Advanced Stationary Electrical Energy Storage R&D at PNNL

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Funded by the Energy Storage Systems Program of the U.S. Department Of Energy through Pacific Northwest National Laboratories

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EES technologies and PNNL focus

Electrical energy

Direct Storage in charges

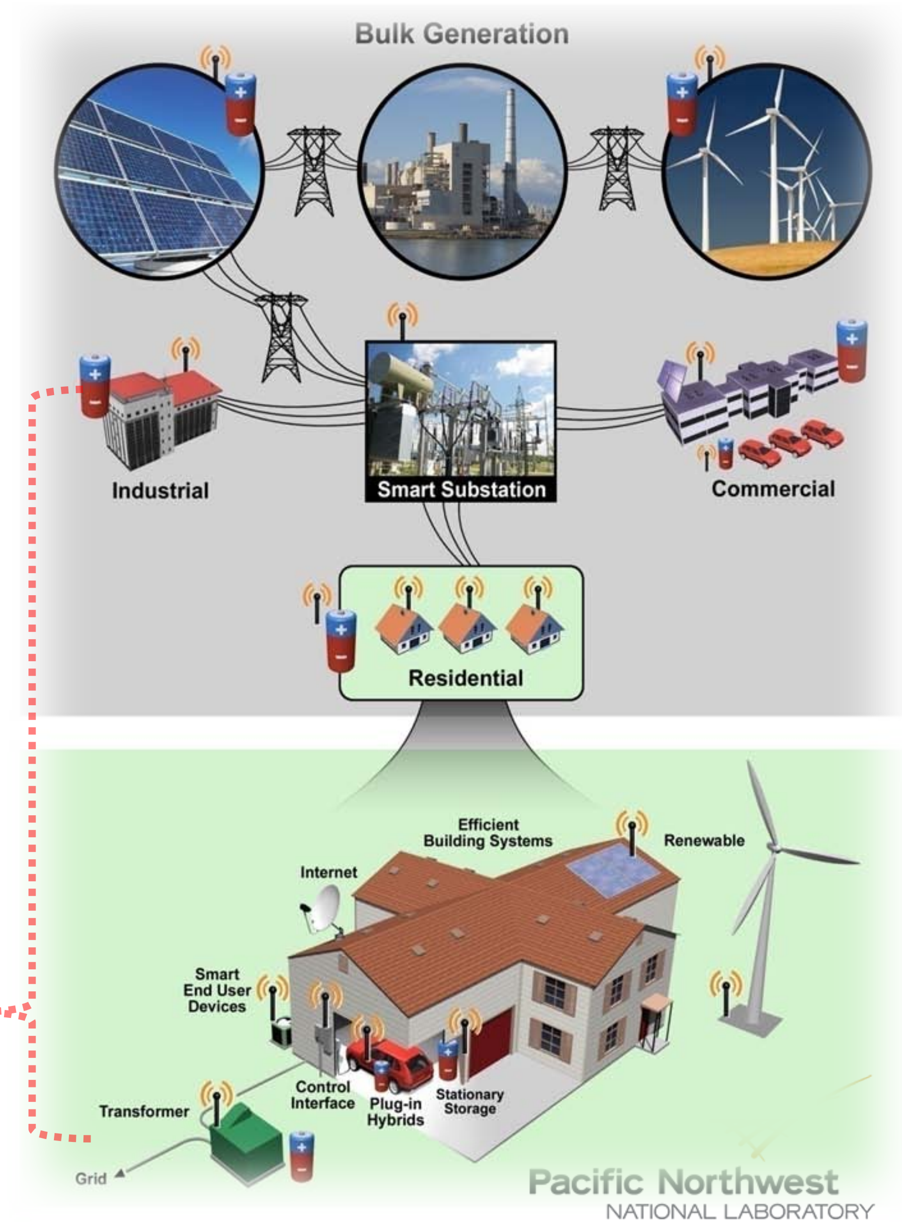
Electrical charges:
Capacitors

Indirect storage via energy conversion

Kinetic energy:
flywheels

Potential energy:
pump hydro,
compress air

Chemical energy:
batteries



PNNL strategy in stationary EES R&D

EES R&D at PNNL

Collaboration with industries, universities, etc.

Grid analytics on EES

- Roles of storage in US grids
- Value, locations, targets
- Cost and performance requirements

EES Technologies

Novel redox flow batteries, MWhs

New gen Na-batteries, up to MWhs

Low cost, long life Li-ion, community storage

…

Materials

- Materials synthesis,
- Ionic membrane
- Mixed conducting electrodes
- …

Crosscutting science

Computer Modeling

- Mass/charge transport
- Electrical fields
- Flow, thermal, …

Advanced diagnostic study, NMR, TEM, etc.

- Basic chemistry
- Materials structure
- Physical properties

Electrochemical study

- Electrochemical activity
- Reaction kinetics
- Performance/chemistry/structure

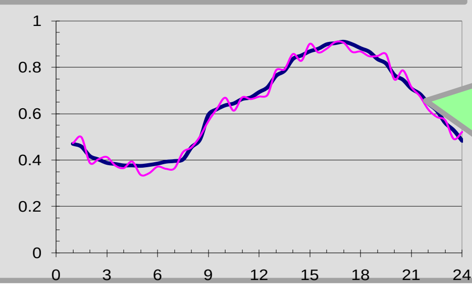
Grid analytics on energy storage technologies
(discussed by Dr. Kintner-Meyer)

Meeting Balance Requirements

Actual production

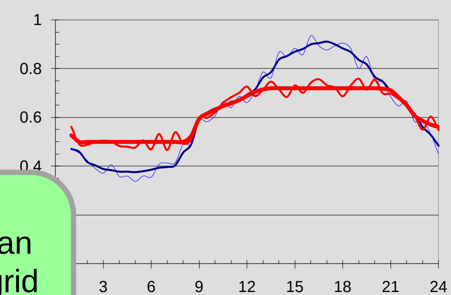
Generation schedule

Real-time operation



Energy storage is an valuable grid assets to provide balance services

Arbitrage



Infrastructure deferment

when

- Located at strategic location in bulk power to reduced congestion
- In distribution system/home to reduce distribution congestion

Reliability value

Economic value

Redox flow battery RD&D

Materials, components, technology R&D

- Redox electrolytes
- Electrodes-bipolar plate
- Membranes/separators
- Other stack components
- Modeling & Simulation
- Design and prototype

PNNL
Other labs
Universities
Industries
Small business

→ Core team

Demonstration commercialization

- Scale up
- System design/engineering
- Demonstration
- Production

Battery manufacturers
Utilities
……

→ Vertical team

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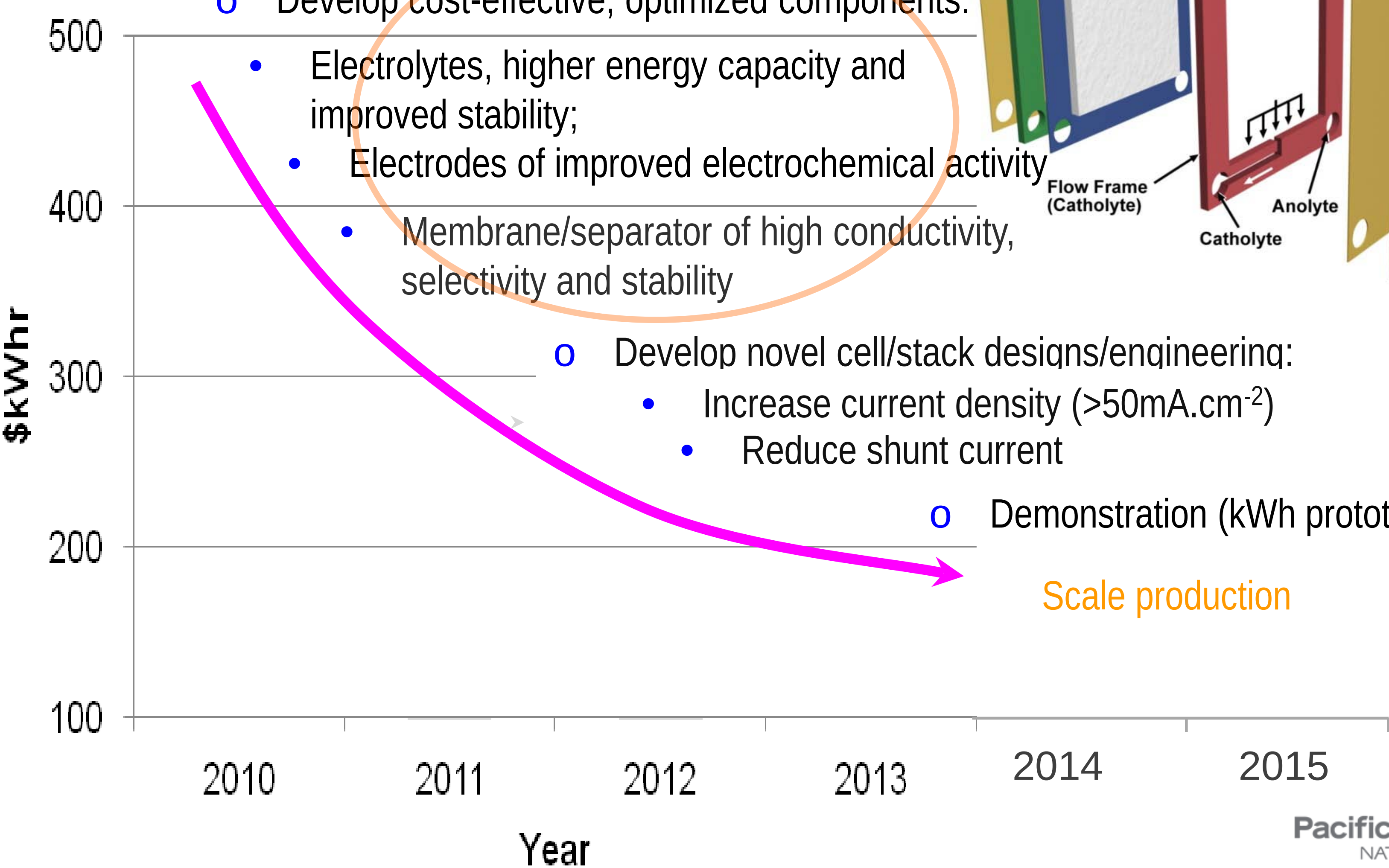
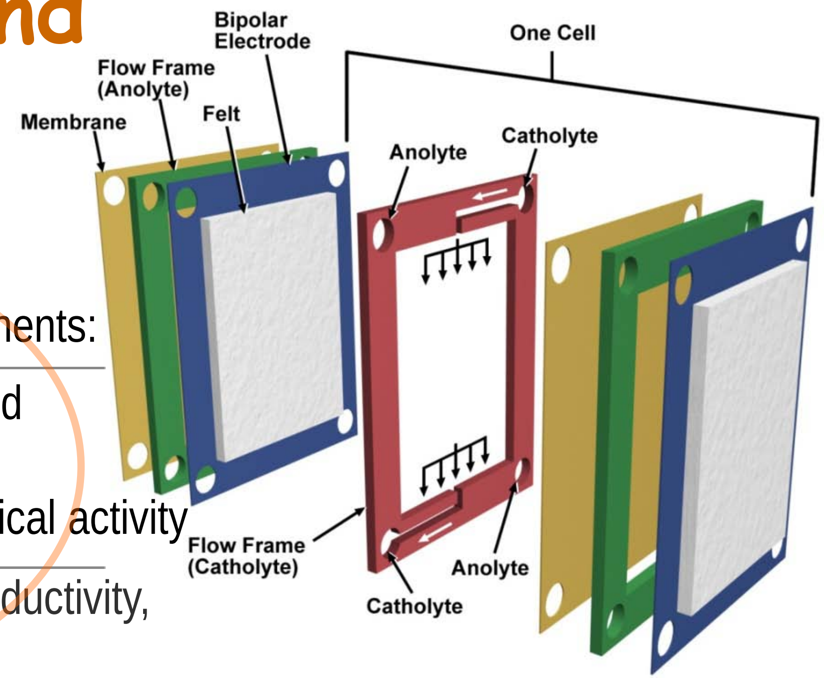
Toward cost reduction and commercialization



Current focus

- Develop cost-effective, optimized components:
  - Electrolytes, higher energy capacity and improved stability;
  - Electrodes of improved electrochemical activity
  - Membrane/separator of high conductivity, selectivity and stability
- Develop novel cell/stack designs/engineering:
  - Increase current density (>50mA.cm^{-2})
  - Reduce shunt current
- Demonstration (kWh prototype)

Scale production



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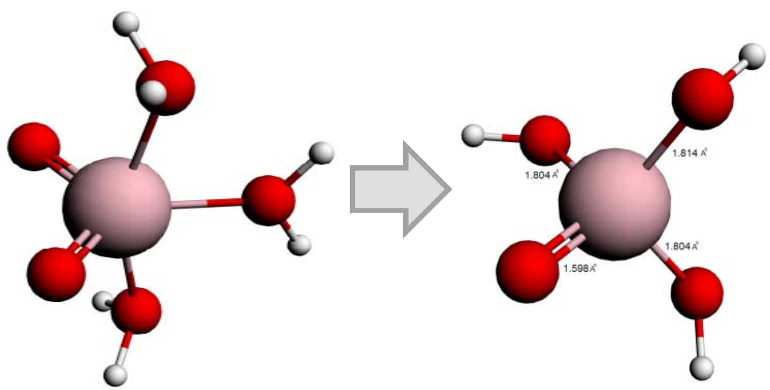
Electrolyte development



$$[VO_2 3H_2O]^+ \rightarrow VO(OH)_3 + H_3O^+$$

$$2VO(OH)_3 \rightarrow V_2O_5 \cdot 3H_2O \Downarrow$$

- ❑ Alternative redox couples to all V:

  Fe^{3+}/Fe^{2+} vs. V^{3+}/V^{2+}, …

- ❑ Supporting electrolytes:
  - ➢ Chloride acid
  - ➢ Sulfate-chloride mixed acid

    (to be discussed by Dr. Liyu Li)

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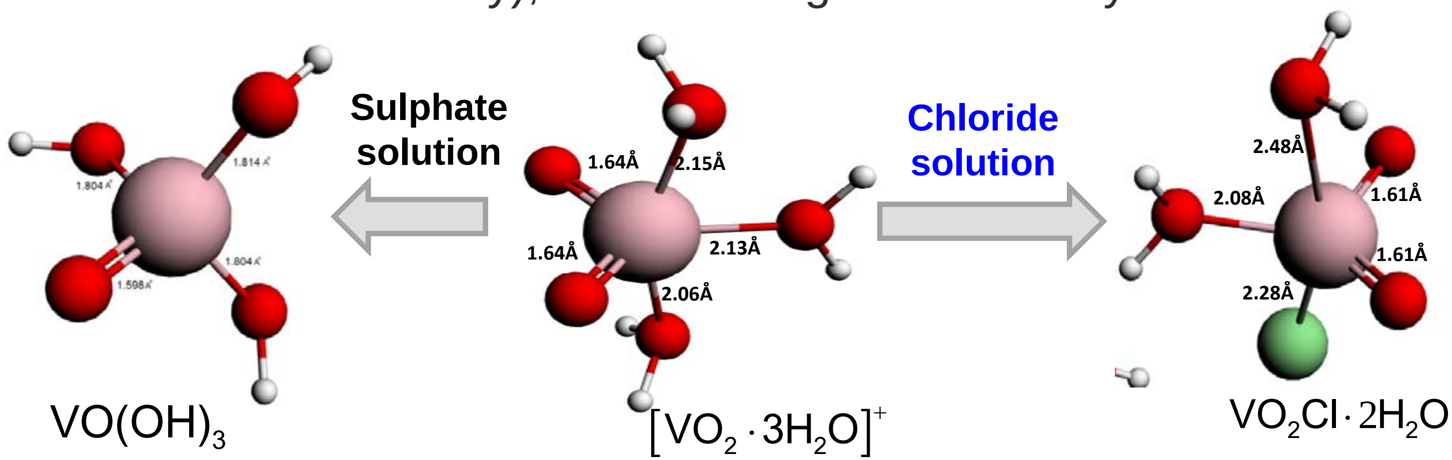
Stability of chloride electrolytes

V specie	-5°C		25°C		40°C	
	sulfate	Chloride	sulfate	Chloride	sulfate	Chloride
V^{2+}	**2M (419 h)**	2.3M (>20 d)	2M (>30 d)	2.3M (>20 d)	2M (>30 d)	2.3M (>20 d)
V^{3+}	**2M (634 h)**	**2.3M (96 h)**	2M (>30 d)	2.3M (>20 d)	2M (>30 d)	2.3M (>20 d)
V^{4+} (VO^{2+})	**2M (18 h)**	2.3M (>20 d)	**2M (95 h)**	2.3M (>20 d)	2M (>30 d)	2.3M (>20 d)
V^{5+} (VO_2^+)	2M (>30 d)	2.3M (>20 d)	2M (>30 d)	2.3M (>20 d)	**2.2M (95 h)**	2.3M (>20 d)

- Energy capacity up to 2.3M V over 0~50°C (1.7 M and 10~40°C for current sulfate chemistry), due to change in chemistry:



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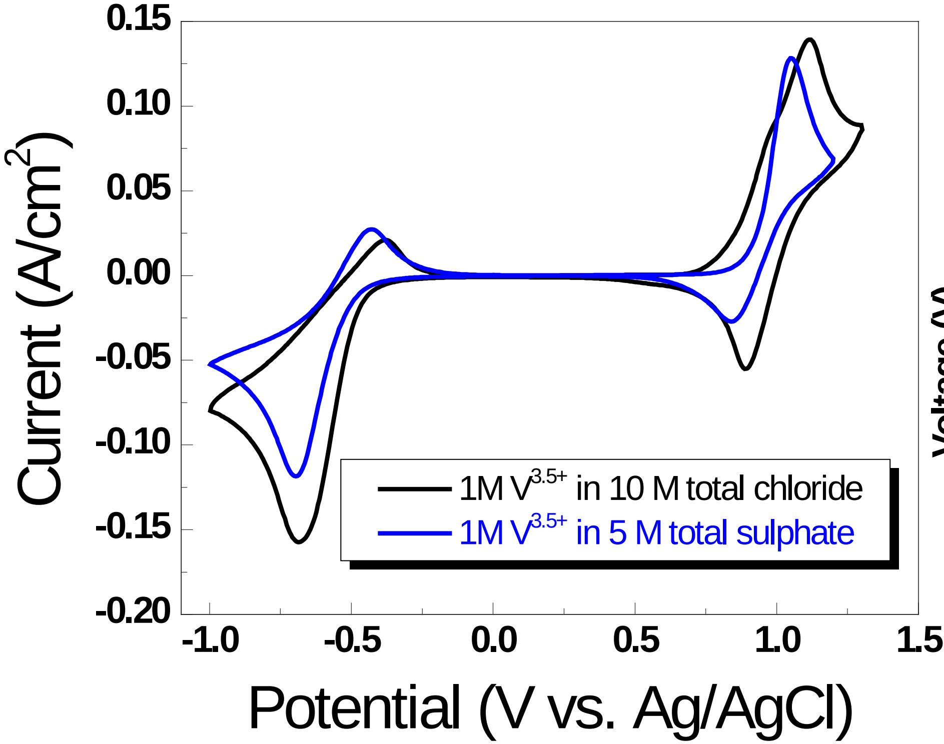
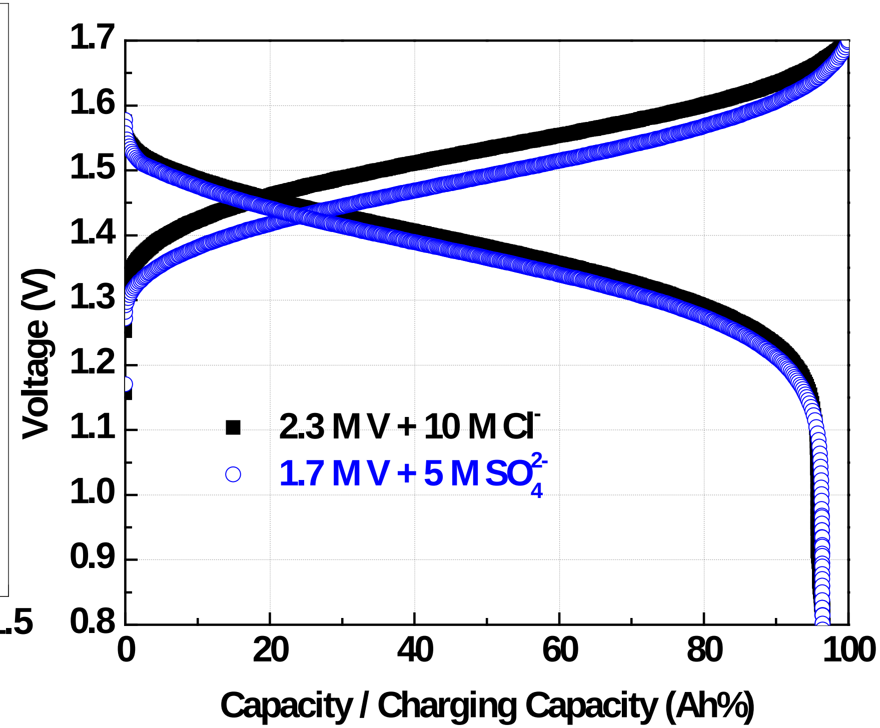
Electrochemical properties of all V chloride system





Chloride system shows higher charging and discharging potential for the same condition.

Positive: $[VO_2 \cdot 3H_2O]^+ + 2H^+ + e \underset{C}{\overset{D}{\rightleftarrows}} [VO \cdot 4H_2O]^{2+} \quad E^o = 1.0\,V$

$VO_2Cl \cdot 3H_2O + 2H^+ + e \underset{C}{\overset{D}{\rightleftarrows}} [VO \cdot 4H_2O]^{2+} + Cl^- \quad E^o = 1.0 + \alpha$

Negative: $V^{2+} \underset{C}{\overset{D}{\rightleftarrows}} V^{3+} + e \quad E^o = -0.25\,V$

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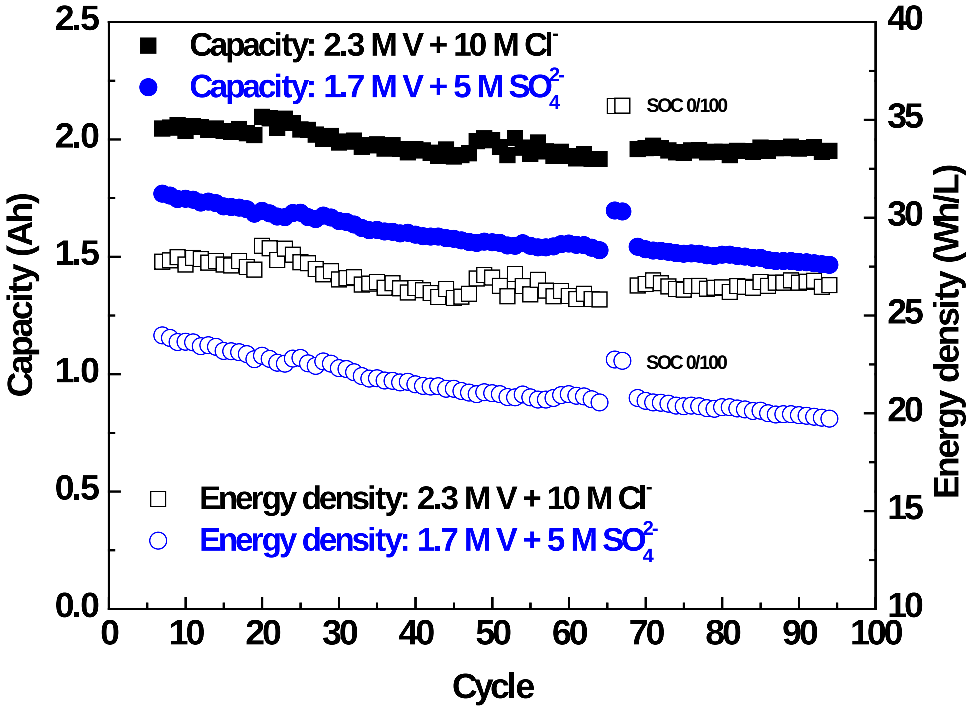
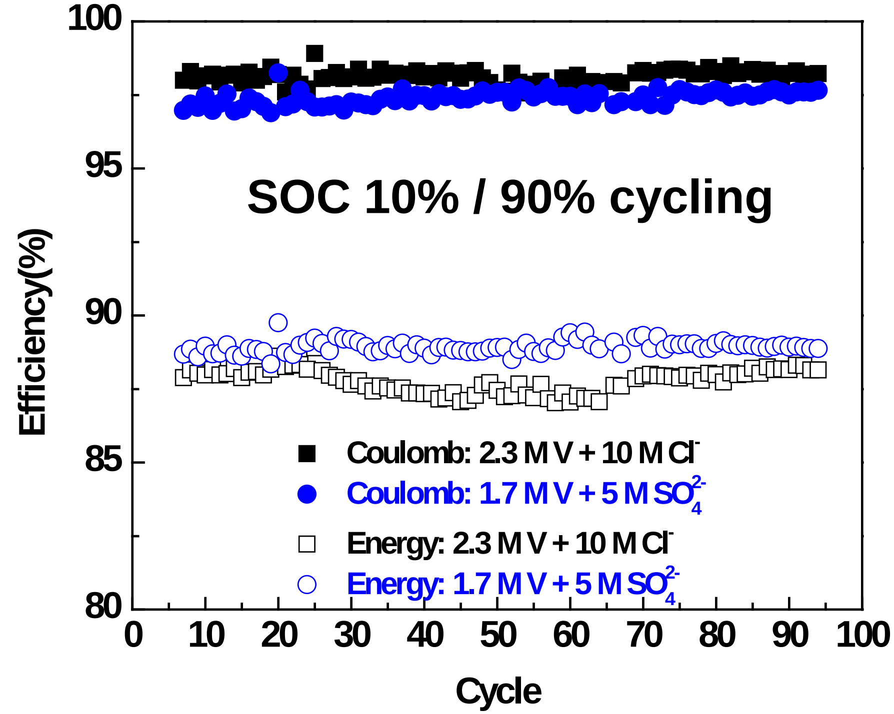
Performance of all V chloride batteries





	Chloride	Sulphate
7th	2.05 Ah	1.77 Ah
94th	1.95 Ah	1.46 Ah
Loss	**0.06%/cy**	**0.24%/cy**

- Chloride system shows better and stable performance

  30% energy density improved; Lower capacity loss

- Negligible, if any, chlorine gas evolution

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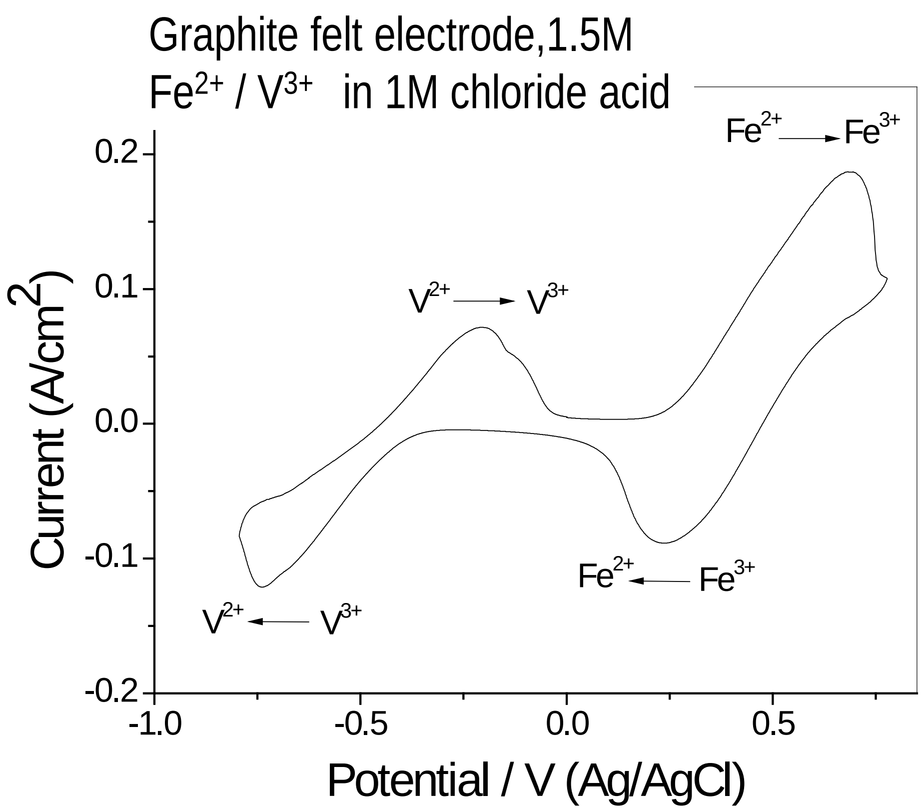
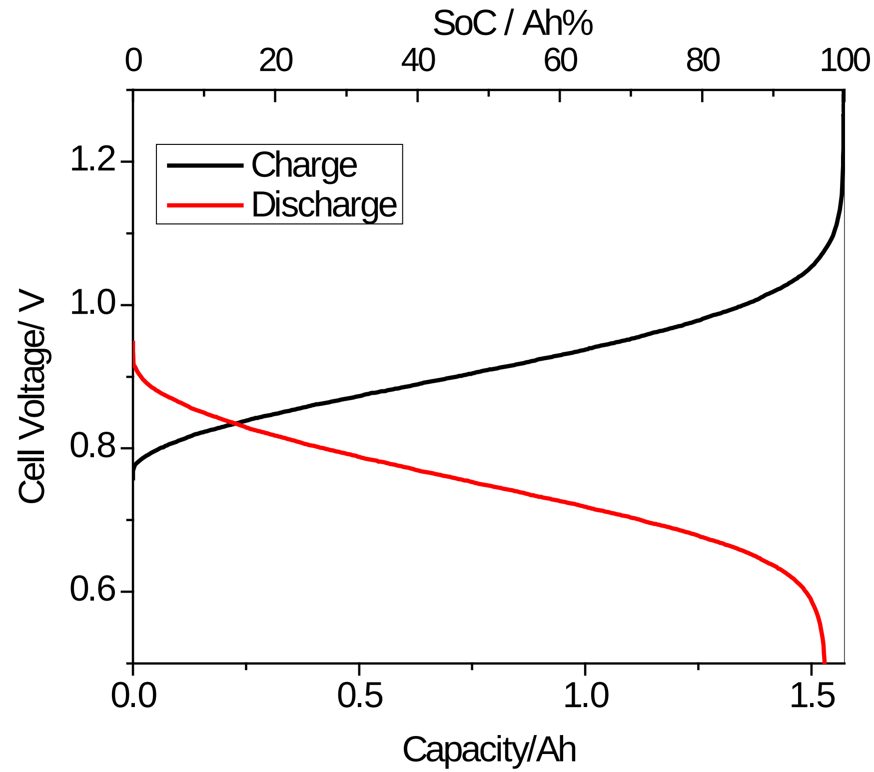
Electrochemical properties of Fe/V redox couples





- Fe^{3+}/Fe^{2+} (positive) vs. V^{3+}/V^{2+}, E_o=1.02 V
- Advantages over Fe/Cr system: no H_2 evolution and without catalysts
- Over V/V system: significantly improved chemical compatibility by avoiding high oxidant V^{5+}, allowing use of low cost materials, e.g. separator

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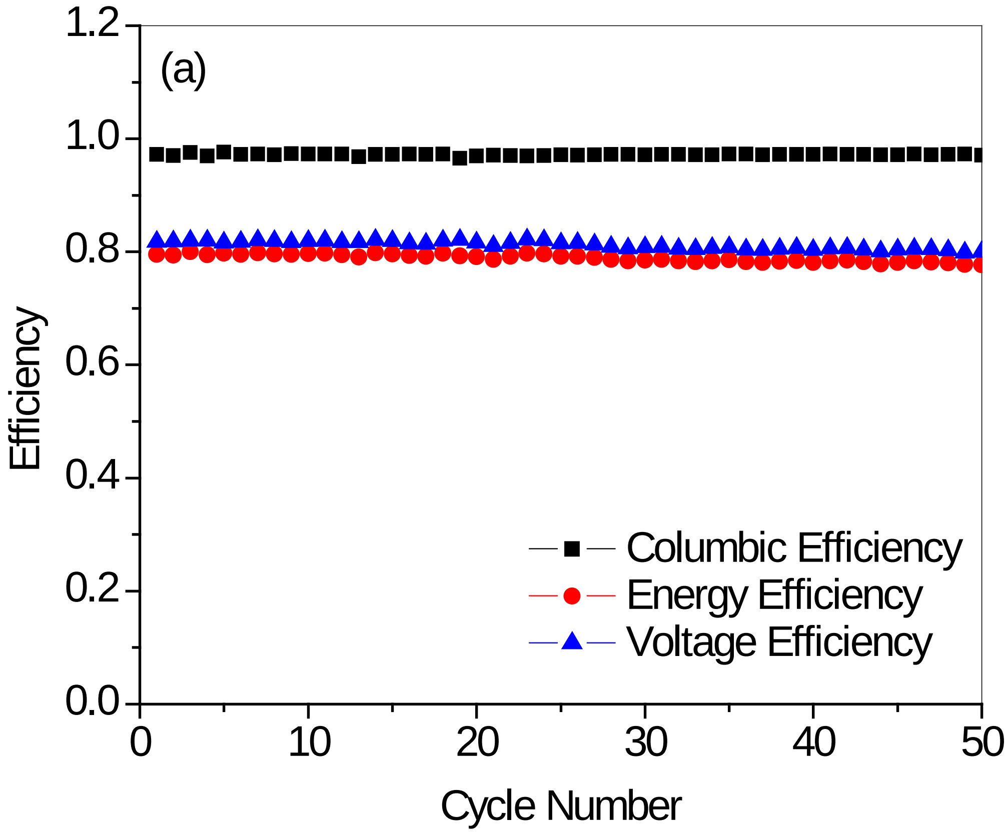
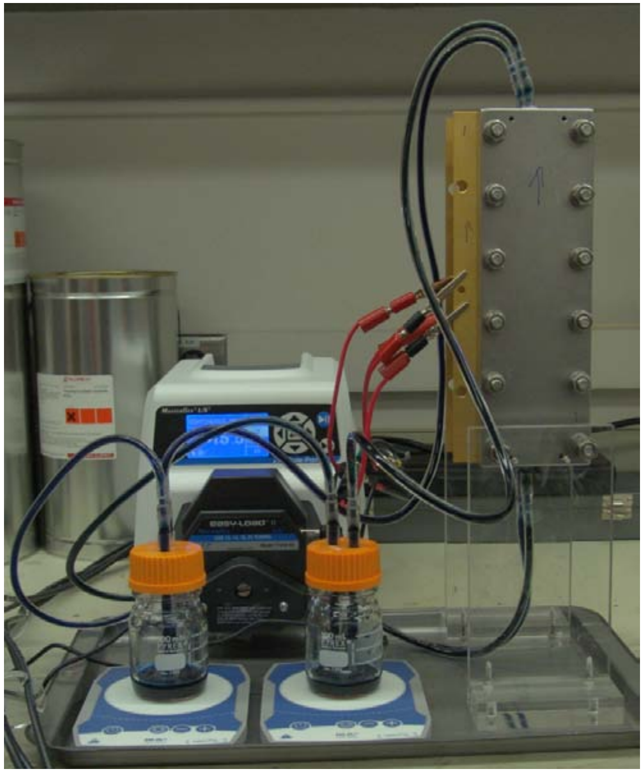
Battery performance of Fe/V chloride system





On going research on the electrolyte system with higher concentration and improved efficiency

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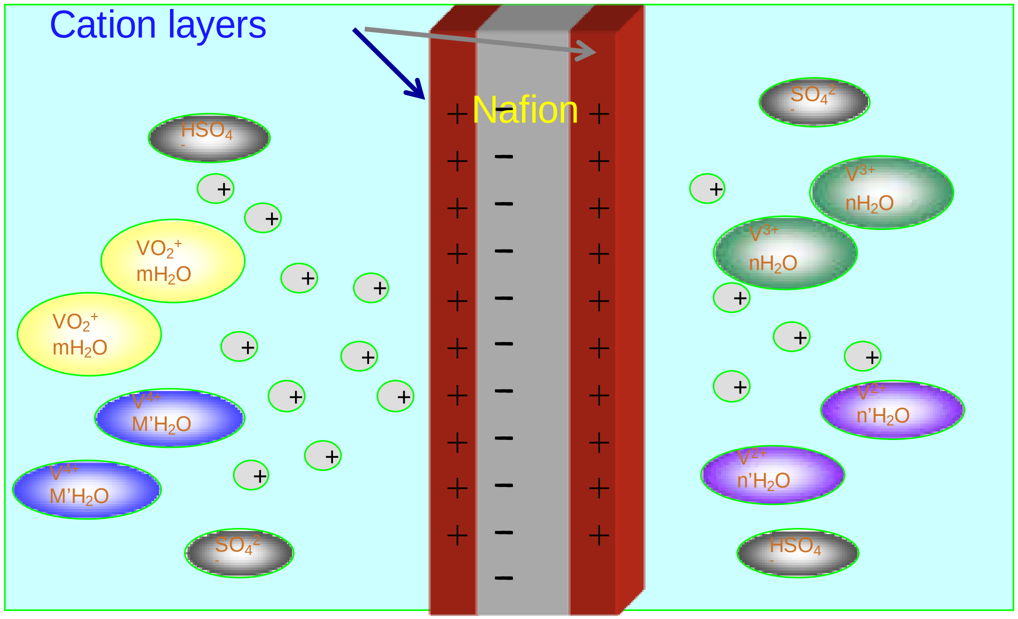
Membrane/separator development

- Develop cost-effective, optimized membranes or separators that can demonstrate high ionic conductivity, selectivity and mechanical/chemical durability through collaboration with universities, among national labs, industries

  - Nafion modification
    - Surface coating (PPR, PANI)
    - Nano-composite doping with SiO_2
  - Hydrocarbon membrane:
    - S-Radel and SPEEK
    - Degradation Mechanism

  Collaborated with Prof. Mike Hickner of Penn State



After Huamin Zhang

- Future focus on optimization of Nafion and searching its low cost alternatives via collaboration with ORNL, SNL, Penn State, DuPont, …

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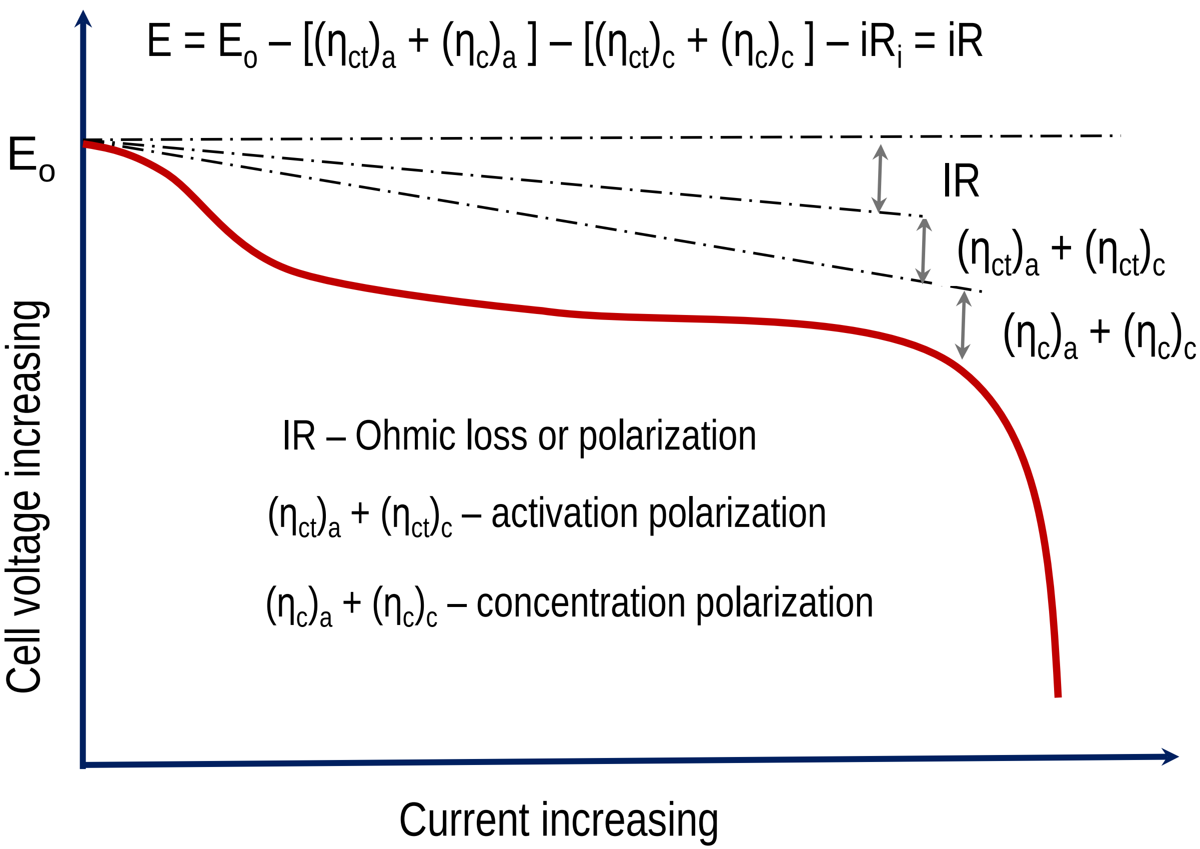
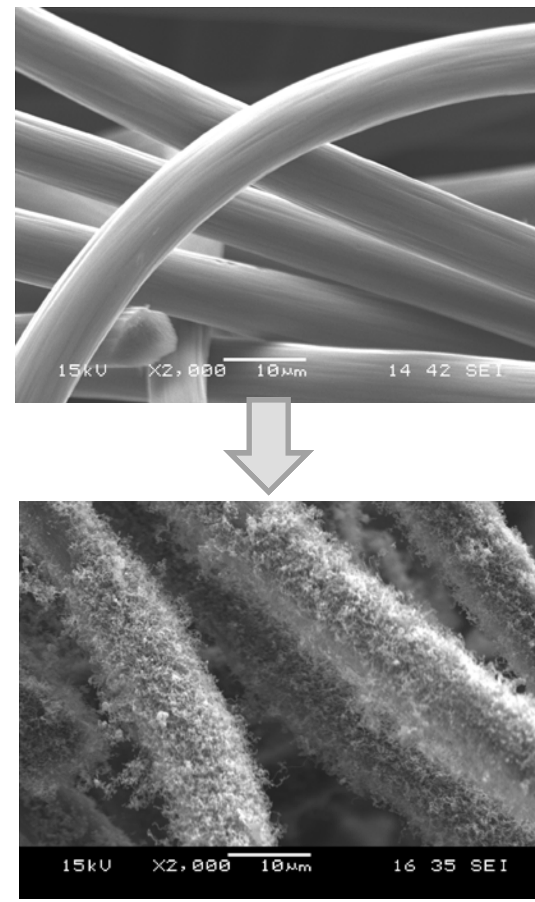
Electrodes/bi-polar plates of improved electrochemical activity

- Improve carbon/graphite electrode activity and current capability by modifying surface chemistry and structure/microstructure
- Carried out thermal oxidation, doping and nanostructuring





Na-batteries

Electrochemical storage that utilize Na- or Na-containing electrodes and a Na^+ conducting electrolyte, either solid or liquid

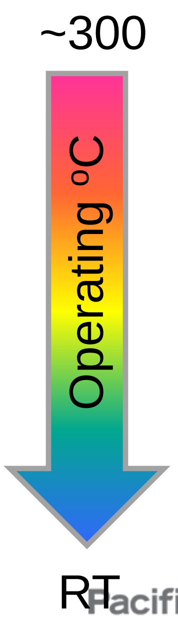
Why Na-battery chemistries?

- ❑ Li-resources constrains;
- ❑ Low cost of raw materials

- ❑ Na-beta alumina electrolyte batteries (SBB)

  Na-S or Na-Ni/NaCl
- ❑ Na-NaSicon electrolyte batteries
- ❑ Na-ion (aqueous or

  non aqueous electrolyte) batteries



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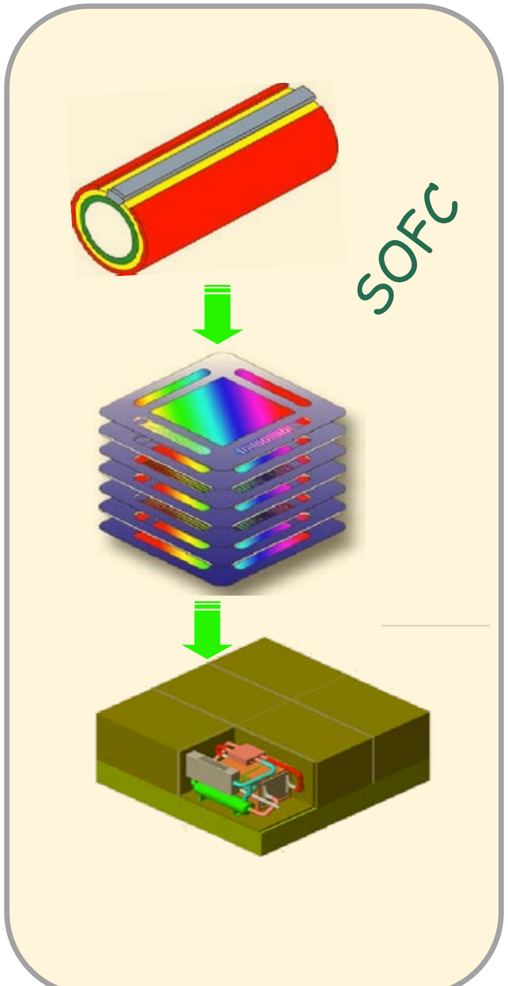
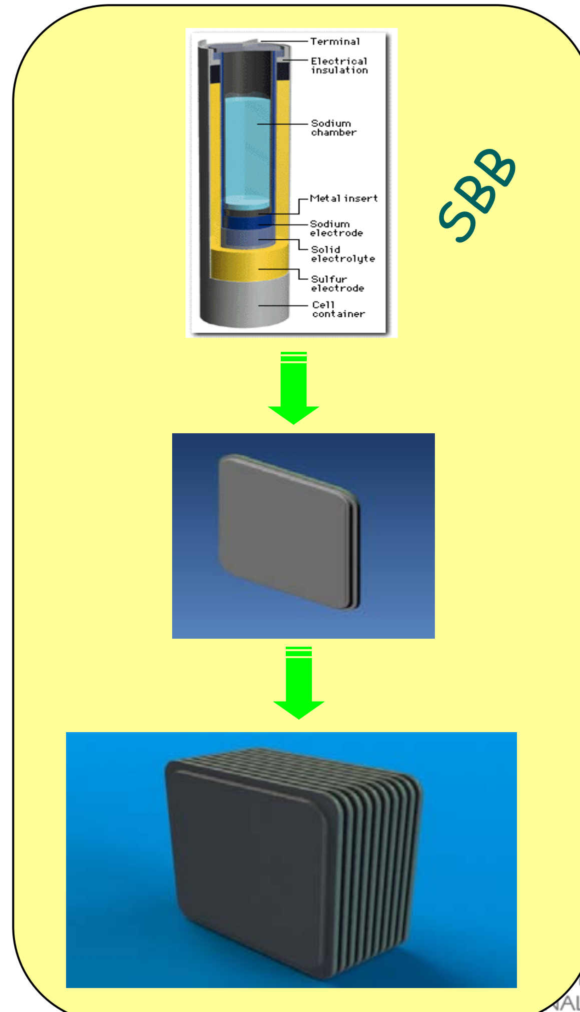
Development of Planar SBB

- PNNL (supported by DOE-ARPA-E, with Eagle Pitcher (lead)) is developing new generation Na-beta batteries that can meet economic and performance requirements for wide market penetration

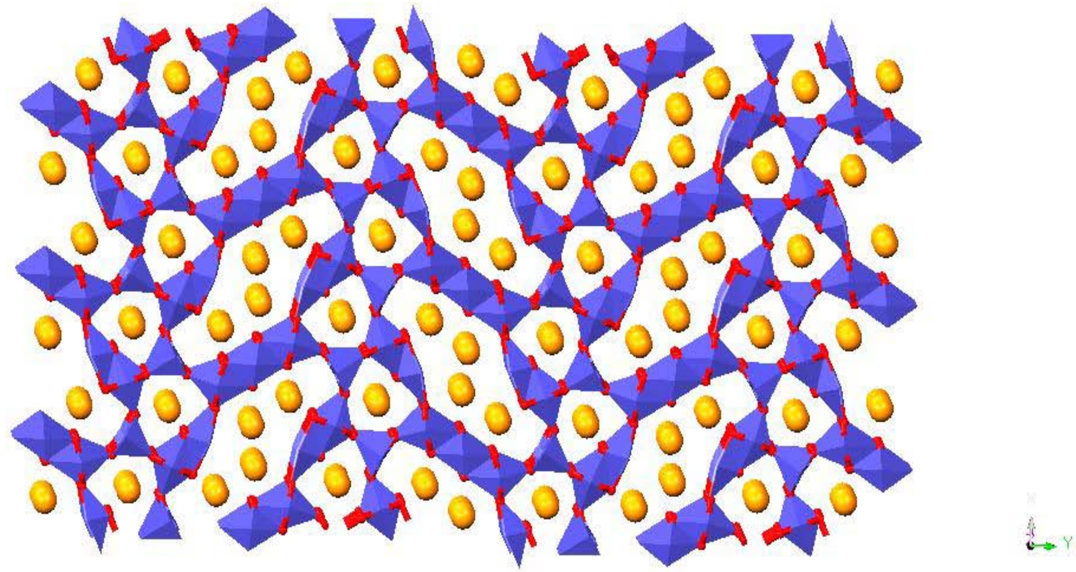


To be discussed by Dr. Vince Sprenkle

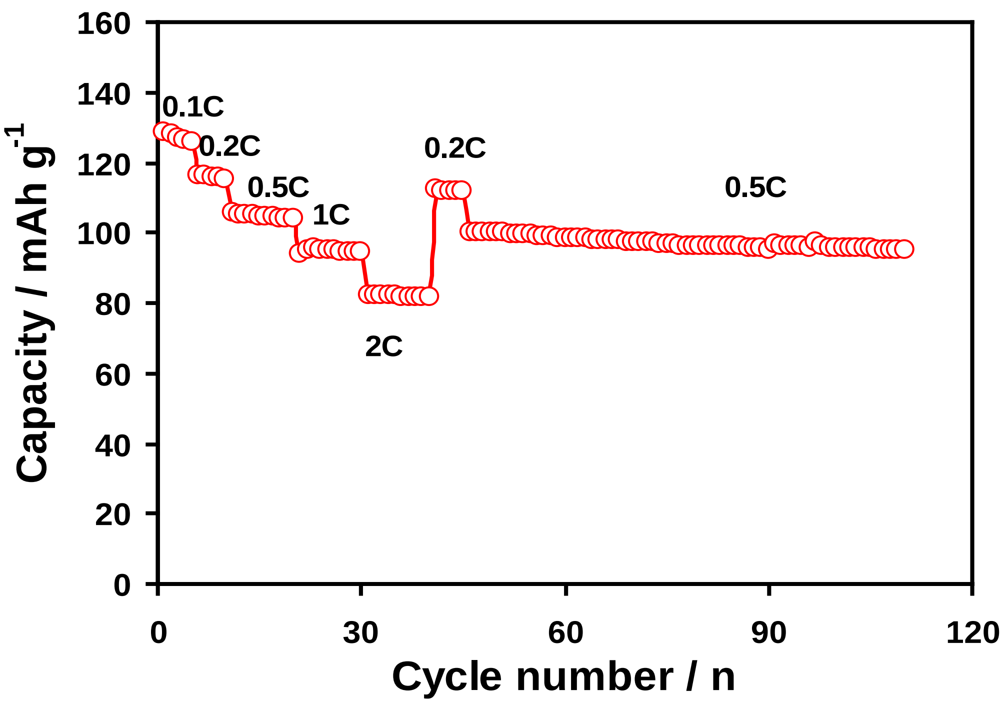


Na-ion battery development

- Search materials and structures that are capable of facile Na^+ insertion/ deinsertion, and develop low cost Na-ion batteries



orthorhombic $Na_4Mn_9O_{18}$



To be discussed by Dr. Jun Liu

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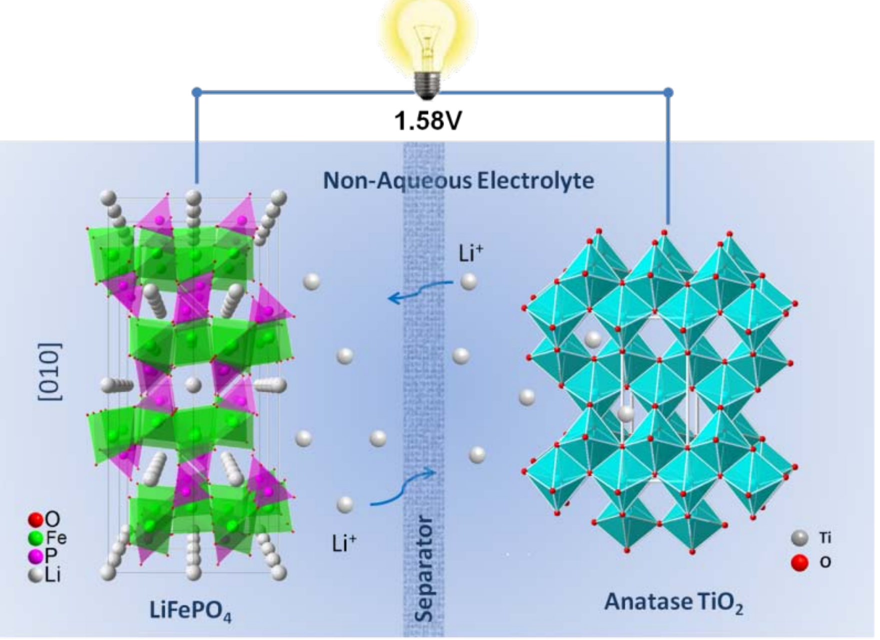
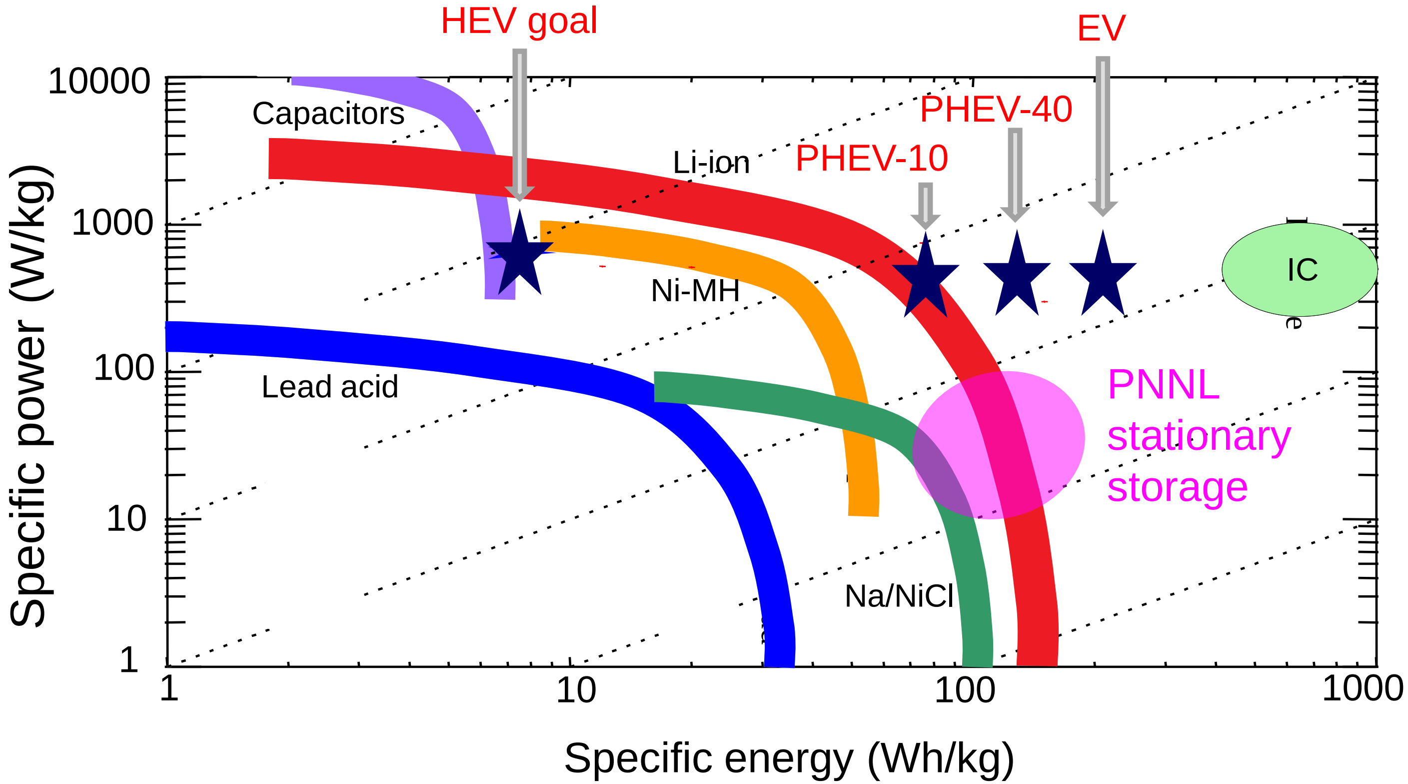
Unique Li-ion for community storage

- Long cycle life (>6,000 cycles)
- Low cost (<$250/kWh)
- Low P/E (≤0.5)
- Easy heat management





To be discussed by Dr. Choi

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Summary and Future Work

- PNNL has adopted an systematic approach in searching suitable technologies, including novel redox flow batteries, Na-batteries and low cost, long life Li-ion batteries, for distribution and community storage.
- Substantial progress has achieved in development and optimization of key materials components and cell designs, which include new redox flow battery electrolytes, electrodes and electrolytes for planar Na-beta alumina batteries, etc.
- Future work will focus on cell scale up, stack design and engineering, while continuing efforts on materials/components, through collaboration with academia, industries, and among national labs.

Please follow other talks from PNNL for further information.

Acknowledgements

- DOE-OE Energy Storage Program: Dr. Imre Gyuk,
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- Staff at PNNL:

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  Liyu Li, Soowhan Kim, Gordon Xia, Wei Wang, Vijayakumar Murugesan, Dean Matson, Jianlu Zhang, Yuliang Cao, Birgit Schwenzer, Feng Chen, …

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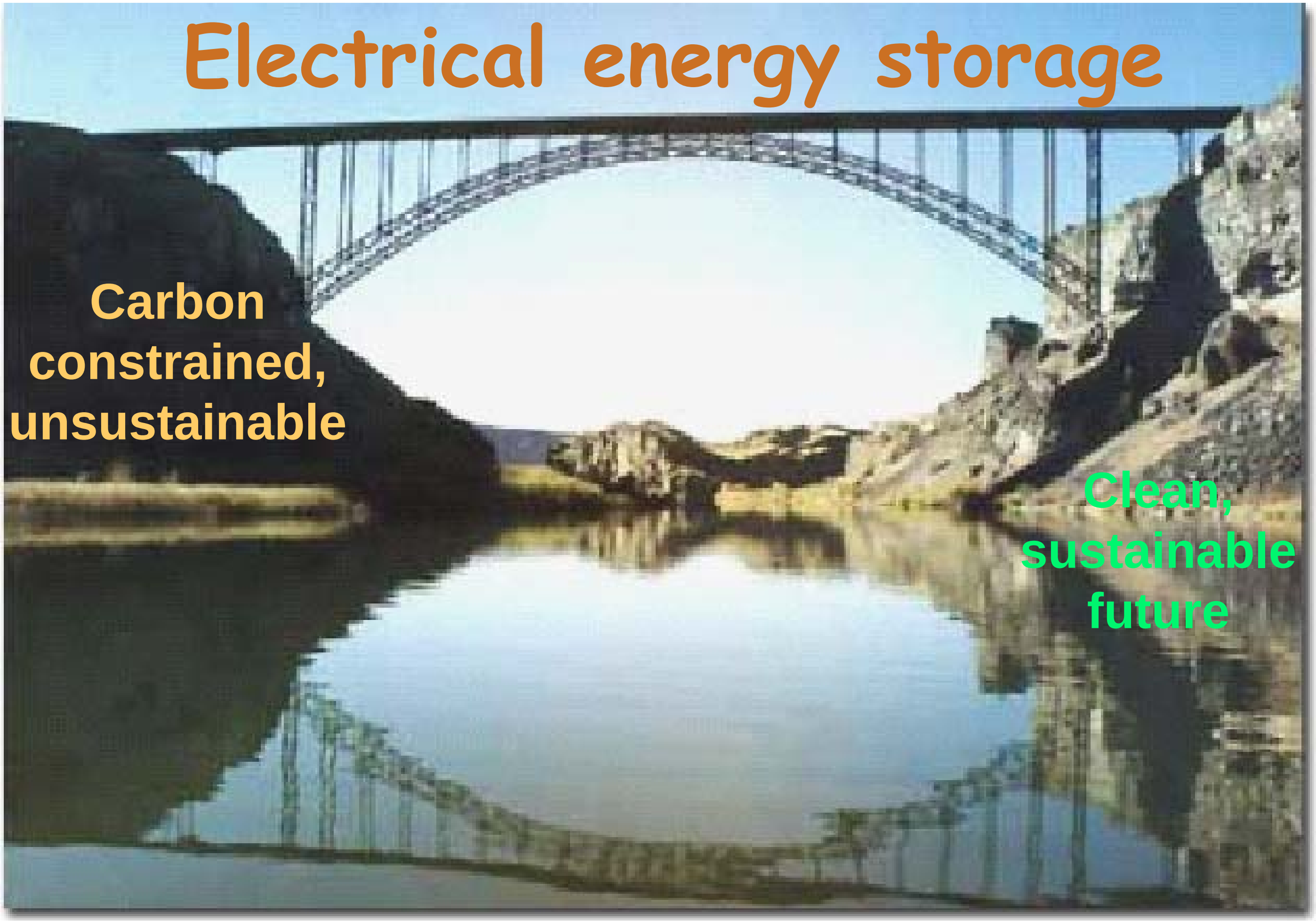

THANK YOU FOR YOUR ATTENTION

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