Study of Olivine Phosphates as Cathodes for Lithium Ion Batteries

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ABSTRACT

Electronic structure calculations for olivine phosphates (LiMPO$_4$) are done with correlation effects taken into account. Heavier TMs in olivines lead to greater ionic character and higher potential for lithium extraction. However, LiFePO$_4$ has a lower potential due to the enhanced stability of FePO$_4$ with half filled d-orbitals. Variation in electrochemical potential is explained in terms of charge transfer during delithiation.

INTRODUCTION

Transition metal olivine phosphates have emerged as the cathode material of choice in lithium ion battery systems specially for electric vehicle application. Lithium iron phosphate due to its low cost, high cyclability, good thermal stability, environmental friendliness and adequate energy density (~170 mAh/g) has been widely commercialized. One Laptop per Child project uses LiFePO$_4$ for batteries. The low electrical conductivity of the olivine phosphates has been overcome by using carbon black coated nano-particles instead of bulk materials. Other members of this series and mixed phosphates are being studied as possible cathodes with better electrochemical characteristics compared to LiFePO$_4$. We have carried out Density Functional Theory (DFT) based electronic structure calculations and 3D mapping of charge transfer during lithiation/de-lithiation to explain the observed trends in these materials.

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
- 920 eV wavefunction cutoff and Brillouin zone sampling through Monkhorst-Pack k-mesh of 3x4x4
- Energy minimization with respect to lattice parameters and atomic positions
- Bader scheme for charge analysis

Phonon simulation using Density Functional Perturbation Theory (DFPT) with Quantum Espresso: Structural stability
- Spin dependent GGA approximation with Perdue-Burke-Ernzerhof exchange correlation functional
- Ultrasoft Pseudopotential
- 30 Ryd wavefunction cutoff, 240 Ryd charge density cutoff and Brillouin zone sampling through 8 irreducible k-points
- Lattice parameters and atomic positions optimization
- Implementation of Acoustic Sum Rule (ASR)

From the ground state energies of the lithiated, delithiated structures and lithium, one can calculate the electrochemical potential against standard lithium electrode (lithium intercalation potential).
Considering that entropic and volume changes are negligible, the Gibbs free energy difference can be approximated with the ground state energy difference.
Thus, the electrochemical potential can be evaluated from the equation

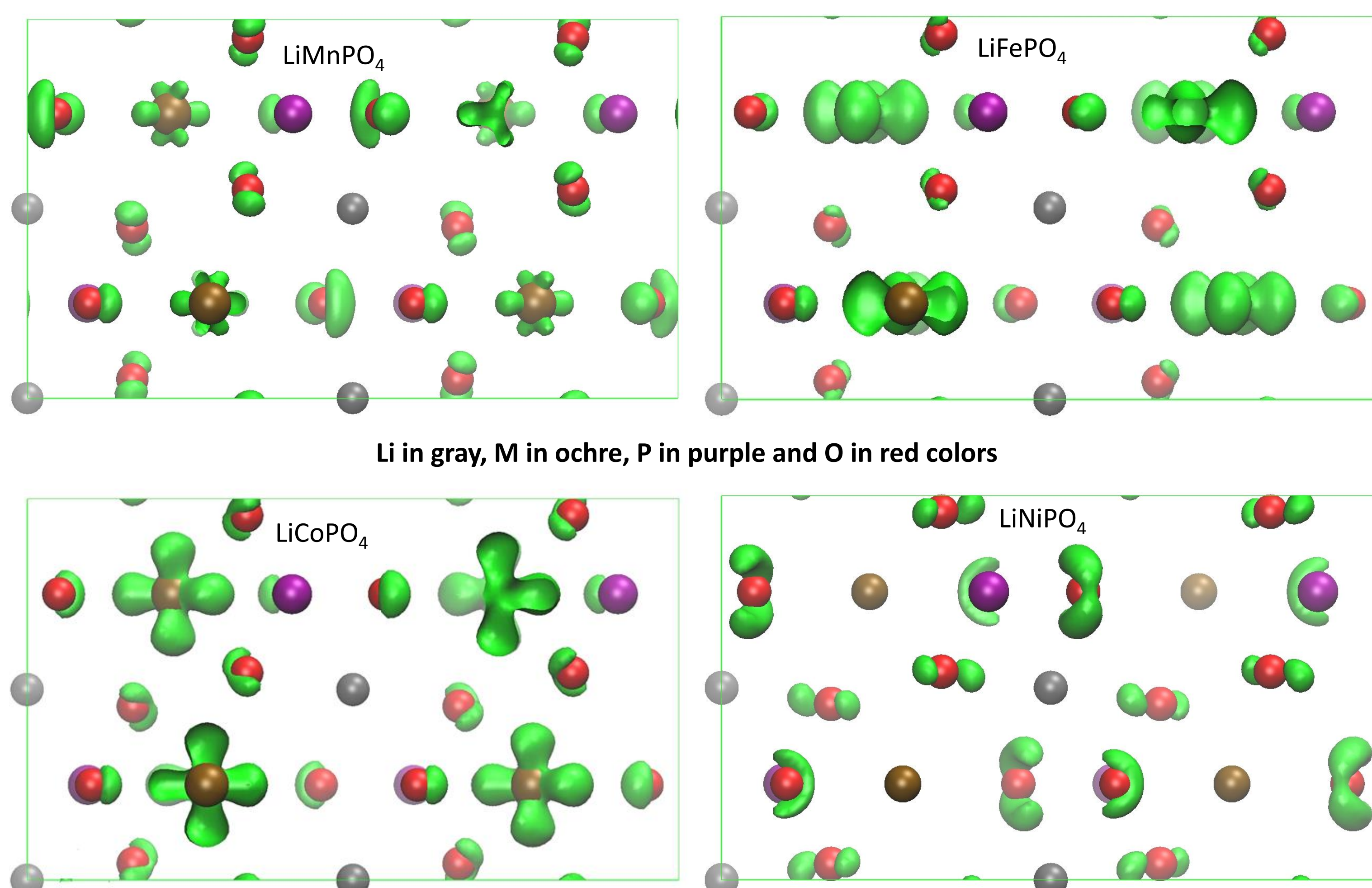$$V = \frac{E_{MPO_4} + E_{Li} - E_{LiMPO_4}}{nF}$$

where, V = Electrochemical potential, E$_x$ = Ground state energies of respective materials, F = Faraday's constant, and n = total charge transferred. Charge transfer maps can be obtained from the difference between real space charge density of lithiated and de-lithiated compound.
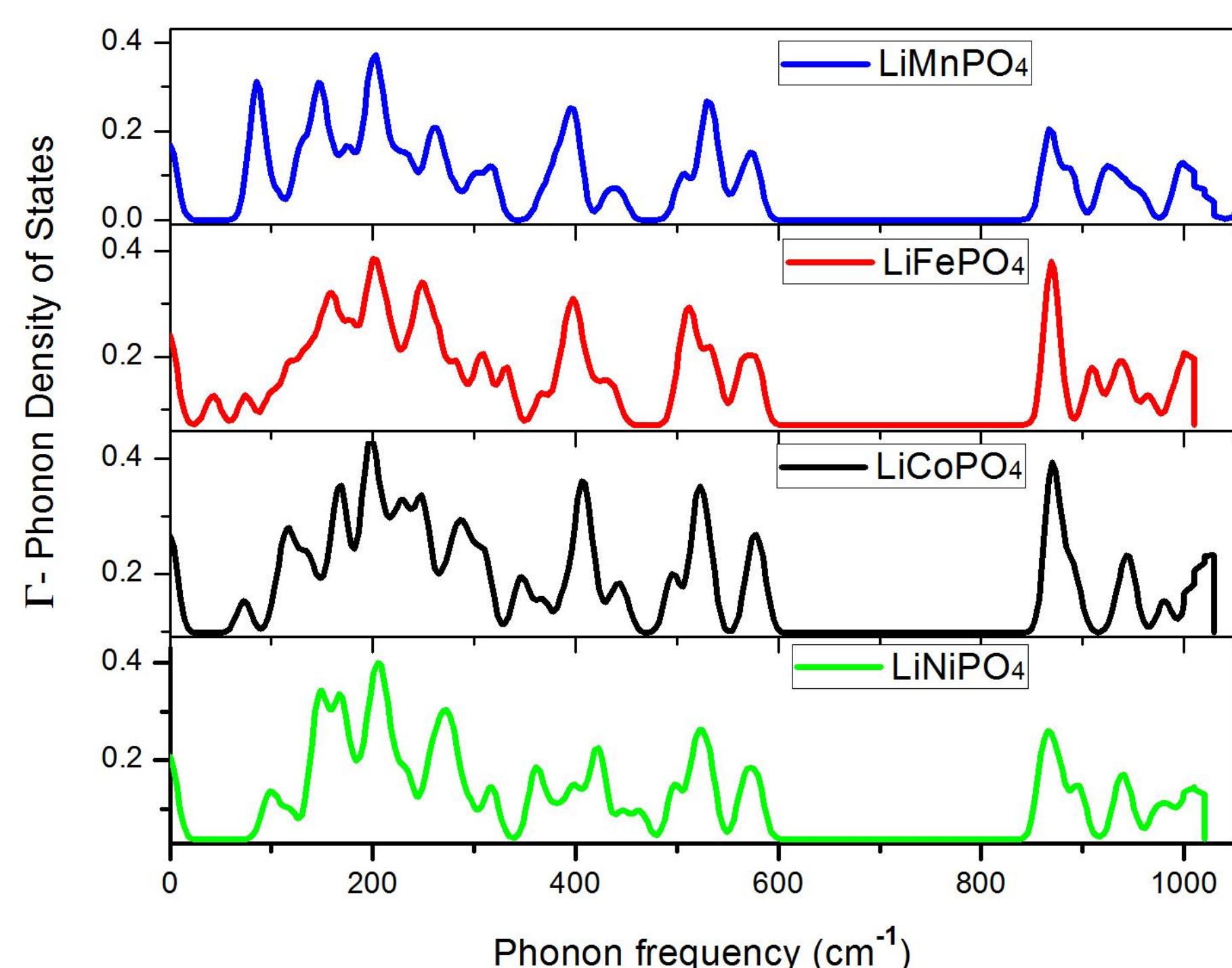
Structural Parameters from simulation

Materials	Lattice parameters in Å (experimental)			Lattice parameters in Å (DFT)				Volume change due to de-intercalation (Theoretical)
	a	b	c	a	b	C	Cell vol. (Å³)	
LiMnPO$_4$	10.44	6.09	4.75	10.62	6.18	4.79	314.7	-5.29%
LiFePO$_4$	10.33	6.01	4.69	10.41	6.06	4.75	300.6	-4.25%
LiCoPO$_4$	10.20	5.92	4.70	10.24	6.00	4.75	291.6	-1.91%
LiNiPO$_4$	10.03	5.85	4.68	10.12	5.91	4.72	282.4	-5.64%

- Later TM compounds have lower unit cell volume
- Low volume change during Li-intercalation makes these cathodes ideal

3D plot charge transfer during de-lithiation

Li in gray, M in ochre, P in purple and O in red colors

Total Density of States for olivine phosphates

Position of TM d-orbitals and O p-orbitals in LiMPO$_4$
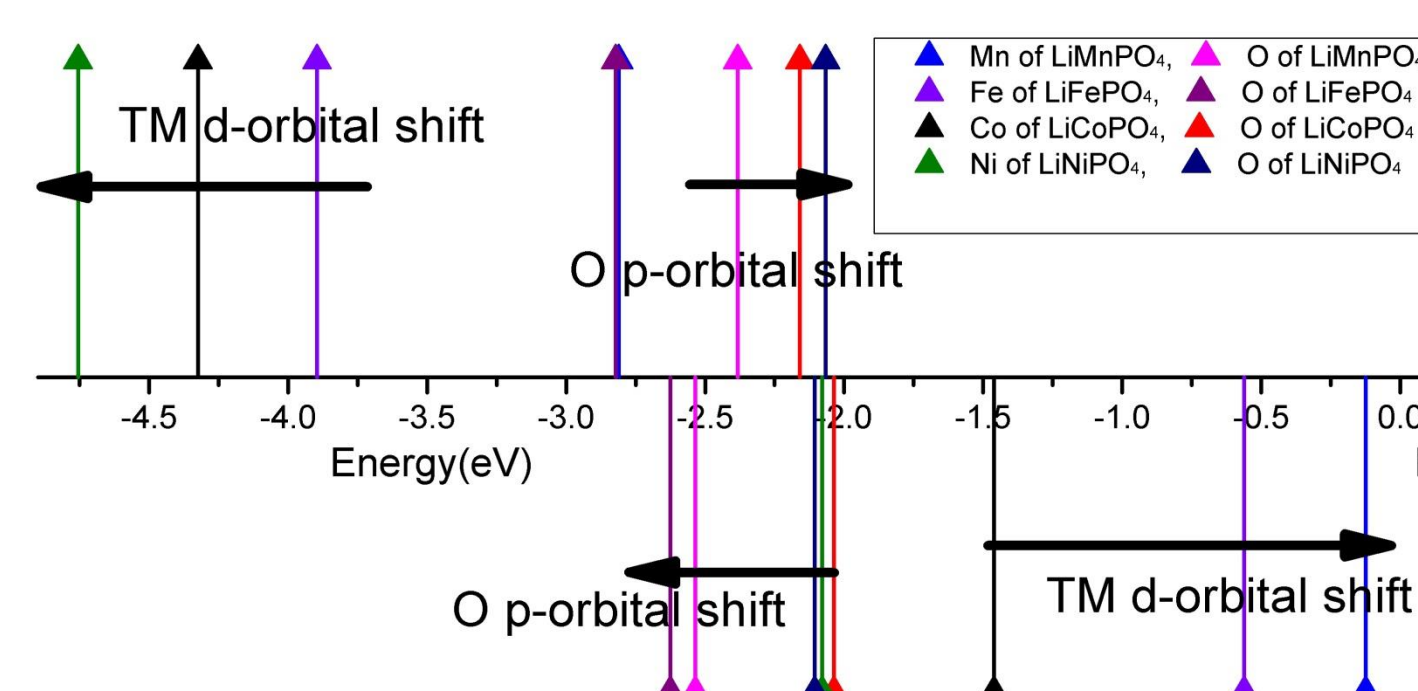
- In later TM compounds, d-orbitals are much deeper in energy and oxygen p-orbitals are placed closer to Fermi energy
- Energy level difference between d-orbital and O p-orbital increases from Mn to Ni
- Heavier olivine phosphates have more ionic character due to less hybridization.

Charge transferred to oxygen during deintercalation of lithium leads to high electrochemical potential

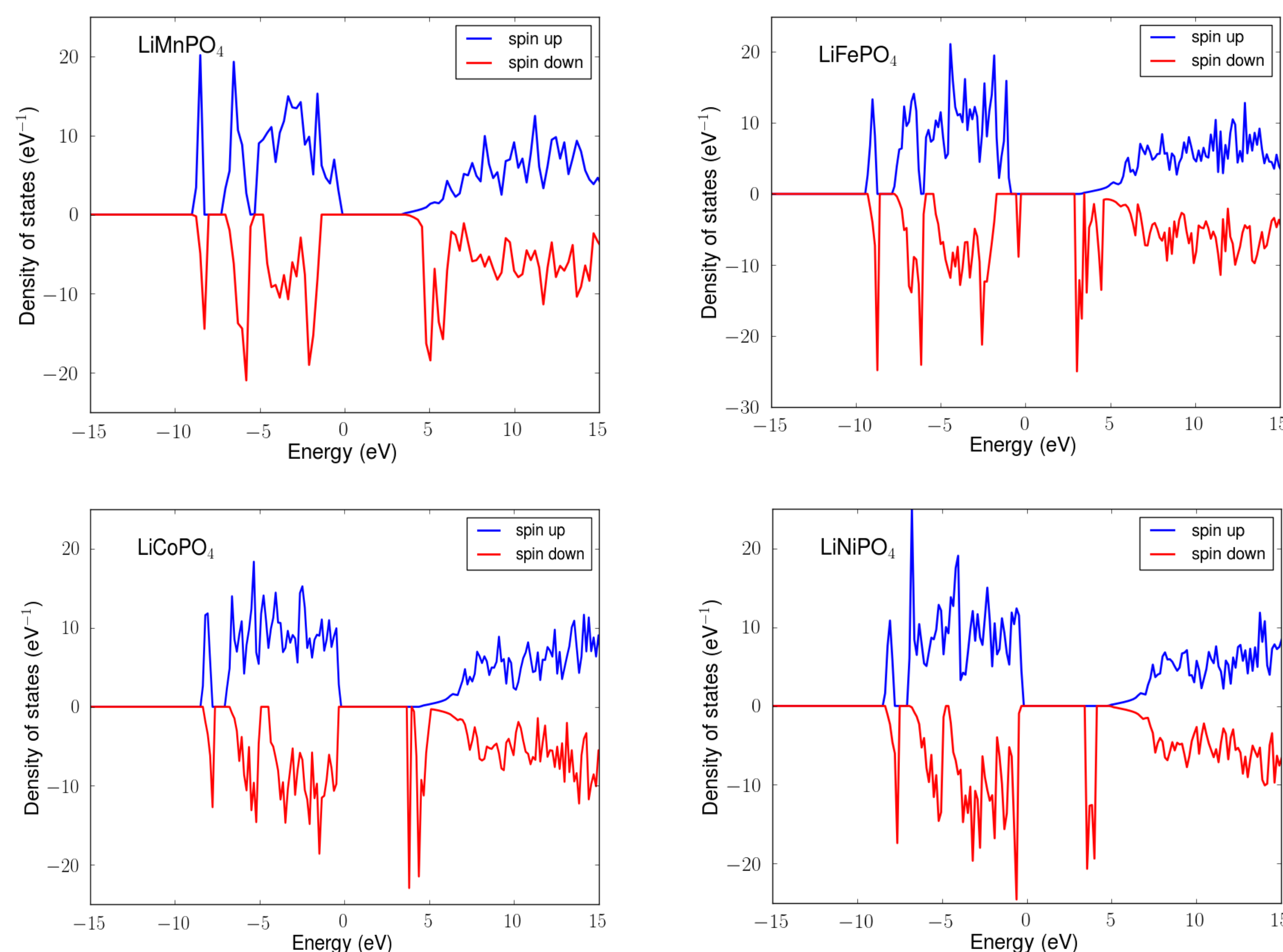| Material	Electrochemical potential for LiMPO$_4$/Li cell (V)	% of Li charge transferred to Oxygen
LiMnPO$_4$	4.2	54.8
LiFePO$_4$	3.51	45.6
LiCoPO$_4$	4.62	55.6
LiNiPO$_4$	5.11	83.6

Vibrational spectra at Brillouin zone centre

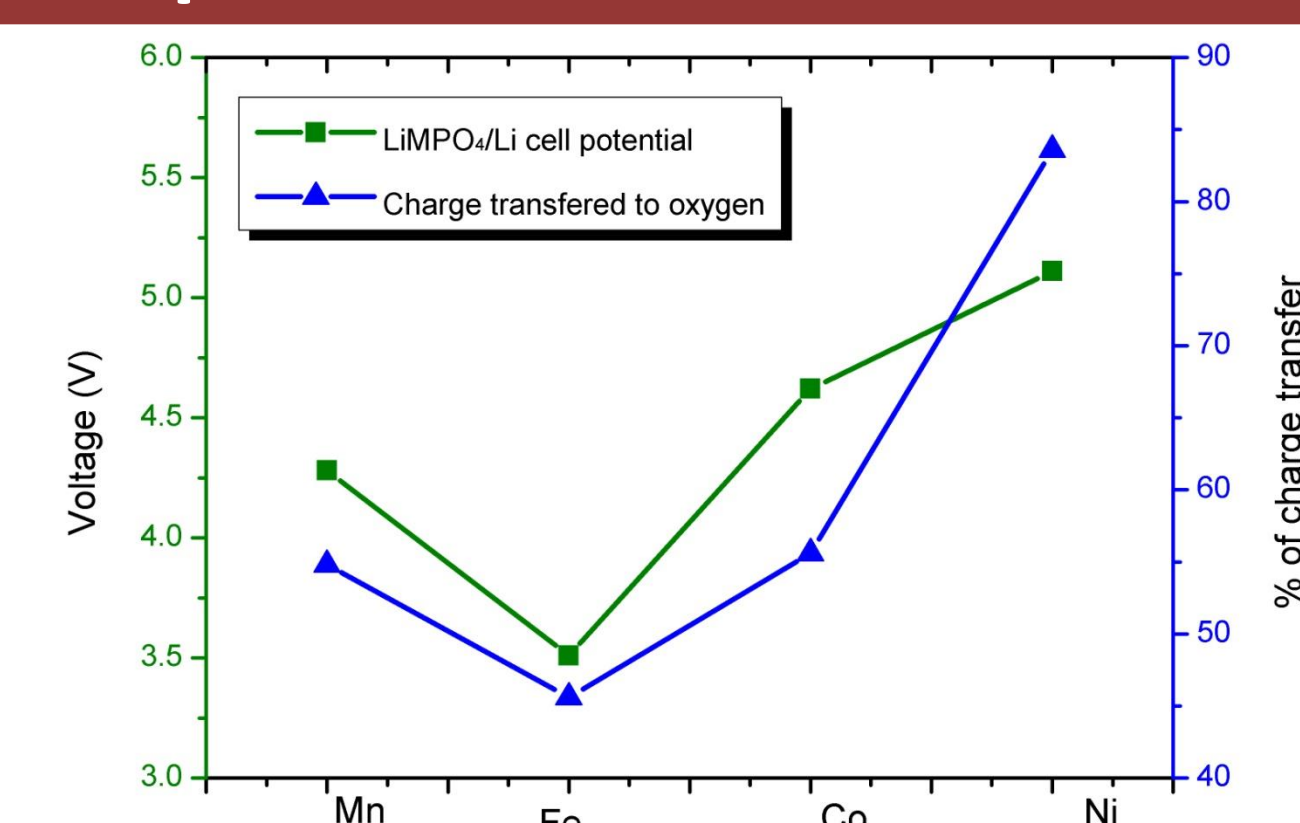- All olivine phosphates have stable vibrational modes
- A large number of low frequency mode shows less contribution to Gibbs free energy

✓ Being more electronegative, charge transfer to oxygen leads to lower electrostatic energy and hence higher voltage.

✓ With the exception of LiFePO$_4$ heavier TM olivines with more d-electrons have high Li-intercalation potential.

✓ FePO$_4$ is stable due to the half filled d-orbital. So, it is relatively easy to de-intercalate lithium from LiFePO$_4$ giving only ~3.5V.

Acknowledgments