

Supporting Information

Surface Changes of $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ in Li-Ion Batteries using In Situ Surface-Enhanced Raman Spectroscopy

Chao-Yu Li^{1,2,}, Yang Yu³, Chen Wang², Yirui Zhang⁴, Shi-Yao Zheng², Jian-Feng Li², Filippo Maglia⁵, Roland Jung⁵, Zhong-Qun Tian^{2,*}, Yang Shao-Horn^{1,3,4}*

¹Research Laboratory of Electronics, MIT, Cambridge, Massachusetts 02139, USA

²State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Xiamen University, Xiamen, China

³Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts 02139, USA

⁴Department of Mechanical Engineering, MIT, Cambridge, Massachusetts 02139, USA

⁵BMW Group, Petuelring 130, 80788 München, Germany

Corresponding Authors

* Zhong-Qun Tian (zqtian@xmu.edu.cn)

* Chao-Yu Li (li_chaoyu@outlook.com)

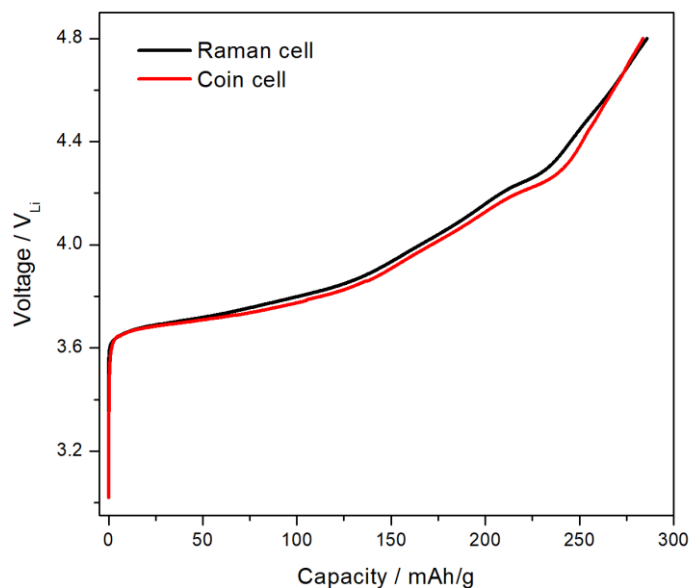


Figure S1. First charge curves of NMC811 composite electrode using an electrochemical Raman cell (black) and a coin cell (red). In the coin cell, a NMC811 electrode is fully covered by Li counter electrode. Both the composite electrodes were charged to 4.8 V_{Li} at a current of ~27.5 mA/g_{NMC}.

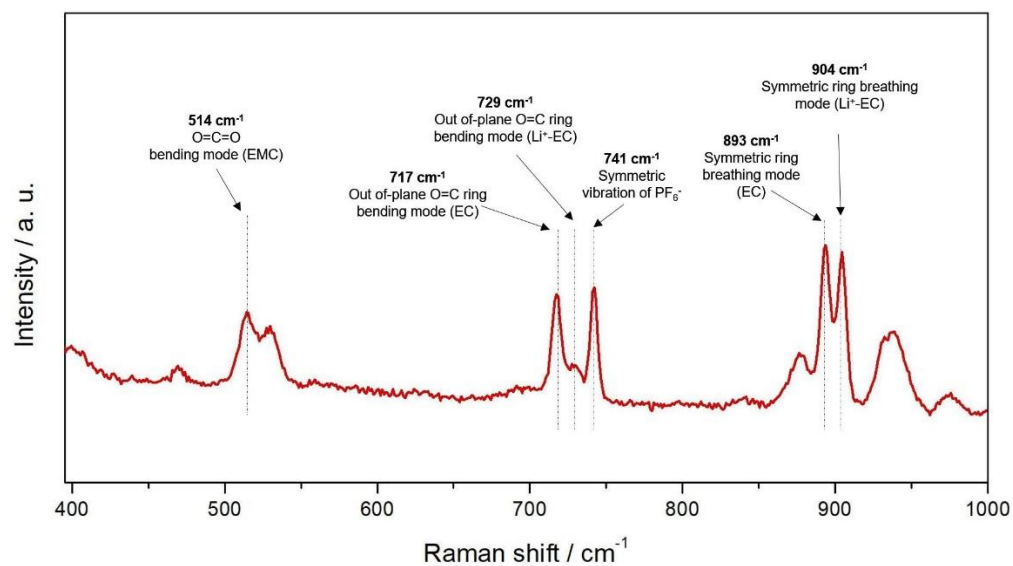


Figure S2. Raman spectrum of LP57 electrolyte [1 M LiPF₆ in a 3:7 EC/EMC electrolyte] and corresponding Raman peak assignments based on literature data¹⁻³.

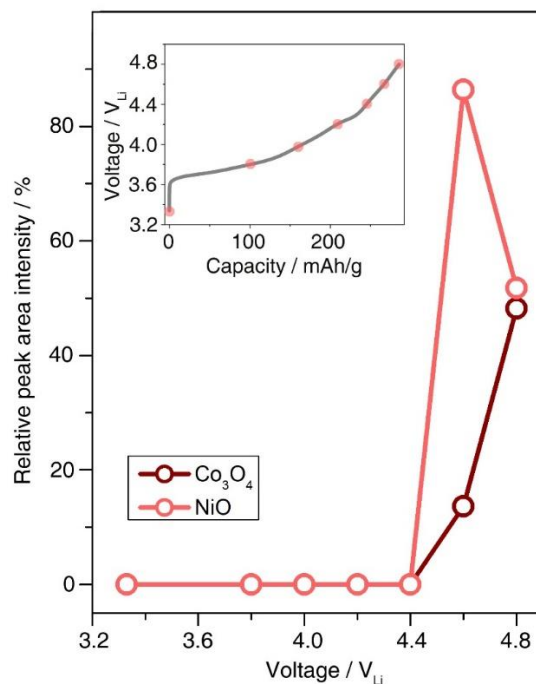


Figure S3. Potential-dependent relative Raman peak area intensities of Co_3O_4 and NiO species on NMC811 composite electrode surface. The inset presents electrochemical profile of NMC811 composite electrode charged to 4.8 V_{Li} at a current of ~ 27.5 mA/g_{NMC}, where the light red spots denote the voltages for Raman acquisitions.

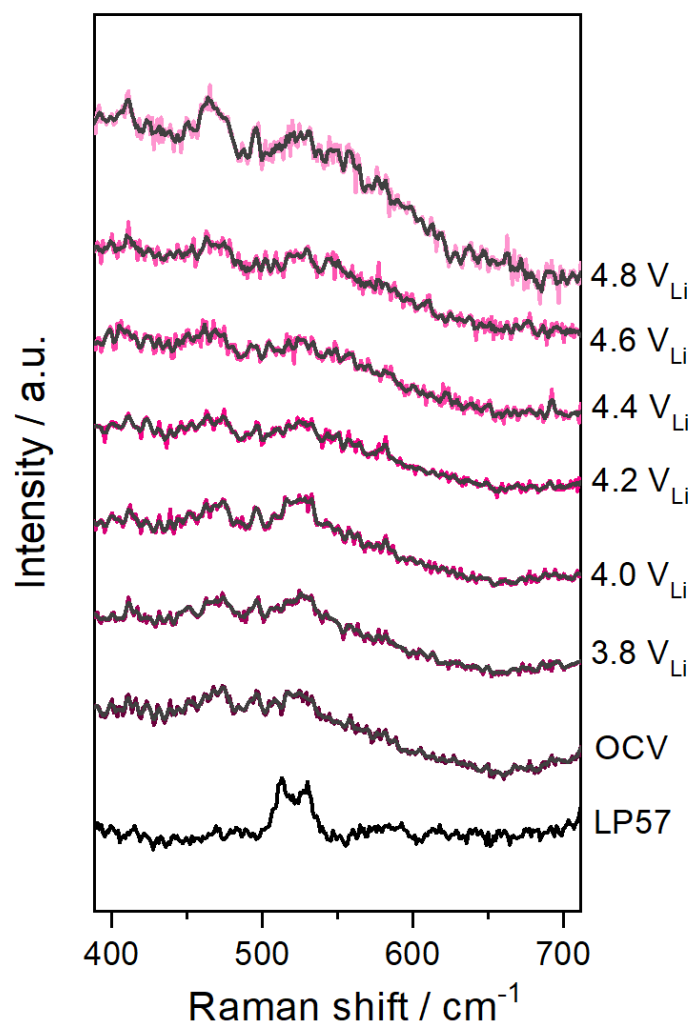


Figure S4. *In situ* electrochemical normal Raman spectra of an NMC811 composite electrode as a function of voltage in presence of LP57 electrolyte (1 M LiPF₆ in 30%EC and 70%EMC). The black curves represent the smoothed results.

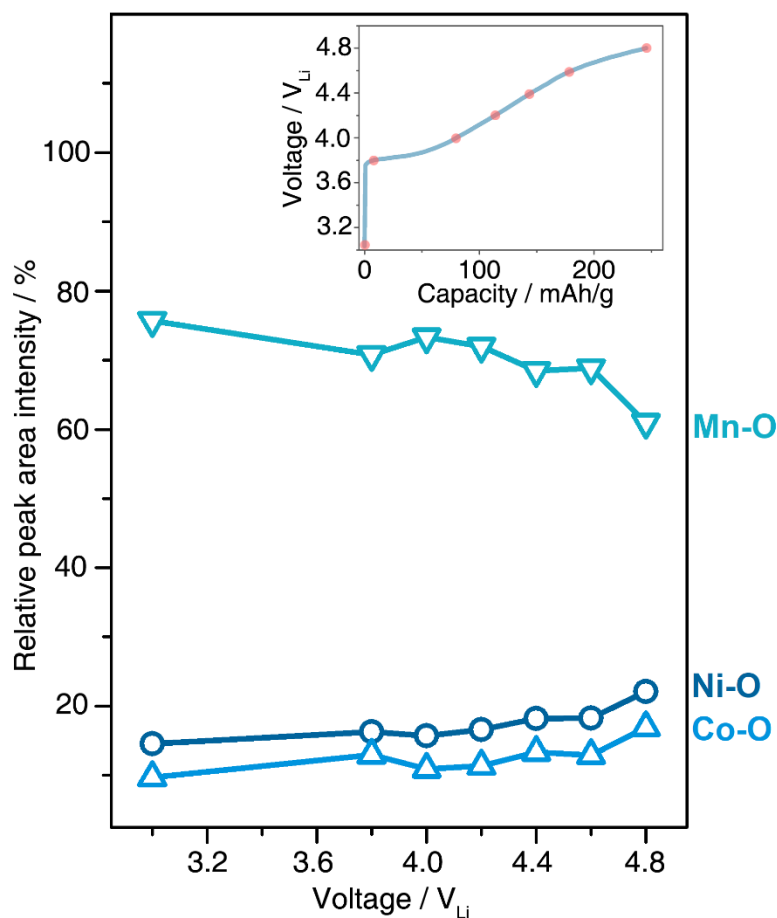


Figure S5. Potential-dependent relative Raman peak area intensities of E_g modes of Ni-O, Co-O and Mn-O bonds on NMC111 composite electrode surface. The inset shows electrochemical profiles of NMC111 composite electrodes charged to 4.8 V_{Li} at a current of 27.5 mA/g_{NMC} (C/10 rate), where the light red dots denote the voltages of Raman acquisitions.

References

1. Katon, J. E.; Cohen, M. D., The Vibrational Spectra and Structure of Dimethyl Carbonate and its Conformational Behavior. *Can. J. Chem.* **1975**, 53, 1378-1386.
2. Hyodo, S.-A.; Okabayashi, K., Raman Intensity Study of Local Structure in Non-Aqueous Electrolyte Solutions—I. Cation-Solvent Interaction in LiClO₄/Ethylene Carbonate. *Electrochim. Acta* **1989**, 34, 1551-1556.
3. Klassen, B.; Aroca, R.; Nazri, M.; Nazri, G. A., Raman Spectra and Transport Properties of Lithium Perchlorate in Ethylene Carbonate Based Binary Solvent Systems for Lithium Batteries. *J. Phys. Chem. B* **1998**, 102, 4795-4801.