ARPA-E Program Proposal: Selective Ion Conductors and the Future of the Electrochemical Cell

Paul Albertus
ARPA-E Program Director
Dec 1, 2015

Program team: Sue Babinec, Scott Litzelman, Scott Himmelberger

Outline

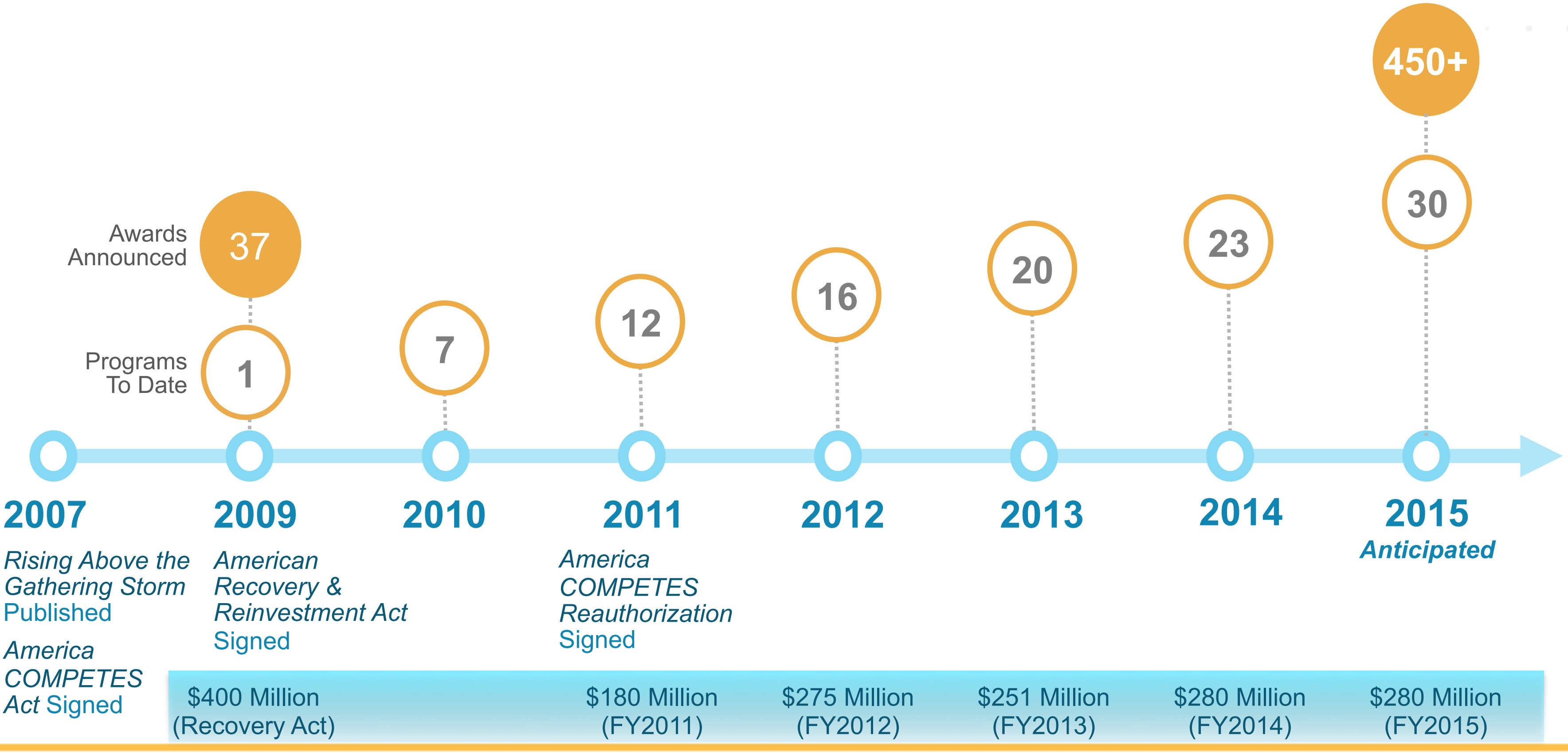
- **ARPA-E background and status of this program**

- Program overview (5 min)

- Program overview (20 min)

ARPA-E's History

In 2007, The National Academies recommended Congress establish an Advanced Research Projects Agency within the U.S. Department of Energy



Awards Announced 37

Programs To Date 1

7

12

16

20

23

30

450+

2007

Rising Above the Gathering Storm Published

America COMPETES Act Signed

2009

American Recovery & Reinvestment Act Signed

2010

2011

America COMPETES Reauthorization Signed

2012

2013

2014

2015

Anticipated

$400 Million (Recovery Act)

$180 Million (FY2011)

$275 Million (FY2012)

$251 Million (FY2013)

$280 Million (FY2014)

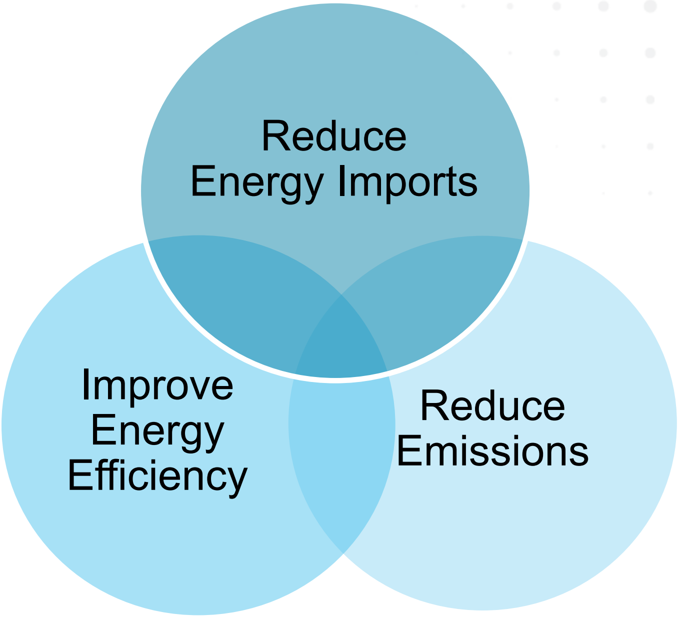
$280 Million (FY2015)

arpa·e

CHANGING WHAT'S POSSIBLE

ARPA-E Authorizing Legislation

Mission: To overcome long-term and high-risk technological barriers in the development of energy technologies



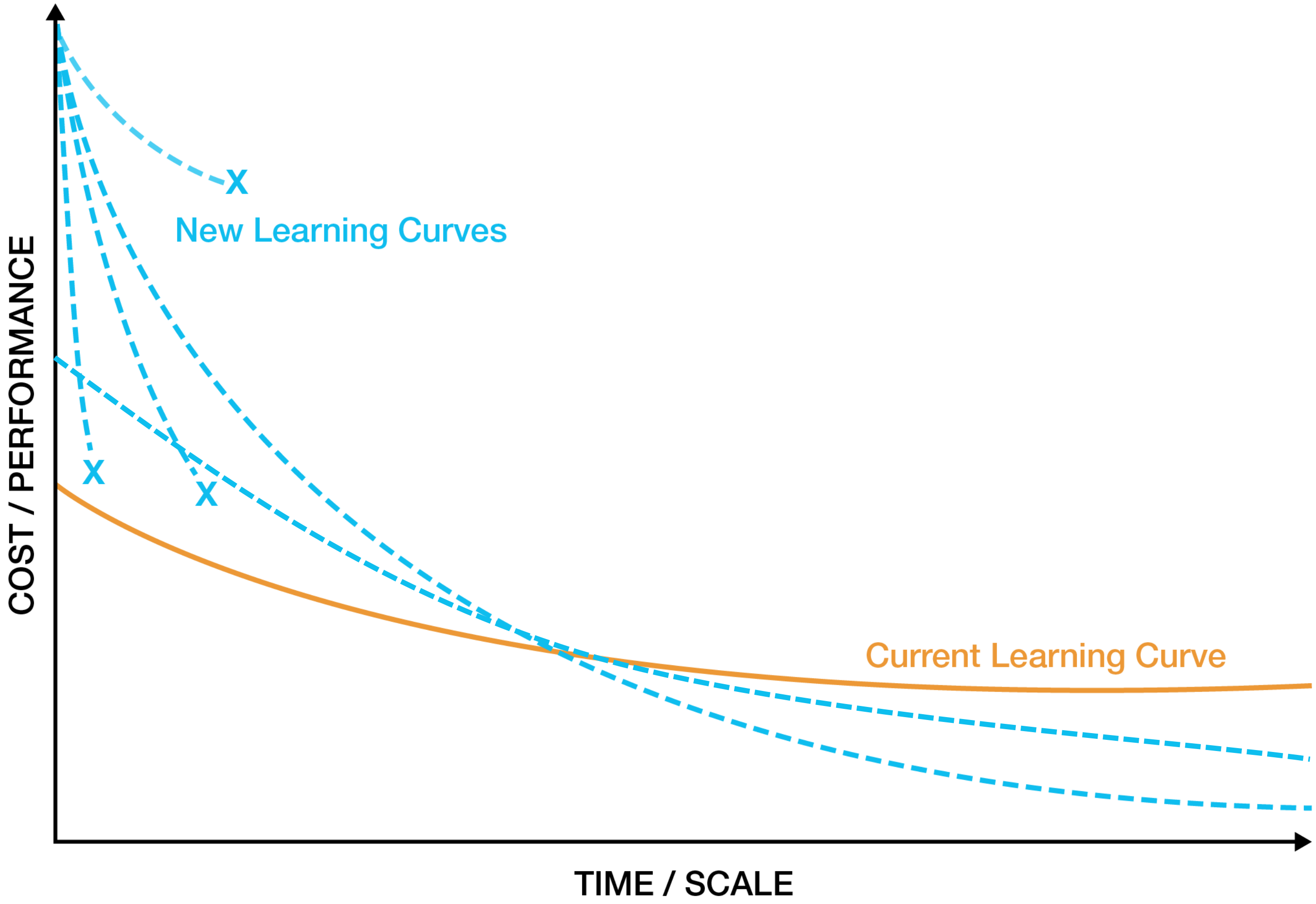
Goals: **Ensure America's**

- Economic Security
- Energy Security
- Technological Lead in Advanced Energy Technologies

Means:

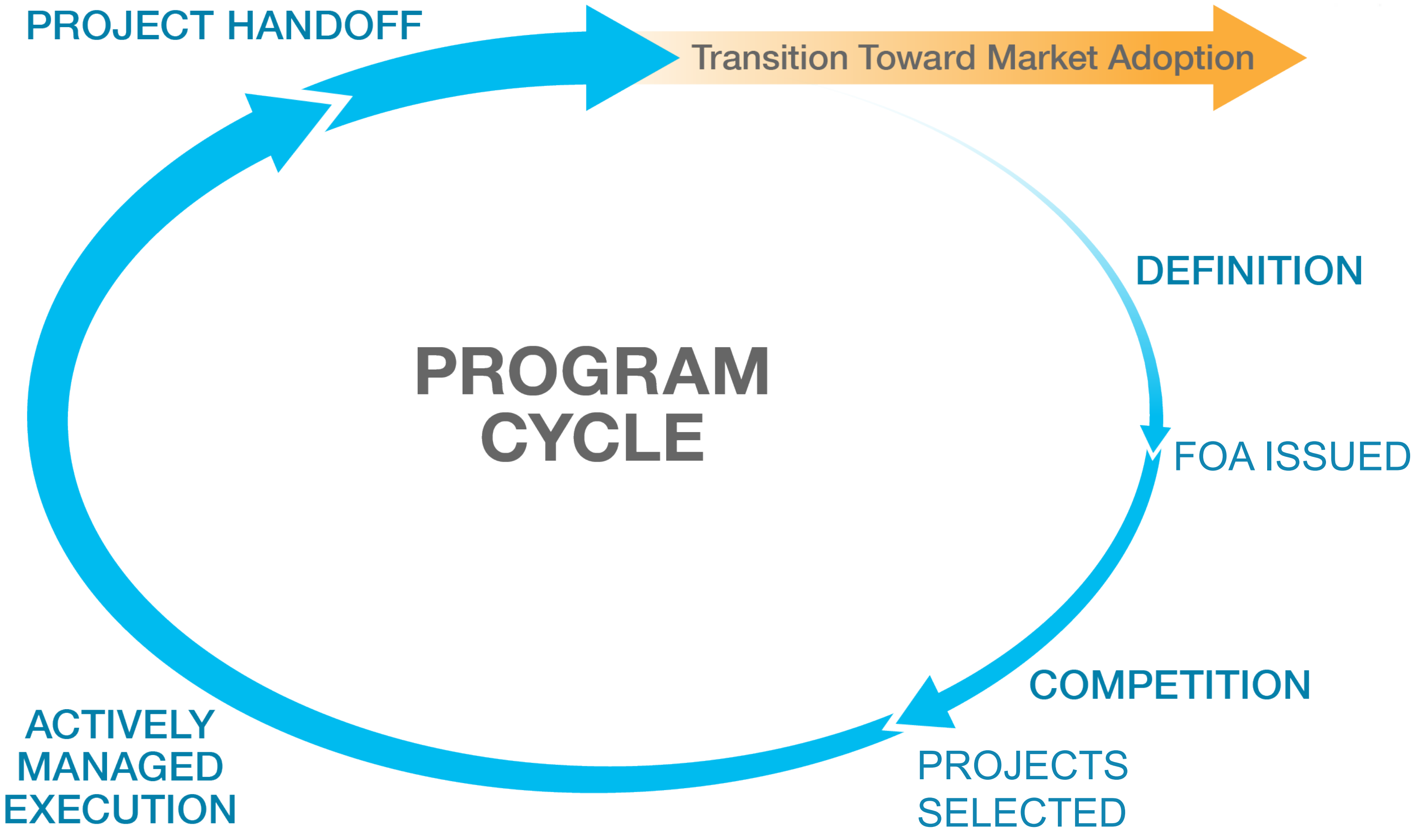
- Identify and promote revolutionary advances in fundamental and applied sciences
- Translate scientific discoveries and cutting-edge inventions into technological innovations
- Accelerate transformational technological advances in areas that industry by itself is not likely to undertake because of technical and financial uncertainty

Creating New Learning Curves



ARPA-E Process

ARPA-E Program Directors and Tech-to-Market Advisors develop programs and guide project teams



CHANGING WHAT'S POSSIBLE

https://arpa-e-foa.energy.gov/

FOA = Funding Opportunity Announcement

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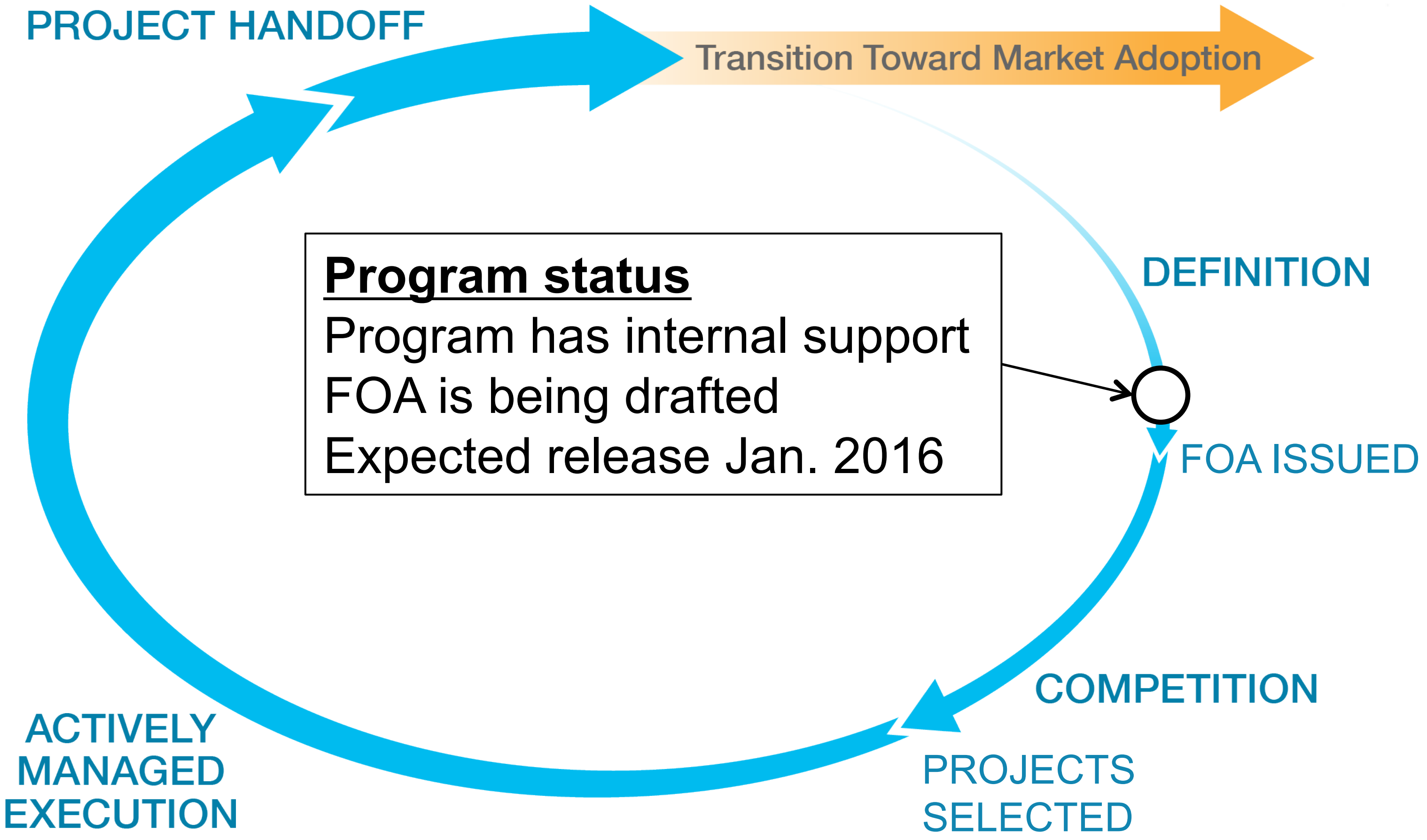
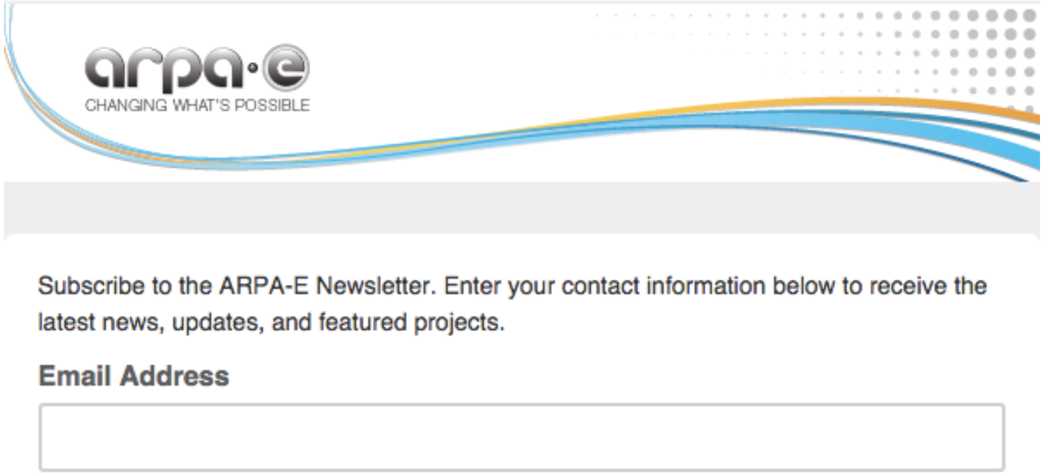


<u>Program status</u>
Program has internal support
FOA is being drafted
Expected release Jan. 2016

https://arpa-e-foa.energy.gov/
FOA = Funding Opportunity Announcement

How to engage with ARPA-E

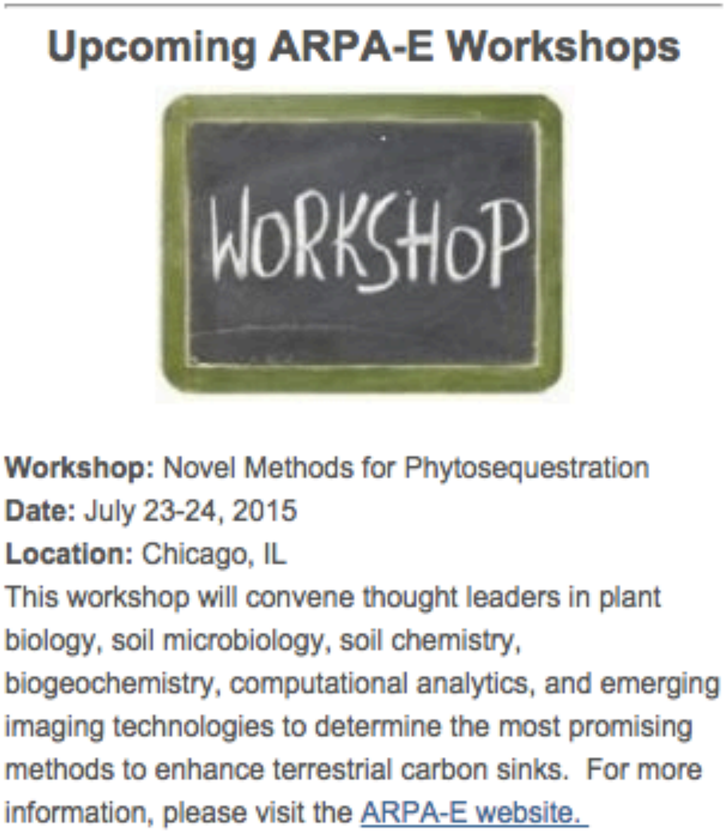
Sign up for the newsletter



Subscribe to the ARPA-E Newsletter. Enter your contact information below to receive the latest news, updates, and featured projects.

Email Address

Engage prior to FOA release



Upcoming ARPA-E Workshops

Workshop: Novel Methods for Phytosequestration
Date: July 23-24, 2015
Location: Chicago, IL
This workshop will convene thought leaders in plant biology, soil microbiology, soil chemistry, biogeochemistry, computational analytics, and emerging imaging technologies to determine the most promising methods to enhance terrestrial carbon sinks. For more information, please visit the ARPA-E website.

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- ARPA-E background and status of this program
- **Program overview (5 min)**
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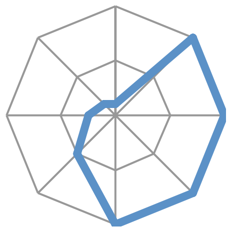
The problem: having it all, and at the same time

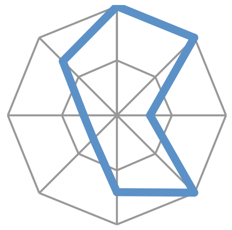
Current reality: tradeoffs among properties of ion conductors severely limit electrochemical cell improvements

Liquid

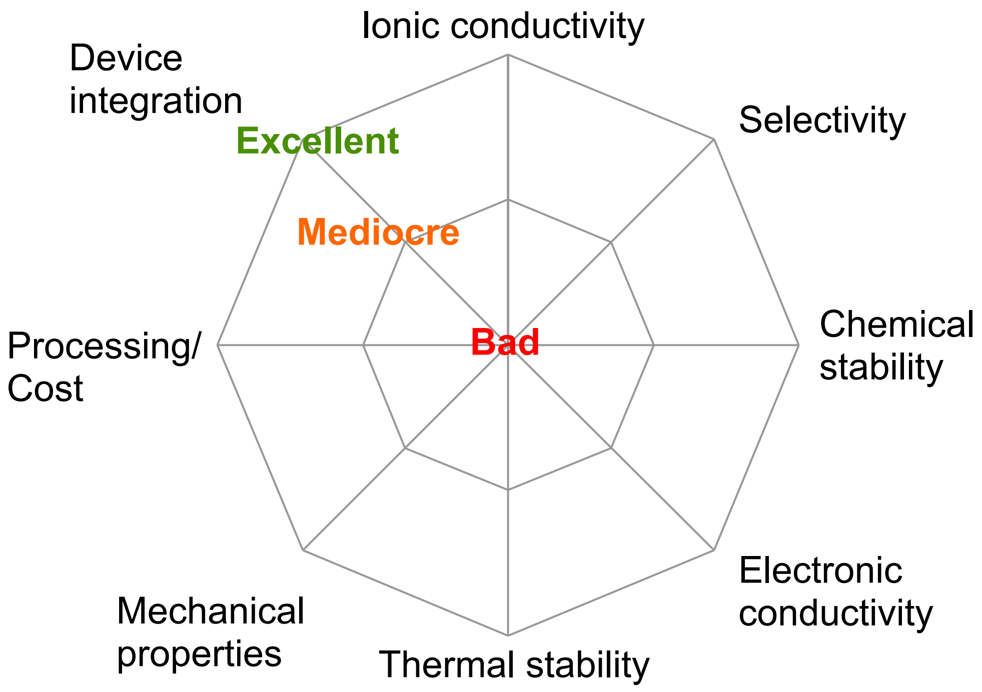
Nafion



LiPON



LGPS



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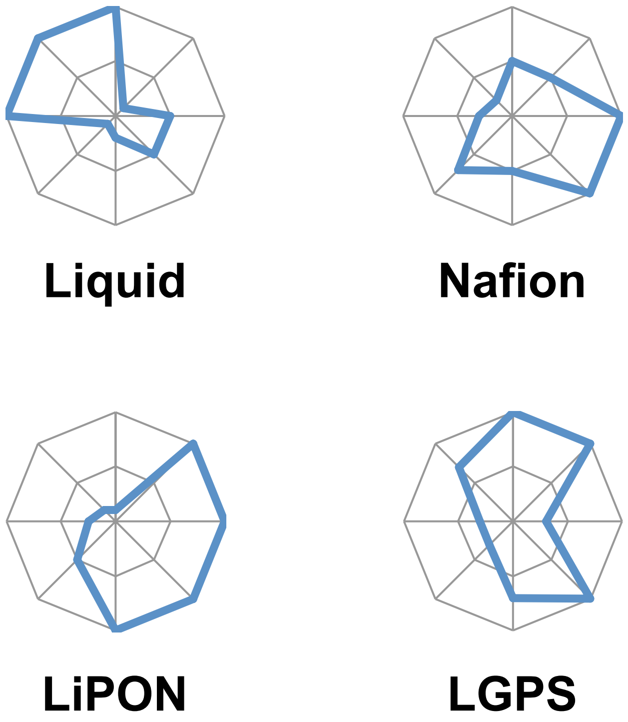
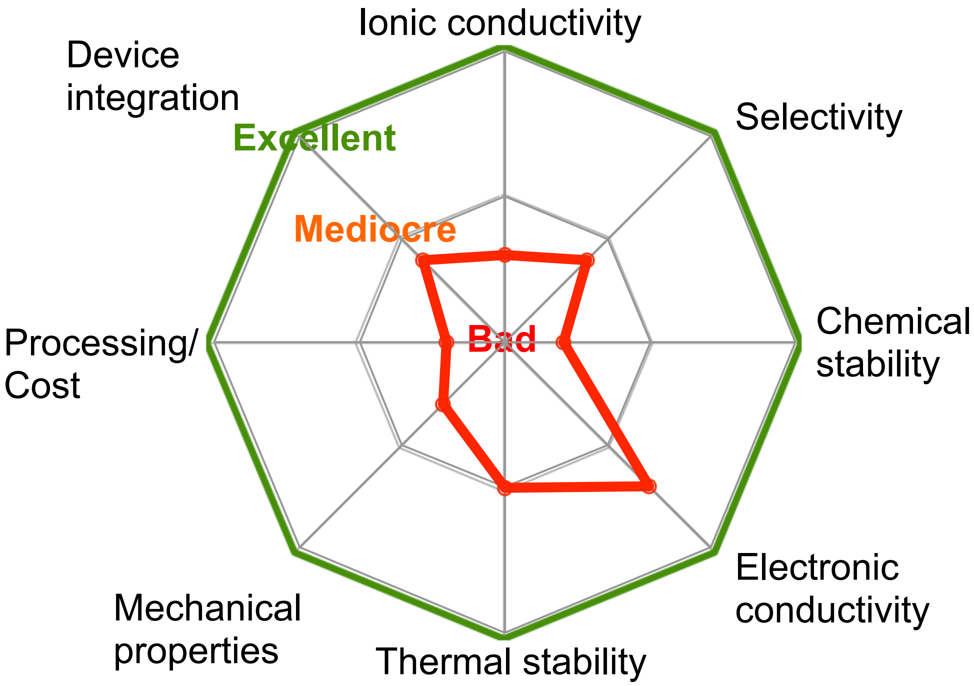
This program: *from the beginning* seek to overcome *fundamental property tradeoffs*

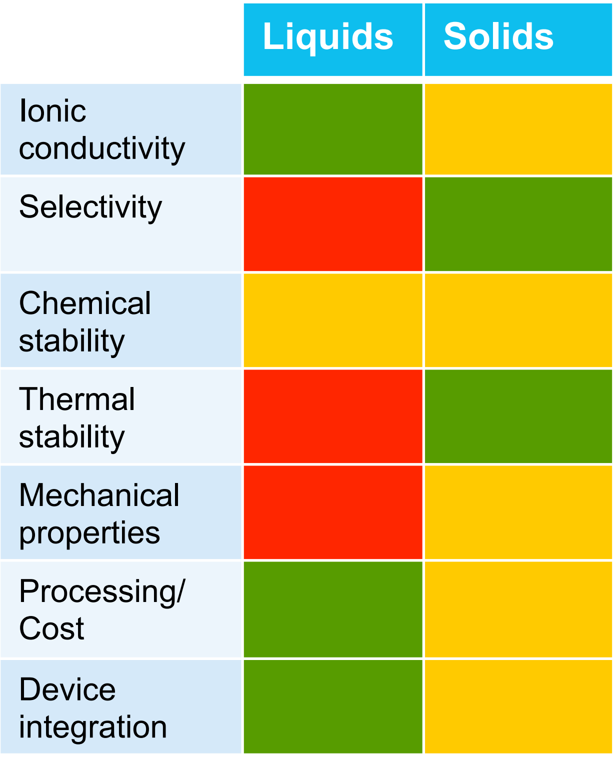




The problem: having it all, and at the same time

Liquids are SOA, but have fatal flaws

Solids need improvement, no fatal flaws



	Liquids	Solids
Ionic conductivity	🟩	🟨
Selectivity	🟥	🟩
Chemical stability	🟨	🟨
Thermal stability	🟥	🟩
Mechanical properties	🟥	🟨
Processing/ Cost	🟩	🟨
Device integration	🟩	🟨

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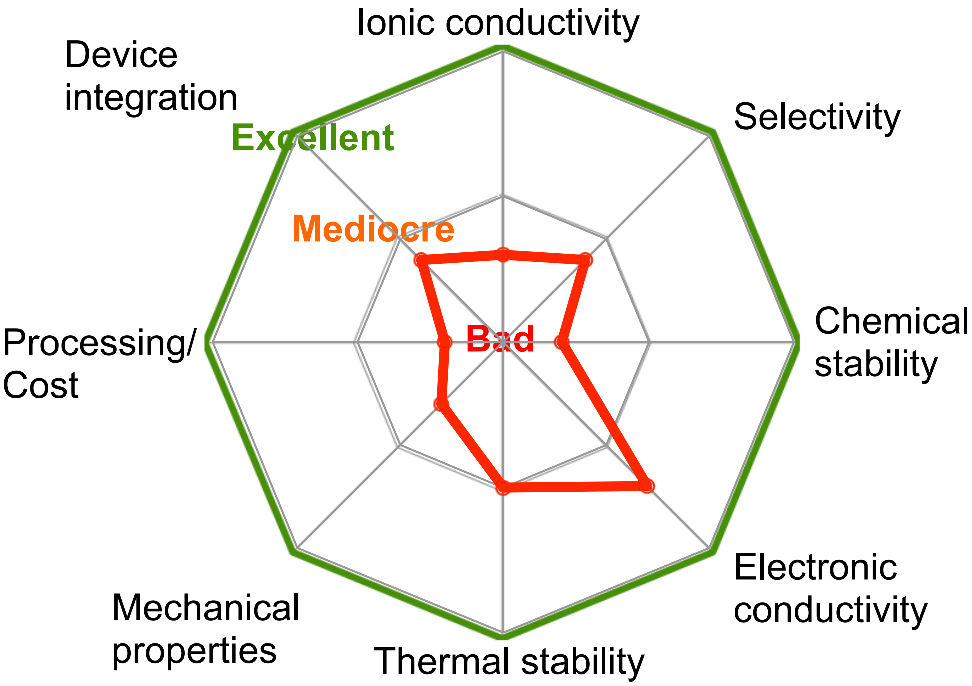


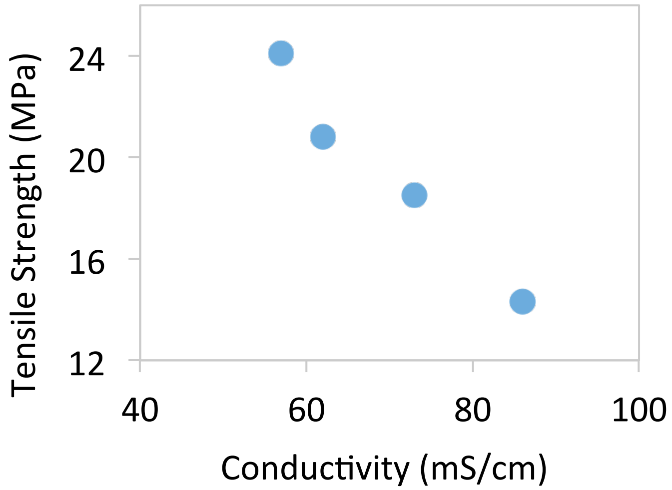
Sample approach: break free from tradeoffs

Example: a common tradeoff in alkaline polymer membranes

Independent variable:
Ion Exchange Capacity
(Charge carrier concentration)

Dependent variables

- ↑ conductivity
- ↓ mechanical properties (swelling)
- ↓ chemical stability



Ran et al., *Scientific Reports*, 4 (2014)
Pan et al., *Energy Environ. Sci.*, 7 (2014)

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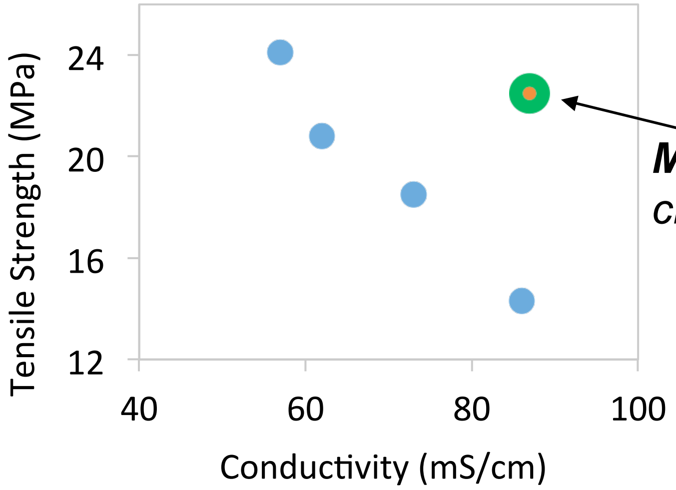
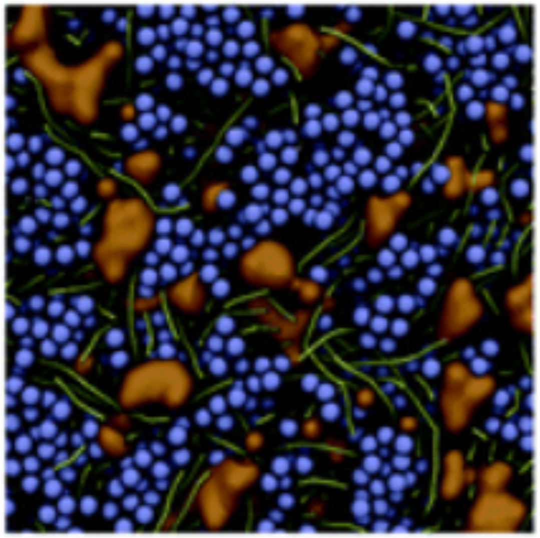


Morphology engineering
creates separate phases



Ran et al., *Scientific Reports*, 4 (2014)
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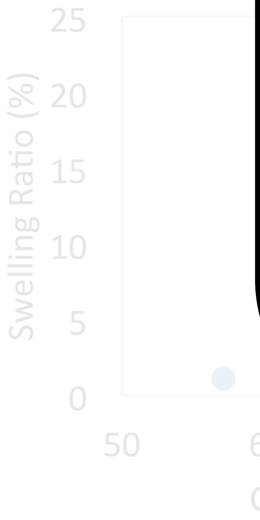
Sample approach: break free from tradeoffs

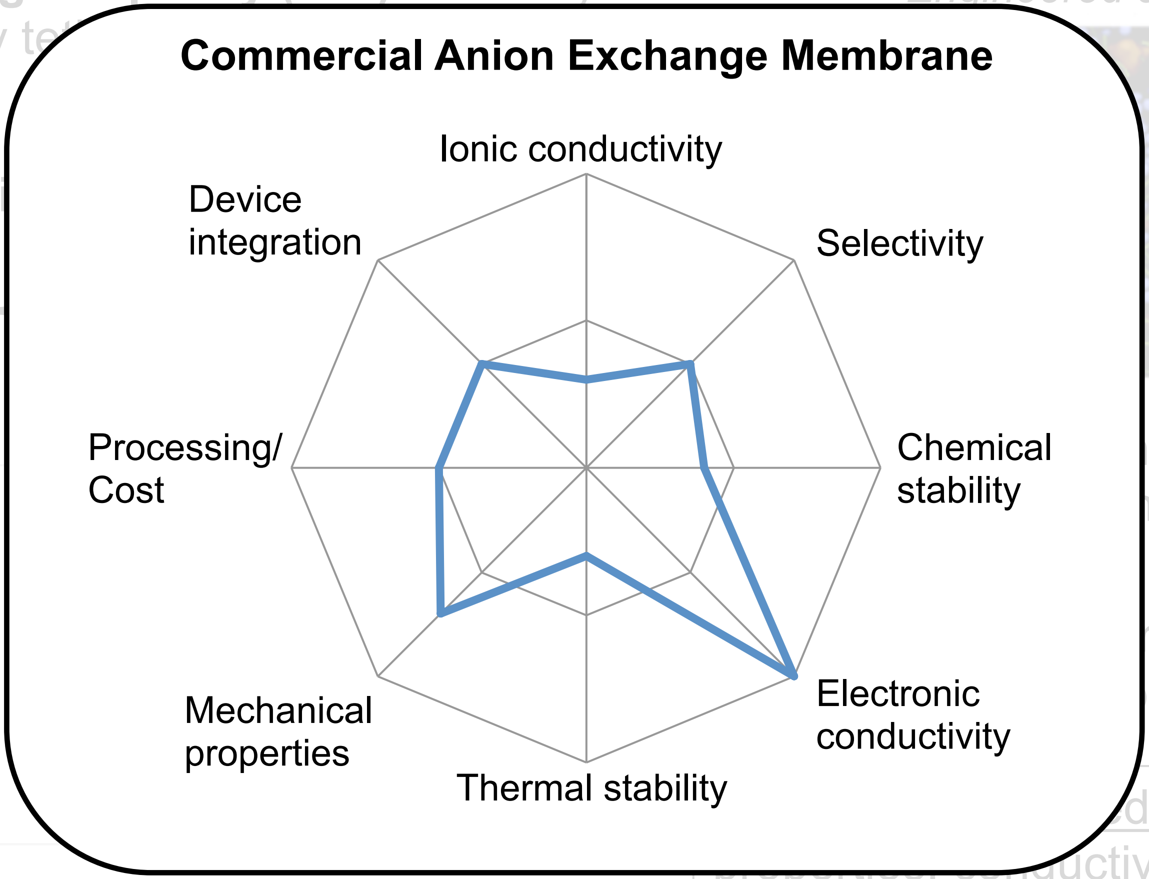
Ion Exchange Capacity (IEC) – density of covalently te

backbone

↑ conductivi

↑ swelling –





Engineered channels

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Ran et al., *Scientific Reports*, 4 (2014)
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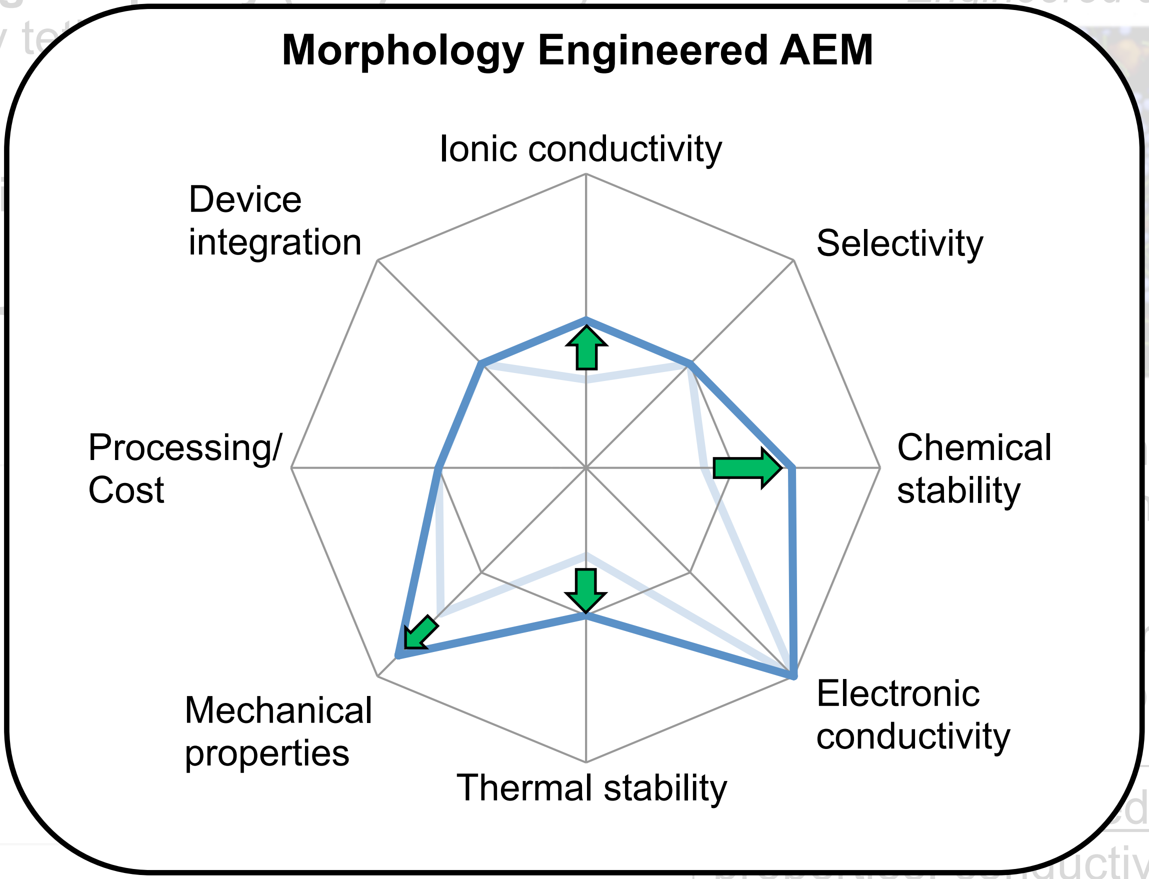

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Unifying program vision: cross-cutting technical approaches to overcome property tradeoffs

- Morphology engineering
- Polymer/inorganic composites
- Advanced processing of ceramics and glasses, including lower-temperature and continuous processing
- Fluorine chemistry for stability
- Self-forming mechanisms
- Conductive phases with enhanced properties
- …

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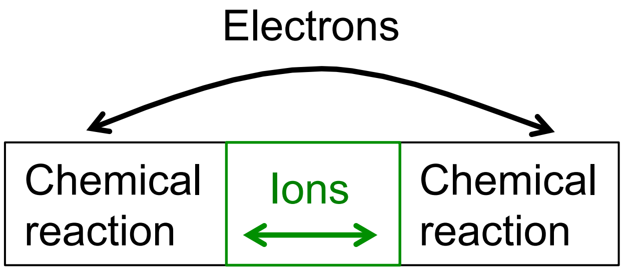
The electrochemical cell and the program focus

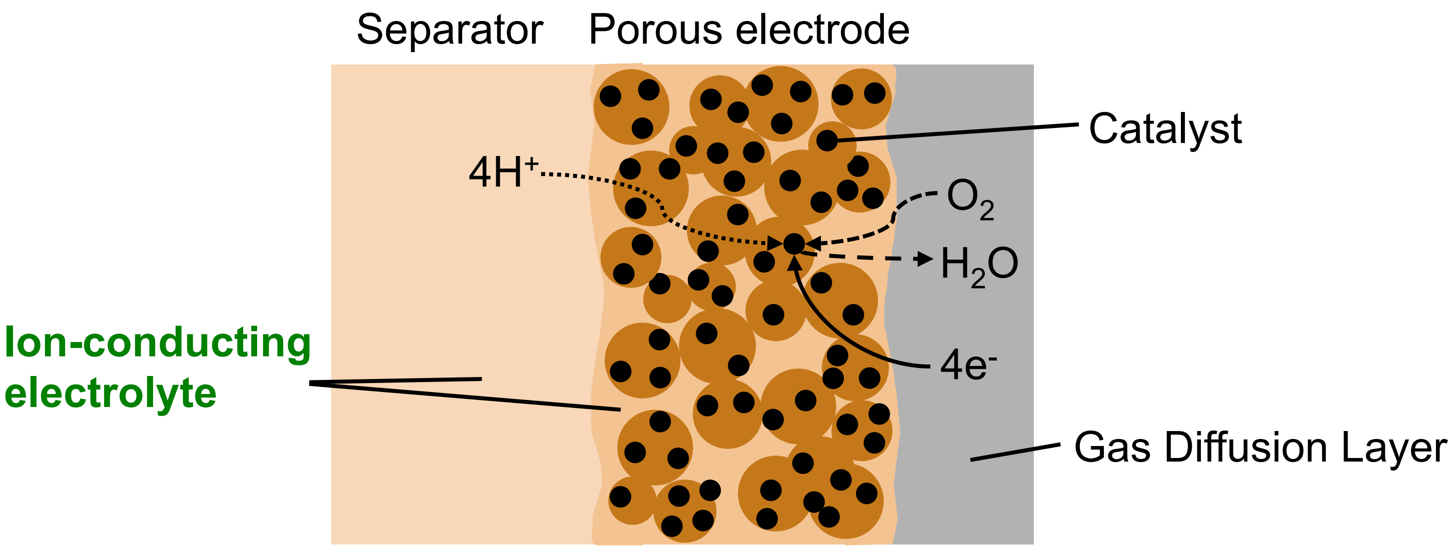
Electrochemical cell: schematic



Electrochemical cell: benefits

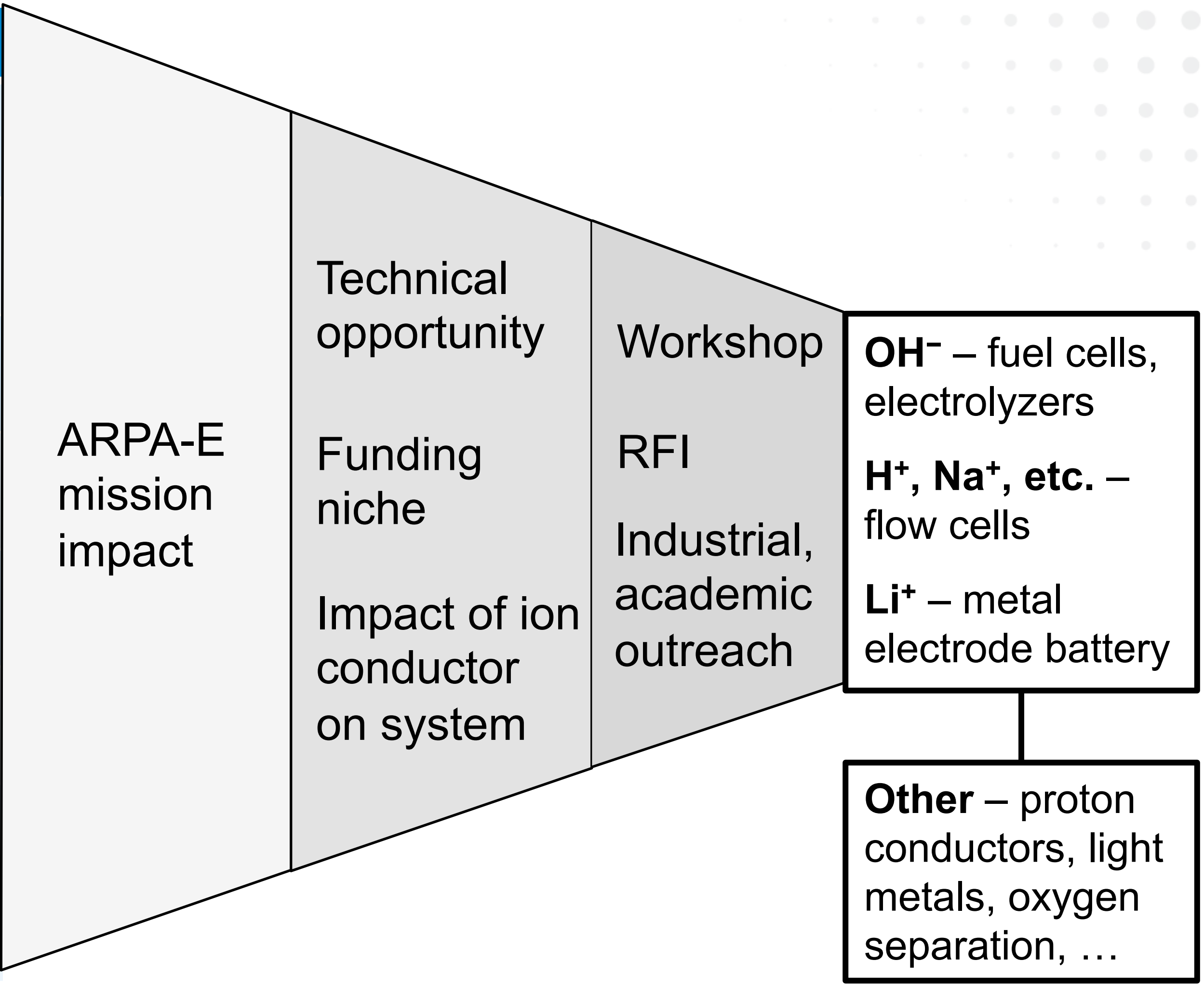
- Link chemical reactions with electron flow.
- High energy efficiency (90% RTE DC-DC possible)
- Scalable (milli-Watts to Mega-Watts)

Program focus: Ion-conducting electrolyte



We have defined categories from a broad space

Ion	Use
Li^+	Metal electrode, flow, and molten salt cells
OH^-	Stationary fuel cells, electrolyzers
H^+	Flow cells and stationary fuel cells
Mg^{2+}, Al^{3+}	Light metal production
O^{2-}, e^-	Air separation, Syn gas
H^+, e^-	Stationary fuel cells, electrosynthesis
Na^+	Metal electrode, AMTEC, Flow cells
…	…



ARPA-E mission impact

Technical opportunity

Funding niche

Impact of ion conductor on system

Workshop

RFI

Industrial, academic outreach

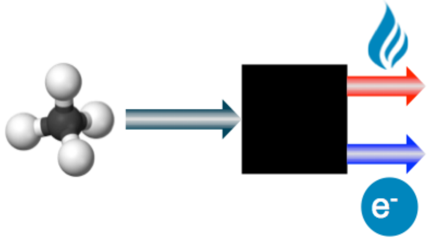
OH^- – fuel cells, electrolyzers

H^+, Na^+, etc. – flow cells

Li^+ – metal electrode battery

Other – proton conductors, light metals, oxygen separation, …

Program impacts span applications



Category	Application	Device Impact	Application Impact	Energy Impact
AEM	**CHP**	↓15% system cost	↑50% CHP adoption[1]	Energy ↓1% GHG ↓0.6%
	Vehicle Fuel Cells	↓25% system cost	10% FCV adoption	Oil ↓7% GHG ↓1%

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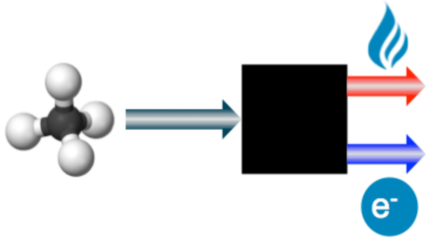
[1] White House 2020 goal

[2] Combined Heat and Power: A Clean Energy Solution, U.S. DOE and EPA (2012)

Program impacts span applications



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Flow Cell	**Grid Energy Storage**	<$100/kWh system cost	Enable >30% renewable penetration	GHG ↓

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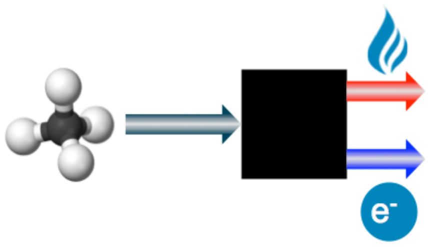

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Flow Cell	**Grid Energy Storage**	<$100/kWh system cost	Enable >30% renewable penetration	GHG ↓
Lithium	**Electric Vehicles**	<$125/kWh battery packs	↑10% EV adoption	Energy ↓1% Oil ↓3% GHG ↓1%

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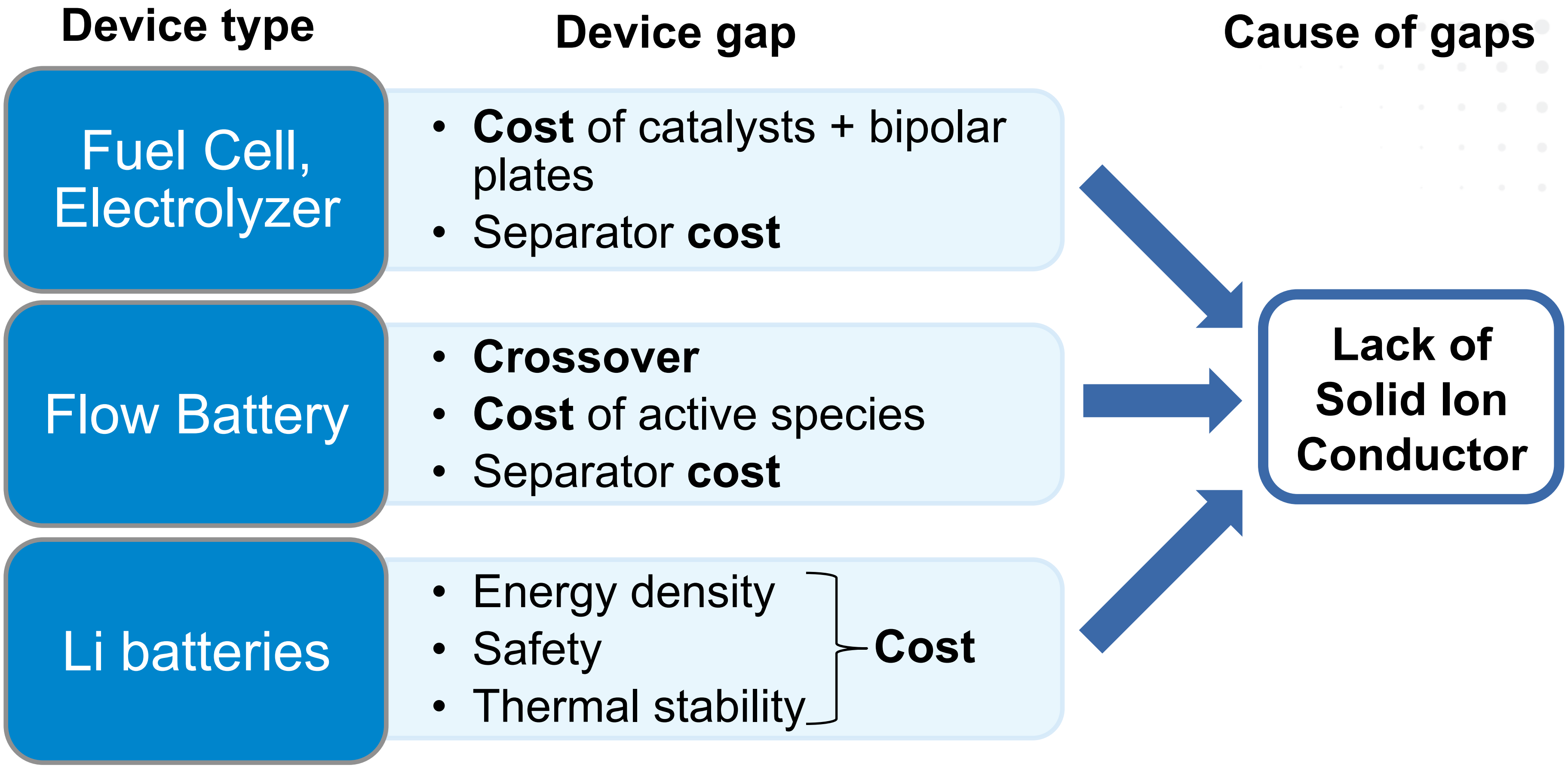
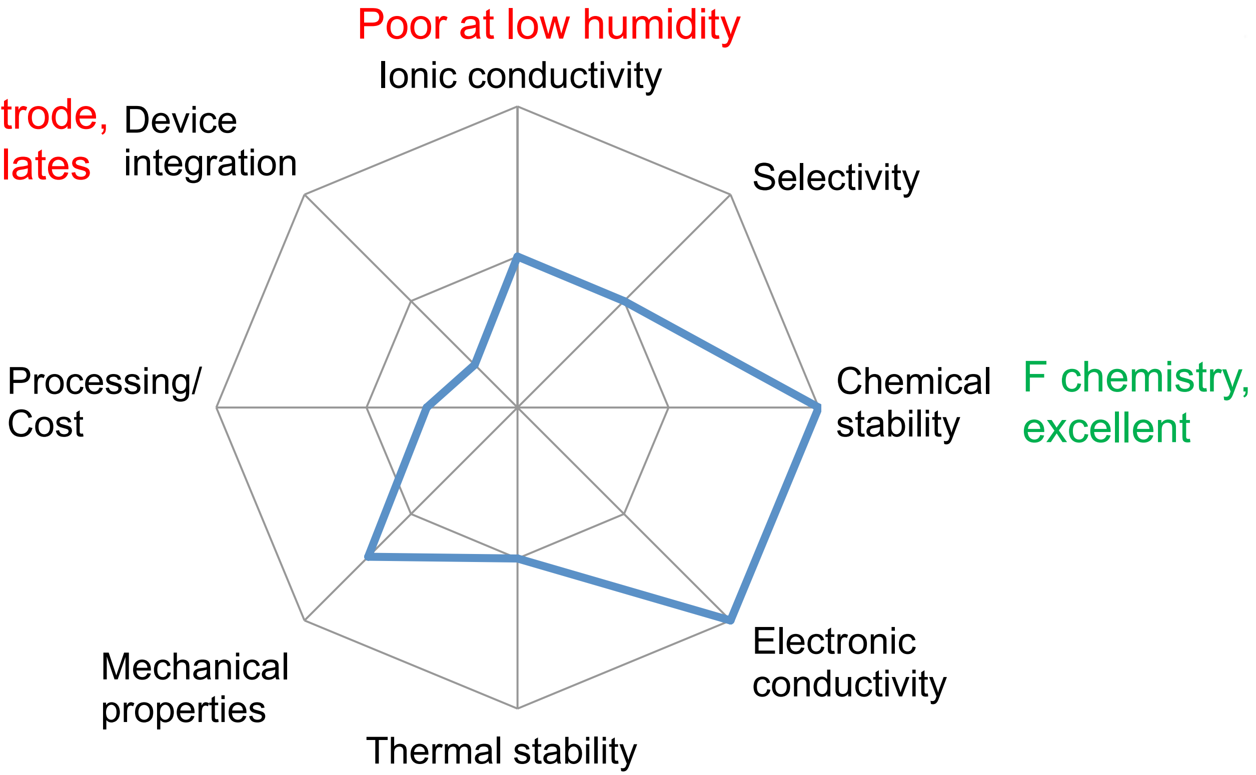
Problem: device gaps are limiting success



Device type	Device gap	Cause of gaps
Fuel Cell, Electrolyzer	• **Cost** of catalysts + bipolar plates • Separator **cost**	**Lack of Solid Ion Conductor**
Flow Battery	• **Crossover** • **Cost** of active species • Separator **cost**	
Li batteries	• Energy density • Safety • Thermal stability } **Cost**	

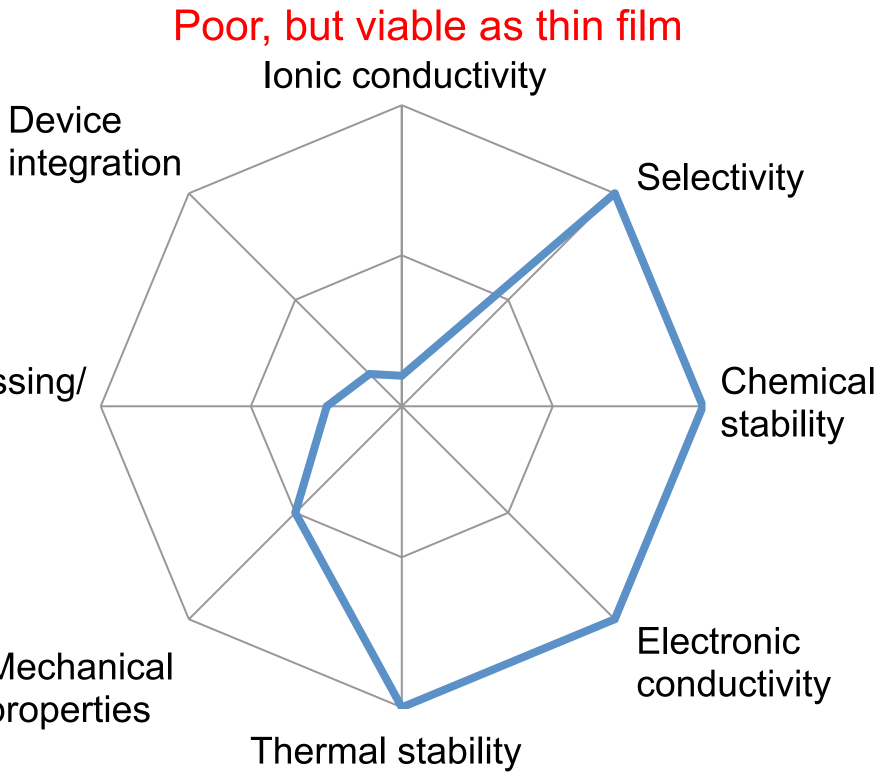
Solid ion conductor gaps example: Nafion

Nafion (H^+, other cations)



Solid ion conductor gaps example: LiPON

LiPON (Li^+ conductor)



Poor, but viable as thin film

Thin film only

Sputter deposited

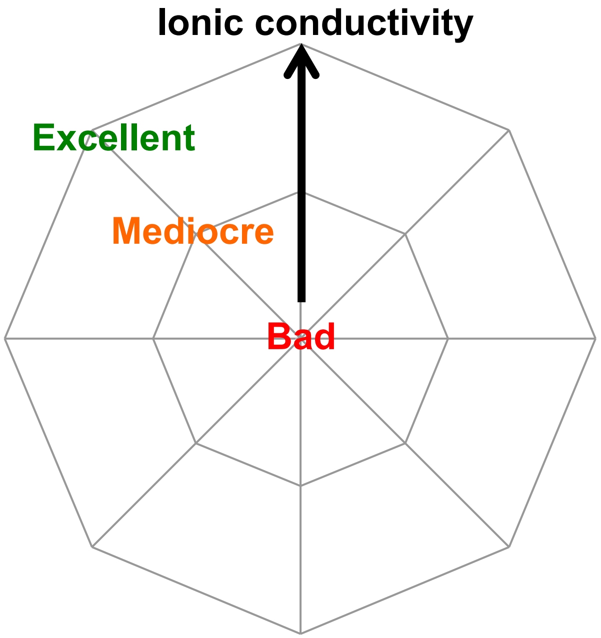
Excellent, >40k cycles

No Li dendrites

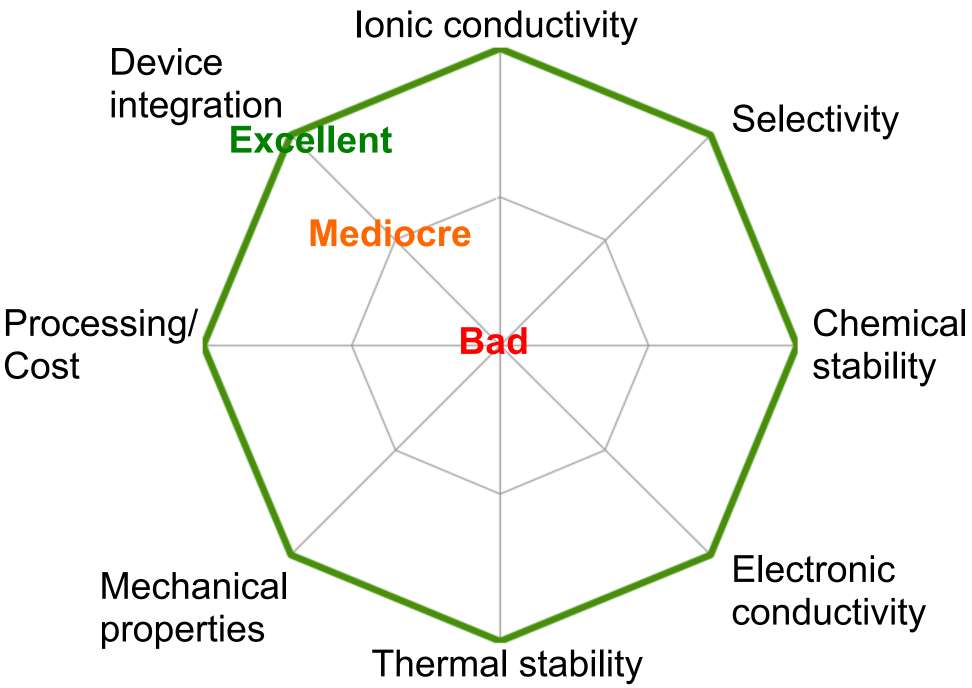
What approach does this program take?

- *From the beginning*, address the full set of relevant attributes.

Today's research



This program



Example: paradigm of much of today's research

LETTERS

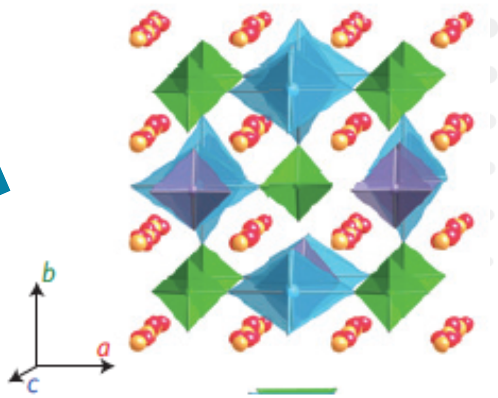
PUBLISHED ONLINE: 31 JULY 2011 | DOI: 10.1038/NMAT3066

nature materia

A lithium superionic conductor

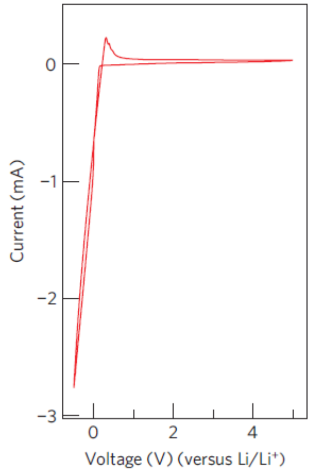
Noriaki Kamaya[1], Kenji Homma[1], Yuichiro Yamakawa[1], Masaaki
Masao Yonemura[2], Takashi Kamiyama[2], Yuki Kato[3], Shigenori Ha amoto[3]
and Akio Mitsui[4]

Solid conductivity equal to liquid!



But…

"Chemical Stability"



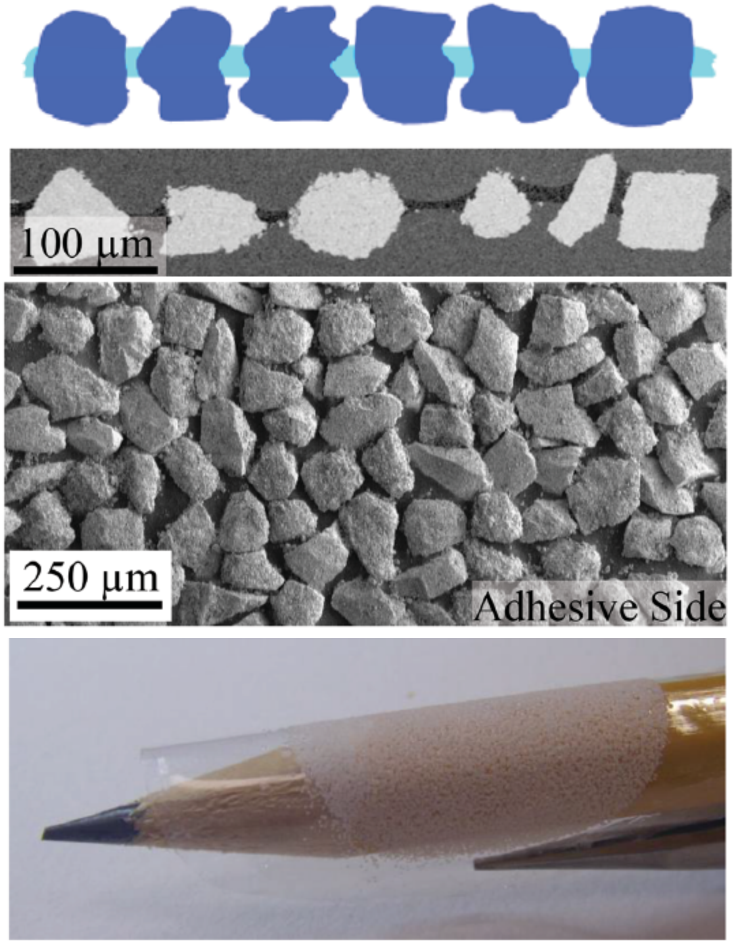
Material is not truly stable across a wide potential window

Other open questions:

- Mechanical properties
- Thermal stability
- Processing
- Device integration

Overcoming tradeoffs: Li^+ conductor

Li^+-conducting composite membrane



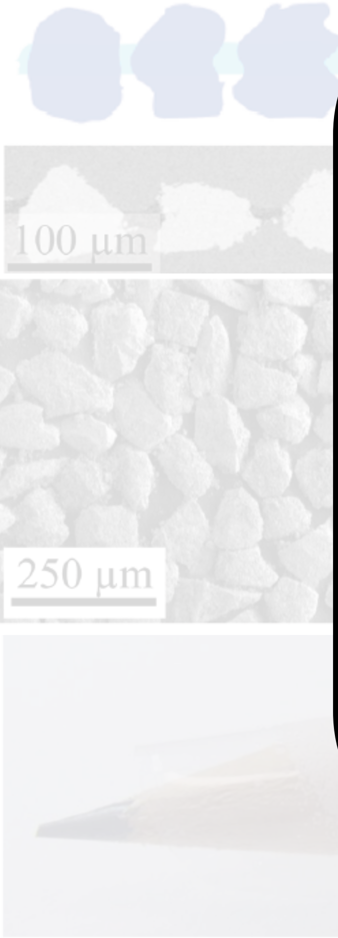
- Highlights of this paper:
  - Membrane suitable for **roll-to-roll processing**.
  - Polymer chosen for **chemical and thermal stability** in typical battery electrolytes.
  - **Eliminate processing** solid ceramic particles into a dense membrane.
  - **Measurement of Li dendrite formation** carried out.

Aetukuri et al., Advanced Energy Materials, 2015.

Ceramic: $Li_{1.6}Al_{0.5}Ti_{0.95}Ta_{0.5}(PO_4)_3$
Polymer: poly olefin

Overcoming tradeoffs: Li$^+$ conductor

Li$^+$-conducting composite membrane



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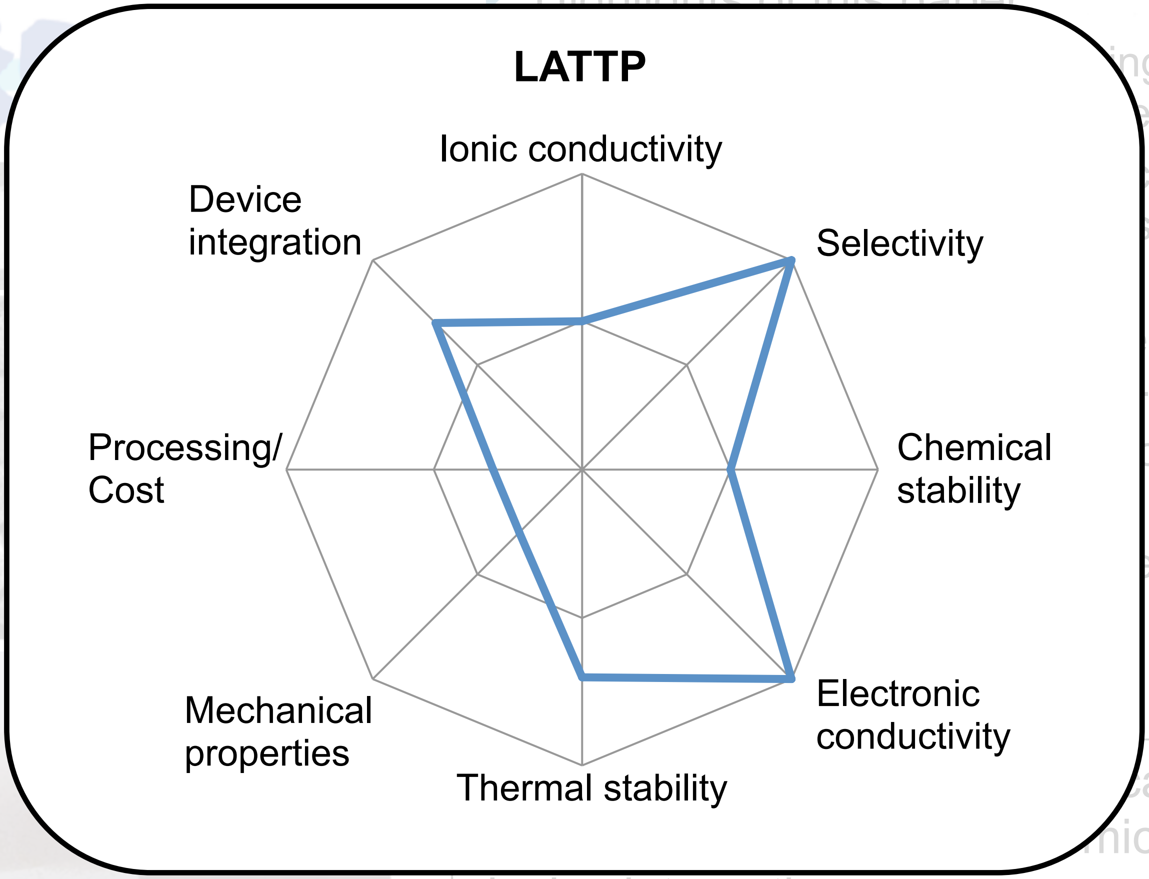

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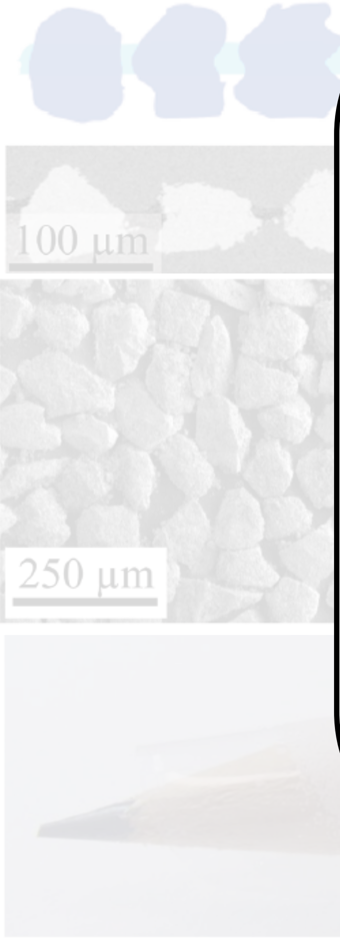

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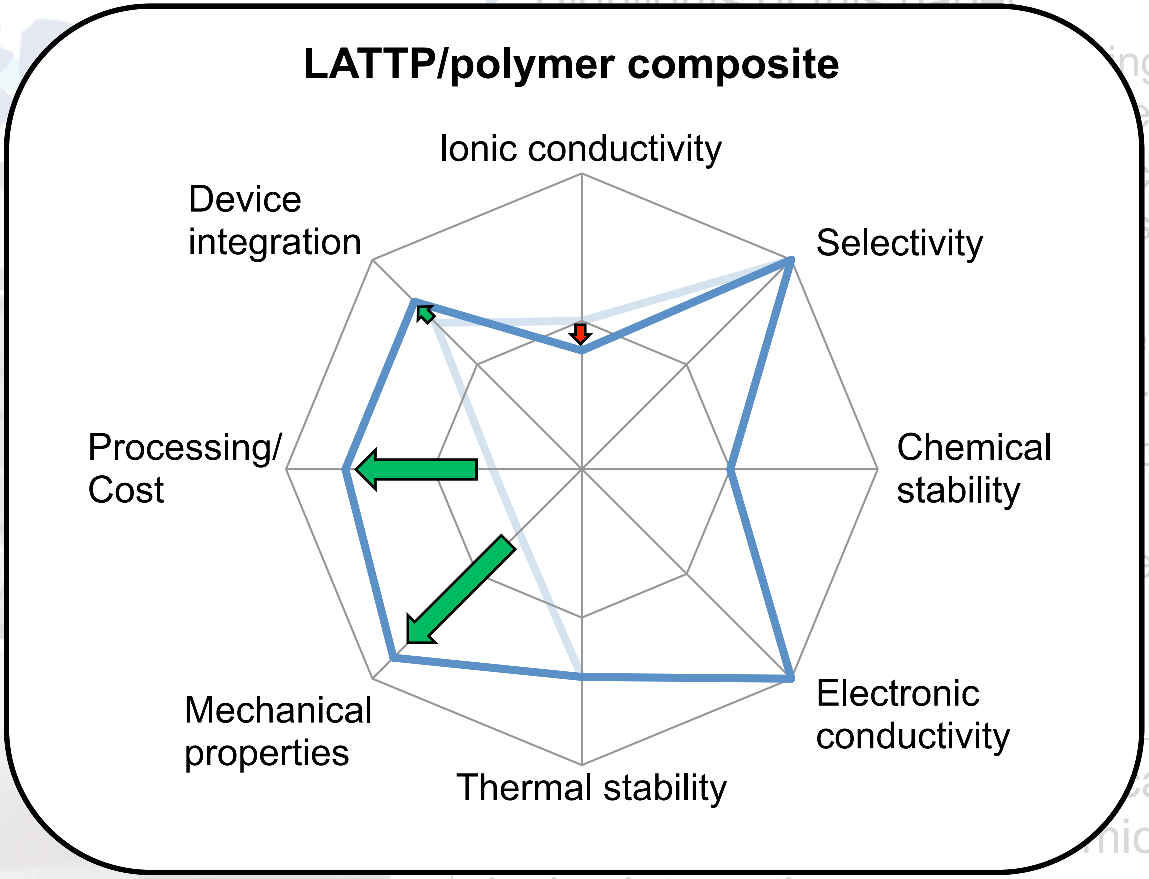


LATTP/polymer composite

Aetukuri et al., Advanced Energy Materials, 2015.

Ceramic: $Li_{1.6}Al_{0.5}Ti_{0.95}Ta_{0.5}(PO_4)_3$
Polymer: poly olefin

Overcoming tradeoffs: Flow battery membrane

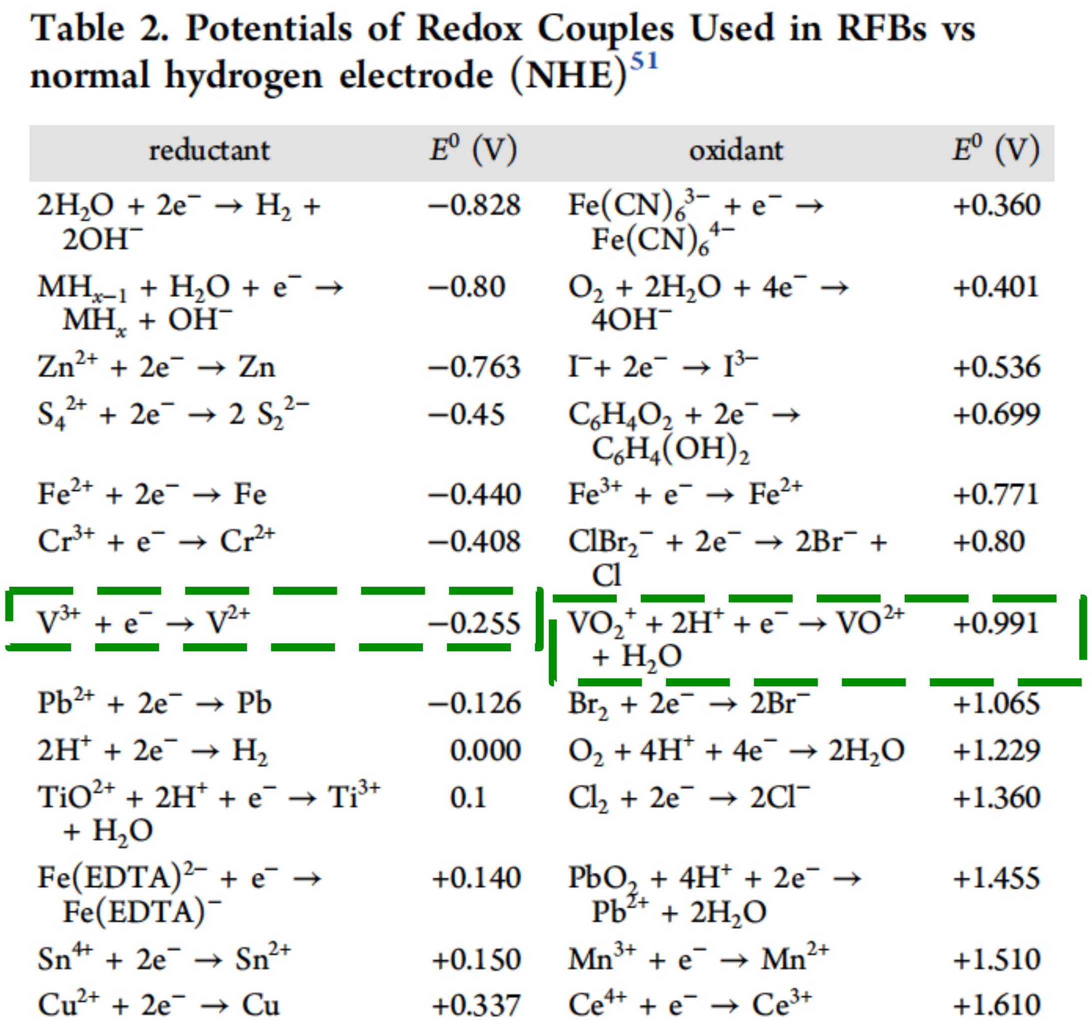
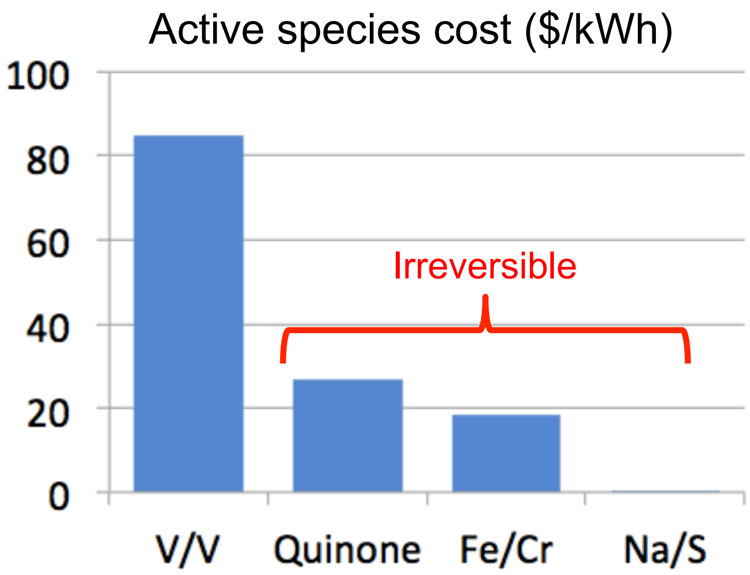


Table 2. Potentials of Redox Couples Used in RFBs vs normal hydrogen electrode (NHE)[51]

reductant	E^0 (V)	oxidant	E^0 (V)
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.828	$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	+0.360
$MH_{x-1} + H_2O + e^- \rightarrow MH_x + OH^-$	−0.80	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.401
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.763	$I^- + 2e^- \rightarrow I^{3-}$	+0.536
$S_4^{2+} + 2e^- \rightarrow 2\ S_2^{2-}$	−0.45	$C_6H_4O_2 + 2e^- \rightarrow C_6H_4(OH)_2$	+0.699
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.440	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.408	$ClBr_2^- + 2e^- \rightarrow 2Br^- + Cl$	+0.80
$V^{3+} + e^- \rightarrow V^{2+}$	−0.255	$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	+0.991
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.065
$2H^+ + 2e^- \rightarrow H_2$	0.000	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229
$TiO^{2+} + 2H^+ + e^- \rightarrow Ti^{3+} + H_2O$	0.1	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.360
$Fe(EDTA)^{2-} + e^- \rightarrow Fe(EDTA)^-$	+0.140	$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	+1.455
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.150	$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.510
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337	$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.610

Crossover limits commercial chemistries to those where it is reversible

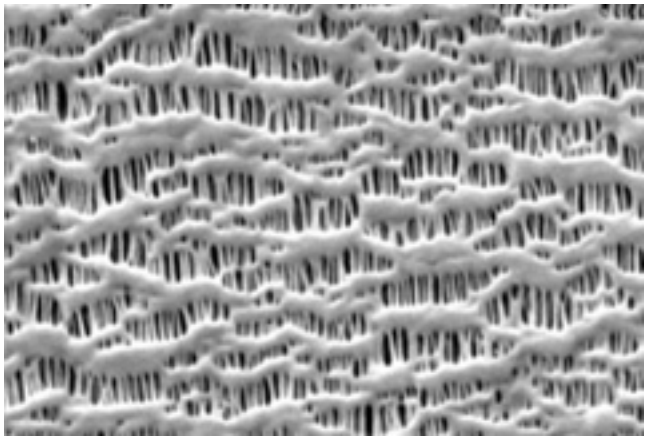
Many low-cost flow battery chemistries have **irreversible crossover**



Soloveichik, *Chemical Reviews*, 2015.

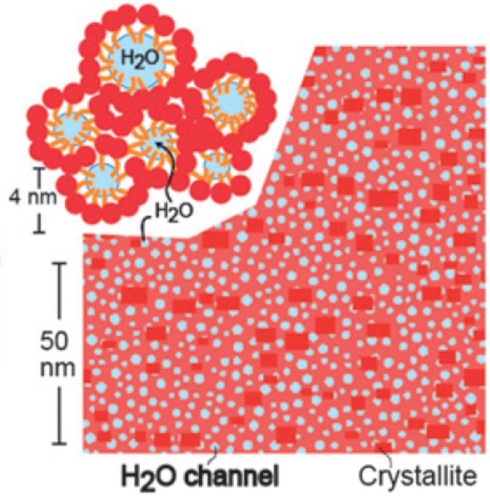
Overcoming tradeoffs: Flow battery membrane

Porous membrane



Cycles with crossover that is irreversible: 2

Typical ionomer



Cycles with crossover that is irreversible: 20

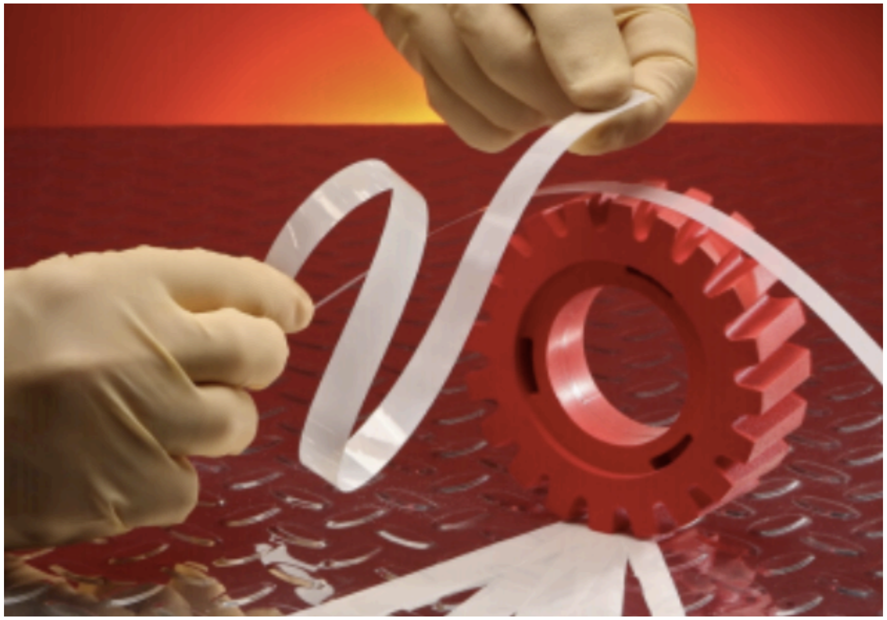
Other

?

Cycles with crossover that is irreversible: >5000

Inorganic?

Overcoming tradeoffs: Flow battery membrane



3YSZ from ENrG Inc.

- 20 to 40 microns thick
- Flexible
- 20 to 25 nm rms surface roughness
- Can be made in a R2R format

Thin oxide-conducting ceramics can be made for R2R processing

But there are also Na^+-conducting ceramics with ~1E-3 S/cm at 25°C

This could give us:

- >5000 cycles
- 0.1 V membrane loss @ 100 mA/cm^2
- <10 $/kWh membrane cost @ 5h discharge

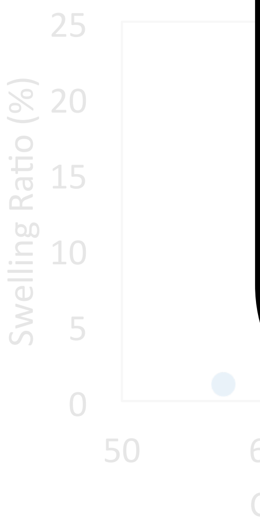
Overcoming tradeoffs: Flow battery membrane

Ion Exchange Capacity (IEC) – density of covalently te

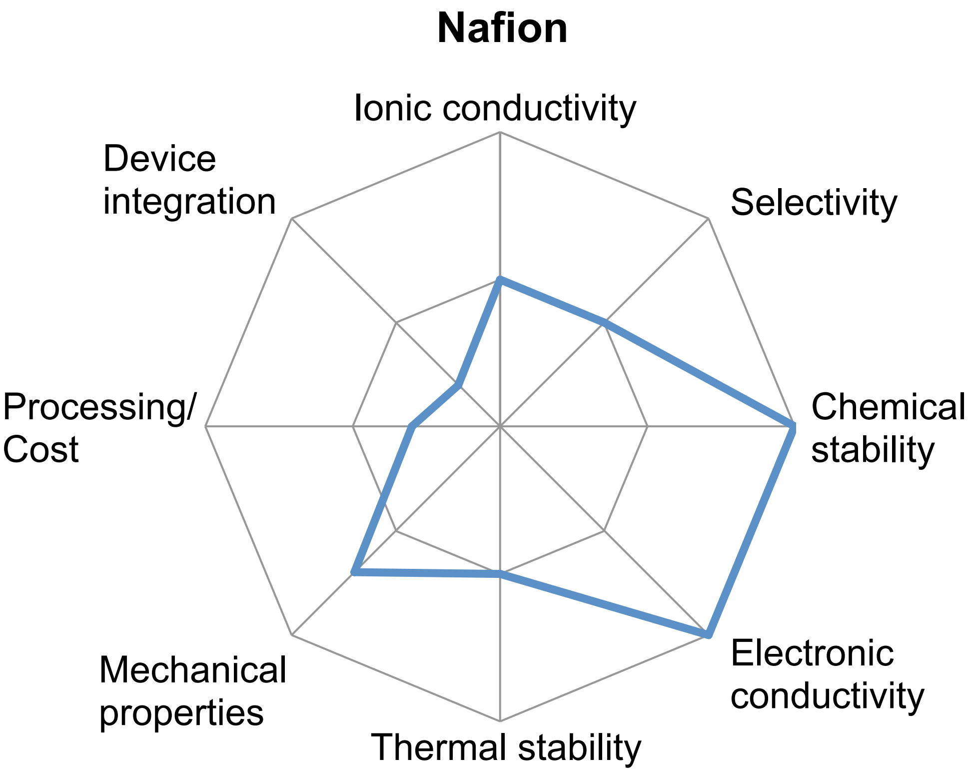
backbone

↑ conductivi

↑ swelling –



Engineered channels



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d: mechanical

properties, conductivity, chemical

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Ran et al., *Scientific Reports*, 4 (2014)
Pan et al., *Energy Environ. Sci.*, 7 (2014)

Overcoming tradeoffs: Flow battery membrane

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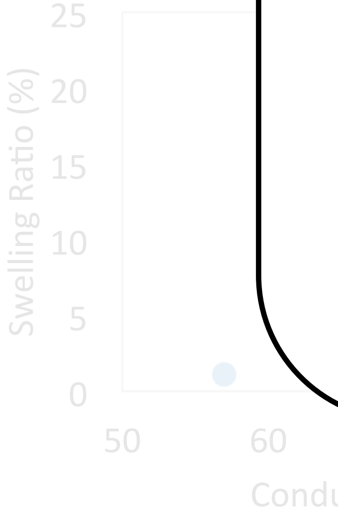
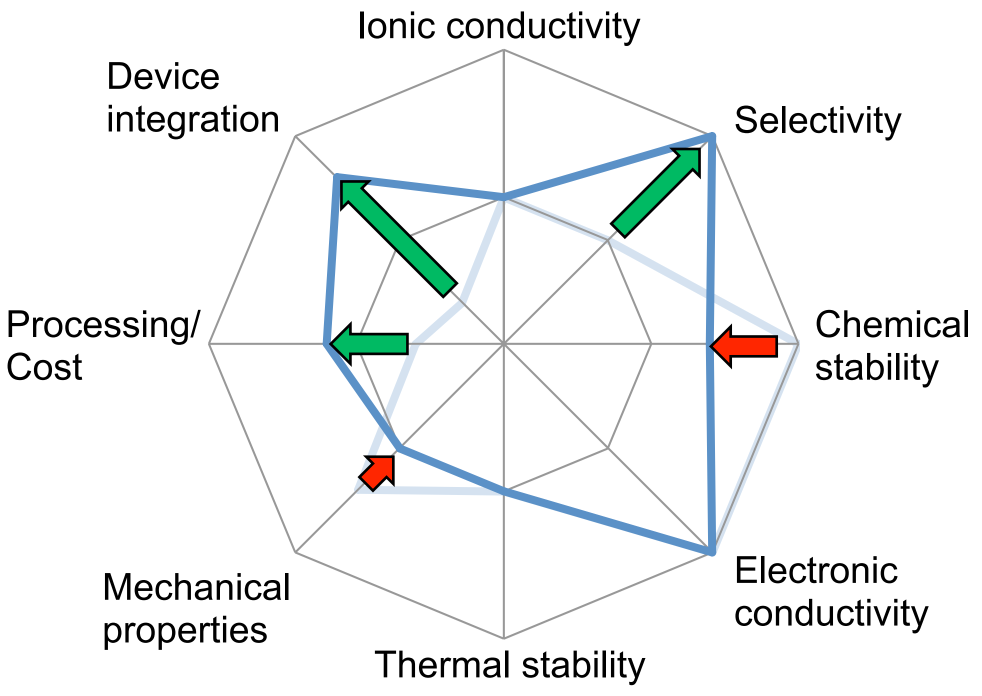


Novel processed Na-conducting ceramic



Engineered channels

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Ran et al., *Scientific Reports*, 4 (2014)
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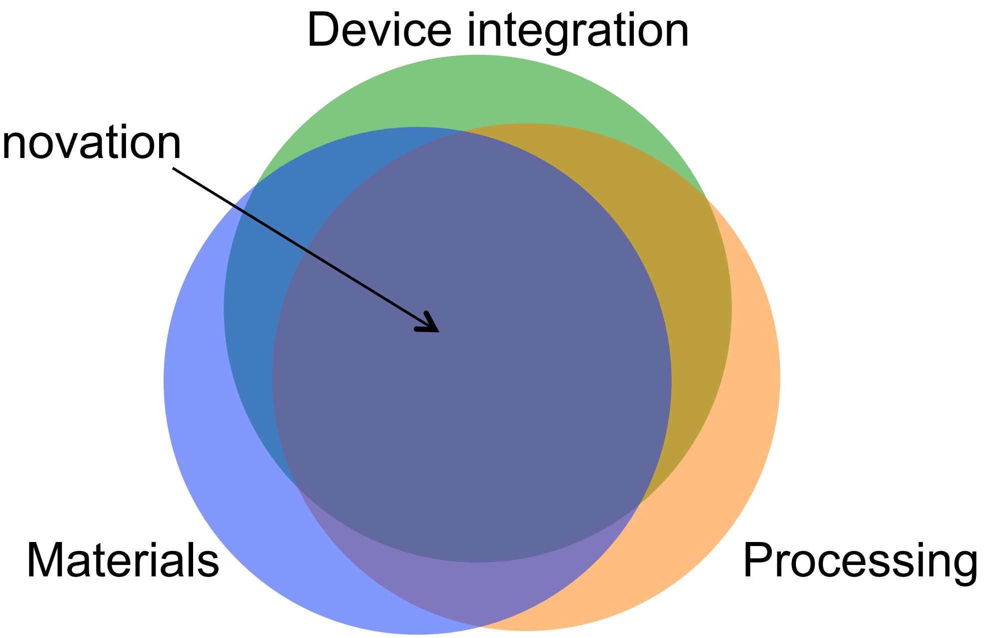
Where will the innovation happen?

Device integration

Materials

Processing

Innovation primarily at the intersections



Foundational science and engineering

- solid state ionics
- inorganic chemistry
- solid state chemistry
- polymer-polymer compos.
- functional glasses
- polymer-ceramic compos.
- mechanical properties
- thin film deposition
- organic chemistry
- photoelectrochemistry
- analytical mat. sci.
- process engineering

Key deliverables summary

This is a **critical component program** focused on delivery of high-performance solid ion conductors with an **area of at least 100 cm^2**.

	Alkaline conductors	**Selective conductors for flow batteries**	**Li^+ conductors**	**Other**
Key metrics	• **Chemical stability** of >10k hours at pH 14 and 80°C • **Cost** at volume of <10 $/$m^2$ • **Area-specific resistance** of 0.02 Ω-cm^2 at 80°C and 100% RH • **Tensile strength** of 20 MPa • **Mechanical durability** of 20k RH cycles	• **Negligible crossover** that enables >5000 cycles • **Cost** of active + separator of <40 $/kWh • **Area-specific resistance** of <0.5 Ω-cm^2	• **Enable use of Li metal** with modulus and microstructure to prevent Li penetration • **Cost** at volume of <10 $/$m^2$ • **Chemical stability** of 0 to 4.5 V • **Area-specific resistance of** <5 Ω-cm^2	

Device testing is necessary, but the program focus is component development, not device optimization

This is a single program, not three

The concepts for overcoming tradeoffs do not apply to just one materials class or application

Potential cross-cutting topics

- Fluorination: is there a lower cost way to achieve chemical stability?
- Binding polymers with inorganics when mechanics, charge transfer resistance, and other properties are important.
- Are new low-T ceramics fabrication approaches such as flash sintering scalable?
- Can we extend existing self-forming mechanisms to new materials?

Related Fall 2015/Spring 2016 MRS symposia	
EE6	Liquid-Solid **Interfaces** in Electrochemical Energy Storage and Conversion Systems
EE7	**Mechanics** of Energy Storage and Conversion
MD1	Materials, Interfaces and Devices **by Design**
MD2	Tuning Properties by **Elastic Strain Engineering**
B	Stretchable and Active **Polymers and Composites** for Energy and Medicine
T	**Strength** and Failure at the Micro- and Nanoscale
LL	**Materials and Architectures** for Safe and Low-Cost Electrochemical Energy Storage Technologies
PP	Materials, Interfaces and **Solid Electrolytes** for High Energy Density Rechargeable Batteries

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New community: Solid ion conductors that overcome property tradeoffs and create a pathway to commercial application

Questions