Electronic structure of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$:

Effect of local correlation and non-local exchange

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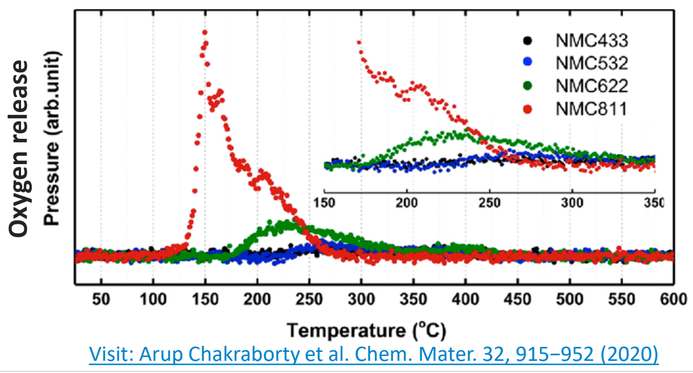
Introduction

- **NMC532** ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$) is a layered-structure oxide materials used as a **cathode** in **Li-ion batteries**.
- Improved performance compared to individual layered materials (e.g., LNO, LMO, LCO) in terms of **high energy density**, **safety**, and **less structural degradation**.
- Relatively **higher initial discharge capacity** and **higher capacity retention** amongst several representative compositions (e.g., NMC622 and NMC811).

Motivation

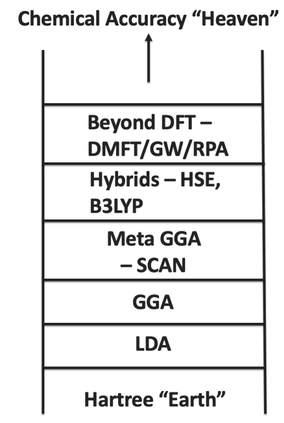
- Regarding the degradation by **singlet oxygen evolution**, why is NMC532 relatively more stable than other compositions upon heating?
- What **electronic properties** can be addressed from DFT calculations with different degrees of localization?
- Study the relative effect of **disorder** and **ionic positions** in the supercell.



Visit: Arup Chakraborty et al. Chem. Mater. 32, 915–952 (2020)

Computational Methods

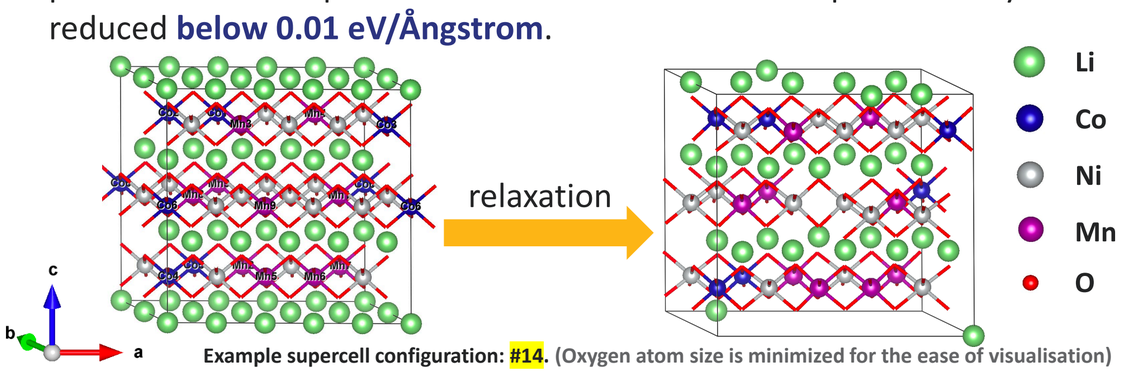
- **D**ensity **F**unctional **T**heory **(DFT)** calculations were performed using **V**ienna **A**b initio **S**imulation **P**ackage **(VASP).**
  - Basis set: **P**rojector **A**ugmented **W**ave method **(PAW)**
  - **P**erdew-**B**urke-**E**rnzerhof functional **(PBE)**
  - **PBE** functional with static **Hubbard U** correction **(PBE +U)**
    - Renormalized Coulomb potential
    - A more accurate modelling for the local correlations in transition metal (TM) d orbitals.
  - **H**eyd–**S**cuseria–**E**rnzerhof **(HSE06)**
    - Hybrid functionals
    - DFT + Hartree Fock (HF)
    - 25% exact (HF) exchange + 75% PBE exchange + 100% PBE correlation energy



Visit: John Perdew et al. AIP Conference Proceedings 577, 1 (2001)

Structural Optimization

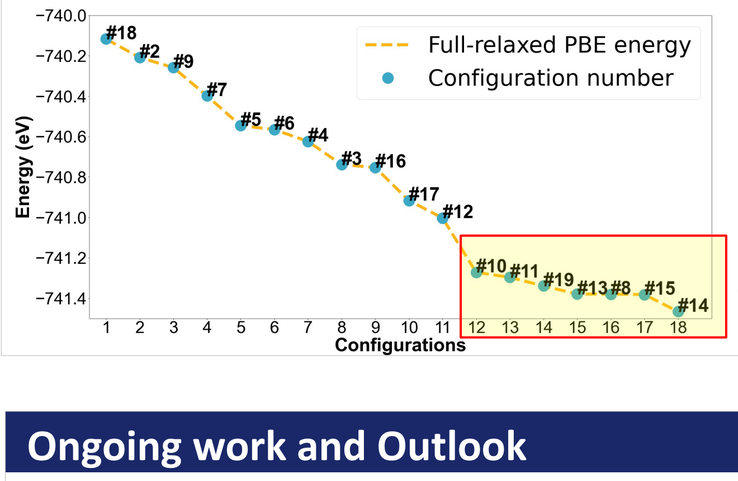
- In **V**isualisation for **E**lectronic **S**truc**t**ural **A**nalysis **(VESTA)**, **18 supercells** were built in the scale of **5x2x1**, each in a different motif consisting of **120 atoms**, with Li and TM ions in alternating layers.
- All the structures underwent relaxation, where ion positions and lattice parameters were optimized till the **maximum force** experienced by ions reduced **below 0.01 eV/Ångstrom**.



Example supercell configuration: #14. (Oxygen atom size is minimized for the ease of visualisation)

Energy Minimization

- Energy minimization for relaxed structures using **PBE**.
- Their energy results were recorded according to the **self-consistent field method (SCF)**: the **energy difference** calculated for the same structure in the last iteration of calculation was **converged within 0.000001 eV**.
- Energy difference across different structures:
  - **Max.** ΔE : ~ 1.3482 eV (between **#18** and **#14**)
  - **Min.** ΔE : ~ 0.0004 eV (between **#13** and **#8**)
- Lowest energy configuration is found: **#14** (confirmed again by **PBE+U, HSE06**)

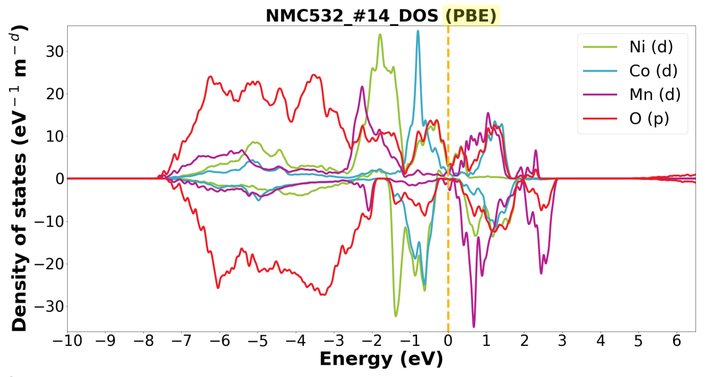


#	ΔE compared to #14 (eV)
...	...
10	+0.1912
11	+0.1694
19	+0.1268
13	+0.0867
8	+0.0862
15	+0.0844
14	0.0000

Results and Conclusions

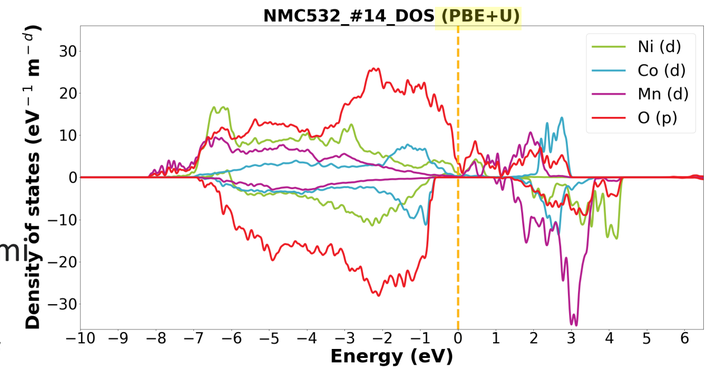
PBE

- **Generalised Gradient Approximation (GGA)**
- DOS plot shows the hybridization of TM d orbitals with O p orbitals.
- Energy levels localised around Fermi level = 0 eV, no observable band gap.
- **Metallic state.**



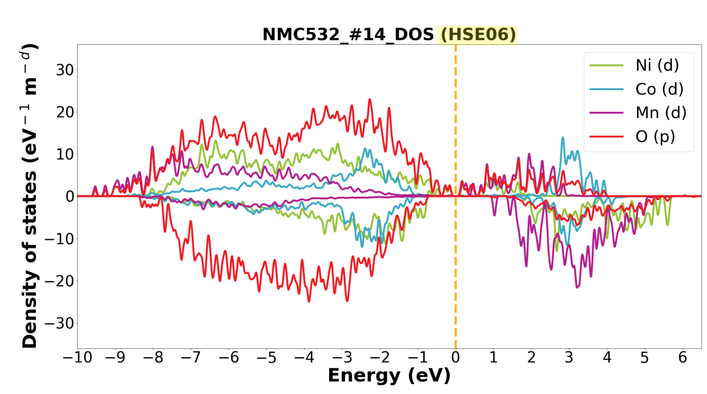
PBE + U

- **U value** applied:
  - strength of the effective on-site **Coulomb** interactions
  - later TM ions, larger value
  - U_{Ni} = 6 eV; U_{Co} = 5 eV; U_{Mn} = 4.5 eV.
- **J value** applied:
  - strength of the effective on-site **Hund's coupling.**
  - $J_{Ni} = J_{Co} = J_{Mn}$ = 0.9 eV
- **Half-metallic state:** Zero density of states around Fermi level for the down spin electrons.
- Band gap for down spin ~ 1.11 eV



HSE06

- **Hybrid functional using non-local Fock exchange**
- **Semi-conductor / insulator:** Small band gap
- Band gap for down spin ~ 1.22 eV
- Band gap for up spin ~ 0.17 eV



Ongoing work and Outlook

- Using DFT-relaxed NMC532 structures, **GW** and **Dynamical mean field theory (DMFT)** can be performed to explore the exact role of correlations in these ground states, and their excited states.
- The set of DFT-calculated extended Bloch eigenstates may be downfolded to the correlated orbitals using **Wannier projection,** and **accurate charge analysis** may be performed**.**
- This would bring the particular focus on how the battery's state of charge influences the **oxidation states** of the species involved, which will eventually unveil the **degradation mechanism of singlet oxygen ($^1O_2$) generation**.

Intern bio

Junpei Shi is a 2nd year undergraduate studying Chemistry at Imperial College London, with an interest in renewable energy and the battery sector.

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