A novel double-structured LiMn$_{0.85}$Fe$_{0.15}$PO$_4$ – LiFePO$_4$ core-shell materials for rechargeable lithium-ion batteries

Seung-Min Oh$^{a, b}$, Seung-Taeg Myung$^c$, Jin Beom Park$^a$, Bruno Serosi$^a$, Khalil Amine$^a$, and Yang-Kook Sun$^a$$^{a,b}$

$^a$ Department of WCU Energy Engineering, $^b$ Department of Chemical Engineering, Hanyang University, Seoul 133-791, Republic of Korea
$^c$Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747, Republic of Korea
$^d$Department of Chemistry, University of Rome Sapienza, 00185, Rome, Italy
$^e$Electrochemical Technology Program, Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

Introduction

Olivine-type LiFePO$_4$ has been extensively studied owing to its low cost, environmental friendliness, and in particular, superior thermal stability at the deeply charged state. Use of a carbon coating significantly improved the intrinsic poor electronic conductivity, to $< 10^{-10}$ S cm$^{-1}$, from $\sim 10^{-8}$ S cm$^{-1}$ at room temperature, and therefore, this material has undergone intensive investigation for large-scale lithium battery applications. [1,2] LiMnPO$_4$ which is an isomorph of LiFePO$_4$ is a more promising electrode material than LiFePO$_4$ as a result of its higher operation voltage (4.1 V vs. Li/Li$^+$). However, LiMnPO$_4$ also suffers from poor electronic conductivity ($< 10^{-10}$ S cm$^{-1}$) and cycle life due to Mn dissolution, like Mn spinel. High energy density is required for mid- to large-scale batteries and other energy storage applications. This constraint necessitates use of micron-sized particles to yield high volumetric energy density and reliable battery performance. [3]

In this study, we synthesized the new concept of double-structured LMFP/LFP materials varying LiFePO$_4$ outer layer thickness onto LiMn$_{0.85}$Fe$_{0.15}$PO$_4$ bulk, for practical LIB systems through fine tuning of physical characteristics such as tap density, porosity, and spherical morphology and investigated its electrochemical performance and thermal stability.

Experimental

To synthesize the bulk hydrates, H$_3$PO$_4$ (Sigma-Aldrich, ≥ 85 wt%, solution in water) and ethanol were poured into a continuously stirred tank reactor (capacity of 4 L). Next, Mn(NO$_3$)$_2$$\cdot$4H$_2$O and Fe(NO$_3$)$_3$$\cdot$9H$_2$O were dissolved in a continuously stirred tank reactor (capacity of 4 L). Next, ≥ (≤ 10$^{-10}$ S cm$^{-1}$) and cycle life due to Mn dissolution, like Mn spinel. High energy density is required for mid- to large-scale batteries and other energy storage applications. This constraint necessitates use of micron-sized particles to yield high volumetric energy density and reliable battery performance. [3]

In this study, we synthesized the new concept of double-structured LMFP/LFP materials varying LiFePO$_4$ outer layer thickness onto LiMn$_{0.85}$Fe$_{0.15}$PO$_4$ bulk, for practical LIB systems through fine tuning of physical characteristics such as tap density, porosity, and spherical morphology and investigated its electrochemical performance and thermal stability.

To synthesize the bulk hydrates, H$_3$PO$_4$ (Sigma-Aldrich, ≥ 85 wt%, solution in water) and ethanol were poured into a continuously stirred tank reactor (capacity of 4 L). Next, Mn(NO$_3$)$_2$$\cdot$4H$_2$O and Fe(NO$_3$)$_3$$\cdot$9H$_2$O were dissolved in ethanol with a molar ratio of 0.85:0.15. The dissolved metal solution was poured into the reactor and then reactor stirred (1000 rpm) for 4 hr at 40 °C to obtain a gray-green micron-sized Mn$_{0.85}$Fe$_{0.15}$PO$_4$ hydrate powder (see SI-Fig. 2). The precipitated powders were filtered, washed, and added to the reactor with distilled water. The as-synthesized bulk hydrates were transferred to the next reactor. Then, Fe(NO$_3$)$_3$$\cdot$9H$_2$O and H$_3$PO$_4$ were separately dissolved in distilled water with a molar ratio of 1:1. Next, sucrose was dissolved in an aqueous solution of Fe(NO$_3$)$_3$$\cdot$9H$_2$O at 0.2 to 1 molar ratio of Fe(NO$_3$)$_3$$\cdot$9H$_2$O. The prepared aqueous solution was pumped into a continuously stirred tank reactor (capacity of 4 L), which added bulk precursor with distilled water. An aqueous NH$_4$OH solution was also pumped into the reactor to control the solution pH. The concentration (2 M), pH (2), temperature (50 °C), and stirring speed (1000 rpm) of the resulting mixture were precisely controlled. The resulting Mn$_{0.85}$Fe$_{0.15}$PO$_4$–FePO$_4$ hydrate powders were filtered, washed, and vacuum-dried at room temperature, then heat-treated at 500 °C for 1 h in air to obtain a crystalline anhydrous Mn$_{0.85}$Fe$_{0.15}$PO$_4$ powder precursor, which was poured into an ascorbic acid solution (3 wt%).

The latter was dried at 110 °C to obtain ascorbic acid-coated Mn$_{0.85}$Fe$_{0.15}$PO$_4$ powders that were mixed with a stoichiometric amount of Li$_2$CO$_3$ (lithium source) and pitch (2 wt%) as a second carbon source. The resulting mixture was calcined for 15 h at 700 °C in a furnace purged with an Ar/H$_2$ (96/4 by vol %) mixture. Powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) using Cu-Ka radiation was performed to identify the crystal structure of the synthesized material. Electrochemical properties of the synthesized powders were evaluated using a 2032-type coin type cell.

Results and discussion

A LiMn$_{0.85}$Fe$_{0.15}$PO$_4$ particle modified by LiFePO$_4$ layer (thickness of 0.5 μm) was cross sectioned by a focused ion beam cut (Fig. 1a). The microscopic images indicate numerous pores in both the bulk and outer layer (Figs. 1b and c). The primary particles seem to agglomerate more densely in the outer layer than the particle bulk due to the smaller particle size of LiFePO$_4$ (Fig. 1c). Relatively thick carbon layer, which is seen in the outer layer, is mainly associated with carbonization of ascorbic acid and pitch (Fig. 1d). The carbon covers the primary particles in both bulk and outer layer and the surface of the outer layer at the decades of nanometer level. The EELS image also indicates an open network of interconnected nano-sized pores distributed throughout the interior of the particles.

References