INL/CON-21-62018-Revision-0

Lithium Metal as an Anode in Electrochemical Energy Storage

April 2021

Changing the World's Energy Future

Corey Michael Efaw, Luis A Diaz Aldana, Tedd E Lister, Bin Li, Eric J Dufek, Michael F. Hurley

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Lithium Metal as an Anode in Electrochemical Energy Storage

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Energy Storage & Transfer

Reversible energy storage at varied scales

- Energy delivery & new grid technology
- (Hybrid) Electric vehicles (HEV, EV)
- Sustainability – long lifetime with low environmental impa

Table I List of Estimated Global Lithium End-Use Applications[a]

Applications	Market share, %	Products
Batteries – portable electronics; hybrid cars; electric vehicles; grid storage applications	35	Li_2CO_3; LiOH; Li metal; lithium hexafluorophosphate ($LiPF_6$) electrolyte salts; lithium chloride (LiCl); Li alloys; lithium cobalt oxide ($LiCoO_2$); and other Li electrode compositions
Ceramics and glass	32	Spodumene – $LiAl(SiO_3)_2$; Li_2CO_3
Lubricants and greases	9	LiOH
Air treatment; continuous casting mould flux powders; polymer production; primary Al production	5; 5; 4; 1	Li organometallics; Li metal; LiCl; lithium aluminium hydride ($LiAlH_4$); butyl lithium; lithium citrate
Other uses such as in medicine as antidepressants, bipolar disorder	9	Li compounds

Li, L. et al, *Johnson Matthey Tehnol. Rev.* **62**, 161 (2018).

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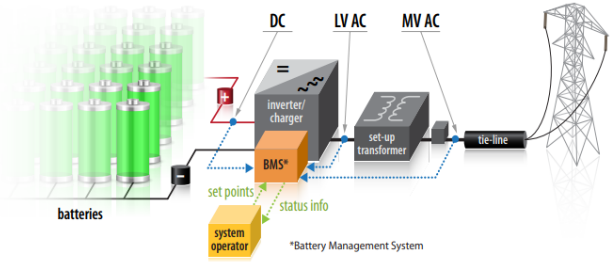
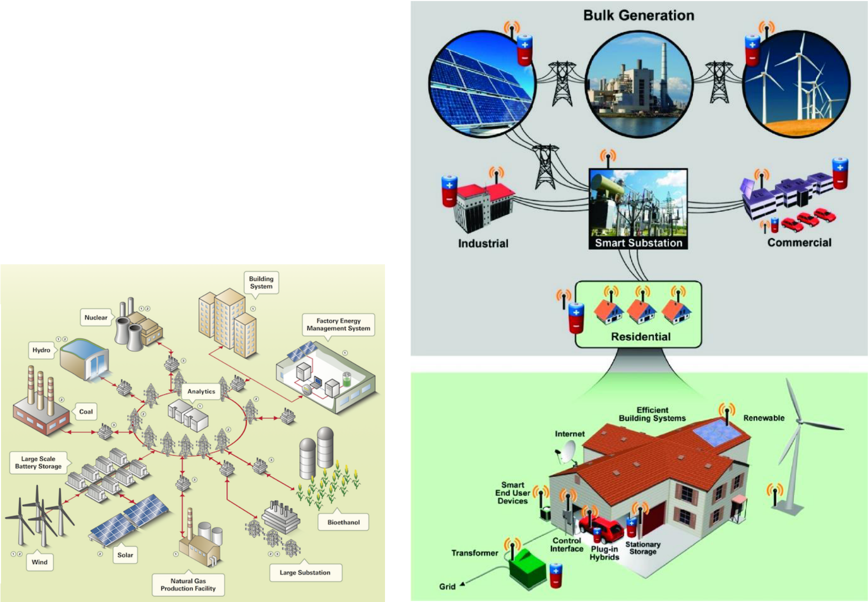
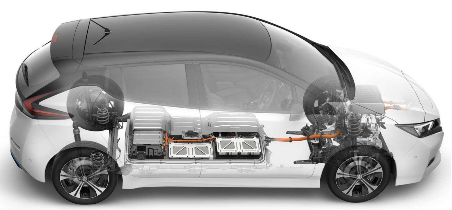


Denholm, P. "Greening the Grid: Utility-Scale Battery Storage." Webinar. Clean Energy Solutions Center. February 28, 2019.

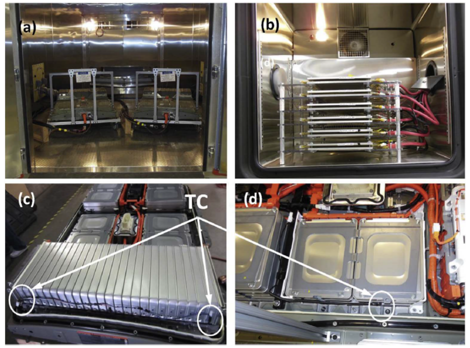


Ulissi, U., Lithium-ion and beyond: safer alternatives, Thesis (2018).

Rivian.com



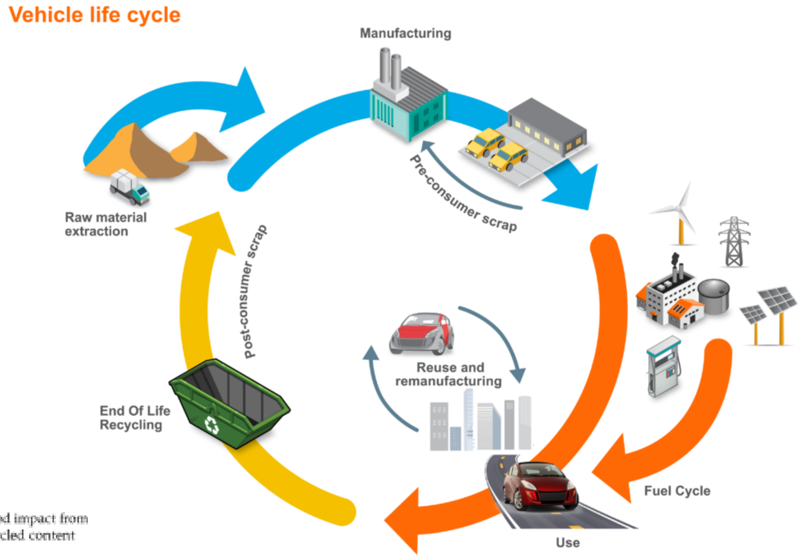
Insideevs.com



Tanim, T. et al., *J. Power Sources* **381**, 56 (2018).

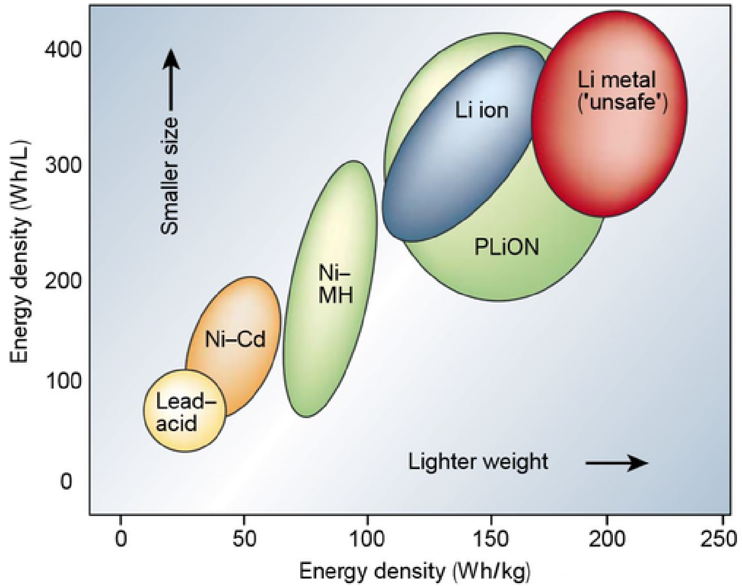
Sustainability Lifecycle

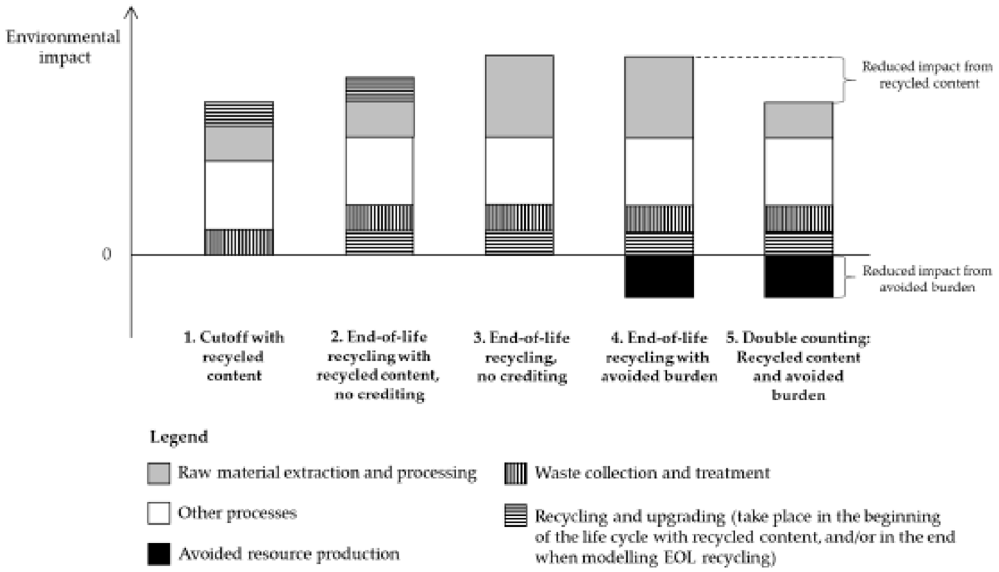
- Life Cycle Assessment (LCA)
  - Environmental impact is seen throughout a material's lifecycle
- Focus on next-generation battery materials
  - Extraction Methodologies
  - Usage (lithium metal example)
  - Reuse & Recycling



ahssinsights.org/

D. Deng, *Energy Science and Engineering* **3**(5), 385 (2015).





Nordelöf, A. et al., *Batteries* **5**, 51 (2019).

Extraction Methodologies

Geothermal waters

Underground brine reservoir

Hard rock mining

https://www.bbc.com/future/article/20201124-how-geothermal-lithium-could-revolutionise-green-energy

Extraction Methodologies

CALIFORNIA
ENERGY COMMISSION

Energy Research and Development Division

FINAL PROJECT REPORT

Selective Recovery of Lithium from Geothermal Brines

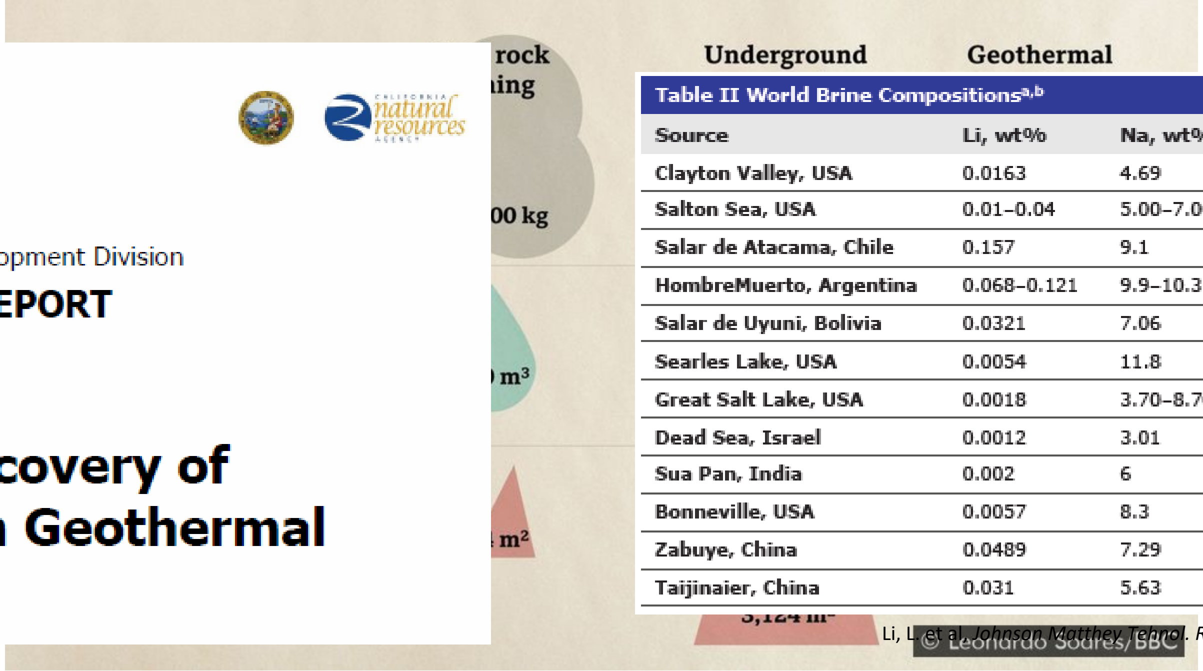


Table II World Brine Compositions[a,b]					
Source	Li, wt%	Na, wt%	Mg, wt%	K, wt%	Ca, wt%
Clayton Valley, USA	0.0163	4.69	0.019	0.4	0.045
Salton Sea, USA	0.01–0.04	5.00–7.00	0.07–0.57	1.30–2.40	2.26–3.9
Salar de Atacama, Chile	0.157	9.1	0.965	2.36	0.045
HombreMuerto, Argentina	0.068–0.121	9.9–10.3	0.018–0.14	0.24–0.97	0.019–0.09
Salar de Uyuni, Bolivia	0.0321	7.06	0.65	1.17	0.0306
Searles Lake, USA	0.0054	11.8	–	2.53	0.0016
Great Salt Lake, USA	0.0018	3.70–8.70	0.5–0.97	0.26–0.72	0.026–0.036
Dead Sea, Israel	0.0012	3.01	3.09	0.56	1.29
Sua Pan, India	0.002	6	–	0.2	–
Bonneville, USA	0.0057	8.3	0.4	0.5	0.0057
Zabuye, China	0.0489	7.29	0.0026	1.66	0.0106
Taijinaier, China	0.031	5.63	2.02	0.44	0.02

Li, L. et al. *Johnson Matthey Technol. Rev.* **62**, 161 (2018).

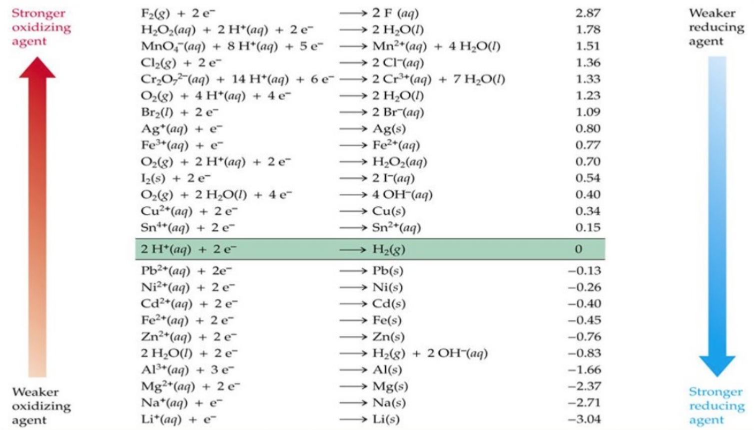
https://www.bbc.com/future/article/20201124-how-geothermal-lithium-could-revolutionise-green-energy

Takeaway: aqueous lithium mining is advantageous over mineral extraction methods

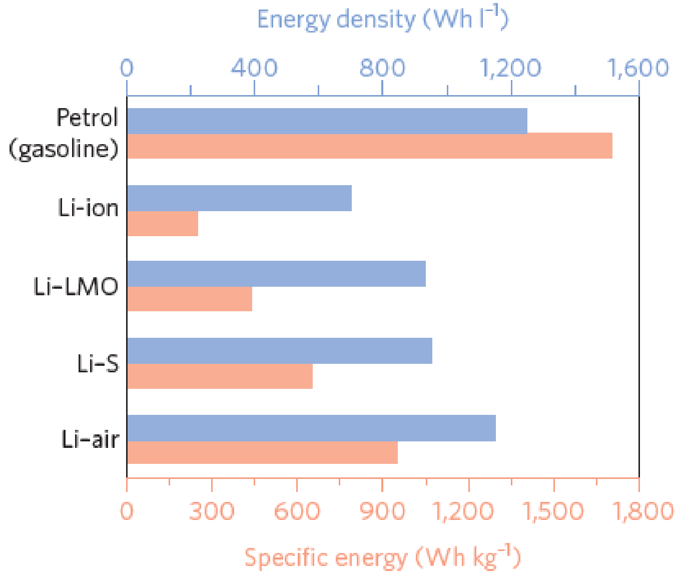
Usage – Lithium Metal Anode

Advantages:

- High theoretical capacity ($C_t \approx$ 3,860 mAh/g)
- Negative reduction potential (-3.04 V vs. SHE)
- Lightweight metal (6.94 g/mol)



$F_2(g) + 2e^-$	$\longrightarrow 2F(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

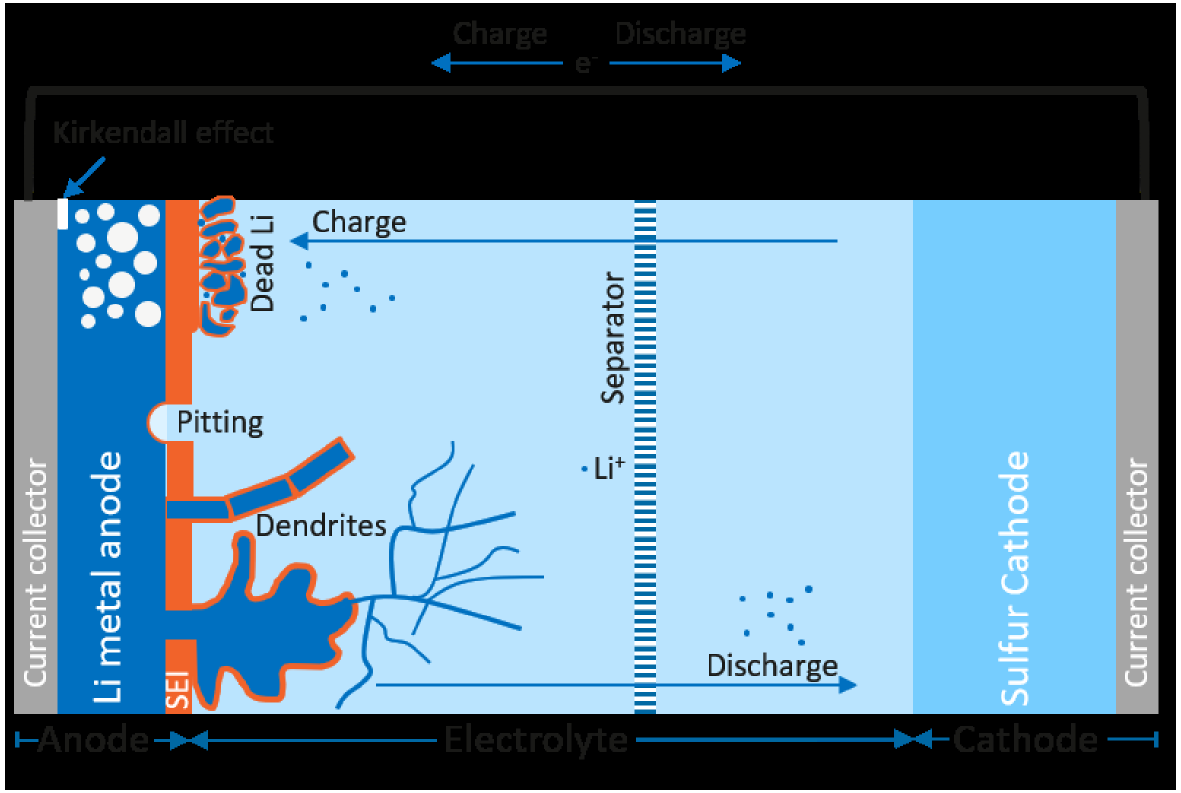


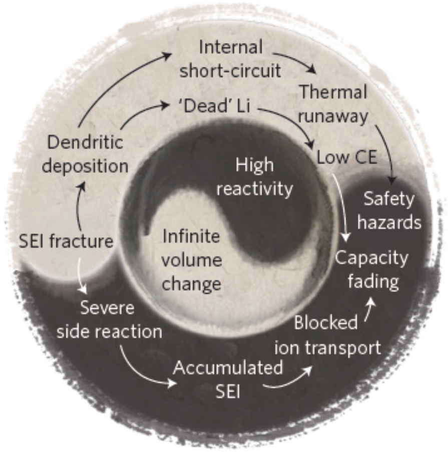
Lin, D. et al, *NNano* **12**, 194 (2017).
Park, J., “Principles and Applications of Lithium Secondary Batteries”
Lu, Y. and Yang, Y., *J. Nanomaterials*, 2016.

Manufacturing & Usage – Lithium Metal Anode

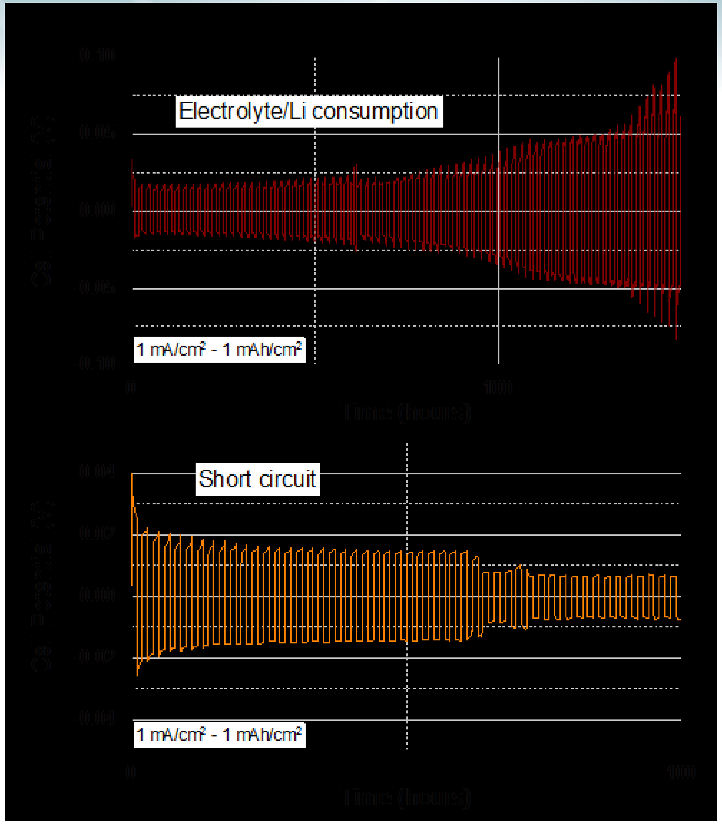
Disadvantages:

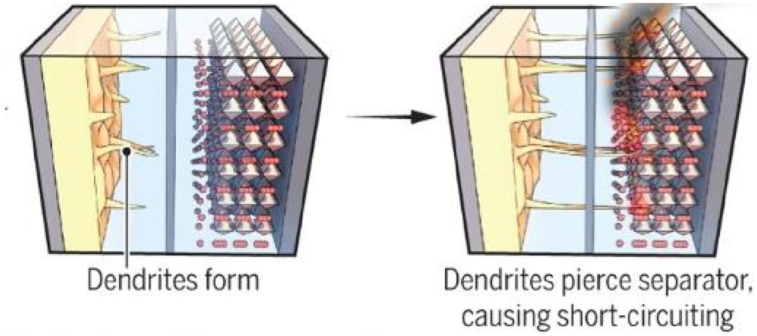
- Low Coulombic efficiency (CE)
- Poor cycle life – side reactions
- Safety – short circuits





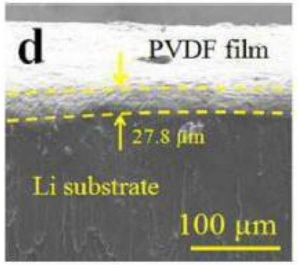
Lin, D. et al, *NNano* **12**, 194 (2017).

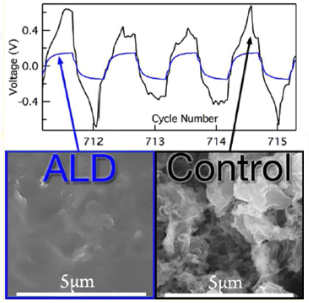


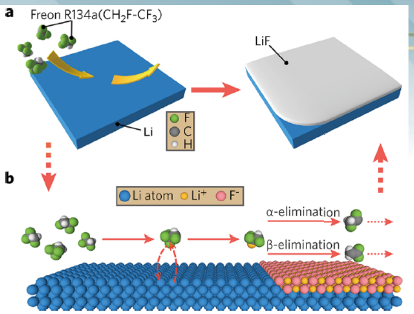


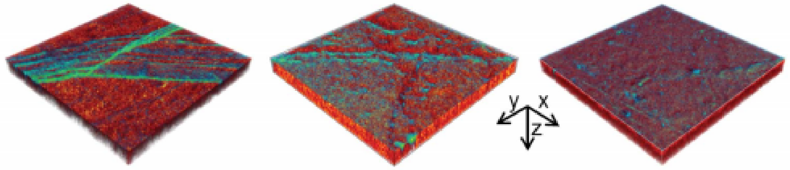
Mukhopadhyay et al, *Science* **359**, (2018).

Methods of Stabilizing Li-metal



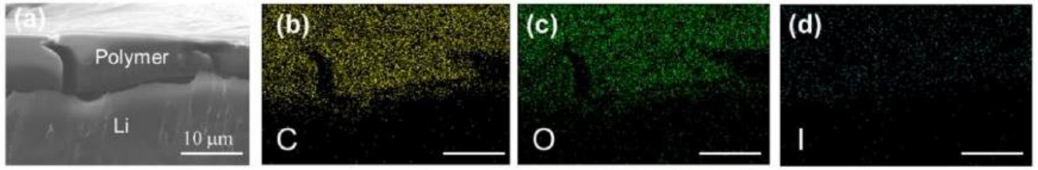


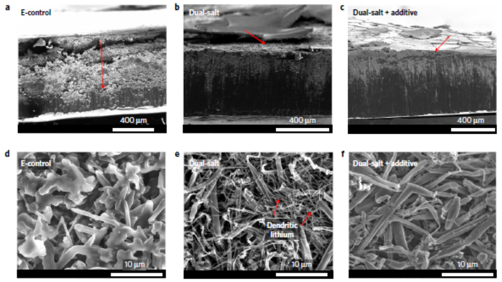


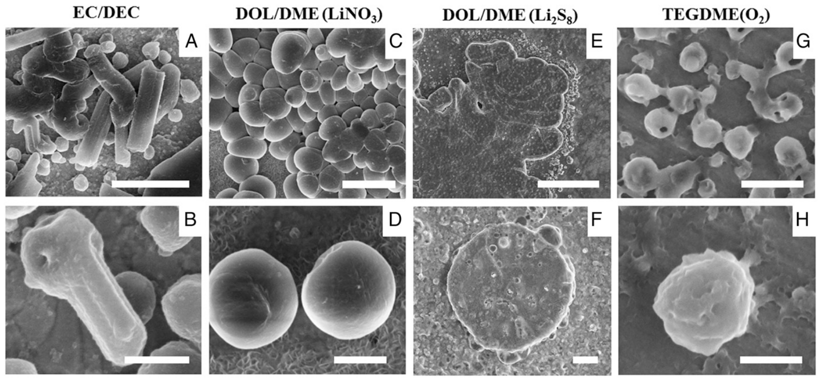


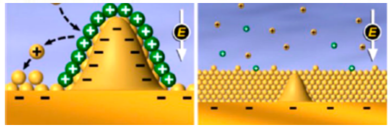
Interface Engineering

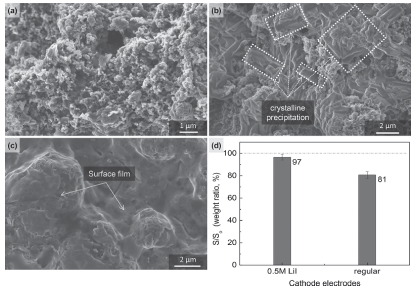
Gao, Z. et al, *Chinese Chemical Letters* **30**, 525 (2019).
Kazyak, E. et al, *Chem. Mater.* **27**, 6457 (2015).
Lin, D. et al, *Nano Lett.* **17**, 3731 (2017).
Zhou, H. et al, *J. Mater. Chem. A* **6**(12), 4883 (2019).
Meyerson, M. L. et al, *J. Mater. Chem. A* **7**, 14882 (2019).





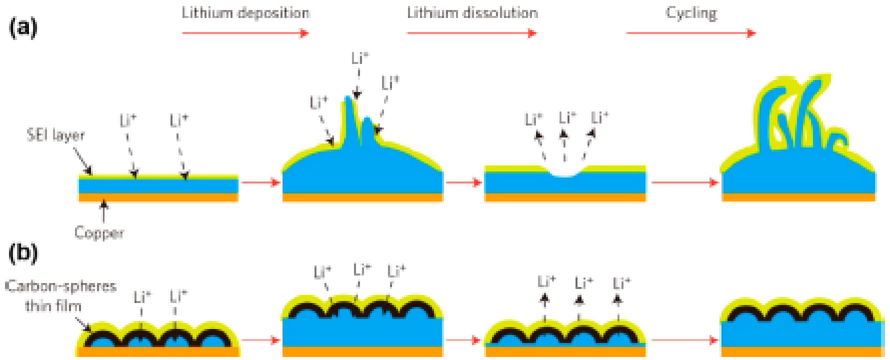


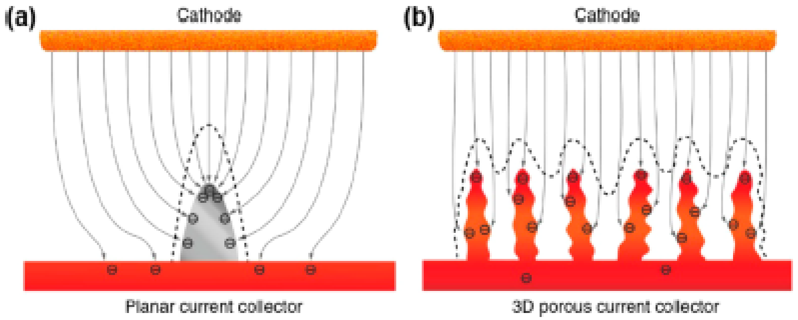




Electrolyte Engineering

Zheng, J. et al, *Nat. Energy* **2**, 17012 (2017).
Shi, F. et al, *PNAS* **114** (46), 12138 (2017).
Wu, F et al, *Adv. Mater.* **27**, 101 (2015).
Ding, F. et al, *J. Am. Chem. Soc.* **135**, 4450 (2013).





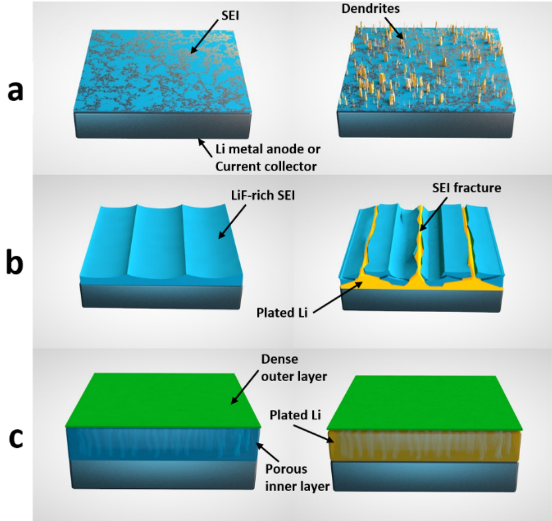
3-D Architectures

Zheng, G. et al, *Nat. Nanotechnol.* 9, 618 (2014).
Yang, C.-P. et al, *Nat. Commun.* **6**, 8058 *(*2015).

Interface Engineering – "Coatings"

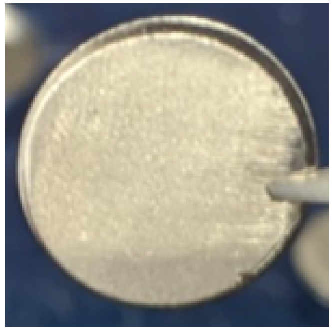
- Treatment of lithium must be simplistic – applicable to large-scale production
  - "Coating-like" Artificial Solid Electrolyte Interphase (SEI)
    - Electrochemically & mechanically stable

- Surface characterization
  - SEM, XPS, & AFM: chemical and morphological analysis
- Electrochemical testing
  - Symmetric cells & Li||LFP, Li||S cells



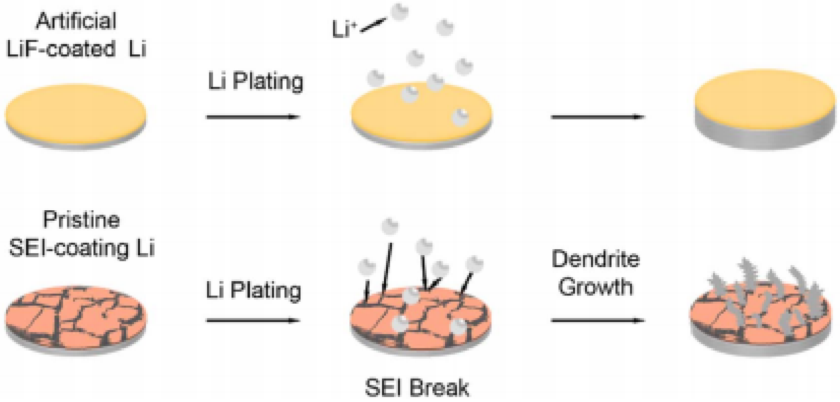
C. M. Efaw et al, submitted to *Materials Today.*

<u>Polished Li</u>



<u>Dense LiF</u>

<u>Porous LiF</u>

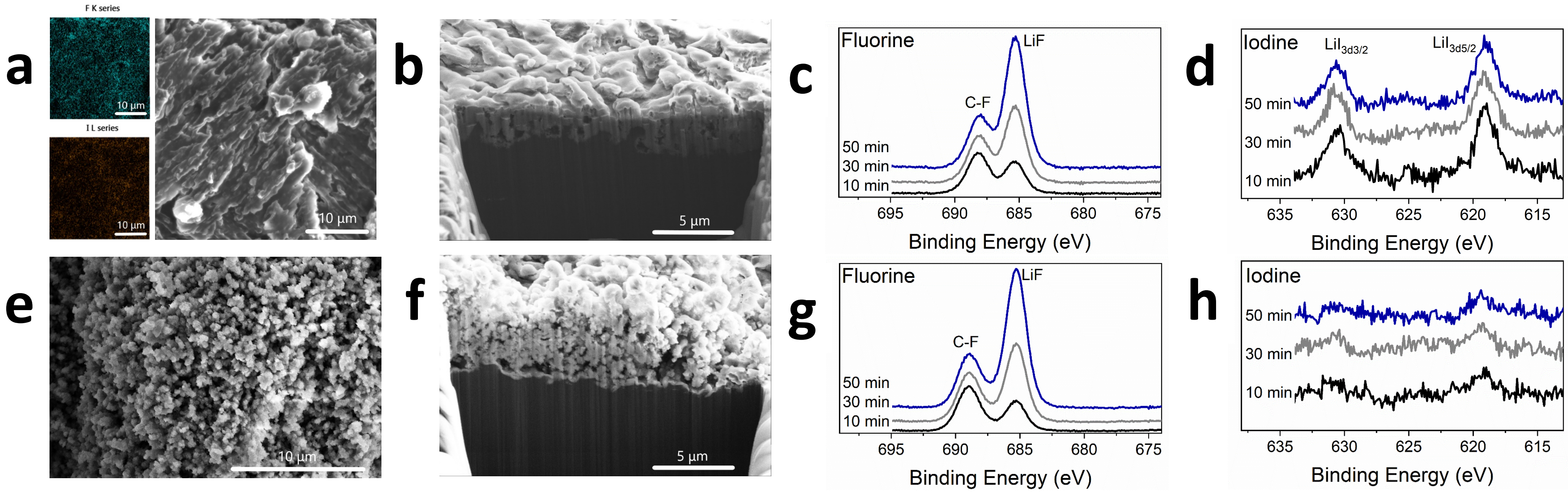


J. Lang et al, *Energy Storage Materials* **16**, 85 (2019).

Bi-Layer Coating Formulation

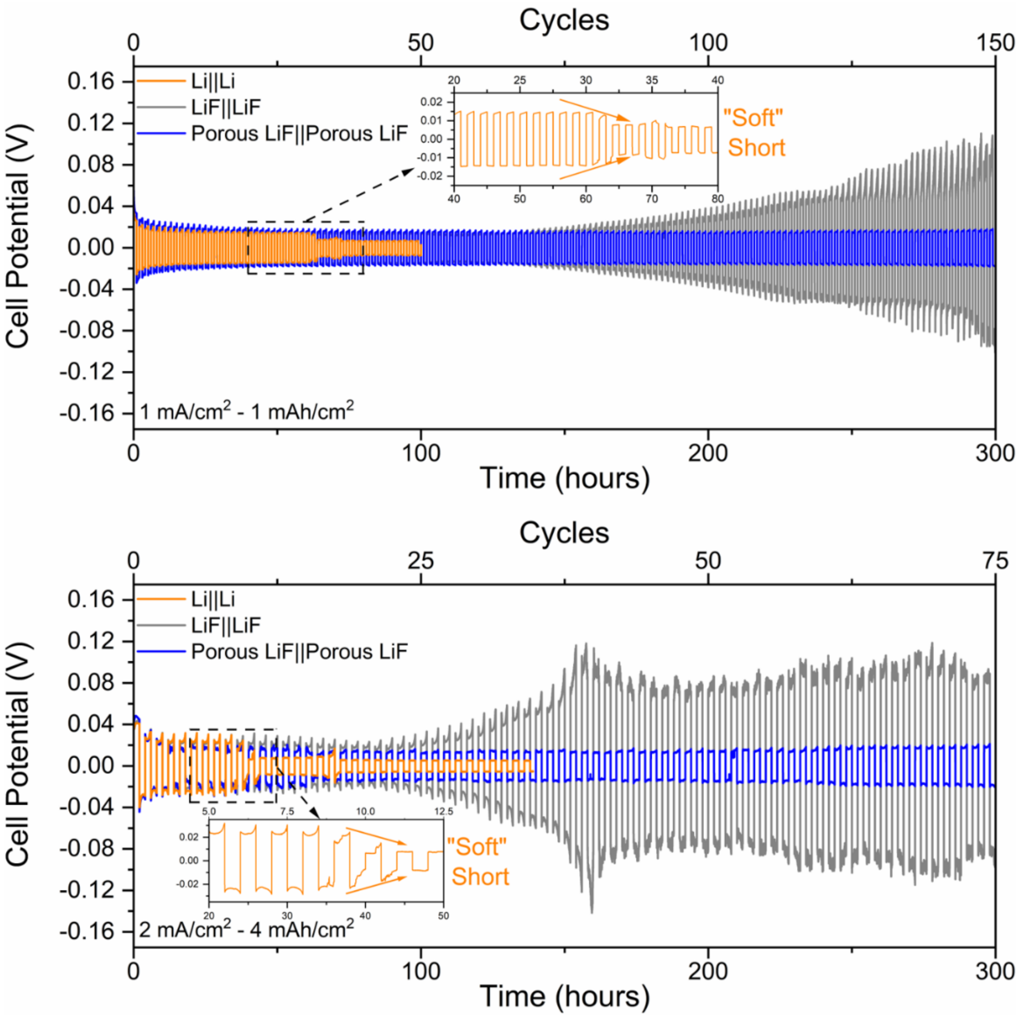
1) Mixed coating of LiI & LiF

2) Porous LiF-rich coating

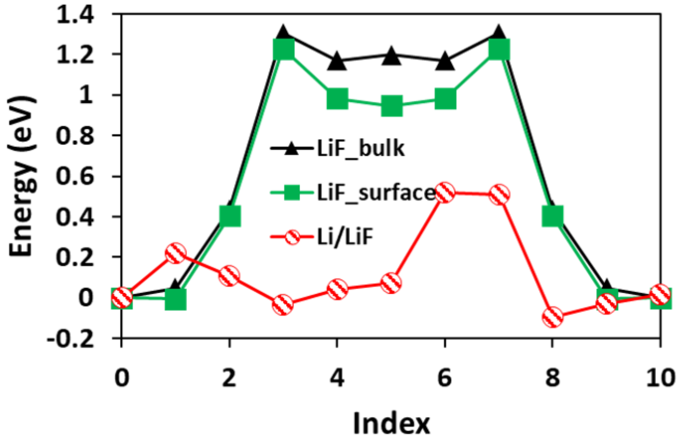


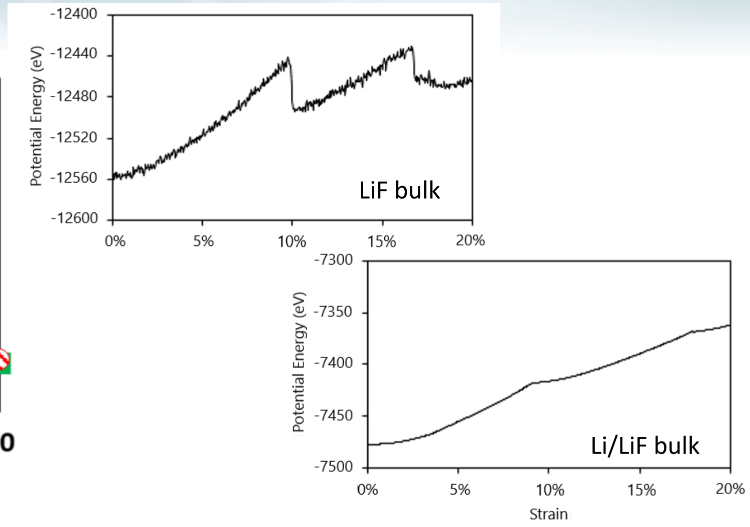
C. M. Efaw et al, submitted to *Materials Today.*

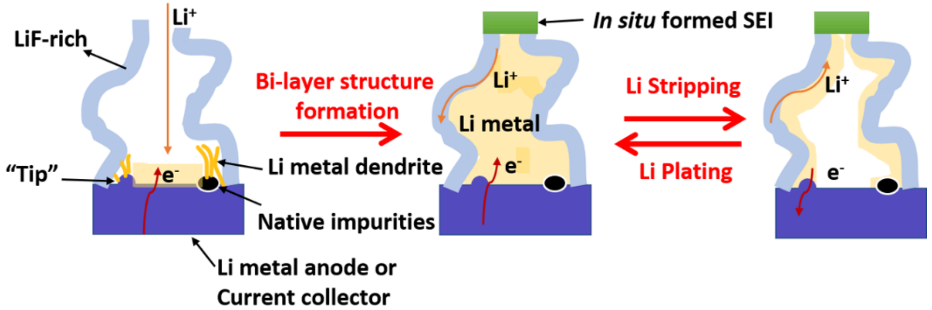
Cell Performance

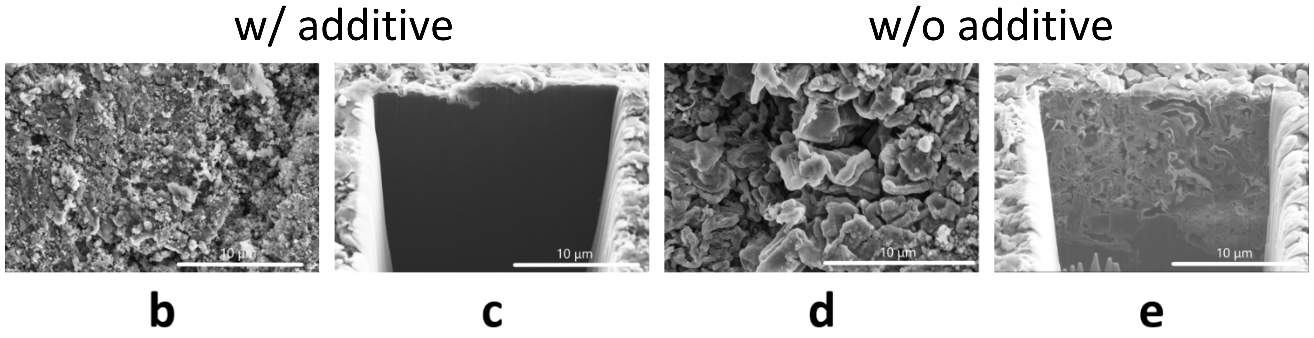


C. M. Efaw et al, submitted to *Materials Today.*



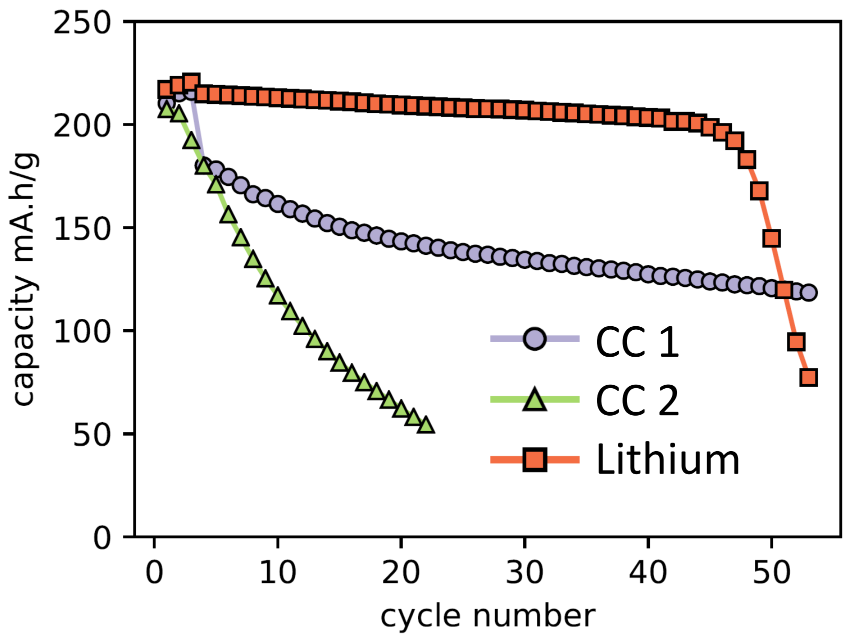






Other Viable Cell Routes

- Beyond Li – Na, Ca, Mg, Zn, Al
- Li-Ion Batteries
  - Lower theoretical capacity, needs redesign
- Anode-less Batteries
  - Manufacturing ease
- Solid-state Batteries
  - New interfacial processes at play



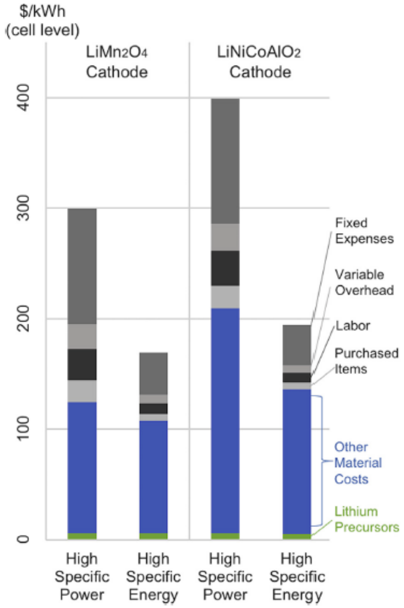
Reuse & Recycling Methodologies

- Refining methodologies
  - Direct Recycling
    - Blended mixture, cathode-targeted
  - Pyrometallurgy – incineration, smelting
    - Requires large scale facilities, high energy, high CO_2
  - Hydrometallurgy – acid leaching
    - Economically viable, slow processing, toxicity concerns
  - Electrochemical methods
    - Variety in methods, assisted to older methods

- Extraction capabilities for cathode-materials, poor for Li
  - Not a major factor in production/recycling costs

- Second-life use of EV batteries for grid applications

Argonne National Laboratory



Li, Z. et al, *Resources, Conservation & Recycling* **149**, 20 (2019).
Ciez, R.E. and Whitacre, J.F., *Nature Sustainability* **2**, 148 (2019).
Ciez, R.E. and Whitacre, J.F., *Journal of Power Sources* **320**, 310 (2016).
Diaz, L.A. et al, *Resources, Conservation & Recycling* **161**, 104900 (2020).
Nordelöf, A. et al., *Batteries* **5**, 51 (2019).
Zhang, L. et al, *Journal of Hazardous Materials* **58**, 122840 (2020).
Valant, C. et al, *Batteries* **5**, 8 (2019).

Social Life Cycle Assessment (S-LCA)

- Additional risk assessments
  - Child labor
  - Corruption
  - Occupational hazards
  - Poverty
- Evaluate these risk factors along the supply chain
  - Raw material extraction
  - Components
  - Cell production
  - Pack assembly

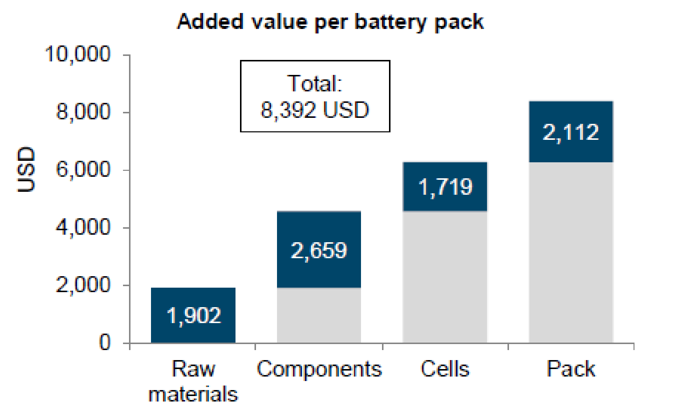
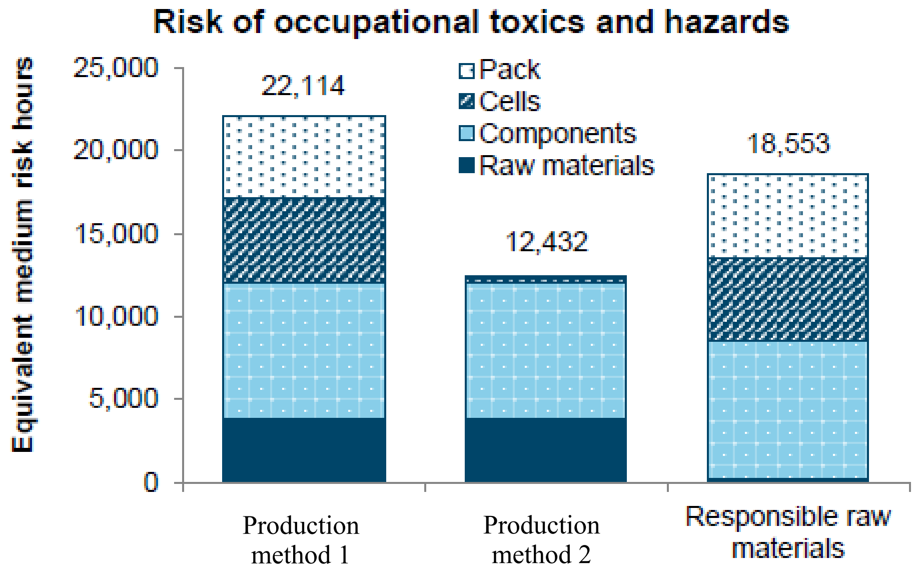


Fig. 2 Breakdown of added value for the battery pack along the supply chain

Thies, C. et al, *Procedia CIRP* **80**, 292 (2019).



Conclusions

- Metal corrosion is a sustainability issue
- Thinking outside the box – lithium is a metal; corrosion is an issue in this field
- Intersectionality present that members of STEM can collaborate