Tuning of Thermal Stability and Ni/Li Disordering in Layered $Li(Ni_xMn_yCo_z)O_2$

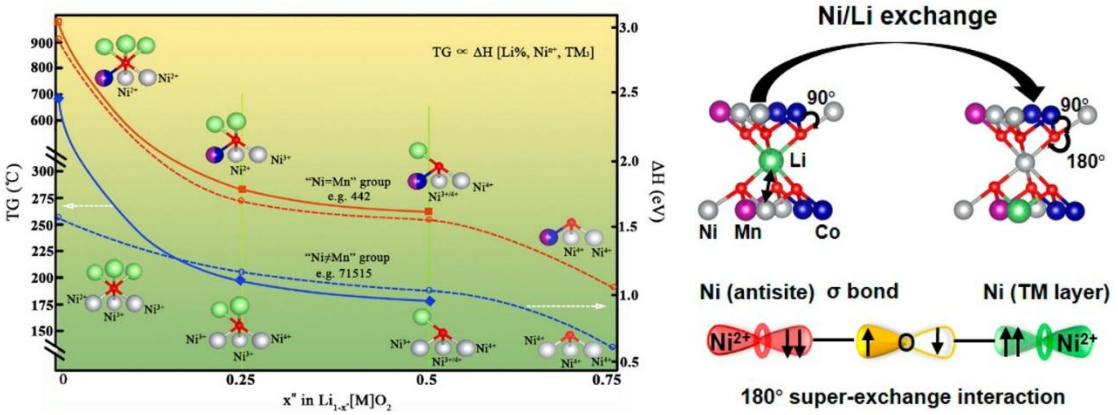
Jiajie Liu, Jiaxin Zheng, Tongchao Liu and Feng Pan

School of Advanced Materials, Peking University, Shenzhen Graduate School
Shenzhen 518055, People's Republic of China

E-mail: 1601111598@sz.pku.edu.cn

Using ab initio calculations combined with experiments, we clarified how the thermal stability of $Li(Ni_xMn_yCo_z)O_2$ (NMC) (x + y + z = 1) can be tuned by the most unstable oxygen, which is determined by the local coordination structure unit (LCSU) of oxygen $(TM(Ni, Mn, Co)_3{-}O{-}Li_{3-x'}$, shown in **Scheme 1a**). Under this model, the synergistic effect between Li vacancies and raised valence state of Ni during delithiation process can aggravate instability of oxygen, and oxygen coordinated with more nickel (especially with high valence state) in LSCU becomes more unstable at a fixed delithiation state. The Ni/Li mixing would decrease the thermal stability of the "Ni=Mn" group NMC materials but benefit the thermal stability of "Ni-rich" group, because the Ni in the Li layer would form 180° Ni−O−Ni super exchange chains in "Ni-rich" NMC materials. Mn and Co doping can tune the initial valence state of Ni, local coordination environment of oxygen, and the Ni/Li disorder, thus to tune the thermal stability directly.

Using extensive ab initio calculations combined with experiments, a super-exchange interaction between transition metals is reported (shown in **Scheme 1b**), which plays a dominating role in tuning the Ni/Li disordering in NMC materials. Under this scheme, we also propose a new charge compensation mechanism that describes that after Ni^{3+}/Li^+ exchange the nearest Co^{3+} transforms to Co^{4+} in Ni-rich NMC materials. On the basis of this theory, the existence of Co^{4+} in the pristine Ni-rich NMC samples was predicted for the first time, which was further confirmed by our synchrotron-based soft X-ray absorption spectroscopy.



Scheme 1. Schematic illustration for (a) the tuning of thermal stability in a delithiation process; (b) 180 °Ni^{2+}−O−Ni^{2+} super-exchange interaction.

References:

[1] J. Zheng, T. Liu, Z. Hu, Y. Wei, X. Song, Y. Ren, W. Wang, M. Rao, Y. Lin, Z. Chen, J. Lu, C. Wang, K. Amine, F. Pan, J. Am. Chem. Soc. 2016, 138, 13326-13334.

[2] J. Zheng, G. Teng, C. Xin, Z. Zhuo, J. Liu, Q. Li, Z. Hu, M. Xu, S. Yan, W. Yang, F. Pan, J. Phys. Chem. Lett. 2017, 8, 5537-5542.