

# ORIGINS OF HCMR<sup>TM</sup> CATHODES DEGRADATION

V. Battaglia, G. Chen, W. Chen, G. Liu, D. Membreno, K. Persson, A. Shukla, L. Terborg,  
T. Yi and R. Kostecki

*Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory  
1 Cyclotron Road, Berkeley, CA 94720, USA  
r\_kostecki@lbl.gov*

High capacity manganese rich (HCMR<sup>TM</sup>) materials are promising candidates for commercial Li-ion battery positive electrodes for applications in electric and plug-in hybrid electric vehicles.<sup>1</sup> These oxides, also denoted as  $x\text{LiMO}_2 - (1-x)\text{LiMnO}_3$  ( $M = \text{Co, Mn, Ni}$ ), deliver a high discharge capacity ( $>240$  mAh/g) at operating voltages exceeding 3.5 V vs. Li/Li<sup>+</sup>.<sup>2</sup> However, these materials have significant limitations and suffer from high first cycle irreversible capacity loss, impedance rise and voltage fade during cycling.<sup>2-4</sup>

This study provides an overview about possible scenarios which could lead to the DC resistance rise observed within a cycle and with cycle life in high capacity manganese rich positive electrode materials (HCMR<sup>TM</sup>). The structure and possible structural changes of the pristine and aged HCMR<sup>TM</sup> material are discussed. Preliminary evaluations of the material suggest a single phase, aperiodic crystal consisting of monoclinic domains. *In situ* Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and potentiostatic intermittent titration technique (PITT) are discussed providing information about structural changes of the surface, surface layer formation and Li<sup>+</sup> diffusivity. Raman spectroscopy suggests transformation to a spinel like structure after aging and FTIR spectroscopy indicates dynamic formation of a surface film, growing with cycle number. The Li<sup>+</sup> diffusivity in HCMR<sup>TM</sup> varies as a function of potential and correlates strongly with DC-R behavior. Changes in impedance as well as in cell parameters during and with cycling show morphology and topology changes of the HCMR<sup>TM</sup> material. The electrode composite and the material itself contribute to the long term impedance rise with prolonged cycling.

## Acknowledgements

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, under the Applied Battery Research for Transportation (ABR) Program and Award Number DE-EE0006443.

## References

1. M. M. Thackeray, S. H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek and S. A. Hackney, *J Mater Chem*, **17**, 3112 (2007).
2. Y. Li, M. Bettge, B. Polzin, Y. Zhu, M. Balasubramanian and D. P. Abraham, *J. Electrochem. Soc.*, **160**, A3006 (2013).
3. K. J. Carroll, D. Qian, C. Fell, S. Calvin, G. M. Veith, M. F. Chi, L. Baggetto and Y. S. Meng, *Phys Chem Chem Phys*, **15**, 11128 (2013).
4. D. Mohanty, A. S. Sefat, S. Kalnaus, J. L. Li, R. A. Meisner, E. A. Payzant, D. P. Abraham, D. L. Wood and C. Daniel, *J Mater Chem A*, **1**, 6249 (2013).