ENERGY STORAGE:
Battery Technologies for Grid Storage and E-Mobility

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ENABLING TECHNOLOGIES IN THE MODERN GRID

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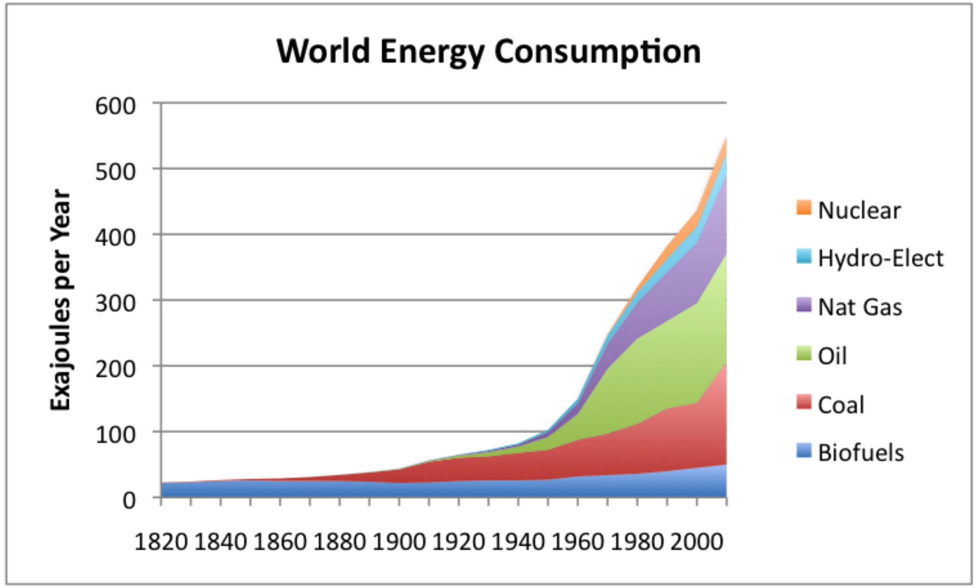
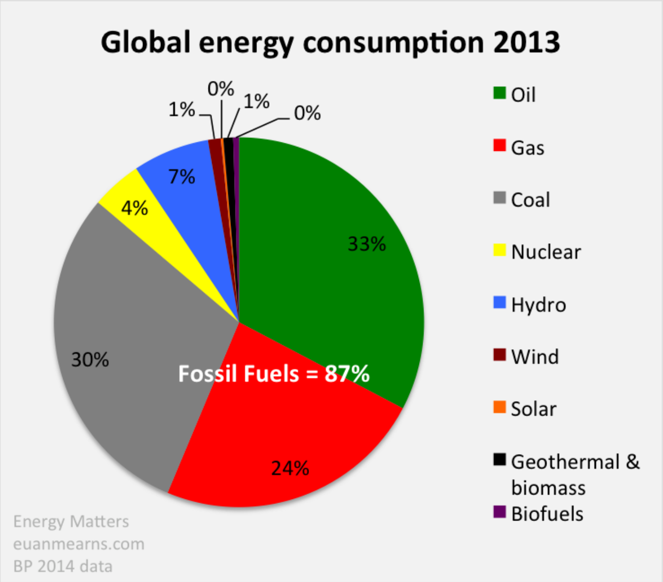
GLOBAL ENERGY OUTLOOK





Energy Use
China: 23%
USA: 17%
India: 5%

Population
China: 1.38 Billion
USA: 0.33 Billion
India: 1.35 Billion

- Energy is a central societal issue, impacting our way of life, economy, national security, environment, and public health; fossil-fuel use causes CO_2 emission and global warming
- World's energy consumption is projected to triple in 2100 based on moderate population and economic growth
- Energy is the greatest challenge (#1 problem) facing humanity in the 21st century

HUMANITY’S TOP 10 PROBLEMS

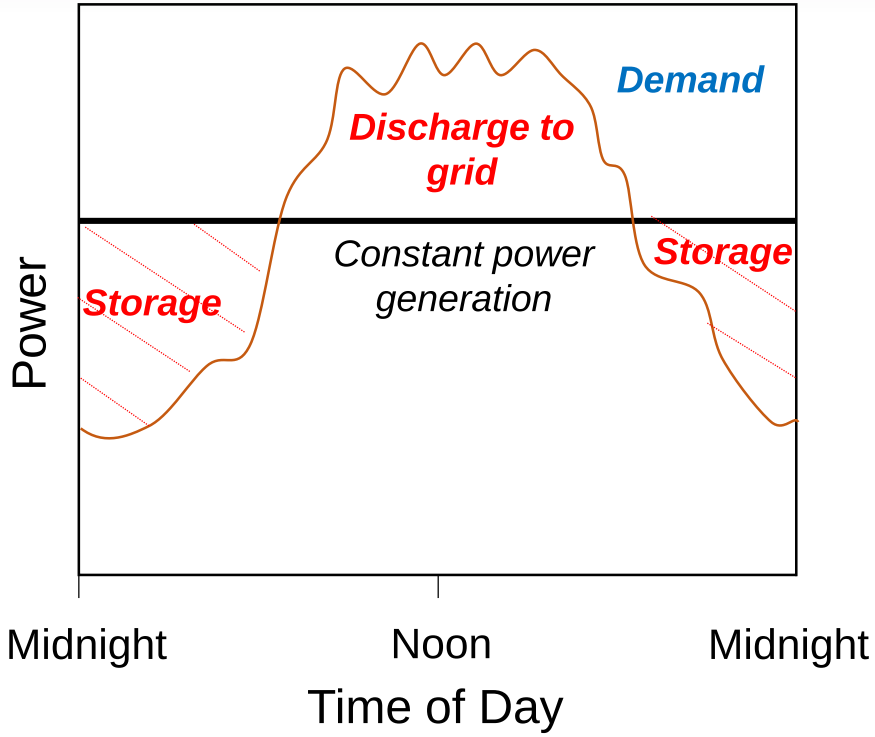
Humanity’s Top Ten Problems for next 50 years

1. **ENERGY**
2. WATER
3. FOOD
4. ENVIRONMENT
5. POVERTY
6. TERRORISM & WAR
7. DISEASE
8. EDUCATION
9. DEMOCRACY
10. POPULATION

2003	**6.3**	**Billion People**
2050	**8-10**	**Billion People**

Smalley Institute, Rice University

WHAT IS THE SOLUTION?

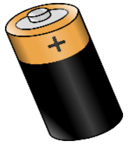


The energy challenge
Finite fossil fuel supply, pollution

Solution?

Renewable energy (solar, wind)
Intermittent: storage is the bottleneck

Option?

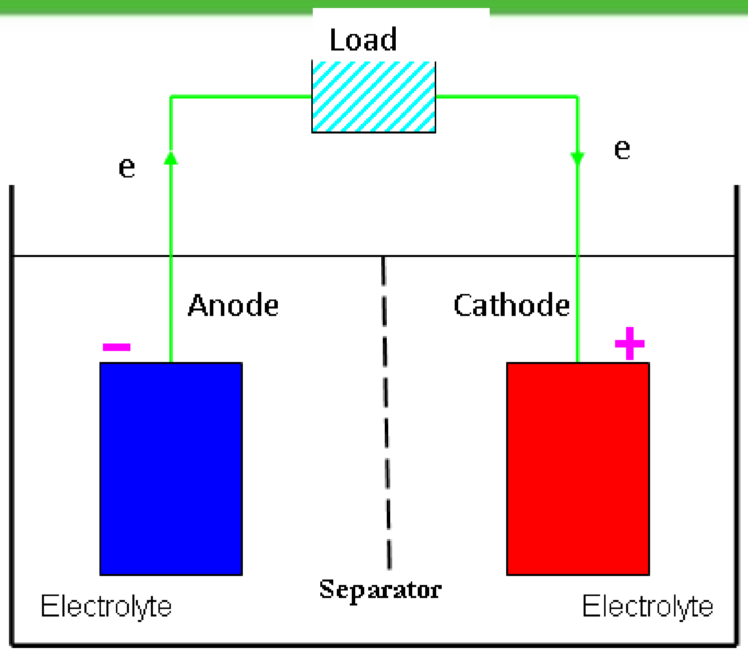


Battery technologies
Cost, energy, charging time, life, safety

Transportation
Uncontrolled pollution
Electric vehicle

- Storage is critical for renewable energy use
- With a storage technology, conventional power plants can also be operated more efficiently

ELECTROCHEMICAL CELL



Galvanic cell – cell at discharge

Anode reaction: oxidation, removal of electron

$M \rightarrow M^{n+} + ne^-$ (*e.g.*, $Zn \rightarrow Zn^{2+} + 2e^-$)

Cathode reaction: reduction, addition of electron

$X + ne^- \rightarrow X^{n-}$ (*e.g.*, $Cl_2 + 2e \rightarrow 2Cl^-$)

Faraday's first law:

Mass of a substance reacting or being produced at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.

Faraday's second law:

For a given quantity of electricity, the masses of different substances reacting or being produced at the electrodes are directly proportional to the equivalent masses of the substances.

Electrolytic cell – cell at charge: reverse reaction will occur

Cathode: M

Anode: X

BATTERY PERFORMANCE PARAMETERS

Cell voltage $V_{op} = V_c - V_a$

Gravimetric capacity $Q_g = Q/m$ Ah/kg

Gravimetric energy density $= Q_g V_{op}$ Wh/kg

Gravimetric power density $= I_g V_{op}$ W/kg

Volumetric capacity $Q_v = Q/V$ Ah/L

Volumetric energy density $= Q_v V_{op}$ Wh/L

Volumetric power density $= I_v V_{op}$ W/L

C rate $= I_d / Q_n$ = discharge current / nominal capacity

A *C* rate of *t* implies that the nominal capacity of the cell is delivered in 1/t hours under the specified current density.

Coulombic efficiency, $q_c = Q_d / Q_c$ = discharge capacity / charge capacity

Charging factor, $f = 1 / q_c$

Energy efficiency, $q_E = q_c (V_d / V_c) = (Q_d / Q_c) (V_d / V_c)$

A $q_C < 1$ implies unwanted side reactions resulting in production of heat

A $q_E < q_C$ implies a deviation of the discharge and charge curves from OCV

Cycle life: limiting value is 70 – 80 % of the nominal capacity

User time = energy density = (cell voltage) x (amount of charge stored in the form of ions)

DESIGNING A CELL

Electrode reaction	E^0 (V)
$Li^+ + e \rightarrow Li$	-3.01
$K^+ + e \rightarrow K$	-2.92
$Ca^{2+} + 2e \rightarrow Ca$	-2.84
$Na^+ + e \rightarrow Na$	-2.71
$Mg^{2+} + 2e \rightarrow Mg$	-2.38
$Al^{3+} + 3e \rightarrow Al$	-1.66
$Zn^{2+} + 2e \rightarrow Zn$	-0.76
$Fe^{2+} + 2e \rightarrow Fe$	-0.44
$Co^{2+} + 2e \rightarrow Co$	-0.27
$Ni^{2+} + 2e \rightarrow Ni$	-0.23
$H^+ + e \rightarrow \frac{1}{2}H_2$	0.00
$Cu^{2+} + 2e \rightarrow Cu$	0.34
$Ag^+ + e \rightarrow Ag$	0.80
$Pd^{2+} + 2e \rightarrow Pd$	0.83
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	1.23
$Cl_2 + 2e \rightarrow 2Cl^-$	1.36
$F_2 + 2e \rightarrow 2F^-$	2.87

Materials Parameters

- **Energy density (user time)**

- voltage (electrode potentials)
- degree of Li^+ insertion

- **Power density (charging time)**

- electronic conductivity
- lithium-ion conductivity

- **Cycle life (battery life)**

- reversibility, stability

- **Cell fire (safety)**

- oxygen release, flammability

- **Environmental impact**

- toxicity

- **Cost**

BATTERY PARAMETERS OF $Zn\text{-}Cl_2$ SYSTEM

Amount of charge transferred or stored = (I x t) Coulomb or A s = nN_AeN_m = nFN_m

Faraday constant F = N_ae = (6.023 x 10^{23} mol^{-1}) (1.6 x 10^{-19} C) = 96,497 C or A s = 96,487 A s / (60 x 60 s/h) = 26.8 A h

$Zn\text{-}Cl_2$ Battery:

$Zn \rightarrow Zn^{2+} + 2e^-$	E^o = 0.76 V
$Cl_2 + 2e \rightarrow 2Cl^-$	E^o = 1.36 V
$Zn + Cl_2 \rightarrow ZnCl_2$	Cell voltage = 0.78 + 1.36 = 2.12 V

Capacity of Zn = (26.8 Ah) (2 electrons) / (65.4 g/mol) = 0.82 Ah/g or 1.22 g/Ah

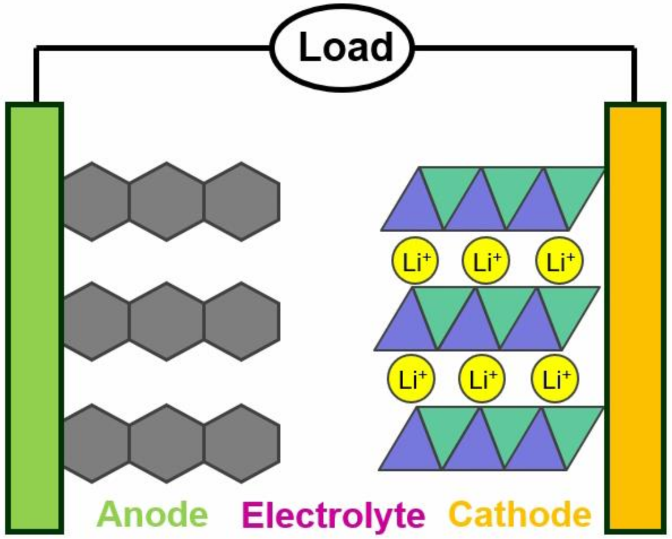
Capacity of Cl_2 = (26.8 Ah) (2 electrons) / (71 g/mol) = 0.76 Ah/g or 1.32 g/Ah

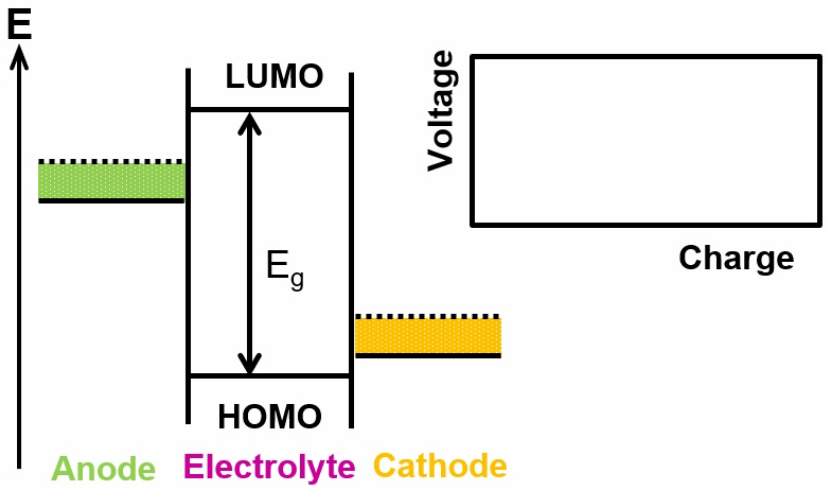
Capacity of $Zn\text{-}Cl_2$ system = (1.22 + 1.32) g/Ah = 2.54 g/Ah = 0.394 Ah/g

Capacity of $ZnCl_2$ = (26.8 Ah) (2 electrons) / 136.4 g/mol) = 0.394 Ah/g or 2.54 g/Ah

Energy density of $Zn\text{-}Cl_2$ system = (0.394 Ah/g) (2.12 V) = 0.835 Wh/g

LITHIUM-ION BATTERY: HOW DOES IT WORK?





Charge: $LiCo^{3+}O_2 + C_6 \rightarrow Li_{1-x}Co^{(3+x)+}O_2 + Li_xC_6$

Discharge: $Li_{1-x}CoO_2 + Li_xC_6 \rightarrow LiCoO_2 + C_6$

WHERE ARE WE WITH BATTERY TECHNOLOGIES?

Lithium-ion batteries

- insertion-reaction electrodes (layered oxide cathodes and graphite anode)
- conversion-reaction anodes (Si, Sn, Sb, P, etc.)

Sodium-ion batteries

- early stages; lower cost; lower energy density than lithium-ion
- insertion-reaction cathodes (layered, polyanion) and hard carbon anode (grid)

Multivalent-ion batteries (Mg-ion, Zn-ion, Ca-ion, Al-ion)

- lower voltages, diffusional limitations, lack of electrolytes

Metal-sulfur batteries (Li, Na, Mg, Ca, Al)

- poor e^-/ion transport; crossover; kinetic limitations with multivalent ions

Metal-air batteries

- nonaqueous systems are difficult; aqueous systems have the potential (grid)

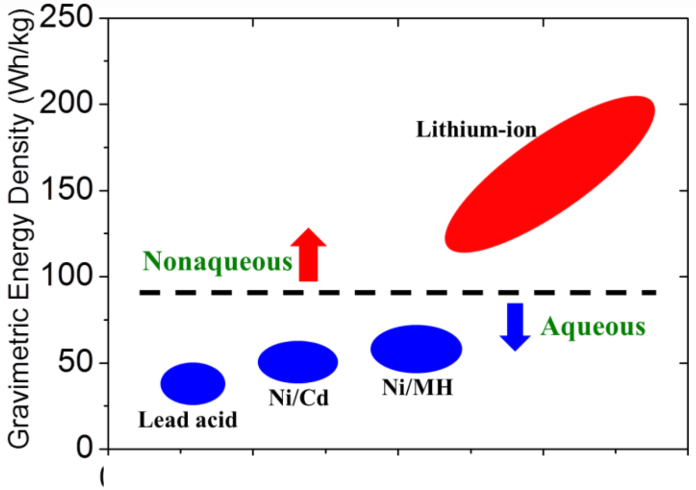
Redox flow batteries

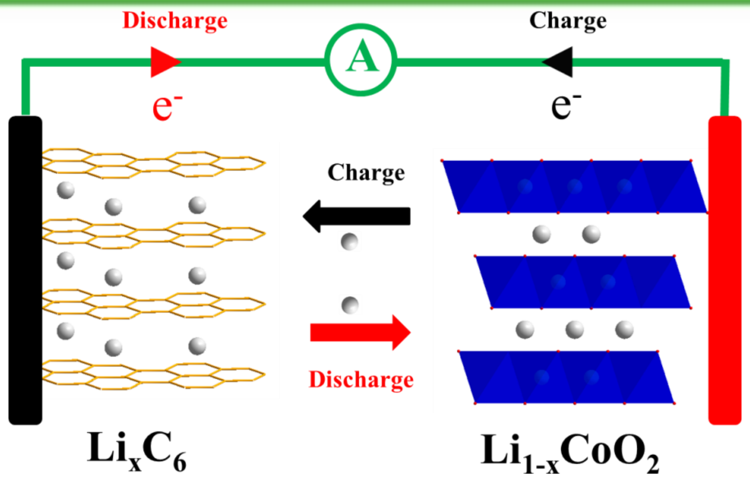
- appealing for grid storage; suffer from serious chemical crossover (efficiency) (grid)

All-solid-state batteries

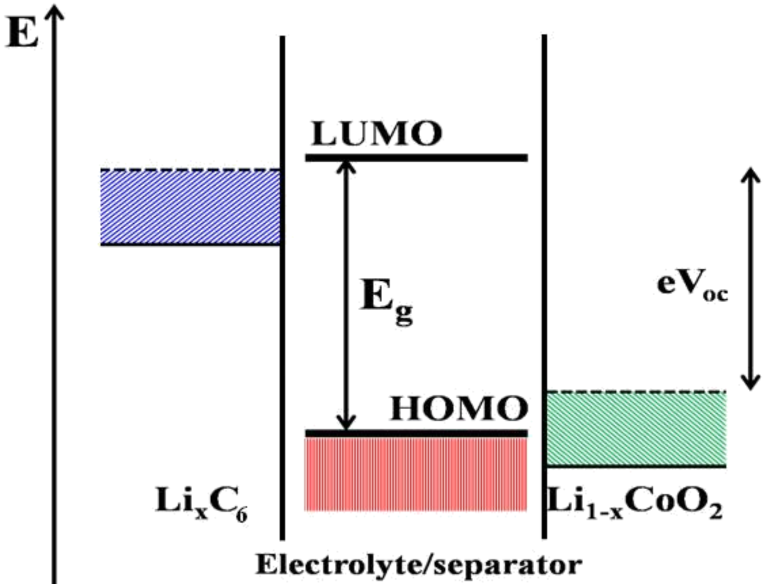
- better safety; suffer from interfacial charge transfer, manufacturability

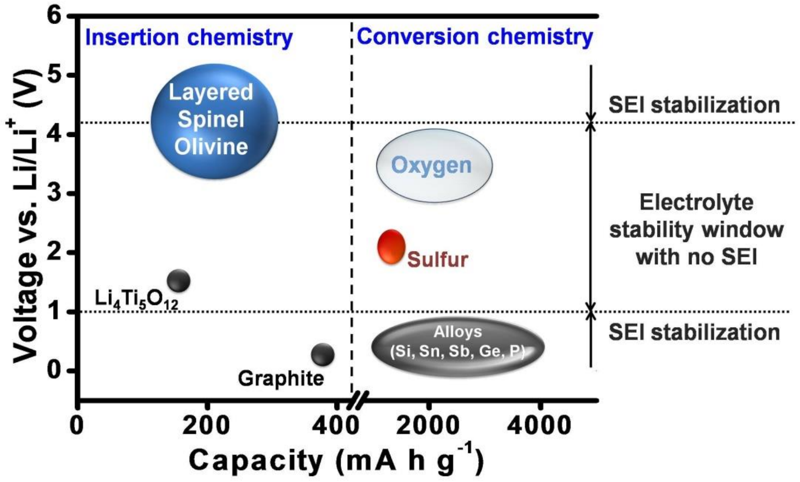
RECHARGEABLE BATTERIES

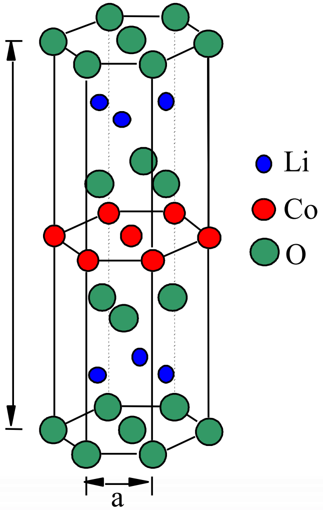


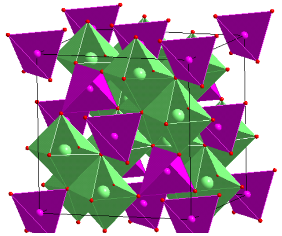


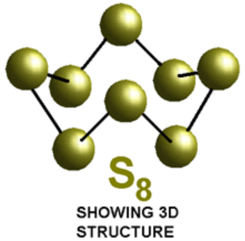
$V_{oc} = (\mu_{Li(c)} - \mu_{Li(a)})/nF$

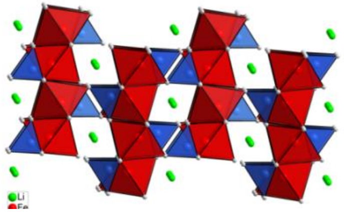








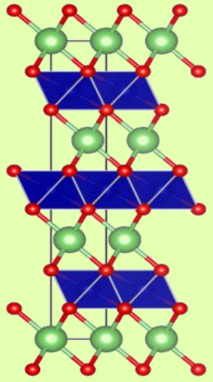




A. Manthiram, *MRS Bulletin* **41**, 624 (2016)
A. Manthiram, *ACS Central Science* **3**, 1063 (2017)

EVOLUTION OF CATHODE CHEMISTRY

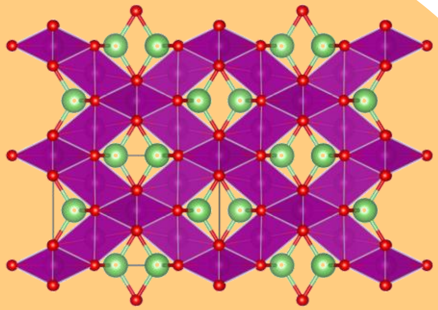
Layered
$LiCoO_2$



Mizushima, Jones, Wiseman, & Goodenough, 1980

(Japan)

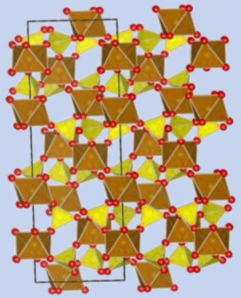
Spinel
$LiMn_2O_4$



Thackeray, David, Bruce, & Goodenough, 1983

(South Africa)

Polyanion
$Li_xFe_2(XO_4)_3$
(X = S, Mo, and W)

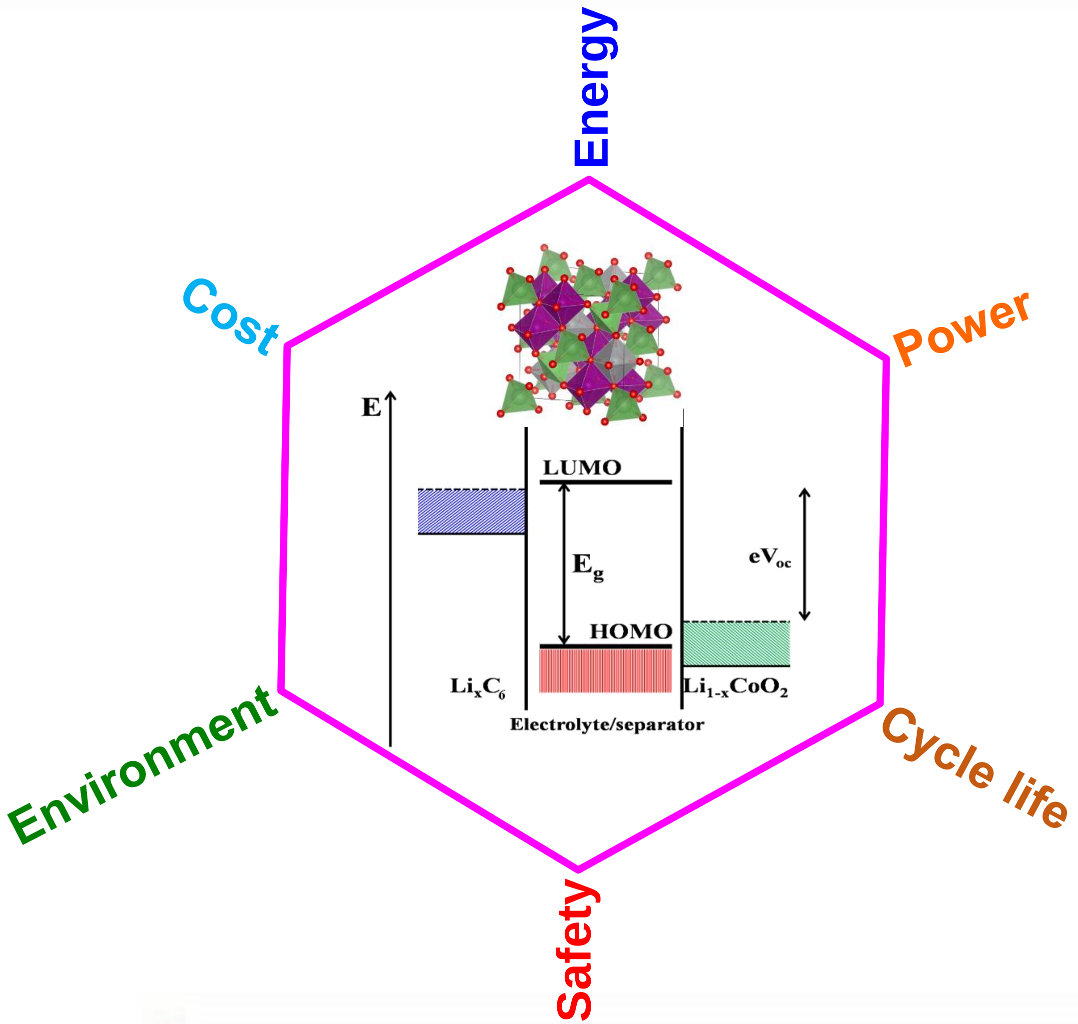


Manthiram & Goodenough, 1987 & 1989

(India)

University of Oxford and
University of Texas at Austin

CHOOSING A BATTERY TECHNOLOGY



- The priority in performance parameters and choosing a specific battery technology depend on application

  Portables: energy (user time), life

  E-mobility: energy (driving range), cost, safety, life

  Grid storage: cost, life, power, safety, energy

Additional parameters to be considered

- Operating temperature: -40 to 65 ^oC
- Fast charge with acceptable safety

LIMITS OF CATHODES

A battery consists of an anode, a cathode, and an electrolyte

Cost

Cathode is the most expensive (50% of the materials cost)

Li: 250,000 tons Co: 120,000 tons Ni: 2,000,000 tons

Energy

Capacity (< 200 mAh g^{-1}), voltage (< 4.3 V), voltage step

Life

Structural, chemical, dissolution, crossover, lithium trapping

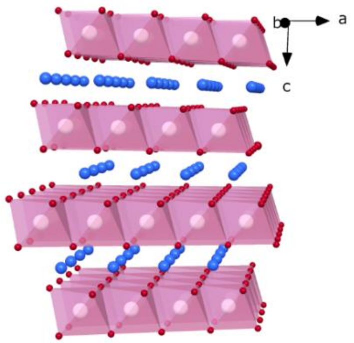
W. Li, E. Erickson, and A. Manthiram, *Nature Energy* **5**, 26 (2020)

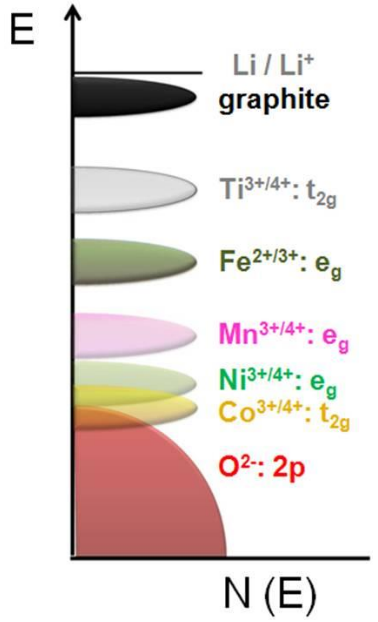
CURRENT RESEARCH IN MY GROUP

Roadmap

- Lithium-ion batteries: low-cobalt and cobalt-free oxide cathodes
  - near term (portable, EV, grid)
- Lithium-ion batteries: nanocomposite metal foil anodes
  - near to medium term (portable, EV, grid)
- Lithium-sulfur and sodium-sulfur batteries
  - Medium to long term (portable, EV, grid)
- Redox flow batteries with a solid electrolyte
  - Long term (grid)
- Sodium-ion, multivalent-ion, all-solid-state, lithium-metal batteries

WHY $LiMO_2$ CATHODES WITH Ni, Mn, AND Co?





Ion	Octahedral CFSE	Tetrahedral CFSE	Octahedral-site stabilization energy
Mn^{3+}: d^4	$t_2^3e^1$: -0.6 Δ	$e^2t_2^2$: -0.18 Δ	-0.42 Δ
Ni^{3+}: d^7	$t_2^6e^1$: -1.88 Δ	$e^4t_2^3$: -0.53 Δ	-1.35 Δ
Co^{3+}: d^6	$t_2^6e^0$: -2.4 Δ	$e^3t_2^3$: -0.27 Δ	-2.13 Δ

- $M^{3+/4+}$ ion characteristics/behavior are determined by
  - position of metal:3d band relative to that of O^{2-}:2p band
  - stability of metal ions in octahedral vs. tetrahedral sites
- **High-Ni oxides:**
  - high capacity, tap density, volumetric energy, and rate
  - cycle, thermal, air instabilities: involves bulk and surface of both electrodes (cathode and anode) and electrolyte

Chemical stability:
Mn > Ni > Co

Structural Stability:
Co > Ni > Mn

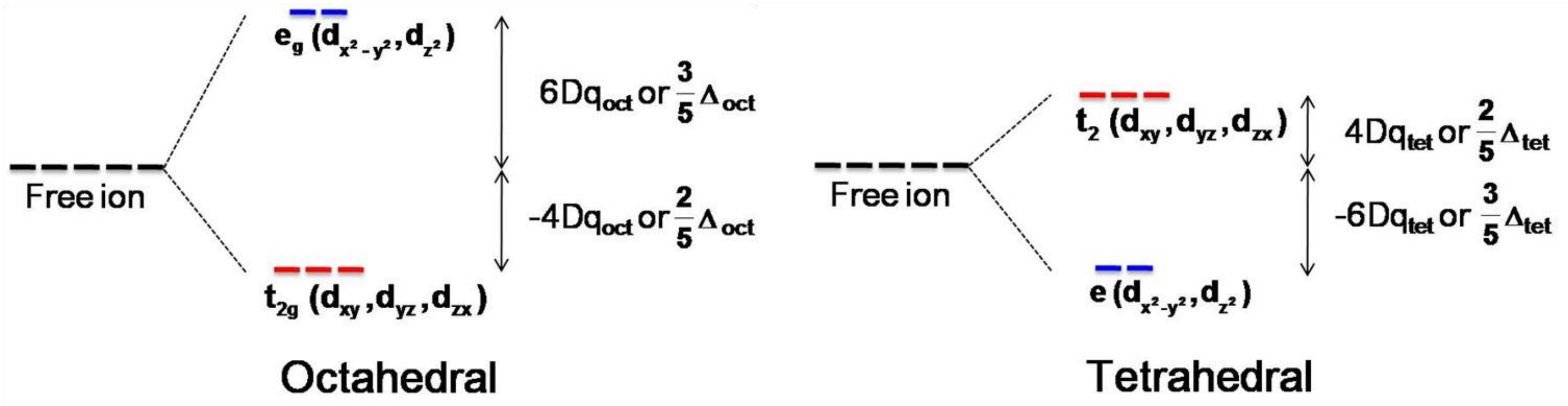
Conductivity:
Co > Ni > Mn

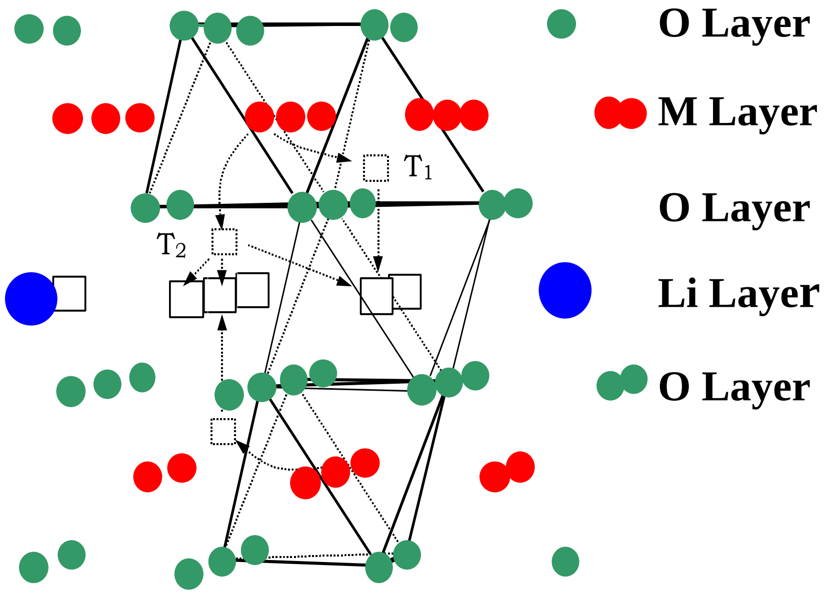
Abundance:
Mn > Ni > Co

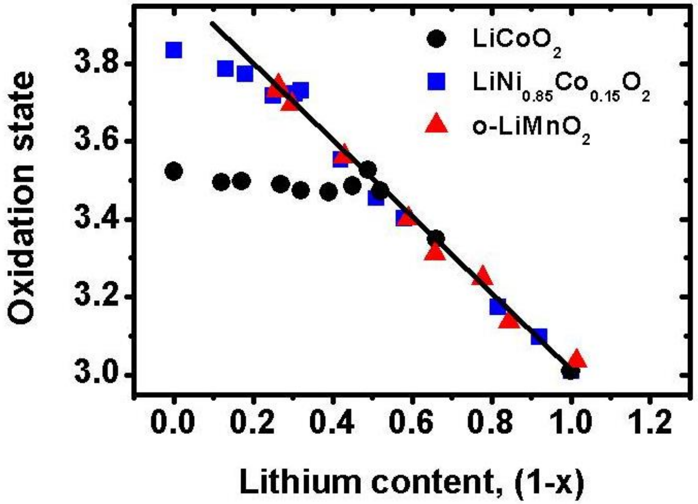
Affordability (low cost)
Mn > Ni > Co

Environmental:
Mn > Ni > Co

CHEMICAL AND STRUCTURAL INSTABILITY



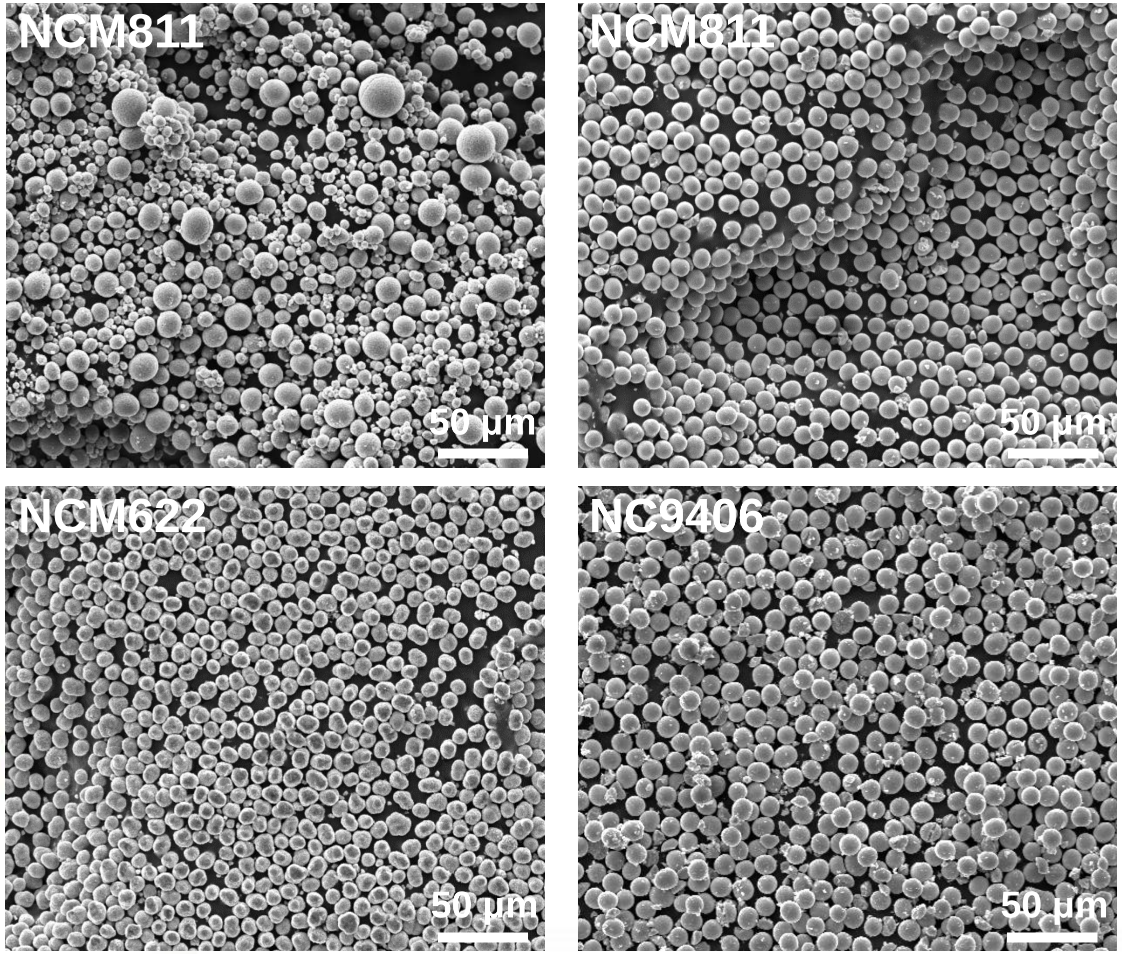


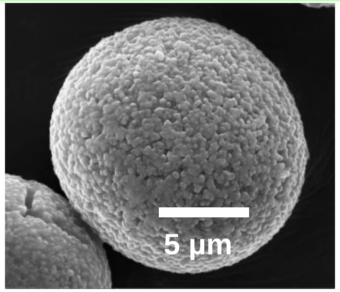


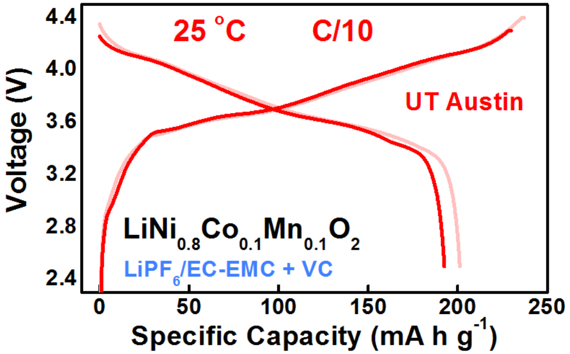
R. V. Chebiam, F. Prado, and A. Manthiram, *Electrochem. Commun.* **3**, 624 (2001)
S. Venkatraman and A. Manthiram, *Chem. Mater.* **14**, 3907 (2002)
S. Venkatraman, Y. Shin, and A. Manthiram, *Electrochem. Solid State Lett.* **6**, A9 (2003)

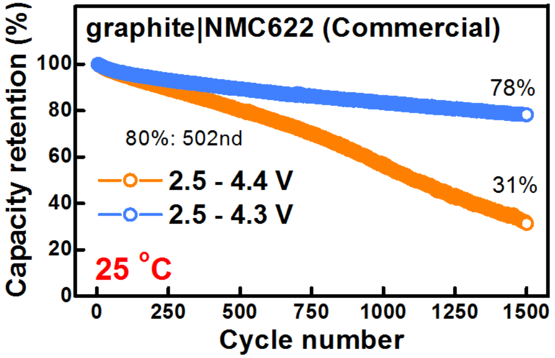
ROLE OF COMPOSITION AND MORPHOLOGY

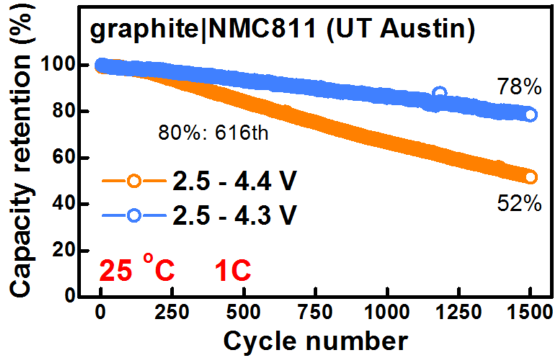
Commercial | **UT Austin**

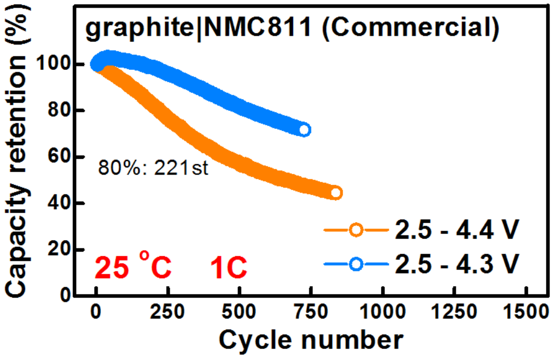




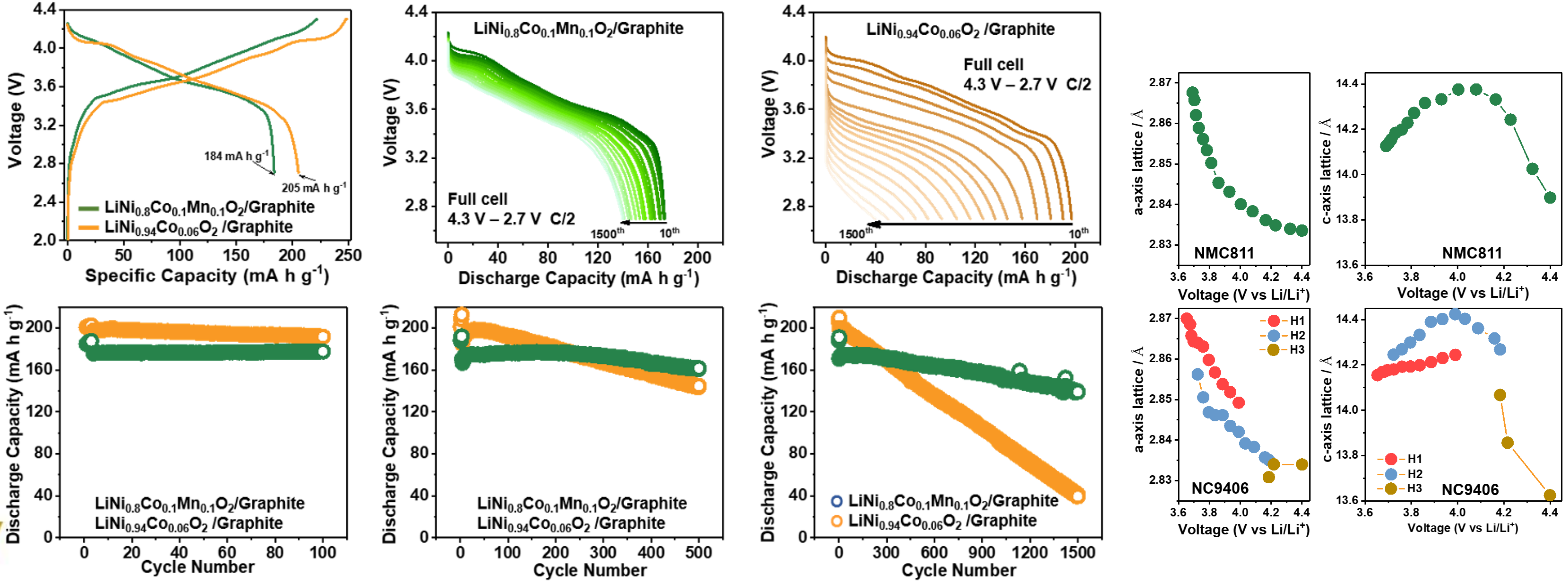








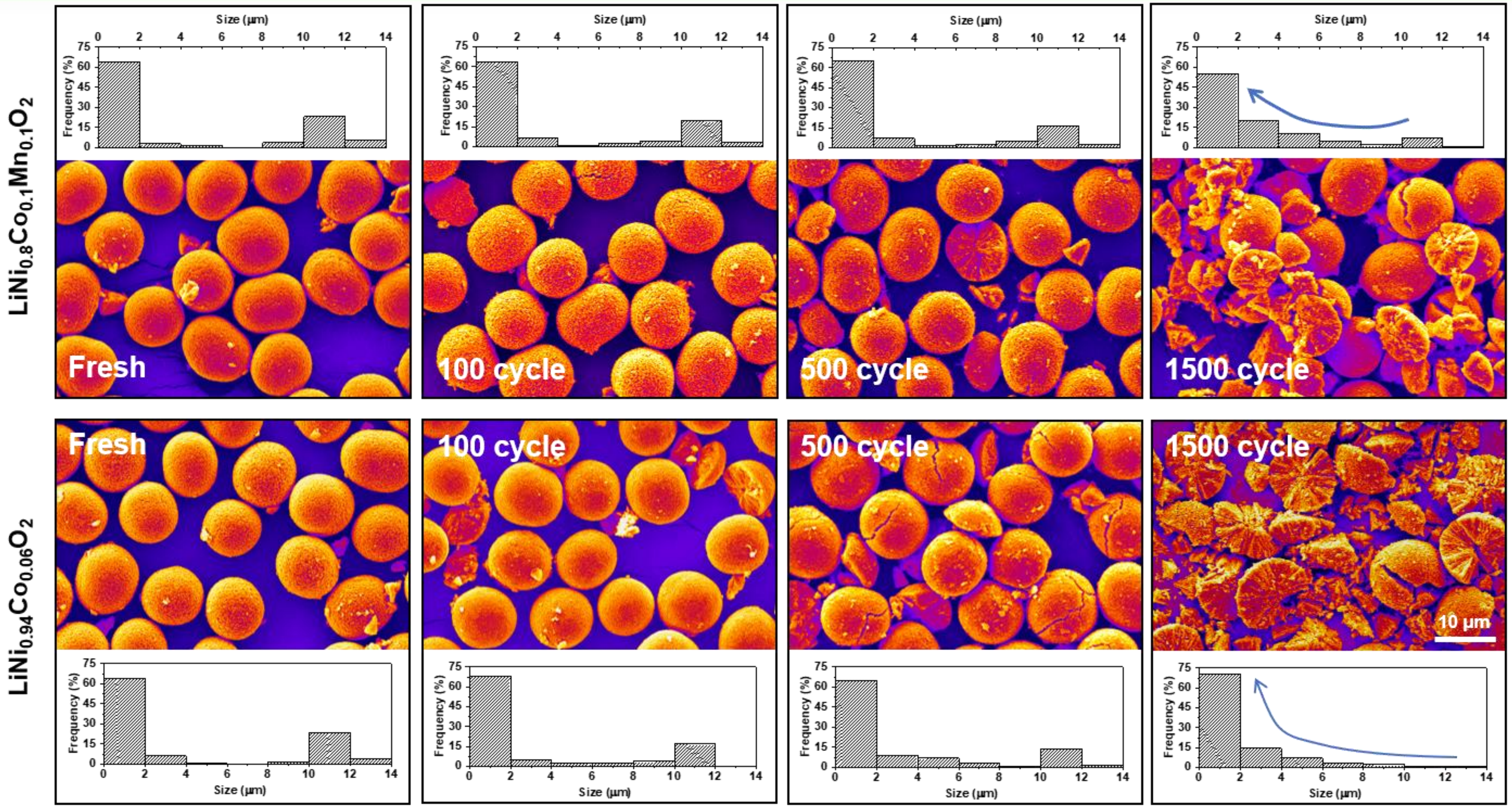
EFFECT OF NICKEL CONTENT

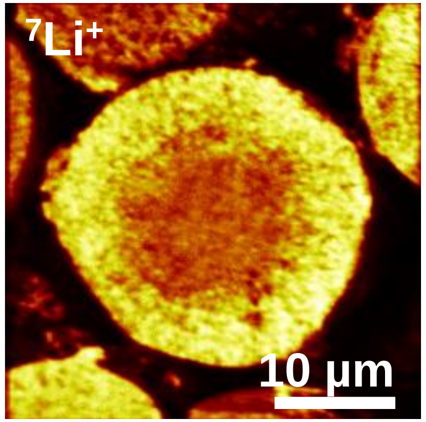


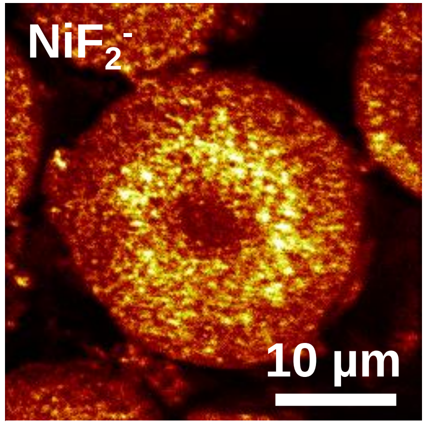
J. Li and A. Manthiram, *Advanced Energy Materials* **9**, 1902731 (2019)

- NC 9406 offers higher capacity, but suffers from severe capacity fade than NMC 811 (1,500 cycles)

EFFECT OF NICKEL CONTENT



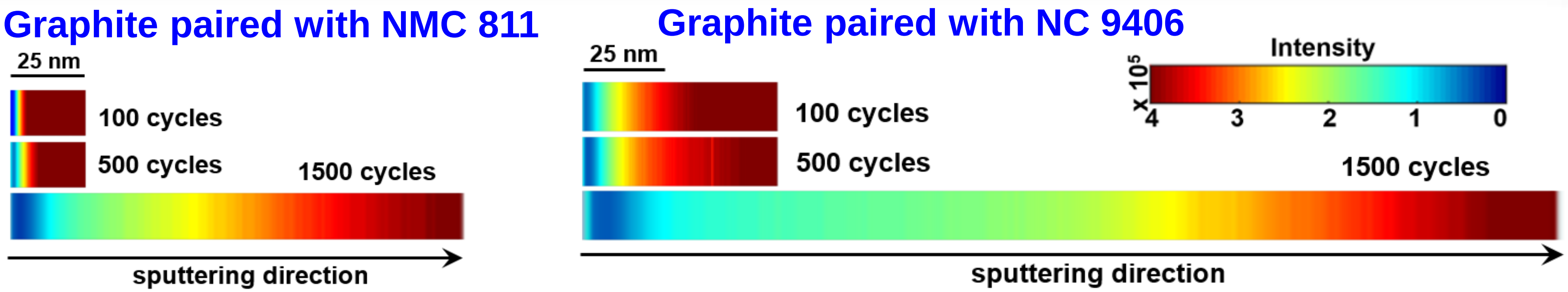




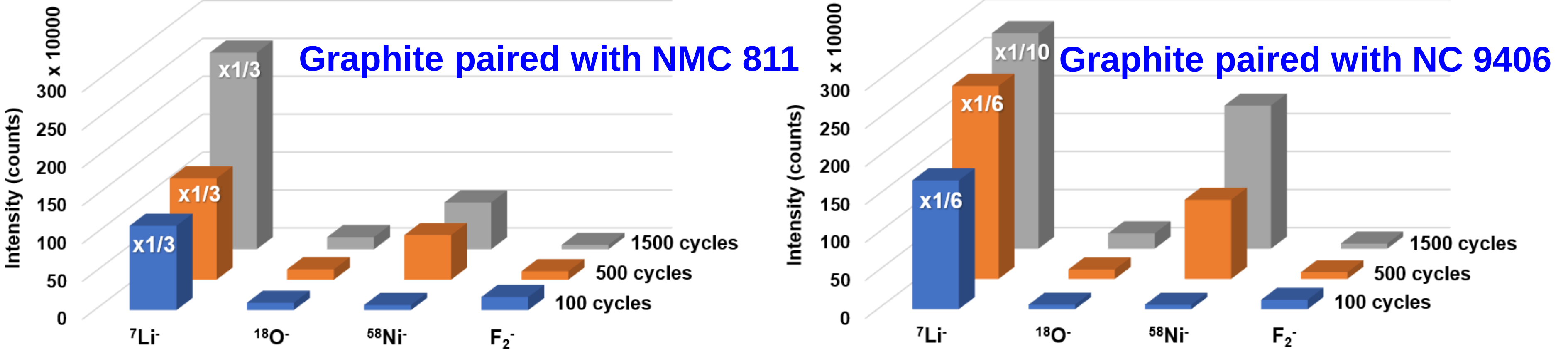
J. Li and A. Manthiram, *Advanced Energy Materials* **9**, 1902731 (2019)

- NC 9406 shows severe cracking & pulverization at large number of cycles (1,500 cycles)

EFFECT OF NICKEL CONTENT



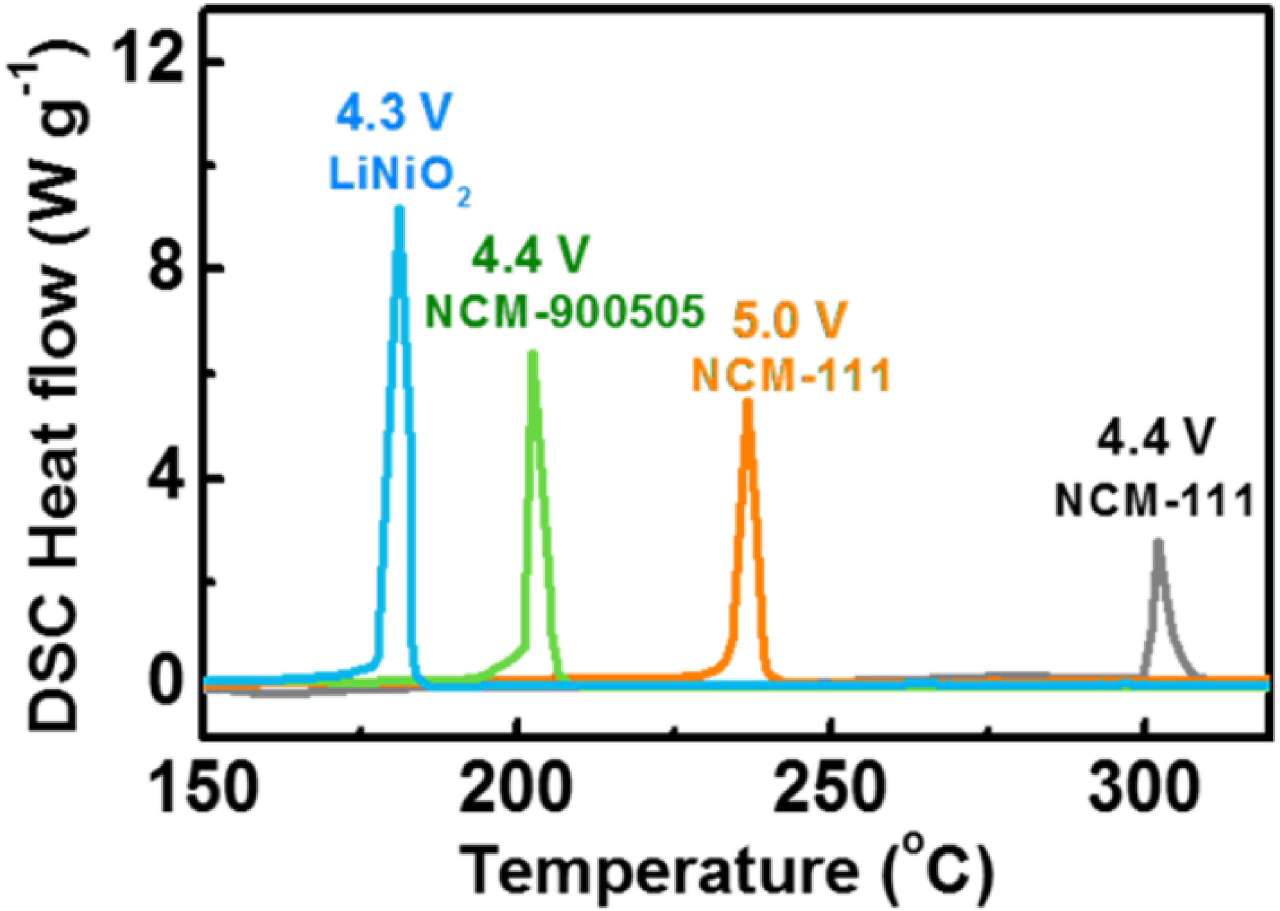
- AEI on graphite paired with NC 9406 is much thicker than that paired with NMC 811



J. Li and A. Manthiram, *Advanced Energy Materials* **9**, 1902731 (2019)

- NC 9406 exhibits more severe transition-metal dissolution and Li trapping than NMC 811

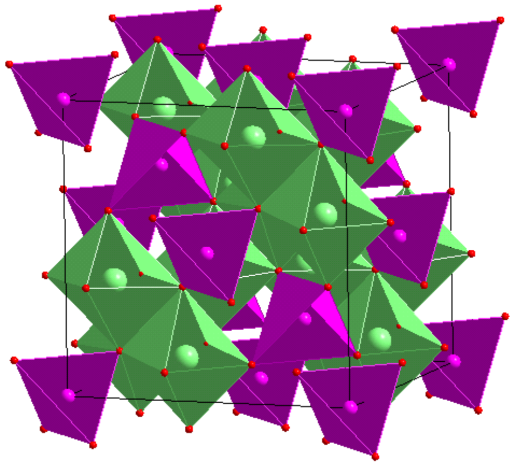
THERMAL STABILITY OF NMC CATHODES



M	MO	M_3O_4	M_2O_3	MO_2
Mn	√	√	√	√
Co	√	√	√	X
Ni	√	X	X	X

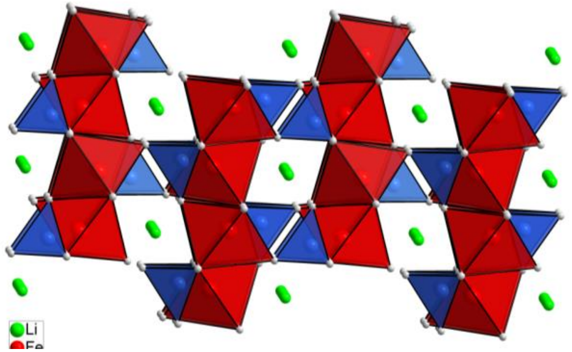
- Thermal stability and safety decrease with increasing nickel content or energy density

SPINEL $LiMn_2O_4$ AND OLIVINE $LiFePO_4$



Advantages:
- Mn is inexpensive and environmentally benign
- Offers high rate capability and safety due to good structural stability (3-d edge-shared MnO_6 octahedra) and chemical stability ($Mn^{3+/4+}$:e_g band lying well above O^{2-}:2p)

Problem:
- Severe capacity fade at elevated temperatures (55 ^{o}C) due to Mn dissolution in presence of H^+ (HF) generated from $LiPF_6$ with trace amount of water in the electrolyte



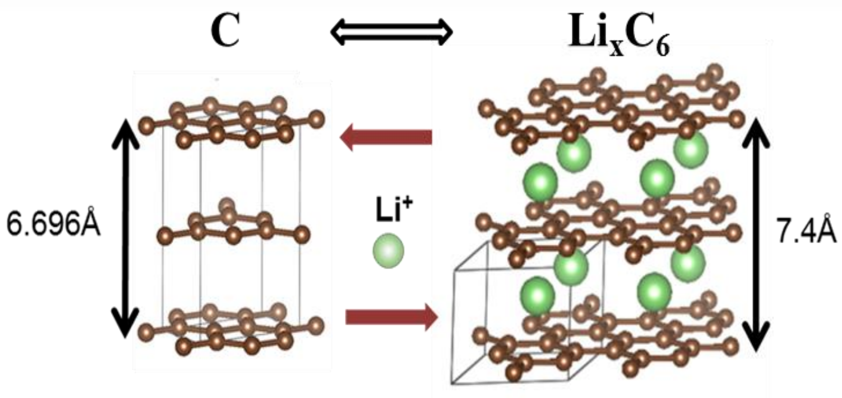
Advantages:
- Fe is inexpensive and environmentally benign
- Offers high-rate capability and safety due to good structural stability (covalent PO_4 groups) and chemical stability ($Fe^{2+/3+}$:e_g band lying well above the O^{2-}:2*p)*

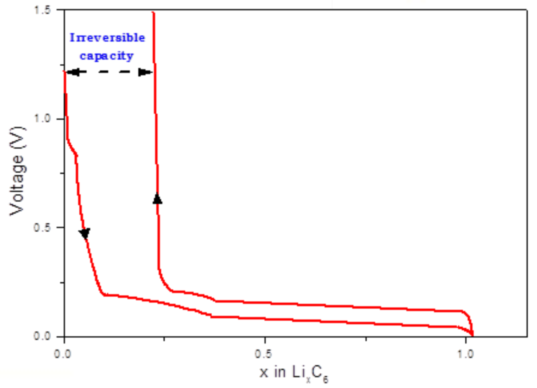
Problem:
- Poor electronic and lithium-ion conductor (one-dimensional Li^+ diffusion)
- Needs to be made as small particle and decorated with conductive carbon

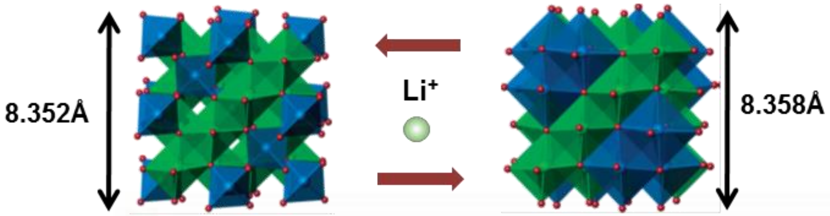
COMPARISON OF VARIOUS CATHODES

Electrode Material	Cell Voltage (V)	Capacity (Ah/kg)	Specific Energy (Wh/kg)	Advantages Disadvantages Applications
Layered $LiNi_{1-x-y}Mn_xCo_yO_2$ Cathode	~ 4	140	560	Expensive; toxic; safety concerns; 50 % capacity utilized; 2D structure; good structural stability; portable devices, electric vehicles, grid storage
Spinel $LiMn_2O_4$ Cathode	~ 4	120	480	Inexpensive; environmentally benign; better safety; 3D structure; high rate capability; severe capacity fade; eliminated from use
Olivine $LiFePO_4$ Cathode	~ 3.4	160	560	Inexpensive; environmentally benign; excellent safety; 1D structure; low Li^+ and electronic conductivity; low volumetric energy; high processing cost; grid storage
Carbon Anode	~ 0.1	370	—	Inexpensive; environmentally benign; maximizes cell voltage; SEI layer and lithium plating; safety concerns; all applications

GRAPHITE AND SPINEL LTO ANODES







Graphite

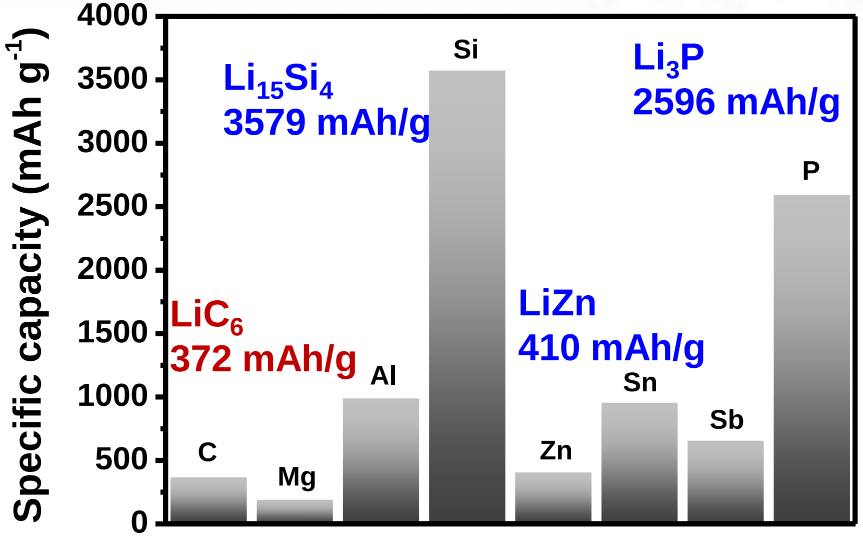
- Operating voltage of ~ 0.1 V maximizes cell voltage, but lies above the LUMO of electrolyte, resulting in solid-electrolyte interface (SEI) layer formation, Li plating under fast charge, and safety concerns
- SEI layer is electronically insulating and lowers graphite surface below the LUMO of electrolyte, allowing operation
- Volume change: < 10 %; low tap density (< 1 g cm^{-3})

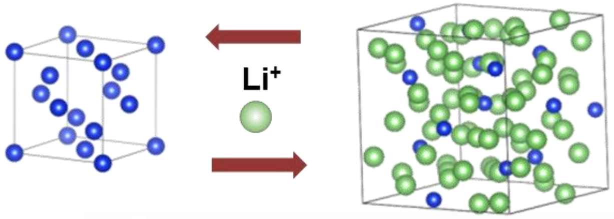
Spinel $Li[Ti_{1.67}Li_{0.33}]O_4$ = $Li_4Ti_5O_{12}$

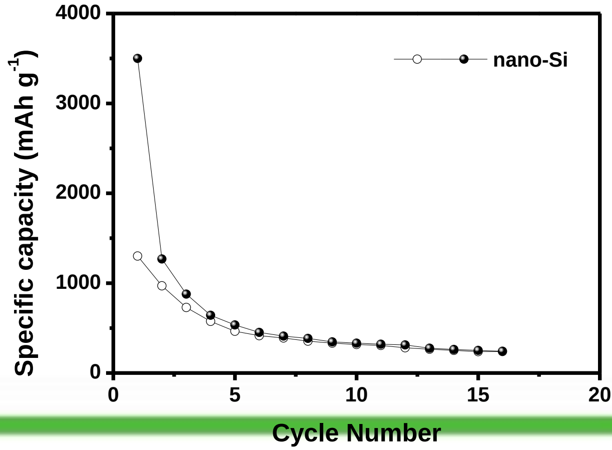
- Additional Li insertion into empty16c sites
  $Li_4Ti_5O_{12} + 3Li^+ + 3e^- \rightarrow Li_7Ti_5O_{12}$
- Operating voltage of ~1.5 V (flat) with ~ 170 mAh/g avoids SEI formation, but lowers energy density
- Volume change: < 0.2 % (zero-strain)

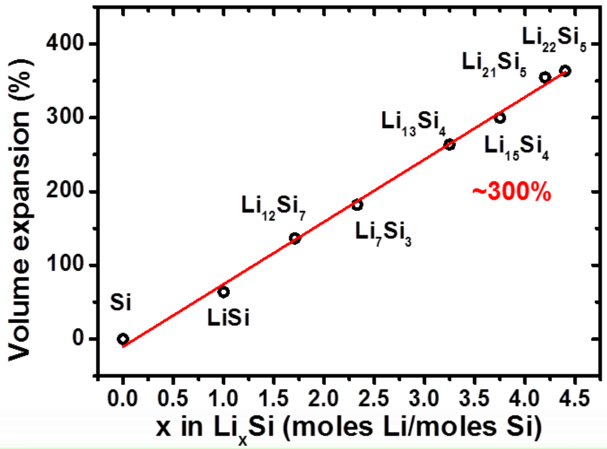
ALTERNATIVE ANODES: METAL ALLOYS

Element	Lithiated phase	Volume expansion (%)	Average operating voltage (V)	Specific capacity (mAh g^{-1})
Si	$Li_{15}Si_4$	280	0.3	3579
Sn	$Li_{22}Sn_5$	244	0.5	993
Sb	Li_3Sb	147	0.948	660
Bi	Li_3Bi	126	0.82	385
Zn	LiZn	98	0.3	410
P	Li_3P	300	0.85	2596



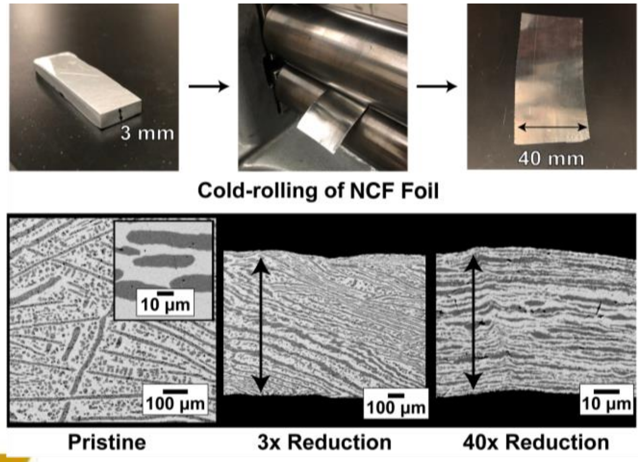


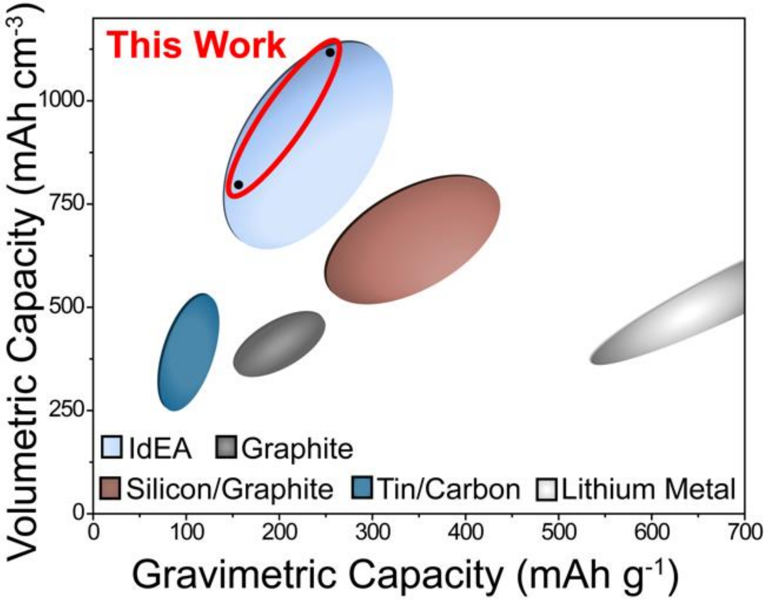


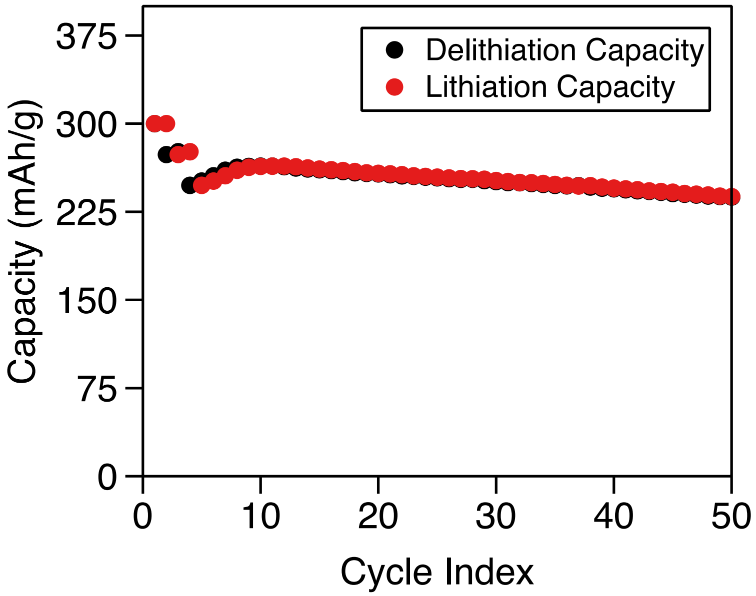


LOW-COST, FAST-CHARGE, SAFER ANODES

- Currently, graphite is the only anode for lithium-ion batteries; it restricts charge rate and cause safety hazards
- Attempts to replace graphite with others (e.g., silicon, tin) via nanostructuring have largely been unsuccessful!
- Interdigitated eutectic alloy (IdEA) anodes with the active material and current collector integrated offer an alternative with fast-charge, safety, and higher volumetric energy density at a lower cost , *e.g.*, Al-Sn, Zn-Sn

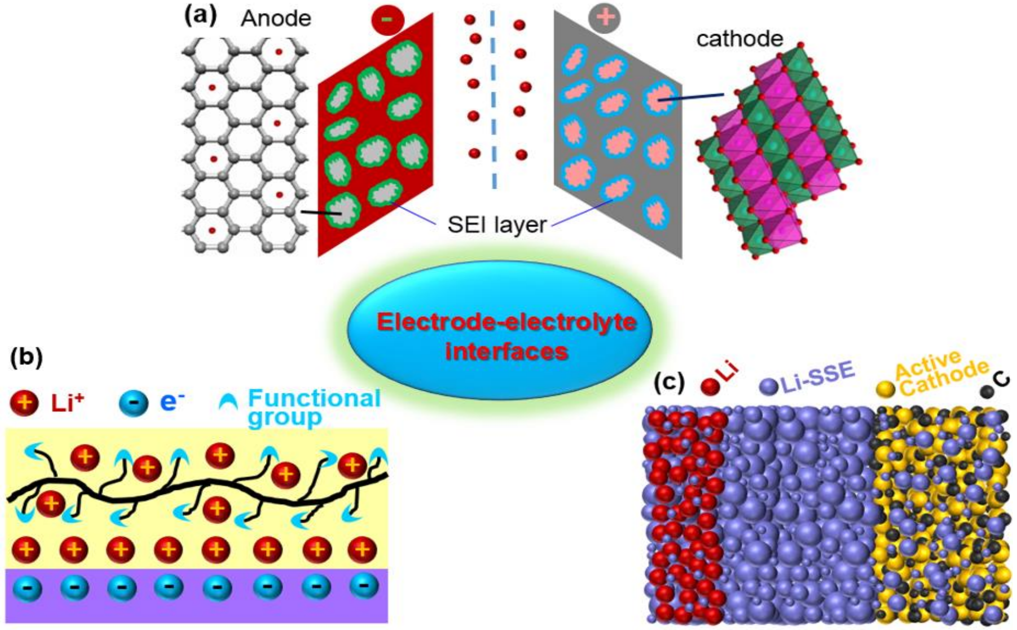


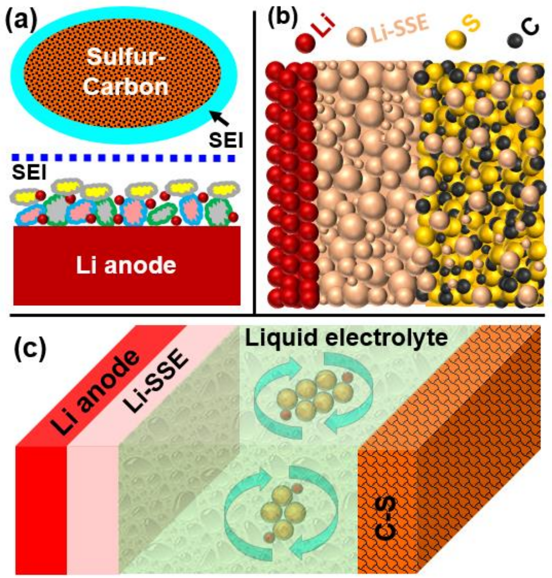


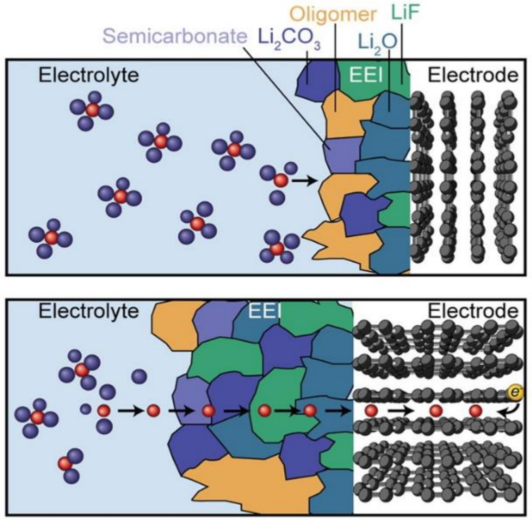


K.J. Kreder, B.T. Heligman and A. Manthiram, *ACS Energy Letters* **2**, 2422-2423, (2017)
B.T. Heligman, K.J. Kreder, and A. Manthiram, *Joule* **3**, 1051 (2019)

ELECTRODE-ELECTROLYTE INTERFACES



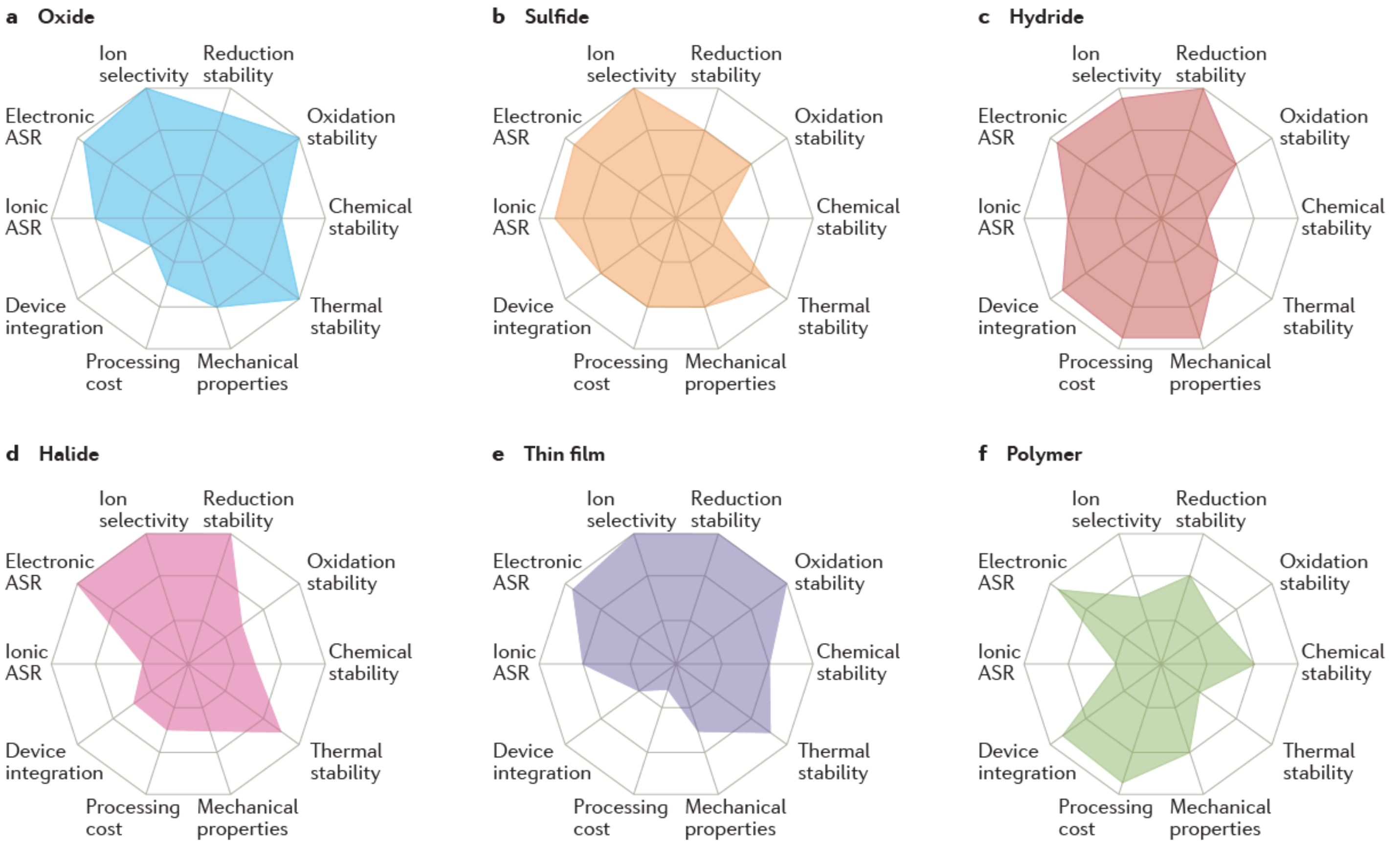


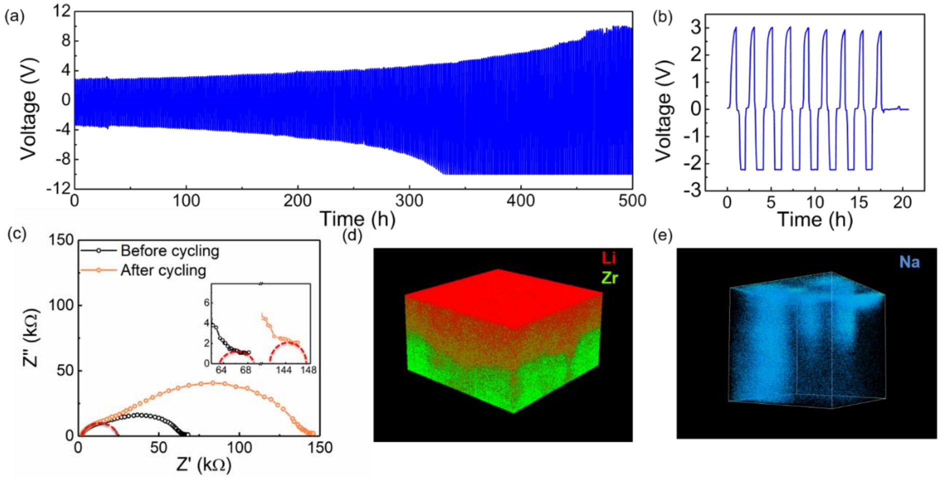


X. Yu and A. Manthiram, *Energy & Environmental Science* **11**, 527 (2018)
X. Yu and A. Manthiram, *Accounts of Chemical Research* **50**, 2563 (2017)
Manthiram, X. Yu, S. Wang, and A. Manthiram, *Nature Review Materials* **2**, 16103: 1-16 (2017)

- Electrode-electrolyte interface play a dominant role in impacting the overall long-term performance -
  - solid-electrolyte interphase (SEI) formation, dendrite growth and safety hazards, sluggish charge transfer across the interface and limited charge-discharge rate, *etc.*

ALL-SOLID-STATE BATTERIES

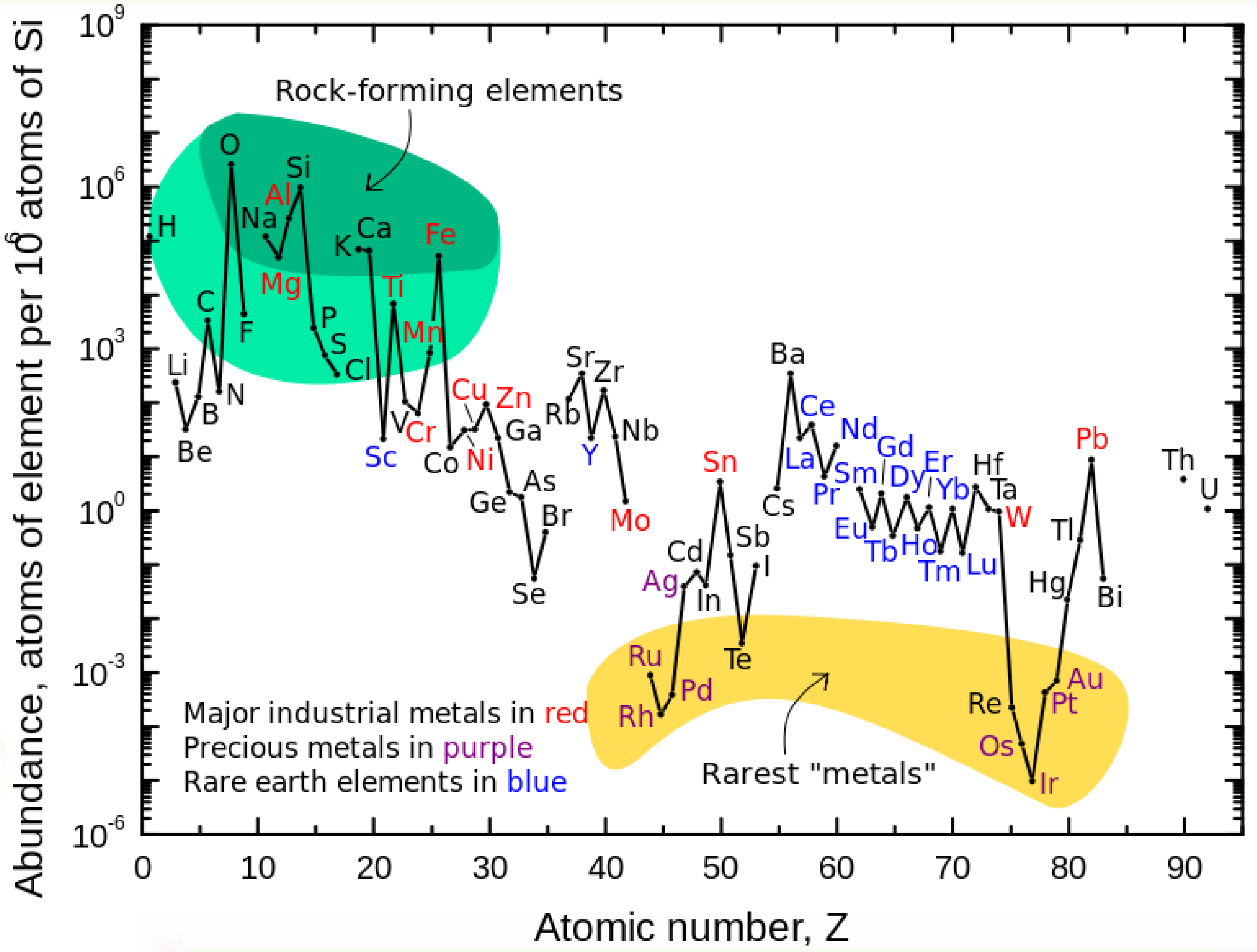




- Current technology is based on solid electrodes and liquid electrolyte
- All-solid-state batteries can provide better safety and higher energy density
- Faced with numerous materials challenges and performance issues

S. Wang, H. Xu, W. Li, A. Dolocan, and A. Manthiram, *Journal of American Chemical Society* **140**, 250 (2018)
A. Manthiram, X. Yu, and S. Wang, *Nature Review Materials* **2**, 16103 (2017)

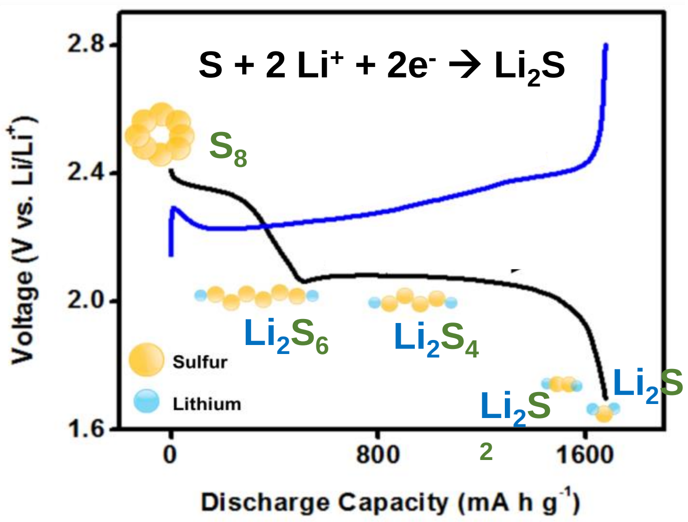
SUSTAINABLE, LOW-COST TECHNOLOGIES

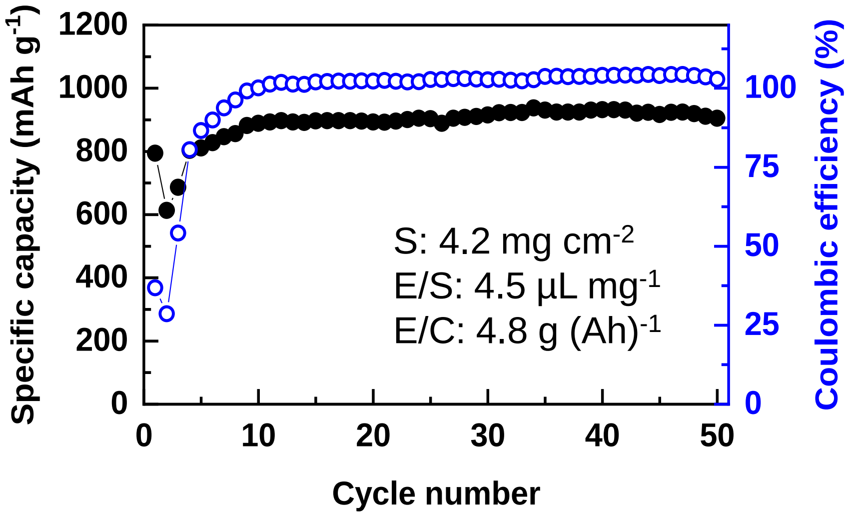


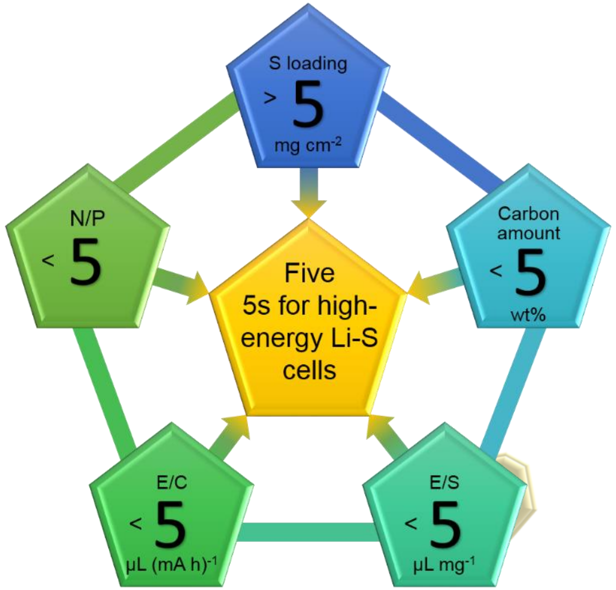
- Cost is the critical parameter for grid storage to be competitive
- Large-scale deployment of E-mobility and grid storage with batteries will drive the raw materials cost drastically up
- Certain raw materials could be localized in certain parts of the earth, which could lead to geopolitical issues
- In order to have a sustainable technology, it is imperative to develop technologies with earth abundant materials

METAL-SULFUR BATTERIES

- Poor electronic conductivity: low utilization, low sulfur content
- Polysulfide migration: poor cyclability, self discharge, low efficiency
- Large volume change: low electrochemical utilization, capacity fade
- Lithium-metal anode: degradation, short cycle life, safety concerns

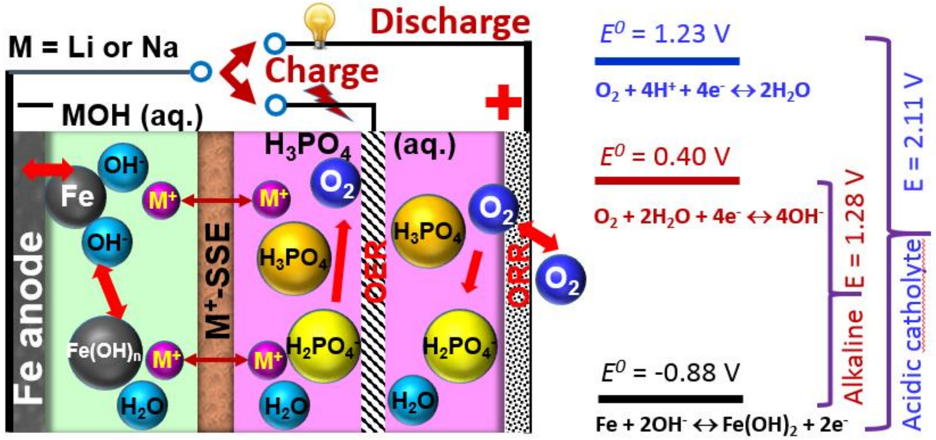


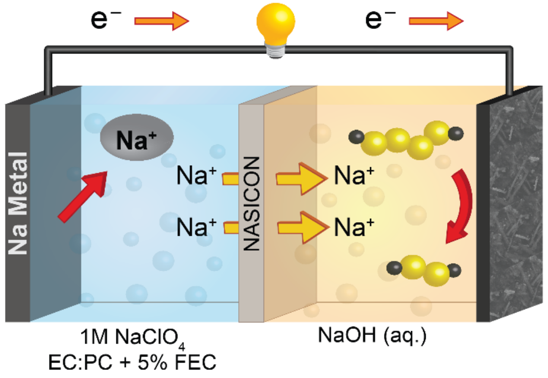


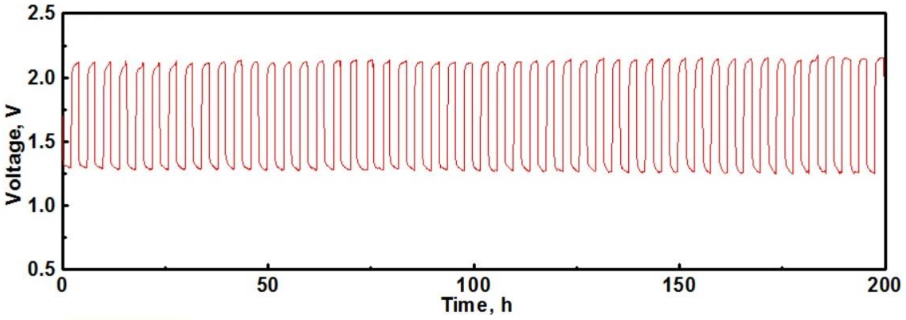


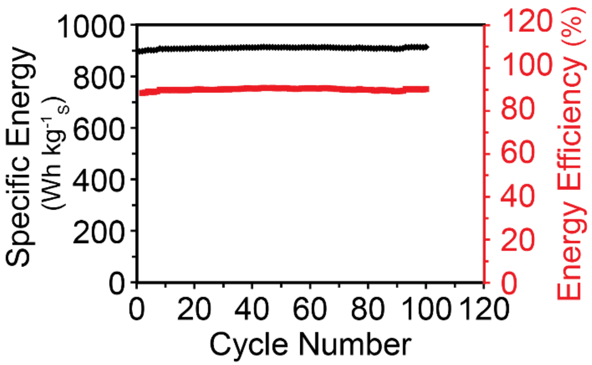
S.-H. Chung and A. Manthiram, *Advanced Materials* **31**, 1901125 (2019)
A. Bhargav, J. He, A. Gupta, and A. Manthiram, *Joule* (2020)

FLOW BATTERIES WITH A SOLID ELECTROLYTE









- Flow batteries offer great promise for grid storage, separating the power and energy requirements
- Conventional flow batteries suffer from chemical crossover, limiting the efficiency
- Crossover can be eliminated with the use of a solid electrolyte, offering the advantage of having entirely different chemicals and media on the two electrodes
  - aqueous vs. nonaqueous
  - acidic vs. basic

L. Li and A. Manthiram, *Advanced Energy Materials* **5**, 1502054 (2015)
X. Yu and A. Manthiram, Nature Review Materials **2**, 16103: 1 – 16 (2017)

SUMMARY:
WHERE ARE WE HEADED?

- ***Insertion-reaction electrodes:*** beginning to transform the transportation sector (EV), and has the potential to penetrate the utility industry (grid storage, distributed generation, …..)

- ***Conversion-reaction electrodes:*** huge volume change, continuous electrode-electrolyte interfacial reaction (severe SEI), chemical crossover, capacity fade, …..

- ***Metal anodes:*** dendrites, severe SEI, poor cycle life, efficiency, safety, …..

- ***Multivalent ion:*** lower voltages, diffusional limitations, lack of electrolytes …..

- ***Solid electrolytes:*** could mitigate crossover, dendrite, and safety problems, but suffers from charge-transfer resistance, mechanical integrity, manufacturability, ...

- ***New battery chemistries with solid electrolytes and liquid/gaseous electrodes:*** potential to be a low-cost, safe, sustainable flow option for grid storage

ROAD MAP FOR ENERGY STORAGE

Near-term and long-term perspectives

- Current Li-ion: ~ 250 W h kg^{-1}
- Future Li-ion: high-Ni cathode with graphite anode (~ 300 W h kg^{-1})
- Li: high-Ni cathode with lithium-metal anode (~ 400 W h kg^{-1})
- Sulfur cathode with lithium-metal anode (~ 500 W h kg^{-1})
- Na-ion and Na: layered oxide, sulfur, carbon, Na metal, … (250 – 450 W h kg^{-1})
- Flow batteries with solution electrodes for grid
- Li, Na, Zn, Fe: mediator-ion solid electrolyte and solution/solid electrodes for grid

WHAT IS INVOLVED?
WHERE DOES INDIA STAND?

Infrastructure for electric vehicles
Charging stations, battery replacement

↑

Cell integration and packaging
Cost, reliability, safety, maintenance

↑

Cell manufacturing
Cost, performance, reliability, charging time

↑

Materials development
Cost, performance, durability, charging time

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India SMART UTILITY Week 2019

ACKNOWLEDGMENT

ISGF India Smart Grid Forum

Ph.D. graduated: 60; M.S. graduated: 26; postdocs completed: 80; undergraduates: 45
Current: Ph.D. students: 20; postdocs: 8; undergraduates: 2; visiting students: 2

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