



Full paper

New liquid carbon dioxide based strategy for high energy/power density LiFePO₄Jieun Hwang^a, Ki Chun Kong^b, Wonyoung Chang^c, Eunmi Jo^c, Kyungwan Nam^d, Jaehoon Kim^{a,e,*}^a School of Mechanical Engineering, Sungkyunkwan University, 2066 Seobu-ro, Jangnan-gu, Suwon, Gyeonggi-do 16419, Republic of Korea^b CM Partner INC, 810, Seoul Techno Park, 232, Gongneung-ro, Nowon-gu, Seoul 01811, Republic of Korea^c Center for Energy Convergence, Korea Institute of Science and Technology, Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea^d Department of Energy and Materials Engineering, Dongguk University, Seoul 04620, Republic of Korea^e Sungkyun Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, 2066 Seobu-ro, Jangnan-gu, Suwon, Gyeonggi-do 16419, Republic of Korea

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ABSTRACT

A liquid carbon dioxide (*l*-CO₂) based coating approach is developed for ultrathin, uniform, and conformal carbon coating of hierarchically mesoporous LiFePO₄ (LFP) nano/microspheres for fabricating high-energy-density and high-power-density carbon coated LFP (C-LFP) with long-term cyclability. The unique properties of *l*-CO₂ result in an ultrathin carbon layer (1.9 nm) distributed all over the primary nano-sized LFP particles (20–140 nm in diameter), forming a core (LFP)-shell (carbon) structure. This unique structure provides facile penetration of liquid electrolytes and rapid electron and Li-ion transport. C-LFP exhibits high reversible capacity, high energy and power density (168 mAh g⁻¹ at 0.1 C, 109 Wh kg⁻¹ and 3.3 kW kg⁻¹ at 30 C, respectively) with excellent long-term cyclability (84% cycle retention at 10 C after 1000 cycles). In addition, the ultrathin and uniform carbon layer of the mesoporous microspheres allows a high tap density (1.4 g cm⁻³) resulting in a high volumetric energy density (458 Wh L⁻¹ at a 30 C rate). Furthermore, C-LFP presents a high capacity and stable cycling performance under low-temperature and high-temperature environment. Well-developed carbon coating approach in this study is simple, scalable, and environmentally benign, making it very promising for commercial-scale production of electrode materials for large-scale Li-ion battery applications.

1. Introduction

Olivine-structured lithium iron phosphate (LiFePO₄, LFP) is considered one of the most promising cathode materials for next-generation, large-scale Li-ion batteries (LIBs) such as those required for electric vehicles (EVs), plug-in hybrid electric vehicles (PHEVs), and energy storage systems (ESSs) [1–6]. The two most promising approaches to improve the electrochemical performance of LFP are reducing its particle size to the nanometer scale and carbon coating its surface. Reduction in particle size can improve the diffusion of Li ions into one dimension channels in the LFP phase, and this helps improve the power density [7,8]. However, nanometer-sized LFP exhibits very low tap densities (< 1.0 g cm⁻³), which in turn causes low volumetric energy density. In addition, even though the high surface area of the particles—caused by reducing the particle size—provides fast Li-ion transport from the electrolyte to the electrode surface, it also leads to undesirable side reactions at the electrode-electrolyte interface (e.g.,

Fe²⁺ dissolution), which have detrimental effects on the long-term cyclability. Carbon coating the LFP surface can inhibit side reactions at the electrode-electrolyte interface and surface oxidation caused by air/water under ambient conditions. In addition, the inherently low electronic conductivity of pristine LFP can be improved by applying a carbon coating, leading to enhanced power density. However, incorporation of a large amount of carbon in thick layers decreases both the volumetric and gravimetric energy densities and hinders Li-ion diffusion into the active phase [5]. Efforts to decrease the carbon content, on the other hand, can lead to incomplete carbon coverage of the LFP surface, which lowers the power density and fails to inhibit side reactions.

Recently, hierarchically mesoporous nano/micro structures, in which nanosized primary particles are loosely aggregated by forces such as van der Waals interactions and form micron-sized porous particles, have received considerable attention because hierarchical structures exhibit the advantages of both nanosized particles (e.g., fast

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