fabrication procedures remained the same as the PPBT-based electrodes.

2.3. Electrochemistry

Stainless-steel coin cells were used for electrochemical measurements. Lithium metal, purchased from MTI corp., was used as a counter electrode and 1 M $LiPF_6$ in ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 by weight), purchased from BASF, was used as the electrolyte. Before electrochemical testing, the capacity of each coin cell was confirmed by charging and discharging at a current density of 40 mA g^{-1} (~0.05 C), using an Arbin battery cycler. Cycling and rate capability testing was then performed on the Arbin battery cycler. Electrical impedance spectroscopy (EIS, Metrohm Autolab PGSTAT101) measurements were conducted in the frequency range from 0.1 MHz to 0.1 Hz.

2.4. Microscopic characterization

FE-SEM images were observed on the surface view of the electrodes using a Zeiss Ultra-60 FE-SEM with an accelerating voltage of 5 kV using the high vacuum mode at room temperature. Elemental analysis was conducted using energy dispersive x-ray spectroscopy (EDS, Oxford Aztec software). Transmission electron microscopy (TEM) images of Fe_3O_4 powders were obtained using a Hitachi HT7700 TEM. First the Fe_3O_4 (or PEG-Fe_3O_4) powders were dispersed in ethanol and then the solution was drop-cast onto Formvar Film 200 Mesh Copper grids (Electron Microscopy Sciences).

TEM images of selected nondischarged electrodes were obtained by embedding the samples in resin. Ultrathin electrode sections were cut with an ultramicrotome and placed on TEM grids to obtain cross-sections. TEM for cross-sectioned electrodes was collected using a JEOL JEM 1400 transmission electron microscope equipped with a Gatan CCD camera.

Transmission X-ray microscopy–X-ray absorption near-edge structure (TXM–XANES) images of the nondischarged electrodes were collected at Beamline 8BM at the Advanced Photon Source, Argonne National Laboratory. XANES image series were collected by scanning from 7092 to 7192 eV across the Fe K-edge with a step size of 2 eV (for a total of 50 steps) and one image per step. Image series were collected with an exposure time of 30s and binned camera pixels of 2 × 2 (approximately 39 × 39 nm^2). Additional 2 × 2 binning was used during data processing resulting in 78 nm × 78 nm pixel resolution. Analysis of the TXM data was accomplished by least-squares combination fitting of each binned pixel to standard phases of Fe_3O_4 and FeO using a customized MatLab program developed at Beamline X8C, NSLS-1, Brookhaven National Laboratory. The public domain Java image processing program Image J [32] was used to analyze the distributions of areas where Fe_3O_4 was detected from the TXM images. After spatial calibration, a color threshold and sizing algorithm was applied to produce tabular data. The entire TXM image (40 μm × 40 μm) was analyzed for each electrode type.