Tutorial: Batteries (incl. K-Ion Batteries)

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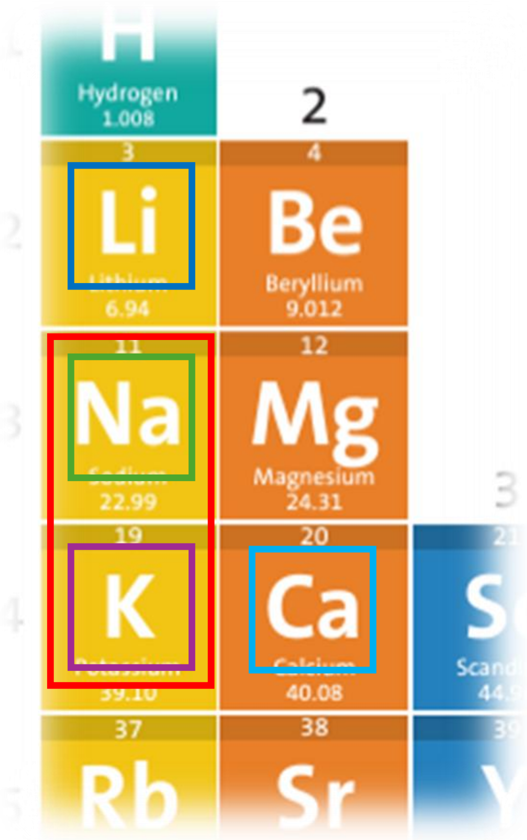
Outline

- A bit about what I research
- A quick recap of battery development
- The holy grail Li-ion battery
- Next generation Li-ion battery
- Beyond Li batteries – K-ion (vs. Na-ion) battery

A bit about what I research

THE FARADAY INSTITUTION

Saleable and green synthesis of LIB cathodes (w/ Prof. Darr, UCL Chem)



The Leverhulme Trust

Ca-ion intercalation chemistry & materials

UCL

Na solid-state electrolytes & interfaces (w/ Dr Rettie, UCL Chem Eng)

THE ROYAL SOCIETY

UKRI Engineering and Physical Sciences Research Council

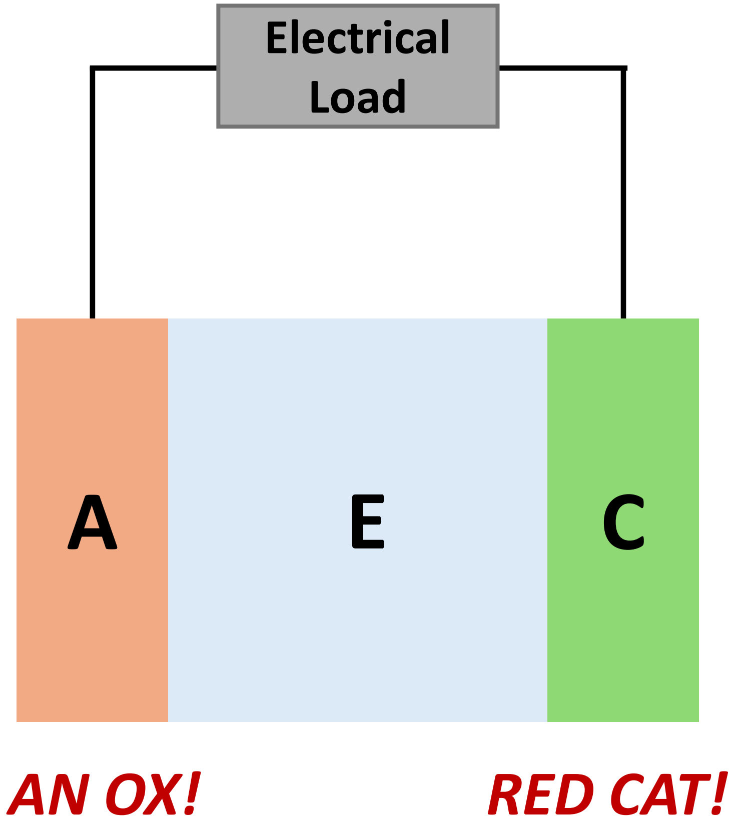
Na/K metal anode manufacture & S cathode chemistry

UKRI Engineering and Physical Sciences Research Council

K-ion battery electrode materials with defects

Xu group

A battery is an electrochemical cell

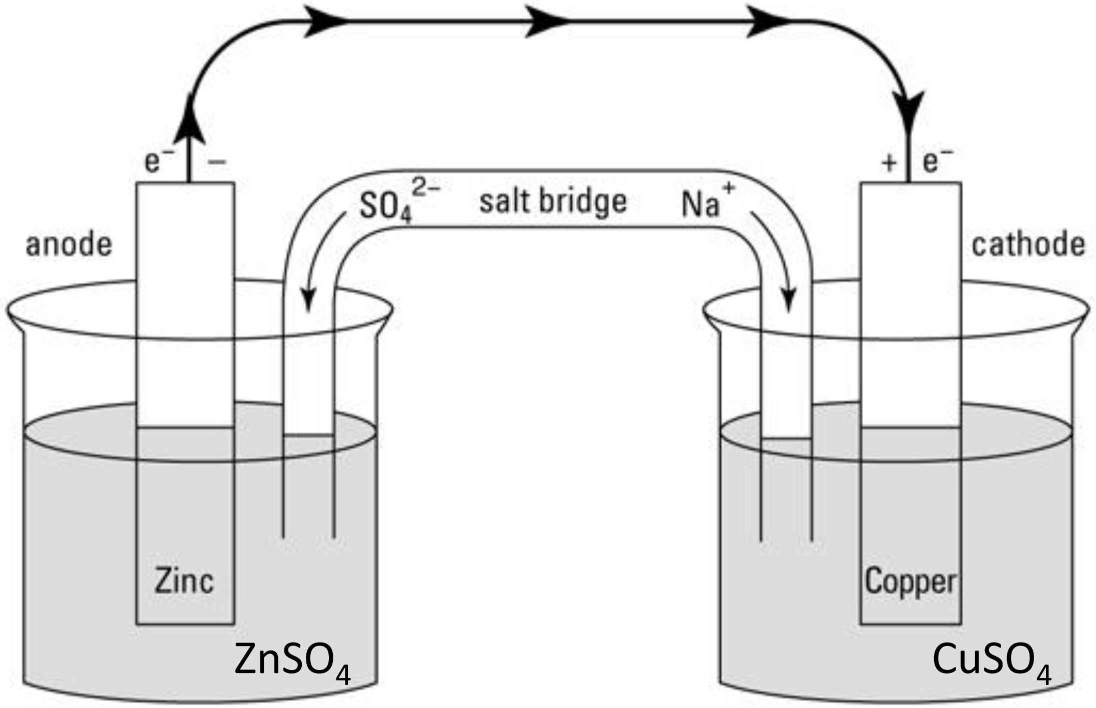


An electrochemical cell includes 3 components:

- Anode (A): oxidation reaction, releasing electrons
- Cathode (C): reduction reaction, accepting electrons
- Electrolyte (E): conducting ion flow, electronically insulating, electrochemically inactive

An electrochemical cell converts chemical energy to electricity through a discharge process.

Look back history: Daniell cell



John Frederic Daniell, FRS
https://en.wikipedia.org/wiki/John_Frederic_Daniell
Daniell cell
https://en.wikipedia.org/wiki/Daniell_cell

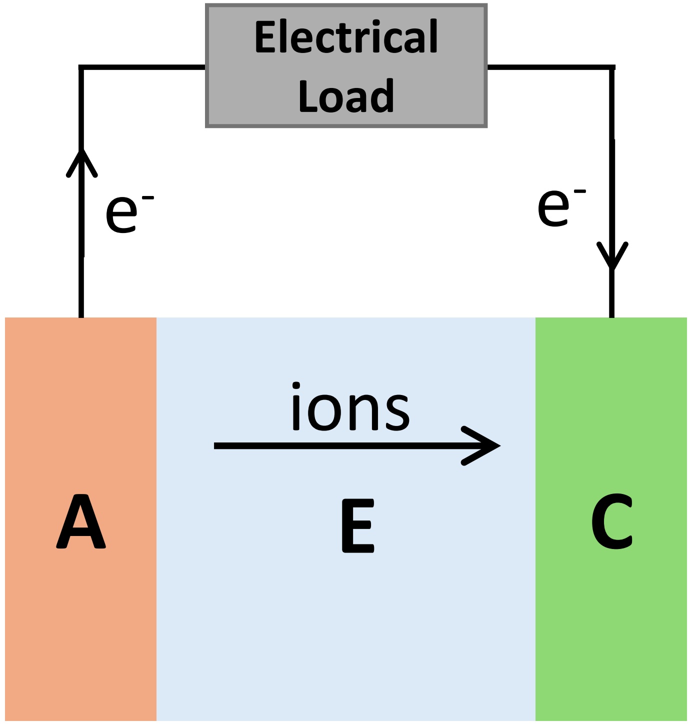
Anode: $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

Overall: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

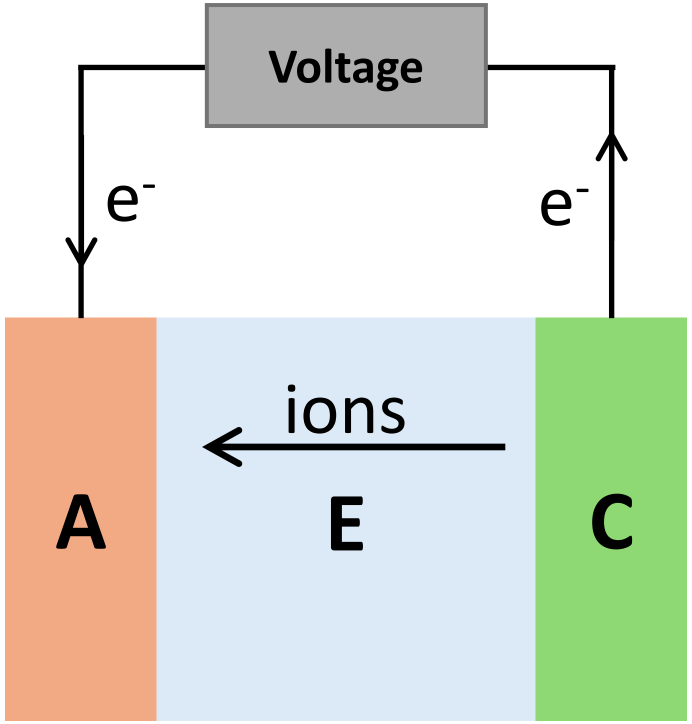
Primary battery vs. secondary battery

Primary battery: low-cost general commodity applications or niche market



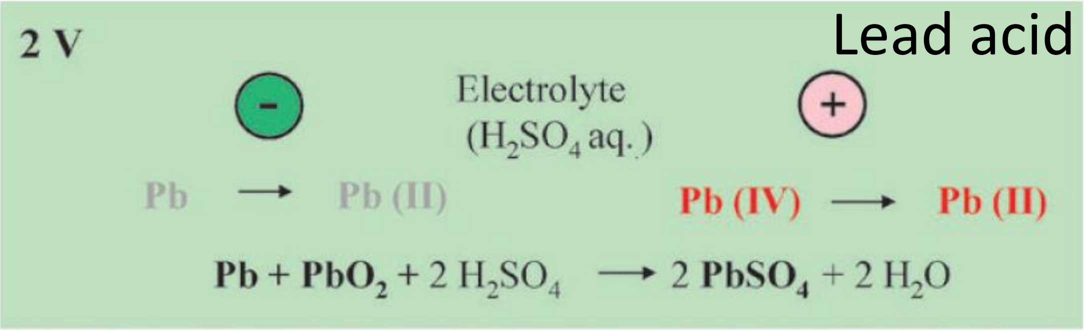
Discharge $A \rightarrow A^{n+}$
$C \rightarrow C^{n-}$

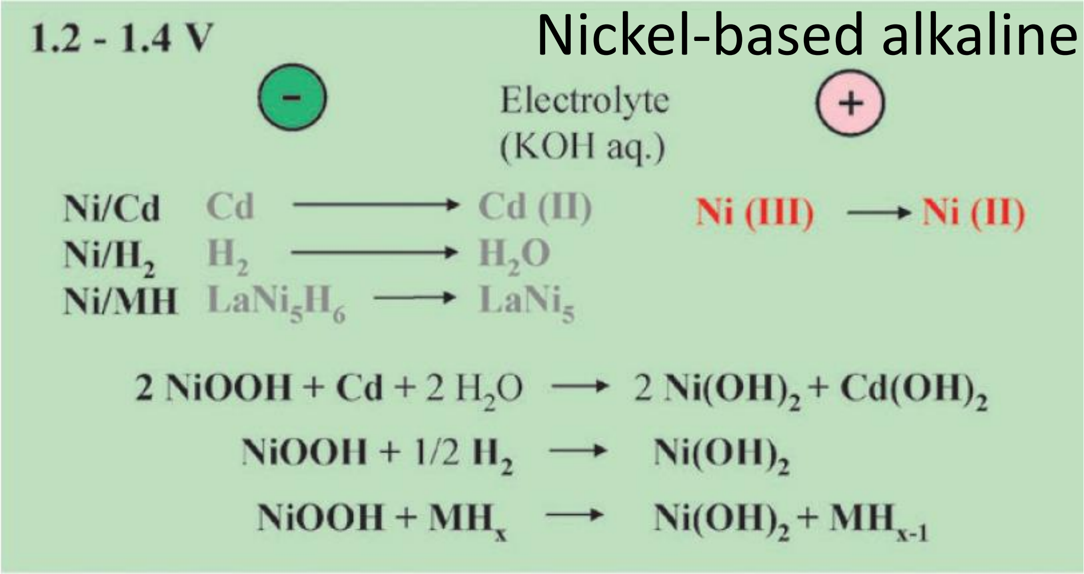
Secondary battery: diverse applications

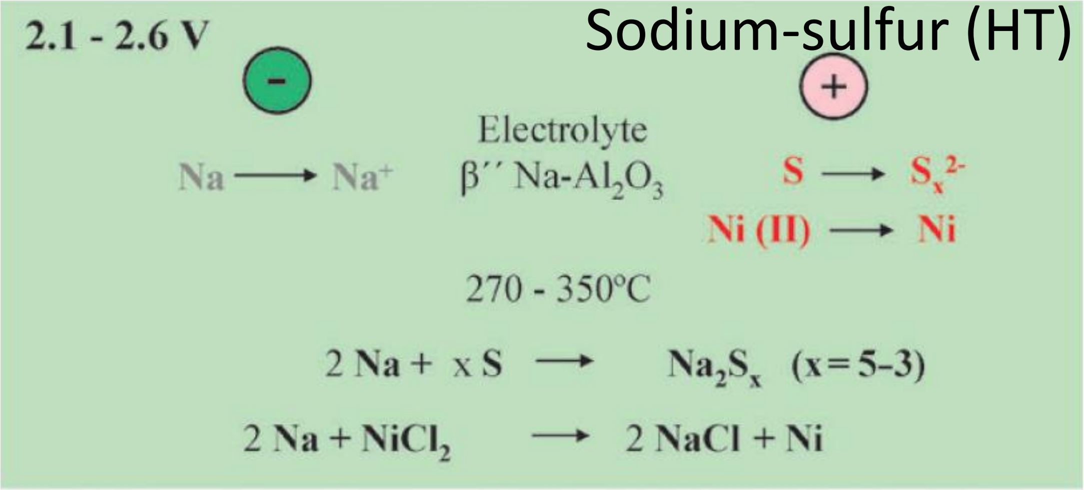


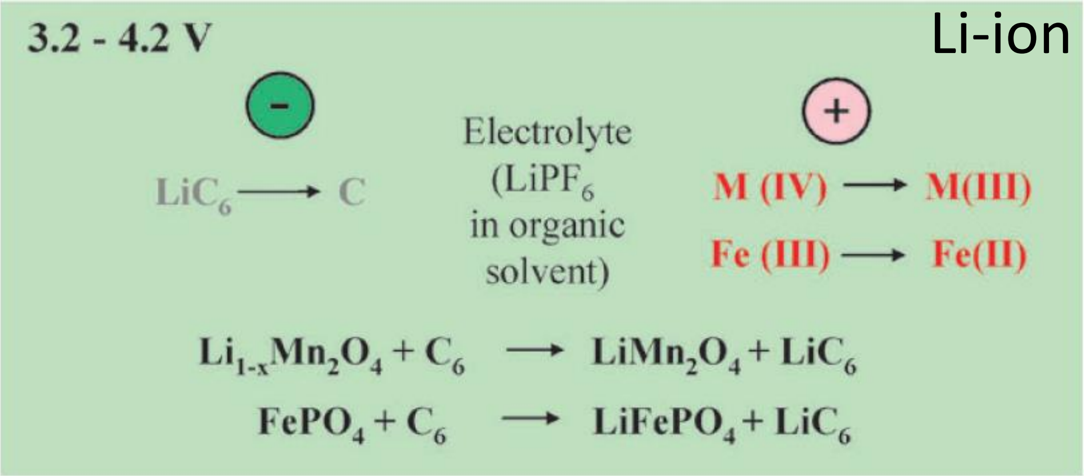
Charge $A^{n+} \rightarrow A$
$C^{n-} \rightarrow C$

Main rechargeable battery chemistries









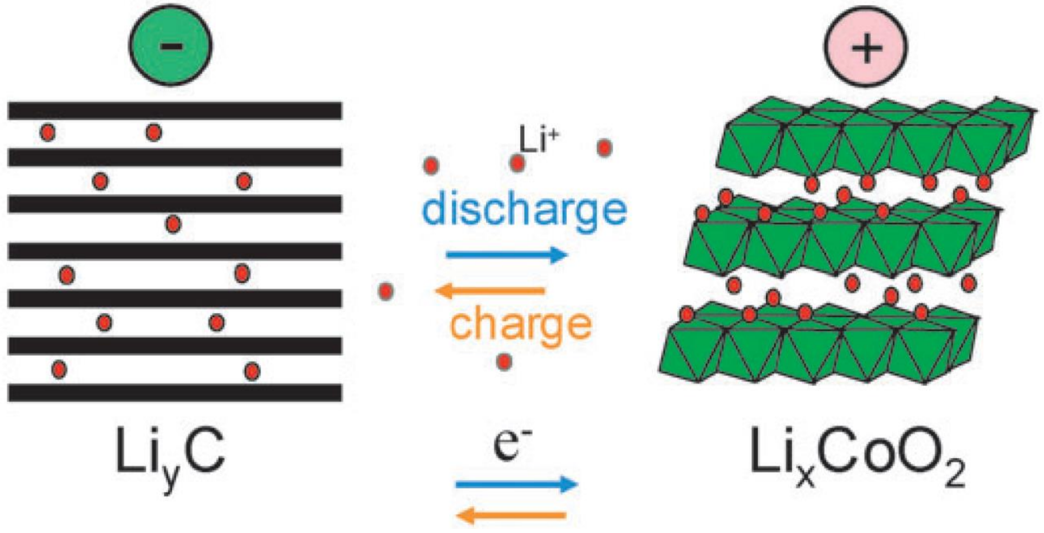
Chem. Soc. Rev. **2009**, *38*, 2565

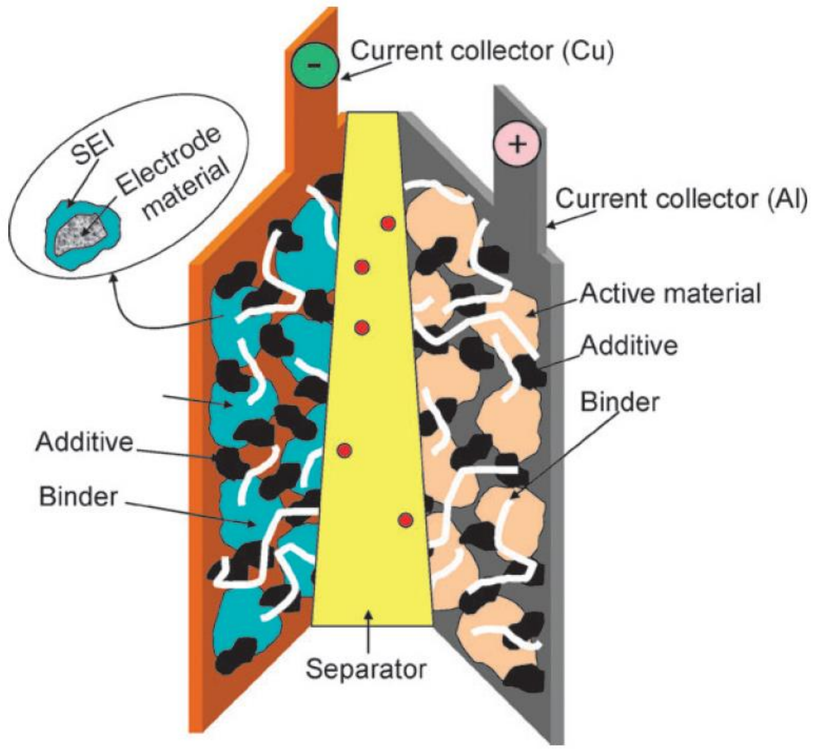
Li-ion battery (LIB)

Mechanism: lithium intercalation chemistry (solid state chemistry)

Why Li-ion?

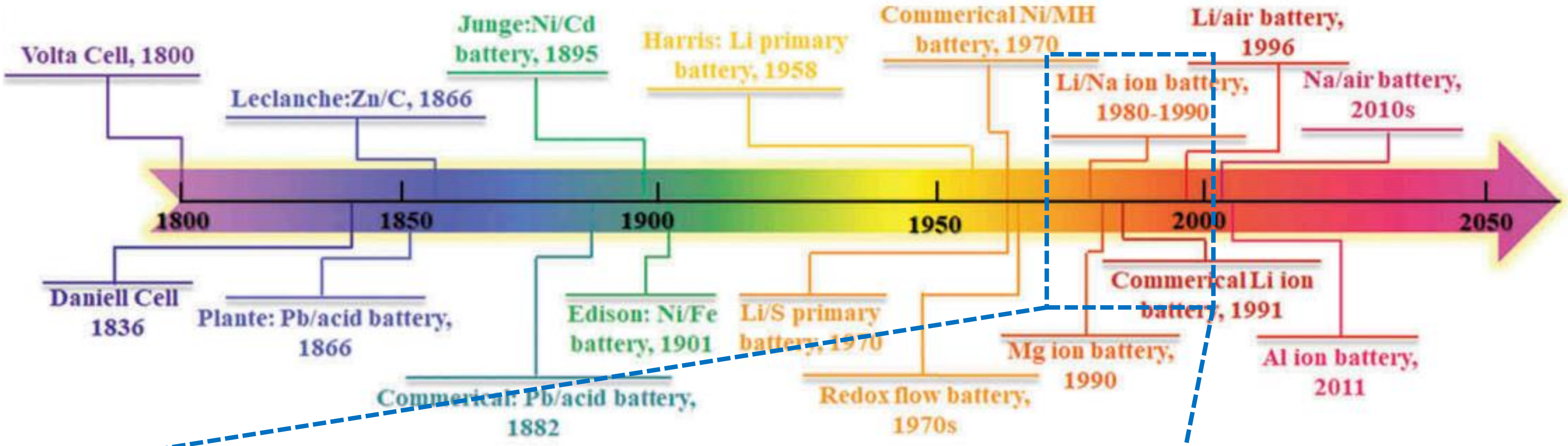
- Smallest and lightest cation as charge carrier
- Occupy empty interstices in host materials
- Move fastest in host materials
- Provide high energy stored in host materials





Chem. Soc. Rev. **2009**, *38*, 2565

Battery development



DOI: 10.1080/10667857.2018.1474005

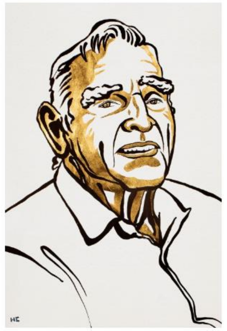
Intercalation cathodes

- Li intercalation in metal disulfides (70's)
- Li-TiS_2 battery (Whittingham, 70's and 80's)
- $LiCoO_2$ cathode (Goodenough, 1979)
- $LiMn_2O_4$ cathode (Thackeray, 1984)
- $LiFePO_4$ cathode (Goodenough, 1997)

Anode materials

- Reversible Li intercalation in graphite (1976)
- Rocking-chair battery demonstrated with $LiCoO_2$ (Goodenough, 1980)
- $LiCoO_2$-hard carbon battery commercialized (Sony, 1991)

Noble Prize in Chemistry 2019



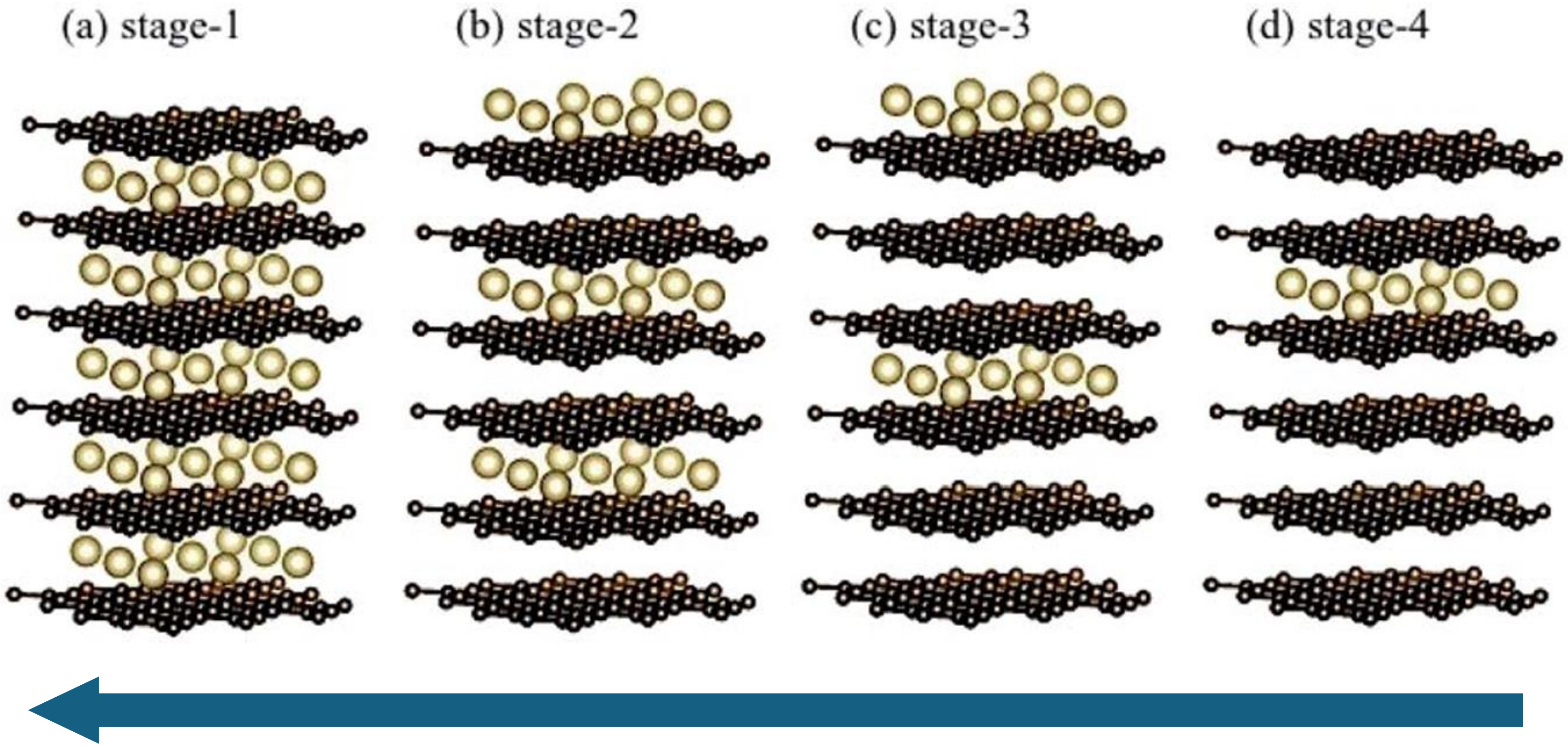
John B. Goodenough
Prize share: 1/3

M. Stanley Whittingham
Prize share: 1/3

Akira Yoshino
Prize share: 1/3

LIB anode: intercalation in graphite

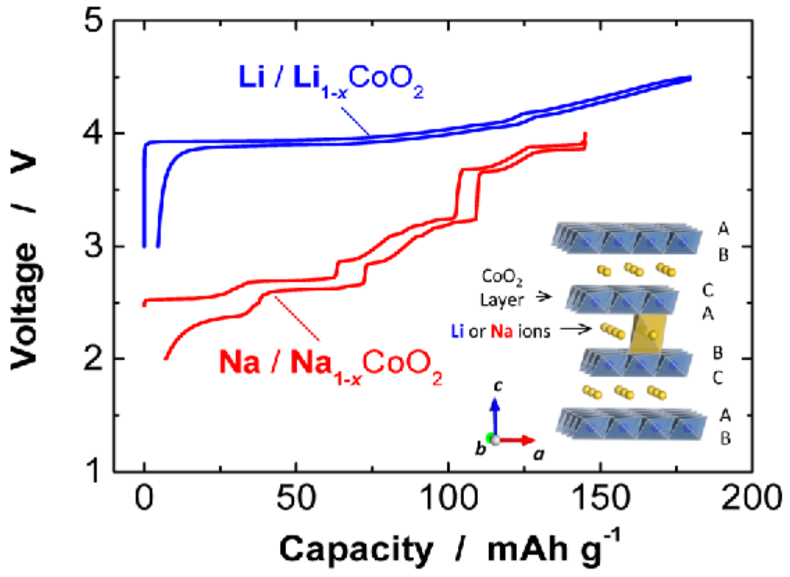
Graphite can accommodate ions in its interlayer space. Stoichiometry depends on the size of the ions, e.g., LiC_6 (372 mAh g^{-1}) vs. KC_8 (279 mAh g^{-1})



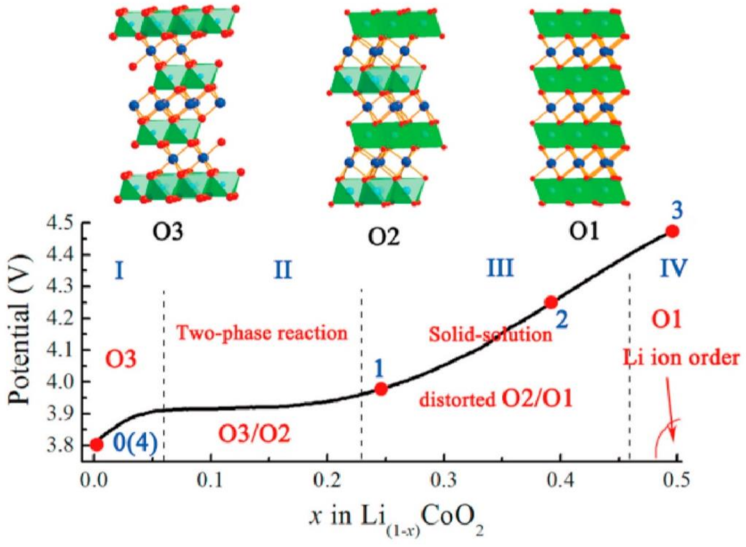
Staging: one interlayer space is completely filled before intercalation starts in another layer due to interlayer expansion upon intercalation.

RSC Adv. **2020**, *10*, 23573

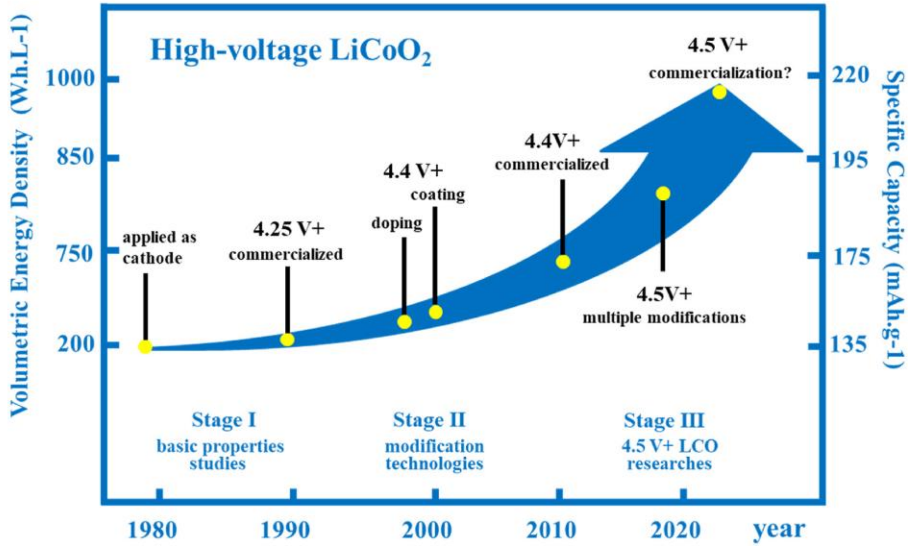
LIB cathode Gen1: layered $LiCoO_2$ ($Co^{3+/4+}$)



$Li_{1-x}CoO_2$ discharge-charge profiles
Chem. Rev., 2014, 114, 11636



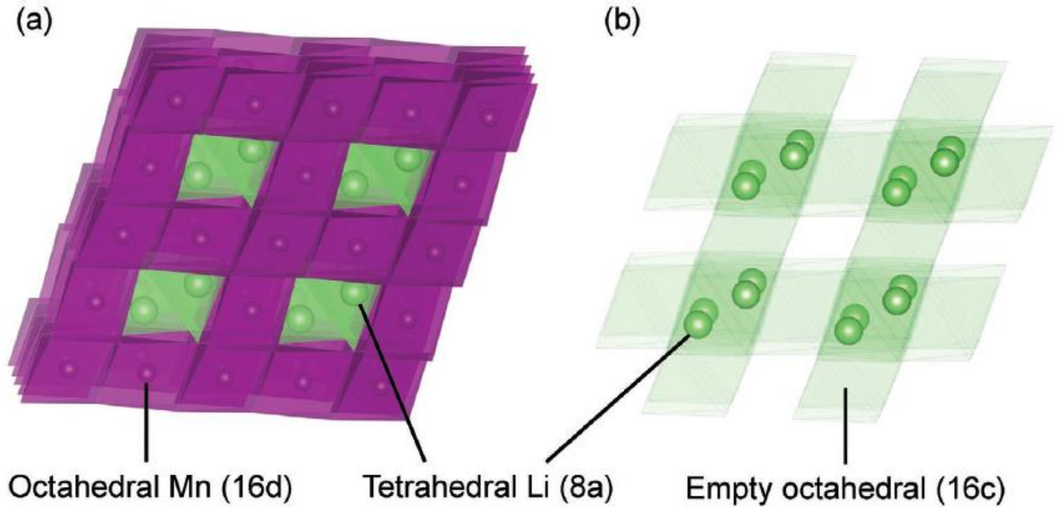
Phase change of $Li_{1-x}CoO_2$ during charge ($0.5 \le x \le 1$)
J. Power Sources, 2020, 460, 228062



Development roadmap of $LiCoO_2$
J. Power Sources, 2020, 460, 228062

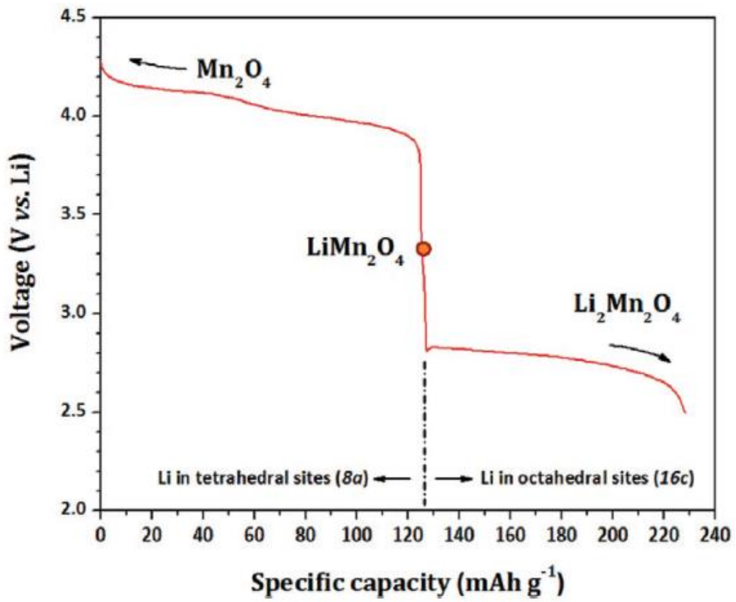
- Li^+ deintercalation at $0.5 \le x \le 1$ causes irreversible structural change
- Co is expensive (relative to Ti, Fe, and Mn) and toxic

LIB cathode Gen2: spinel $Li_{1-x}Mn_2O_4$ ($Mn^{3+/4+}$)



(a) Crystal structure of and (b) Li^+ diffusion tunnel in $LiMn_2O_4$

Adv. Energy Mater., 2020, 2000997

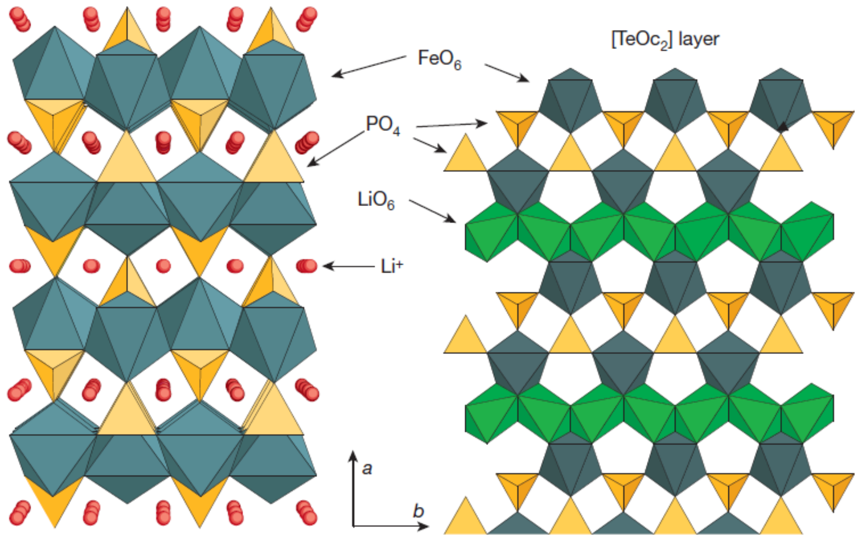


Mn_2O_4 discharge profiles

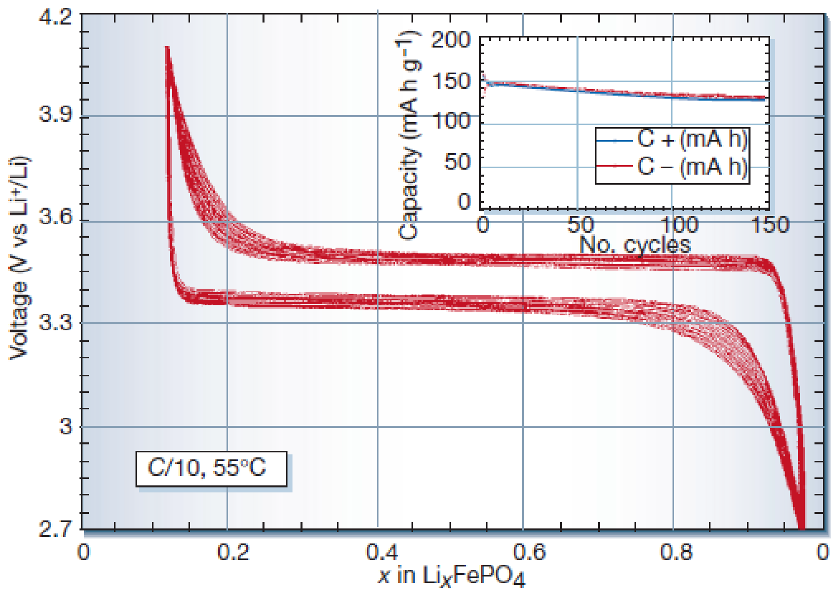
J. Am. Chem. Soc., 2013, 135, 1167

- High voltage as a cathode (4.0 V)
- Li^+ deintercalation varies at $0 \le x \le 1$ (vs. $0.5 \le x \le 1$ in $Li_{1-x}CoO_2$)
- Presence of Mn^{3+} gives a Jahn-Teller distortion that limits cycling
- Rather slow Li^+ movement and poor e^- conductivity

LIB cathode Gen3: olivine $LiFePO_4$ ($Fe^{2+/3+}$)



Crystal structure of olivine $LiFePO_4$
Nature, 2001, 414, 359



Discharge-charge curves of olivine $LiFePO_4$.
Nature, 2001, 414, 359

- Li^+ deintercalation varies at $0 \le x \le 1$ (vs. $0.5 \le x \le 1$ in $Li_{1-x}CoO_2$)
- Relatively low voltage as a cathode (~3.5 V) – Mn-doped $LiFePO_4$ (LMFP)
- Rather slow Li^+ movement and poor e^- conductivity

Most important performance parameter

High power density
(Fast charge)

Low cost
(Recycling)

High energy density

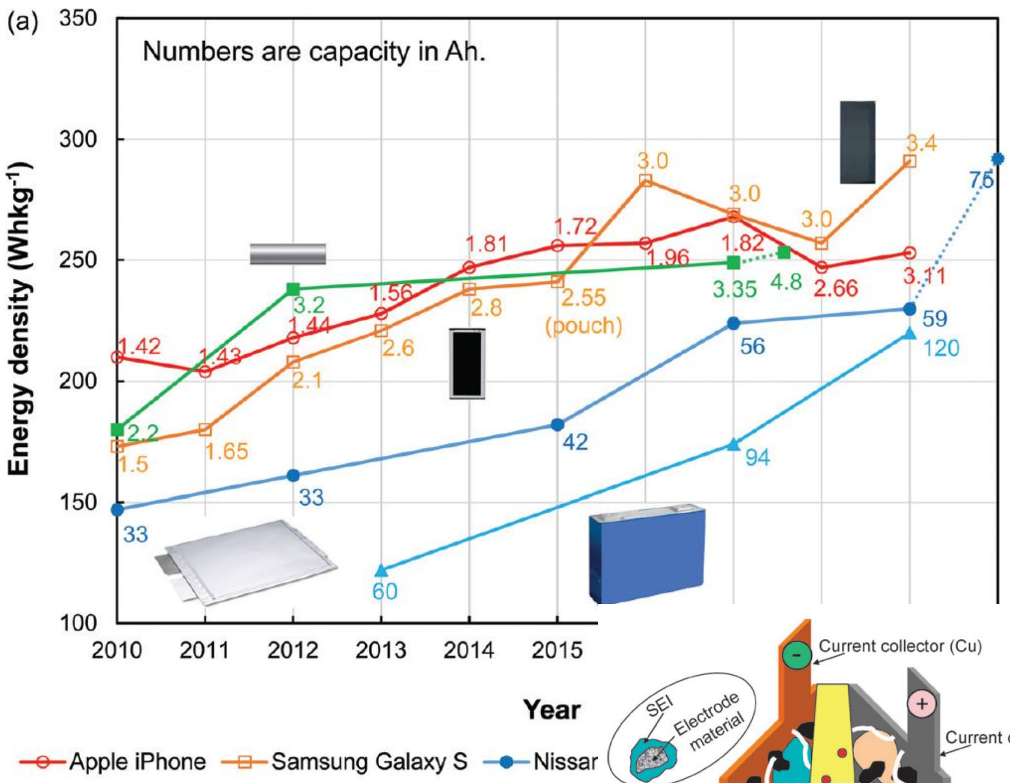
Long lifetime

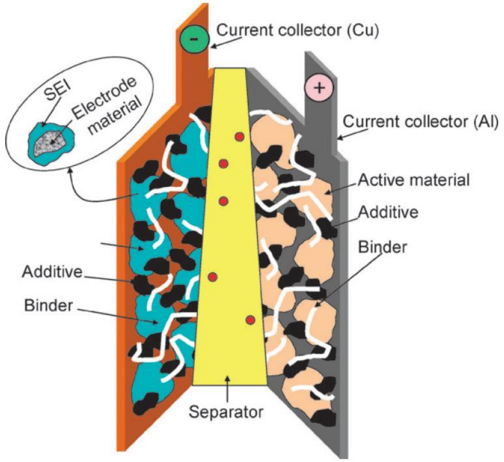
High safety

Energy density determines the maximum potential of a battery.

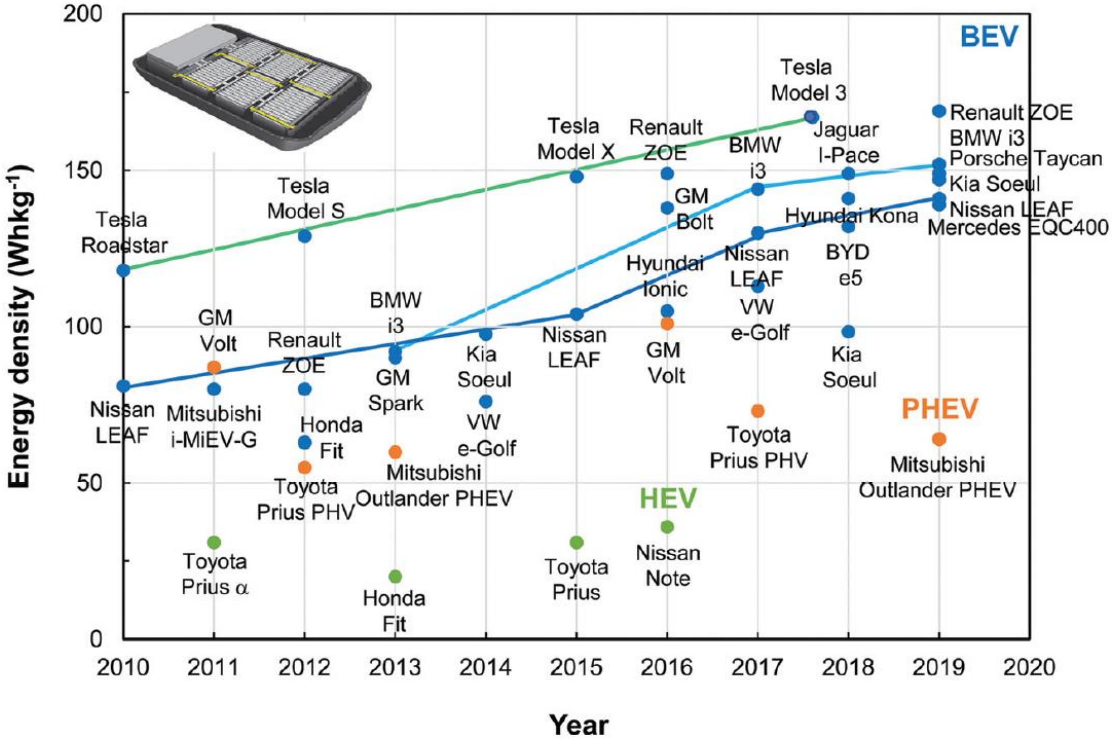
- The value of a battery is evaluated by the total usable energy (W h), and the price of a battery is often represented by the price of energy (\$ kW^{-1} h^{-1}), because this measure can compare any kind of battery regardless of battery size or weight.
- If the energy density (W h kg^{-1}) of a battery is improved, it contributes to a decrease in the cost of energy in the battery.

Trends in energy densities of LIB cells





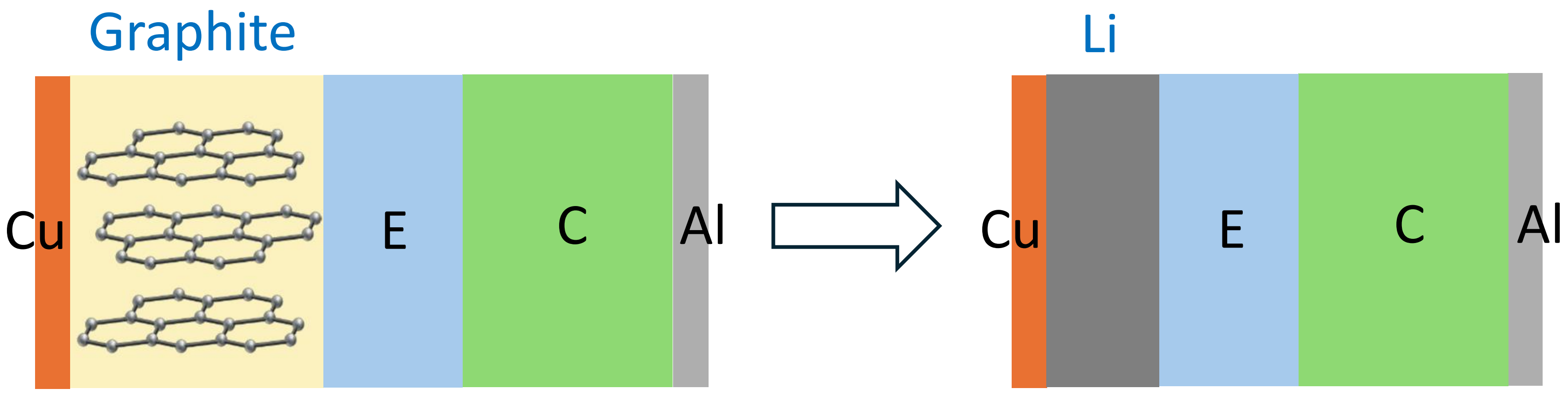
LIB cells



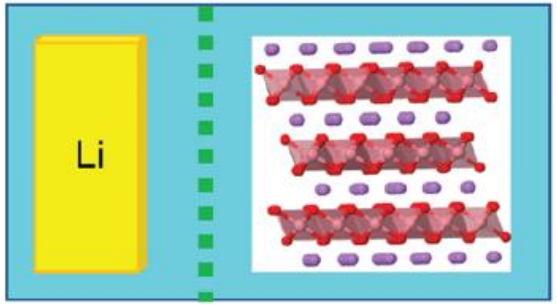
LIB Packs including battery management system (BMS) and battery thermal managing system (BTMS)

Mater. Horiz. **2020**, *7*, 1937

Next generation LIBs: higher energy density – Li metal anode

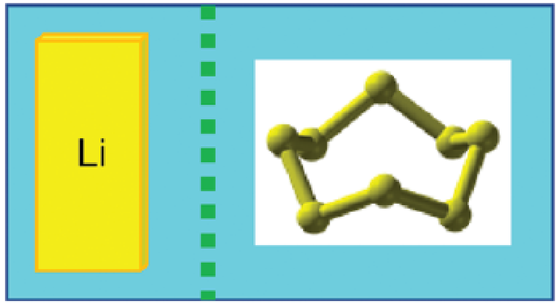


Li-ion battery → Li metal battery



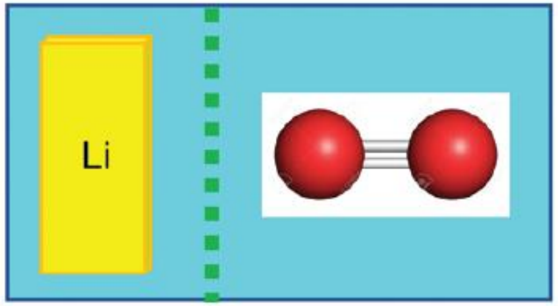
$Li_{1-x}MO_2 + x\,Li^+ + x\,e^- \rightleftharpoons LiMO_2$

Li metal battery
(intercalation cathode)



$S_8 + 16\,Li^+ + 16\,e^- \rightleftharpoons 8\,Li_2S$

Li-S battery
(conversion cathode)



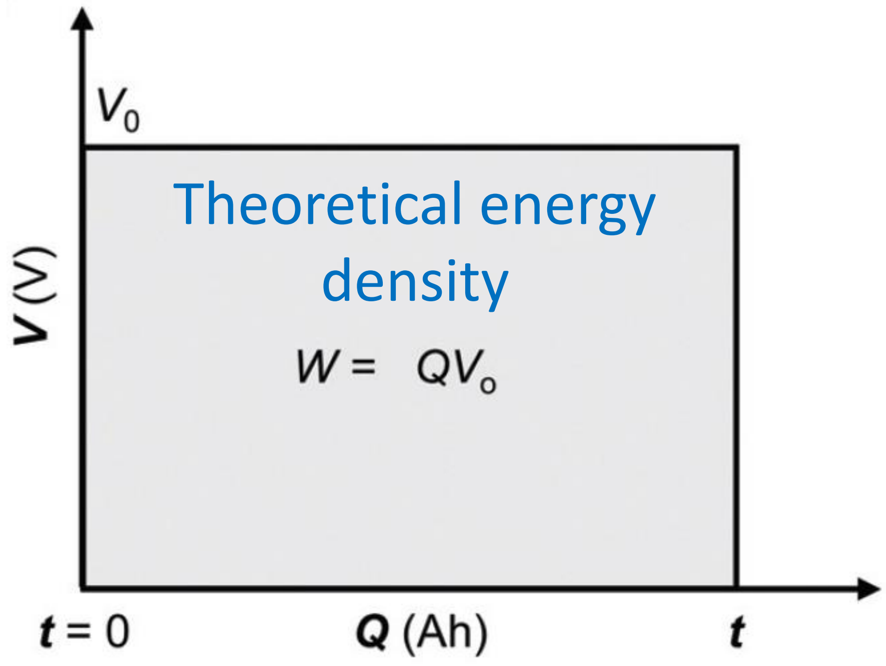
$O_2 + 2\,Li^+ + 2\,e^- \rightleftharpoons Li_2O_2$

Li-O_2 battery
(conversion cathode)

Mater. Horiz. **2020**, *7*, 1937

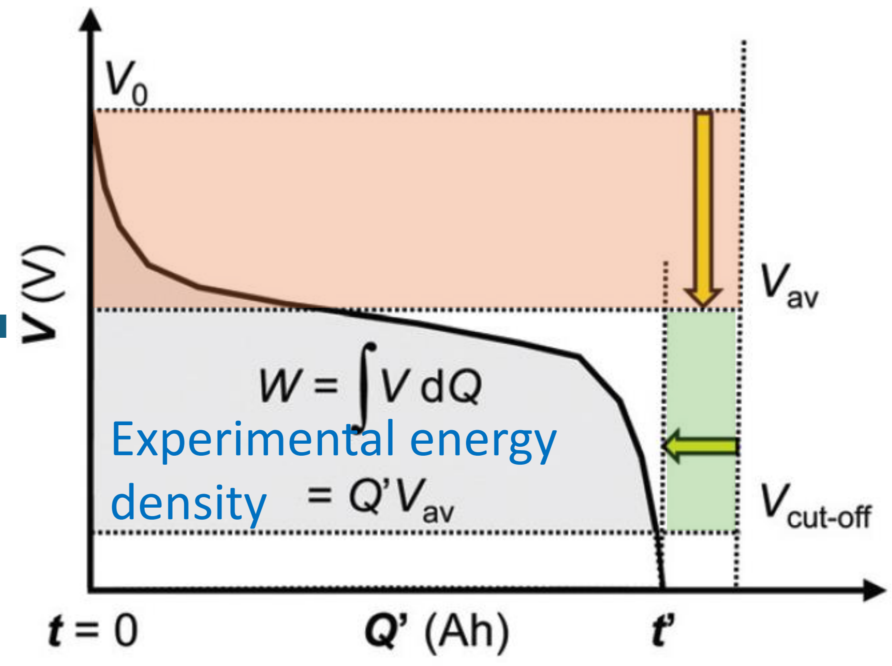
The gap between theoretical and practical energy density

Theoretical voltage determined by redox pair(s)



Theoretical capacity $Q = nF$

Experimental voltage affected by the internal resistance R



Experimental capacity Q' affected by discharge current i

Mater. Horiz. **2020**, *7*, 1937

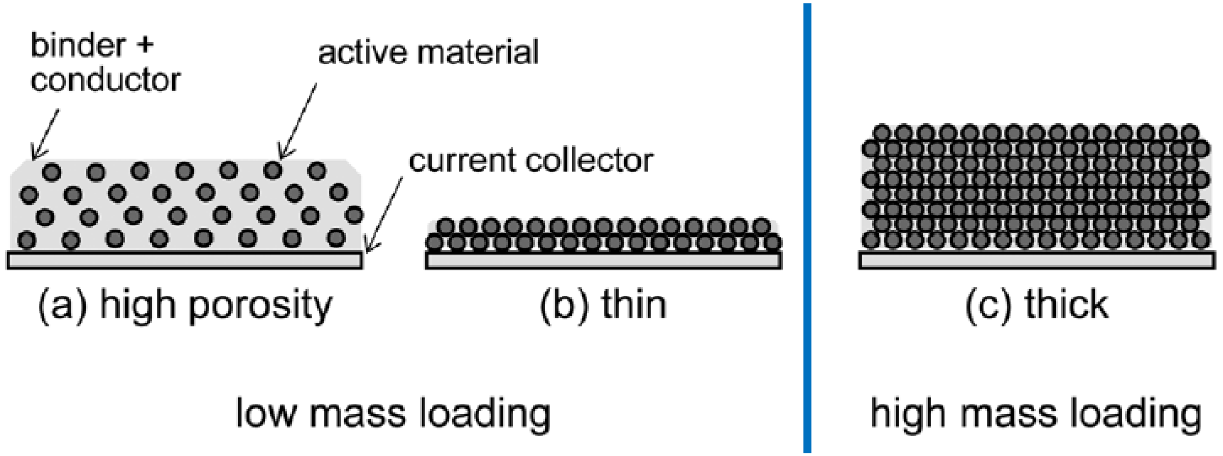
Key technological parameters in improving energy density – cathode coating

- Mass loading of active materials
  - Increasing the loading of active material (>90%)
  - Optimizing ink formulation (conductive carbon, binder, solvent, etc.)

- Thickness and porosity of electrodes

↗ Higher reversible capacity

↘ Lower ratio of active material

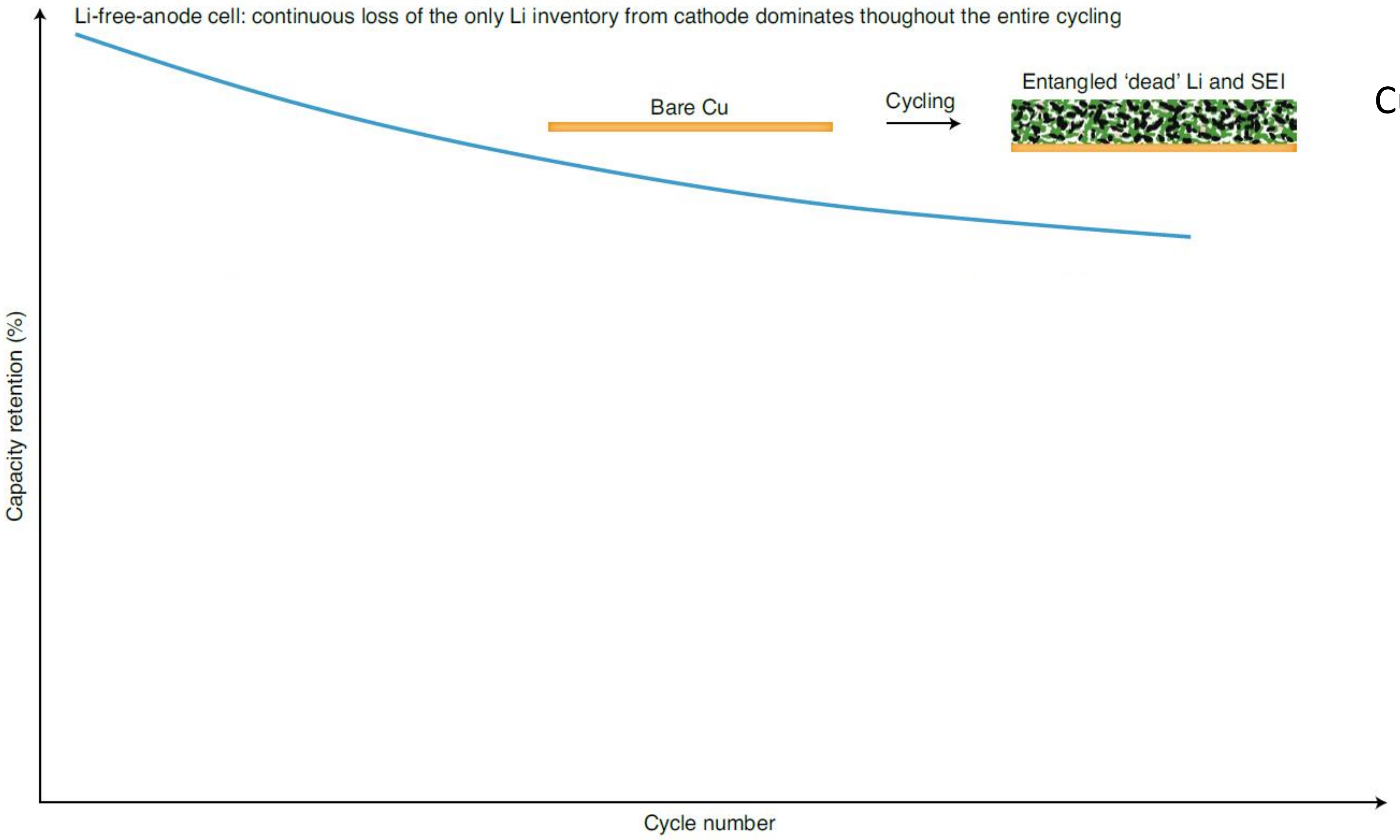


↗ Higher ratio of active material

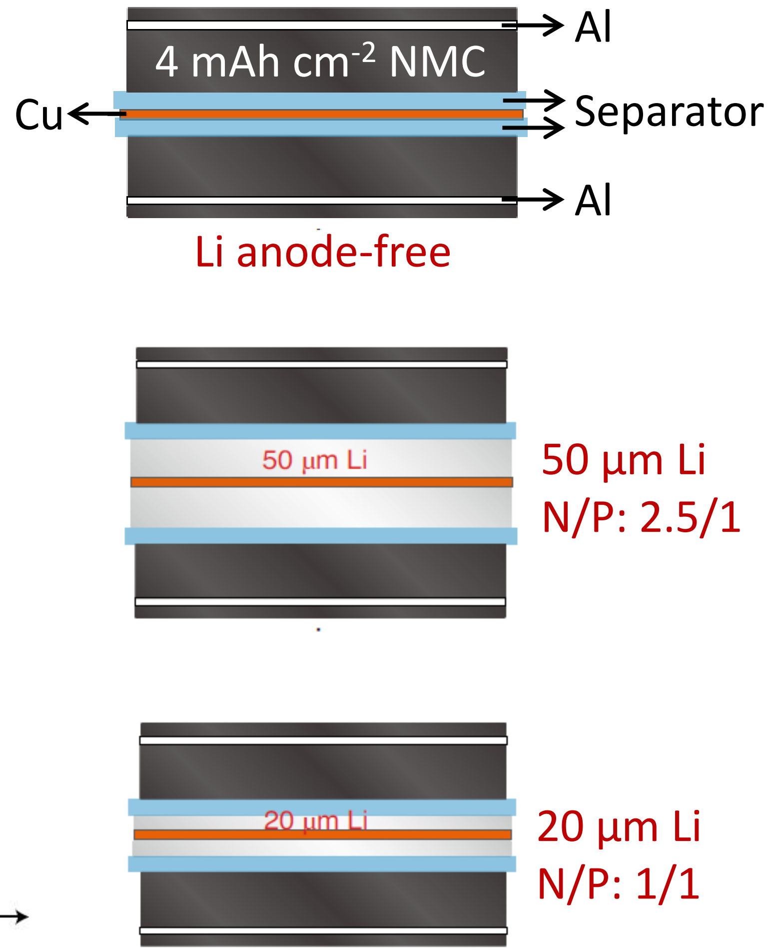
↘ potential polarization

Mater. Horiz. **2020**, *7*, 1937

Improving energy density – anode/cathode pairing (N/P ratio)



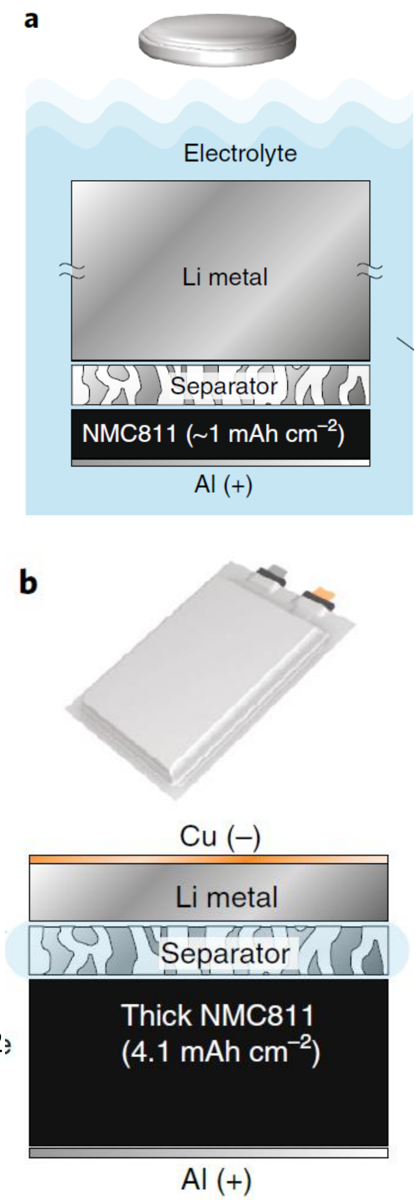
One repeating layer of double-sided pouch cell

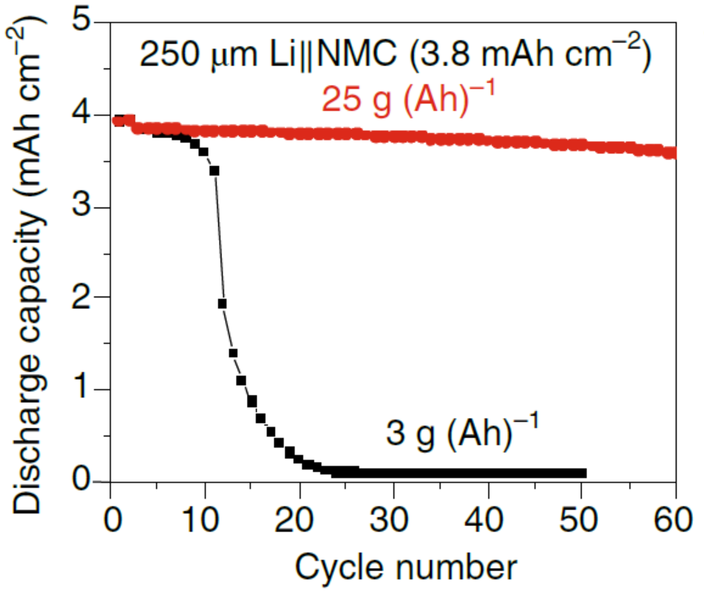


Nat. Energy **2021**, *6*, 723

Improving energy density – electrolyte amount (E/C ratio)

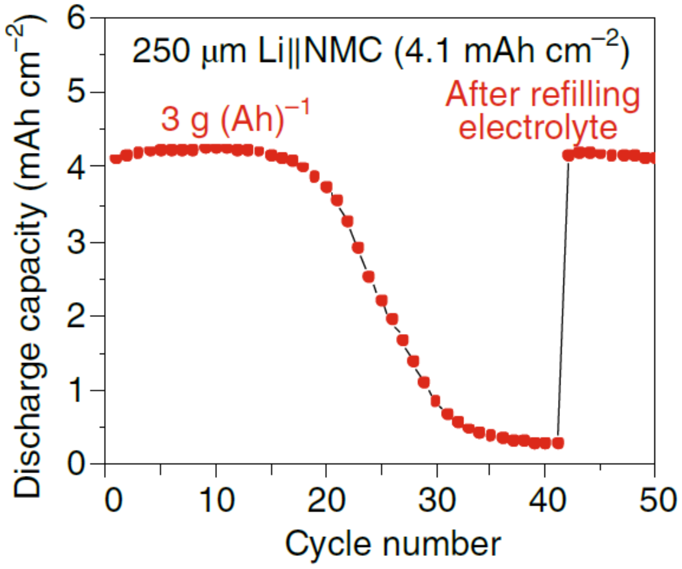
<u>Coin cell</u>
Flooded electrolyte: ≥75 μL
Cathode loading: 1 mAh cm^{-2}
E/C ratio: ≥70 g $(Ah)^{-1}$





Capacity dropping significantly when reducing E/C ratio

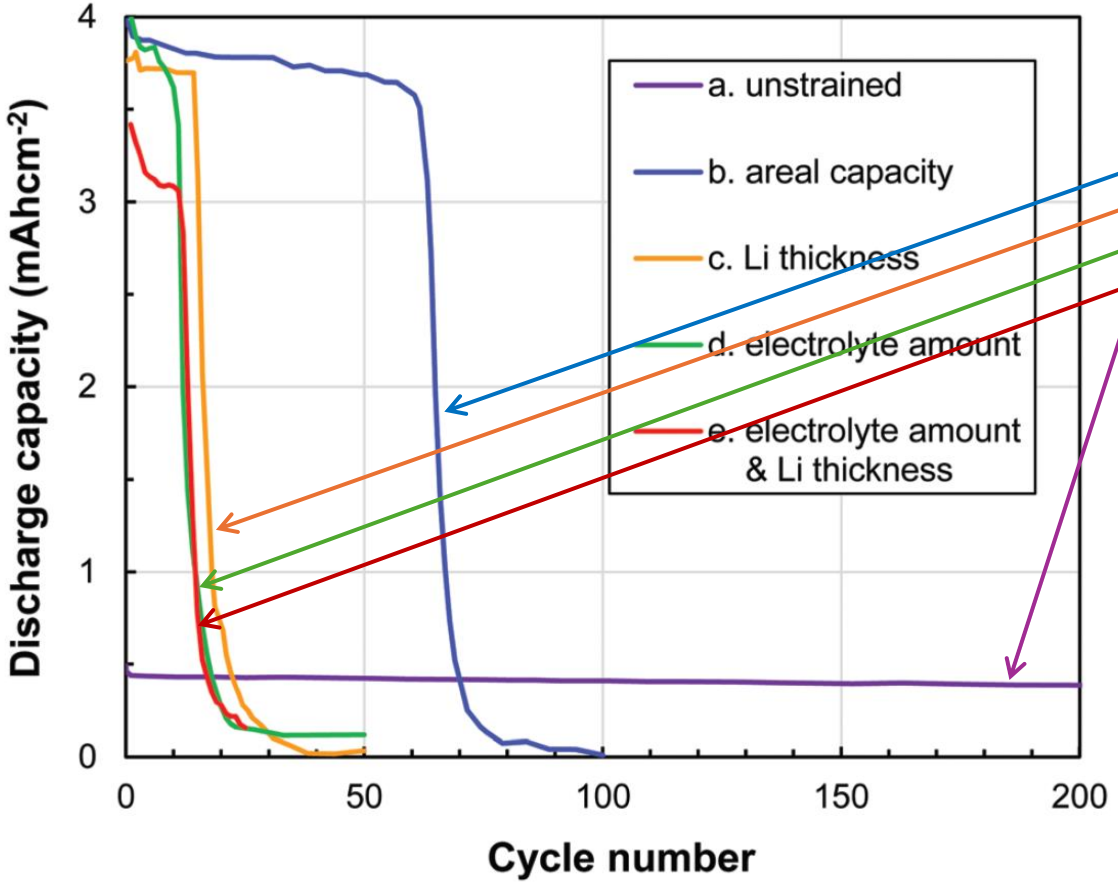
<u>Pouch cell</u>
Lean electrolyte
Cathode loading: ~4 mAh cm^{-2}
E/C ratio: ~3 g $(Ah)^{-1}$



Capacity recovered when replenishing electrolyte – electrolyte consumption by thick Li anode

Nat. Energy **2019**, *4*, 180

For example (Li/NCM622)

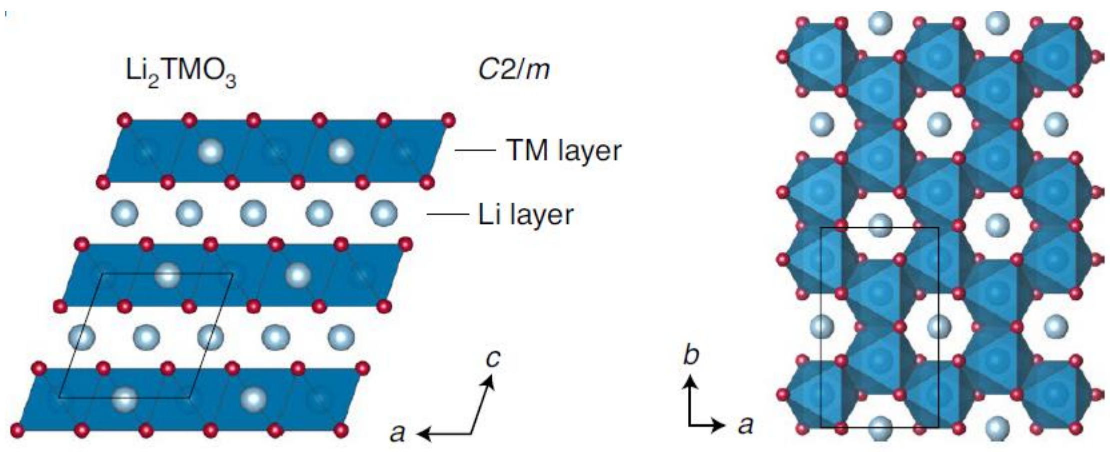


Expt.	Areal capacity (mA h cm^{-2})	Li thickness (μm, N/P)	Electrolyte amount (μl, g A h^{-1})	Charge/discharge rate (mA cm^{-2}, C-rate)	Cycle life (number)
a	0.45	250, 173	100, 210	0.90, 2	>300
b	3.8	250, 20	100, 25	0.76, 0.2	63
c	3.7	50, 4	100, 25	0.74, 0.2	16
d	3.8	250, 20	11, 3	0.76, 0.2	12
e	3.5	50, 4	11, 3	0.70, 0.2	12

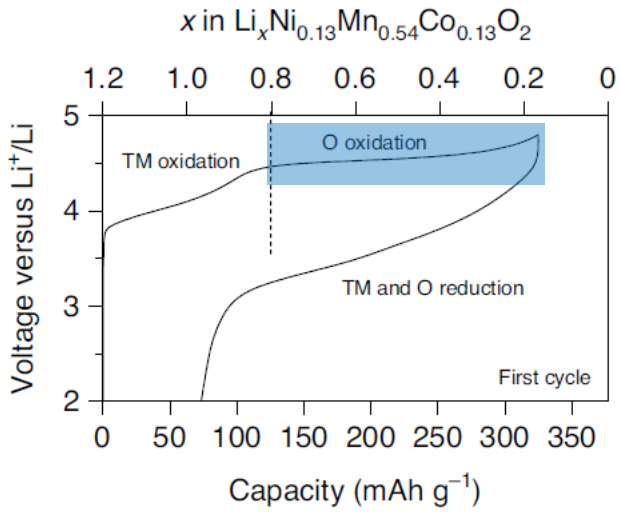
- Unstrained: flooded electrolyte, high N/P ratio, large electrode area
- Small electrode area and large areal capacity
- Low N/P ratio, large areal capacity
- Lean electrolyte, large areal capacity
- Low N/P ratio, lean electrolyte, and large areal capacity

Joule **2019**, *3*, 1094

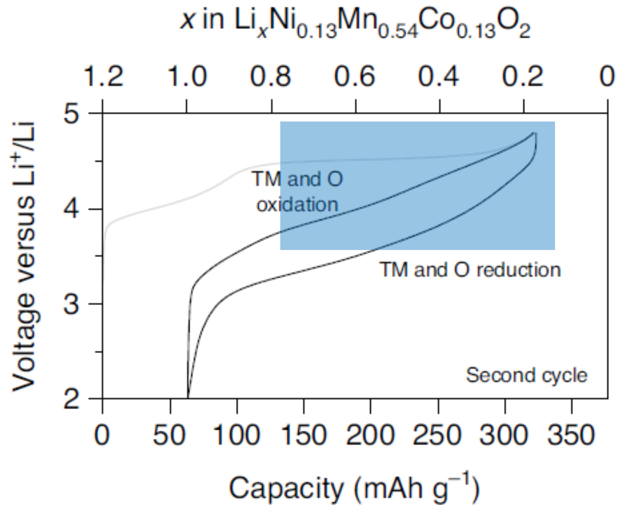
Next generation LIBs: higher energy density – Li-rich & O-redox cathodes



Parent crystal structure of layered Li-rich O-redox cathodes, $LiTMO_3$ ($Li[Li_{1/3}TM_{2/3}]O_2$), e.g., $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ ($Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$)



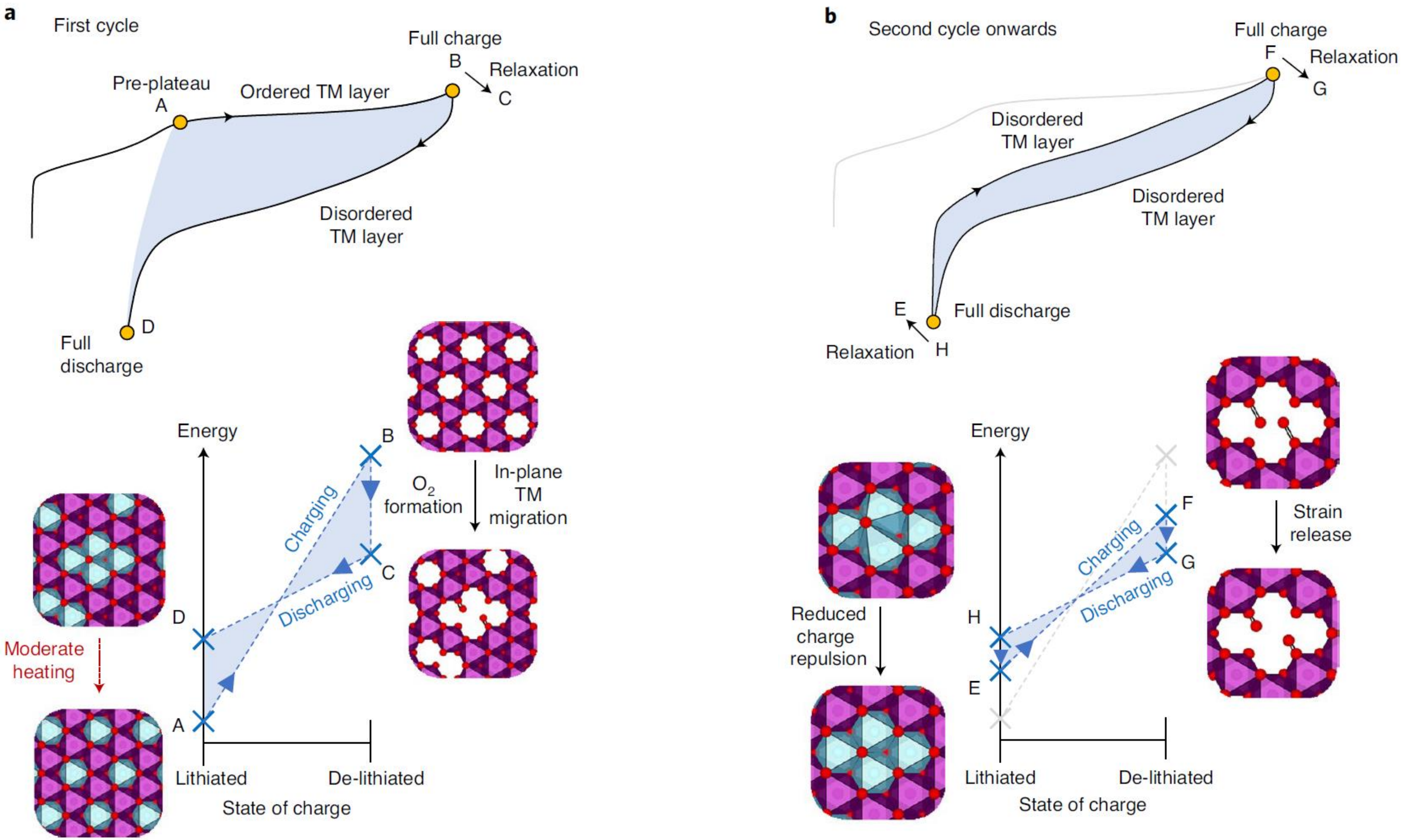
The oxidation of O^{2-} is typically accompanied by a high voltage plateau (~4.5 V vs. Li^+/Li for 3d cathodes) on charging followed by an S-shaped discharge profile.



Irreversible O-redox activity is seen from the second charging onwards, showing the loss of high-voltage plateau – **voltage hysteresis**

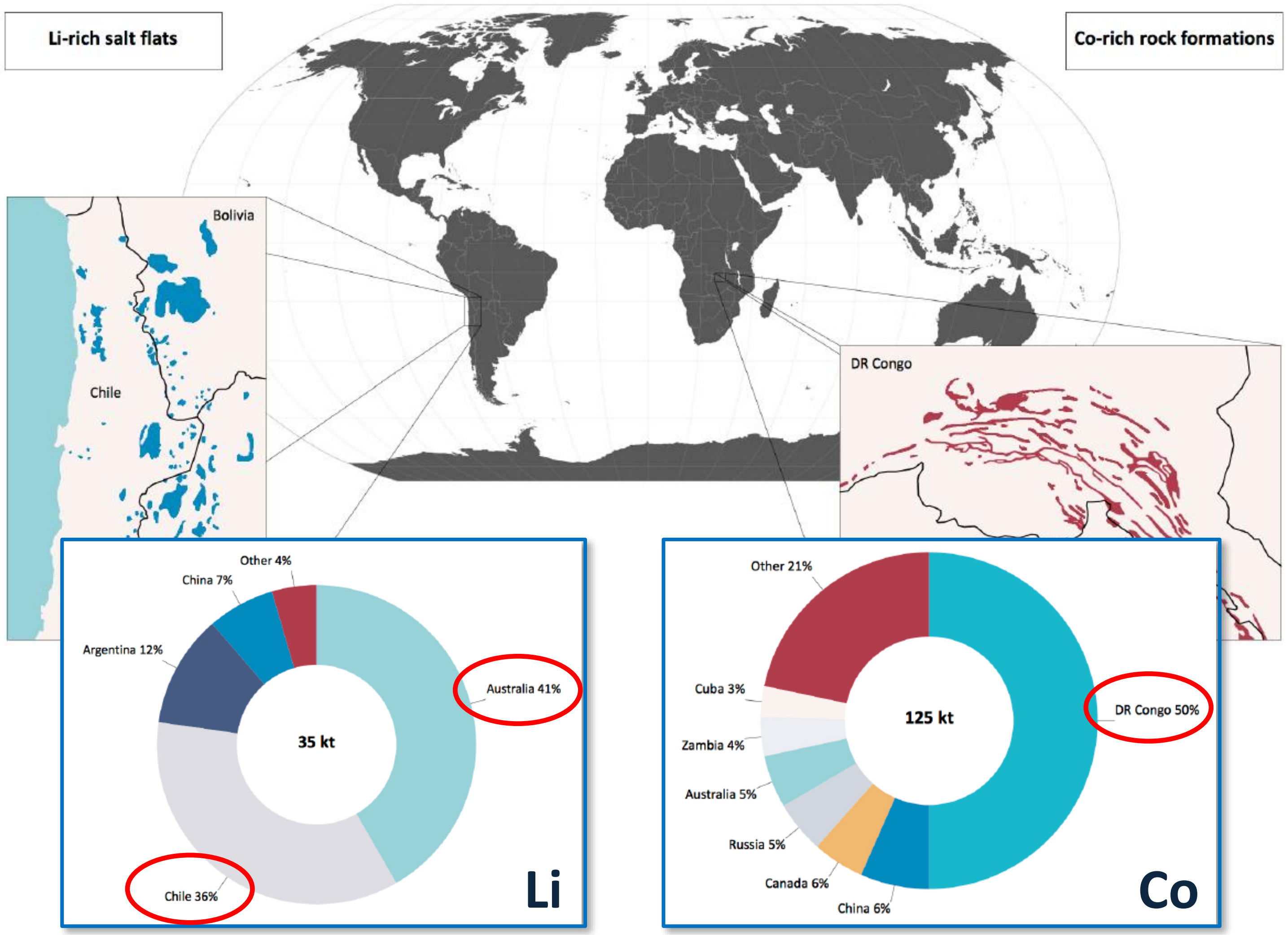
Nat. Energy **2021**, *6*, 781

Voltage hysteresis

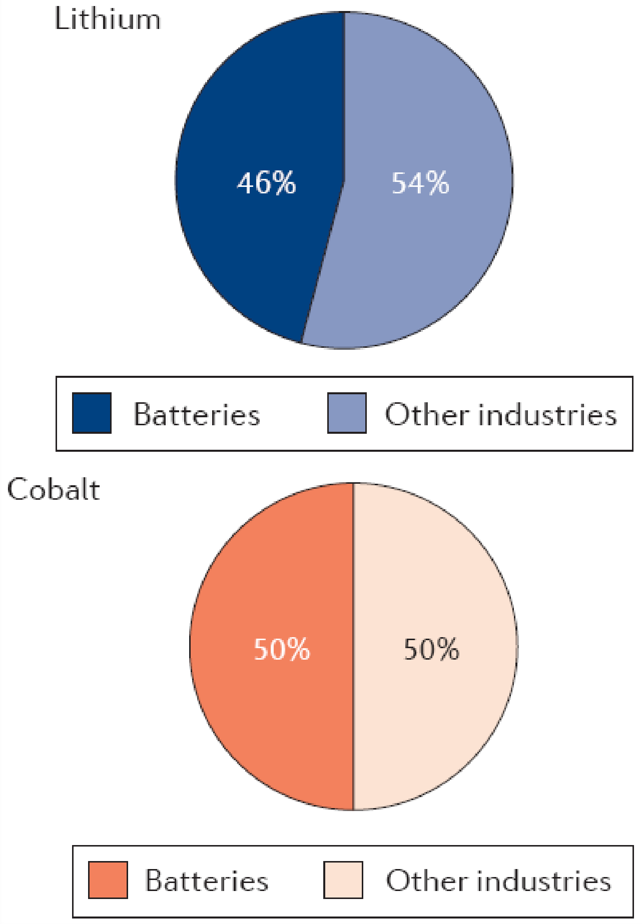


Nat. Energy **2021**, *6*, 781

Next generation batteries: beyond lithium (sustainability is key)



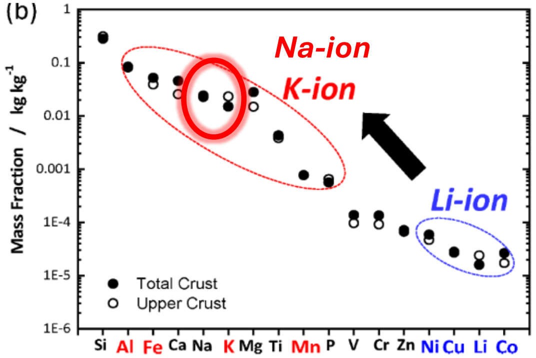
Battery industry's present share of the demand for lithium and cobalt



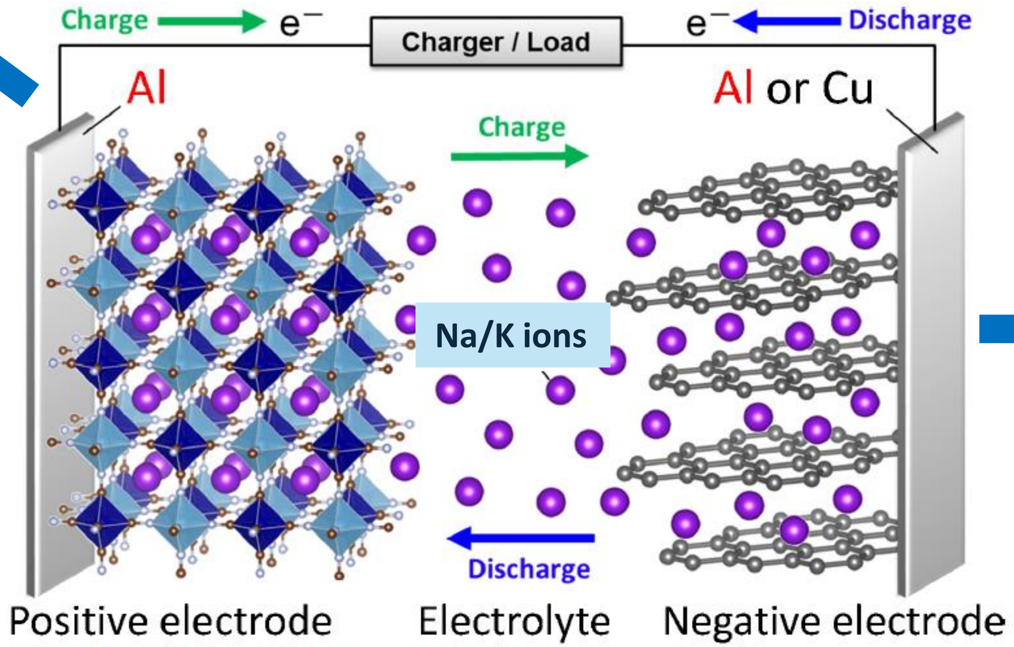
Nat. Rev. Mater. **2018**, 18013; *U.S. Geological Survey, Mineral Commodity Summaries* **2017**

Na-ion battery (NIB) & K-ion battery (KIB)

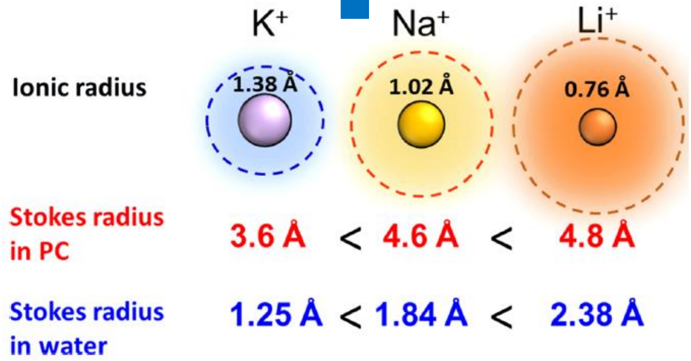
- ❑ High abundance



- ❑ Al: $1165 (K) vs.
  Cu:$3829 (Li) per ton



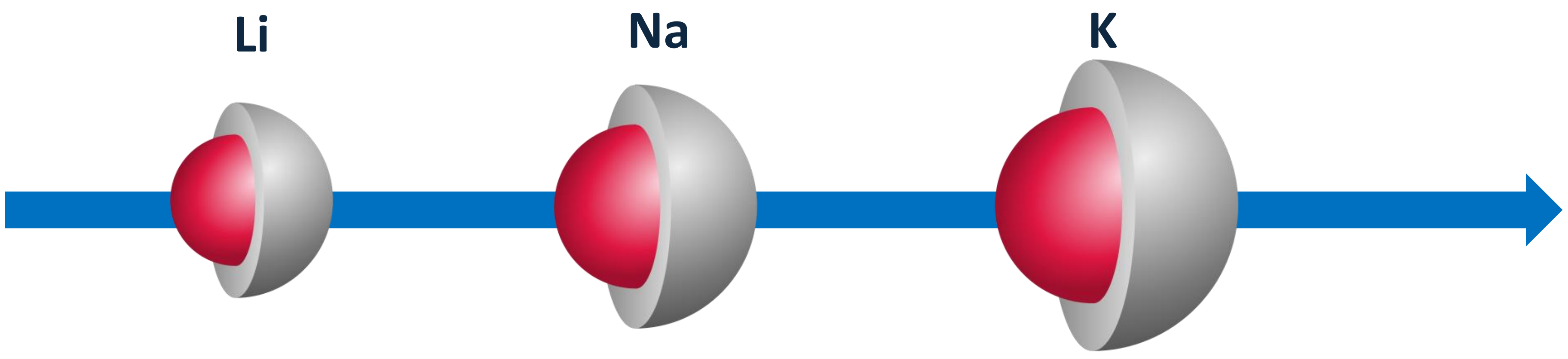
- ❑ Ionic conductivity (in PC):
  K: 15.2 & Na: 9.1
  vs. Li: 8.3 S cm^2 mol^{-1}

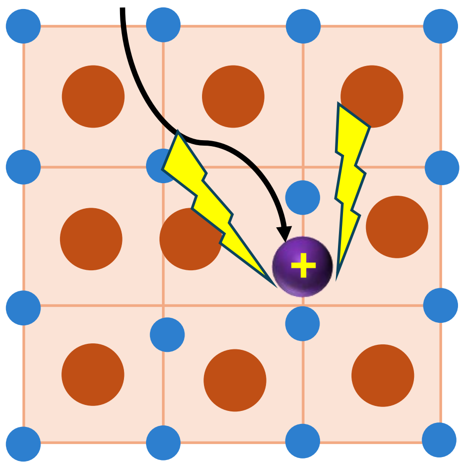


- ❑ Desolvation energy (in PC):
  K: 119.2 & Na: 158.2
  vs. Li: 215.8 kJ mol^{-1}

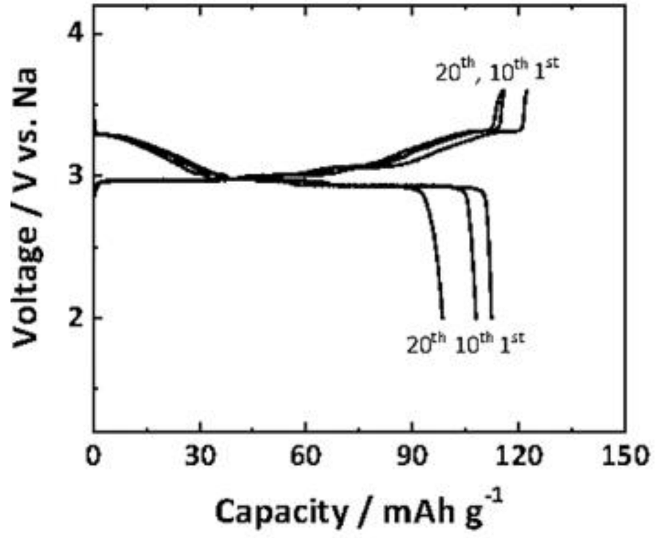
Chem. Rev. **2014**, *114*, 11636 & **2020**, *120*, 6358

Challenges of NIBs and KIBs

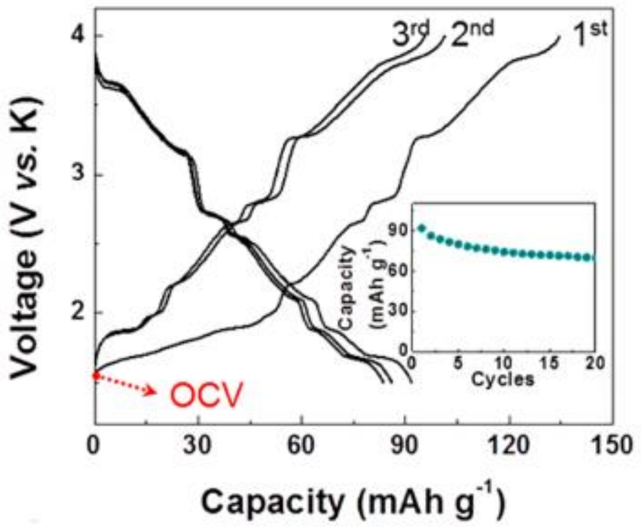


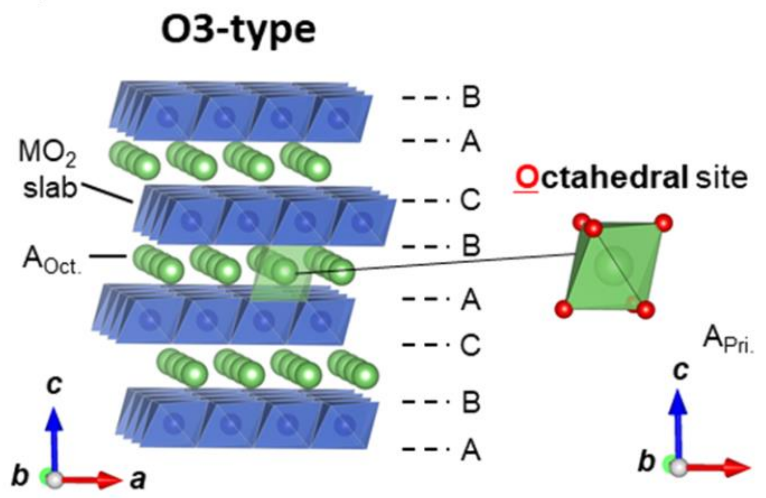


Na||O3-$NaCrO_2$



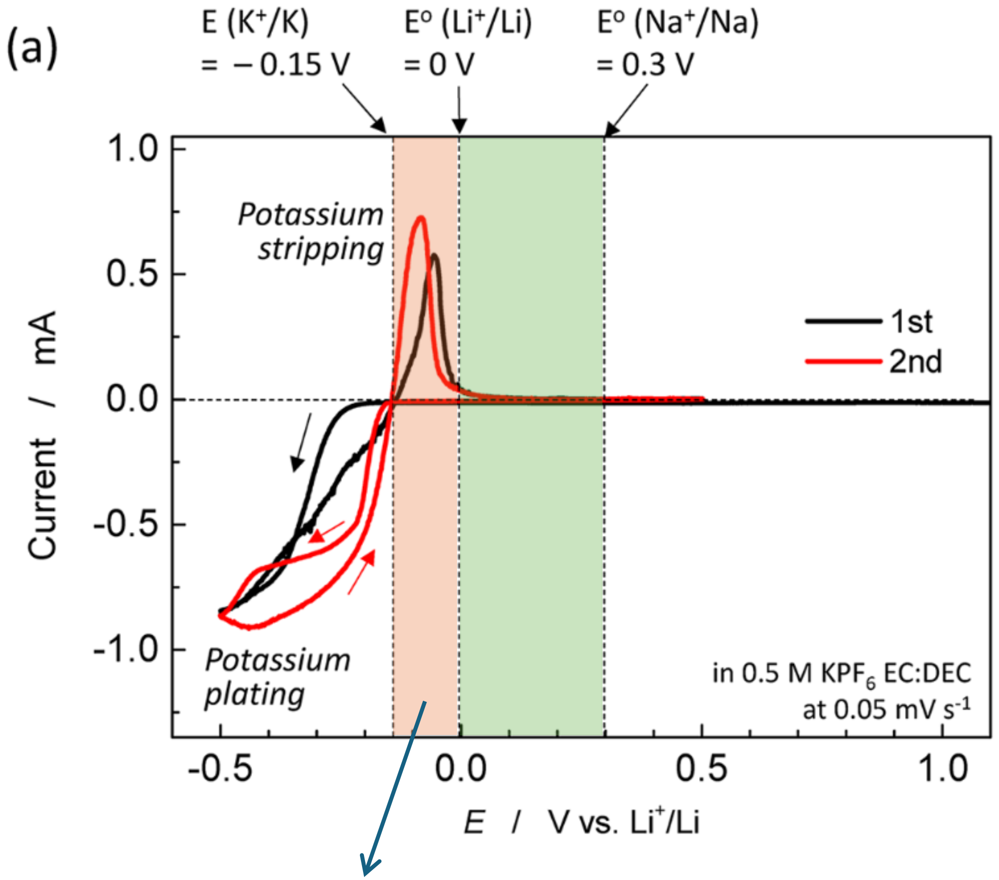
K||O3-$KCrO_2$



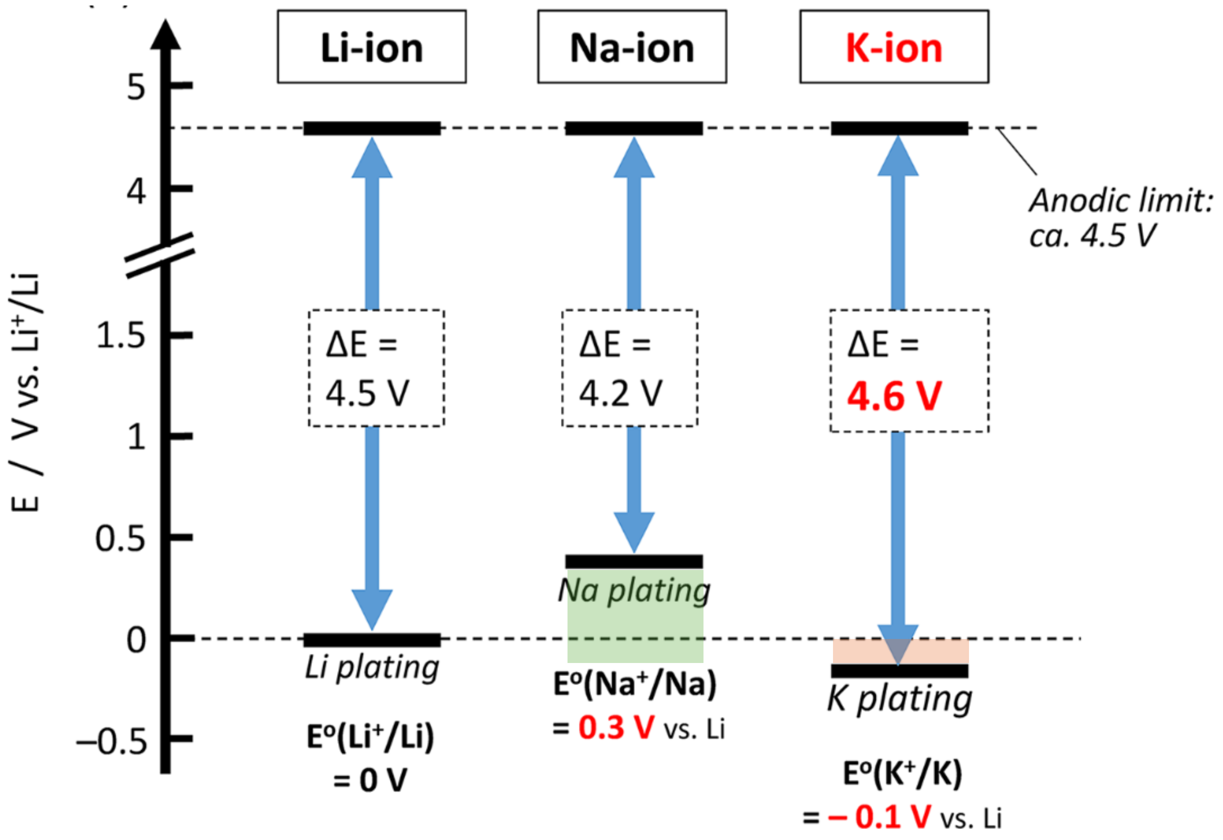


Chem. Rev. **2020**, *120*, 6358; *Chem. Mater.* **2018**, *30*, 6532

KIBs vs. NIBs: plating potential

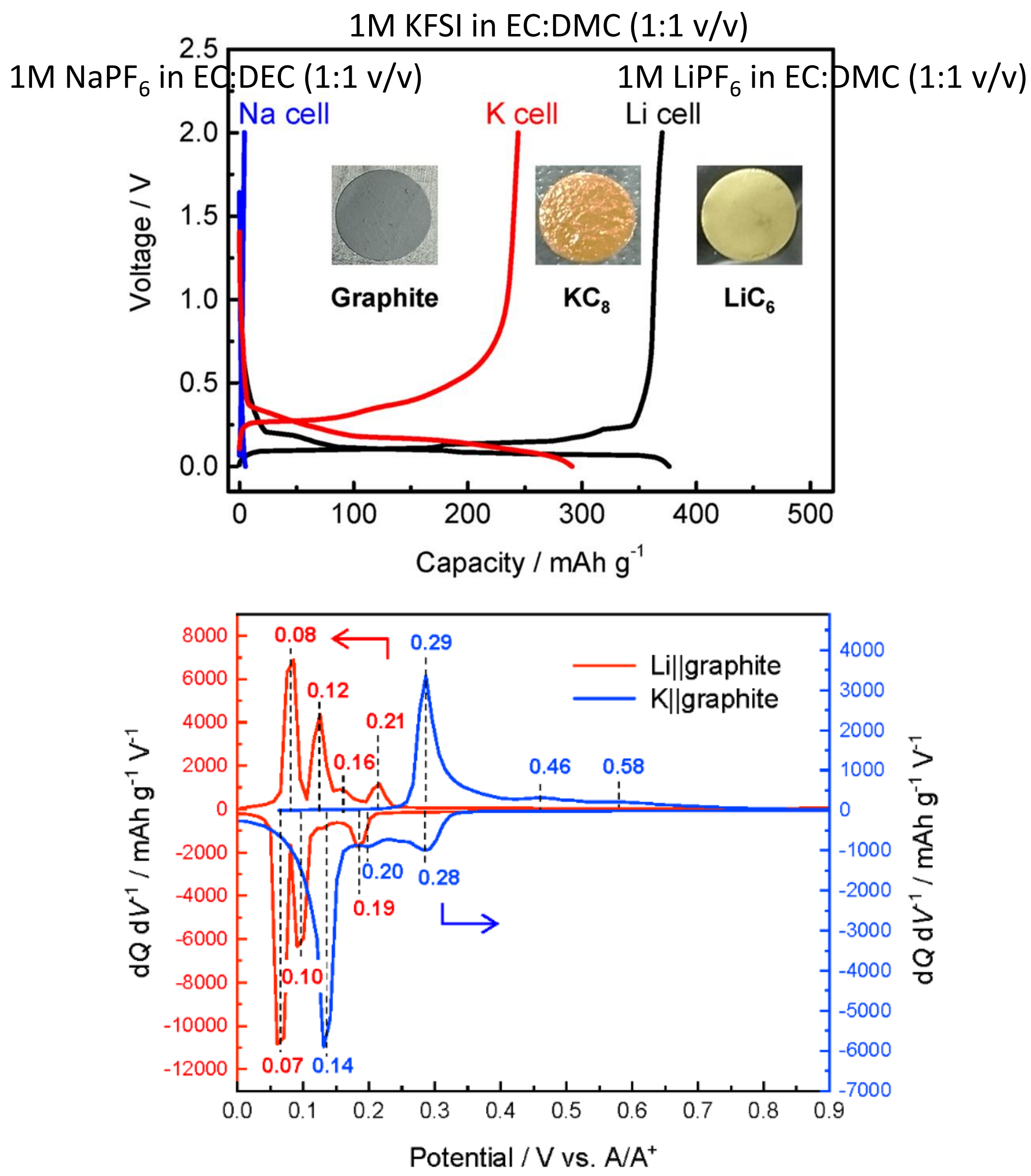


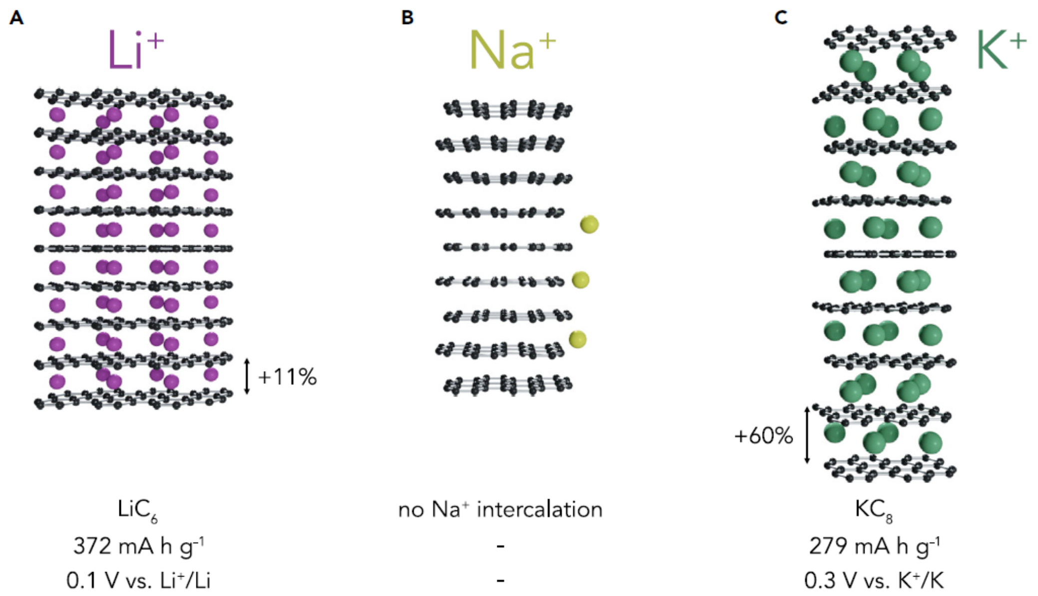
0.15 V lower

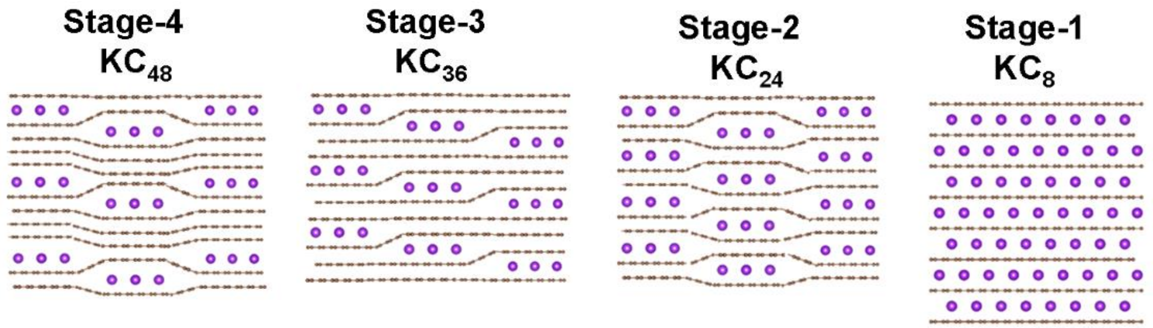


Electrochem. Commun. **2015**, *60*, 172

KIBs vs. NIBs: intercalation in graphite – a staging process



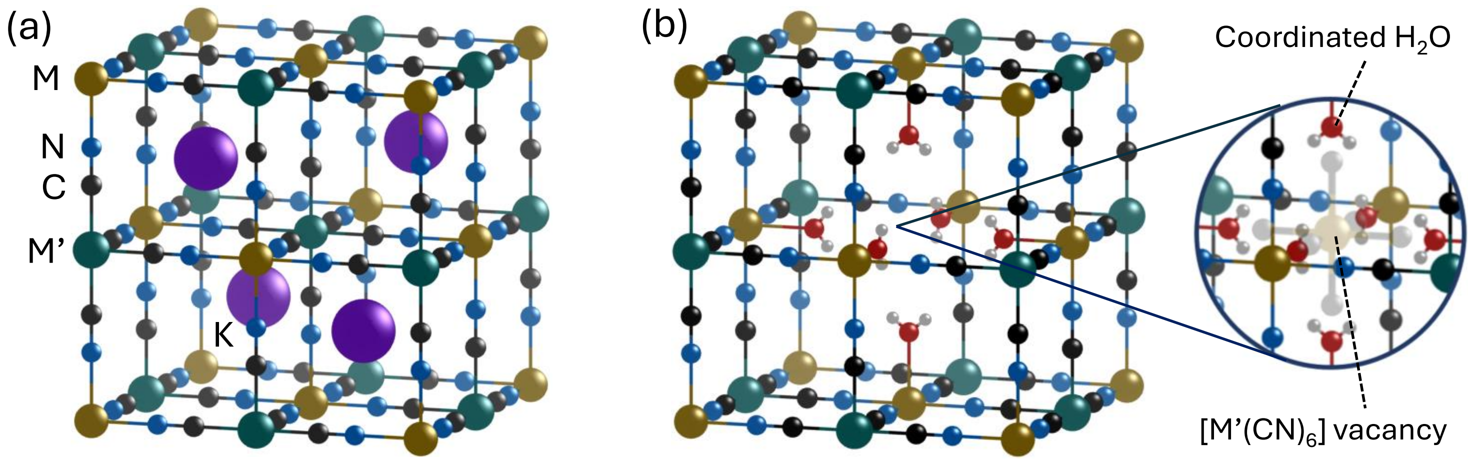


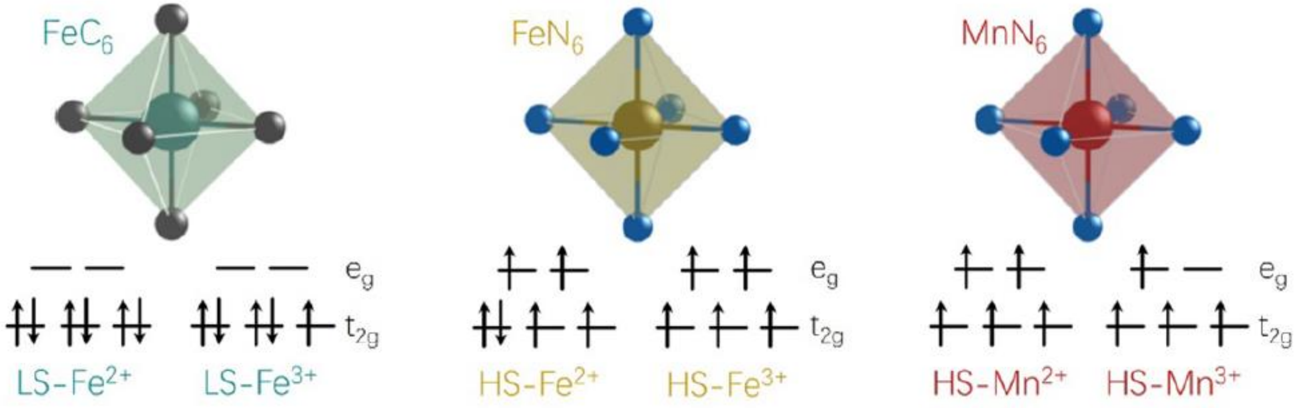


Chem. Rec. **2018**, *18*, 459; *Chem* **2020**, *6*, 2442

KIBs vs. NIBs: intercalation in Prussian blue analogues (PBAs)

$K_xM[M'(CN)_6]_{1-y}\cdot\square_y\cdot zH_2O$ (M' = Fe, M = TM, $\square$ = anion vacancy)



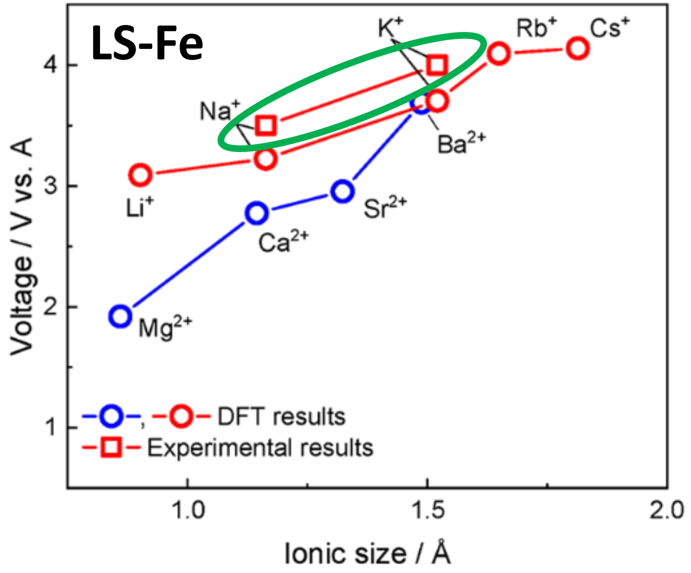


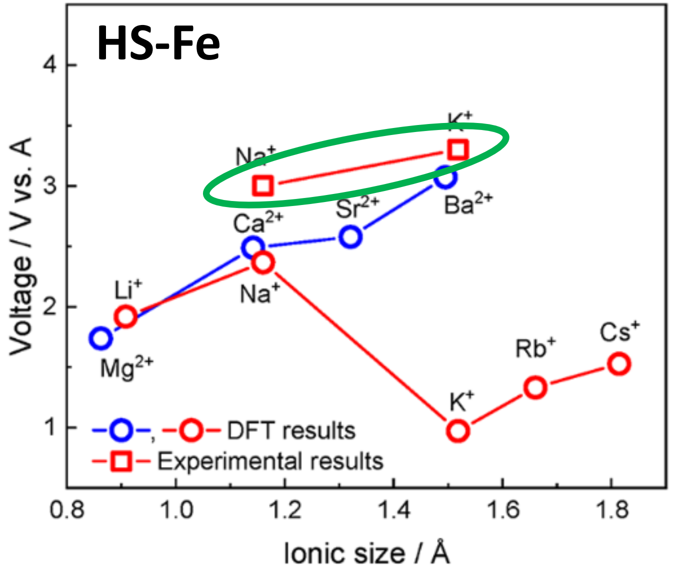
- Open framework
- Large interstitial sites
- Directional ion diffusion channels
- Versatile TMs

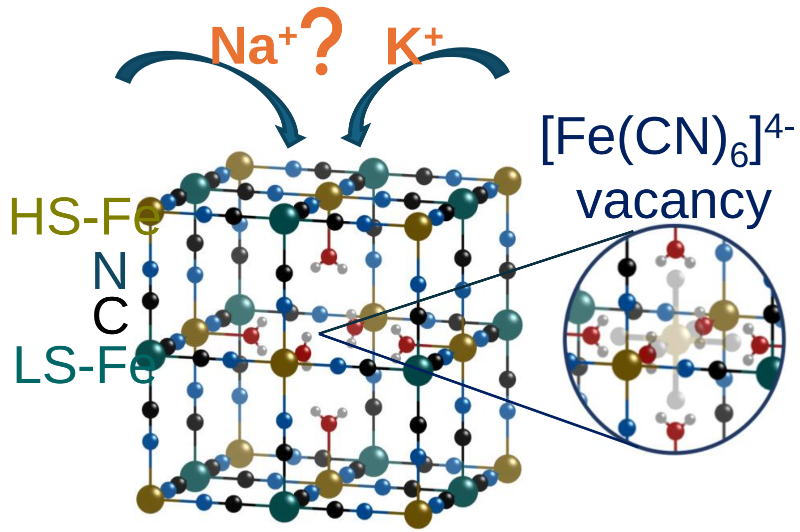
- Two-step redox process involving low-spin (LS) Fe connecting to C and high-spin (HS) TM connecting to N
- Phase transition

JPhy. Energy **2023**, *5*, 021502

KIBs vs. NIBs: intercalation in Prussian blue analogues (PBAs)







- The PBA framework prefer intercalation of large sized ions.
- K-intercalation voltage is higher than Na-intercalation voltage – higher energy density

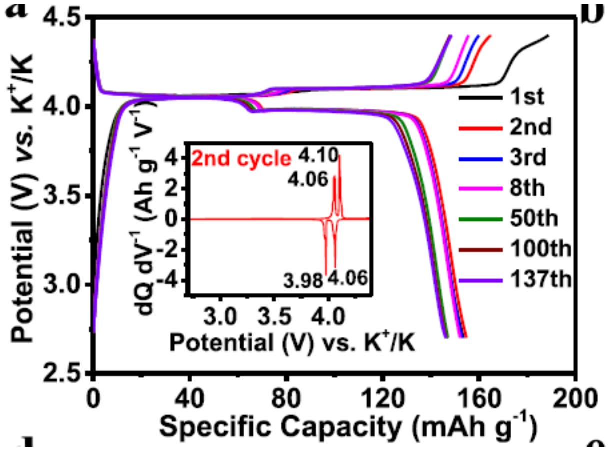
"Incorporating K-ions in the cathode materials for sodium-ion batteries"

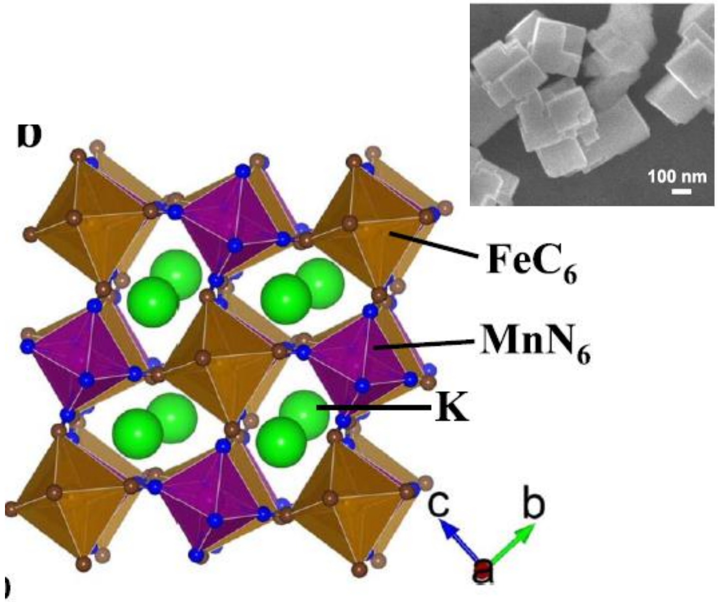
3B6 Materials Discovery/High Entropy Materials
11:20 Tuesday, Room: Gielgud

Chem. Rec. **2018**, *18*, 459; *J. Phys. Chem. Lett.* 2013, 117, 21158

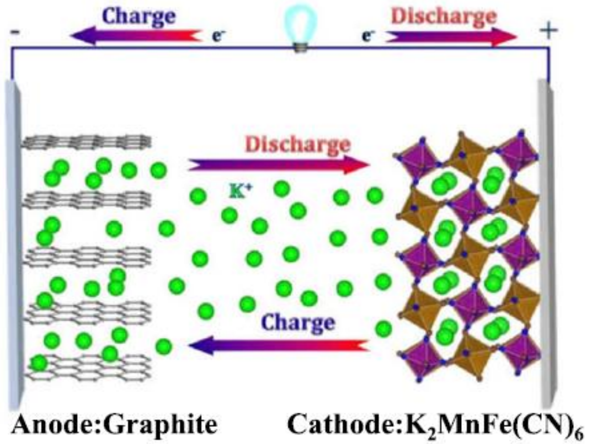
PBAs for KIBs: promising results

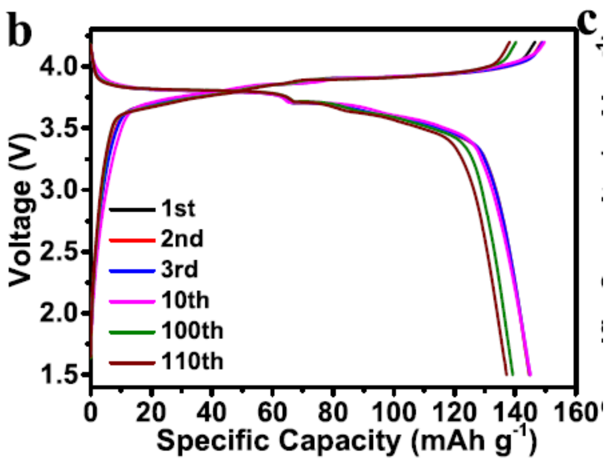
Half cell





Full cell

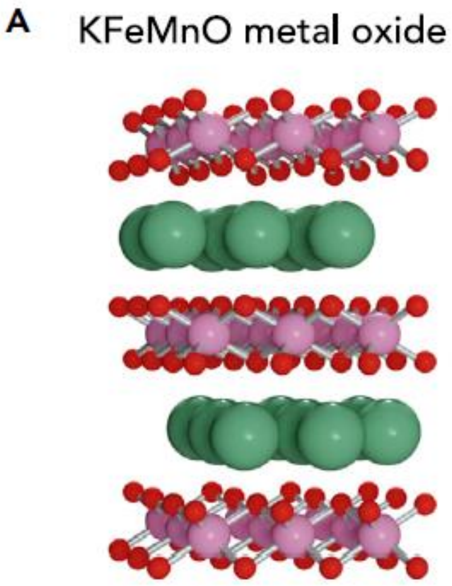


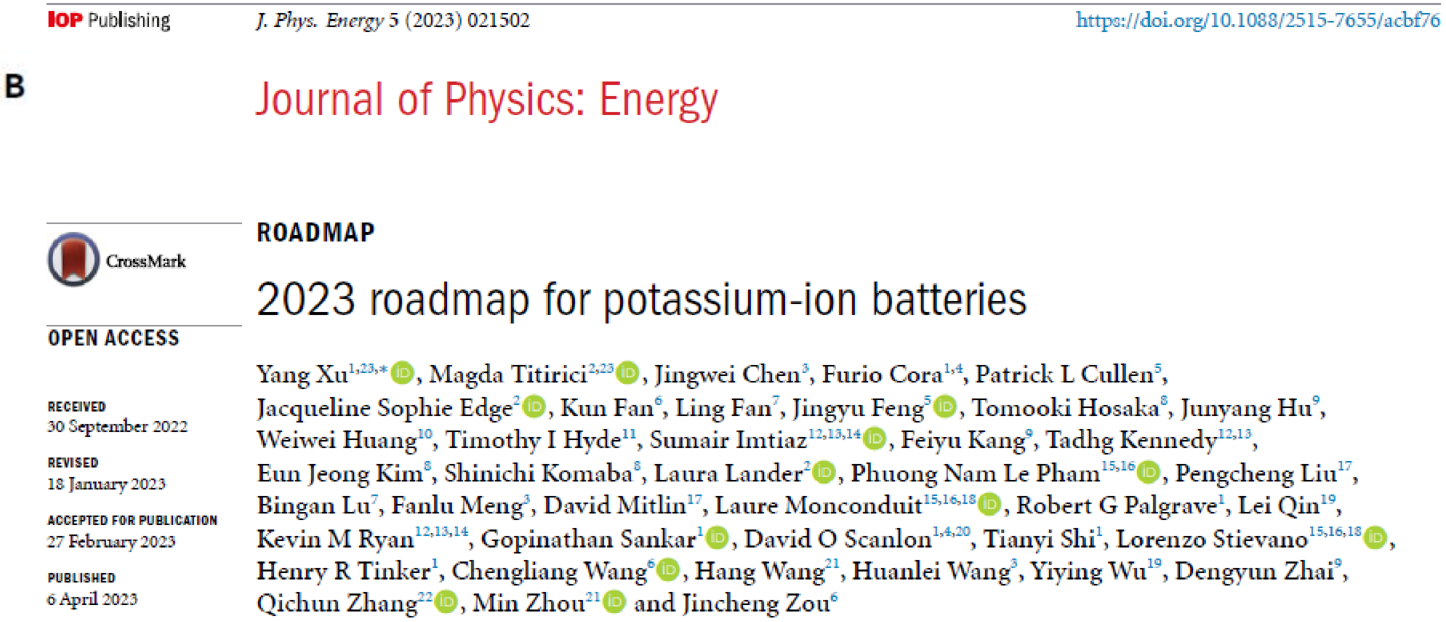


- 140-150 mAh g^{-1} half-cell capacity
- >95% retention @100 cycles @ 15 mA g^{-1}
- >90% retention @ 300 cycles @ 30 mA g^{-1}
- ~140 mAh g^{-1} full-cell capacity
- Similar retention as half cells
- 331.5 Wh kg^{-1} (cathode+anode)

Nat. Commun. **2021**, *12*, 2167

Other KIB cathodes

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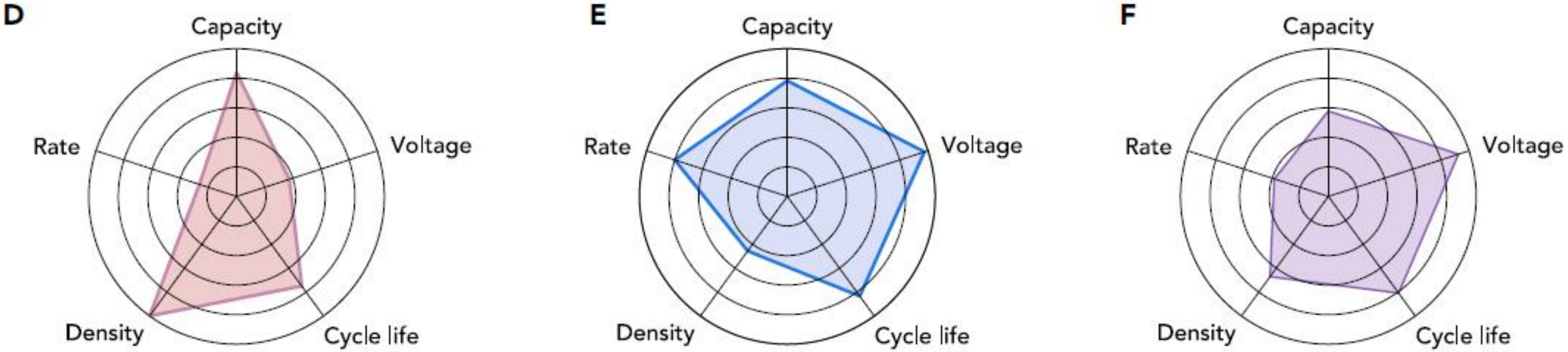
ROADMAP

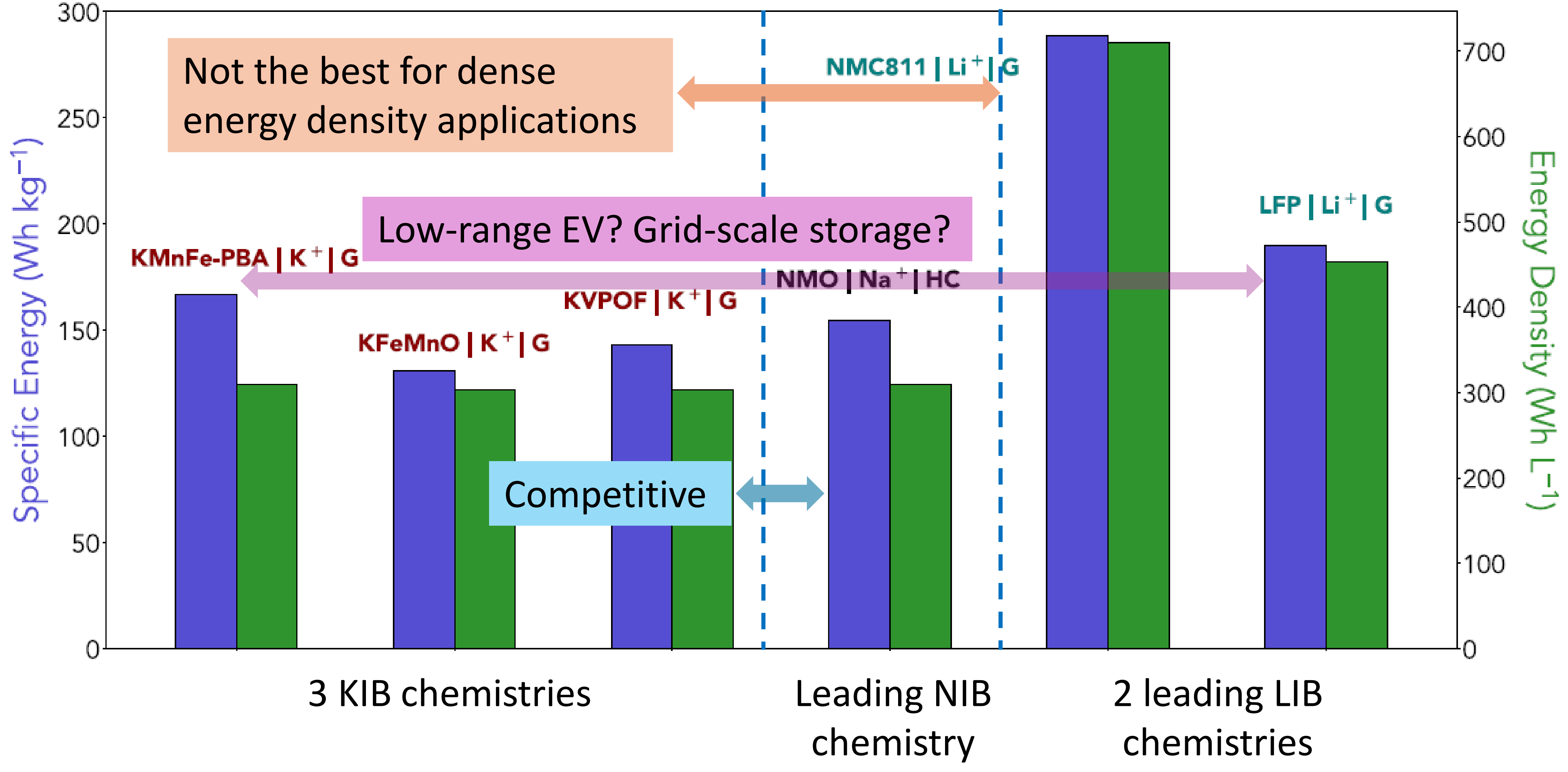
2023 roadmap for potassium-ion batteries

Yang Xu[1,23,*], Magda Titirici[2,23], Jingwei Chen[3], Furio Cora[1,4], Patrick L Cullen[5], Jacqueline Sophie Edge[2], Kun Fan[6], Ling Fan[7], Jingyu Feng[5], Tomooki Hosaka[8], Junyang Hu[9], Weiwei Huang[10], Timothy I Hyde[11], Sumair Imtiaz[12,13,14], Feiyu Kang[9], Tadhg Kennedy[12,13], Eun Jeong Kim[8], Shinichi Komaba[8], Laura Lander[2], Phuong Nam Le Pham[15,16], Pengcheng Liu[17], Bingan Lu[7], Fanlu Meng[3], David Mitlin[17], Laure Monconduit[15,16,18], Robert G Palgrave[1], Lei Qin[19], Kevin M Ryan[12,13,14], Gopinathan Sankar[1], David O Scanlon[1,4,20], Tianyi Shi[1], Lorenzo Stievano[15,16,18], Henry R Tinker[1], Chengliang Wang[6], Hang Wang[21], Huanlei Wang[3], Yiying Wu[19], Dengyun Zhai[9], Qichun Zhang[22], Min Zhou[21] and Jincheng Zou[6]



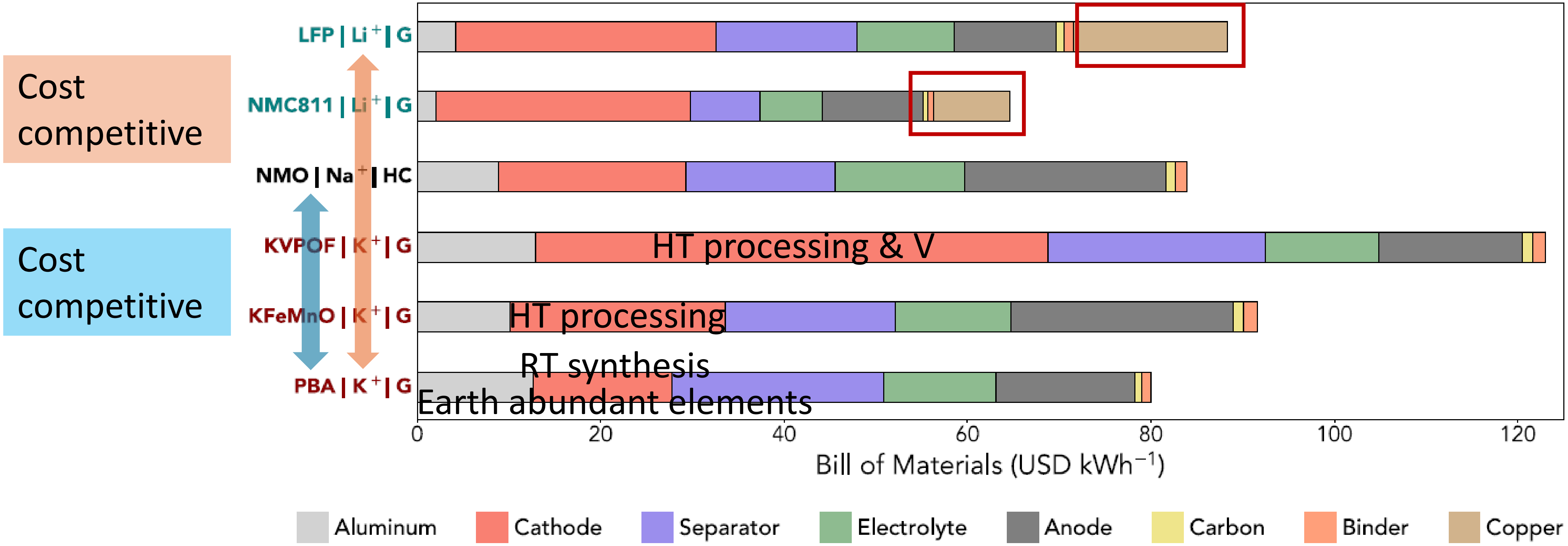
Chem **2020**, *6*, 2442

Techno-economic model of KIBs – energy density



Chem **2020**, *6*, 2442

Techno-economic model of KIBs – cost



- Currently no cycling data of full cell KIBs with realistic form factors
- Results only relevant if reasonable cycling performance (>1000 cycles) can be demonstrated for the full cell PBA KIB
- More sophisticated techno-economic models required to further the analysis

Chem **2020**, *6*, 2442

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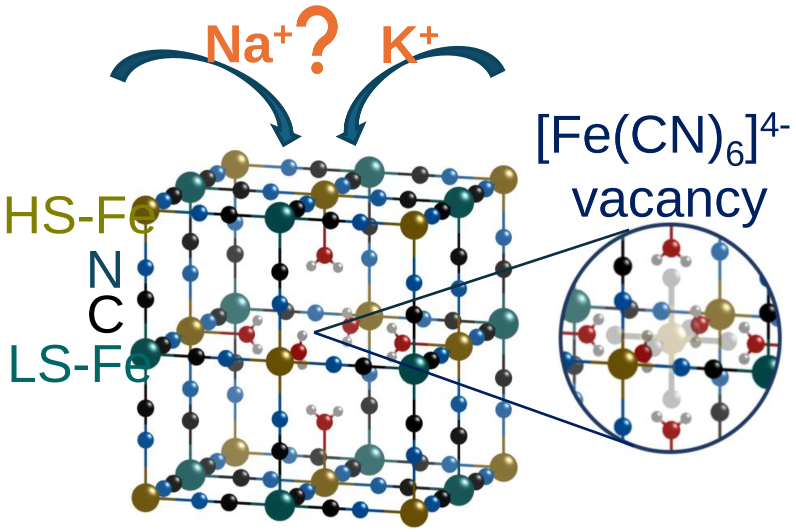

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Thank you for your attention!

XU GROUP xulab.uk

Get in touch if you are interested in my research, collaborating, or joining my group (y.xu.1@ucl.ac.uk)