applied sciences

MDPI

Supplementary Materials: Metal Release Mechanism and Electrochemical Properties of $Li_x(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$

Blake G. Hudson and Sara E. Mason *

Department of Chemistry, University of Iowa, Iowa City, IA 52240, USA; blake-hudson@uiowa.edu
* Correspondence: sara-mason@uiowa.edu

Figure S1: Shown is the optimization of the RFT model using the four selected descriptors used to train the model. Figure S1 (a) indicates the model does not improve in training R^2 value beyond 5 trees and (b) does not improve past four nodes. These values are used to parameterize our model when predicting ΔG_1 values.

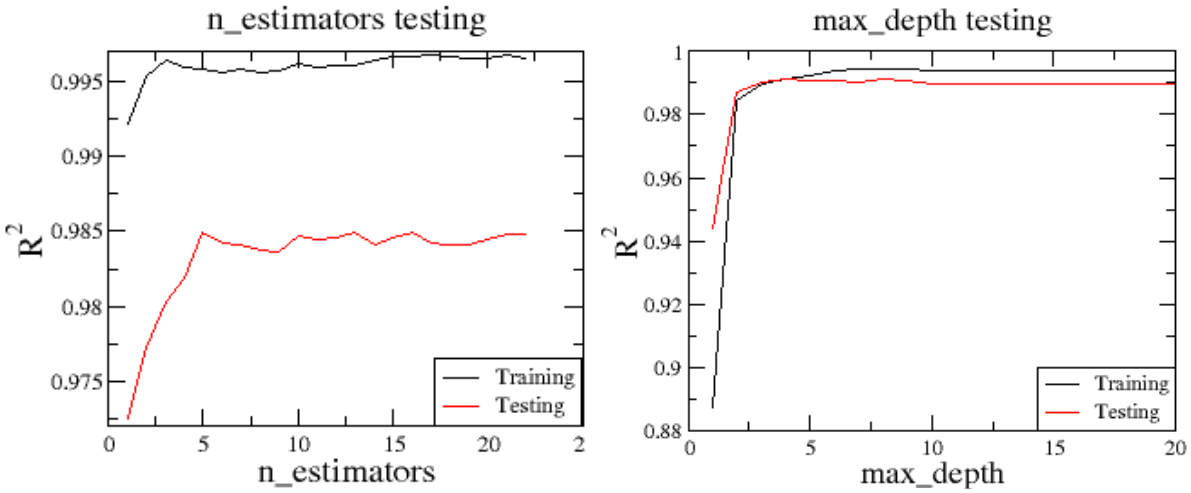

Figure S1: Optimization of the RFT model starting with optimization of the number of trees (a) and number of nodes (b). Training R^2values are displayed in black and testing values in red.

Figure S2: Initial descriptors used to train the RFT model were BV_vac, Charge_vac, Mag_vac, as well as the same three descriptors for the six neighboring metals to the vacancy site. This model obtains accurate ΔG_1 predictions shown in (a). A caveat of using these descriptors is the order of importance varies each time model is run, (b,c), making trends undecipherable as the identity of metal site 4 (or any other neighboring site) is ambiguous and even more so in compositionally tuned structures that do not have perfectly alternating metal surfaces. Moving forward, when considering neighboring metal sites, we will use the summation of their magnetic moments as the spin pairing of the vacancy site and metal environment have shown to govern metal release as seen in previous work[15]. Reducing surrounding metal descriptors to $\Sigma\rho_s$ simplifies interpretation of RFT results and is transferable to other materials beyond NMC that have different coordination environments of surface metals.

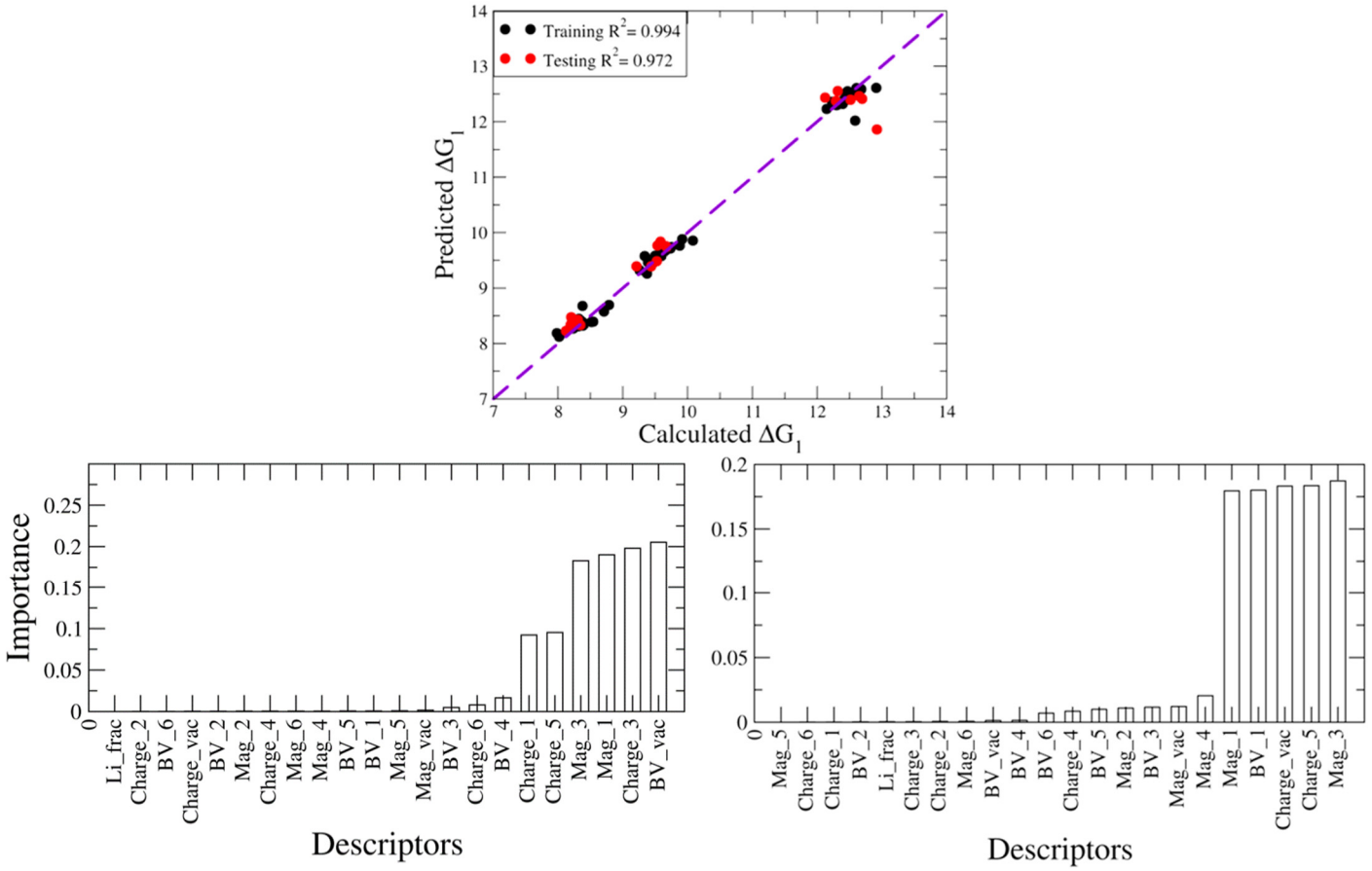

Figure S2:(a) Top: Initial descriptors used to train the RFT model give accurate ΔG_1 predictions shown by an excellent testing R^2 value. When the RFT model is run numerous times, the order of descriptor importance varies seen in (b, c).

Figure S3: PDOS of Co and Mn d-states over the lithium fractions $Li_{1.00}$ to $Li_{0.44}$. Oxidation states of these metals is not expected to change until going below Li_x=0.33 and show no changes in electron density for our configurations tested. Cobalt shows comparable densities between the up and down states suggesting a d^6 configuration and a nominal oxidation state of 3+ (a). Mn has no spin-down electrons shown by all the green density located above E_F and more spin-up density below E_F than the unoccupied states indicating a d^3 configuration or Mn^{4+} (b).

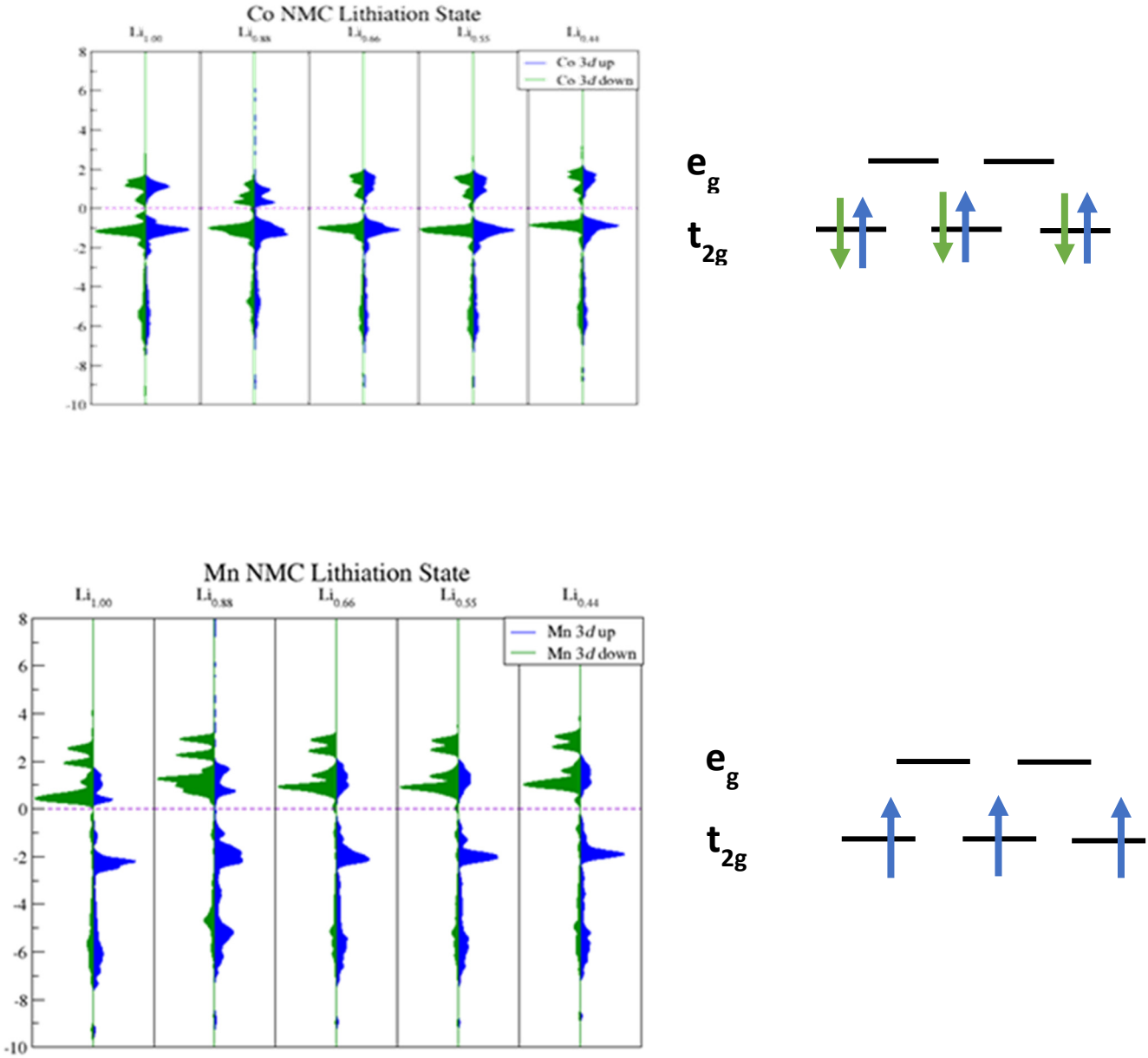

Figure S3: PDOS of Co (a) and Mn (b) d-states across lithium fractions in the charge cycle. Delithiating to $Li_{0.44}$ does not induce any changes to either Co or Mn electron fillings.