Measuring the impact of voltage fade for selected layered Li-intercalating oxides

Martin Bettge[1], Yan Li[1,2], Kevin Gallagher[1], Ye Zhu[1], Qingliu Wu[1], Wenquan Lu[1], Ira Bloom[1], Daniel P. Abraham[1]

[1] *Argonne National Laboratory, Chemical Sciences and Engineering Div., Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA*
[2] *Materials Science Program, University of Rochester, RC Box 270216, Rochester, NY 14627-0216, USA*

Voltage fade of layered Li-intercalating oxides is a materials-specific phenomenon in which the equilibrium electrochemical potential of the active material decreases over time and/or cycle number. It is caused by irreversible structural changes within the oxides that may involve the relocation of transition metals from the metal- to the Li-layer and ultimately lead to the formation of a spinel-like arrangement [1, 2]. This phenomenon reduces the energy content of the electrochemical cell continuously throughout cycling and complicates state-of-charge (SOC) determination for effective battery management.

Voltage fade has previously been observed in layered-oxide systems [3], but several issues remain largely unaddressed: no comprehensive study currently exists that establishes structural and experimental conditions for this potential decay to occur. In fact, it is not even clear whether the impact of voltage fade is technologically relevant. Also, no formal description of voltage fade and its measurement exists. The latter one is especially important to successfully address the other issues and shed light on the underlying physical mechanisms leading to the fade. This presentation will outline a proposed methodology to measure and track voltage fade and highlight a few materials and experimental conditions to show when voltage fade is significant.

This methodology uses a resistance-corrected average voltage to track and quantify voltage fade. Since the composition-dependent cell voltage $U(q)$ affects the measured average voltage $\bar{U}$, the change in average voltage from cycle to cycle (or over time) can be used to define voltage fade. The many polarization losses that affect charge and discharge behavior can be corrected for using low-current cycling and an average cell resistance for additional correction. For each charge and discharge, we can then compute a resistance-corrected average voltage which is essentially an average open-circuit potential for the compositional region of interest.

This methodology will be discussed and will be specifically used to investigate the extent of voltage fade for several layered oxides. The materials of interest include some that are currently of technological interest, such as $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ ("NCA"), $Li_{1.05}(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ ("NMC"), and $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (a Li- and Mn- rich NMC, expressed in the two-component notation as $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}$) [4], as well as some other Li-rich oxide materials. Examination of these materials shows that voltage fade is common for many, if not all, layered oxides when cycled to 4.7V *vs.* Li^{+}/Li. In most cases, the decay rate of the resistance-corrected average voltage is found to be on the order of a few millivolts per cycle, often with a slightly faster decay in the beginning. Over the course of about 20 cycles, the largest degree of fade is found in a Li-rich $Li_{1.2}Mn_{0.4}Fe_{0.4}O_2$ oxide with a ~14mV decrease per cycle;

the smallest degree is found in NCA with only ~1.5mV per cycle.

Particular attention will also be paid to the Li- and Mn-rich NMC. Figure 1 shows its decreasing average voltage as a function of cycle number. Here, the uncorrected and corrected voltages are shown for charge and discharge. The decay rate is also found to be a function of the cycling window and temperature: it increases when cycled to higher voltages (up to 4.7V *vs.* Li^{+}/Li) and at elevated temperatures (55°C). For this material, voltage fade significantly reduces the material's energy density and outweighs energy losses due to capacity loss and resistance rise under standard cycling conditions (i.e. 2.0 – 4.7V *vs.* Li^{+}/Li at 30°C) in improved composite electrodes. However, despite its significant voltage fade, the Li- and Mn-rich NMC exhibits the highest energy density after 20 cycles among the materials investigated.
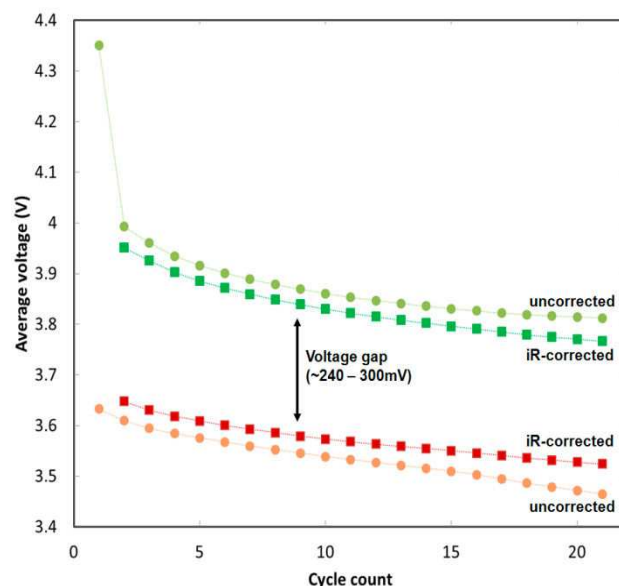

Figure 1. Average voltages, corrected and uncorrected, as a function of cycle number for the Li- and Mn- rich NMC *vs.* Li^{+}/Li. Average voltages during charge are plotted in green and those during discharge are plotted in red. Voltage fade and hysteresis are apparent. The connecting lines are only shown to serve as a guide to the eye.

References

[1] A.R. Armstrong, N. Dupre, A. J. Paterson, C. P. Grey, P.G. Bruce, Chem. Mater. 2004, **16**, p. 3106-3118

[2] J. R. Croy, K. Gallagher, M. Balasubramanian, Z. Chen, Y. Ren, D. Kim, S.-H. Kang, D. W. Dees, M. M. Thackeray, J. Phys. Chem. C, 2013, **117**, p. 6525–6536

[3] P. G. Bruce, A. R. Armstrong, R. L. Gitzendanner, J. Mater. Chem., 1999, **9**, p. 193-198

[4] Y. Li, M. Bettge, B. Polzin, Y. Zhu, M. Balasubramanian, D. P. Abraham, J. Electrochem. Soc., 2013, **160** p. A3006-A3019