Investigation into Rigid Band Approximation (RBA) of Na-ion Battery Materials

Jerry Kappuzha, Yi-Ting Cheng, Christopher J Bartel
kappu006@umn.edu | cems.bartel.umn.edu

Minnesota Supercomputing Institute
University of Minnesota
Driven to Discover®

Design of Materials on Computers
DMC LAB
Bartel Research Group

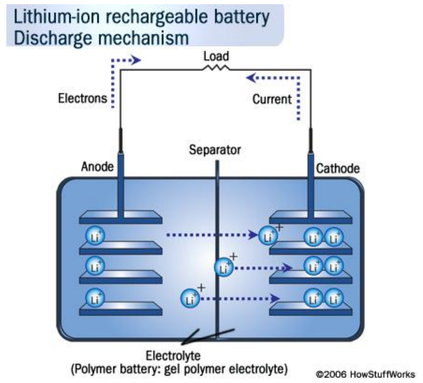
Computational Tools Simulate Battery Lifecycle

b-initio VASP ienna imulation ackage

Out now! LOBSTER
Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction

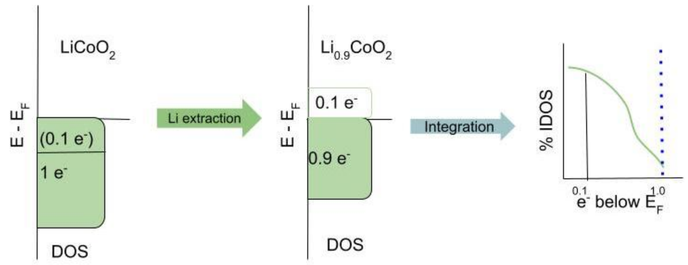
- Computational tools save time and resources in screening new materials candidates for batteries
- VASP models materials at atomic scale, using DFT estimates of Schrodinger equation to obtain lowest energy ground state [1]
- LOBSTER projects VASP data onto local atomic orbitals, allowing specific chemical-bonding based analysis [2]

Rigid-Band Approximation (RBA) in Batteries



- Batteries rely on redox principles to work and are characterized by their mechanism of transporting ions and electrons between anode and cathode
- Intercalation cathode materials are a type of material where Li ions are inserted between layers of crystal lattice, being highly reversible, and rely on cation redox (image: [3]
- When analyzing intercalation materials, RBA is assumed where, during discharge, the Fermi level changes, but not the electronic structure
- Quantifying error in RBA for a specific battery material can better characterize the redox mechanism, allowing for better understanding and usage of such materials
- Applying this to study Na-ion battery materials, the eco-friendlier alternative, to Li-ion battery materials, can further advancements in materials design for batteries, by saving time and resources in determining characteristics of battery materials

Approximating RBA Error Through IDOS

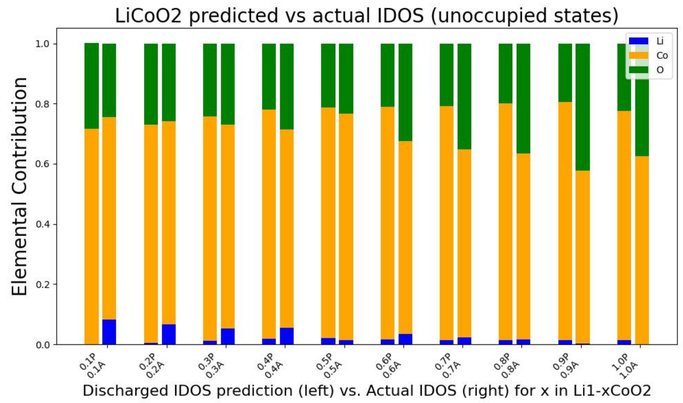


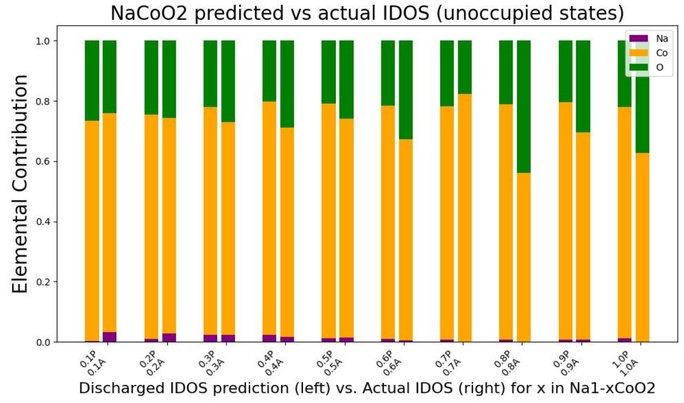
- Integrated Density of States (IDOS) represents electronic structure through contribution of electrons to structure per each element in material
- Unchanged electronic structure means unchanged elemental contribution, and thus unchanged IDOS, IDOS
- Quantified error in RBA of LiCoO2 and NaCoO2, Na-analog of LiCoO2, by measuring IDOS of the recently extracted electron in incrementally extracted states (i.e. Li0.9CoO2) and comparing with the IDOS of the corresponding electron of the fully discharged structure (LiCoO2)
- Dramatic changes in IDOS between extracted electron and electron in discharged structure signify error in assumption of RBA and highlight other redox mechanisms present in intercalation material
- Experimental Data determine anion redox (and thus not intercalation) starts occurring in LiCoO2 after extraction of 0.5 electrons and in NaCoO2 after 0.3 electrons, thus dramatic IDOS changes should be seen at corresponding values

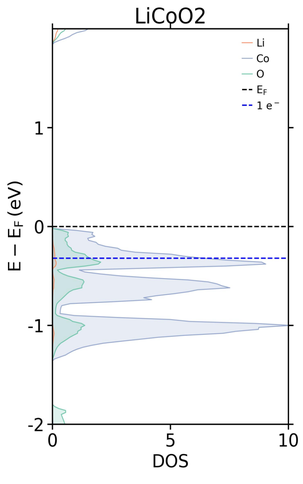
References

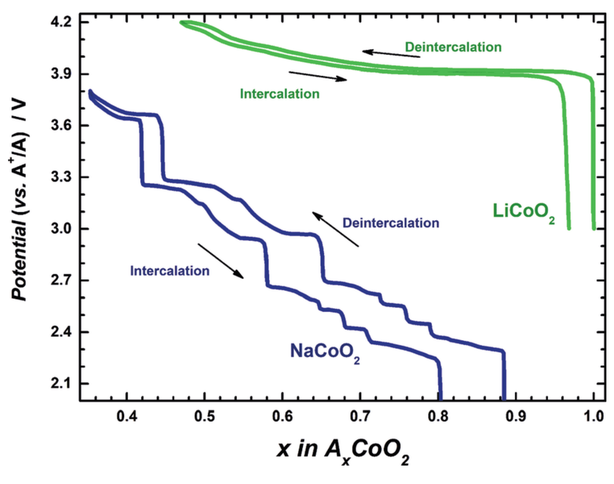
(1) Hafner, J. Ab-Initio Simulations of Materials Using VASP: Density-Functional Theory and Beyond. *Journal of Computational Chemistry* **2008**, *29* (13), 2044–2078. https://doi.org/10.1002/jcc.21057.
(2) Nelson, R.; Ertural, C.; George, J.; Deringer, V. L.; Hautier, G.; Dronskowski, R. LOBSTER: Local Orbital Projections, Atomic Charges, and Chemical-Bonding Analysis from Projector-Augmented-Wave-Based Density-Functional Theory. *Journal of Computational Chemistry* **2020**, *41* (21), 1931–1940. https://doi.org/10.1002/jcc.26353.
(3) Nayak, P. K.; Yang, L.; Brehm, W.; Adelhelm, P. From Lithium-Ion to Sodium-Ion Batteries: Advantages, Challenges, and Surprises. Angewandte Chemie (International ed. in English) 2018, 57 (1), 102–120. https://doi.org/10.1002/anie.201703772.
(4) Bobby. How Does Intercalation Work in Batteries? News about Energy Storage, Batteries, Climate Change and the Environment. https://blog.upsbatterycenter.com/intercalation-work-batteries/.

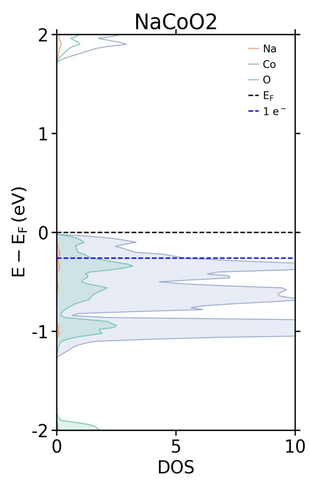
IDOS in LiCoO2 vs NaCoO2











- Dramatic deviations in IDOS show up for LiCoO2 after 0.5 electrons for LiCoO2 and after 0.3 electrons for NaCoO2
- Experimental Data in the form of Voltage Curve lines up with calculated data, smoother voltage curve generally indicates cation redox, and thus intercalation, voltage curve with increased "jaggedness", indicate anion redox, and thus another method called conversion [4]
- For future work, this method can be applied to more battery materials being analyzed, and quantitively applying these deviations can shed more light on to levels of each redox mechanism within a certain battery material
- Applying this method can shorten the amount of time and resources needed to discover new battery materials, promoting newer more sustainable technologies within the space