

Transition metal oxides as cathodes for lithium ion battery: structure, stability and substitution effects



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ABSTRACT

Density Functional Theory (DFT) based first-principles simulations, Bader charge analysis and density of states of three layered transition metal oxide cathode materials (LiXO_2 , $X=\text{V, Co, Ni}$) were carried out. A theoretical basis for the effect of Al substitution in LiCoO_2 is proposed. The stability of these materials in completely lithiated state is shown through phonon calculations based on Density Functional Perturbation Theory (DFPT).

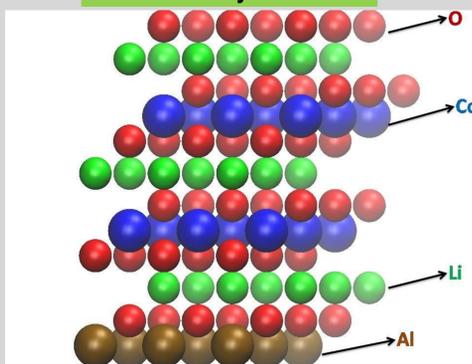
INTRODUCTION

First-principles DFT simulations are computationally demanding but are reasonably accurate in predicting properties of battery cathode materials. Properties relevant to selection of cathode material include electrochemical potential, structural stability, energy/power density and cycle life etc. Computational screening of materials speeds up the process of material discovery by saving on costs of experiments and time. In addition, it helps in developing correlation between properties and structural and chemical aspects. Here we analyze some of these aspects for the three above mentioned oxides. The effect of Al substitution on the electrochemical properties of LiCoO_2 is discussed.

METHODOLOGY

- DFT simulations with GGA+U for
 - Voltage Calculations
 - Bader Charge analysis
 - Density of States Calculations (Using VASP 4.6)
- Energy Level analysis for aluminum substituted materials
- Phonon calculations based on DFPT
 - Structural stability (Quantum Espresso 4.3)

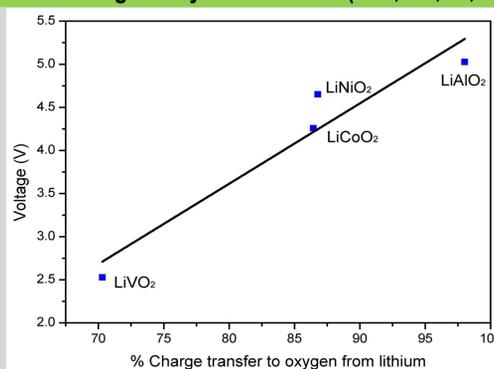
Structure of layered oxides



Structure of hexagonal layered metal oxides (space group no. 166)

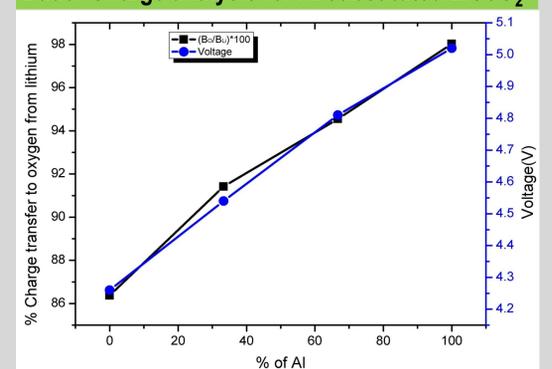
RESULTS & DISCUSSION

Bader Charge analysis for LiXO_2 ($X=\text{V, Co, Ni, Al}$)



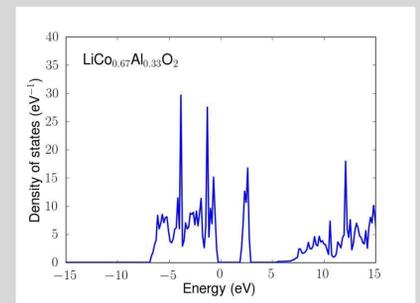
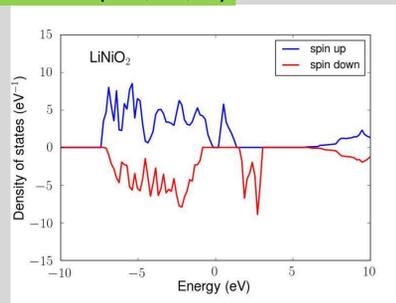
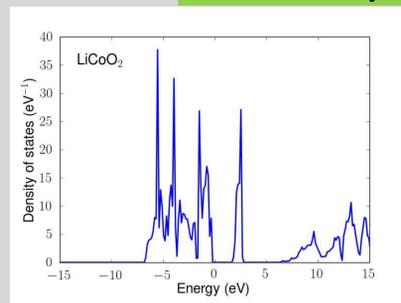
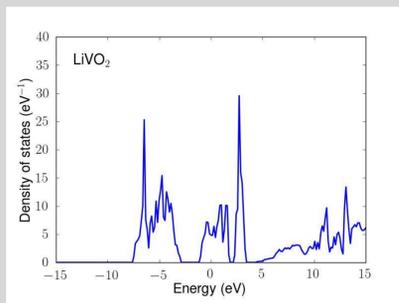
Increase in charge transfer to oxygen from Li results in increase in voltage of LiXO_2

Bader Charge analysis for Al substituted LiCoO_2



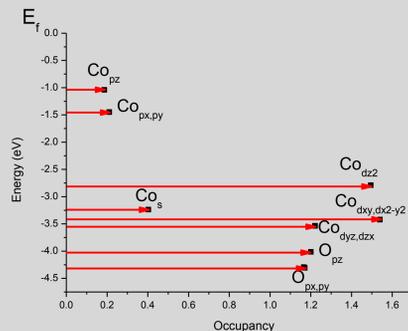
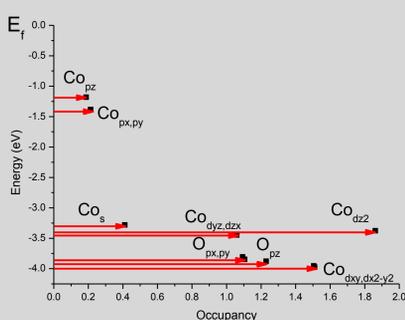
Al substitution for Co results in increase in charge transfer to oxygen from Li and increase in voltage

Electronic density of states for LiXO_2 ($X=\text{V, Co, Ni}$)



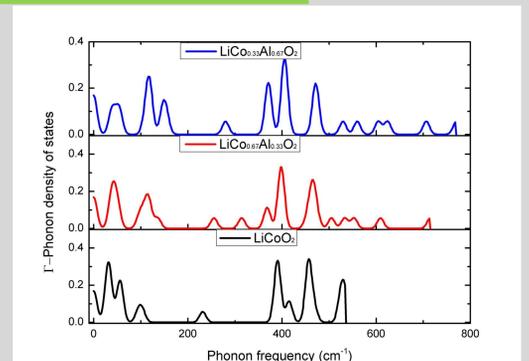
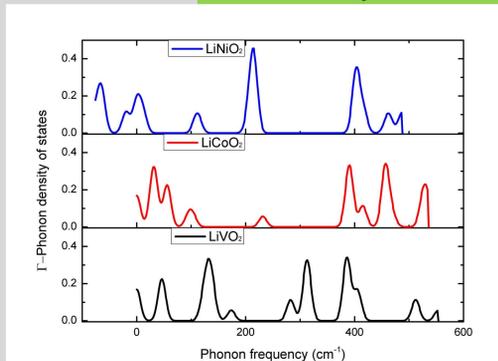
- Average energy levels of individual orbital and electron occupancy of all atoms is calculated from partial DOS.
- The relative positions of O p-orbitals and TM d-orbitals play a role in determining voltage. Oxygen states are deeper in energy and accept the larger share of incoming charge.
- Al substitution increases the separation between O p-orbitals and Co d-orbitals resulting into reduced hybridization and lower electrostatic energy of the lithiated compound.

Energy level diagrams for LiCoO_2 and $\text{LiCo}_{0.67}\text{Al}_{0.33}\text{O}_2$



Orbital energy level diagrams show that relative positions of oxygen p-states with respect to the cobalt d-states change when 33 % of cobalt is substituted with aluminum.

Phonon density of states for LiXO_2 and Al-substituted LiCoO_2



• Zero point phonon DOS shows the vibrational stability of cathode materials

• Aluminum substitution does not introduce unstable modes in LiCoO_2

CONCLUSIONS

- ✓ We propose that ratio of Bader charges of oxygen and lithium correlates with electrochemical potential
- ✓ Higher the electronic charge of lithium which gets transferred to oxygen atoms, greater the electrochemical potential of cathode material.
- ✓ The lower voltage in LiVO_2 is due to increased hybridization as shown by partial DOS.
- ✓ The effect of Al substitution in LiCoO_2 is evaluated using DOS calculations and energy level analysis. The separation between oxygen p-states and Co d-states increases with Al substitution.
- ✓ Phonon calculations confirm that the stability of cathode materials including Al substituted LiCoO_2

ACKNOWLEDGEMENTS

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