Characterization of Cr doped $LiVOPO_4$ as a Novel Cathode for Higher Energy Lithium-ion Batteries Using a First-Principles DFT Approach

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MOTIVATIONS

- As the demand continues to increase, the current batteries are being pushed to their maximum theoretical capacities which inherently increases the safety concerns for consumers
- To meet the consumer demands for both conventional and bulk applications, cope with significant technological developments and address the safety concerns, next-generation, higher energy capacity, and highly efficient batteries must be developed

OBJECTIVES

Overall Objective:

To create a higher energy battery that maximizes the amount of energy capacity and efficiency in a given amount of space while simultaneously addressing the safety concerns posed on consumers

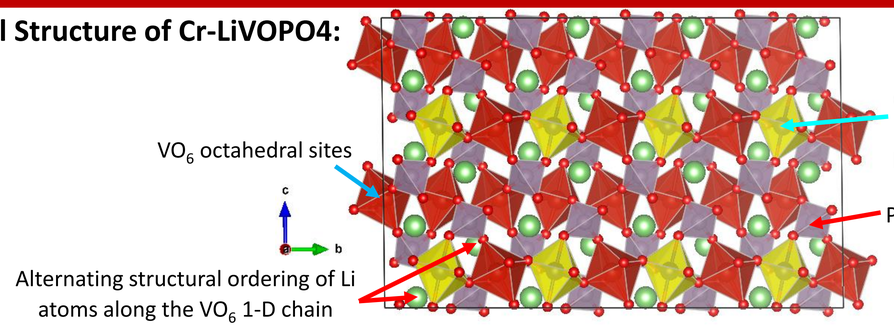
Specific Research Objectives:

The main problem lies within the cathode. A cathode with higher energy capacity, higher ionic and electronic conductivity, a chemically reversible framework, and with low Li-insertion energies must be developed

SOLUTION

- The proposed solution was a Cr-doped $LiVOPO_4$ cathode (with 25% Cr doping)
- Cr was proposed because it can easily localize electrons which is crucial for effortless Li intercalation and battery redox efficiency
- Additionally, Cr has the potential to go to a Cr $^{6+}$ oxidation state whereas vanadium can only go to a V $^{5+}$ gaining extra Li-content per primitive lattice (thus more energy capacity)

Crystal Structure of Cr-LiVOPO4:



CHARACTERIZATION METHODS

Initial Setup

All Ab-initio Density Functional Theory Calculations were done using Vienna Ab-initio Simulation Package (VASP) using the projector augmented-wave approach. All calculations used the Perdew-Burke-Ernzerhof (PBE) functional from the Generalized Gradient Approximation (GGA) class for exchange correlation. The calculations had an energy cutoff of 520 eV, and a Monkhorst-Pack scheme was used to generate a 4x4x4 FFT mesh sampled from the first Brillouin Zone

Summary of First-Principles DFT Characterization

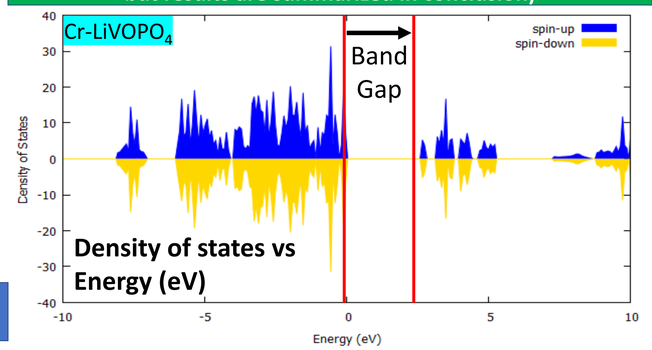
- **Step 1: Structural Relaxation and Optimization**. The lithium content in the undoped LiVOPO4 system was varied to observe the structural change in the crystal framework
- **Step 2: Lithium Insertion Energies.** Lithium content was increased and the change in lithium insertion energies was observed with increasing lithium content
- **Step 3: Addition of Cr dopant.** The Cr dopant was added to the octahedral site near the Li-1 site and all the same calculations done on undoped LiVOPO4 were done again on Cr-LiVOPO4
- **Step 4: DOS Assessment.** Density of States was conducted to assess the band gaps and the occupied electron states of the systems. This data can be used to determine the electronic conductivity of the systems
- **Step 5: Band Structure Evaluation.** The Band Structure was assessed to see the electron valence and conductance bands and visualize the band gaps near the Fermi Level.
- **Step 6: Nudge Elastic Band (NEB).** NEB was used to assess the migration barriers throughout the LiVOPO4 and Cr-LiVOPO4 systems to further observe the ionic mobility within the system

RESULTS

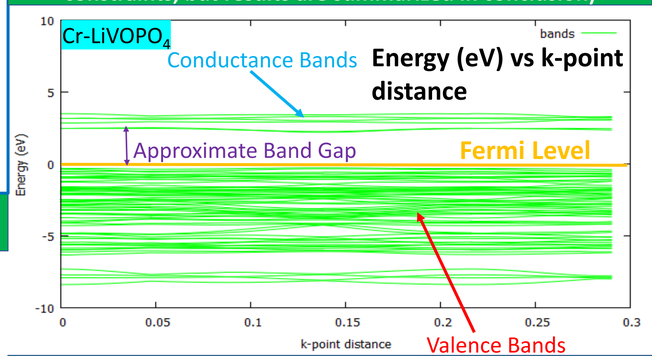
Lithium Insertion Energies

System	1 Li	2 Li	3 Li	4 Li	5 Li
$LiCoO_2$	-10.51 eV	-11.21 eV	-11.69 eV	N/A	N/A
$LiVOPO_4$	(averaged with Li_2)	-5.50 eV per atom	(averaged with Li_4)	-6.13 eV per atom	N/A
Cr-$LiVOPO_4$	(averaged with Li_2)	-4.25 eV per atom	(averaged with Li_4)	-4.80 eV per atom	-4.96 eV

DOS Plots (note: all plots are not shown due to size constraints, but results are summarized in conclusion)



Band Structure Plots (note: all plots are not shown due to size constraints, but results are summarized in conclusion)



The results from the NEB Plots are summarized in the conclusion due to the lack of space for visual graphics

CONCLUSION/NEXT STEPS

Cr-LiVOPO4 proves to an extremely promising cathode for next generation Li-ion batteries. Cr-LiVOPO4 has a chemically reversible framework with full delithation, has extremely low Li-insertion energies (extremely efficient battery redox reactions), has extremely low band gaps (high electronic conductivity and mobility), shows optimal cathode behavior from the NEB plots and has over 2.5x the capacity of current commercial cathodes.

This proposed cathode material will be tested experimentally at Tesla Motors in September of 2020 in the prototypes of the next-generation, all solid state, lithium-metal super batteries