**Outgassing of Ni- and Li-rich Li ion battery cathode materials: the importance of impurities**

Bryan D. McCloskey

Department of Chemical and Biomolecular Engineering, UC, Berkeley

Energy Storage and Distributed Resources Division, LBNL

[*bmcclosk@berkeley.edu*](mailto:bmcclosk@berkeley.edu)

The inability to utilize the entire lithium content in Li-ion battery cathodes and achieve their full theoretical capacity is due, in part, to instabilities at elevated voltages (greater than ~ 4.2 V). To explore the mechanism of the undesirable decomposition in the overcharged, high-voltage limit, we are primarily interested in quantifying the individual and coupled high-voltage decomposition/transformations of the cathode – a lithiated transition metal oxide (TMO) – and the electrolyte – most commonly carbonate blends (ethylene carbonate, diethyl carbonate, etc.) with lithium hexafluorophosphate (LiPF6) as the salt. Previous observations of high-voltage instabilities include TMO surface reconstruction, transition metal dissolution, electrolyte decomposition, and formation of surface species. The picture however is still incomplete, with the dependence on electrolyte and TMO composition not yet fully understood.

A powerful in situ technique to study these instabilities is differential electrochemical mass spectrometry (DEMS), which provides quantitative detection of outgassed volatile species during electrochemical testing. By combining DEMS, isotopic labeling, and a surface carbonate titration, we show that the presence of a contaminant – residual lithium carbonate (Li2CO3) – on the surface of TMOs has a direct correlation with the amount of CO2 and CO evolved, and has a relationship with O2 evolution. By selectively isotopically labeling the residual surface Li2CO3, which remains in small quantities (~ 0.1 wt%) after synthesis, and not the carbonate electrolyte, we further show that up to 4.8 V vs. Li/Li+ on the first charge, carbonate electrolyte degradation negligibly contributes to gas evolution. For the battery research community, our results highlight the importance of quantification of surface contaminants and suggest that further research is needed to fully understand the long-term effects of trace surface Li2CO3.

**Biography**

Bryan D. McCloskey joined the Department of Chemical and Biomolecular Engineering at the University of California, Berkeley in Jan. 2014, and holds a joint appointment as Faculty Engineer in the Energy Storage and Distributed Resources Division at Lawrence Berkeley National Laboratory. His laboratory focuses on characterization of fundamental electrochemical processes to provide guidance for the development of energy storage, electrocatalytic, and corrosion-resistant materials. He was previously a Research Staff Member (2012-2013) and postdoc (2009-2011) at IBM Almaden Research Center, where he worked on understanding fundamental characteristics of electrochemical processes occurring in Li-O2 batteries. His PhD thesis (2009), supervised by Benny Freeman at the University of Texas at Austin, focused on molecular transport through microporous and dense polymeric membranes, with a particular emphasis on membranes for water purification. He received his B.S. (2003) in Chemical Engineering at the Colorado School of Mines where his research, supervised by Drs. Thomas McKinnon and Andrew Herring, focused on employing molecular beam mass spectrometry to characterize aromatic hydrocarbon formation during pyrolysis of cellulosic chars.