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

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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·L^{-1}, benefiting from the joint increments of the specific discharge capacity from 119.5 to 123.7 mAh·g^{-1} and the compacted density from 2.81 to 3.10 g·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: