Moving from Li to Na ion intercalation battery: electronic charge transfer mechanism in cathodes studied with *ab-initio* methods

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OBJECTIVE

Sodium intercalation batteries might prove to be a viable alternative of lithium ion batteries, which is both expensive and in short supply due to unavailability of lithium. Renewable energy sources being crucial to India's energy future, there is a huge need to develop scalable and cost effective storage technology with earth abundant materials to provide load balancing. Moving from lithium to sodium ion intercalation materials, electrochemical properties change significantly and electrochemical potential of intercalation drops. We need to understand those effects through electronic details, thus enabling rational design of Na-intercalation materials with energy storage performance close to existing Li-ion based materials. We do a comparative study of Na and Li intercalation in 3 cathode materials with very different crystal structures to understand this. Two of these, layered cobalt oxide and iron phosphate with olivine structure are host cathode materials for commercial lithium ion batteries. Newly discovered and promising material - iron fluoro-sulfate with tavorite structure is also studied for Li and Na ion intercalation.

METHODOLOGY

Pseudopotential based DFT simulations with Generalized Gradient Approximation (GGA) or Local Density Approximation (LDA) predict the structural and functional properties of majority of materials quite accurately. However, to evaluate the redox potentials for lithium intercalation compounds specially with transition metals, LDA or GGA is not sufficient. To represent the self interaction of d-orbital electrons, GGA + Hubbard U approach is utilized.

Electronic structure calculations using Vienna Ab-initio Simulation Package (VASP)

- ❑ Spin dependent GGA+U approximation with projector augmented wave function technique. Hubbard U-J of 3.3 eV(for CoO_2) 3.71 eV(for $FePO_4$) 4 eV(for $FeSO_4F$)
- ❑ 600 eV wavefunction cutoff and Brillouin zone sampling through Monkhorst-Pack k-mesh of 8×8×1 (for CoO_2) 3×4×4 (for $FePO_4$) 6×6×4 (for $FeSO_4F$)
- ❑ Energy minimization with respect to lattice parameters and atomic positions
- ❑ Bader scheme for charge analysis (atom in molecule AIM approach)

From the ground state energies of the lithiated, delithiated structures and lithium, one can calculate the electrochemical potential. Considering that entropic and volume changes are negligible, the Gibbs free energy difference can be approximated with the ground state energy difference.

$$V = \frac{E_{host} + E_{Li} - E_{Li-host}}{nF}$$

where, V = Electrochemical potential, E_x = Ground state energies of respective materials, F = Faraday's constant, and n = total charge transferred.

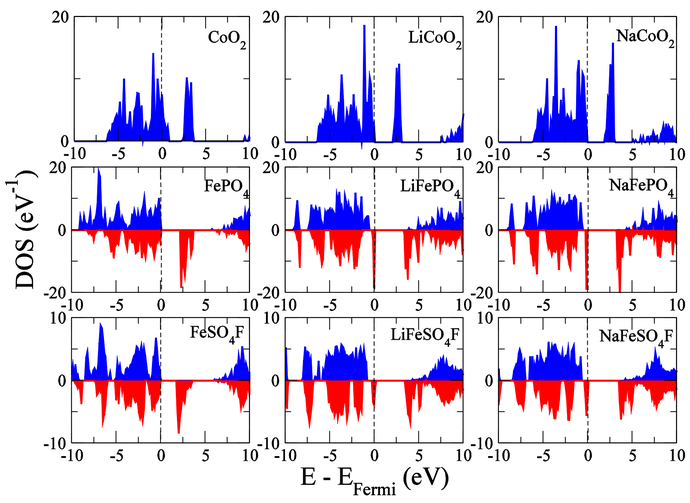
Structural Parameters from simulation

Materials	Lattice parameters in Å (before intercalation)				Lattice parameters in Å (after Li intercalation)				Lattice parameters in Å (after Na intercalation)			
	a	b	c	Cell vol. (Å^3)	a	b	c	Cell vol. (Å^3)	a	b	c	Cell vol. (Å^3)
CoO_2	2.82	2.82	13.85	95.49	2.84	2.84	14.1	98.49	2.91	2.91	15.5	114.0
$FePO_4$	9.95	5.91	4.87	284.2	10.41	6.07	4.74	299.5	10.48	6.26	4.99	328.0
$FeSO_4F$	5.23	5.26	7.34	177.5	5.23	5.54	7.39	190.0	5.18	5.49	7.23	182.8

❑ **Traditional intercalation cathodes, cobalt oxide and iron phosphate shows high volume change for sodium ion intercalation. These are not suitable for Na-cathode application due possibility of structural disintegration on crack formation**

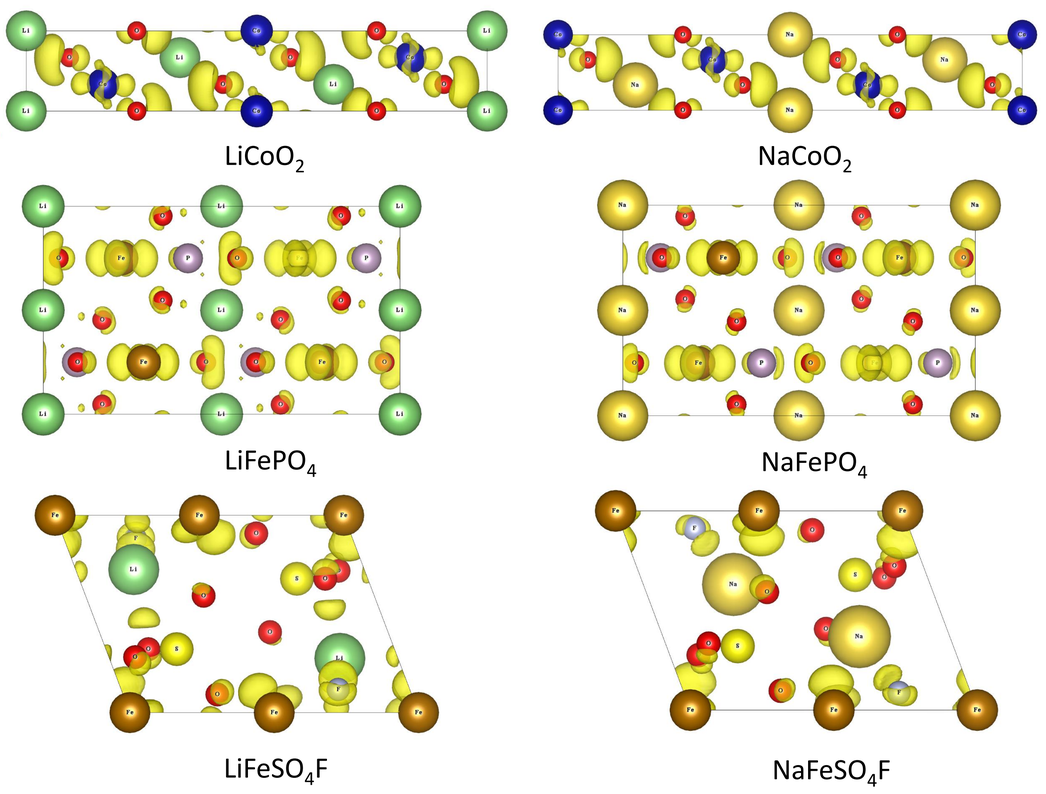
❑ **Newly discovered fluoro-sulfate cathode shows very low volume change on Na-intercalation than Li-intercalation making it very much suitable for sodium ion battery**

Total Density of States for all materials



- ❑ Li and Na intercalation leads to filling up of near Fermi energy valence states
- ❑ It also leads to increase in band gap
- ❑ Down spin states get occupied selectively leading to lowering of magnetic moment in $FePO_4$ and $FeSO_4F$

3D plot of charge transfer during intercalation



❑ **Charge transfer characteristics for both Li and Na intercalation in CoO_2 are very similar, the only difference being, 82% of Li valance charge gets redistributed during intercalation. This is 78% for Na intercalation.**

❑ **Large drop in voltage for Na intercalation from Li intercalation in $FePO_4$ is associated with lower charge transfer from Na (81%) than Li(87%) and higher charge transfer to Fe (50.8% for Na intercalation vs. 46.8% for Li intercalation). The trend is opposite for charge transfer to O (44.3% for Na vs 46.6% for Li). Phosphorous is inert in both the cases.**

❑ **F atoms are more active than O in charge transfer in case of $FeSO_4F$. Li gives up 88% valence charge while Na gives up 82% valence charge. Sulfur stays inert similar to P in $FePO_4$**

Partial Density of States for all materials

- ❑ Cobalt d-states in CoO_2 accept small amount of charge and oxidation state moves from +1.35 to +1.25 for both Li and Na intercalation
- ❑ Conducting states in Co d-orbital moves below Fermi energy on intercalation
- ❑ Lower potential for Na intercalation is due to lower charge transfer, leading to lower stability of $NaCoO_2$ than $LiCoO_2$

- ❑ Iron d^5 state is very prominent in $FePO_4$
- ❑ Intercalation leads to $e_g - t_{2g}$ splitting in down spin d-orbital states.
- ❑ Oxygen states in $NaFePO_4$ show sharper peaks than $LiFePO_4$. Less covalence means lower stability and lower voltage

- ❑ Iron d^5 state is very prominent in $FeSO_4F$ up spin but down spin show $e_g - t_{2g}$ splitting
- ❑ Intercalation leads to large increase in bandwidth of up spin d-orbital states.
- ❑ Oxygen states in $FeSO_4F$ moves to lower energy on intercalation leading to stability. Oxidation state goes from -1.27 to -1.33 (Na case) and -1.37(Li case)
- ❑ Most electronegative element fluorine gains more charge on Li intercalation to give the system more stability than on Na intercalation

Bader charge transfer during intercalation and voltage

Materials	% Bader charge transfer to (after Li intercalation)			% Bader charge transfer to (after Na intercalation)		
	Transition metal	Anion	Voltage (V)	Transition metal	Anion	Voltage (V)
CoO_2	12.3(Co)	87.7(O)	4.19	13.6(Co)	86.4(O)	3.28
$FePO_4$	46.8(Fe)	6.7/46.6(P/O)	3.45	50.8(Fe)	4.9/44.3(P/O)	2.79
$FeSO_4F$	48.5(Fe)	-1.2**/40.7/11.9 (S/O/F)	3.67	55.5(Fe)	1.46/35.4/8.9 (S/O/F)	2.85

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