

Hysteresis and Voltage Fade in Lithium- and Manganese-Rich Transition Metal Oxide Electrodes

Kevin G. Gallagher^a, Jason R. Croy^a, Mahalingam Balasubramanian^b, Michael M. Thackeray

^a Chemical Sciences and Engineering Division,

^b X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois 60439 USA

Lithium- and manganese-rich transition metal layered oxide (LMR-NMC) positive electrodes are a promising candidate to increase the energy density and lower the cost of transportation batteries. In this presentation, we report a direct connection between the observed phenomena of hysteresis and voltage fade in LMR-NMC electrode materials.^{1,2}

Figure 1 displays critical electrochemical measurements on lithium half cells using electrodes of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25}\text{O}_2$, or in standard notation $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.10}\text{O}_2$ (Toda HE5050), that exhibit both the hysteresis and voltage fade phenomena. The galvanostatic cycling curves for the 3rd and 50th cycle show a clear change in both the charge and discharge voltage curves to lower values (i.e. voltage fade). The inset in Figure 1 displays the 3rd cycle dQ/dV with scanning curves measured between 2-4.1 V and 3.7-4.7 V. A significant amount of the lithium sites that are emptied above 4.1 V are not refilled until discharging to a potential of ~ 3.3 V (i.e. a 1 V hysteresis) as communicated by Croy et al.¹

The connection between voltage fade and hysteresis was elucidated in a cycling window study that was undertaken to tease out the accelerating factors related to voltage fade.² The testing protocol measured an IR corrected average voltage before and after an electrochemical cycling window exposure. The cycling windows chosen for the truncated voltage window cycling all included 4.7 V as the high voltage to utilize a large fraction of the total lithium content. The lower voltage window cutoff was varied among different samples to map out the mechanistic space. Figure 2 displays the fade in average OCV on discharge as a function of lower voltage cutoff between the 2nd and 23rd cycles as a function of lower voltage cutoff during the truncated cycles. The greatest voltage fade occurs when cycling from a high voltage, such as 4.7 V, to a lower voltage, below ~ 3.4 V. To explore the calendar time dependence, the cycling data was transformed to a calendar time plot and additional data points were measured. The earlier test protocol was repeated on each of the same samples to put up to 65 cycles on the same coin cells. New coin cells were also made and tested with a potentiostatic hold at 4.7 V for 120, 240, 360, or 480 hours rather than continuous cycling in a truncated window.

Figure 2 (inset) presents the calendar time (total time on test) behavior of all of the different samples. Once again, it is shown that cycling between 4.7 V and 3.2 V accelerates voltage fade more than any other electrochemical exposure. The calendar time study shows a greater extent of voltage fade for the shortest hold of 120 hours relative to the equivalent 2-4.7 V cycling data; however, holding the electrode material at 4.7 V for longer periods of time only modestly increases the extent of voltage fade. From this observation, we may conclude that while calendar time is important, cycling to low potentials is necessary to significantly accelerate voltage fade. Moreover, the same critical potential, ~ 3.2 V, is observed for the hysteresis and voltage fade phenomena.

These observations lead us to some mechanistic insights and in-turn a phenomenological model for the interrelationship between hysteresis and voltage fade.

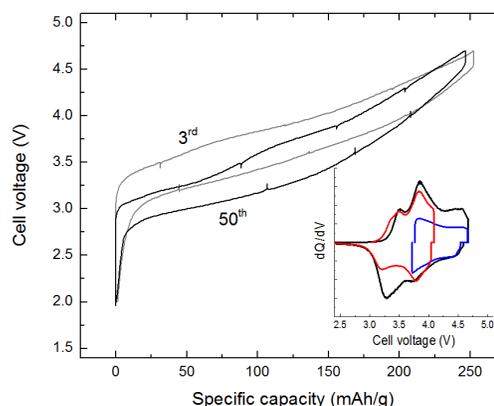


Figure 1. Voltage fade and (inset) hysteresis in the electrochemical profiles of a Li/Toda HE5050 half cell

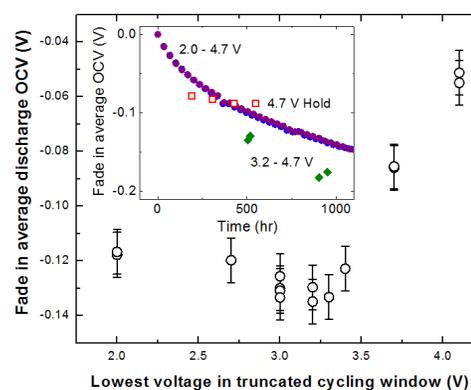


Figure 2. Fade in the average OCV on discharge as a function of the lower cut-off voltage between the 2nd and 23rd cycles (inset) transformed to calendar time.

Acknowledgment

Support from the Vehicle Technologies Program, Hybrid and Electric Systems, in particular David Howell, Peter Faguy, and Tien Duong at the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, is gratefully acknowledged.

The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

References

- 1.) J.R. Croy, K.G. Gallagher, M. Balasubramanian, Z. Chen, Y. Ren, D. Kim, S.-H. Kang, D.W. Dees, and M. M. Thackeray *J. Phys. Chem. C* **117** 6625 (2013).
- 2.) K.G. Gallagera, J.R. Croy, M. Balasubramanian, M. Bettge, D. P. Abraham, A. K. Burrell, M. M. Thackeray *Electrochem. Comm.* DOI: 10.1016/j.elecom.2013.04.022 (2013).