Modeling Co-Extruded Cathodes for High Energy Lithium-Ion Batteries

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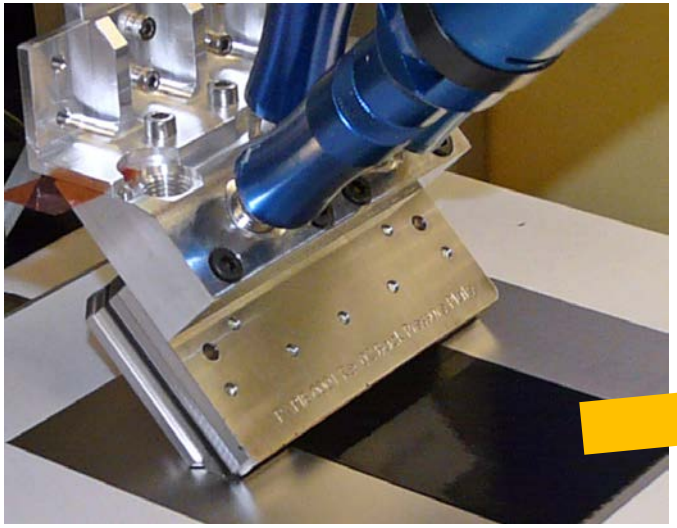
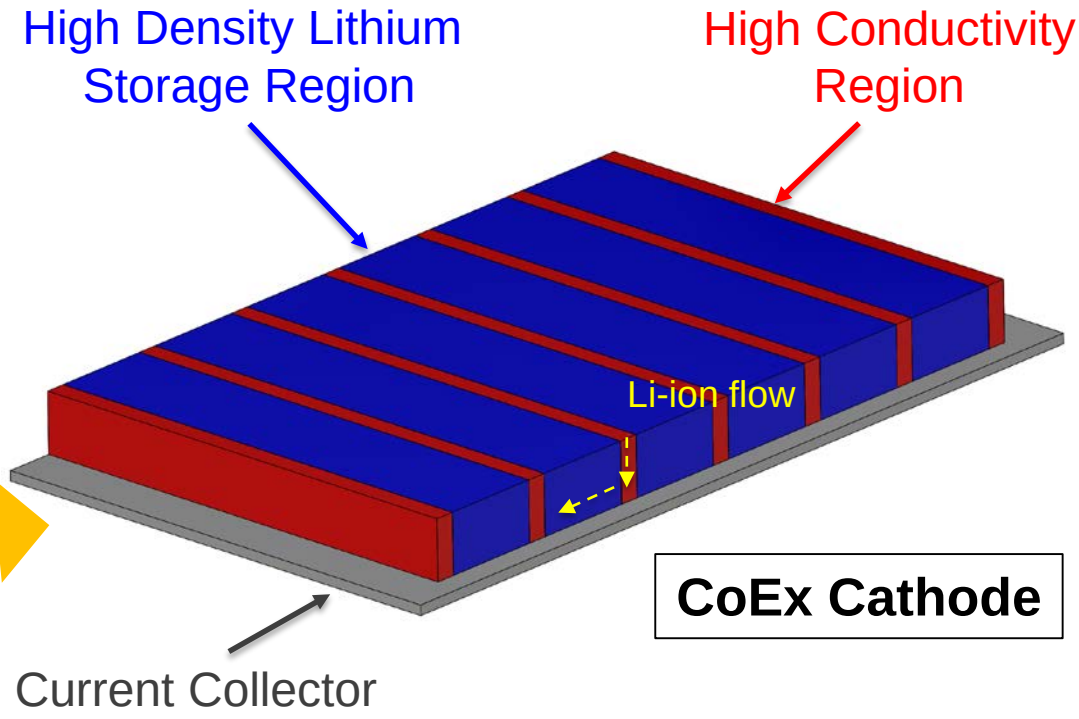
Co-Extrusion (CoEx) for Enhanced Li-ion Transport in Thick Battery Electrodes

Co-extrusion Printhead*





Hypothesis: Using conventional battery materials, thick co-extruded electrodes can change conduction pathways in lithium-ion batteries, decoupling power and energy trade-offs with novel geometry layout

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*ARPA-E Award Number DE-AR0000324

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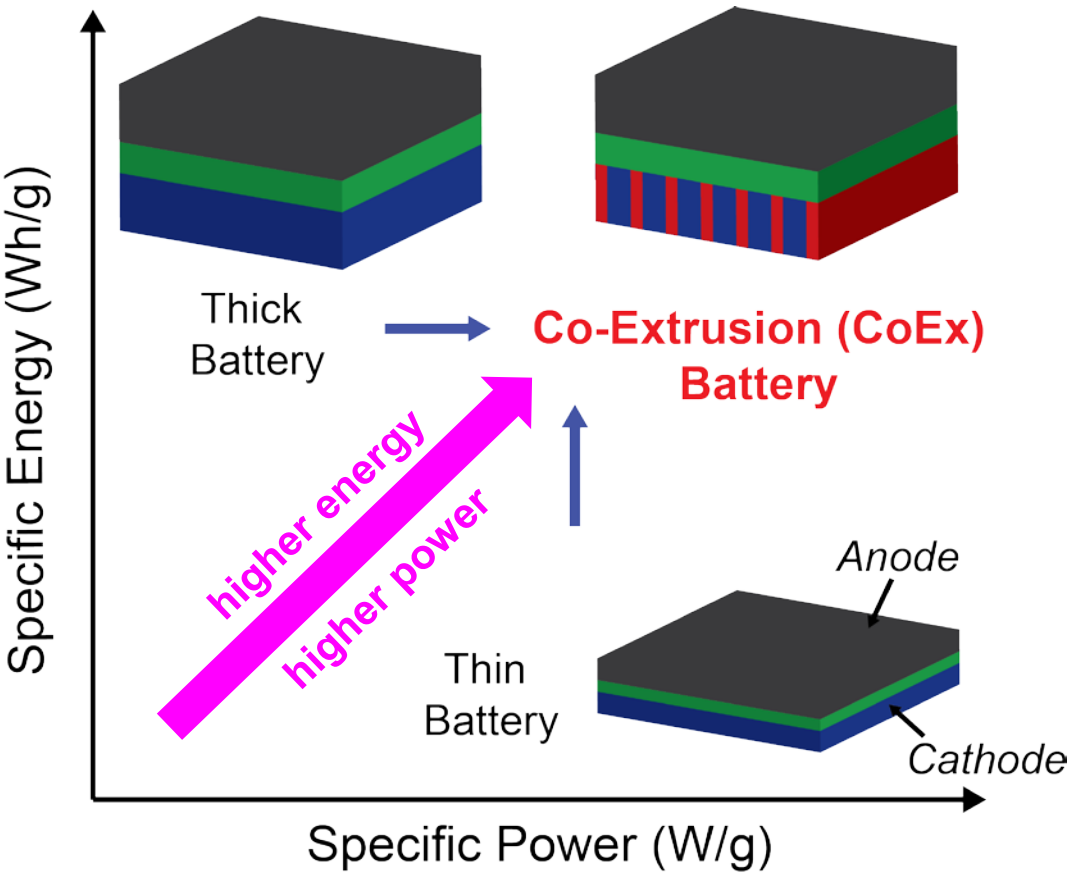
2D and 3D Battery Electrodes



- 2D & 3D battery designs show great promise for high energy and high power batteries
- Large-area, low cost processes are required to realize the benefits of 2D & 3D battery designs → **CoEx**
- Design space for optimal electrode designs is large

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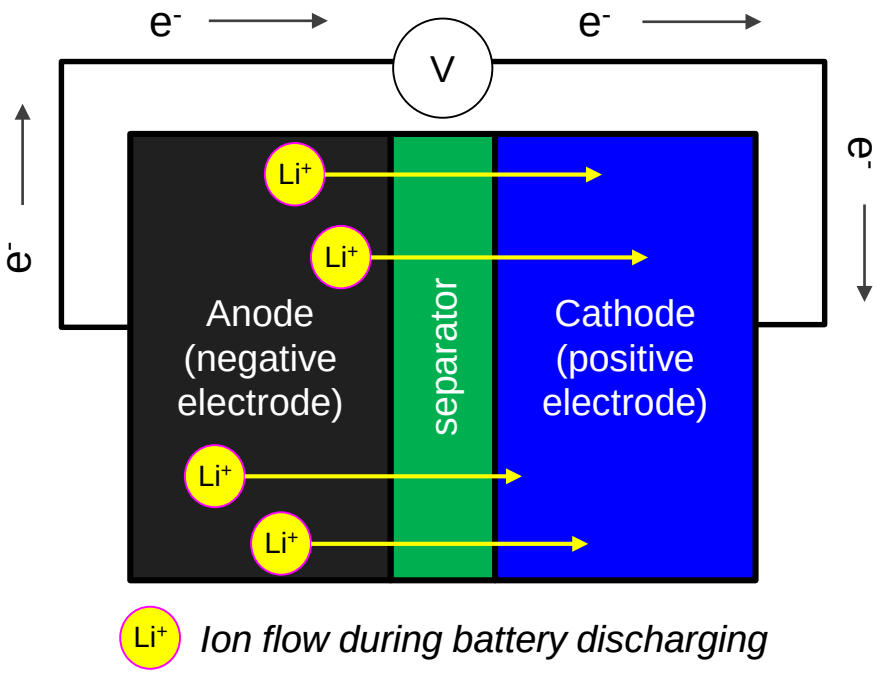
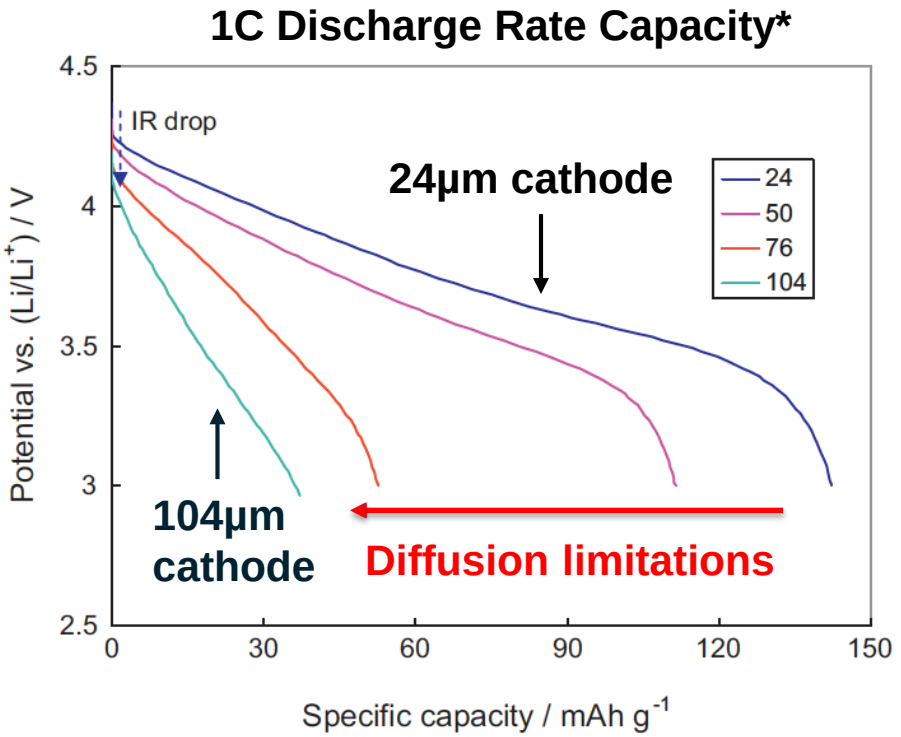
Battery Electrode Trade-offs

- **Thin electrodes** → High power, but increases overhead of current collectors and separators in a battery stack
- **Thick electrodes** → High energy, but diffusion limitations





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* Source: Zheng, et al., Electrochimica Acta, 71, pp. 258-265, 2012.

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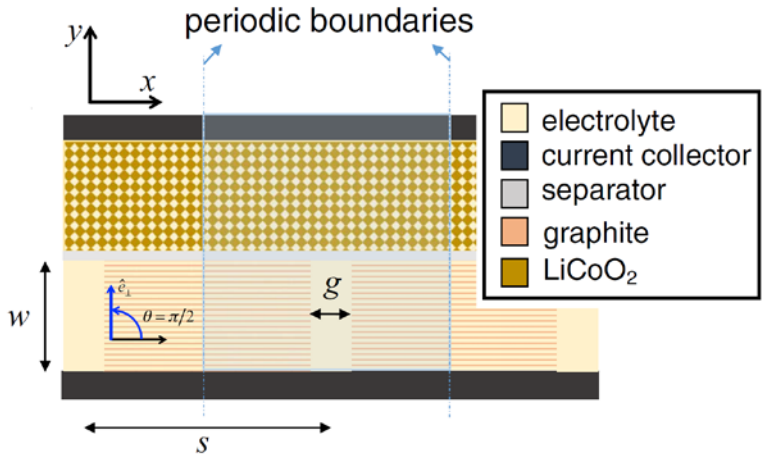
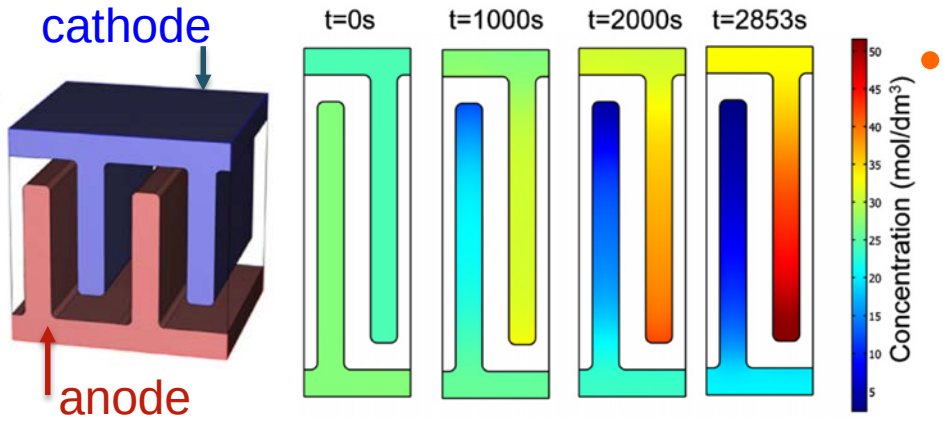
Modeling 2D/3D Battery Electrodes



- Nemani *et al.*, *Journal of the Electrochemical Society*, (2015).
  - A bi-tortuous anode with macro & micro pores increased discharge capacity by >2X
  - Modeling required a 2D form of porous electrode theory to capture anisotropic transport behavior



- Zadin *et al.*, *Journal of Power Sources*, (2016).
  - Used a 2D porous electrode model to study the inhomogeneous lithiation front in interdigitated microbatteries

High fidelity models of electrochemical transport are needed to guide the design of complex electrode architectures

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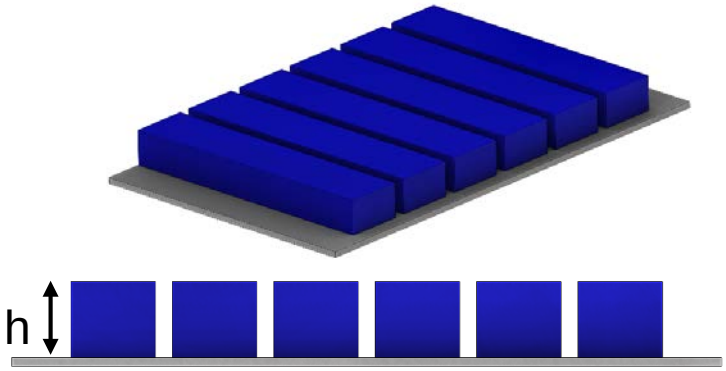
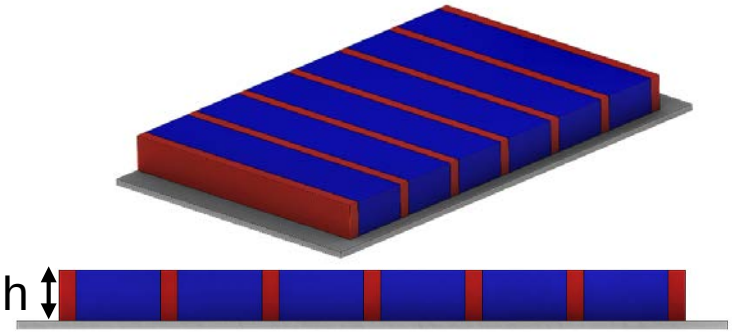
CoEx Electrode Design Space

CoEx 1: Corrugated Design



h = 125 - 400 µm

CoEx 2: Two-material Design



h = 100 - 180 µm

Description	Stripe Width Ratio	Stripe 1 Porosity (%)	Stripe 2 Porosity (%)
Corrugated design with open channels for electrolyte	1:1 to 20:1	33.8 (based on monolithic electrode)	100
Two-material design with a 5-30% porosity differential between the stripes	1:1 to 5:1	30-35	40-60

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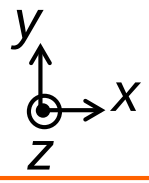
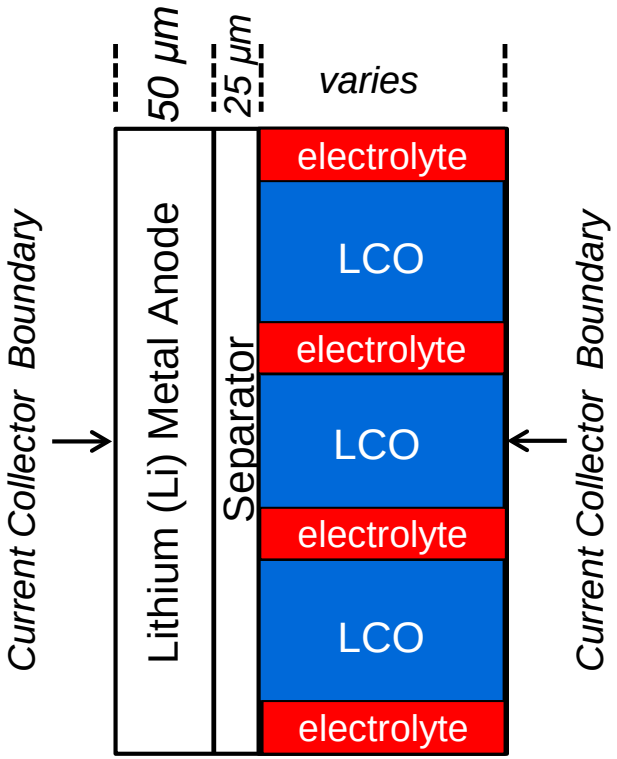
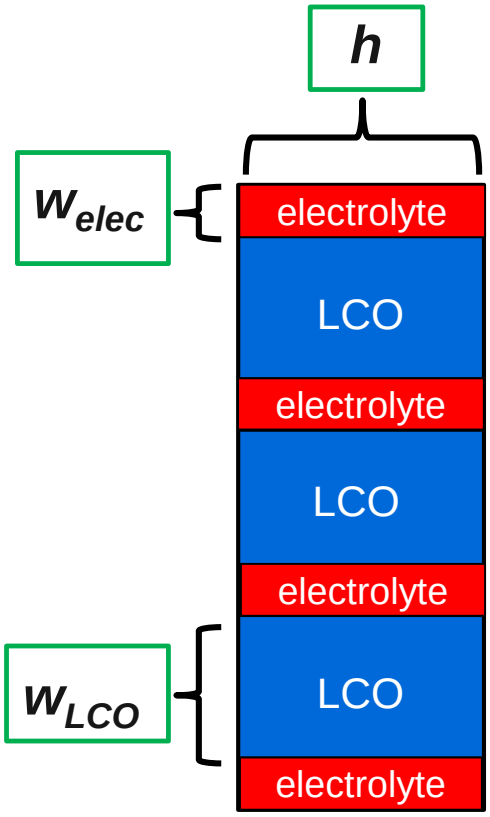
CoEx 1 Geometry Exploration with COMSOL



What are the required thicknesses and feature sizes for a CoEx cathode electrode?



Half Cell Geometry



Cathode Structure

LCO Composition:
52% $LiCoO_2$
14.2% Filler/binder
33.8% Porosity

Electrolyte:
1:1 EC:DMC
1M $LiPF_6$

LCO = Lithium Cobalt Oxide ($LiCoO_2$)

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Model Setup

- Implemented a 2D version of John Newman's Macrohomogeneous porous electrode model[1-3] in COMSOL to model a series 2D CoEx geometries
- Only CoEx cathode geometry is varied → Volume fraction of LCO active material/filler/porosity is constant

LCO = Lithium Cobalt Oxide ($LiCoO_2$)

Charge Conservation & Mass Transport

$$\eta = \phi_s - \phi_l - U$$

$$i_l = -\kappa_{l,eff}\nabla\phi_l + \frac{2\kappa_{l,eff}RT}{F}\left(1 + \frac{\partial \ln f}{\partial \ln c_l}\right)(1 - t_+)\nabla \ln c_l$$

$$\epsilon_l \frac{\partial c_l}{\partial t} = \nabla \cdot \left(D_{l,eff}\nabla c_l\right) + \left(\frac{a i_{loc}}{F}\right)(1 - t_+)$$

$$\frac{\partial c_s}{\partial t} = \nabla \cdot (D_s \nabla c_s)$$

$$i_s = -\sigma_s \nabla \phi_s$$

Chemical Kinetics

$$i_{loc} = i_0\left[e^{\left(\frac{\propto_a F\eta}{RT}\right)} - e^{\left(-\frac{\propto_c F\eta}{RT}\right)}\right]$$

$$i_0 = F(k_c)^{\alpha_a}(k_a)^{\alpha_c}(c_{s,max} - c_s)^{\alpha_a}(c_s)^{\alpha_c}(c_l)^{\alpha_a}$$

1. *M. Doyle, T.F. Fuller, J. Newman, J. Electrochem. Soc. 140 (1993) 1526-1533.*
2. *T.F. Fuller, M. Doyle, J. Newman, J. Electrochem. Soc., 141 (1994) 1-10.*
3. *T.F. Fuller, M. Doyle, J. Newman, J. Electrochem. Soc., 141 (1994) 982-990.*

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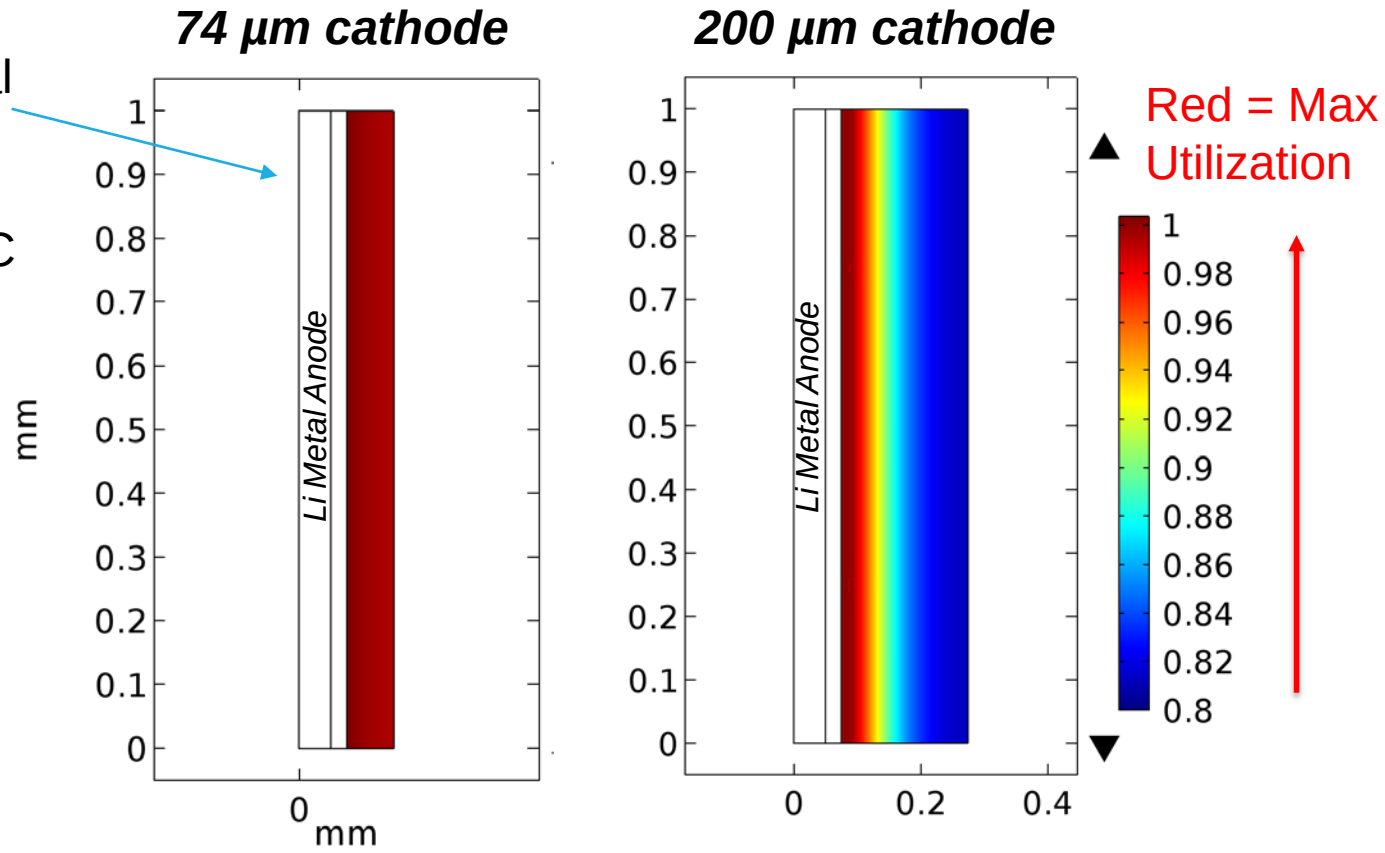
Lithium Utilization Plots – Conventional Cells

(End of a 1C Discharge Cycle)

commercial baseline cell at the end of a 1C discharge



Note: COMSOL model was compared against DUALFOIL and a conventional 1D COMSOL model and before moving to 2D models

Parameters from: G. Ning, R.E. White, B.N. Popov, Electrochimica Acta 51(10) (2006) 2012-2022

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Source: **C.L. Cobb** and M. Blanco, *Journal of Power Sources*, Vol. 249, pp. 357-366, 2014.

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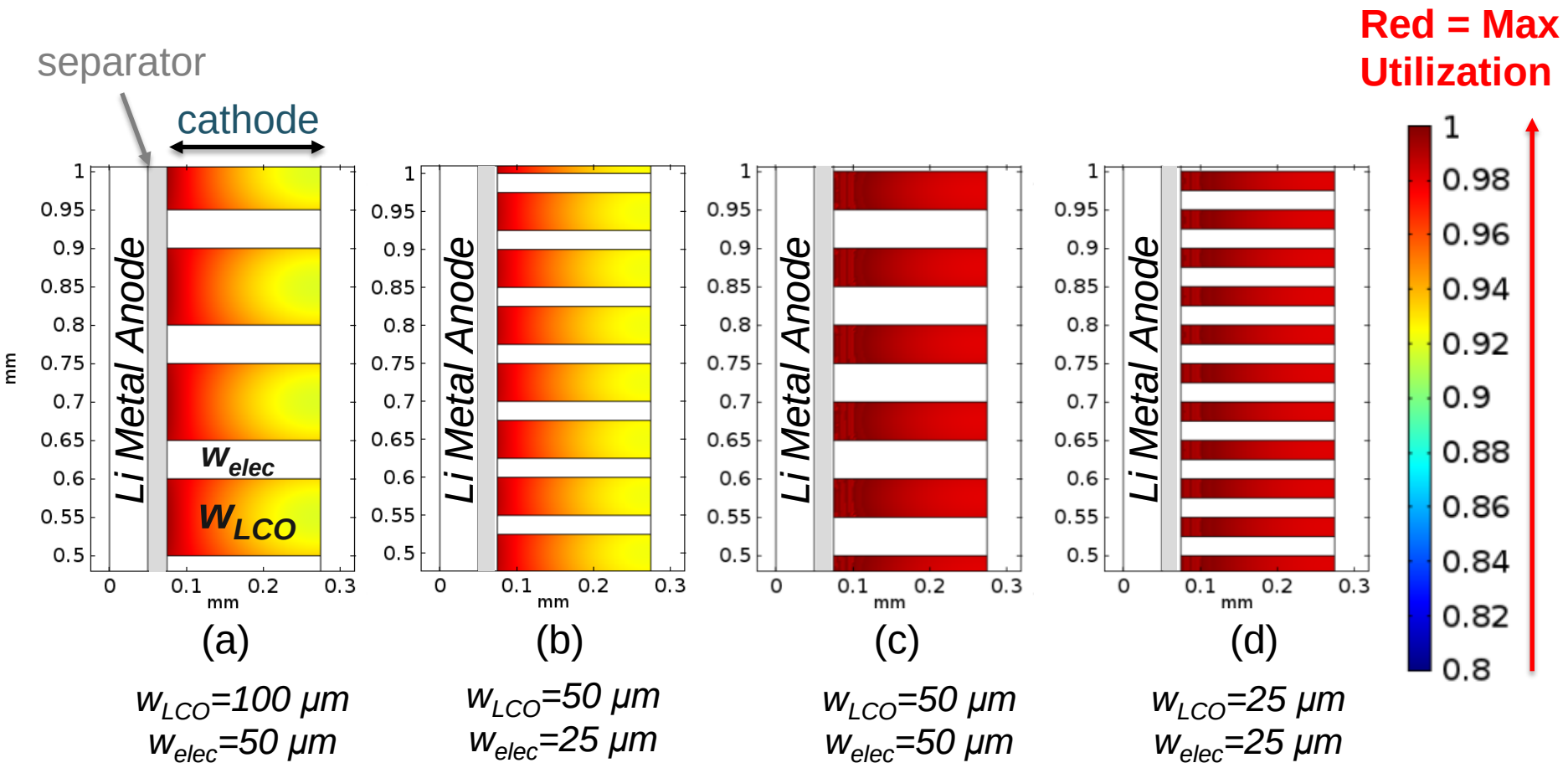
Lithium Utilization Plots – 200 µm Thick CoEx Cathodes
(End of a 1C Discharge Cycle)



(a) w_{LCO}=100 µm, w_{elec}=50 µm

(b) w_{LCO}=50 µm, w_{elec}=25 µm

(c) w_{LCO}=50 µm, w_{elec}=50 µm

(d) w_{LCO}=25 µm, w_{elec}=25 µm

1C discharge rate results shows that designs (c) and (d) have the best performance based on specific capacity

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Source: **C.L. Cobb** and M. Blanco, *Journal of Power Sources*, Vol. 249, pp. 357-366, 2014.

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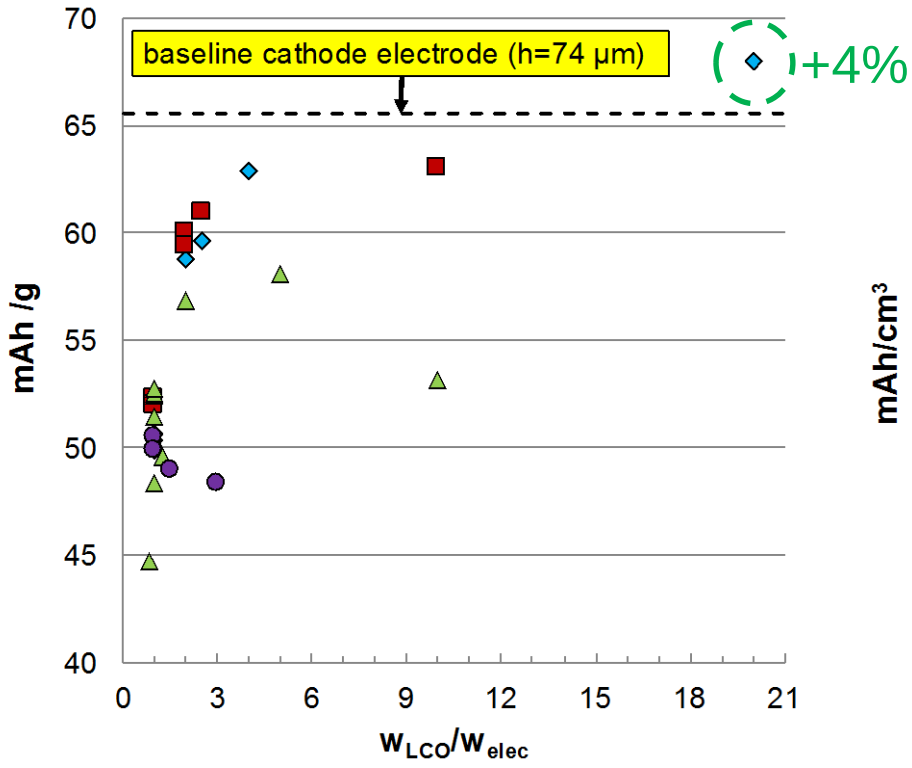
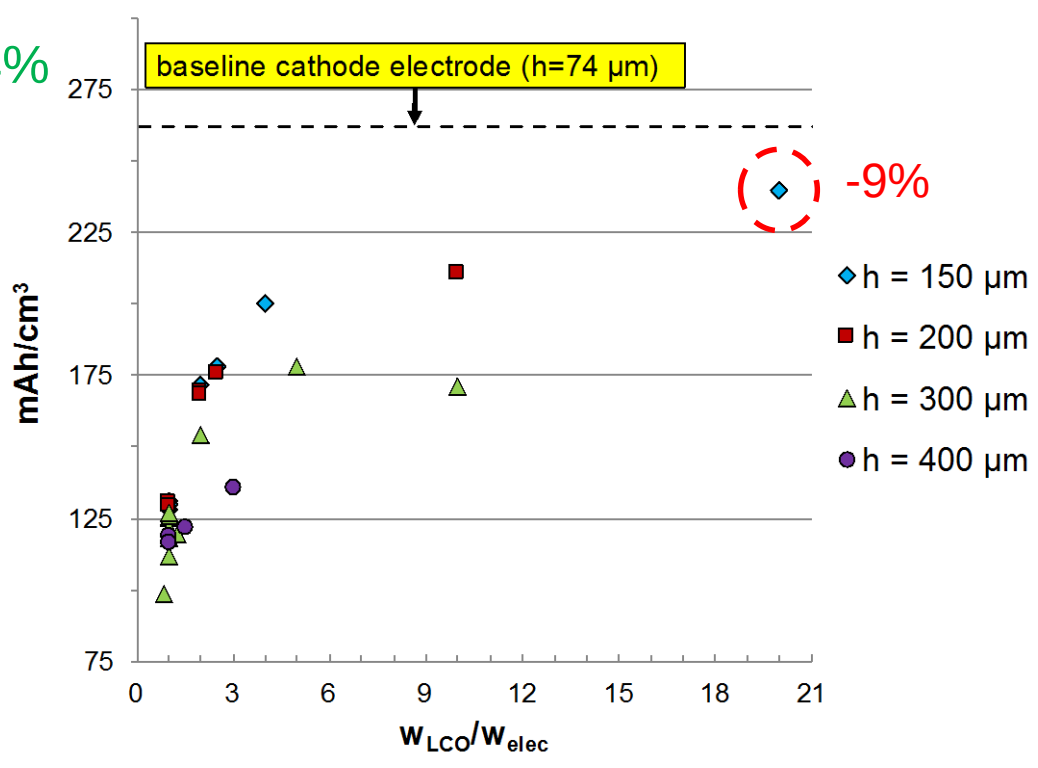
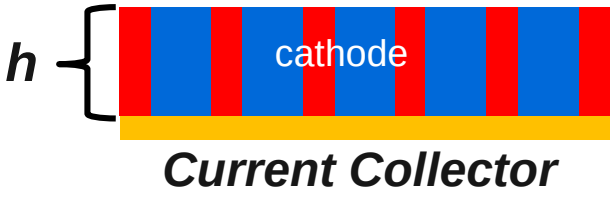
Capacity Based on Total Weight and Volume of Cathode

Gravimetric capacity vs. ratio of co-extruded pillar widths



Volumetric capacity vs. ratio of co-extruded pillar widths





Result: 150 µm thick CoEx cathode with w_{LCO}/w_{elec} = 20 was the best performing design & translates to a ~16% improvement in gravimetric capacity at the pouch cell level

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Source: **C.L. Cobb** and M. Blanco, *Journal of Power Sources*, Vol. 249, pp. 357-366, 2014.

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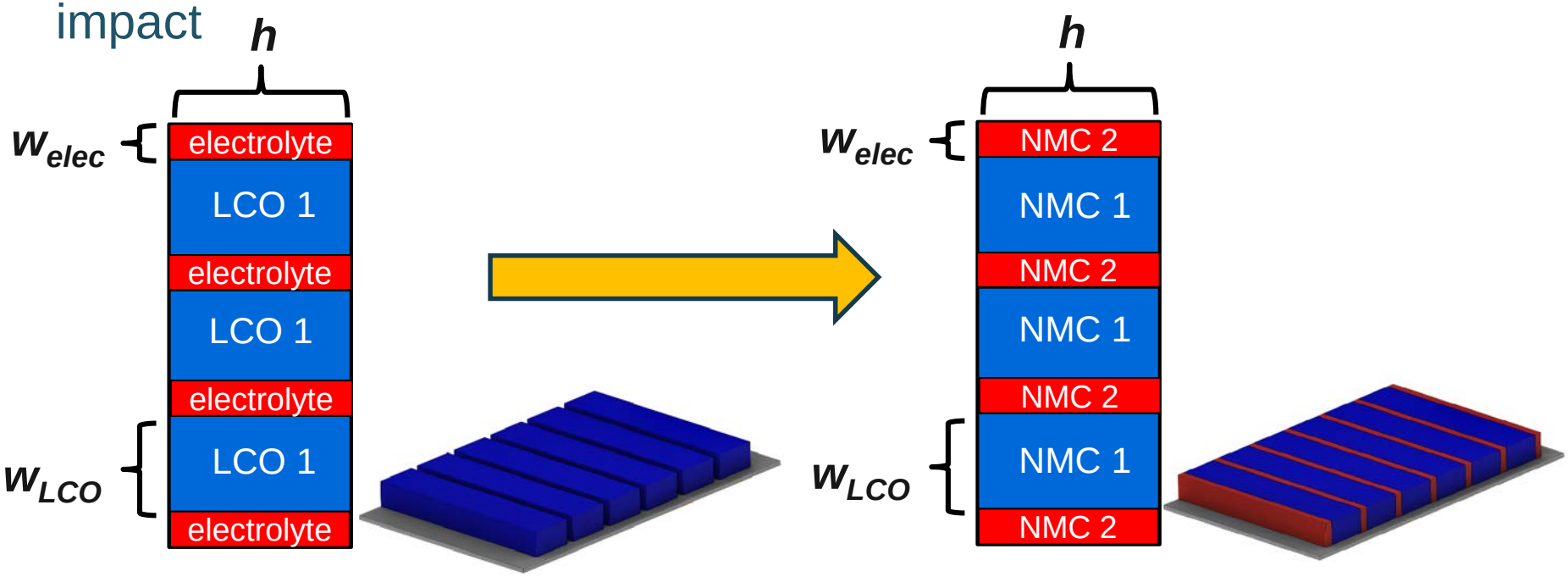
Modeling Summary

- Pure electrolyte channels enhanced lithium utilization in thick cathodes but impacted the total capacity
- Additional modeling is being conducted on structures with higher porosity material in the ‘electrolyte’ regions to reduce total capacity impact



CoEx Structure 1

CoEx Structure 2

(switch to NMC for EV-relevant data)

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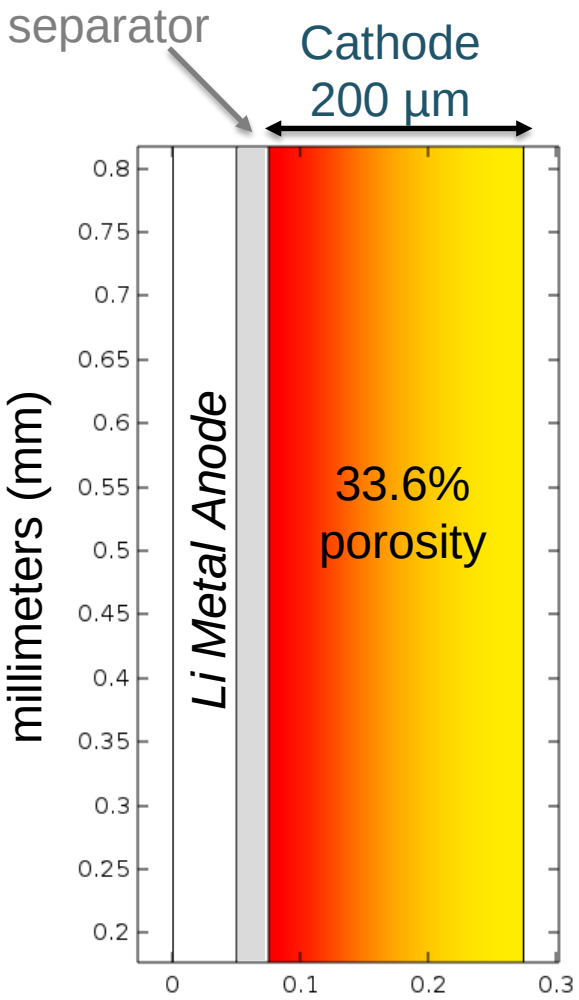
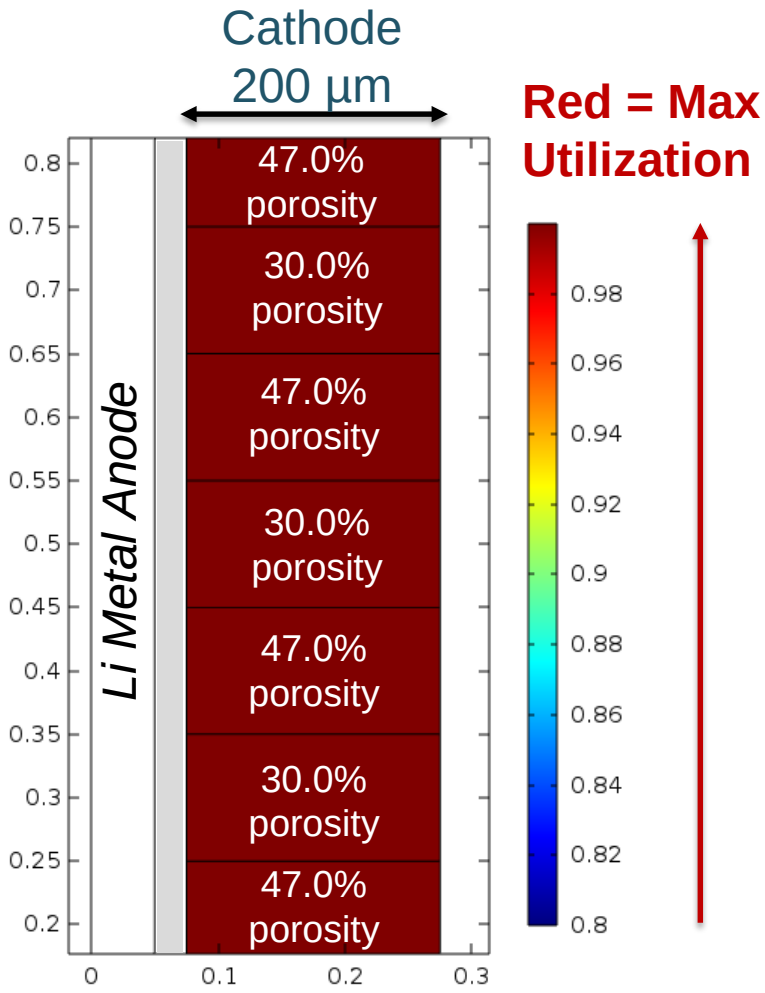
Preliminary Modeling Results for CoEx 2 Structure

(End of a 1C Discharge Cycle)



Monolithic NMC 532
($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$)



CoEx NMC 532
($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$)

Based on parameters from: Wu *et al.*, *Journal of The Electrochemical Society* *159*, no. 4 (2012): A438-A444.

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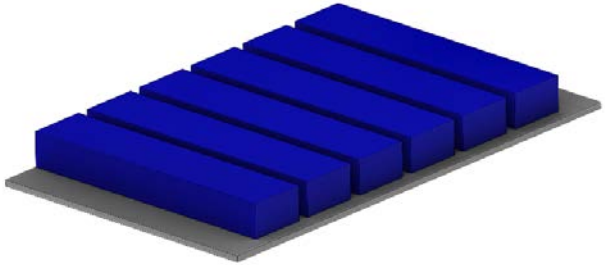
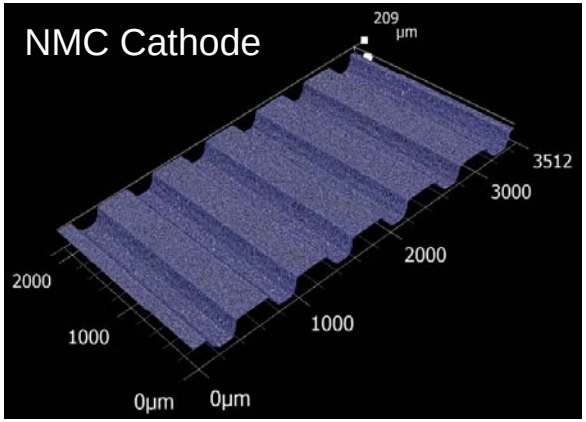
Co-Extrusion (CoEx): Experimental Progress

Co-extrusion Printhead

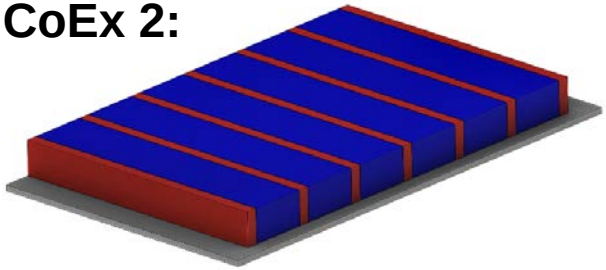
We are currently leveraging ARPA-E investment to optimize the CoEx cathode for Electric Vehicle (EV) applications

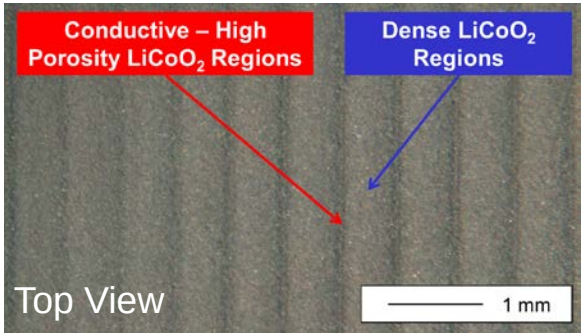
CoEx 1:





CoEx 2:





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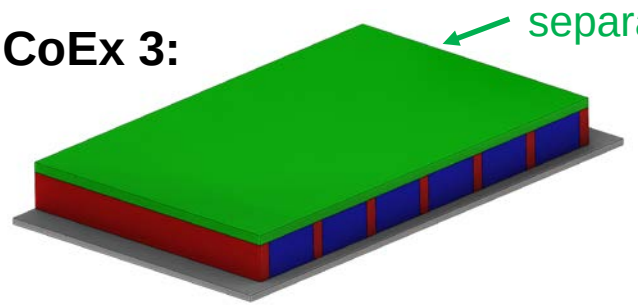
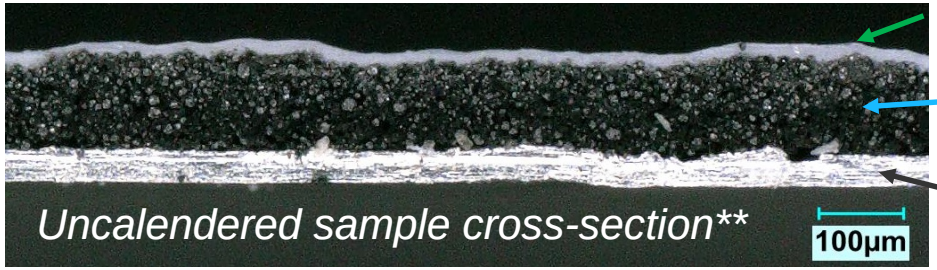
CoEx 3:





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