Synthesis of high-energy-density $LiMn_2O_4$ cathode through surficial Nb doping for lithium-ion batteries

Wensheng Yang, Gang Li, Xu Chen, Yanluo Lu

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China

E-mail: yangws@mail.buct.edu.cn

Because of the scarcity of Ni and Co reserves and the explosive demands of Li-Ni-Co-Mn-O_2 materials for EVs, the prices of Ni and Co rise quickly [1]. Due to the high abundance and low cost of Mn, the spinel $LiMn_2O_4$ is considered as a promising cathode to replace part of $LiCoO_2$ or Li-Ni-Co-Mn-O_2 to reduce the LIBs' cost [2]. However, the practical application of commercial $LiMn_2O_4$ materials is greatly limited because of their low energy density.

In this work, Nb-doped $LiMn_2O_4$ with different amount of Nb were synthesized by high-temperature solid state reaction with the electrolytic MnO_2 (EMD), Li_2CO_3, and Nb_2O_5 as the raw materials. Scanning electron microscopy (SEM) suggests that the morphology of $LiMn_2O_4$ particles transforms from conventional octahedral appearance into truncated octahedral or spherical-like appearances with the Nb doping amount increasing to 0.01 and 0.03, respectively. Besides, the primary particle size also increases from ~200 nm to ~1 μm. Auger electron spectroscopy (AES) and X-ray diffraction (XRD) characterizations confirm that Nb^{5+} enrich in the surficial layer of $LiMn_2O_4$ particles to form a $LiMn_{2-x}Nb_xO_4$ phase. Compared with the pristine $LiMn_2O_4$, the capacity of $LiMn_{1.99}Nb_{0.01}O_4$-based 18650R-type battery increases from 1497 to 1705 mAh with the volumetric energy density increasing from 344 to 392 $Wh{\cdot}L^{-1}$, benefiting from the joint increments of the specific discharge capacity from 119.5 to 123.7 $mAh{\cdot}g^{-1}$ and the compacted density from 2.81 to 3.10 $g{\cdot}cm^{-3}$. Besides, the capacity retention after 500 cycles at 1 C (1500 mA) is also improved by 17.1%. The increased specific discharge capacity is attributed to the more Mn^{3+} caused by Nb^{5+} doping, the reduced grain boundary resistance, and better rate performance. The enhanced cyclic performance is attributed to the reduced specific surface area, which reduces the Mn^{2+} dissolution. It is a significant breakthrough to greatly enhance the energy density of the commercial $LiMn_2O_4$ materials.

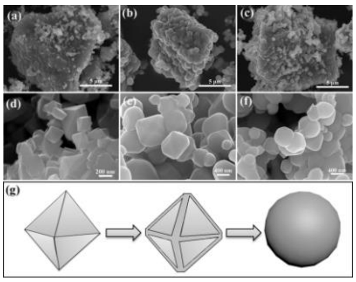

Fig. 1. SEM images of $LiMn_{2-x}Nb_xO_4$: x = (a, d) 0.0, (b, e) 0.004, and (c, f) 0.03.

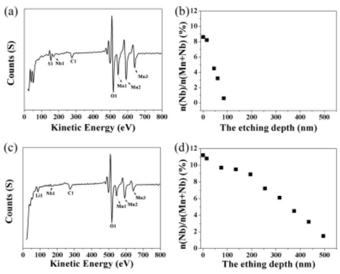

Fig. 2. AES of the $LiMn_{2-x}Nb_xO_4$ particles: x = (a, b) 0.01 and (c, d) 0.06.

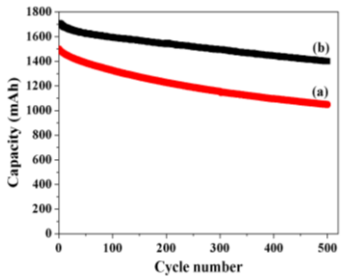

Fig. 3. Cyclic performance of $LiMn_{2-x}Nb_xO_4$-based 18650R-type cell: x=(a) 0.00, (b) 0.01

References:

[1] S. Ahmed, P.A. Nelson, K.G. Gallagher, N. Susarla, J. Power Sources, 342 (2017) 733-740.

[2] P. Albertus, J. Christensen, J. Newman, J. Electrochem. Soc., 156 (2009) A606-A618.