UHMob International Conference – Organic Semiconductors

Charge storage mechanism in metal-organic polymers for alkali-ion battery electrodes

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Acknowledgments

Experiment
Roman Kapaev

Project Leaders
Keith Stevenson
Pavel Troshin

R Kapaev, A Zhugayevych, S Ryazantsev, D Aksyonov, D Novichkov, P Matveev, K Stevenson, Charge storage mechanisms of a π-d conjugated polymer for advanced alkali-ion battery anodes, Chem Sci 13, 8161 (2022)

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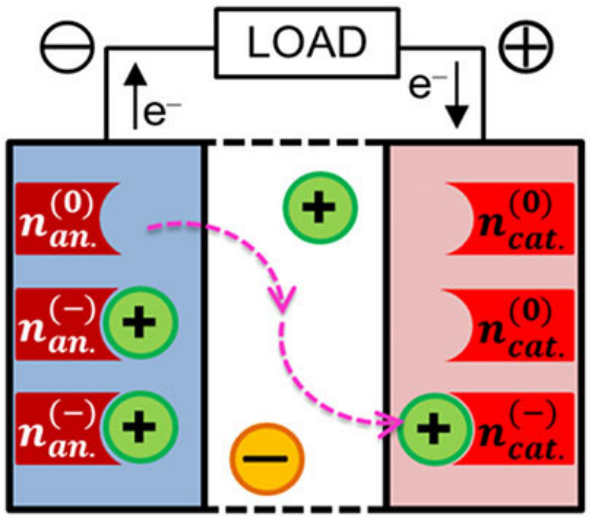
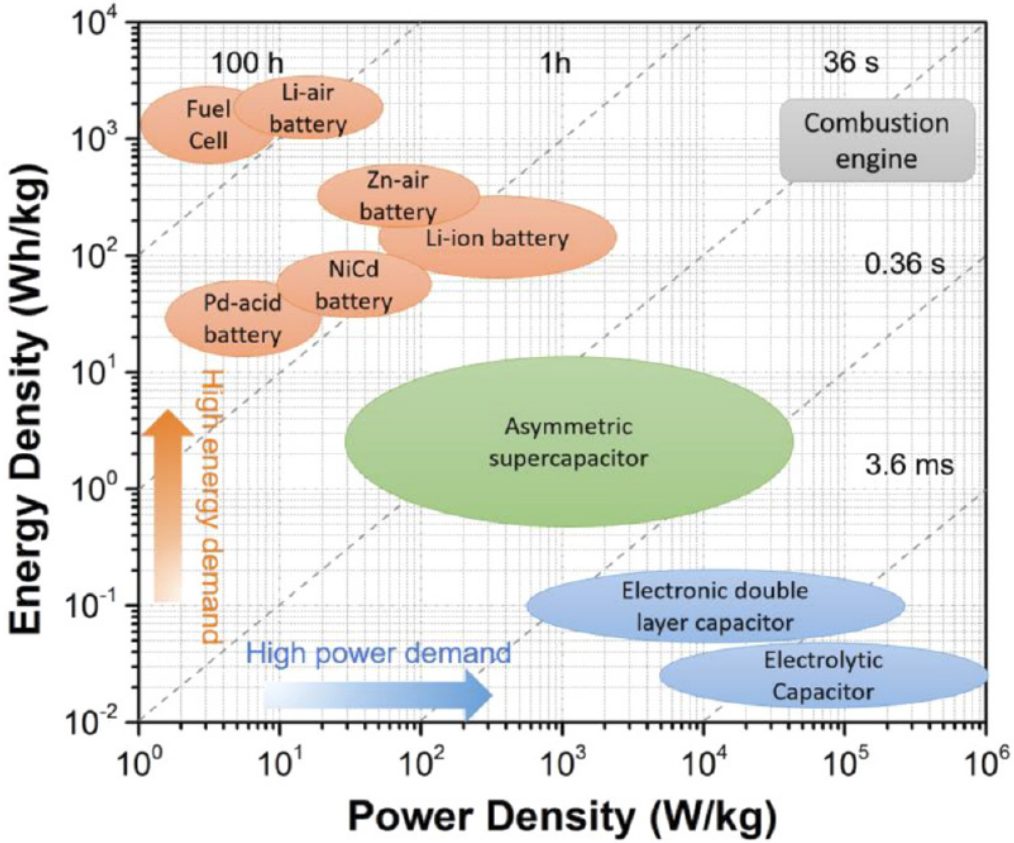
Electrochemical energy storage: Metal-ion batteries



Chem Rev 120, 6490 (2020)



Chem Rev 118, 9233 (2018)

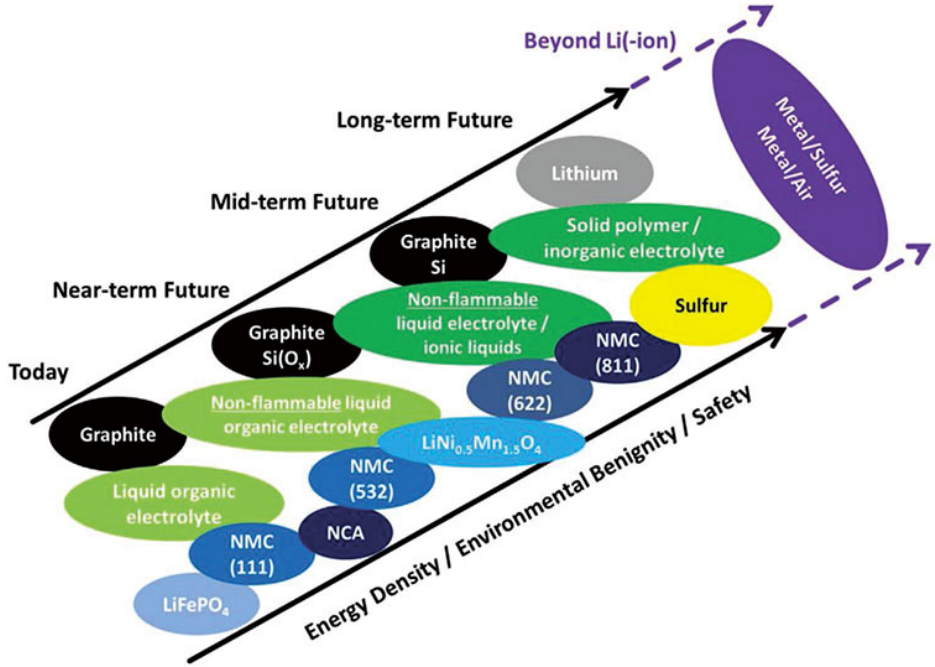
Power and energy, mass and volumetric capacities are the main parameters of a battery from practical perspective...

... More detailed list of parameters for electrodes

- Operational stability, reversibility
- High voltage
- Fast charging
- High ionic mobility
- High electronic conductivity
- Ease of production etc.

No single material can perfectly satisfy all these requirements
$\Longrightarrow$ *organic materials might find their own niche applications*

Possible niche for organic and metal-organic materials



Adv Energy Mater 12, 2102904 (2022)

Among the best are transition metal oxides (NMC, LFP) showing high voltage and operational stability, but

- Not fully reversible e.g. due to cation mixing
- Low ionic mobility (lattice is too rigid)
- Bulk carbon (organics) is added for electronic conductivity
- Graphite (organics) is used as anode

$\Longrightarrow$ *A lot of "opportunities" for organic materials*

Focus of this work: fast charging solid state electrode

(organic materials are soft so it is reasonable to expect fast ion intercalation)

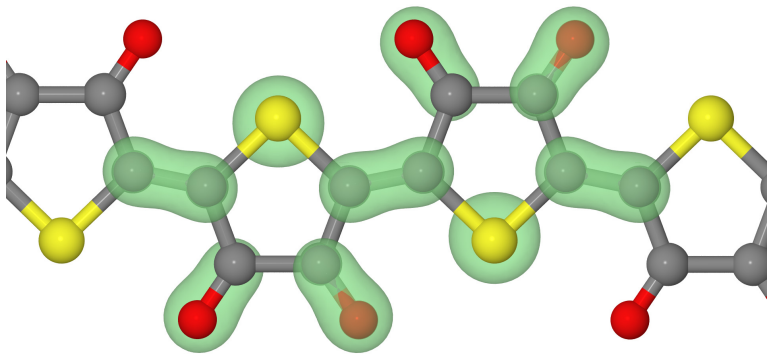
Some common problems of solid organic alkali-ion electrodes:
(easy to synthesize molecular and polymers, no frameworks)

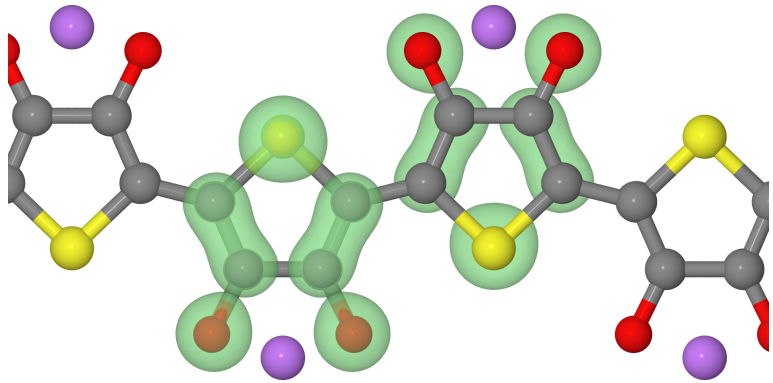
- Technological problems
  - Irreversible changes – creates many other problems
  - Poor electronic conductivity
- Theoretical problems
  - No structural data $\Longrightarrow$
    $\Longrightarrow$ no atomistic model for first-principle modeling
  - Limited material characterization $\Longrightarrow$
    $\Longrightarrow$ no way to cross-validate first-principle models
  - Consequently, very limited understanding of mechanisms
- Fundamental intrinsic problems
  - Organic materials need separated subsystems for
    (1) keeping structural rigidity and transporting electrons, and
    (2) charging or doping *(next slide)*

We are going to address (lucky to) most of these problems except for poor electronic conductivity

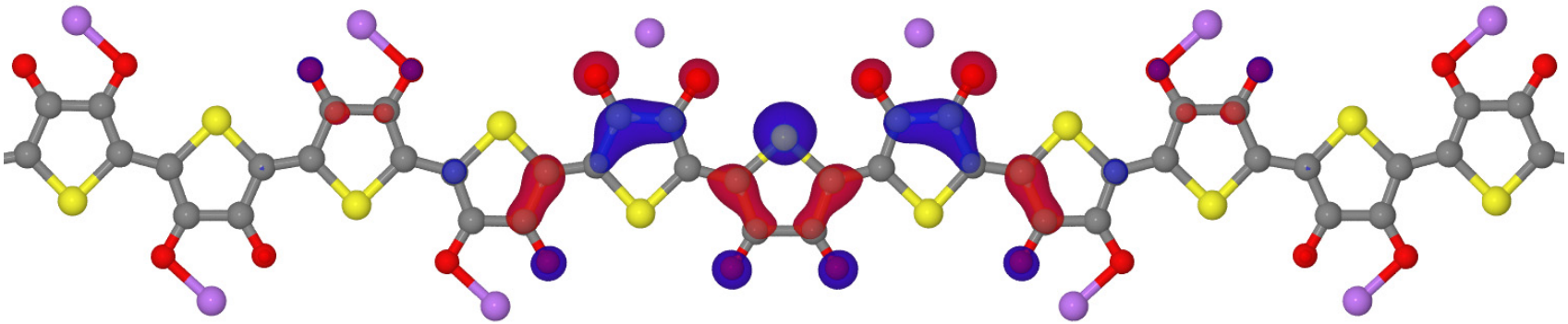
What happens if we dope/charge π-conjugated backbone

A toy model of a flexible polymer with local doping/charging





Upon Li-intercalation $pp\pi$-bonding pattern changes dramatically

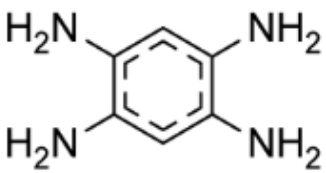


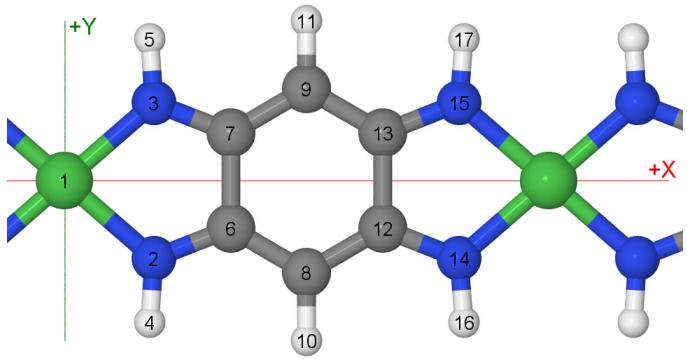
Deep electronic traps appear on Li-deficient monomers (-0.5 eV)

Upon ion intercalation irreversible structural changes are expected

Polymer under study: NiBTA in alkali-ion batteries

(BTA=benzenetetramine, considered alkali metals are Li, Na, K)





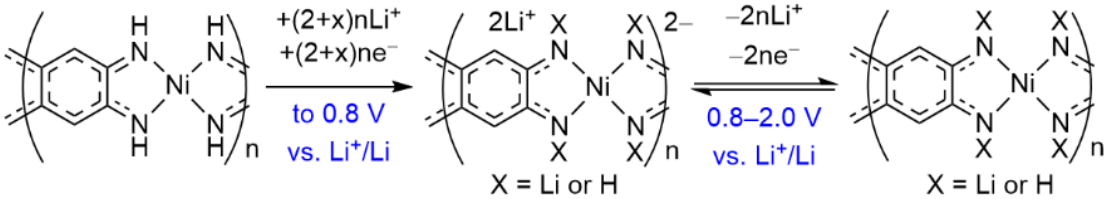
- Good performance in fast-charging metal-ion batteries
- Semicrystalline structure
- Fully reversible changes upon charge/discharge

However published reports contained controversial statements on

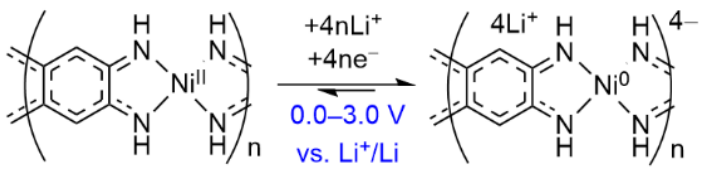
- Intermolecular packing (herringbone or π-stack, ions location)
- Electronic structure (metal or insulator, frontier orbitals)
- Mechanism of operation and role of transition metal...

... Previously proposed charge storage mechanisms

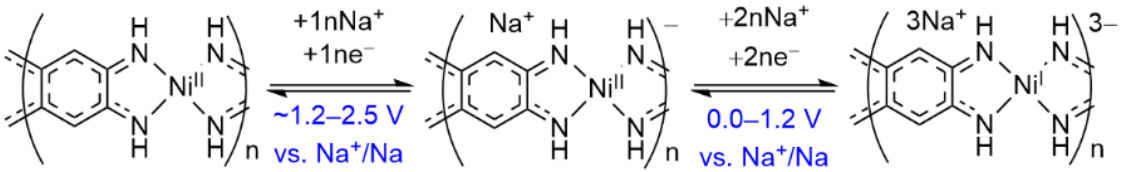
Kapaev *et al.* 2019, ref. 15:



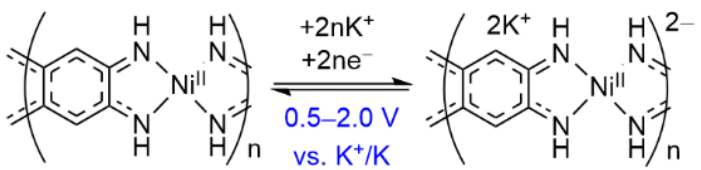
Xie *et al.* 2019, ref. 13:



Chen *et al.* 2019, ref. 14:



Kapaev *et al.* 2020, ref. 16:



The primary goal is to resolve controversies and understand mechanism of operation

Experimental methodology

(synthesis and characterization are performed by Roman Kapaev)

- Operando XRD
- Operando Raman
- UV-Vis-NIR absorption
- Cyclic voltammetry
- Galvanostatic cycling
- Microscopy and elemental analysis (HAADF-STEM and EDX)
- XANES by Sergey Ryazantsev

Rarely a theoretician is given such a comprehensive set of data + the only known to me fully characterized material of its class

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HAADF=High-Angle Annular Dark-Field imaging, STEM=Scanning Transmission Electron Microscopy, EDX=Energy-Dispersive X-ray spectroscopy, XANES=X-ray Absorption Near Edge Structure

Computational methodology

(difference from commonly used approaches for metal-organic electrodes,
in other words, many controversies can be resolved just by choosing the right method)

Intermolecular geometry

- ~~PBE, fitting 3 broad XRD peaks~~ → PBE-D3
- Ad hoc structure prediction followed by ab initio MD

Intramolecular geometry and electronic structure

- ~~PBE, GGA+U, B3LYP~~ → PBE0, CAM-B3LYP
- composite basis of 6-31G* till Ar and TZVP after Ar

Analysis of electronic structure

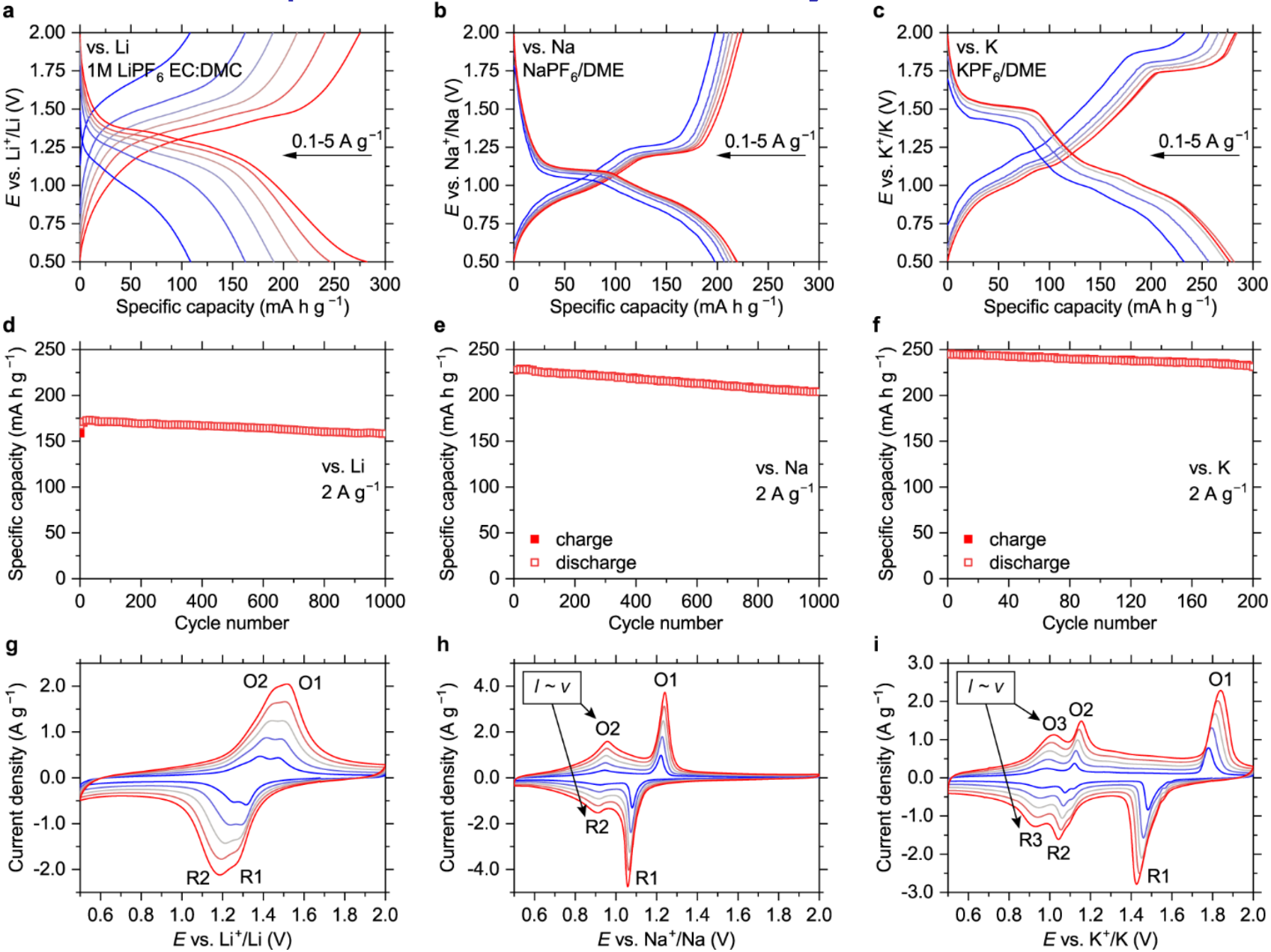
- ~~bands, canonic MO~~ → localized MO and inter-LMO couplings
- ~~charge density~~ → wave-function

Validation

- crystal structure and UV-Vis of oligomers
- use of methods well-benchmarked for semiconductors

MD=Molecular Dynamics, MO=Molecular Orbital, LMO=Localized MO

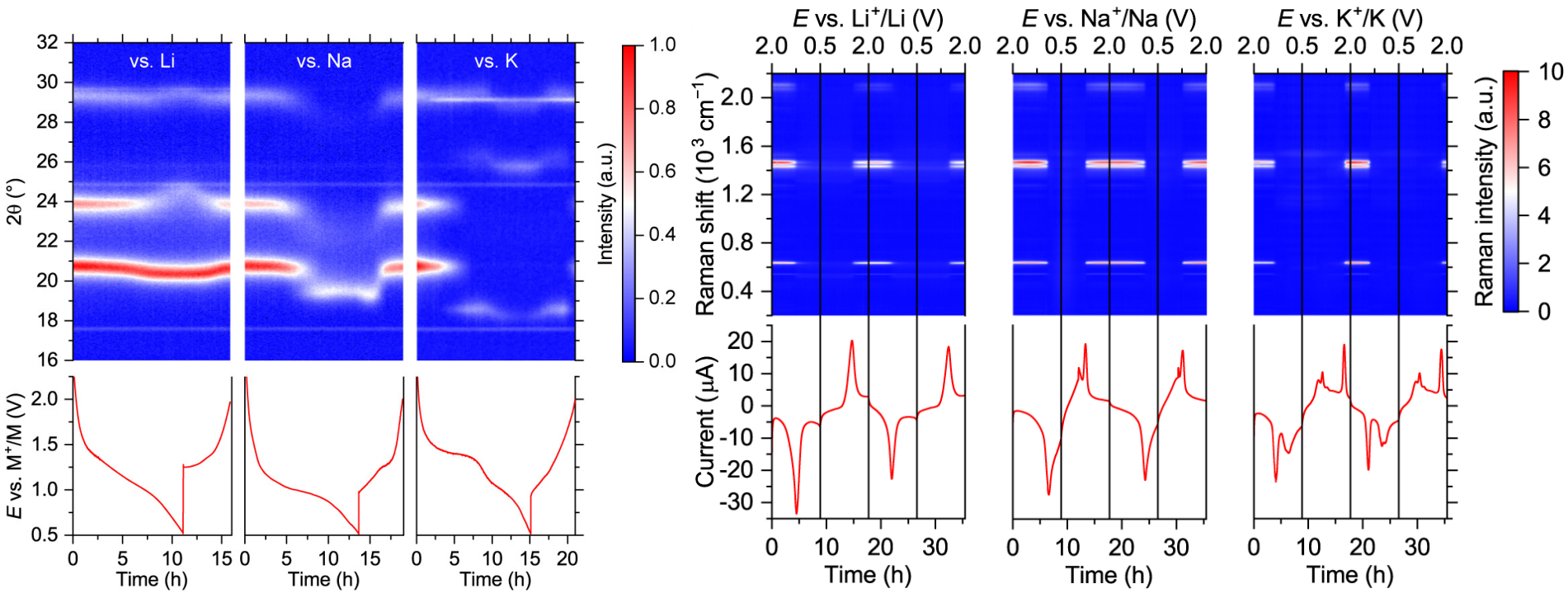
Results: Good performance in battery with metal electrode



Material is stable at high charge-discharge rates

Fully reversible changes upon charge-discharge cycling

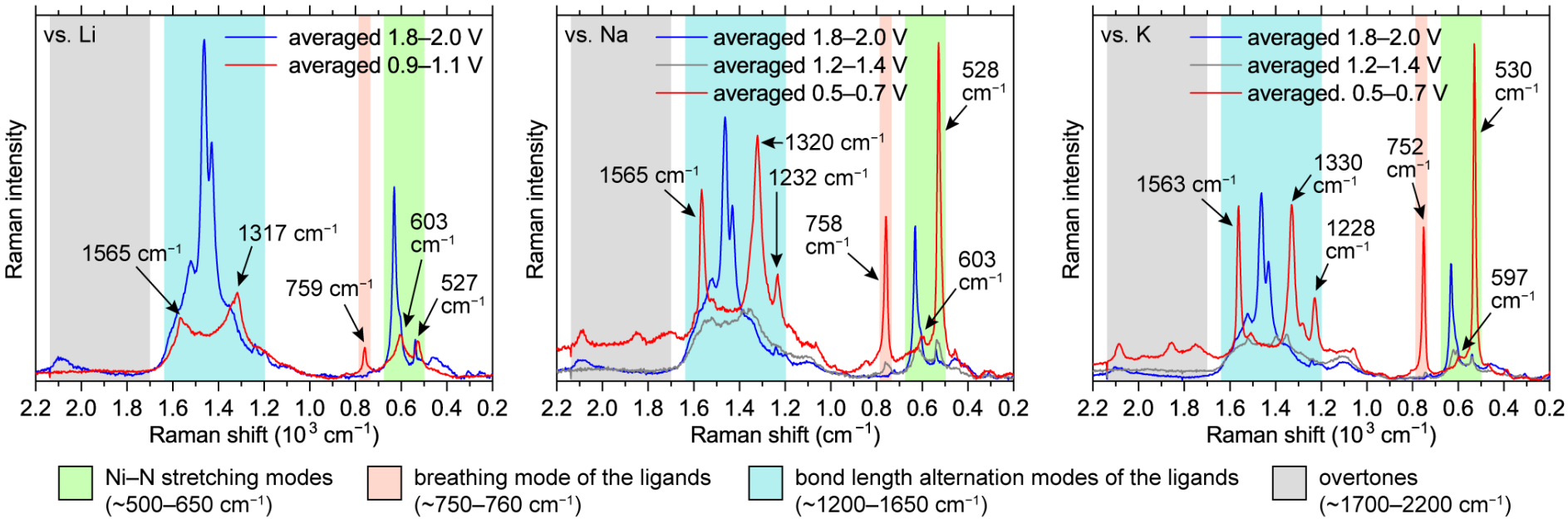
(operando XRD and Raman)



Material has well-defined structure, changes are fully reversible

Resonance Raman spectra have several distinctive peaks

(and new peak appears at 750 cm^{-1} upon alkali ion intercalation)

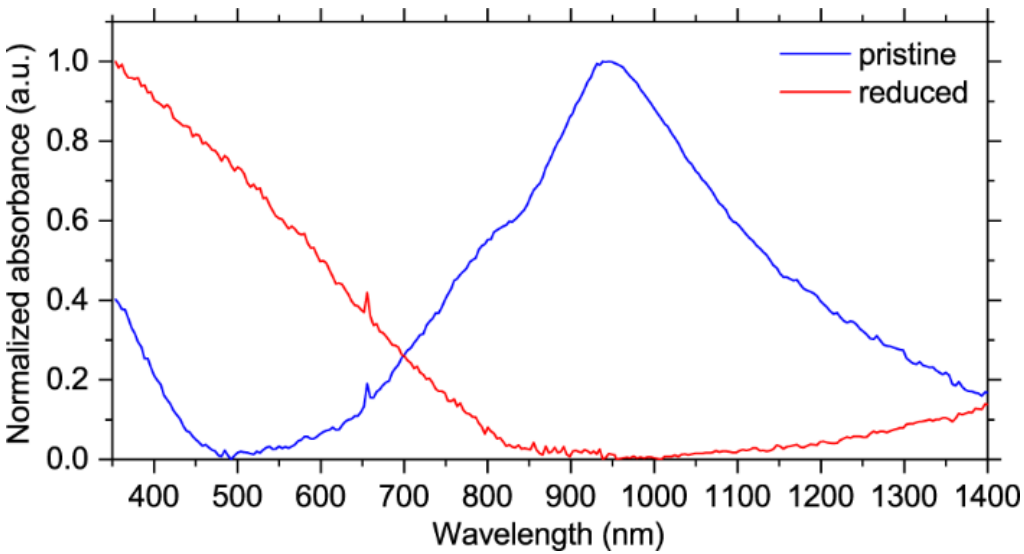


Important for validation of atomistic models

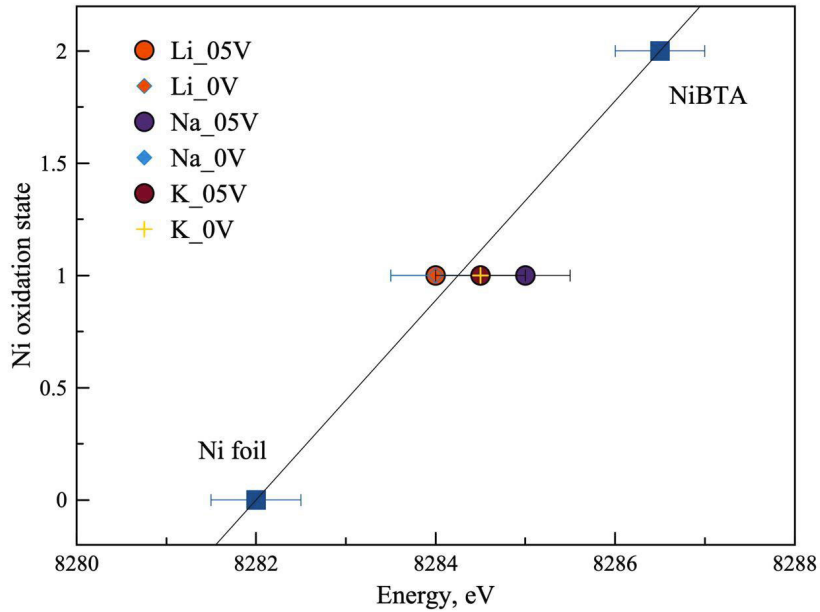
(Raman for intramolecular structure and XRD for intermolecular)

UV-Vis-NIR and XANES spectroscopies are puzzling

(mutually inconsistent and inconsistent with published calculations)



(published calculations show very small gap)



(hypothetical $Ni^{2+} \rightarrow Ni^{+}$ reduction should result in gap reduction)

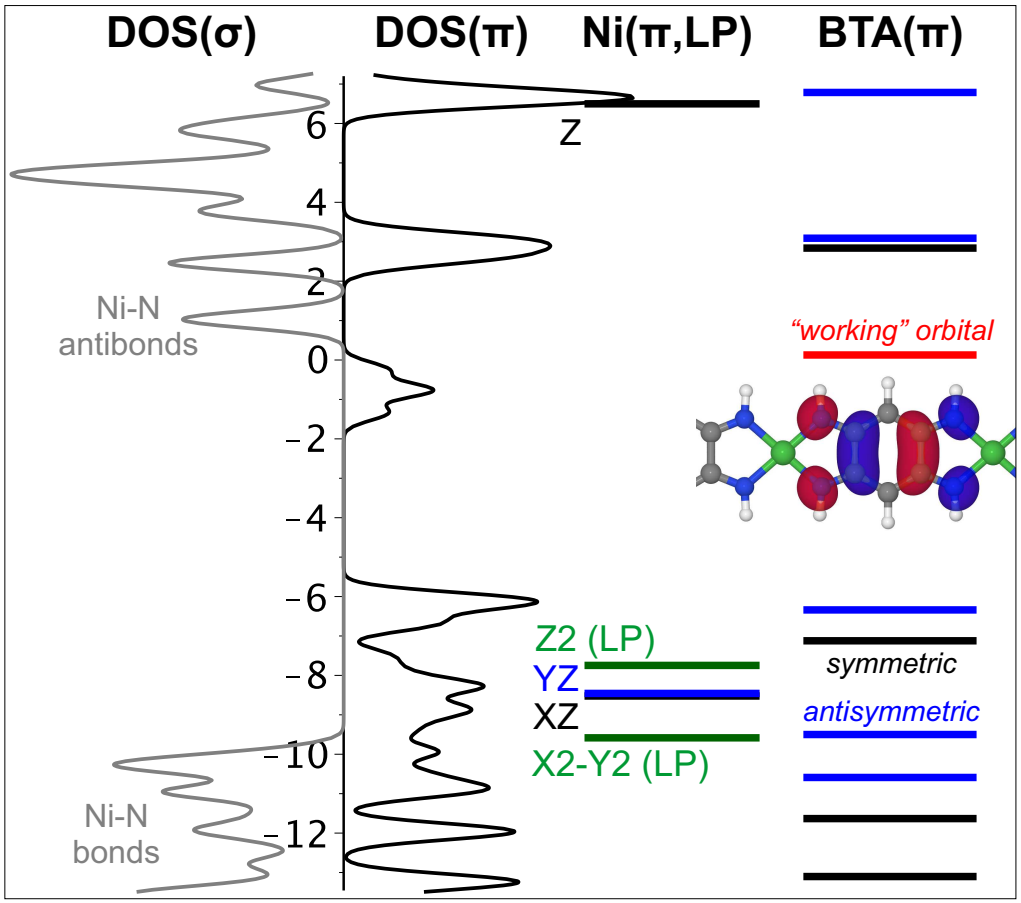
This and other questions to theoreticians:

- Interpretation of spectroscopic data
- Atomic positions (controversial published reports)
- Electronic structure (controversial published reports)
- *Mechanism of operation* (controversial published reports)

Electronic structure of a single polymer chain

(localized molecular orbital analysis of π-system using proper density functional)

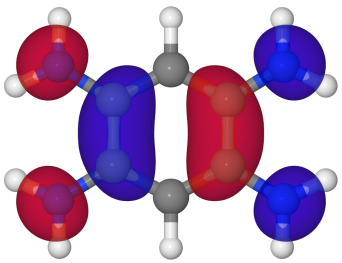
Polymer chain remains planar in operational range up to 2e per Ni

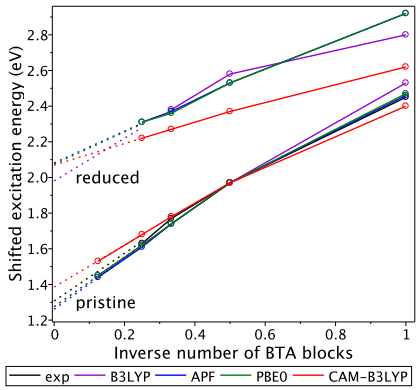


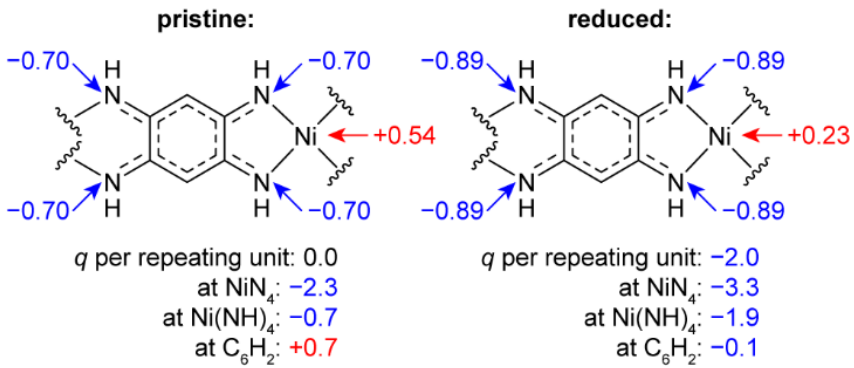
Ni itself is electrochemically inactive but pre-charges (dopes) organic part of the π-conjugated polymer (BTA ligand)*

* in analogy to π-backbonding Ni donates 2e through Ni-N σ-bonds but withdraws them back from BTA π-system, so that formally Ni is in $Ni^{(0)}$ state

... This immediately explains spectroscopic data

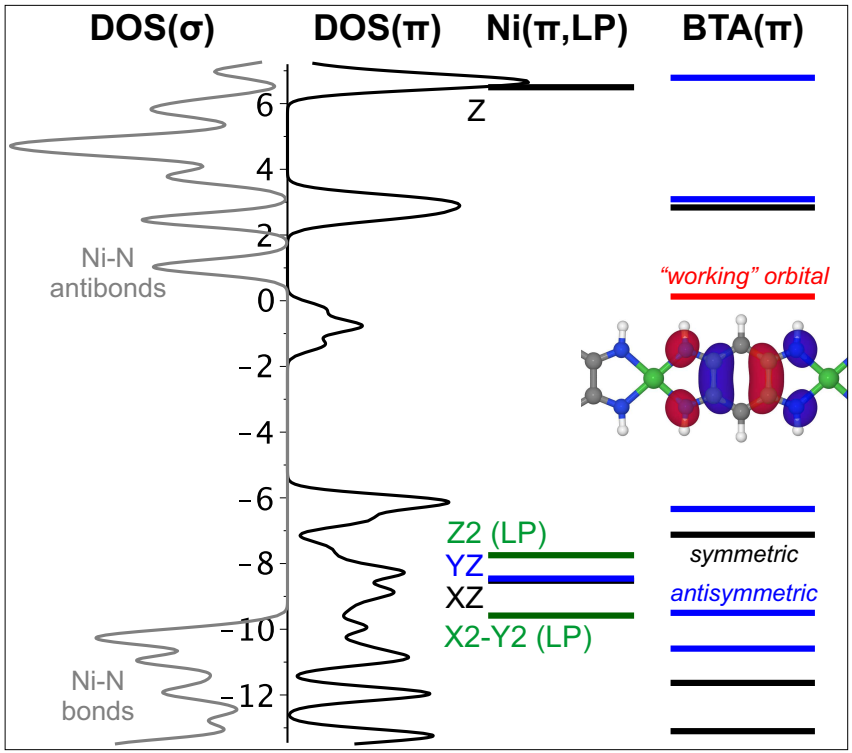






- Optical gap is increased upon reduction because π-system of BTA ligand returns to its normal occupation state in the most stable form of free BTA molecule
- Raman peak at 750 cm^{-1} (breathing mode) is invisible in pristine polymer because of zero electronic density on vertical C-C bonds whose stretching constitutes the breathing
- Linear fit to XANES is valid but with Ni charge rescaled to computed values showing $+0.54$ to $+0.23$ reduction

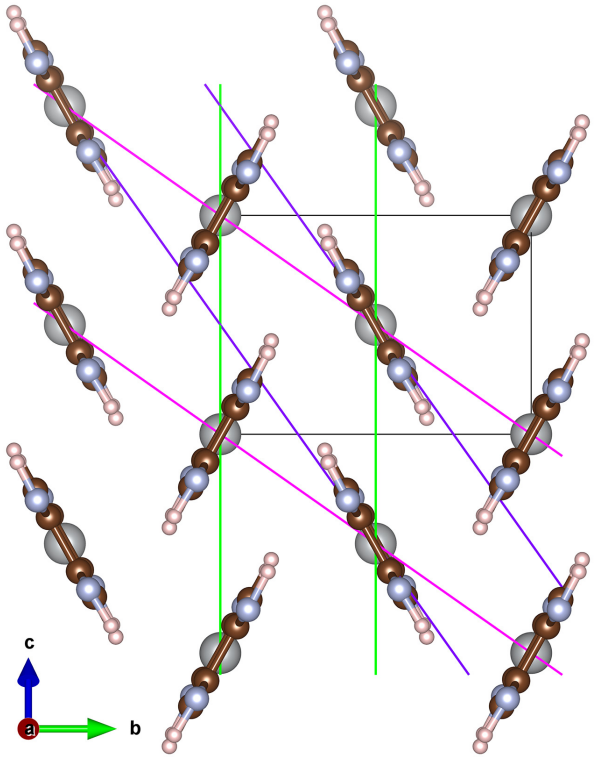
... and also explains structural stability during charging

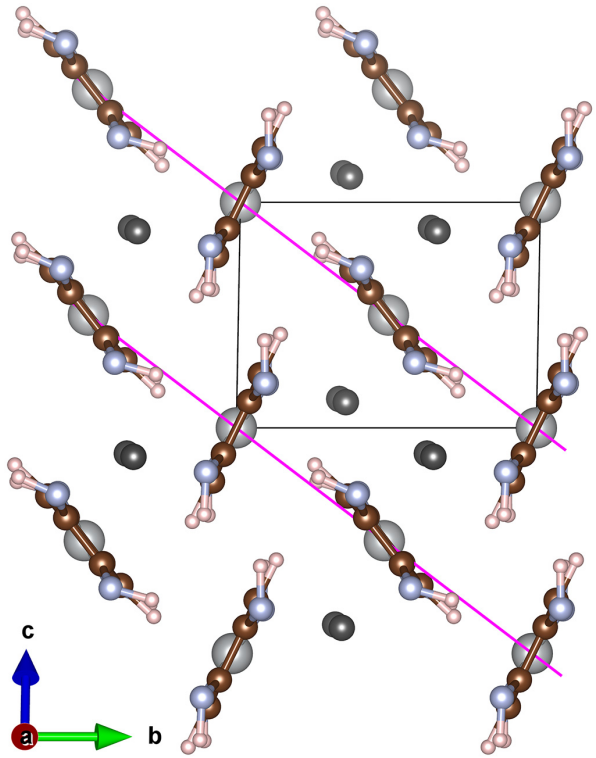


- All bonding molecular orbitals remain intact upon charging with up to 2e per repeating unit
- Further reduction populates Ni-N antibonding orbitals thus loosening the structure

Intermolecular structure and ion intercalation mechanism

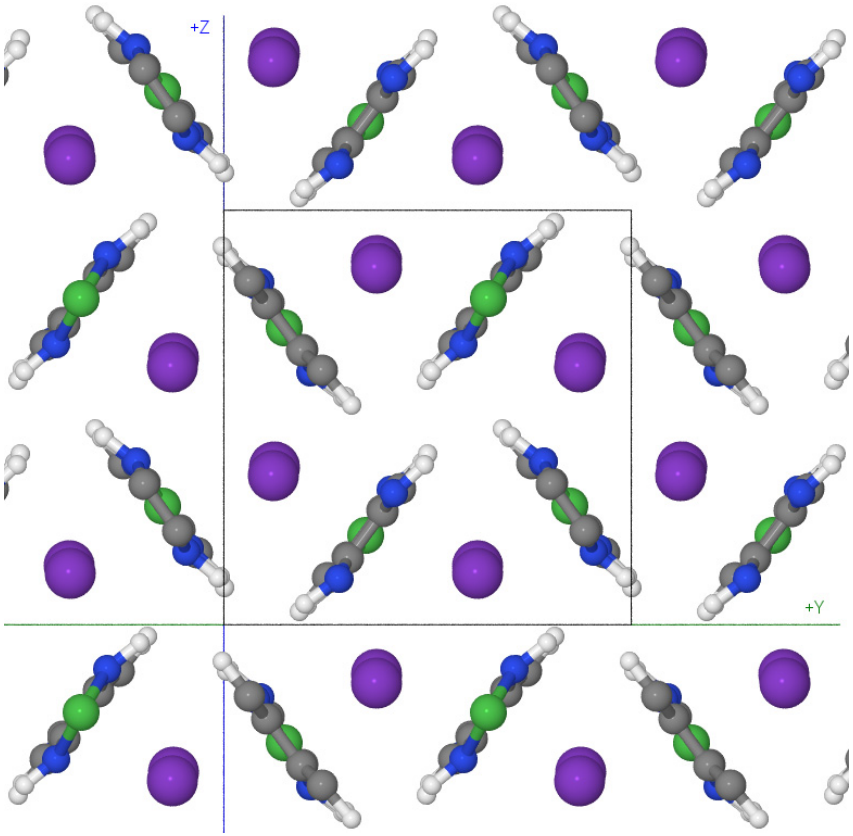
(considered all structures with 2 monomers per unit cell, then ran MD in supercell)

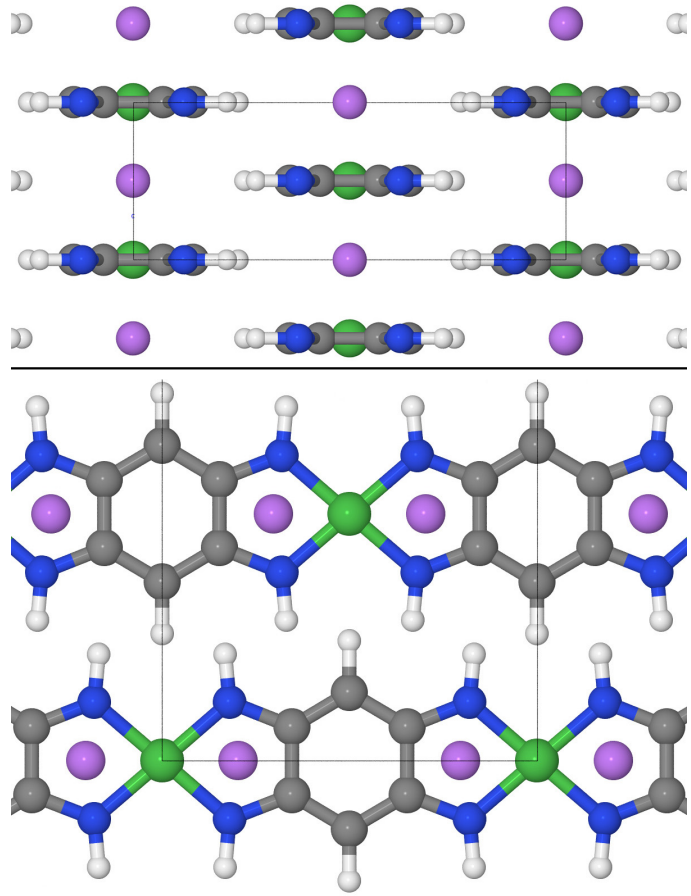




- Pristine material has herringbone packing
- Facile rotations and displacements of polymer chains allows for fast ion intercalation between (011) planes
- Ions intercalate in pairs according to energy estimates
- Small ions (Li) slightly distort the initial structure
- Large ions (K) open wide channels resulting in restructuring...

... Other structures





- Although ab initio MD captures restructuring,
  more XRD peaks are needed to identify Na- and K-ion structures
- π-stacking is stable only for small ions and only with them
- Larger scale MD should help, but force field is required

Summary and Outlook

Metal-organic polymers

- Late transition metal itself is electrochemically inactive but pre-charges (dopes) organic part of the π-conjugated polymer
- Rigid polymers allow for fast reversible alkali-ion intercalation
- More structural characterization and modeling is needed to get details of intercalation of Na and K ions

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Outlook

- NiBTA is not special, so other metal-organic crystalline polymers and molecular solids should be studied to get a broad picture of organic electrode materials
- Can we replace organic material + bulk carbon composite by a single organic material with good electronic conductivity?
- 2D and 3D frameworks might be promising due to enhanced rigidity and electronic transport