High-throughput screening of intercalation electrodes for electrochemical ion-capture and desalination

Sougat Purohit[1], Andreas Kuhlmann[2], Marten Huck[2], Hans-Georg Steinrück[2], Sai Gautam Gopalakrishnan[1]

[1]Department of Materials Engineering, Indian Institute of Science, Bengaluru, India
[2]Institute for a Sustainable Hydrogen Economy (INW), Forschungszentrum Jülich GmbH, Jülich, Germany
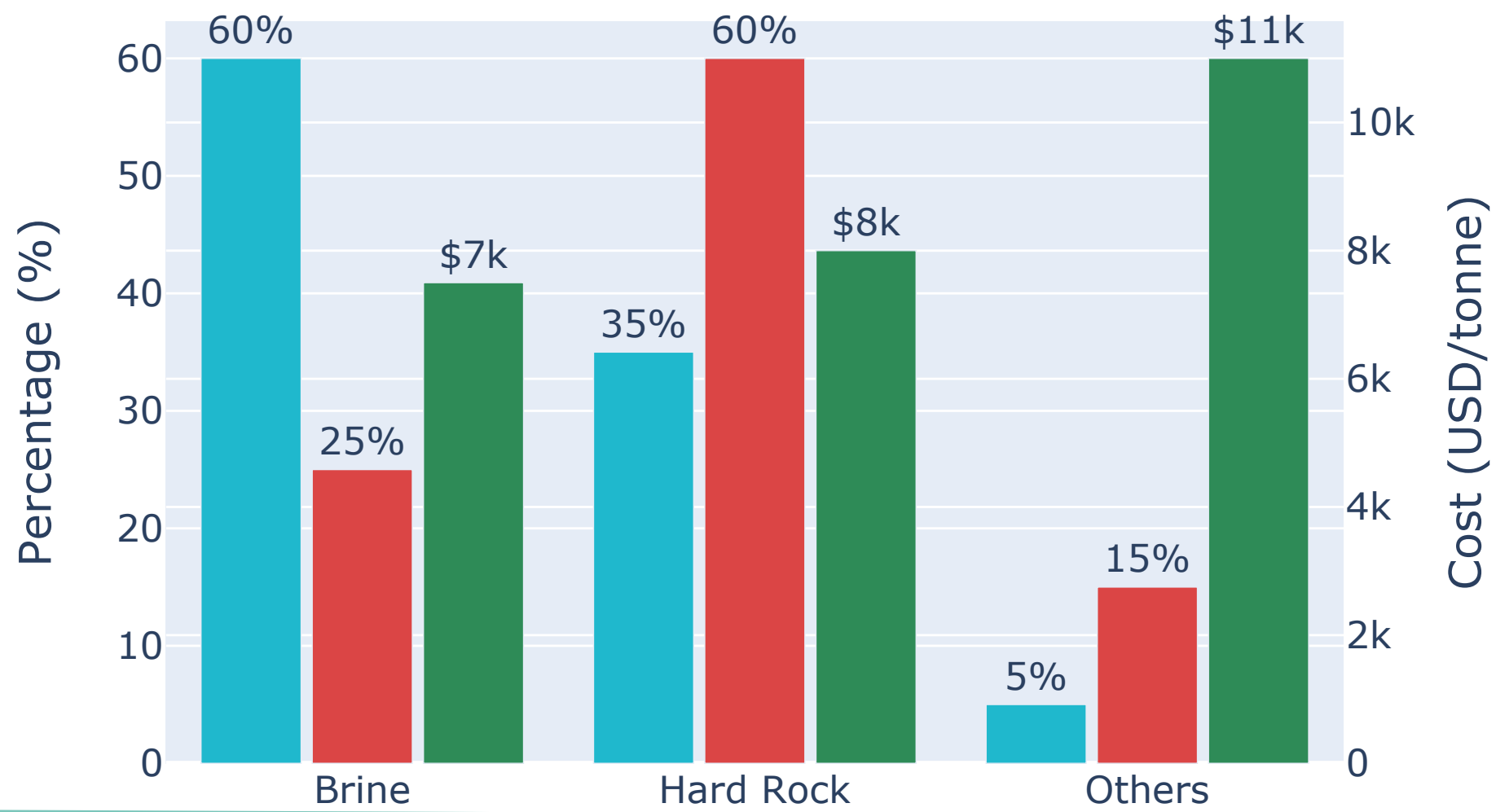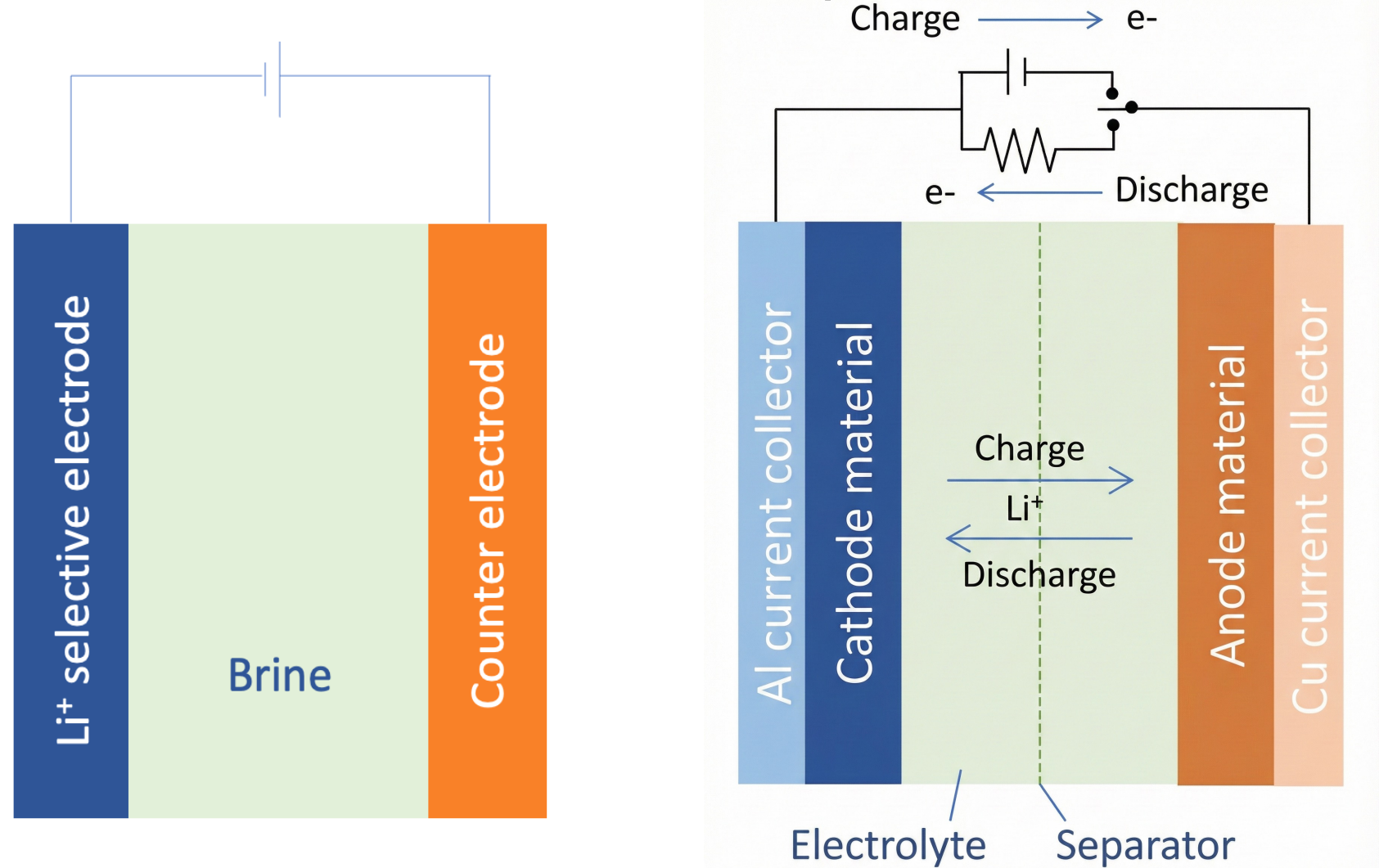
sougatp@iisc.ac.in

INTRODUCTION

- Li in brine sources > Li in rock sources[1]
- Extraction cost from rocks ≈ 2 × cost from brines[1]
- Slow traditional extraction methods from brines
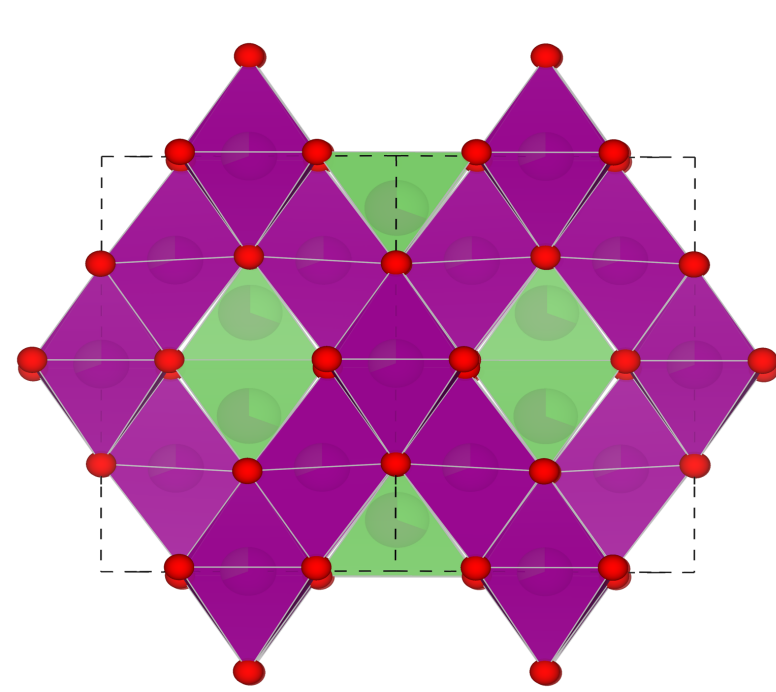

Electrochemical ion-recovery:[2,3]

- Faster, low energy consumption
- Similar to Li-ion Battery (LIB)
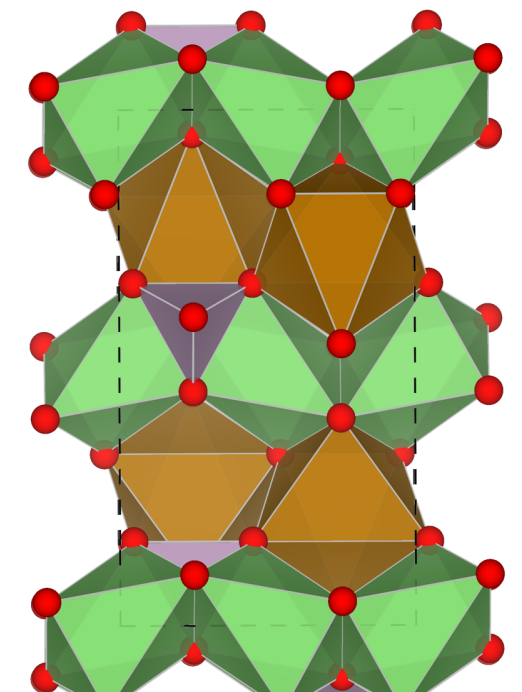- Can handle various brine compositions

Current state of the art electrodes:[2,3]

- Poor cycling stability of $LiMn_2O_4$
- Poor electronic conductivity of $LiFePO_4$
- Can better ion-capturing electrode be found from the pool of battery intercalation cathodes?
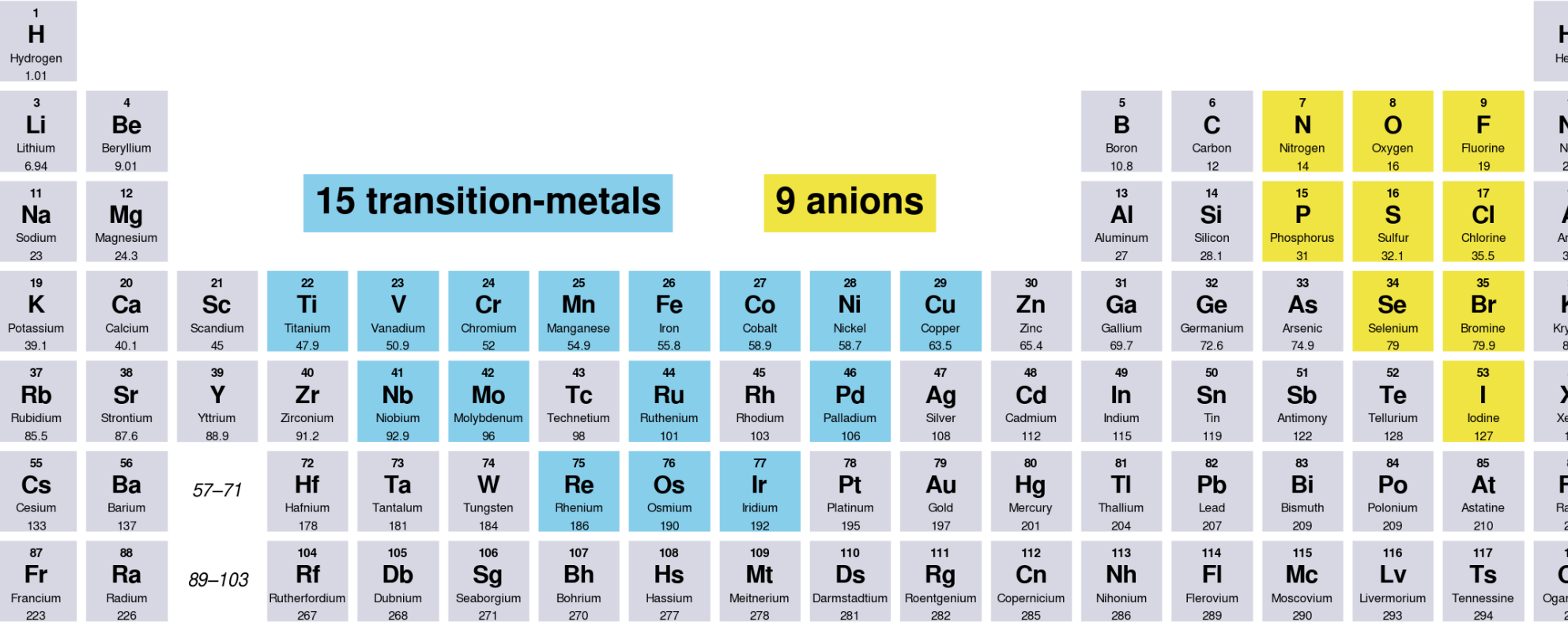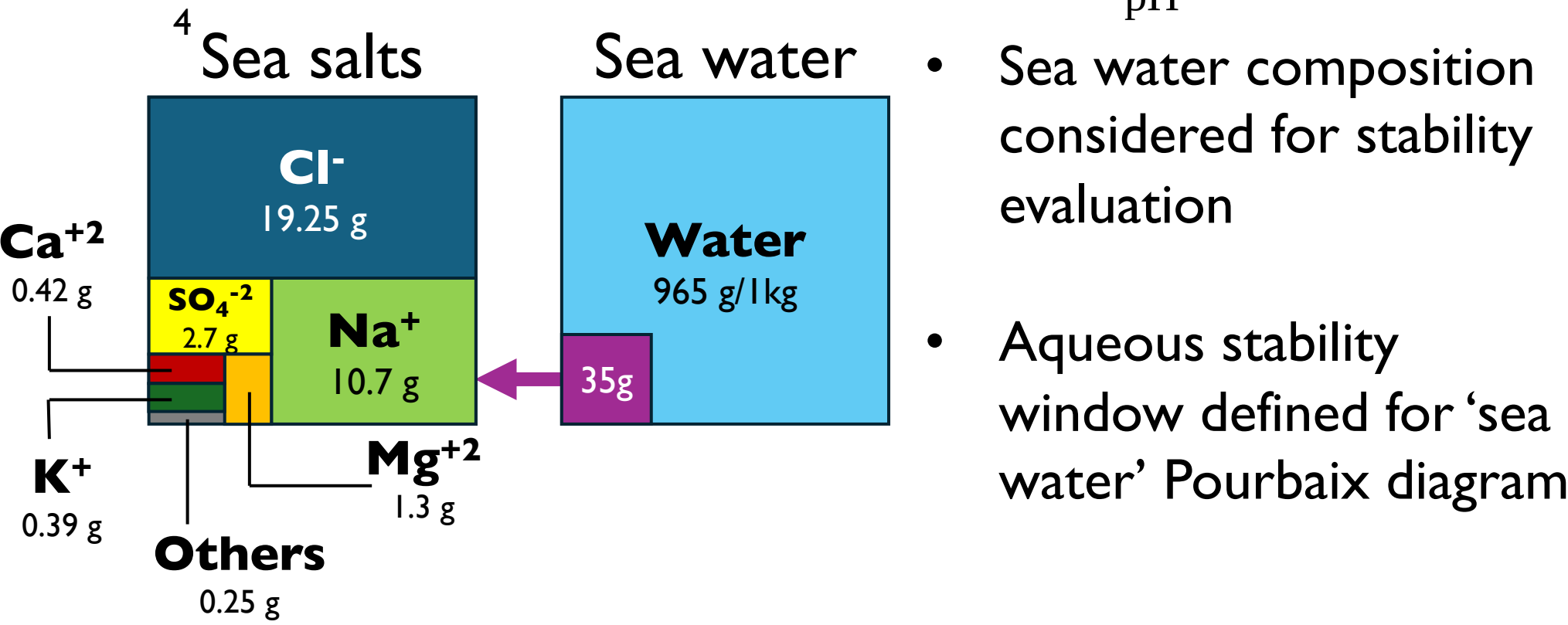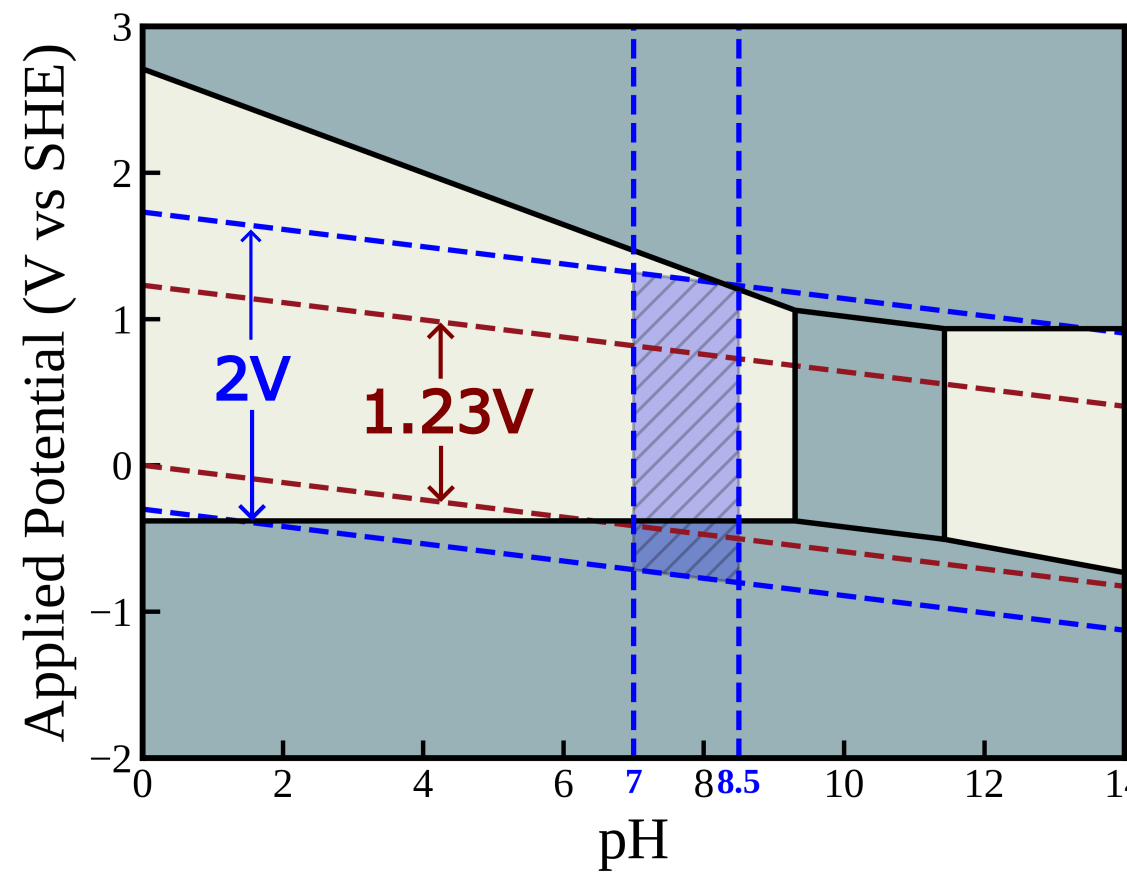

Spinel $LiMn_2O_4$ Olivine $LiFePO_4$

WORKFLOW

1 Query first-principles cathodes data across ions

- All Li / Na / K / Mg / Ca electrodes with at most 3 transition metals and 3 anions from the Materials Project database
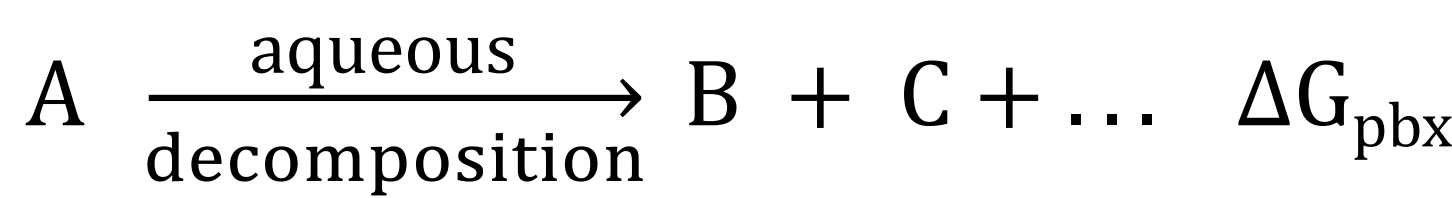

15 transition-metals   9 anions

2 Determine aqueous stability of the cathodes

- Construct Pourbaix diagrams for each electrode
- Aqueous composition affects stability

- Sea water composition considered for stability evaluation
- Aqueous stability window defined for 'sea water' Pourbaix diagram

Sea salts   Sea water

Sea water metastability **criteria** of electrode 'A':[5]

$$A \xrightarrow{\frac{aqueous}{decomposition}} B + C + \dots \quad \Delta G_{pbx}$$

1. At least one of $B, C \dots$ is a solid
2. The solid is non-elemental and doesn't contain the working ion
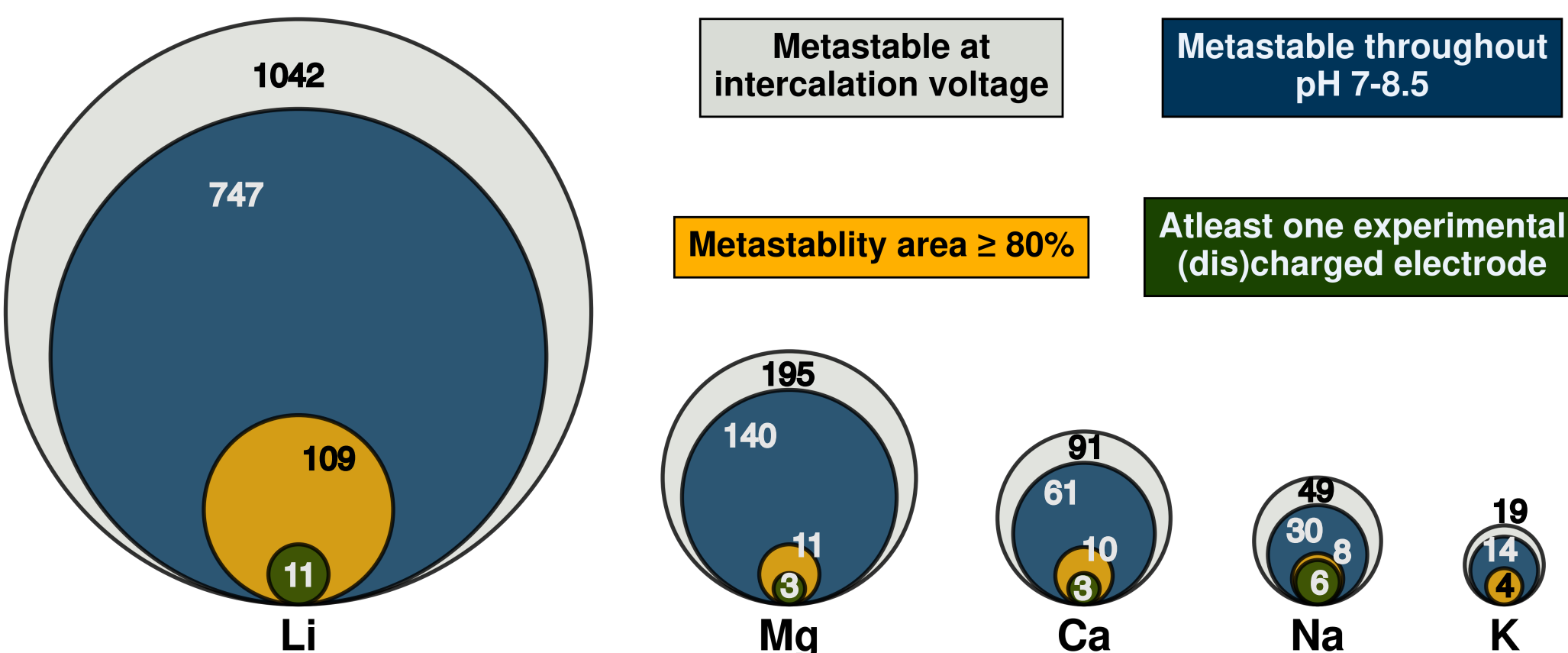3. $\Delta G_{pbx} <$ threshold (0.3 eV atom^{-1} determined from $LiFePO_4$)
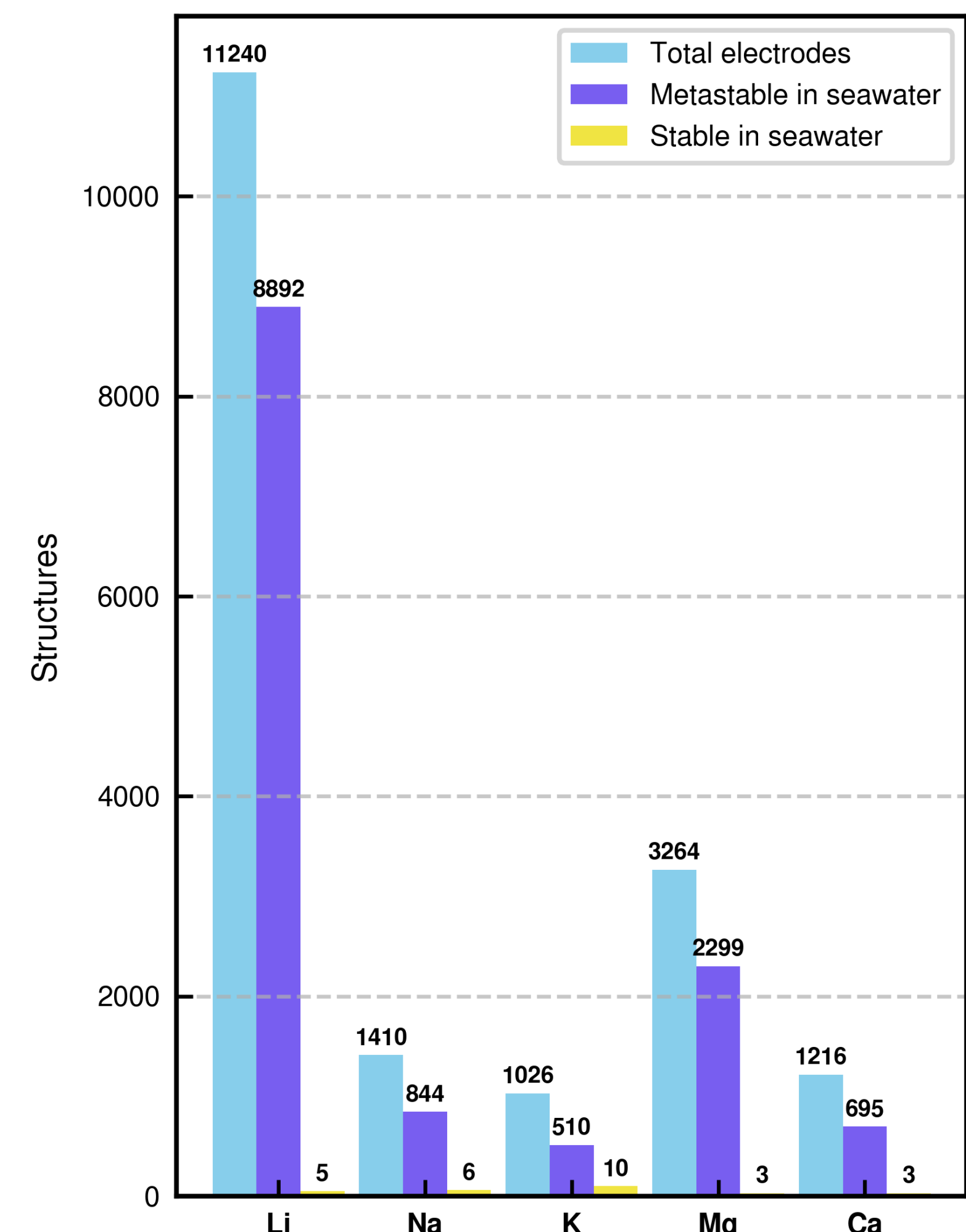
Too many metastable but too few stable electrodes!

3 Calculate the intercalation voltage
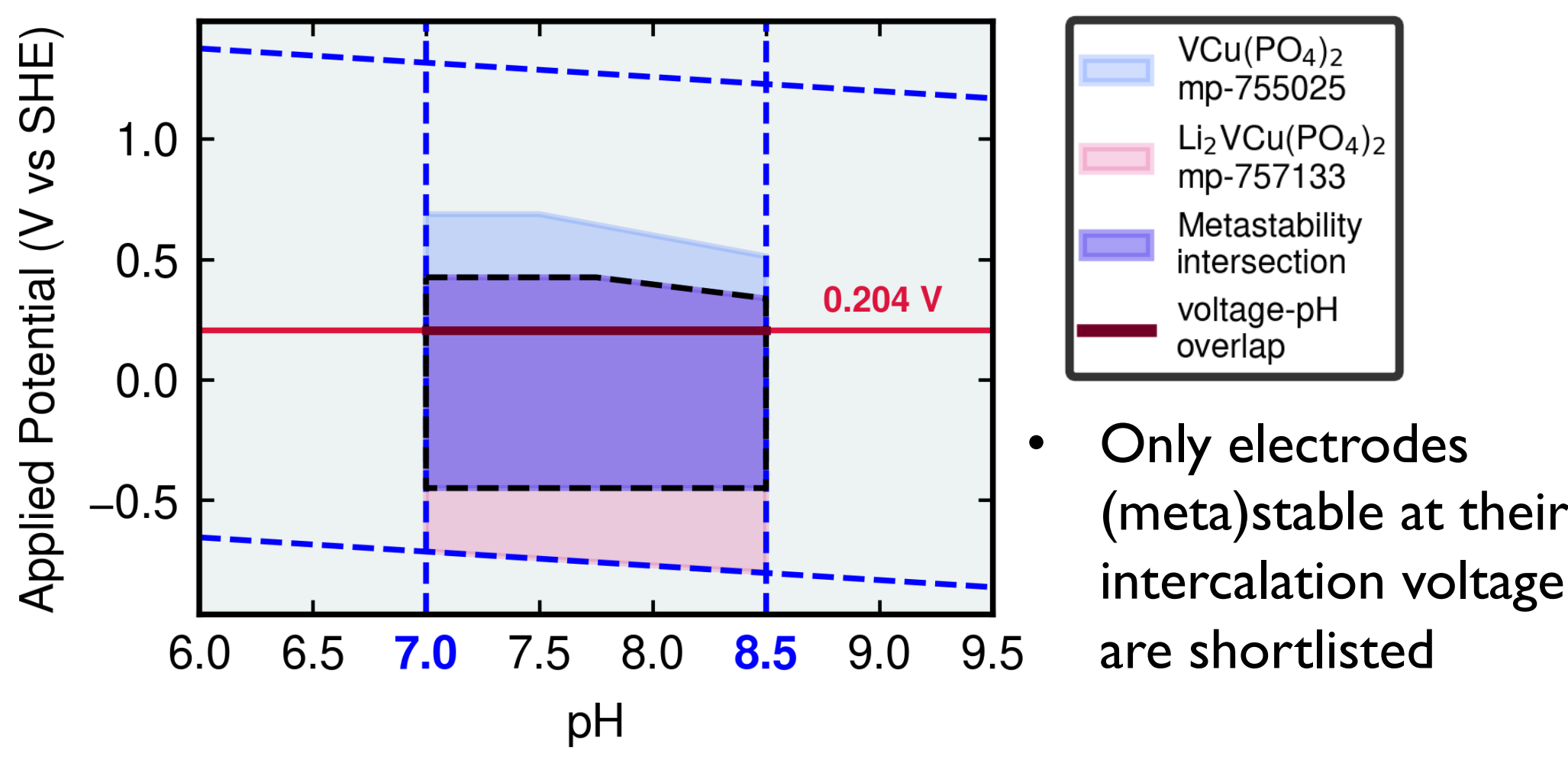
- Only electrodes (meta)stable at their intercalation voltage are shortlisted

Metastable at intercalation voltage
Metastable throughout pH 7-8.5
Metastablity area ≥ 80%
Atleast one experimental (dis)charged electrode
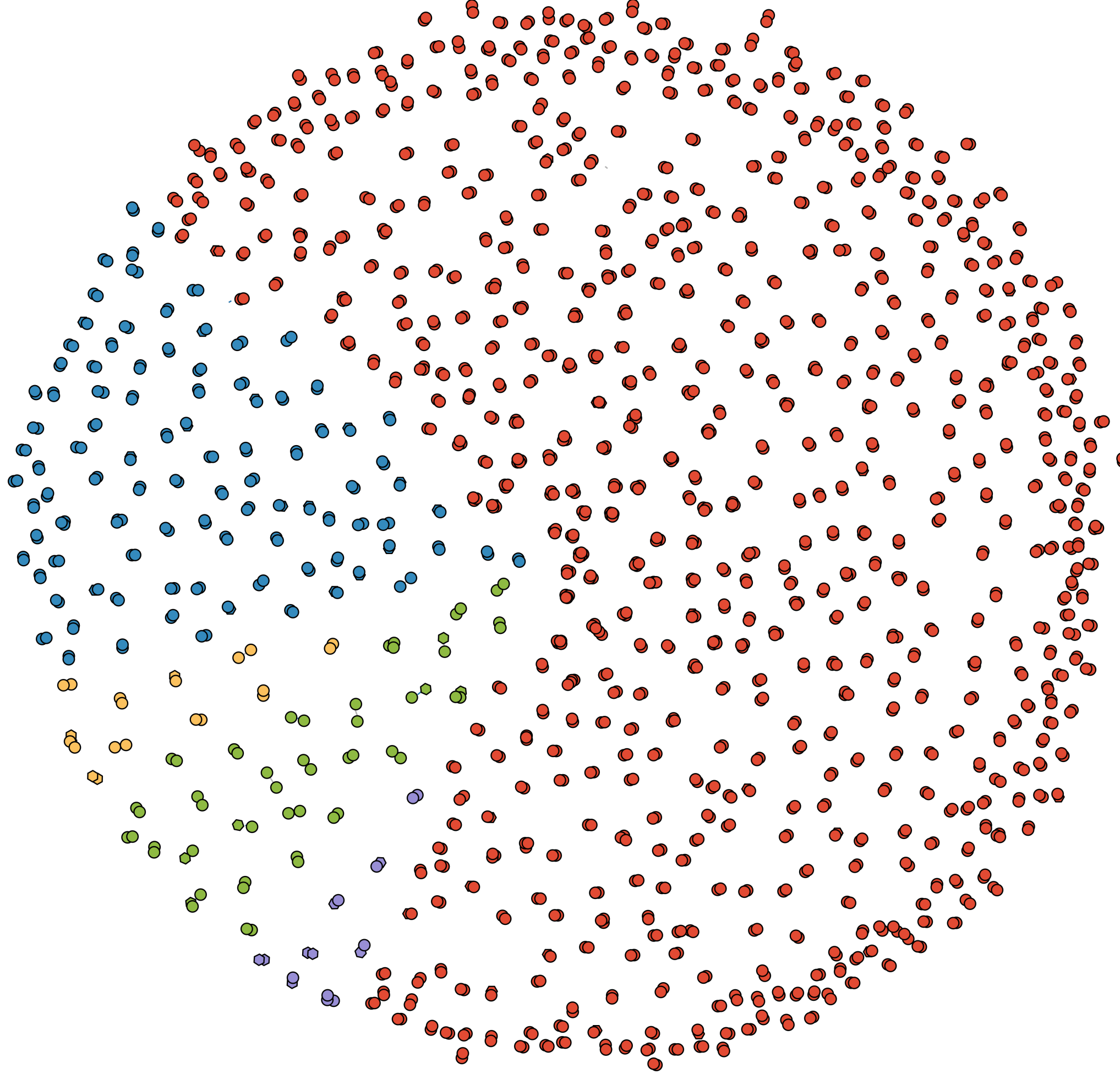
4 Compare frameworks across ions

- Computational graphs are created to identify Li-selective and multi-ion selective (desalination) electrodes
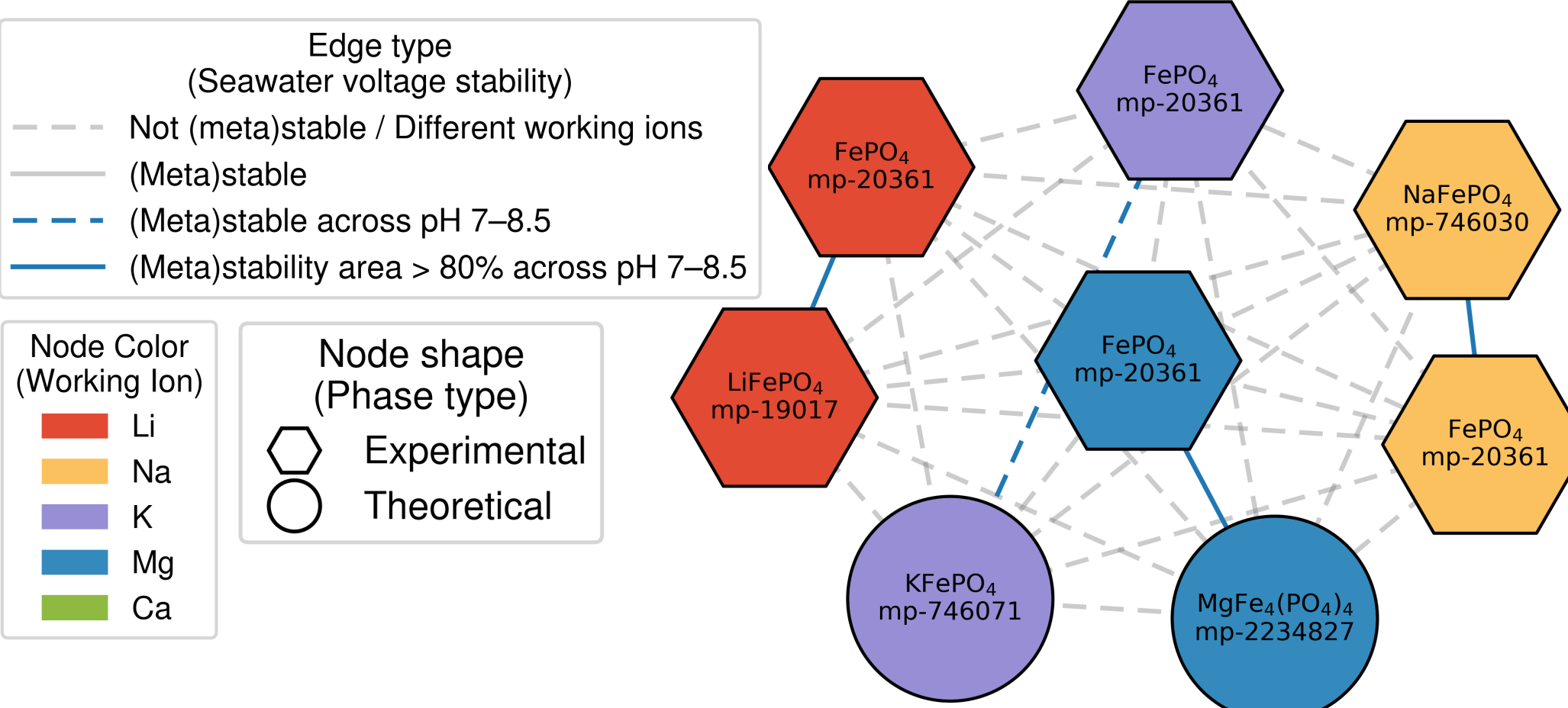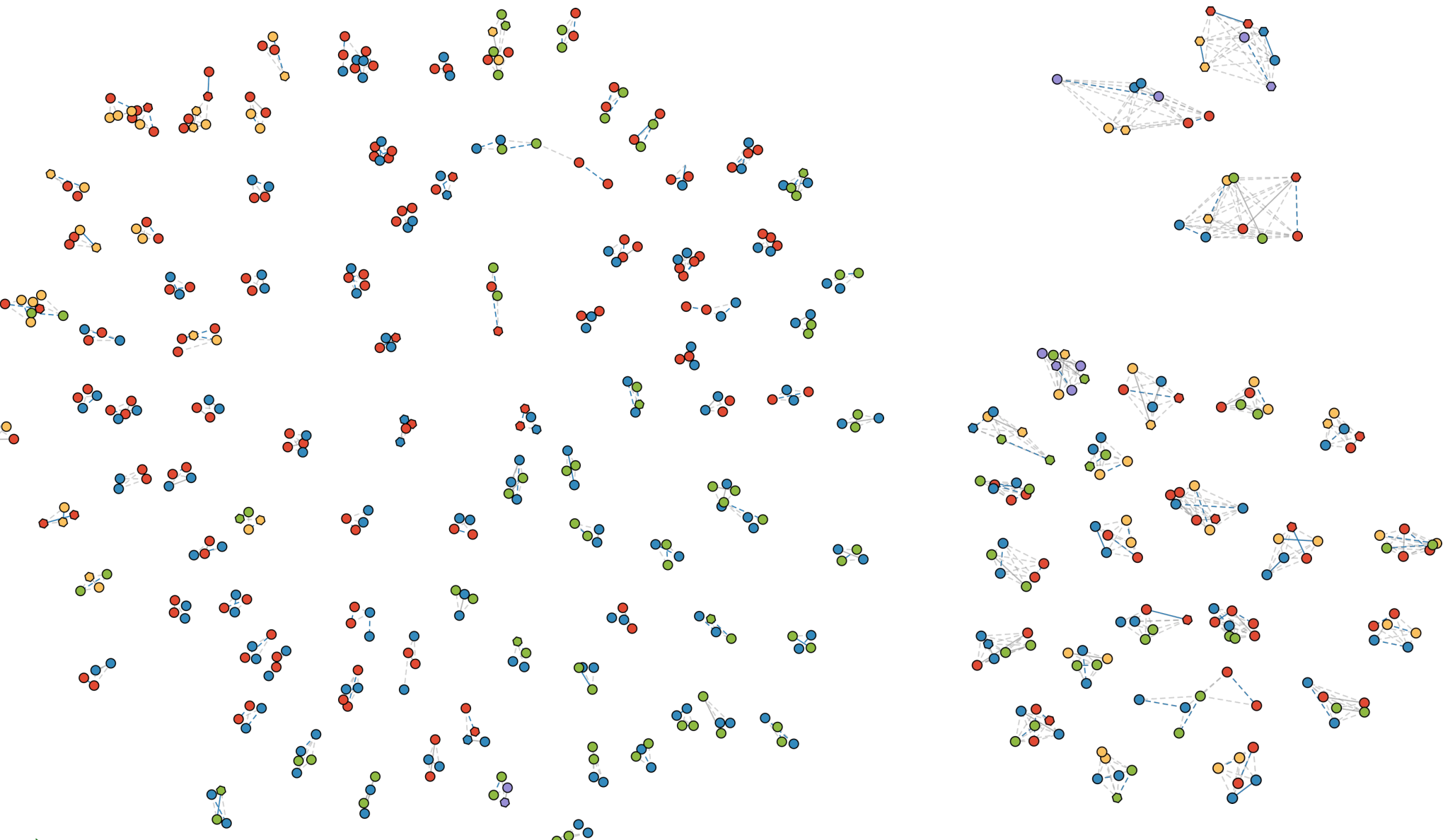

- Strongest candidates are graphs with solid blue edges connecting at east one hexagonal node

RESULTS

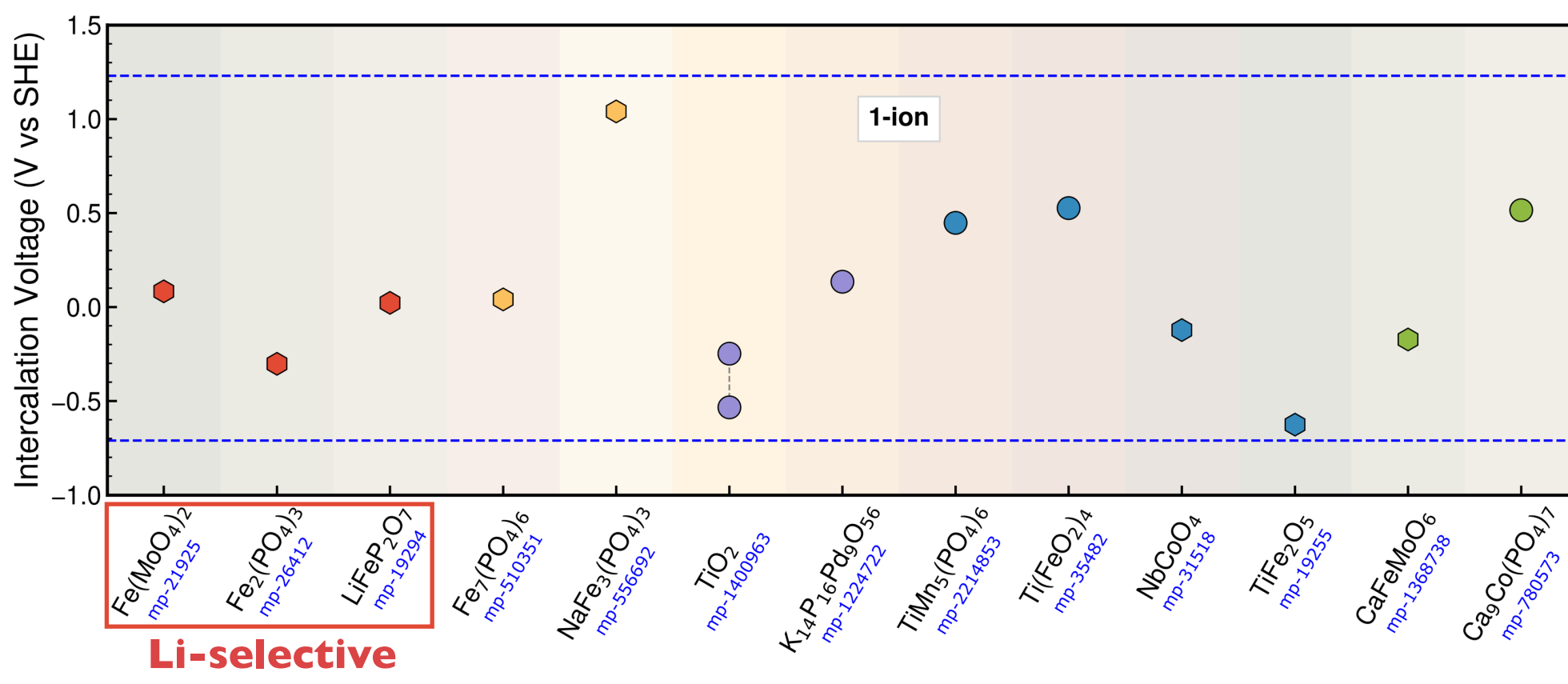- 587 **Li**, 11 **Na**, 8 **K**, 94 **Mg**, and 27 **Ca** selective frameworks (graphs)

- 92 **2-ions**, 22 **3-ions**, 3 **4-ions** and 0 **5-ions** intercalating frameworks (graphs)
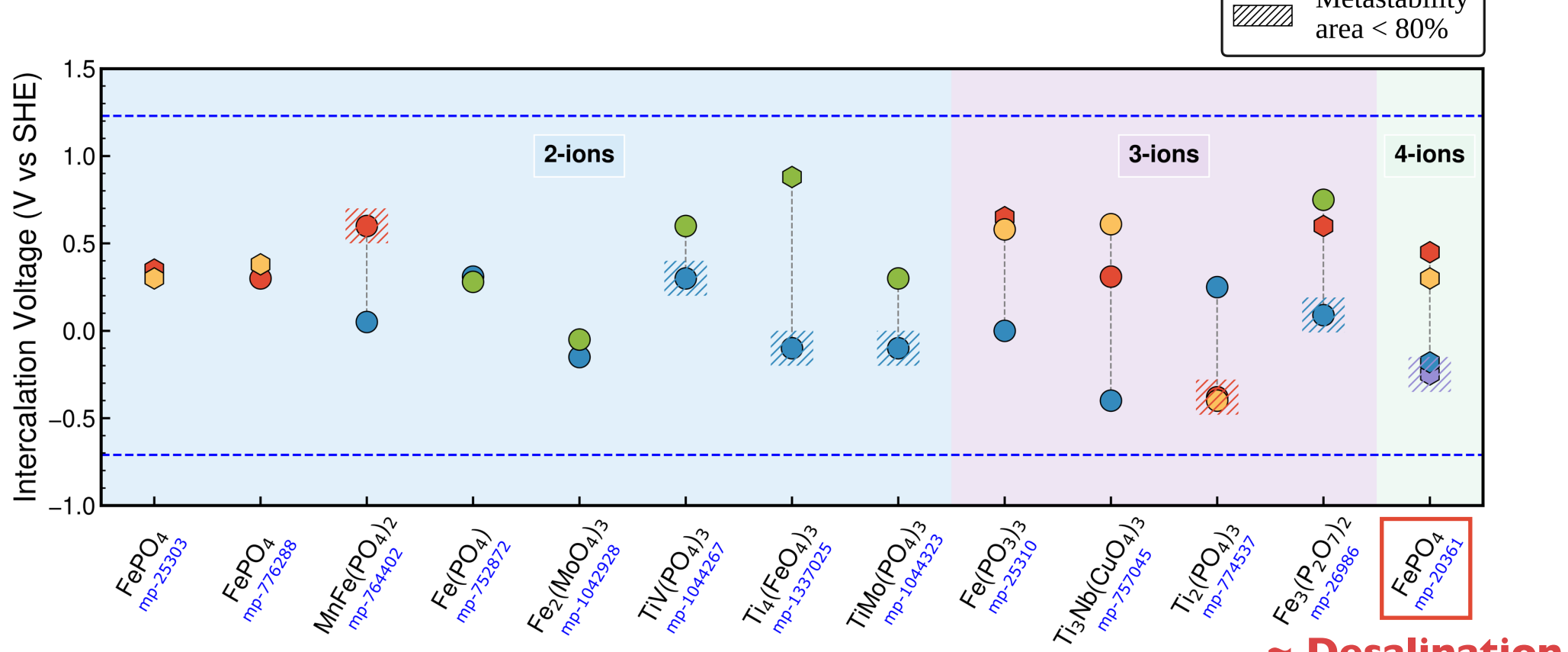

Ion-selective electrodes
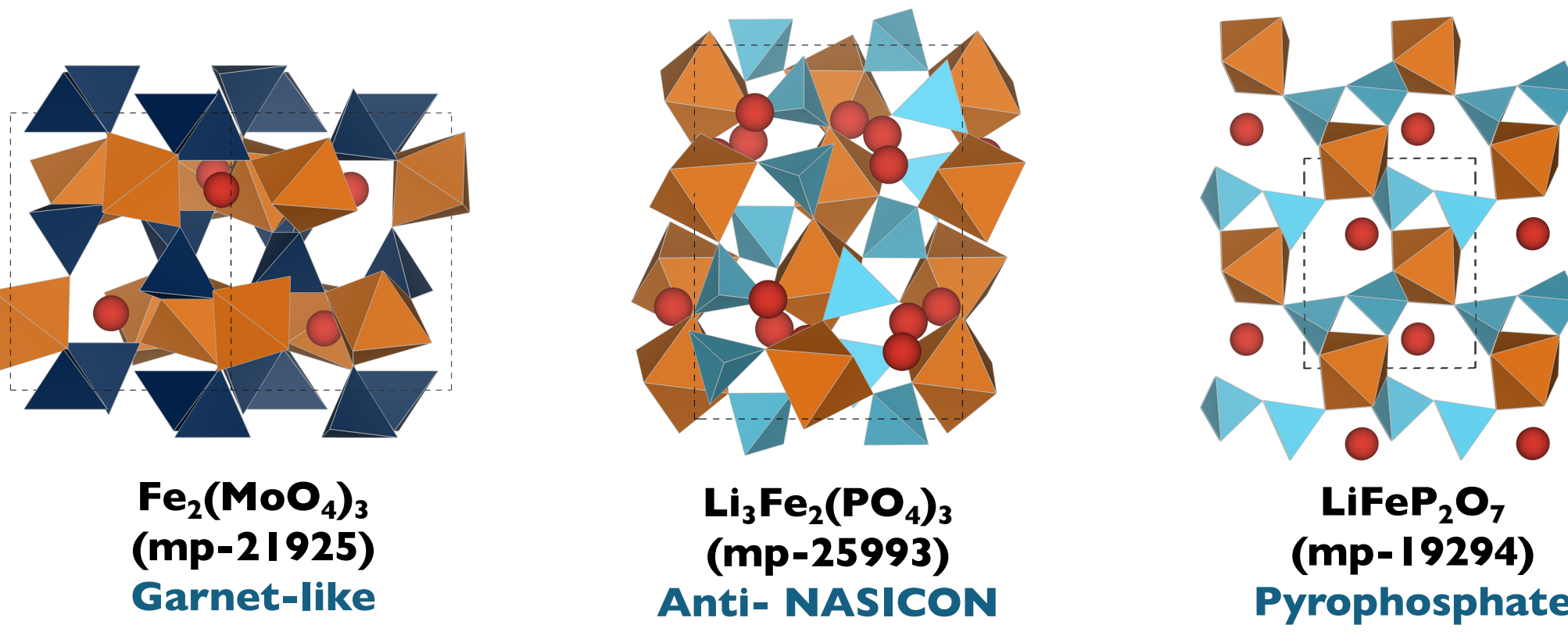
- Identified 13 ion-selective frameworks

Multi-ion-selective electrodes

- Identified 13 multi-ions-selective frameworks

CONCLUSION

1. Developed a framework to evaluate sea water (meta)stability of battery electrodes under operating conditions
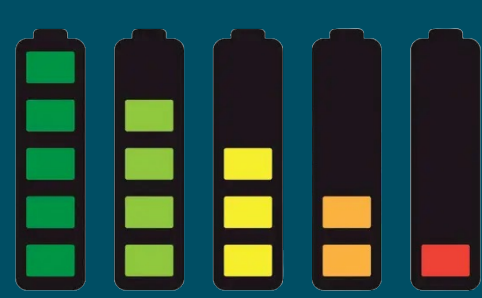2. Identified three new Li-selective electrodes

$Fe_2(MoO_4)_3$ (mp-21925) Garnet-like
$Li_3Fe_2(PO_4)_3$ (mp-25993) Anti- NASICON
$LiFeP_2O_7$ (mp-19294) Pyrophosphate

3. Identified olivine $LiFePO_4$ as a candidate desalination electrode

ACKNOWLEDGEMENTS

REFERENCES

1. surl.li/jaqrbo, surl.lu/wongco
2. Xiong et. al. Matter 2022, 5, 1760-1791
3. Battistel et. al. Adv. Mater. 2020, 32, 1905440
4. en.wikipedia.org/wiki/Seawater
5. Singh et. al. Chem Mater, 29, 10159-10167 (2017)