RUTGERS
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ENERGY STORAGE RESEARCH GROUP
ESRG

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Battery Materials and Issues for Grid Applications

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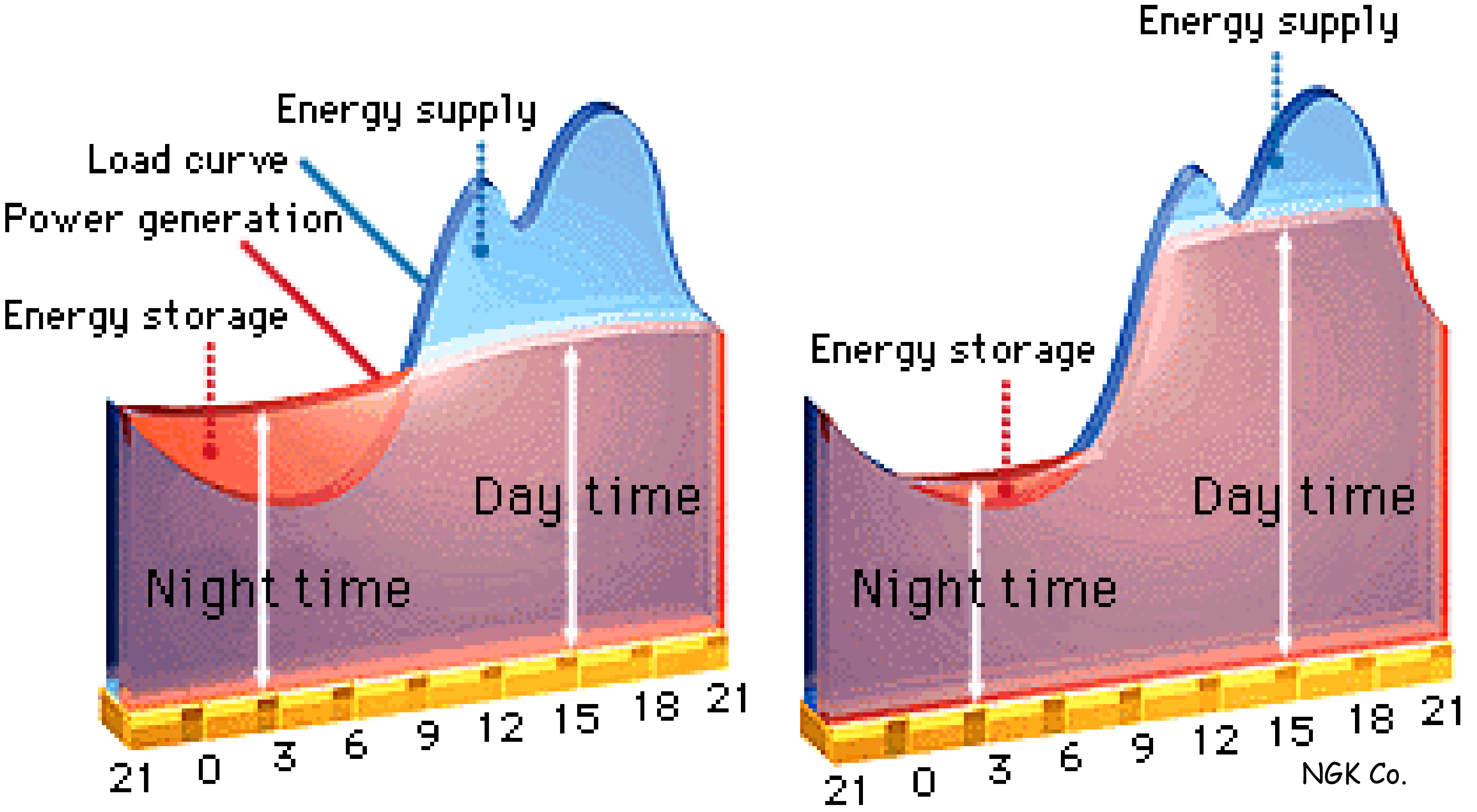
The Challenge Presented by the Grid and Renewable Energy



- Energy Storage is Clearly a Critical Component
- What Path? Electrochemical or Other
- If Electrochemical, what are the options present and future…

Introduction

≠

Burn rubber, not gasoline.

Introducing the Tesla Roadster:

- 100% electric
- 0 to 60 in about 4 seconds
- 135 mpg equivalent
- 250 miles per charge
- about 1¢ per mile*

TESLA ROADSTER

≠

- Energy density
- Safety
- Lifetime/Cost
- Power density

- Safety
- Power/Energy Density
- Lifetime Cost

- Lifetime Cost
- Scalability
- Power/Energy Density
- Safety

Although all have similar list of key performance criteria
Distinctly different priorities

Introduction

Ultra Low lifetime cost Electrochemical Systems for Grid:

Key Requirements:

a. Low Lifetime Cost (25 yr)
b. Charge / discharge efficiency = $
c. Green

Many Options:

- Redox Flow: Vanadium, Zn/Br, others
  Very low cost / scalability → Large applications
- Na/S or $FeCl_2$, $NiCl_4$ (Zebra) (latter safer in failure mode):
  high energy/ Good for localized apps.
- Hybrid ultracapacitors
- Li, Mg and Ca non-aqueous
- Li aqueous
- Regenerative fuel cell
- Symmetric and Asymmetric Supercapacitors

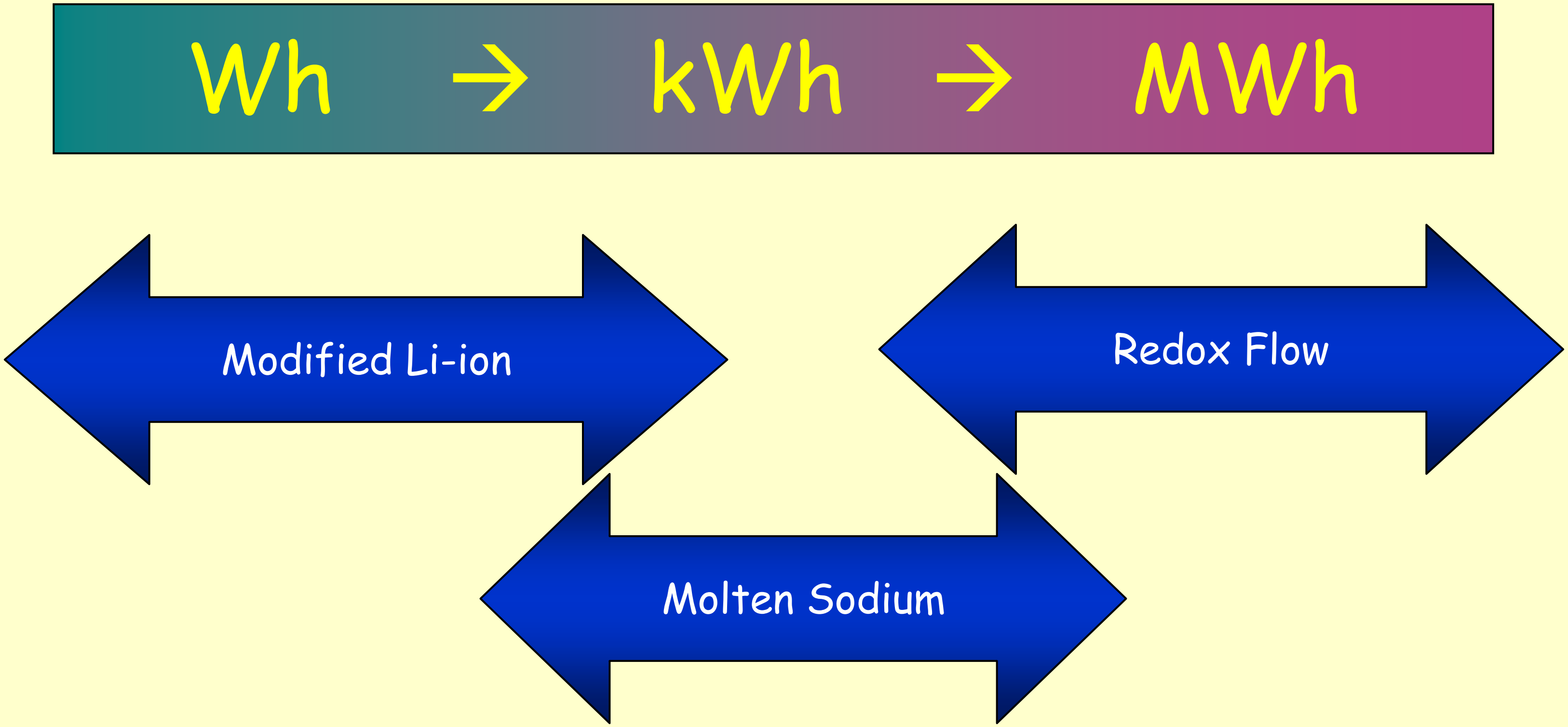
- Which one to choose? depends on application
- For this talk we focus on batteries..

Introduction

Batteries and the grid

We should not hope or look for a single solution, much depends on application

-We will take a look at 3 different options from the materials perspective



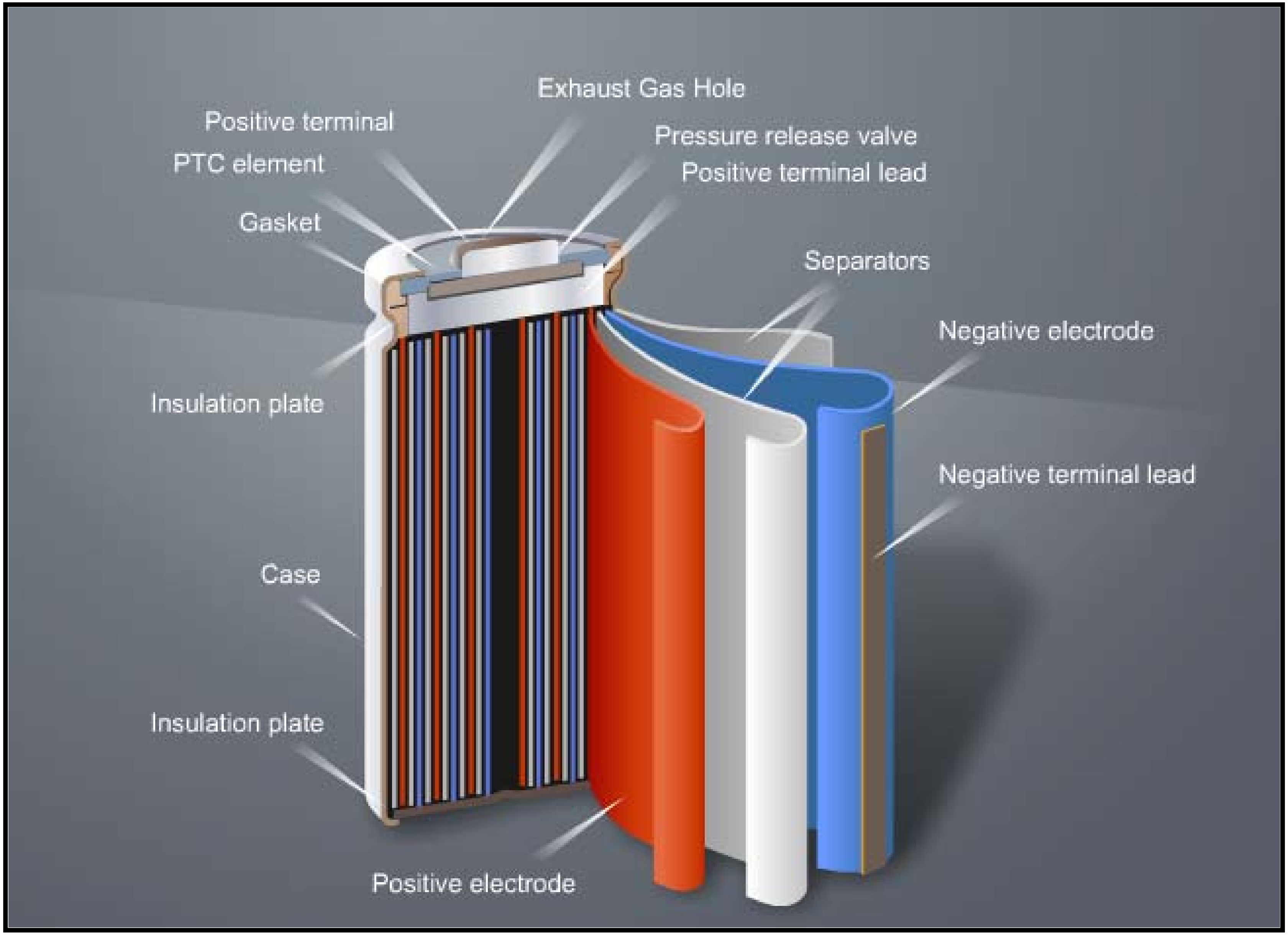
Wh → kWh → MWh

Modified Li-ion

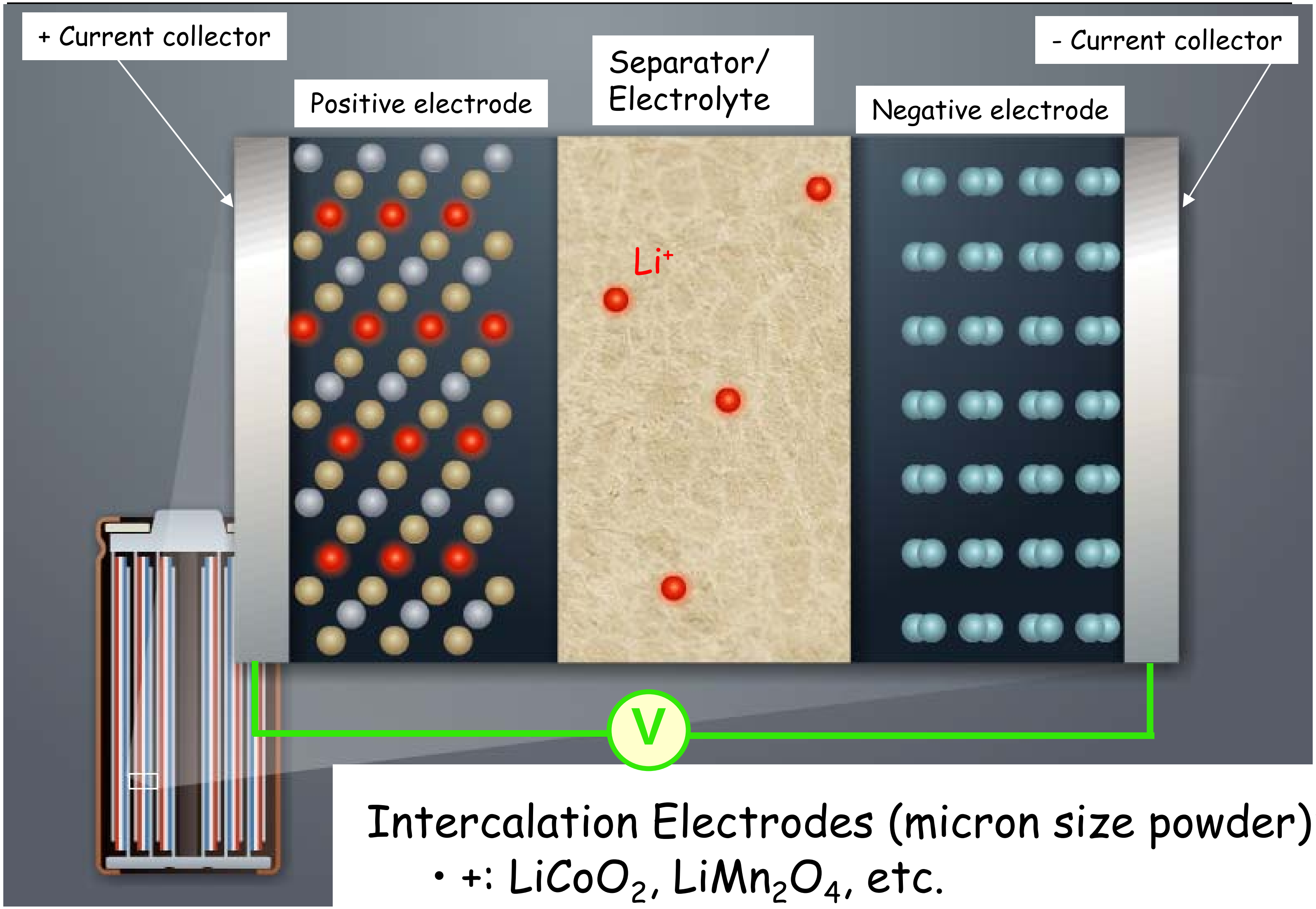
Redox Flow

Molten Sodium

Generic Battery Structure



Batteries: Lithium and Lithium-ion

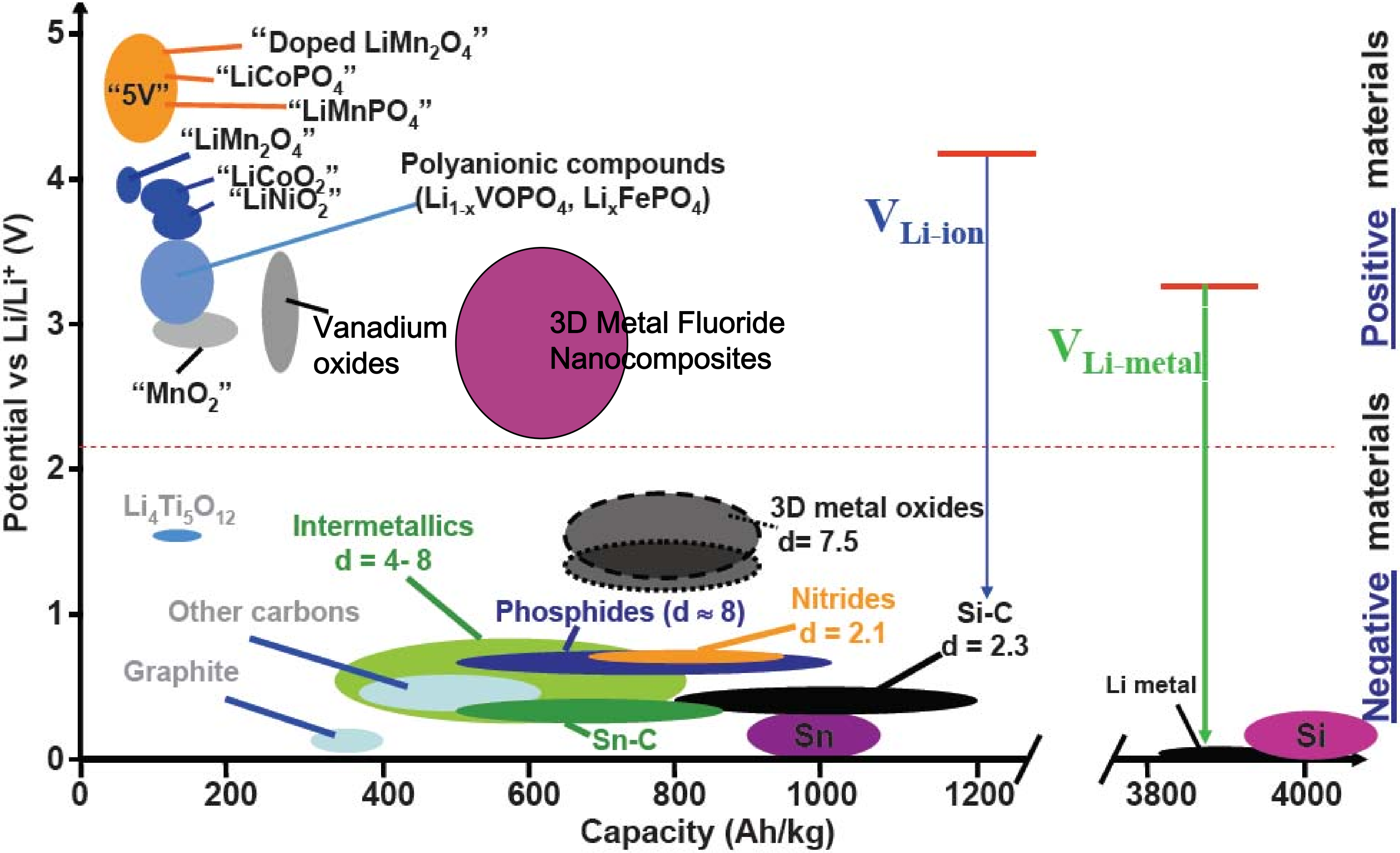


Intercalation Electrodes (micron size powder):

- +: $LiCoO_2$, $LiMn_2O_4$, etc.
- - : Graphite (LiC_6)

- *grid will require alternative approaches…*

The Electrochemical Design of Li Battery Technology



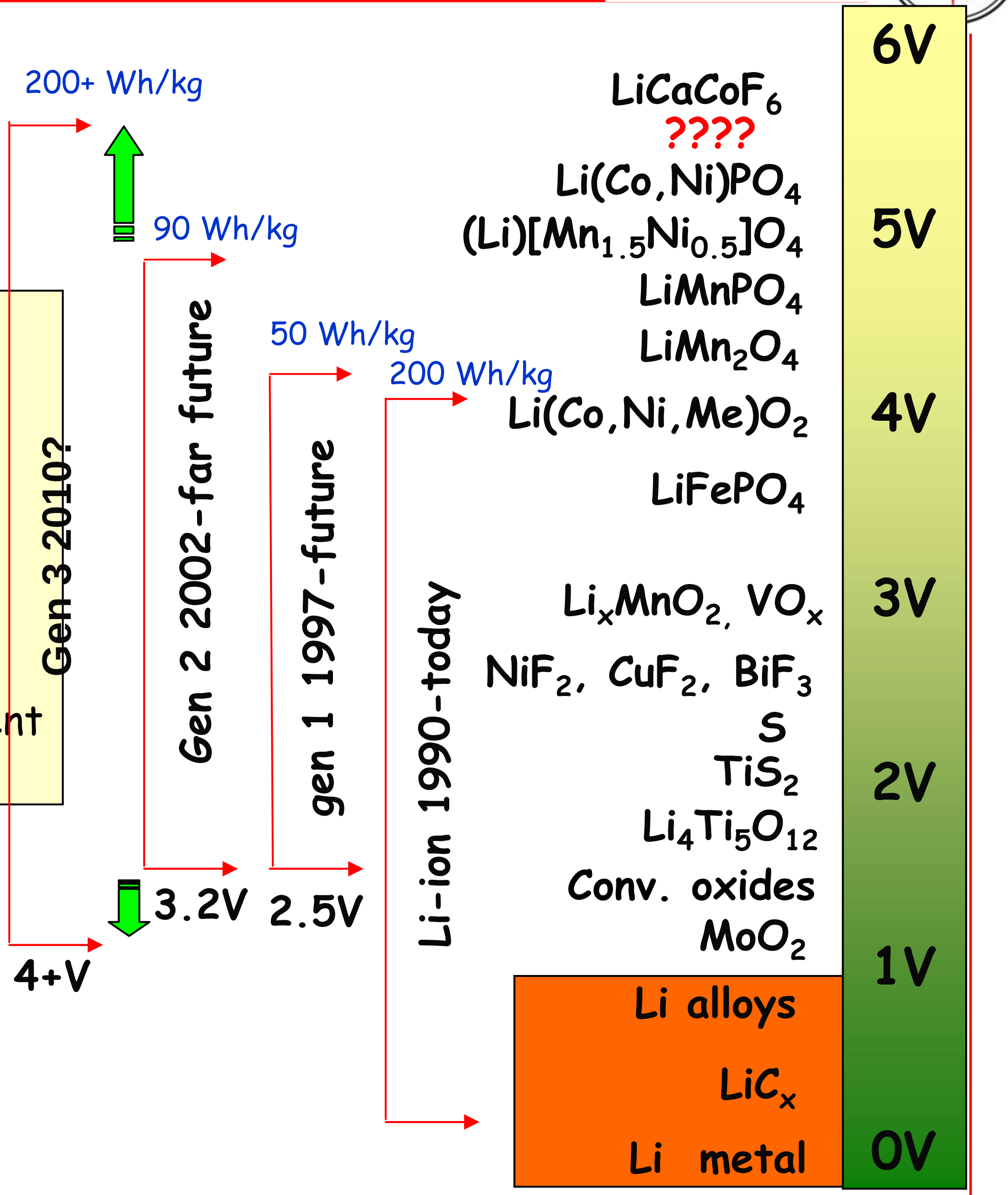
- Wide array of materials departing from today's SOA for portable power

Modified from J.M. Tarascon and M. Armand, Nature, 2001 (359-367)

Large Applications: Window “Shift” Option

Why Window Shift:
Increase potential of - electrode
- Safety: reduced H_2 with H_2O/fire
- Low T Performance: Little SEI
- Fast Charge: No Li plating
- Long Life: Focus electrolytes on one voltage extreme relative to SHE
- Voltage more important than capacity

For high rate applications (usually current density limited)



Gen 3 2010?
200+ Wh/kg
4+V

Gen 2 2002-far future
90 Wh/kg
3.2V

gen 1 1997-future
50 Wh/kg
2.5V

Li-ion 1990-today
200 Wh/kg

$LiCaCoF_6$
????
$Li(Co,Ni)PO_4$
$(Li)[Mn_{1.5}Ni_{0.5}]O_4$
$LiMnPO_4$
$LiMn_2O_4$
$Li(Co,Ni,Me)O_2$
$LiFePO_4$
Li_xMnO_2, VO_x
NiF_2, CuF_2, BiF_3
S
TiS_2
$Li_4Ti_5O_{12}$
Conv. oxides
MoO_2
Li alloys
LiC_x
Li metal

6V
5V
4V
3V
2V
1V
0V

Electric Grid Applications: General Materials: NEEDS

Positive electrodes:

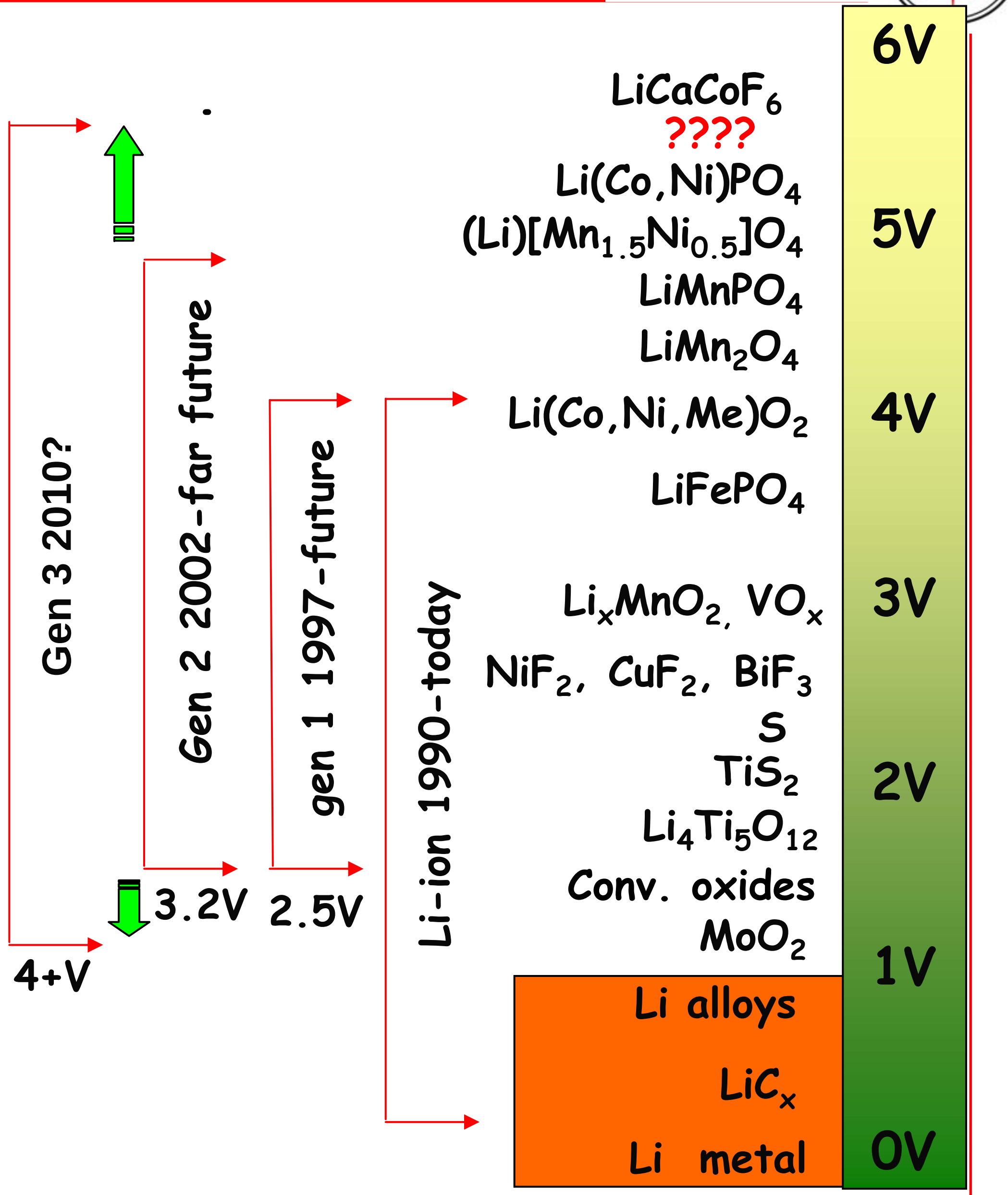
- Path: low cost but high performance: example -phosphates
- Anion stability towards oxidation: inductive polyanion or fluorides
- Material safety = polyanion
- New inductive effect polyanion compounds in 4-5V range

Negative electrode

- lower V than $Li_4Ti_5O_{12}$: 1-1.2V
- higher capacity than LTO

Electrolytes

- Low Cost
- High V stability
- Low flammability
- No vapor pressure
- SHUTTLES



Paths towards ultra low cost: General Materials: NEEDS

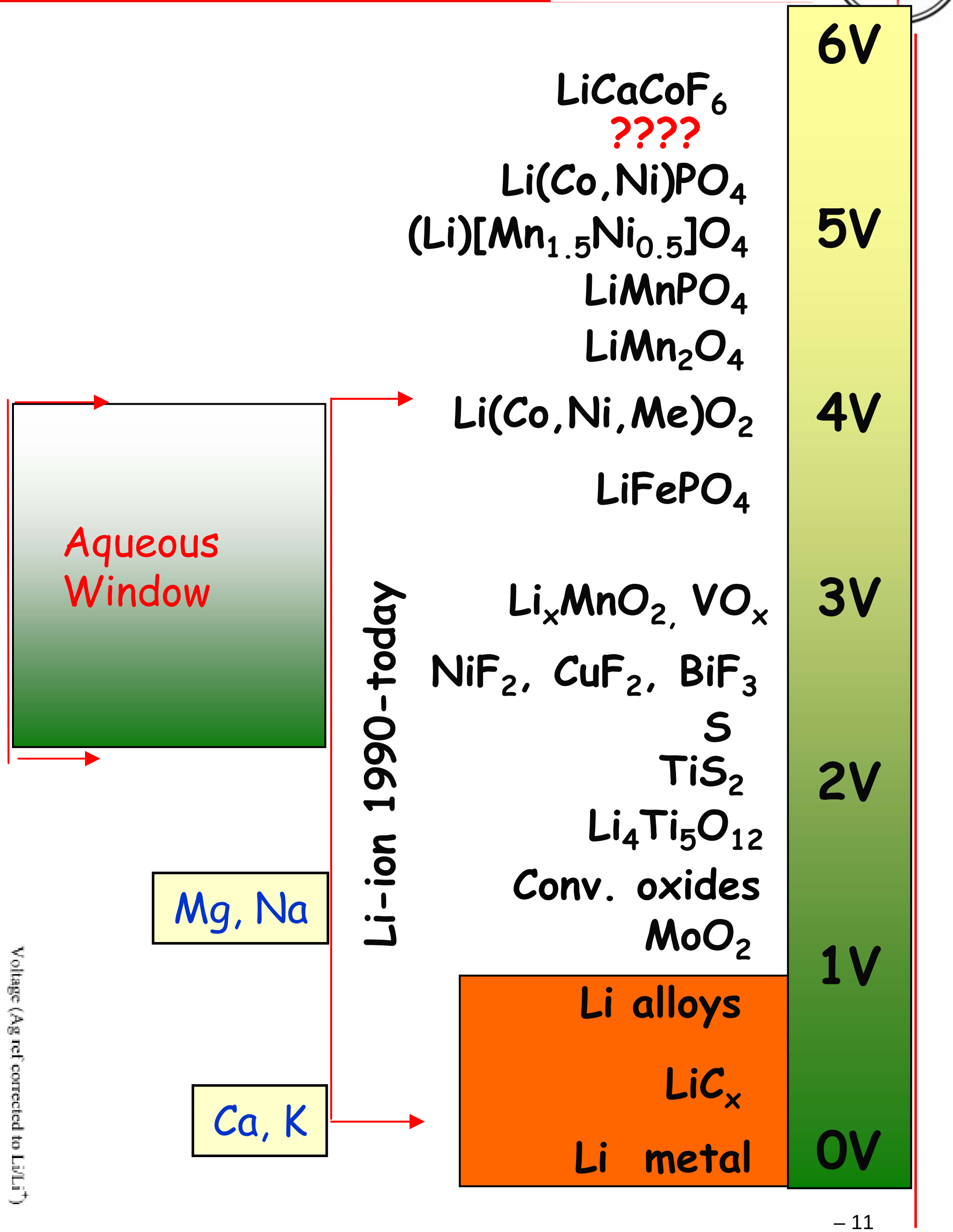
More extreme focus on cost:

Electrolytes:
- low cost salts
- alkali aqueous electrolytes advantages

If alternative guest cation
  - → new electrolytes

Guest Cation:
- Move away from Li^+??
  - supply / price / plating efficiency
- low cost polyvalent
  - Mg^{2+} / Ca^{2+}
- very low cost monovalent
  - Na^+ and K^+

Electrodes:
- If alt. guest → new insertion electrodes



6V

5V

4V

3V

2V

1V

0V

$LiCaCoF_6$

????

$Li(Co,Ni)PO_4$

$(Li)[Mn_{1.5}Ni_{0.5}]O_4$

$LiMnPO_4$

$LiMn_2O_4$

$Li(Co,Ni,Me)O_2$

$LiFePO_4$

Li_xMnO_2, VO_x

NiF_2, CuF_2, BiF_3

S

TiS_2

$Li_4Ti_5O_{12}$

Conv. oxides

MoO_2

Li alloys

LiC_x

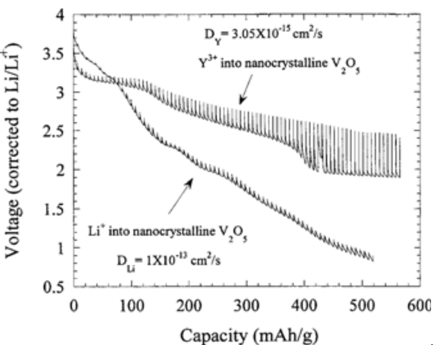
Li metal

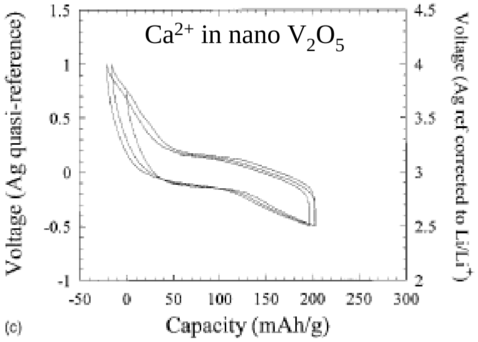
Aqueous Window

Li-ion 1990-today

Mg, Na

Ca, K



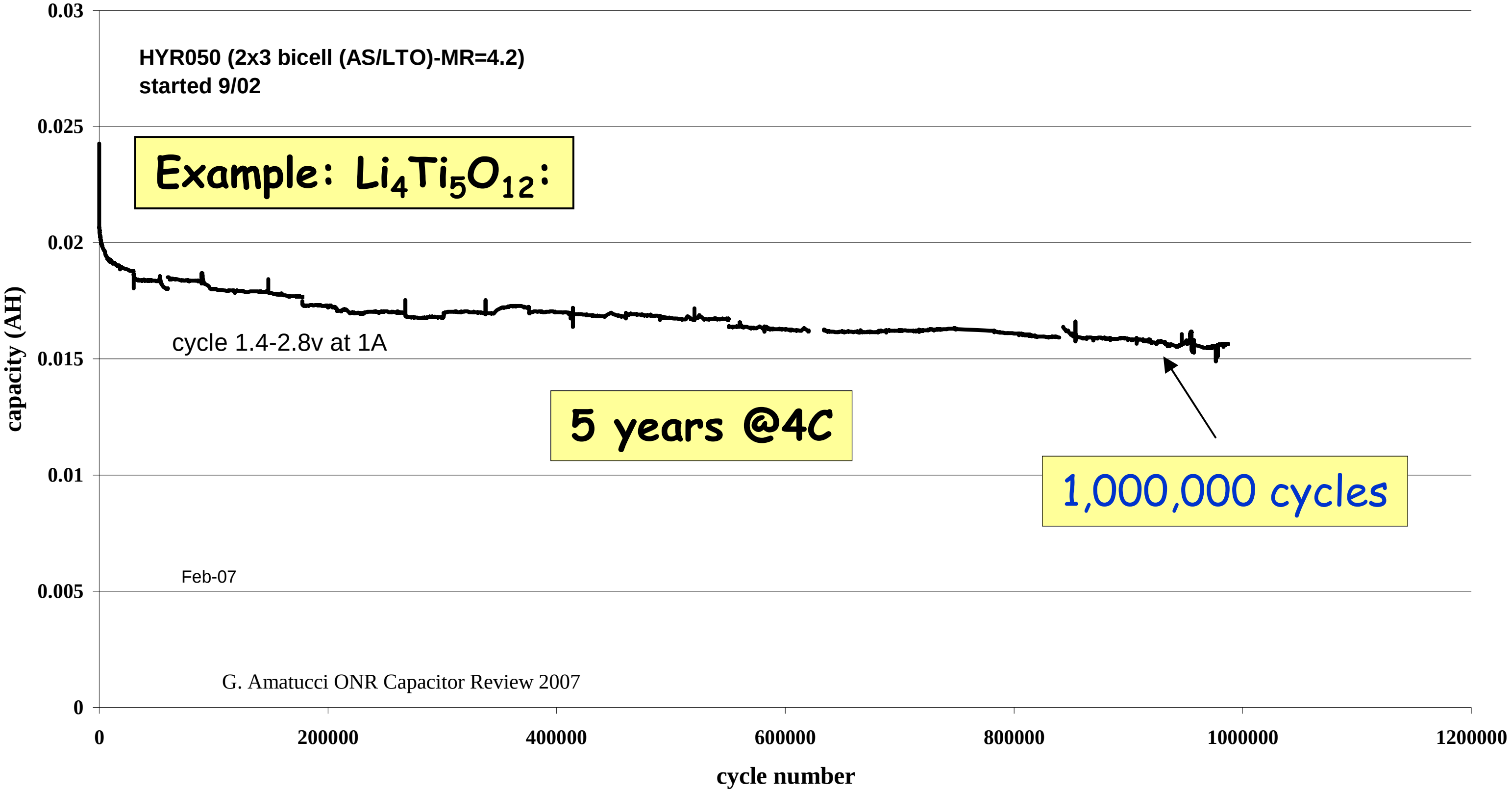


Electric Grid: Electrode Materials: Research Directions

Long life = Low Lifetime Cost

Challenge: Electromechanical destruction

- Route to eliminate <u>one</u> primary source of failure
- Identify new pos. and neg. zero or quasi zero expansion electrodes



Example: $Li_4Ti_5O_{12}$:

5 years @4C

1,000,000 cycles

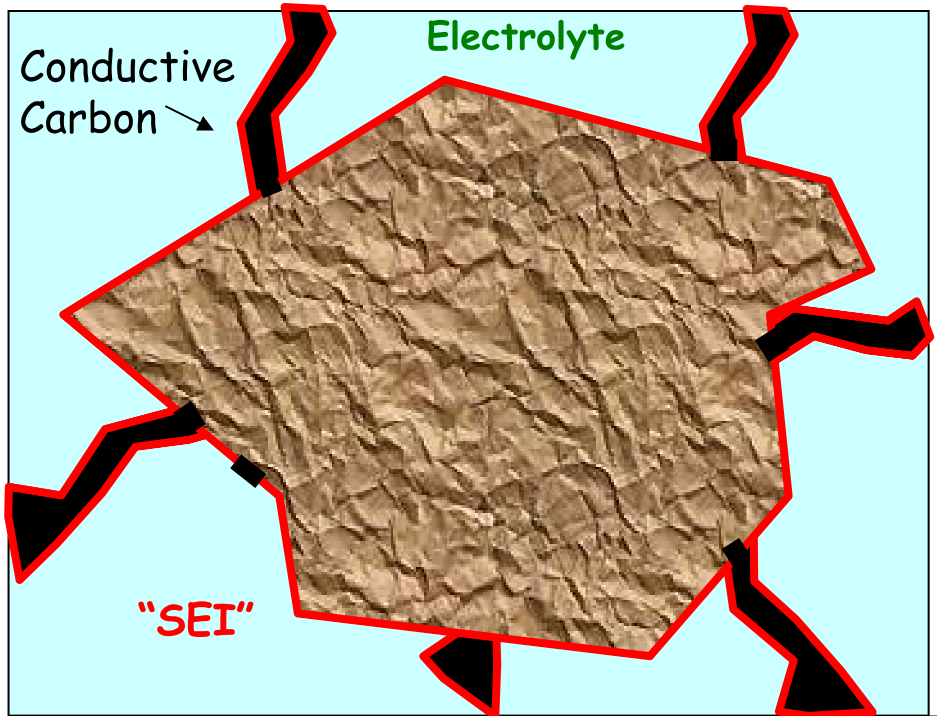
G. Amatucci ONR Capacitor Review 2007

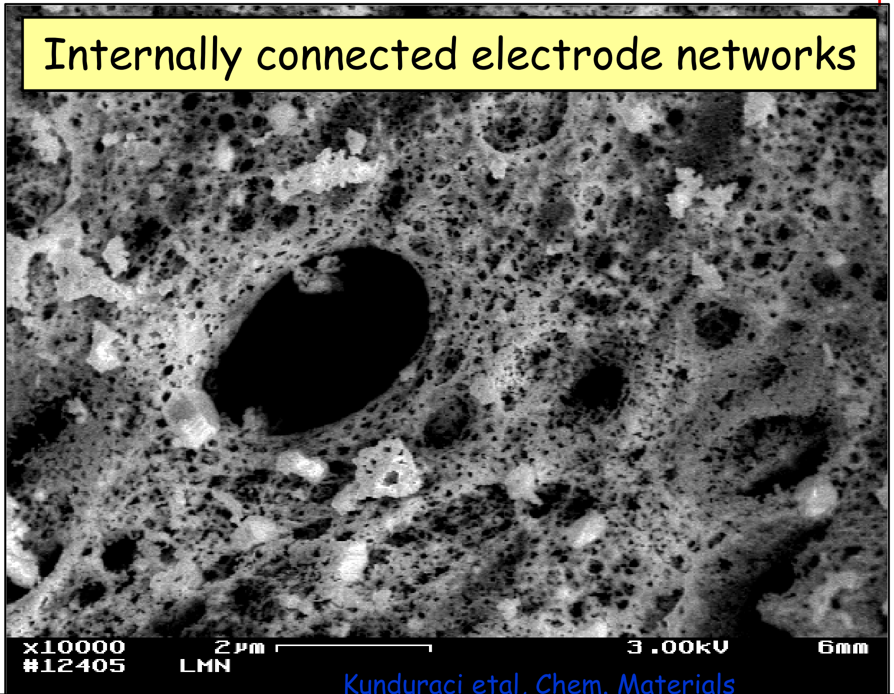
Electric Grid: Electrode Materials: Research Directions

Long life = Low Lifetime Cost

Surface Science: Electrode/electrolyte interface

- Development of interphase to assist low cost electrolytes @ High V
- Electrode passivation (coated electrodes)
- Very effective, but fundamentally flawed
- Entire electronic conductive network must be coated uniformly
    1. New approaches towards in-situ formed inorganic interphases,
    2. Capability to model and predict effectiveness
    3. Stabilization of aqueous electrolytes at V extremes

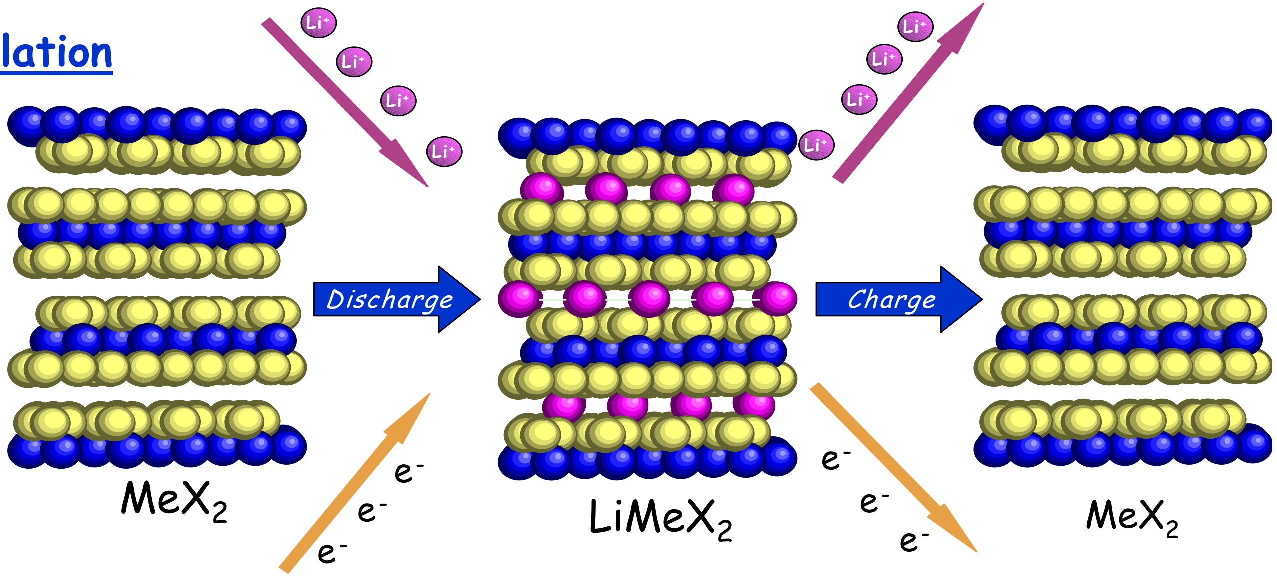



Internally connected electrode networks

Kunduraci etal. Chem. Materials

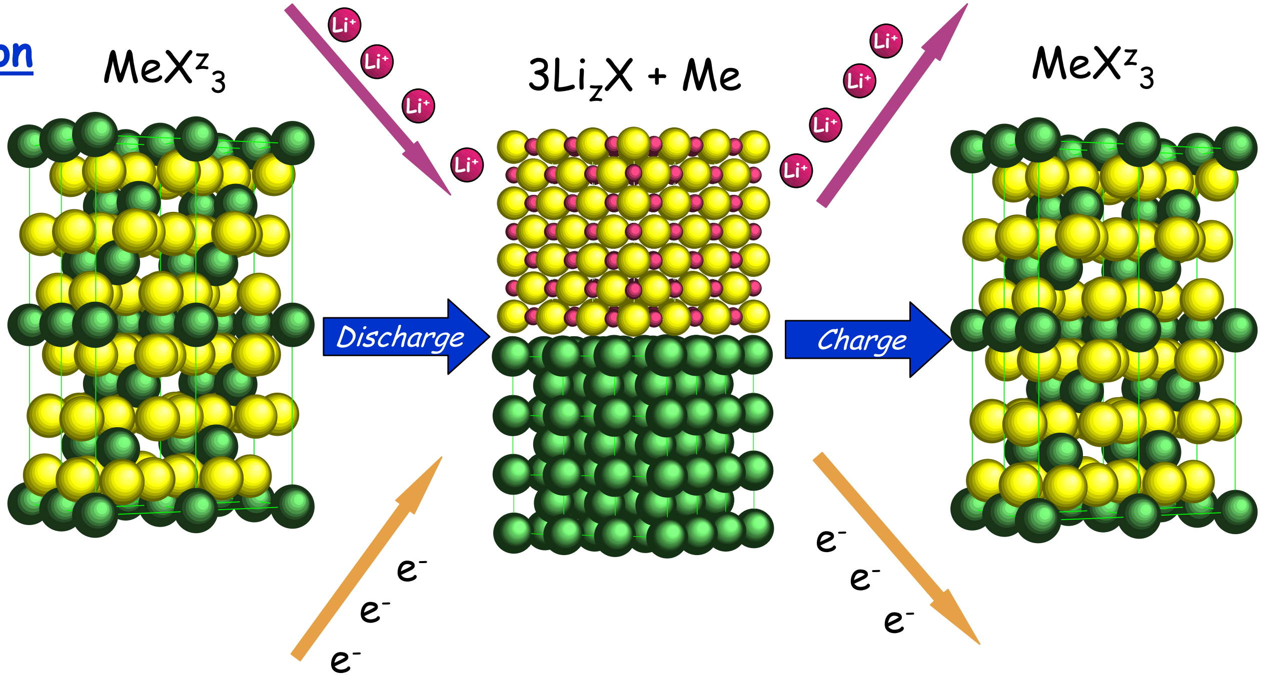
High energy Cathodes: Electrochemical Conversion Processes

Intercalation



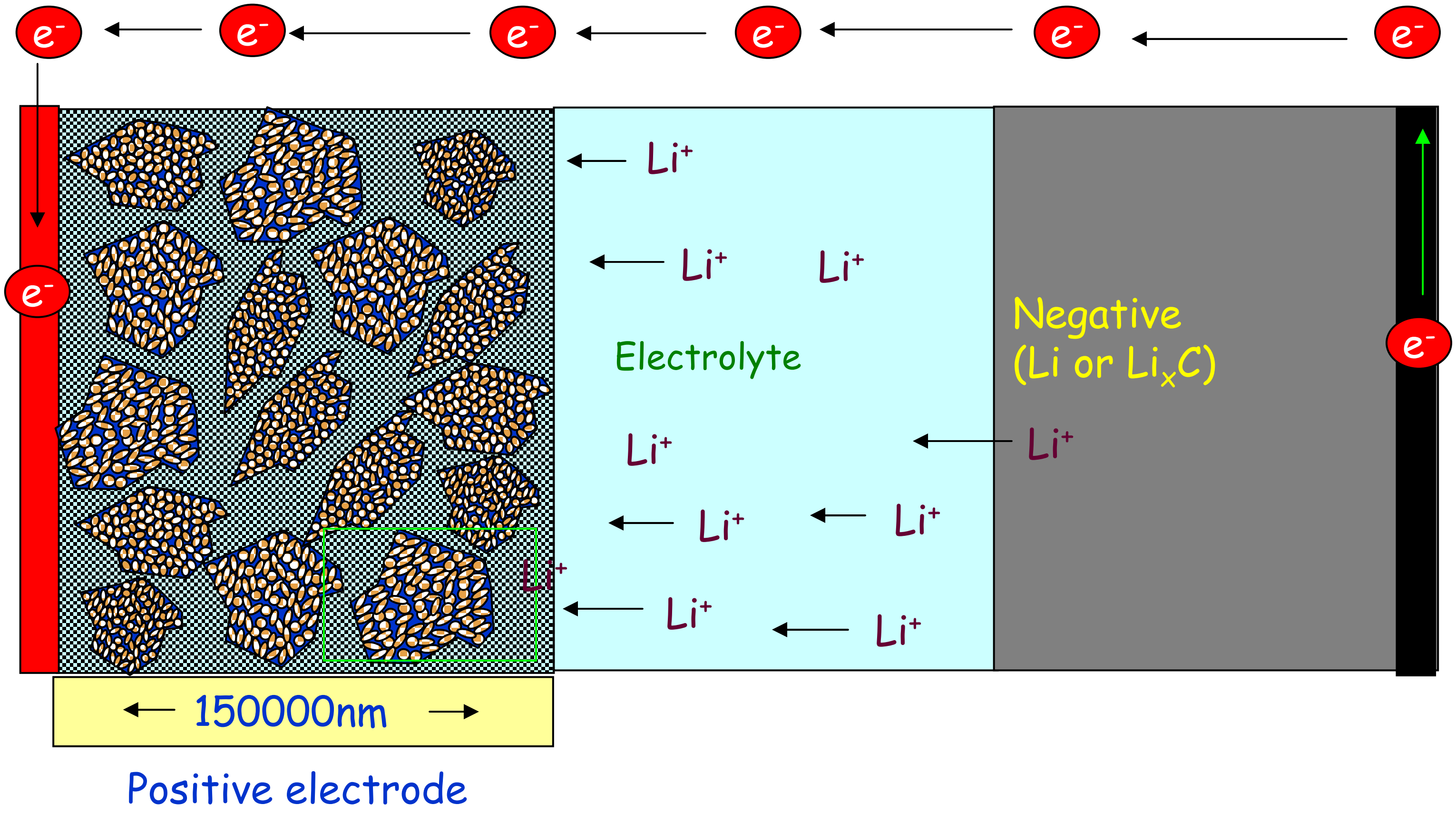
$1e^-$ transfer
<<300 mAh/g

Conversion



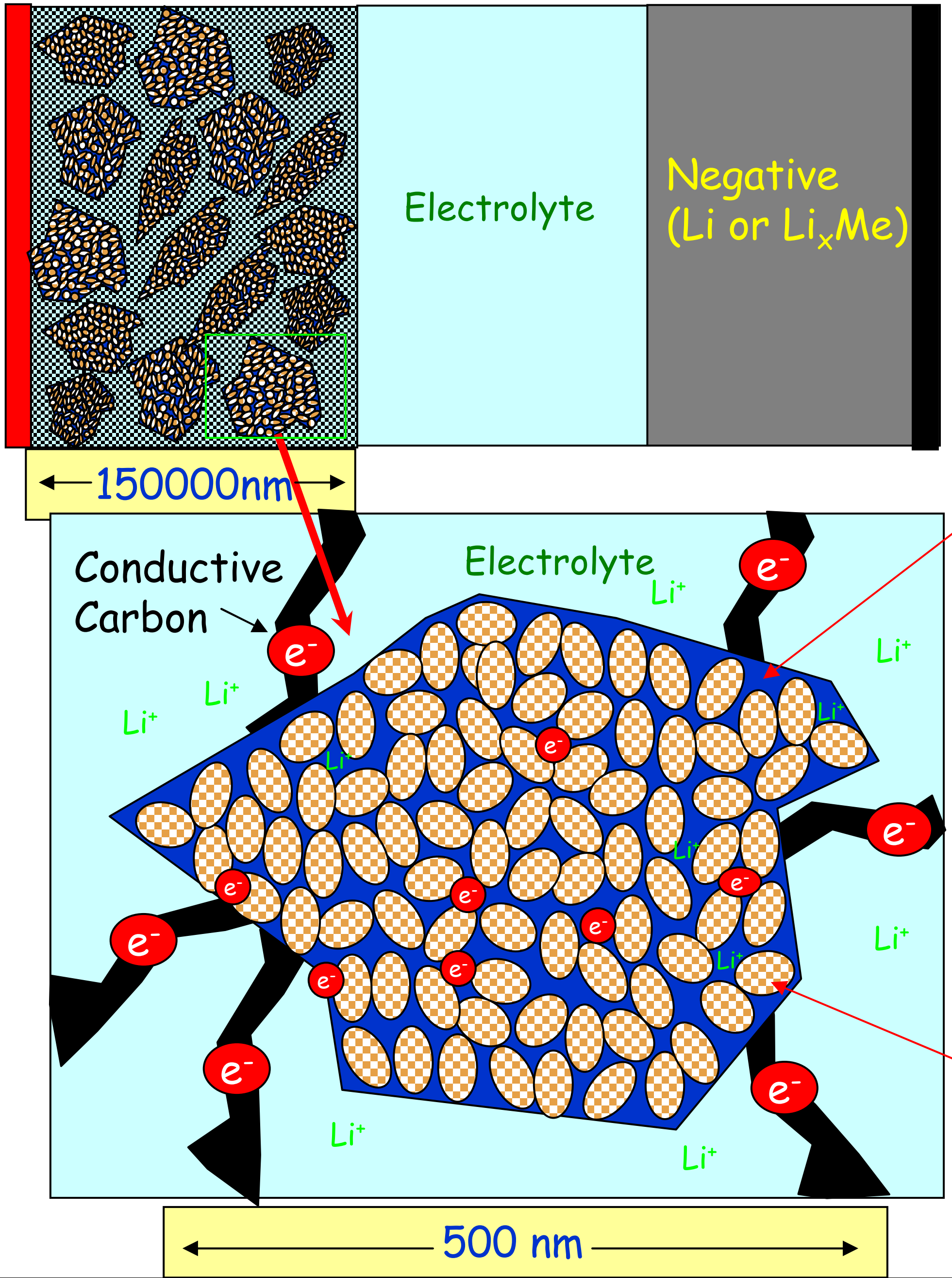
$3e^-$ transfer
>700 mAh/g

Our Own Electrical Grid Issues:



Electrons and Li ions:
The Macroscopic Journey is Just the Beginning...

Enabling Insulating Fluorides:



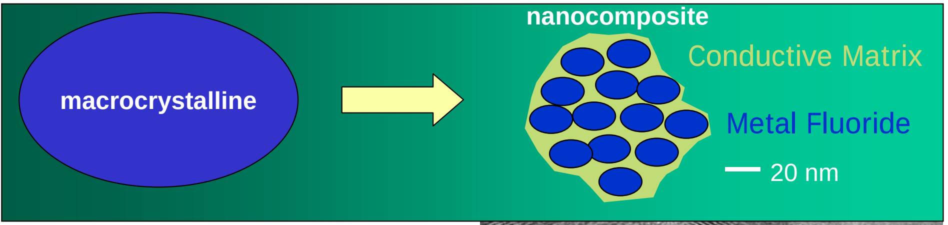
The MeF_x Nanocomposite
- enable transport in insulating MeFs
- reduce volume wrt discrete nano

Mixed Conducting Matrix (MCM)
- High σ_i
- High σ_e
- Mixed conductor

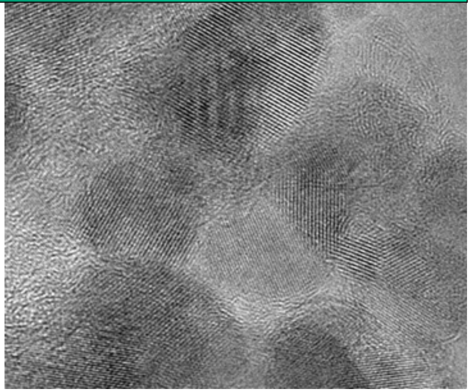
MeF_x nanodomains

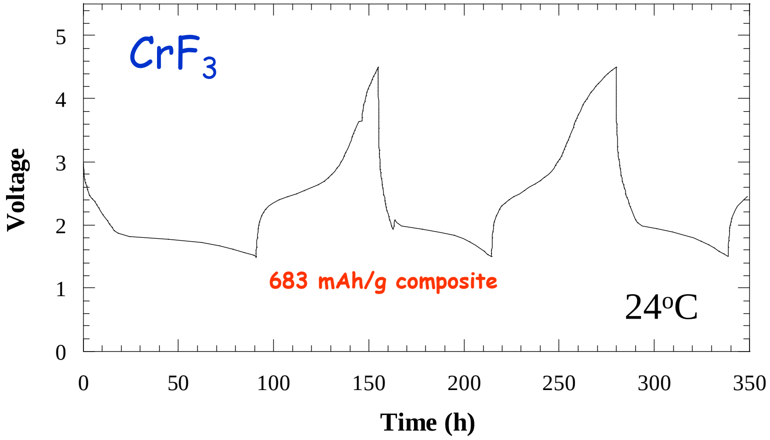
Badway etal. Chem. Matl. (2007)

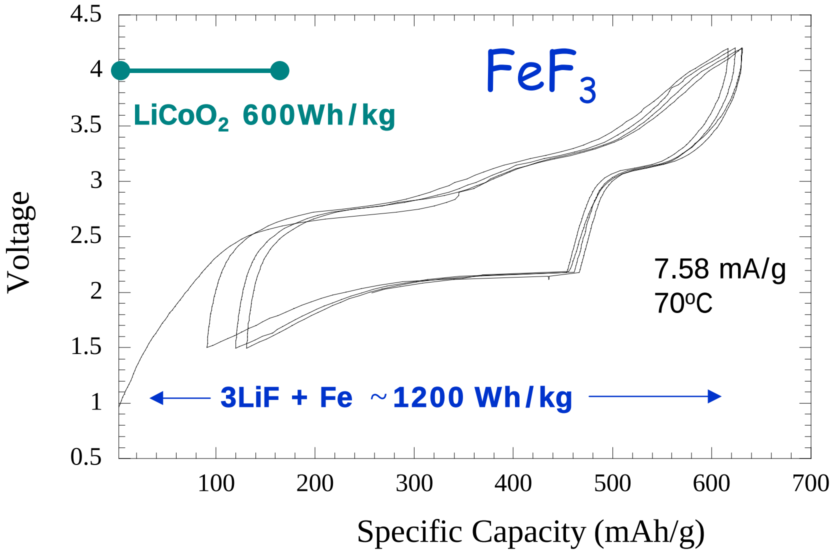
Metall Fluorides

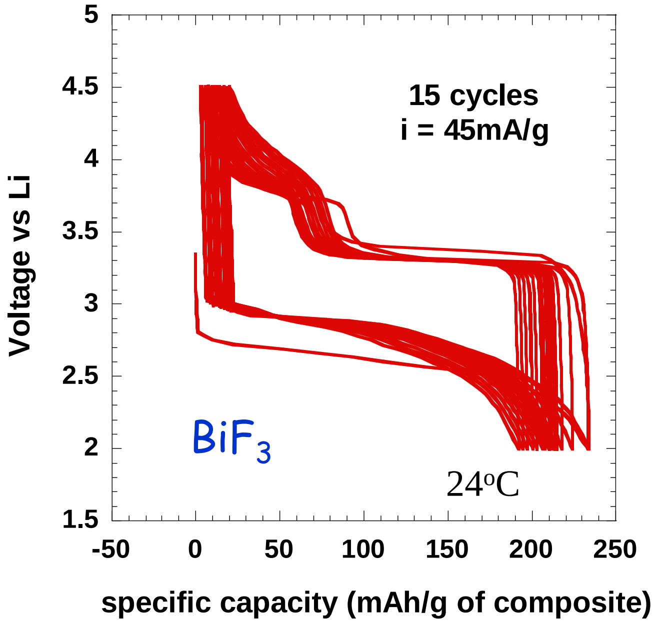


Nanocomposite enabled MeF_z









- Nanocomposites have enabled theoretical a variety of MeF_s
- As with dichalcogenides, polarization needs to be addressed

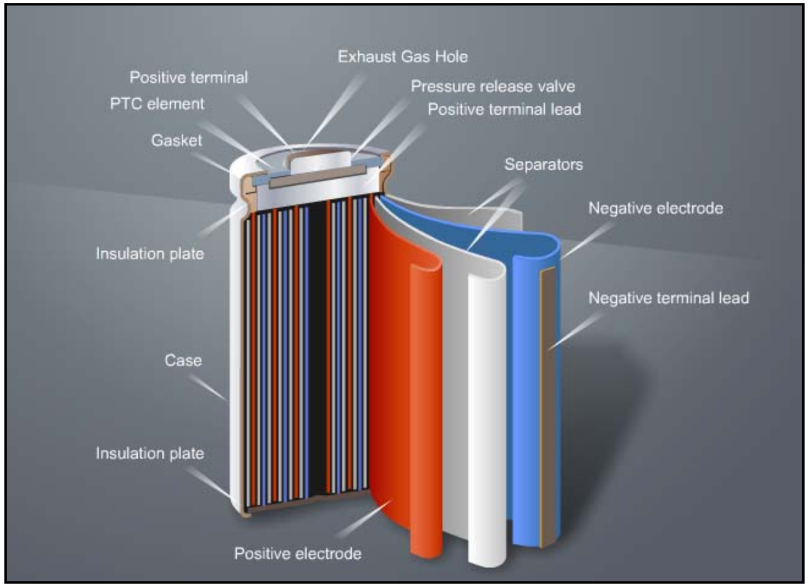
Examples from Badway etal. Rutgers

Batteries, Moving Towards Larger Applications…

Alternatives to Traditional Batteries

The Problem with High Energy Batteries:

- Limited electrode thickness (transport) = very large area cells for >kWh
- Relatively complex designs
- Except for a few exceptions, Li systems have been goals
  - Debatable reserves of Li supply
- Relatively expensive
  - salts/electrolytes
  - highly engineered electrodes
- Can be difficult to control in series
- Aqueous cells lower cost, but lifetime cost is questionable

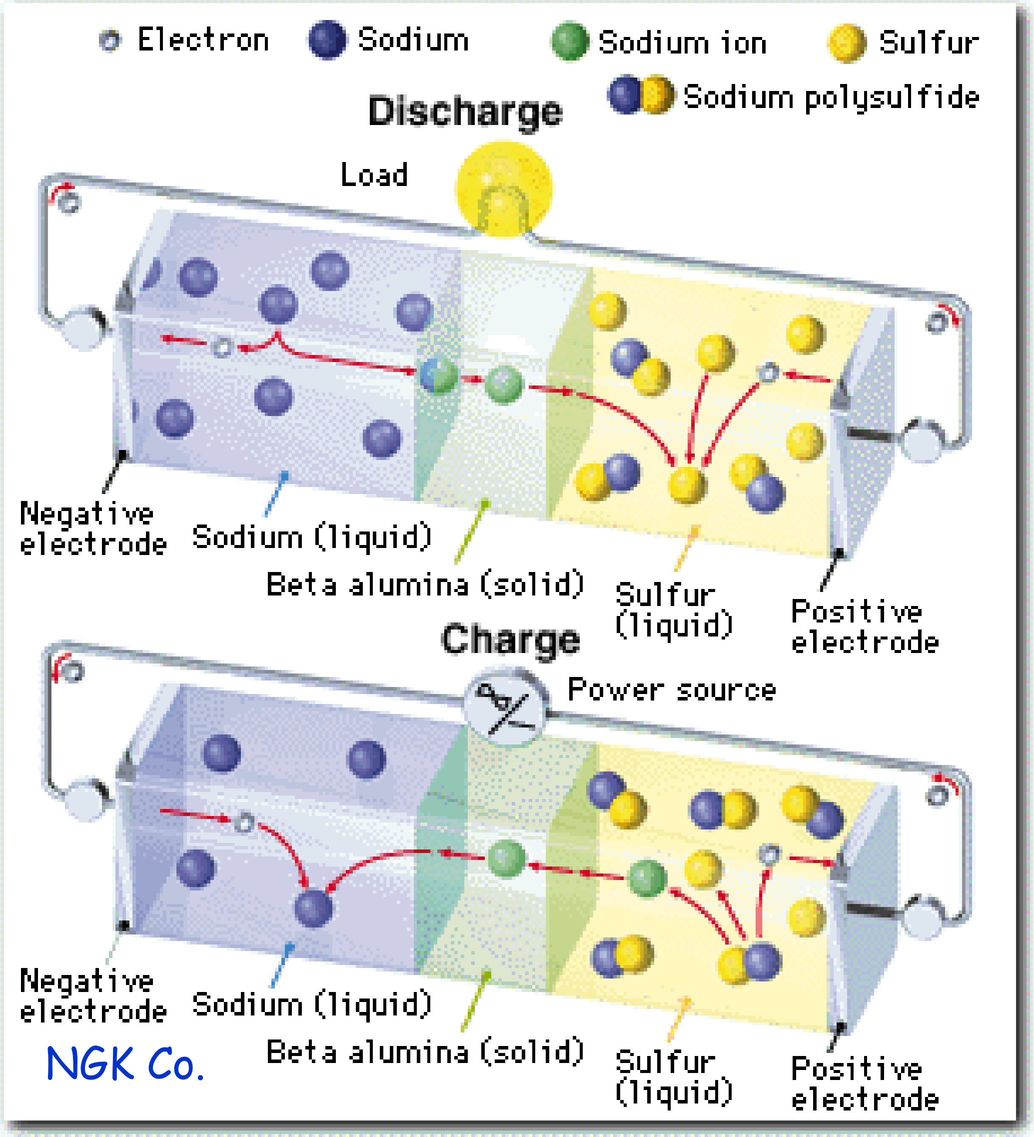


Molten Sodium Technology:

Why??

Low Cost, High Energy , and Abundance of Na

Sodium Sulfur Molten Salts



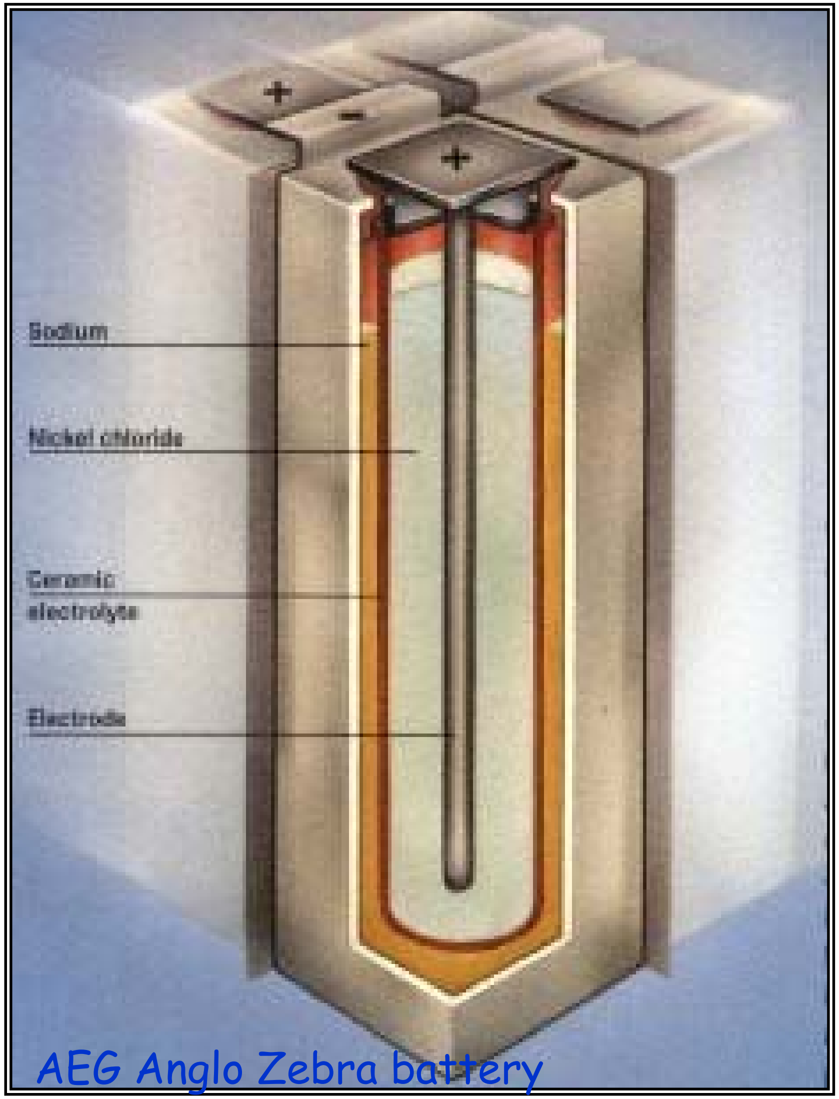
NGK Co.

- $2Na + 3S \rightarrow Na_2S_3$ = 2.08 V
- 300°C
- 89% efficient, very high pulse power
- very inexpensive materials

Hitachi uses 4 2MW NaS systems (NGK)
Tokyo 8 MW system
Both have 58MWh energy
Peak shaving, etc

Very attractive system, work continues in this spirit with the Na metal chlorides…

Na metal Chloride cells and ZEBRA



AEG Anglo Zebra battery

Positive electrode: $MeCl_x$, typivally $NiCl_2$
Electrolyte: B''alumina and $NaAlCl_4$
Negative electrode: Na metal
Operating Temperature: 250 -350°C

Positive electrode Reaction:
$NiCl_2 + 2\ Na^+ + 2e^- \rightarrow Ni + 2\ NaCl$

Negative electrode:
$Na \rightarrow Na^+ + e^-$

Net Reaction:
$NiCl_2 + 2Na \rightarrow 2NaCl + Ni$ (2.58V)

Na metal Chloride cells and ZEBRA

Zebra:

- Similar energy density as NaS (790 vs. 760 Wh/kg theoretical)
- Overcharge resistant relative to Na/S
- Safety in failure mode
- No need for cooling / independent of ambient temperatures
- 20-100 kWh future MWh?
- no self discharge = efficiency
- no gassing
- 100% coulombic efficiency
- 2.58V, 120-150 Wh/kg, 340 Wh/L
- very long calender life (15 years) approx 2000 cycles
- no Na in assembled state
- very robust in series configuration
- current collectors are in thermodynamic equilibrium

Challenges 1:

1. Cost Reduction

- Construction and materials
  - cell fabrication costs
  - much of the complicated B" alumina electrolyte costs have been addressed
  - $FeCl_2$ → Much lower cost and toxicity than $NiCl_2$
  - for similar Wh (728 vs 790 Wh/kg)
    - must address: overcharge to Fe^{3+} → dissolves and attacks B" alumina
    - current collector disadvantages
- Improved Performance = smaller cells = lower cost
  - $CoCl_2$, $CuCl_2$, $SbCl_3$, $MoCl_x$ etc. → must be insoluble in electrolyte
  - container corrosion

Challenges 2:

2. Reduce operation temperature and improved power

Secondary electrolyte melts @ 160°C ,
Na melts @ 97°C but..
Higher temperature needed to improve kinetics of positive electrode and electrolyte

→ Power needs to be improved
    Address positive electrode kinetics
        - control grain size → S
        - mass transport improvement with iodine and bromine
    Pore design
→ Completely new options in Ionic Liquids
→ Alternative solid state electrolytes, Nasicons, etc.
→ Na alloys (Huggins)

Batteries, Moving Towards Even Larger Applications…

Redox Flow Cells

Traditional Batteries:

Positive attributes:

- very efficient recharge cycle
- can be very low cost materials
- non mechanical system
- instantaneous power delivery

Negative attributes

- inefficient design for large scaling
- challenges for scaling (safety, cost, performance)
- difficult charging protocols

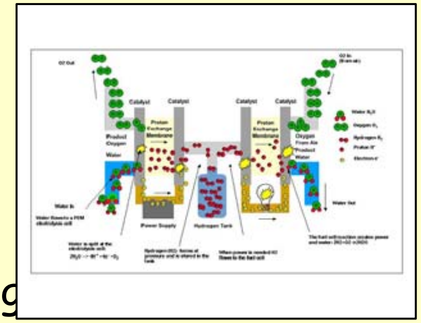
The Hybrid Approach:

Redox Flow Cells

Rechargeable Fuel Cells;

Positive attributes:

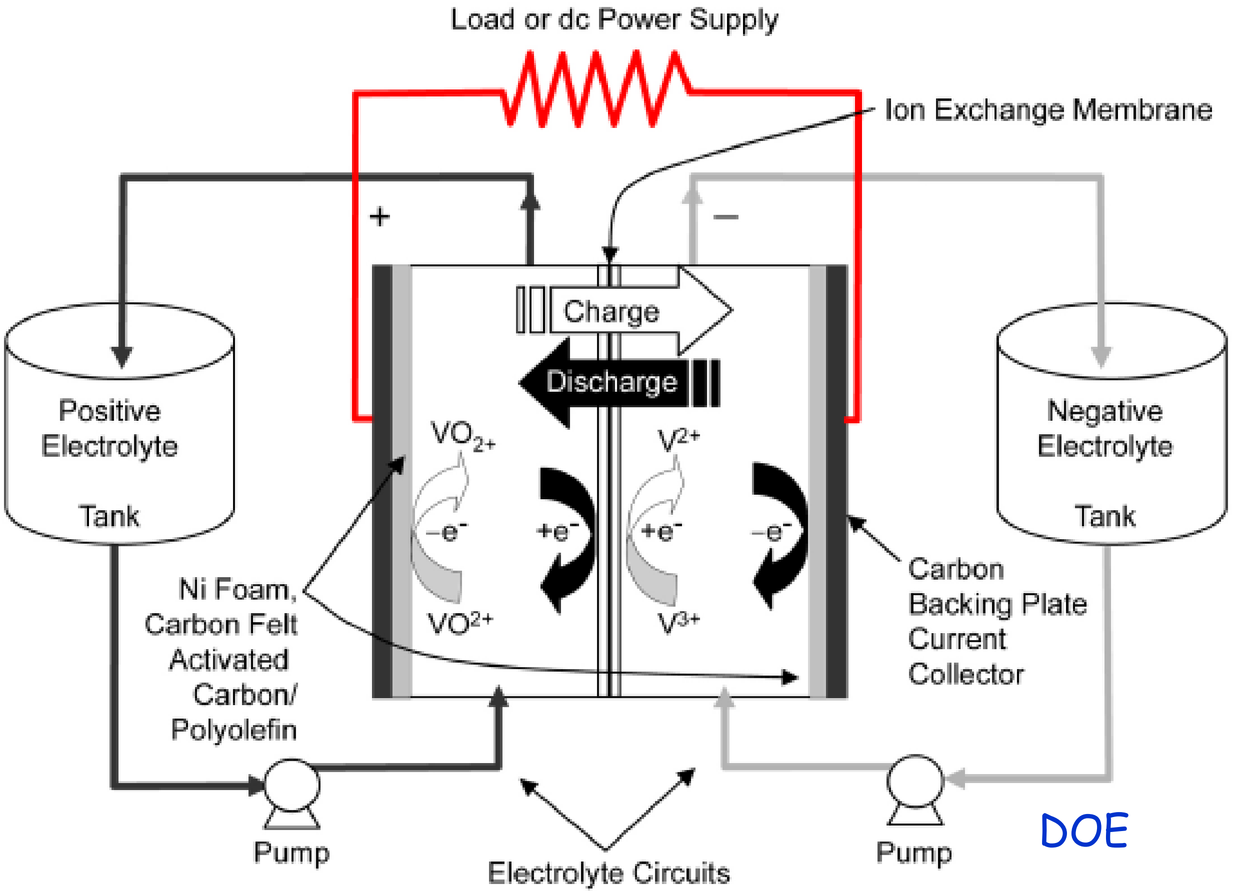
- efficient tank vs. reactor design = high energy density
- easy to scale
- “green”



Serious negative attributes:

- expensive catalysts
- complicated systems, large amount of hydrogen storag
- poor recharging efficiency = $$ and wasted energy
- slow switching time

Grid: peak shaving, renewable support: Redox Flow Cells



DOE

Redox Flow Cells: Fundamentally Attractive to Large Applications

- Reserve tank scalability of fuel cell but..
- Higher efficiency, instantaneous power, low cost, cycle life
- Reconfigurable Parallel / Series cell, Scaleable energy = tank
- Low level needs: improved membranes, improved catalysts, corr. Res.
- High level grand challenge: New green, reversible, stable chemistries,
  - Can We Hybridize with traditional battery approaches?

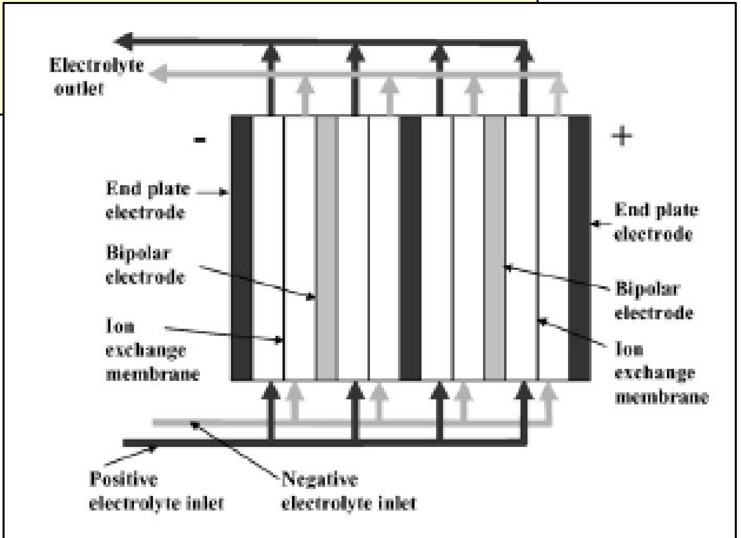
Redox Flow Cells

Positive Attributes (most relate to ease of scaling to high energy):

- Very Low $/Wh over lifetime for large Wh applications
- Very high charge/discharge efficiencies
- Long lifetimes
- High current (approach 1000 mA/cm^2)
- No cell balancing issues
- Tolerance to overcharge/overdischarge (and also under charge/discharge)
- Power conditioning very easy (DC/DC) conversion = # cells
- Charging configuration can be different from discharge (parallel vs series)
- Instantaneous recharging possible if needed
- Power and energy designed separately
    - power = number of cells and size
    - energy= concentration and volume of catholyte and anolyte

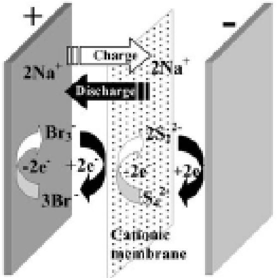
Negative Attributes:

- Requires plumbing / flow pumps
- Best if applied to largest applications >>kW



Present Redox Flow Cell Chemistries

Chemistry	Positive Electrode	Negative Electrode	V
a. Bromine – Polysulfide	$Br^{3-} + 2e^- \rightarrow 3Br^-$	$2S_2^{2-} \rightarrow S_4^{2-} + 2e^-$	1.54
b. Vanadium – Vanadium	$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	$V^{2+} \rightarrow V^{3+} + e^-$	1.3
c. Vanadium – Bromine	$ClBr_2^{2-} + 2e^- \rightarrow 2Br^- + Cl^-$	$VBr_2 + Br^- \rightarrow VBr_3 + e^-$	1.0
d. Iron – Chromium	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$Cr^{2+} \rightarrow Cr^{3+} + e^-$	1.03
e. Zinc – Bromine	$Br^{3-} + 3e^- \rightarrow 3Br^-$	$Zn^{2+} + 2e^- \rightarrow Zn$	1.75
f. Zinc – Cerium	$Zn^{2+} + 2e^- \rightarrow Zn$	$Ce^{3+} \rightarrow Ce^{4+} + e^-$	<2



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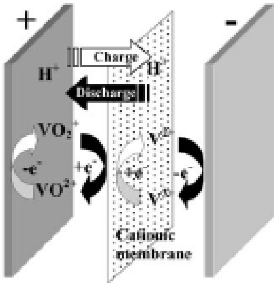

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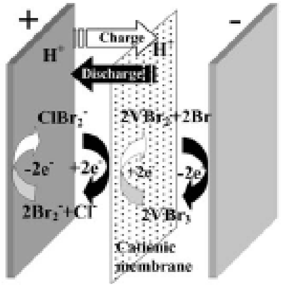

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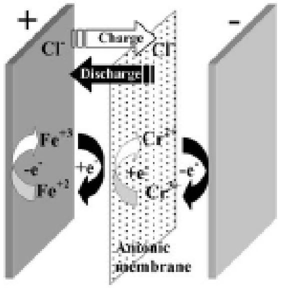

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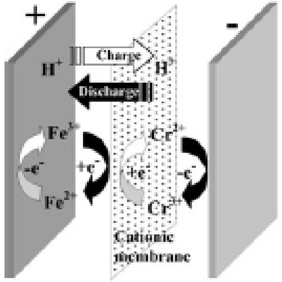

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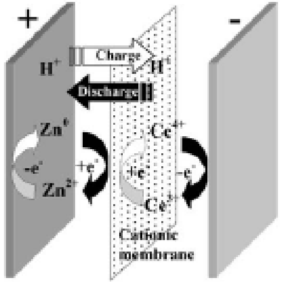

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C. Ponce de Leon, J. Pow. Sources 160 (2006) 716

Redox Flow Technology Materials Challenges

Catholyte and anolyte

- reversible reactions
- all reactants and products are preferably soluble
- wide voltage window
- high concentrations in liquid
- Need high energy
- Need less cost and toxicity

Membrane

- prevent transfer of redox species → needs to be improved
  - but maintain rate
- cation (typical H^+ or Na^+) transport and water

Electrodes

- carbon and carbon composite
- electrode design and materials to further improve power density

Summary

- Batteries offer solutions from < kWh to > MWh
- Materials are key to the success

Which System, Which Materials?

- Primary decision is dictated by cost, scalability and environmental responsibility
- Next generation room to elevated temperature batteries could compete with molten Na
- Redox flow has a large number of advantages of very large applications
- New hybridized chemistries will most likely be developed

The practical challenge:

Little resources are available to focus on electrochemical energy storage for grid
  - Cannot rely on trickle down research from HEV, this is distinctly different in needs
  - Need to focus research and resources on this issue

Distinct progress has been made, great progress will be realized in the future…

Thank You!!