Synthesis, structure and electrochemical performance of Ni-substituted Ru-based Li-rich Cathode Materials ($Li_2Ru_{1-x}Ni_xO_{3-\delta}$)

Shiyao Zheng [a], Feng Zheng [b], Jue Wu [a], and Yong Yang [a]
[a] *Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surface, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005*
[b] *Department of Physics, Xiamen University, Xiamen 361005*

E-mail: zsyxmu2013@163.com

Extensive Studies about high capacity Li-rich cathode materials are being carried out in recent time. The anionic redox reaction in Ru-based Li-rich materials were proved to be more reversible due to higher covalency between Ru with 4d orbitals and O. In this work, a series of Ni-substituted Ru based Li-rich materials are successfully synthesized. Besides, the structural transformation and electrochemical performances of the materials are studied for understanding the mechanism of the anionic redox reaction in Li-rich materials.

The structure of LRO can be indexed to a layered one with a monoclinic C2/c space group, which corresponds to previous works. However, as the amount of Ni rises, a transformation of the diffraction peaks can be observed. It can be found that peak (004) and (131) merge into one from x = 0 to 0.5, and so do peak (-314) and (060), which shows a phase transformation after the Ni-substitution. For x = 0, the LRO material possesses a layered structure, just as mentioned above. However, for $x \geq 0.3$, it can be indexed to a 3D structure with a cubic $Fd\bar{3}m$ space group. Between these two conditions (x = 0.1 and 0.2), a coexistence of both two phases occurs. The corresponding structure and structural transformation of the electrodes during charging/discharging process has been investigated by ex-situ/in-situ XRD experiements and theoretical simulations.

The specific capacity of LRO and LRNO can achieve all ~250 mA g^{-1} for $0 \leq x \leq 0.4$, and diminish a little for x = 0.5. It is obvious to find a new discharge plateau below 2.3 V, which becomes longer as the Ni content rises. This can be related to the phase transformation mentioned above. Besides, according to the dQ/dV curves, the oxidation peak at 4.25 V in LRO, which is commonly considered to be related to oxygen oxidation, shifts to a lower potential. This may indicate a reduction of the oxygen reaction potential as the amount of Ni increases. Besides, the reduction peak at about 3.3 V rises to 3.75 V.

In summarization, a new type of Ni-substituted Ru-based Li-rich materials with a 3D structure was successfully synthesized by a simple solid-state method, and a layered-to-3D structural change occurs on the pristine material of LRNO as the amount of Ni rises, followed by a variation of electrochemical performances. Future work of solid state NMR and XPS experiments will be done in order to study the chemical environment of Li^+ ions and the valance change during charge/discharge process.

References:

[1] Sathiya, M., et al., Chem. Mater. 25 (2013) 1121-1131.
[2] Sathiya, M., et al., Nat. Mater. 14 (2015) 230-238.
[3] D. Seo et al., Nat. Chem. 8 (2016) 692-697
[4] J. Lee et al., Science 343 (2014) 529-522