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Short communication

Toward uniform and ultrathin carbon layer coating on lithium iron phosphate using liquid carbon dioxide for enhanced electrochemical performance

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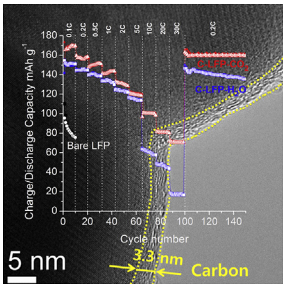
HIGHLIGHTS

- Developing a carbon coating method using liquid carbon dioxide as a solvent.
- Ultrathin and uniform carbon layer coating on $LiFePO_4$ particles.
- Enhanced rate performance of $LiFePO_4$ using small amount of carbon.

GRAPHICAL ABSTRACT



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ABSTRACT

In this communication, uniform and ultrathin carbon coating on $LiFePO_4$ (LFP) particles are performed using liquid carbon dioxide (l-CO_2)-based free-meniscus coating. The uniform and conformal coverage of the carbon layer on LFP with a thickness of 3.3 nm, and a uniform distribution of carbon on the entire surface of the LFP particle are confirmed. The carbon-coated LFP (C-LFP) with a carbon content of 1.9 wt.% obtained using l-CO_2-based coating exhibits a discharge capacity of 169 mAh g^{-1} at 0.1 C and 71 mAh g^{-1} at 30 C, while much lower discharge capacity of 146 mAh g^{-1} at 0.1 C and 17 mAh g^{-1} at 30 C is observed when C-LFP with an optimized carbon content of 6.0 wt.% is prepared using conventional aqueous-based coating.

1. Introduction

In recent years, the development of lithium ion batteries for large-scale applications such as electric vehicles (EV) and energy storage systems (ESSs) has received considerable attention in both

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academic and commercial areas [1,2]. $LiCoO_2$ and graphite, which are currently used for portable electronic devices, are considered not suitable for use in large-scale applications due to the safety concerns and high cost of Co. Lithium phosphates ($LiMPO_4$, M = Fe, Mn, Co) [3], lithium orthosilicates (Li_2MSiO_4, M = Fe, Mn, Co, Ni) [4], lithium titanium oxides ($Li_4Ti_5O_{12}$), and titanium dioxide (TiO_2) [5] are of particular interest as alternative active materials due to their safety, low cost, environmental friendliness, and high theoretical capacities. However, the major drawback of the alternative materials is their inherently low electronic conductivities and low ionic conductivities; thus, these materials typically suffer from poor rate-capability [3–6].

The reduction of particle size to a nanoscale dimension to enhance lithium ion diffusivity [7,8] and carbon coating to increase electronic conductivity [9,10] are the most widely used strategies to improve the performance of the potential active materials. Nano-sized particles, however, also result in other undesirable effects such as poor energy density and poor electron transport by particle agglomeration in conductive additive matrix. In addition, the increased surface area by reducing particle size can increase side reactions at the electrode-electrolyte interface, which leads to degradation of composite electrode and capacity decay [6]. Incorporation of too much carbon content, thick carbon layer coating, and non-uniform carbon coating on individual particles can also deteriorate energy density and battery performance [6,11–13]. For example, a carbon layer that is too thick can hinder lithium ion diffusion at a high charge/discharge rate [13]. The complete, uniform, and thin carbon layer coverage ensures that the particles receive electrons from all directions and the electrons penetrate easily through the carbon layer, resulting in low polarization and high-rate performance [10,14]. Thus, in view of simple composite electrode processing, high energy density, and high battery performance, finding an effective way to coat an ultrathin and uniform carbon layer on micron-sized active materials, that can result in satisfactory rate performance, needs to be given careful attention. Although many approaches have been proposed to form a uniform carbon layer on individual particles such as *in situ* polymerization [14], double carbon coating [15], and chemical vapor deposition [16], considerable efforts are still underway to develop more reliable, simpler, and less-expensive techniques that can produce the complete coverage of the ultrathin carbon layer on irregular-shaped individual particles and particle agglomerates.

In this paper, we describe the first use of liquid carbon dioxide (l-CO_2) for uniform and ultrathin carbon layer coverage on nano-to-micron-sized $LiFePO_4$ (LFP) particles. The extremely low surface tension of l-CO_2 ($0.00195\ J\ m^{-2}$ at 15 °C) makes it an excellent wetting agent and facilitates the penetration of carbon precursors into small pores between particle agglomerates. In addition, the low surface tension of l-CO_2, combined with the ability to decouple the coating from solvent evaporation, can alleviate other non-uniformities caused by high surface tension during solvent drying. The low viscosity of l-CO_2 ($0.000074\ N\ s\ m^{-2}$ at 15 °C) can result in thin films and can facilitate carbon precursor diffusion into small pore structures. In addition to the potential to form uniform coating, l-CO_2 is non-toxic, non-flammable, and abundant, so that sustainable and clean coating process can be possibly developed. In previous literature, it has been shown that highly uniform and ultrathin organic and polymeric film can be coated on a planar substrate or a highly porous water treatment membrane using high-pressure free-meniscus coating (hFMC) with l-CO_2 as the coating solvent [17–20]. Free-meniscus coating is a simple and well-established method to deposit a liquid or a solid film by immersing a substrate in a solution vessel, withdrawing the substrate or draining the solution, and drying the solvent. Herein, we demonstrate that complete coverage of a uniform and ultrathin carbon layer on LFP particles can be obtained by hFMC with l-CO_2 with subsequent calcination at a mild condition.

2. Materials and methods

Detailed description on materials, synthesis of LFP and coating procedure is given in the supplementary data. A schematic representing the synthesis of carbon-coated LFP (C-LFP) using l-CO_2 hFMC is shown in Fig. 1. Details on the l-CO_2 hFMC apparatus are shown in Fig. S1. The LFP particles were placed in a high-pressure coating vessel and sucrose octaacetate (SOA) as a carbon precursor dissolved in l-CO_2 was charged into the vessel. Because of its high solubility in l-CO_2, SOA was used as the carbon precursor in this study. It is noted that other carbon precursors that are well-soluble in l-CO_2 can be also used as carbon precursors. The l-CO_2 solution was drained at the bottom of the vessel, so that SOA was coated on the LFP particles by solution film entrainment. The evaporation of l-CO_2 was controlled by adjusting the evaporation driving force (ΔP) to 2 MPa. The SOA-coated LFP (SOA-LFP) was then calcined under a 5 wt.% H_2/Ar flow condition at 600 °C for 3 h, producing C-LFP-CO_2.

3. Results and discussion

The formation of a highly crystalline LFP phase using a solid-state method can be seen in the X-ray diffraction (XRD) patterns (Fig. S2). All the peaks can be indexed as the olivine LFP phase. Primary LFP particles with sizes of 150–350 nm are highly agglomerated and pores with diameters of 100–250 nm between the particles are observed (Fig. S3). After l-CO_2 hFMC, SOA films on LFP particles and SOA nanowires that are connected between the SOA-LFP agglomerates are visible (Fig. 2a). The SOA nanowires are also observed in SOA-LFP prepared at the low SOA concentrations of 9–20 wt.% (Fig. S4). The evaporation of l-CO_2 during the solution drainage may cause the nanowire to form by SOA precipitation between the particles. After the calcination, the SOA films are not observed in the SEM image (Fig. 2b), but carbon nanowires connected between the particles are clearly visible (Fig. S5). The phase structure of LFP is maintained under the mild carbon coating condition (Fig. S2) and the carbon formation can be confirmed by Raman spectra (Fig. S6). The uniform and conformal coverage of the carbon layer on LFP with a thickness of 3.3 nm is shown in Fig. 2c and Fig. S7. The carbon map shown in Fig. 2d exhibited a uniform distribution of carbon on the LFP particle. Thus, electrons are expected to access the particles from all directions, which is expected to enhance the electrochemical performance of the active material. When a conventional aqueous solution-based carbon coating method is used, however, the LFP surface is not uniformly covered with a thin carbon layer, as shown in Fig. S8 (C-LFP-H_2O) and reported previously [21]. In addition, an amorphous carbon region partially covering the LFP surface is observed. The significantly greater uniform coverage of the carbon layer on LFP prepared using l-CO_2 hFMC is possibly a result of the facilitated penetration of the coating solution and uniform solution entrainment on individual LFP particles by using the benefits of the low surface tension and low viscosity of l-CO_2.

The galvanostatic charge–discharge curves at 0.1 C rate, along with the cycling performance up to 30 cycles of bare LFP, C-LFP-CO_2, C-LFP-H_2O at room temperature, are shown in Fig. 3. The carbon content in the C-LFP is presented in the parenthesis of each sample code. The bare LFP shows a low initial discharge capacity of 90 mAh g^{-1} and a large polarization due to poor electronic conductivity. The Li/C (1.9 wt.%)-LFP-CO_2 cell exhibits an extremely flat voltage plateau at ~3.4 V (vs. Li) during the charge–discharge process, which corresponds to the two-phase solid-state reaction