

Synthesis and Characterization of Ru Doped Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with Improved High-Rate Performance

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Synthesis and Characterization of Ru doped spinel
LiNi_{0.5}Mn_{1.5}O₄ with Improved High-rate Performance
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High operation voltage and reversible capacity make LiNi_{0.5}Mn_{1.5}O₄ with spinel structure a promising candidate for the cathode of next generation lithium ion batteries (1). However, its low conductivity resulting in small accessible capacity and poor cyclic performance at high current rates restricts its application in high power application such as electric vehicles. Nano-sized LiNi_{0.5}Mn_{1.5}O₄ has demonstrated greatly improved high-rate performances through decrease the charge transport length (2-3). However, the use of nanometric material with large surface area may cause detrimental reaction with electrolyte, poor inter-particle contacts and low electrode density. Doping 3d transition metals such as Cr, Fe, Co and Cu (4-7) has been proved as an effective way to improve the electrochemical performance of the LiNi_{0.5}Mn_{1.5}O₄. While doping 4d transition metal with heavier atomic mass is rarely reported mainly due to the consideration of damage of theoretical capacity. Recently our group using 4d transition metal oxide RuO₂ synthesized the novel spinel LiNi_{0.5-2x}Ru_xMn_{1.5}O₄ (x=0.01,0.03,0.05) by simple solid state reaction. Their crystal structure, morphology, chemical composition, and conductivity have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electrochemical impedance spectrum (EIS). The Rietveld refinement analysis of XRD profiles suggests that all synthesized products including LiNi_{0.5}Mn_{1.5}O₄ adopt cubic spinel structure with a space group of *Fd3m* (Fig 1). Selected area electron diffraction (SAED) patterns in [100] zone also confirm the refinement results. The EDS results on single particles indicate that Ru has been successfully doped into the crystal lattice. SEM morphology shows that the particle size ranges between 0.5 and 1 μm. EIS measurement shows that after doping Ru, the room temperature electrical conductivity is several times higher than that of the non-doped LiNi_{0.5}Mn_{1.5}O₄ (Fig 2). Electrochemical performances were measured through cycling batteries between 3 and 5 V at various C rate (1C=147mA/g). The Ru doped LiNi_{0.5}Mn_{1.5}O₄ spinels show outstanding rate capabilities. At 0.2C discharge rate, all of them could deliver nearly 130mAh/g. At 10C discharge rate, the LiNi_{0.4}Ru_{0.05}Mn_{1.5}O₄ can deliver 117mAh/g while the LiNi_{0.5}Mn_{1.5}O₄ can only release only 58mAh/g. Cyclic performance was tested at 10C charge/discharge rate for 500 cycles. The LiNi_{0.5}Mn_{1.5}O₄ initially can deliver 66mAh/g, and less than 40mAh/g can be released at 500th cycle. While, the LiNi_{0.4}Ru_{0.05}Mn_{1.5}O₄ exhibits excellent cyclic performance, which initially can offer 111mAh/g and still maintain 93mAh/g at the 500th cycle (Fig 3). The large accessible capacity and excellent cyclic performance can be attributed to the great improvement in conductivity through doping Ru.

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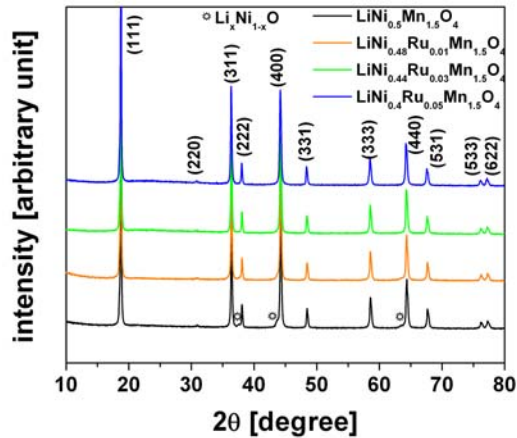


Fig 1(XRD profiles of the LiNi_{0.5-2x}Ru_xMn_{1.5}O₄ (x=0, 0.01, 0.03 and 0.05).)

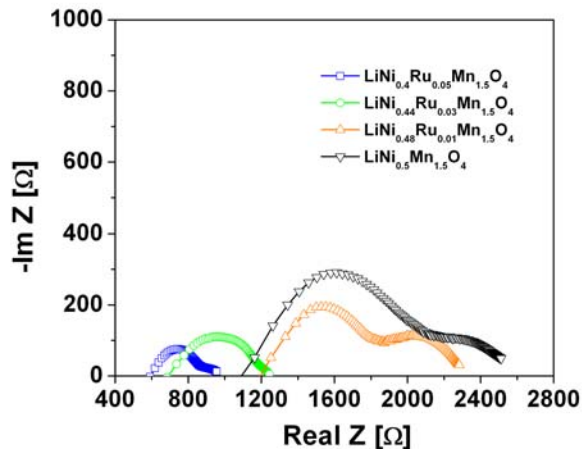


Fig 2 (EIS comparison of the LiNi_{0.5-2x}Ru_xMn_{1.5}O₄ (x=0, 0.01, 0.03 and 0.05).)

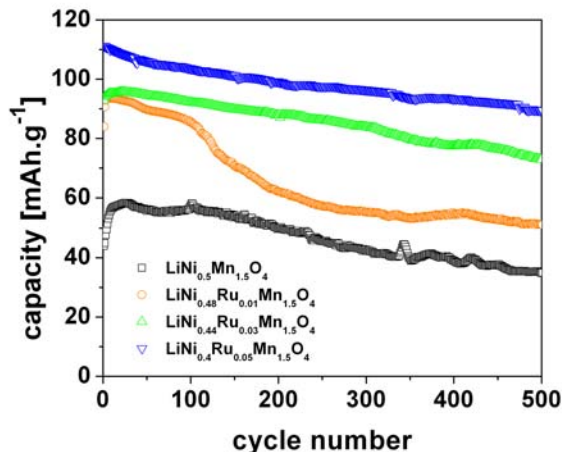


Fig 3 (Cyclic performance of the LiNi_{0.5-2x}Ru_xMn_{1.5}O₄ (x=0, 0.01, 0.03 and 0.05) at 10C charge/discharge rate.)