Electronic Supplementary Material (ESI) for RSC Advances.


Supporting Information:

# Enhanced Capacity and Lower Mean Charge Voltage of Li-Rich Cathodes for Lithium Ion Batteries Resulting from Low-Temperature Electrochemical Activation

Evan M. Erickson,[a] Florian Schipper,[a] Ruiyuan Tian,[a] Ji-Yong Shin,[b] Christoph Erk,[b] Frederick-Francois Chesneau, [b] Jordan Lampert,[b] Boris Markovsky, [a] and Doron Aurbach[a]

[a.] *Department of Chemistry, Faculty of Exact Sciences, Bar-Ilan University, Ramat-Gan, 5290002 Israel*
[b.] *Badische Anilin und Soda Fabrik (BASF), Ludwigshafen am Rhein, Rheinland-Pfalz, Germany*

## 1. Structural Information of the Li-rich Material

A SEM micrograph depicting the morphology of the $0.35LiMn_2O_3 \cdot 0.65Li[Mn_{0.45}Ni_{0.35}Co_{0.20}]O_2$ cathode material is presented in Figure S 1, showing ball-shaped particles with around 5 - 10 µm in diameter.

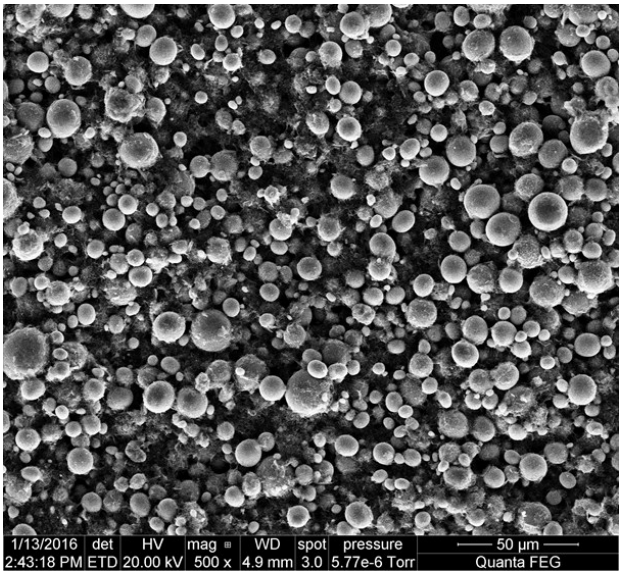


**Figure S 1: SEM micrograph of an uncycled $0.35LiMn_2O_3 \cdot 0.65Li[Mn_{0.45}Ni_{0.35}Co_{0.20}]O_2$ electrode.**

The XRD pattern for uncycled Li-rich powder is presented in Figure S 2 with the resultant derived lattice parameters ( Table S 1).

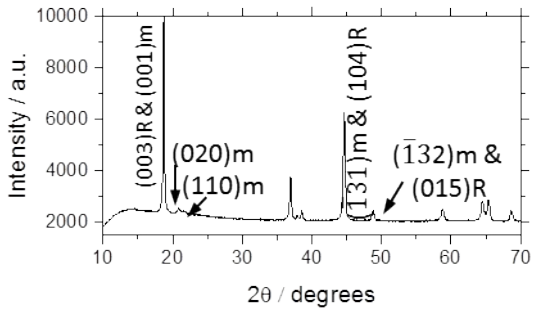


**Figure S 2: XRD pattern from pristine, uncycled Li-rich $0.35LiMn_2O_3 \cdot 0.65Li[Mn_{0.45}Ni_{0.35}Co_{0.20}]O_2$ powder with some reflections indicated.**

| Material | Monoclinic phase | Rhombohedral phase (in terms of hexagonal cell) | Rp value |
|---|---|---|---|
| Pristine (uncycled) | a =4.929(4) Å, b=8.522(9) Å, c =5.029(0) Å, β =109.19° Å | a=2.857(3) Å, c =14.259(6) Å | 2.79% |

**Table S 1: Lattice parameters of monoclinic $Li_2MnO_3$ ($C2/m$) and rhombohedral ($R\bar{3}m$) components of pristine (uncycled) Li-rich $0.35Li_2MnO_3 \cdot 0.65LiNi_{0.35}Mn_{0.45}Co_{0.20}O_2$ powder.**

## 2. Cycling of cells

All cycling results in this manuscript represent the average of 3 - 4 coin cells (vs. Li counter electrodes) with standard deviations used as error bars to ensure confidence in our results. The cells whose results are depicted in Fig. 1 were first cycled to 4.7 V at C/15 (1C defined as 250 $mAhrg^{-1}$) for the first cycle, with a constant voltage step for 3 hrs. The second cycle was performed at a C/10 rate, with this and all subsequent cycles charged to only 4.6 V, utilizing a 30 min constant voltage step. The first two cycles were the "activation steps," performed at 0, 15, 30 or 45 °C, indicated in the legends of Fig. 1 & 2. After the two-cycle activation steps, cells were either cycled at 30 °C (Fig. 1) or 45 °C. The cycling procedure includes a rate capability measurement at first up to 4C (with the same charge and discharge rates). The rate capability test was followed by 3 cycles at C/10 and with the remaining 80 cycles at C/3.

Coin cells were fabricated with 3:7 EC:EMC, 1 M $LiPF_6$ electrolyte, Celgard 2500 polypropylene separators, and ~3 $mg/cm^2$ active Li-rich material electrodes. The electrodes are comprised of 80 % active material, 10 % Solef 5140 PVDF, 5 % C black and 5 % KS6 graphite.

## 3. Differential capacity vs. V plots, over long term cycling.

Figure S 3 depicts the dq/dV curves of electrodes throughout long term cycling. The $Li^+$ extraction from the TM layer is characterized by the most intense peak for the material activated at low T. In the figure, Peak 2 corresponds to $Li^+$ extraction from the TM layer, Peak 3 corresponds to $Li^+$ extraction from the $Li^+$ layer, and peak 4 is likely related to spinel phase redox that is formed due to partial layered-to-spinel transformation in Li-rich electrode materials.

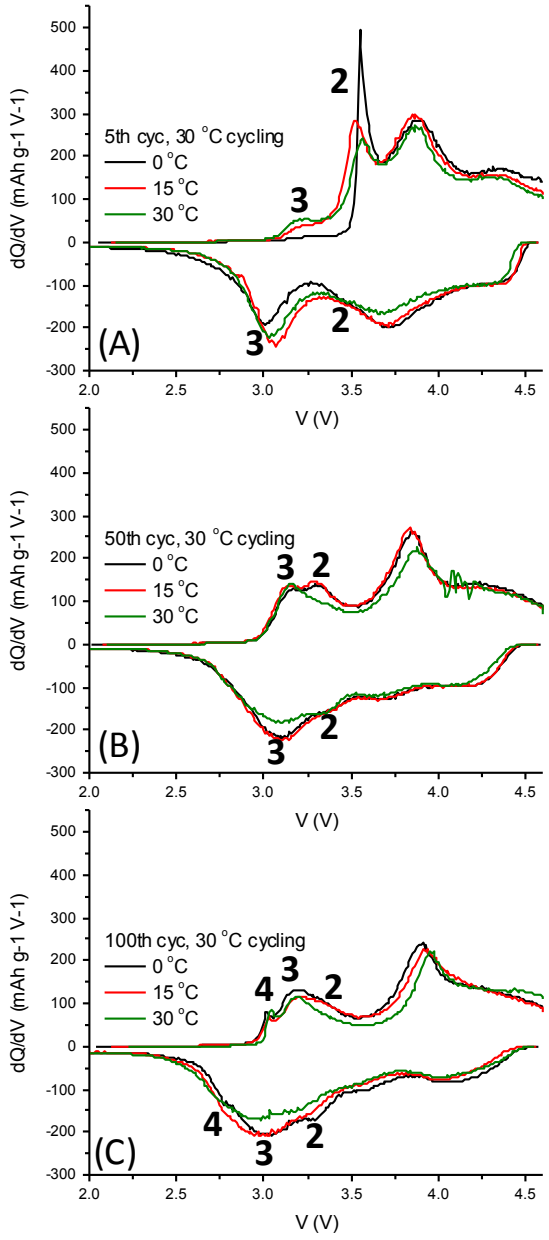


**Figure S 3: Differential capacity vs. voltage plots of the Li-rich material electrodes activated at 0 – 30 °C, cycled at 30 °C, over 100 cycles.**