Supporting Information

Evaluation of Gas Formation and Consumption by Crossover Effect in High Voltage Lithium-Ion Batteries with Ni-Rich NMC Cathodes

Chengyu Mao,[†] Rose E. Ruther,[*,†] Linxiao Geng,[*,†] Zhenglong Li,[†] Donovan N. Leonard,[§] Harry M. Meyer, III,[§] Robert L. Sacci,[‡] and David L. Wood, III[*,†,#]

[†]Energy & Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA.

[§]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

[‡]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

[#]Bredesen Center for Interdisciplinary Research and Graduate Education, University of Tennessee, Knoxville, TN, 37996, USA

Correspondence and requests for materials should be addressed to: R. E. R. (roseruther@gmail.com), L. G. (gengl@ornl.gov) or D. L. W. (wooddl@ornl.gov).

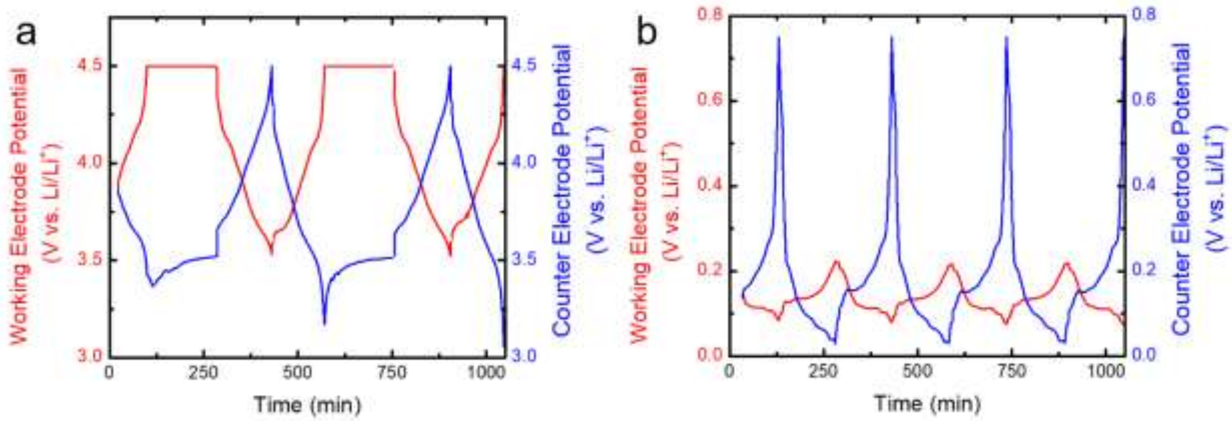

Figure S1. (a) The charge-discharge curves of an NMC811 cathode symmetric cell. (b) The charge-discharge curves of a graphite anode symmetric cell. Voltage profiles are shown for the working and counter electrodes in each cell. The voltage was controlled by incorporating a lithium metal reference electrode in each symmetric pouch cell.

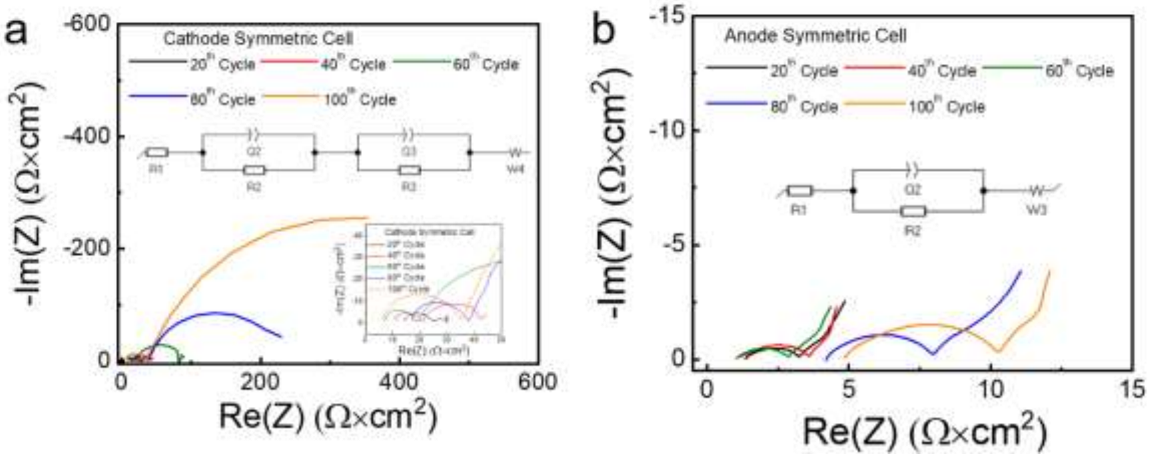

Figure S2. (a) Nyquist plots of the impedance of a cathode symmetric cell. (b) Nyquist plots of the impedance of an anode symmetric cell.

The symmetric cell resistance was calculated by fitting the EIS spectra using the equivalent circuits shown in the inset figures. Here, R is a resistor, Q is a constant phase element, and W is the Warburg element.

For the cathode symmetric cells, R2 and R3 represent interfacial resistance and charge transfer resistance.[1] The sum of R2 and R3 was used to measure the impedance rise shown in Figure 3d. For the anode symmetric cells, interfacial resistance and charge transfer resistance could not be decoupled easily. A single resistor, R2, was used to measure the impedance rise shown in Figure 3d.

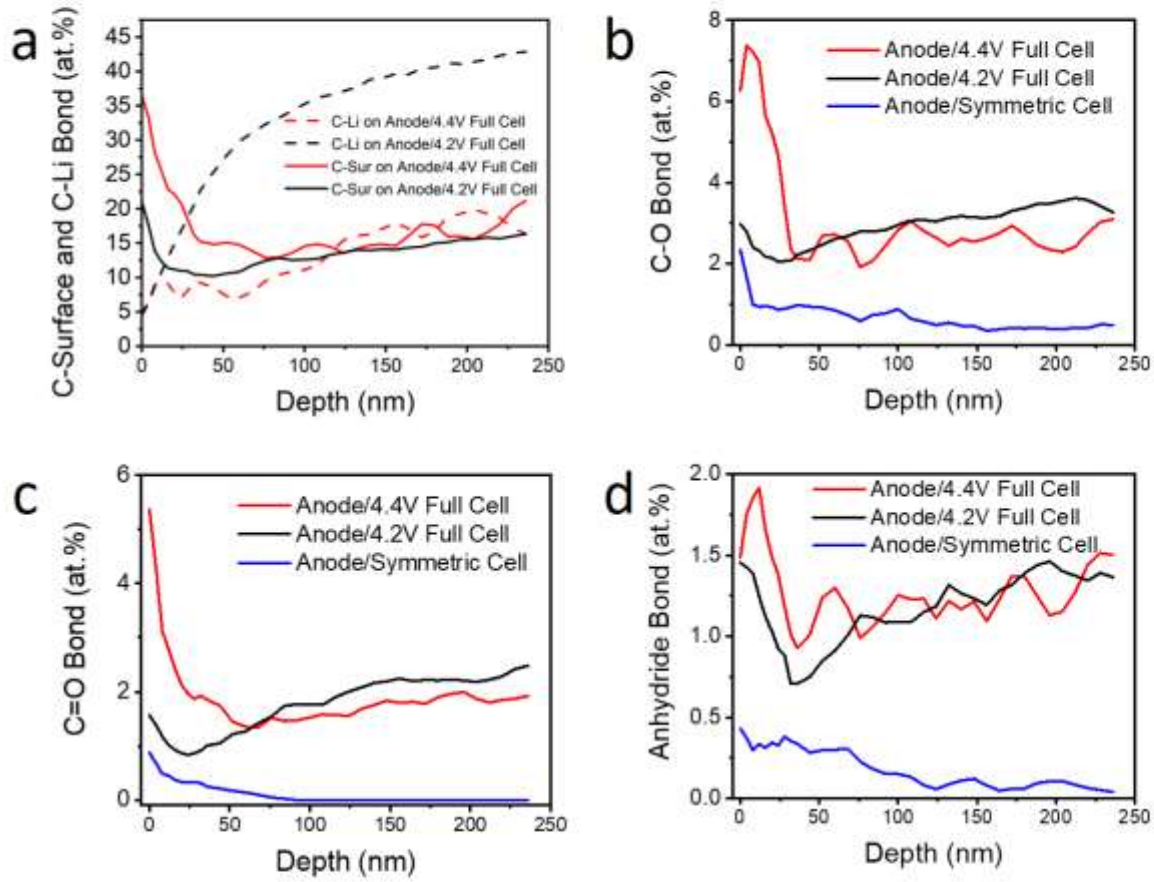

Figure S3. XPS depth profiling of the C 1s spectra of the anode in full and symmetric cells. The C1s spectra were deconvoluted to determine contributions from carbon with different bonding environments. (a) Depth profile of lithiated graphite (C-Li) and all other types of carbon associated with the surface SEI layer (C-Sur). (b) Depth profile of carbon with C-O bonding. (c) Depth profile of carbon with C=O bonding. (d) Depth profile of carbon with anhydride-like bonding.

Figures S3 b, c, and d compare the XPS depth profiles for carbon in different types of bonding environments with oxygen (C-O, C=O, and anhydride) on the anode after cycling in the 4.4 V full cell, 4.2 V full cell, and anode symmetric cell. These types of carbon bonds are typical for the SEI layer that forms on the anode. The concentrations of oxidized carbon are much higher in the full cells than in the anode symmetric cell. This shows that crossover from the cathode plays an important role in determining the SEI chemistry at the anode. Moreover, full cells cycled to 4.4 V have more oxidized carbon than cells cycled to only 4.2 V. Significantly more gas, especially CO_2, was generated during the higher voltage operation. CO_2 and other species generated at the cathode clearly migrated to the anode side and contributed to SEI growth. The changes in SEI chemistry and thickness help to explain the impact of electrode crosstalk on cell performance.

Table S1. GCMS analysis parameters

Column J&W DB-624 Ultra Inert GC Column	
[GC]	[MS]
Vaporization chamber temperature : 200 °C	MS source : 230 °C
oven temperature : 30 °C -> (15°C/min) -> 250 °C (20min)	MS quad : 150 °C
Injection mode : Split	Measurement mode : Scan
Split ratio : 10	Mass range : *m/z* 10 - 250
Carrier gas : Helium	
Control mode : Linear velocity 36.0 mL/min	
Sample injection quantity : 10 μL	

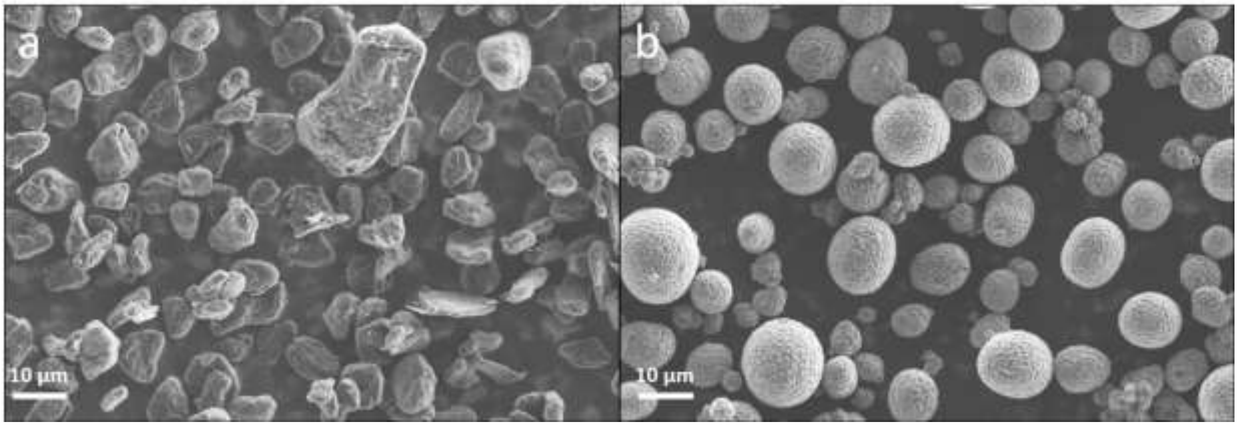

Figure S4. SEM images of (a) graphite powder and (b) NMC811 powder.

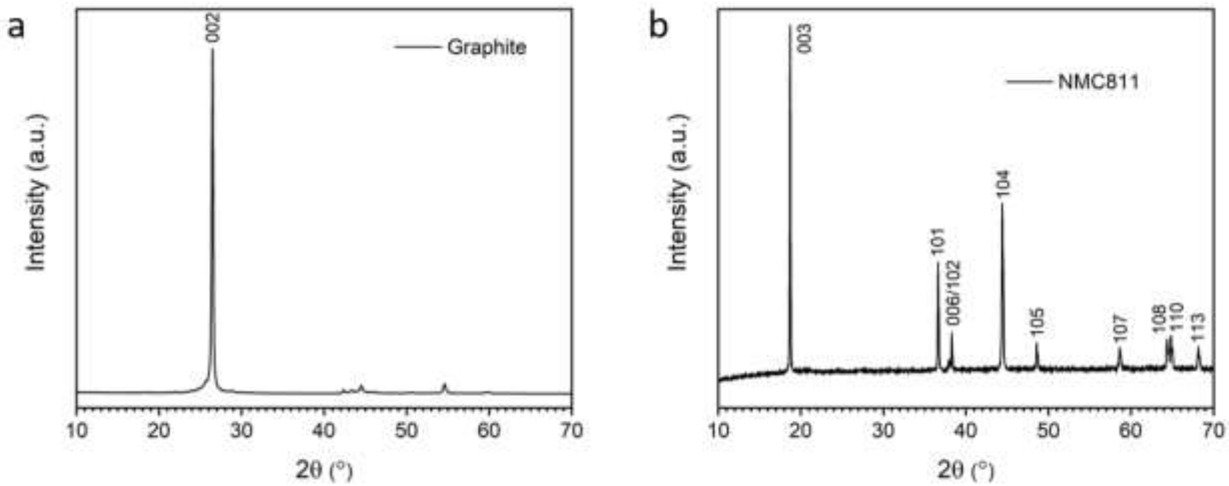

Figure S5. XRD patterns of (a) graphite anode and (b) NMC811 powder.

Reference:

1. An, S. J.; Li, J.; Mohanty, D.; Daniel, C.; Polzin, B. J.; Croy, J. R.; Trask, S. E.; Wood III, D. L. Correlation of Electrolyte Volume and Electrochemical Performance in Lithium-Ion Pouch Cells with Graphite Anodes and NMC532 Cathodes. *J. Electrochem. Soc.* **2017**, *164*, A1195-A1202.