



Energy Storage Technology Advancement
Partnership (ESTAP) Webinar:

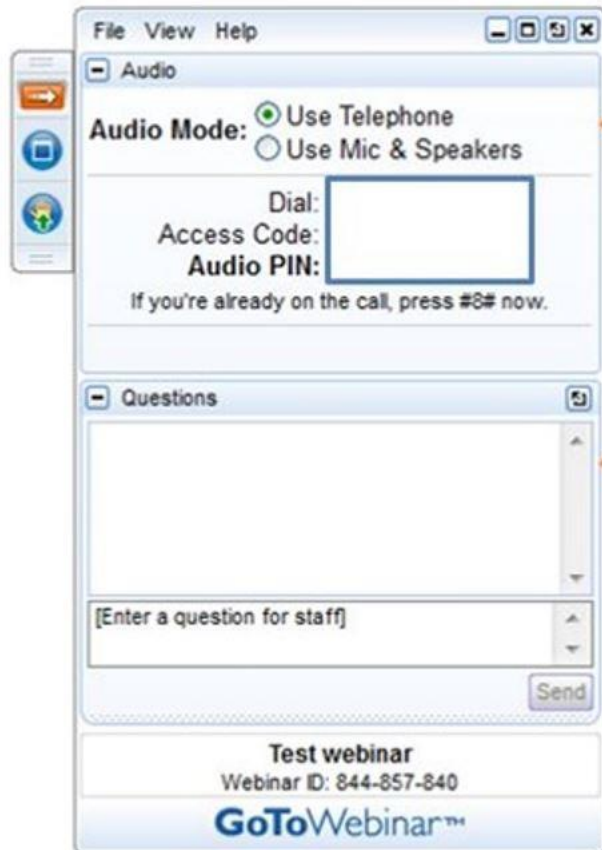
Flow Batteries: New Efforts in R&D

March 23, 2016

Hosted by Todd Olinsky-Paul
ESTAP Project Director
Clean Energy States Alliance



Housekeeping



The screenshot shows the GoToWebinar interface. At the top is a menu bar with 'File', 'View', and 'Help'. Below it is a sidebar with icons for chat, help, and other functions. The main area is divided into two sections: 'Audio' and 'Questions'. The 'Audio' section has a title bar, a menu icon, and two radio buttons: 'Use Telephone' (selected) and 'Use Mic & Speakers'. Below these are fields for 'Dial:', 'Access Code:', and 'Audio PIN:', followed by the instruction 'If you're already on the call, press #8# now.' The 'Questions' section has a title bar, a menu icon, a large text input area, a smaller input area with the placeholder '[Enter a question for staff]', and a 'Send' button. At the bottom, it says 'Test webinar', 'Webinar ID: 844-857-840', and the 'GoToWebinar' logo.

← All participants are in “Listen-Only” mode. Select “Use Mic & Speakers” to avoid toll charges and use your computer’s VOIP capabilities. Or select “Use Telephone” and enter your PIN onto your phone key pad.

← Submit your questions at any time by typing in the Question Box and hitting Send.

This webinar is being recorded.

You will find a recording of this webinar, as well as all previous CESA webcasts, archived on the CESA website at

www.cesa.org/webinars

State & Federal Energy Storage Technology Advancement Partnership (ESTAP)

Todd Olinsky-Paul

Project Director

Clean Energy States Alliance (CESA)



Thank You:

Dr. Imre Gyuk

U.S. Department of Energy,
Office of Electricity Delivery and
Energy Reliability

Dan Borneo

Sandia National Laboratories



ESTAP is a project of CESA

Clean Energy States Alliance (CESA) is a non-profit organization providing a forum for states to work together to implement effective clean energy policies & programs:

State & Federal Energy Storage Technology Advancement Partnership (ESTAP) is conducted under contract with Sandia National Laboratories, with funding from US DOE.

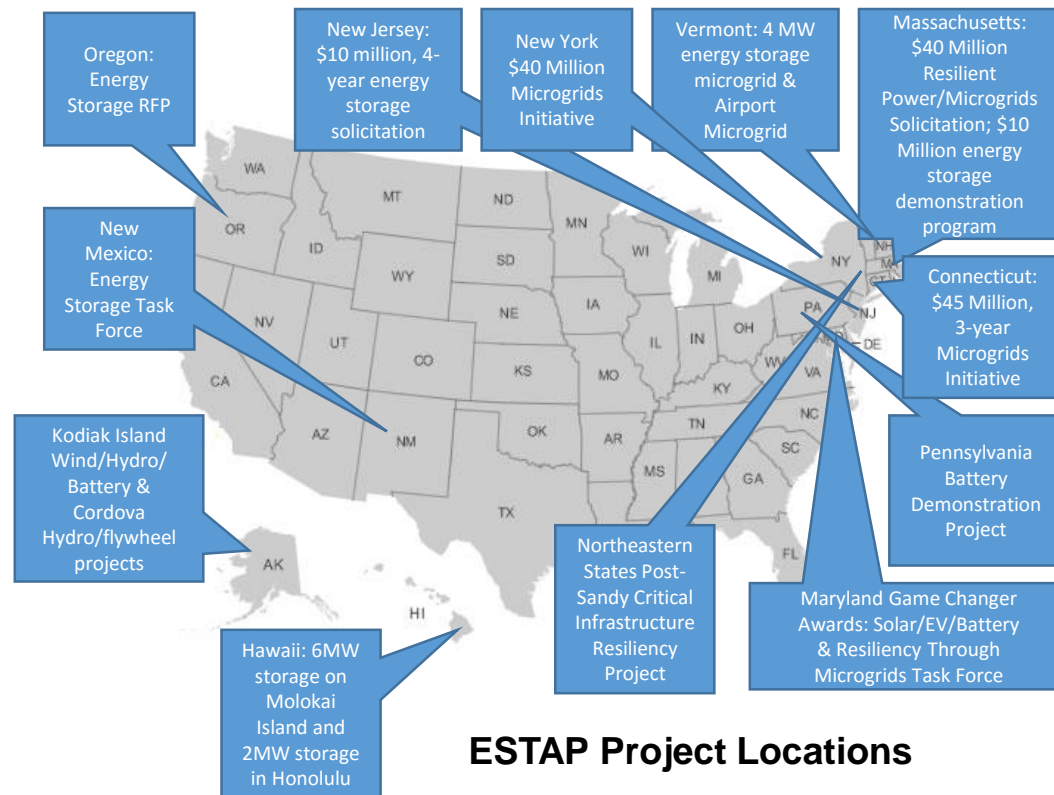
ESTAP Key Activities:

1. Disseminate information to stakeholders

- ESTAP listserv >3,000 members
- Webinars, conferences, information updates, surveys.

2. Facilitate public/private partnerships to support joint federal/state energy storage demonstration project deployment

3. Support state energy storage efforts with technical, policy and program assistance



ESTAP Project Locations



Energy Storage Technology Advancement Partnership

[More CESA Projects](#)

Overview

[ESTAP Resource Library](#)[ESTAP Webinars](#)[ESTAP News](#)[ESTAP Listserv Signup](#)

ESTAP

Project Director: Todd Olinsky-Paul

Contact: Todd Olinsky-Paul, Todd@cleanegroup.org

[SIGN UP FOR THIS e-MAILING LIST](#)

The Energy Storage Technology Advancement Partnership (ESTAP) is a federal-state funding and information sharing project, managed by CESA, that aims to accelerate the deployment of electrical energy storage technologies in the U.S.

The project's objective is to accelerate the pace of deployment of energy storage technologies in the United States through the creation of technical assistance and co-funding partnerships between states and the U.S. Department of Energy.

ESTAP conducts two key activities:

1) Disseminate information to stakeholders through:

- The ESTAP listserv (>2,000 members)
- Webinars, conferences, information updates



NEW RESOURCES

October 14, 2015
Resilience for Free: How Solar+Storage Could Protect Multifamily Affordable Housing from Power Outages at Little or No Net Cost
By Clean Energy Group

September 30, 2015
Webinar Slides: Energy Storage Market Updates, 9.30.15

UPCOMING EVENTS

December 16, 2015
ESTAP Webinar: State of the U.S. Energy Storage Industry,

[More Events](#)

LATEST NEWS

November 30, 2015
Massachusetts Takes the Lead on Resilient

Today's Guest Speaker

- **Dr. Wei Wang**, Senior Scientist, Pacific Northwest National Laboratory (PNNL)



Next Generation Redox Flow Battery Development at PNNL

Wei Wang, Vincent Sprenkle, David Reed, Ed Thomsen, Zimin Nie, Bin Li, Xiaoliang Wei, Brian Koeppel, Baowei Chen, Alasdair Crawford, Vish Viswanathan, Patrick Balducci.

Pacific Northwest National Laboratory

Support from DOE Office of Electricity Delivery & Energy Reliability
Energy Storage Program

**Flow Batteries: New Efforts in R&D Webinar
March 23rd, 2016**



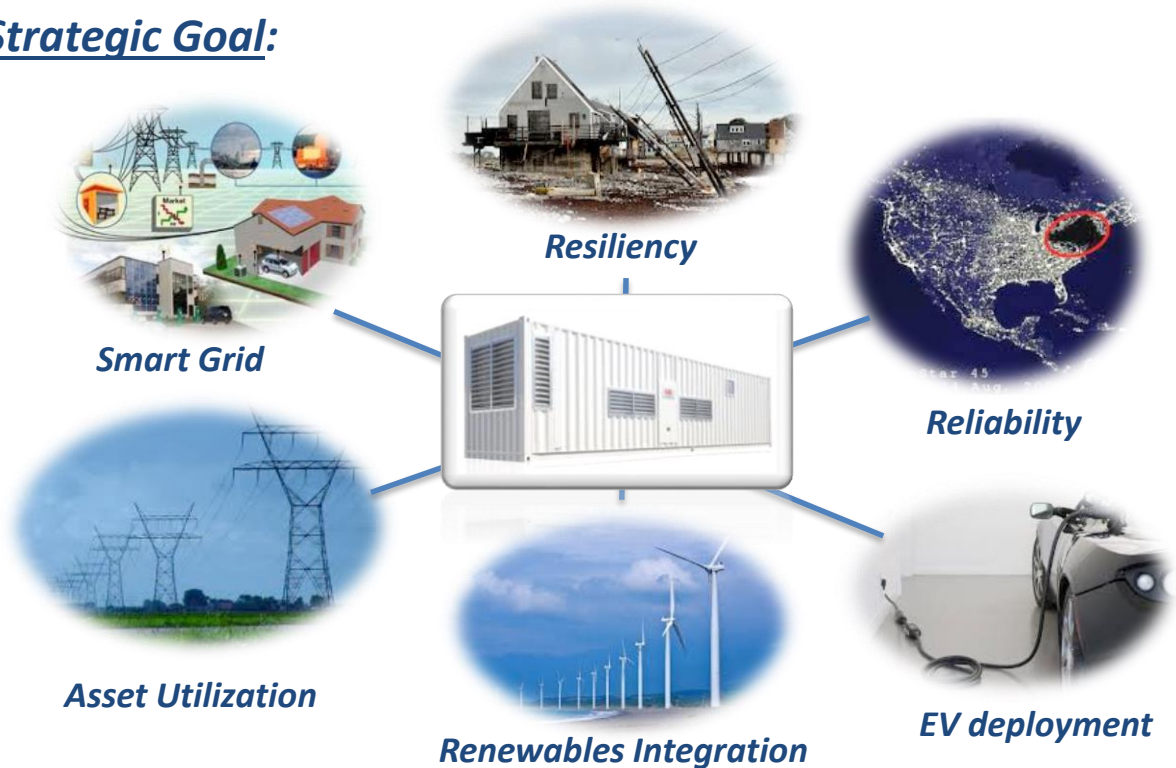
DOE OE Energy Storage Program

Challenges:

- **Cost competitive energy storage technologies**
 - Targeted scientific investigations of key materials and systems
- **Validated reliability & safety**
 - Independent testing of prototypic devices and understanding of degradation.
- **Equitable regulatory environment**
 - Enable Industry, Utility, Developer collaborations to quantify benefits provide input to regulators.
- **Industry acceptance**
 - Highly leverage field demonstrations and development of storage system design tools

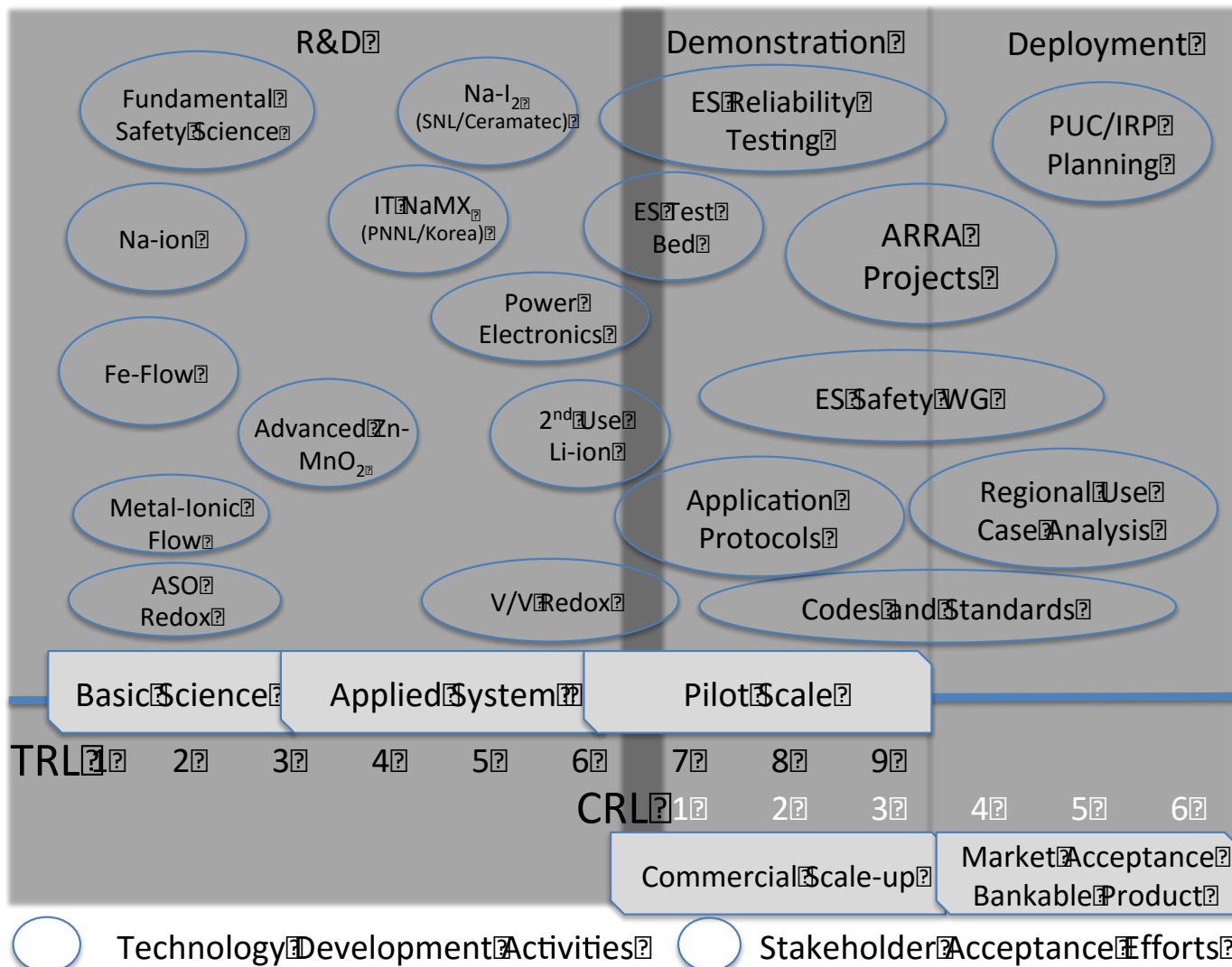
Mission: To enable energy storage to provide multiple benefits for critical grid applications, DOE is accelerating adoption of energy storage through: improving the technology, field demonstrations, and innovative market design.

Strategic Goal:





OE Energy Storage Program Activities



Coordinated effort between Sandia National Laboratory, Pacific Northwest National Laboratory, and Oak Ridge National Laboratory.

PNNL Stationary Energy Storage Development Approach

Competitive Technologies

Market Acceptance

Mixed Acid VRB



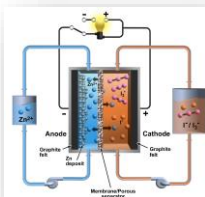
Na Metal Halide



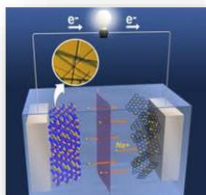
Organic RFBs



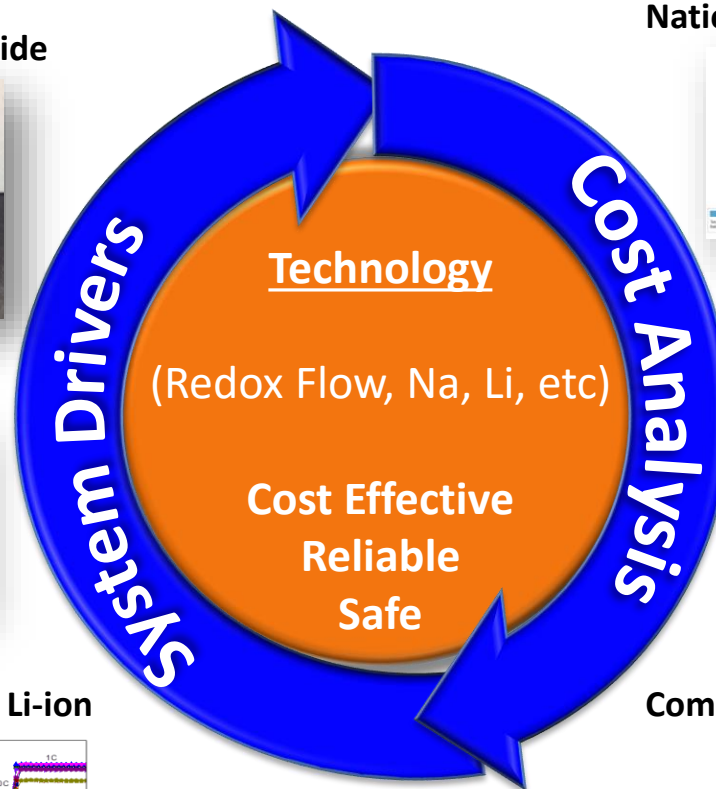
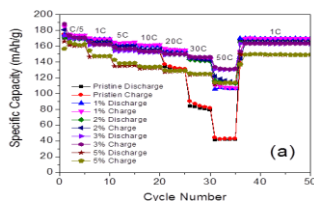
Zn-I RFB



Na-ion



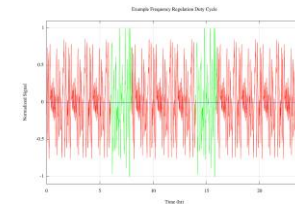
Fast Response Li-ion



National Assessment



Performance Protocols



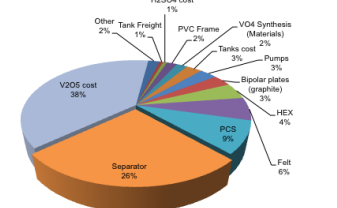
Safety Standards



Bainbridge PSE Case



Component Cost Analysis

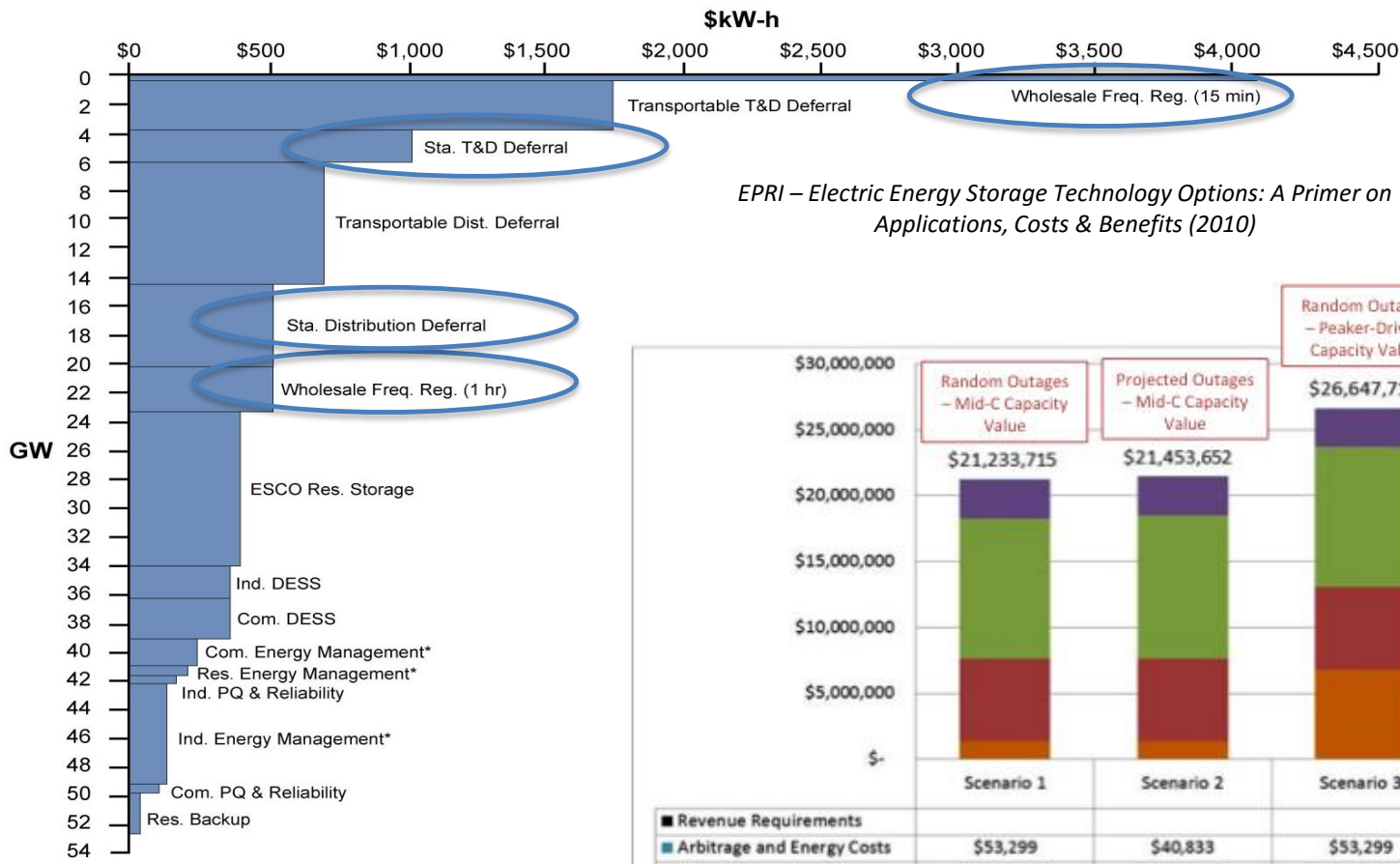


WA CEF

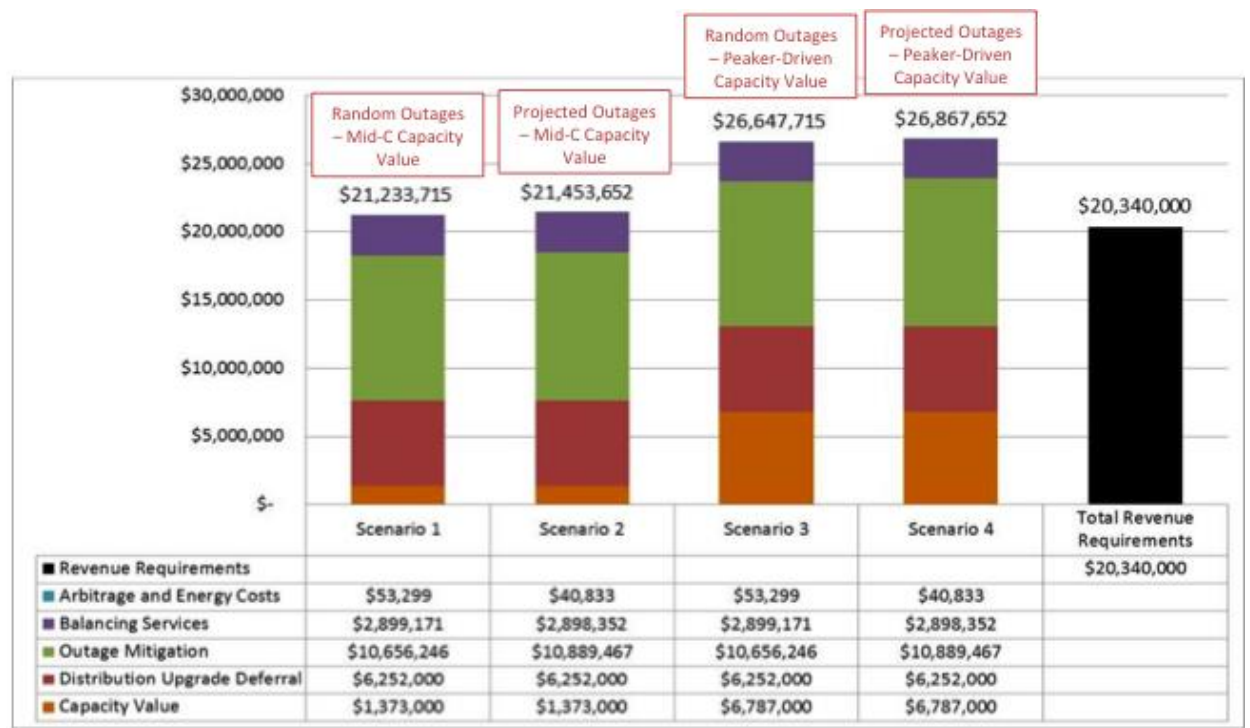


Developing deployable technologies to meet the cost/benefit requirements of the Grid.

Grid Energy Storage Diverse Markets Encourage Bundling and Cost Reduction.



EPRI – Electric Energy Storage Technology Options: A Primer on Applications, Costs & Benefits (2010)



Bundled Services: High degree of flexibility needed from energy storage?

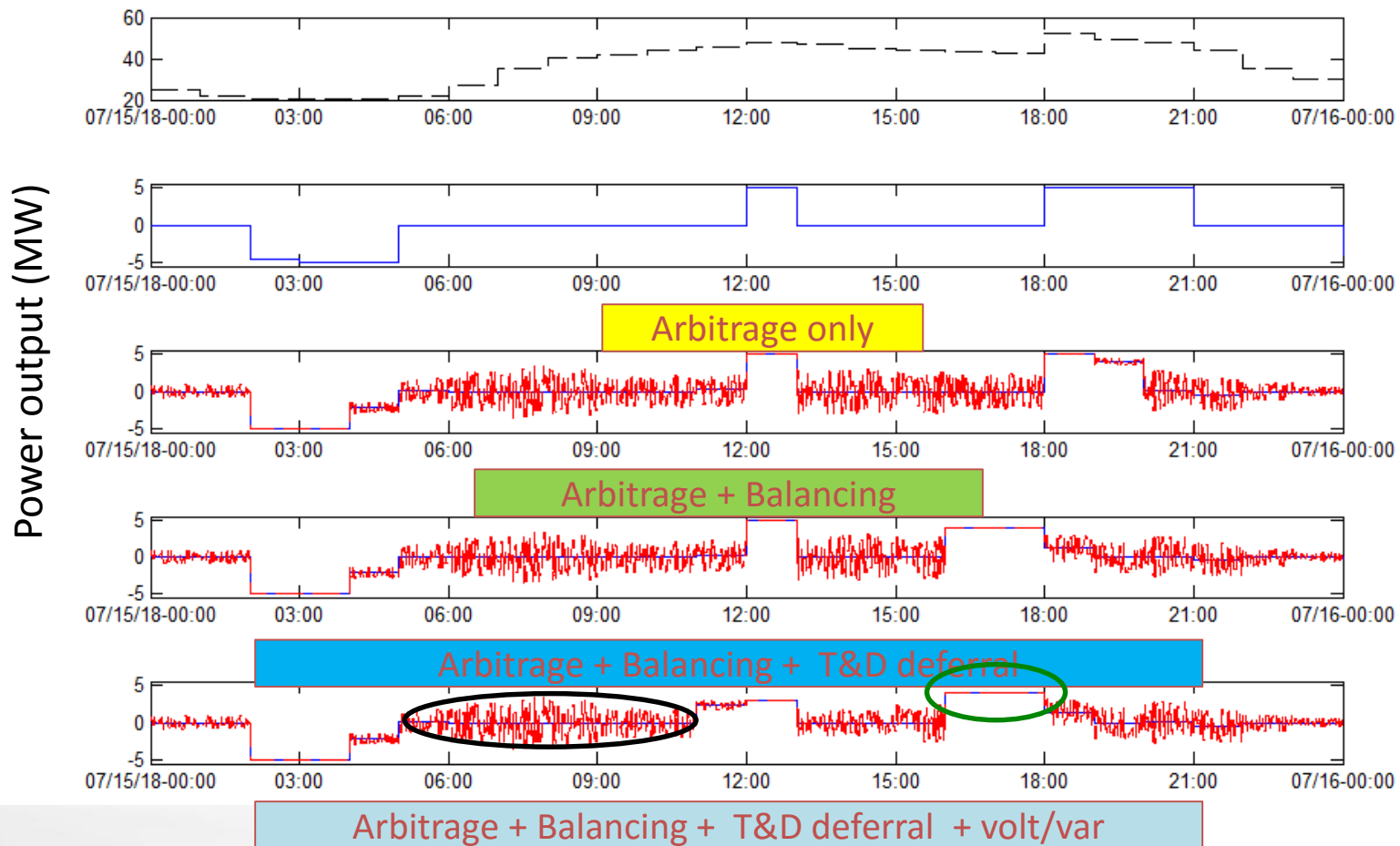
Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

PNNL-23040 Assessment of Energy
Storage Alternatives in the Puget Sound Energy System

Energy price (\$/MWh)

— Scheduled Hourly power
— Actual output minute by minute

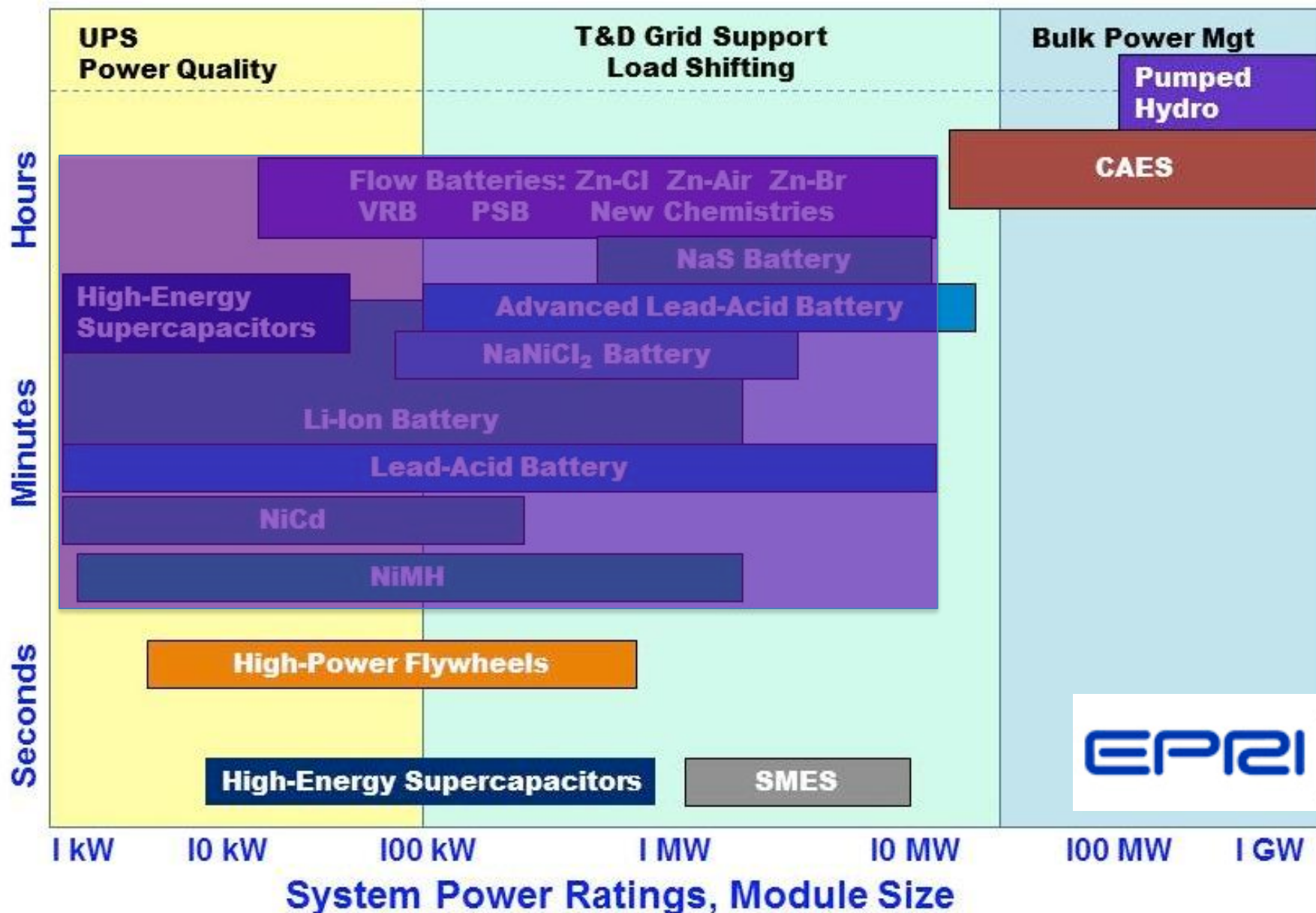


► Want energy storage systems that can provide *for both*:

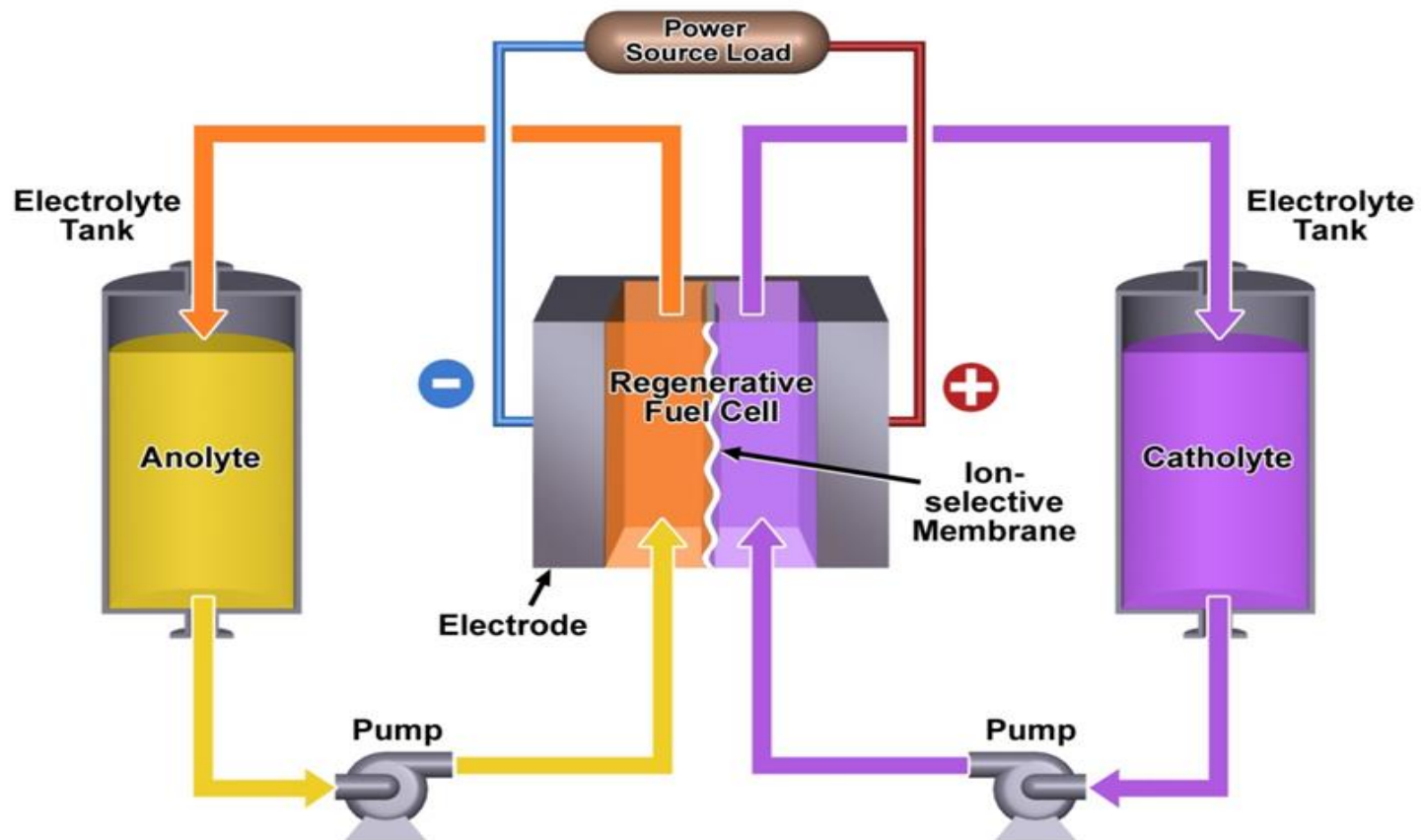
- Fast response balancing services *and*
- Longer duration (2+ hr) deferral and outage mitigation.

Electrical energy storage (EES) Options

Discharge Time at Rated Power



Why Redox Flow Battery?



Key Aspects

- **Power and Energy are separate enabling greater flexibility and safety.**
- **High safety**
- Suitable for wide range of applications 10's MW to ~ 5 kw
- Wide range of chemistries available.
- Low energy density ~ 30 Whr/kg

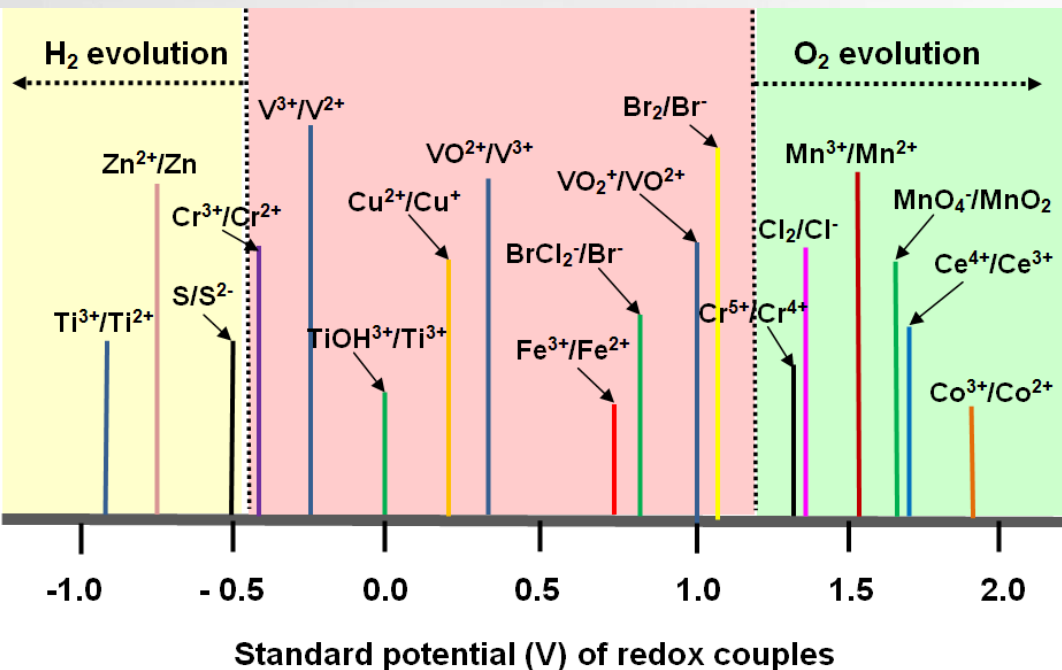
Existing redox systems, advantages/issues

- ❑ ICB: $\text{Fe}^{3+}/\text{Fe}^{2+}$ vs. $\text{Cr}^{3+}/\text{Cr}^{2+}$
- ❑ VRB: $\text{V}^{2+}/\text{V}^{3+}$ vs. $\text{VO}_2^+/\text{VO}^{2+}$
- ❑ PSB: Br_2/Br^- vs. S/S^{2-}
- ❑ ZBB: $\text{Br}^-/\text{Br}^{2-}$ vs. Zn^{2+}/Zn

Multi-100 kW
or MW
demonstrated

Others:

$\text{V}^{2+}/\text{V}^{3+}$ vs. $\text{Br}^-/\text{ClBr}_2^-$;
 $\text{Ce}^{4+}/\text{Ce}^{3+}$ vs. $\text{V}^{2+}/\text{V}^{3+}$;
 $\text{Fe}^{3+}/\text{Fe}^{2+}$ vs. Br_2/Br^- ;
 $\text{Mn}^{2+}/\text{Mn}^{3+}$ vs. Br_2/Br^- ;
 $\text{Fe}^{3+}/\text{Fe}^{2+}$ vs. $\text{Ti}^{2+}/\text{Ti}^{4+}$, ...



- ▶ Temperature stability
- ▶ SoC control
- ▶ Toxicity of Elements
- ▶ Minimal Fire Hazard
- ▶ High Degree of Flexibility

Challenge of traditional sulfuric-acid vanadium electrolyte

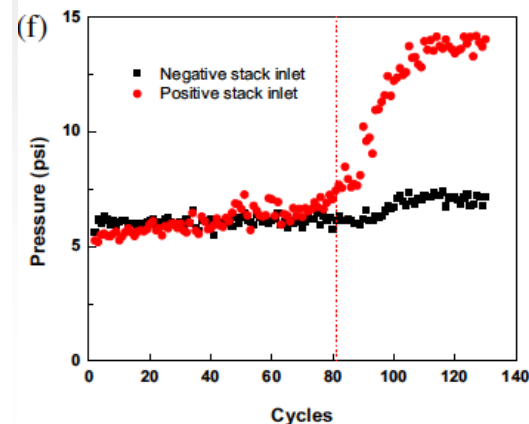
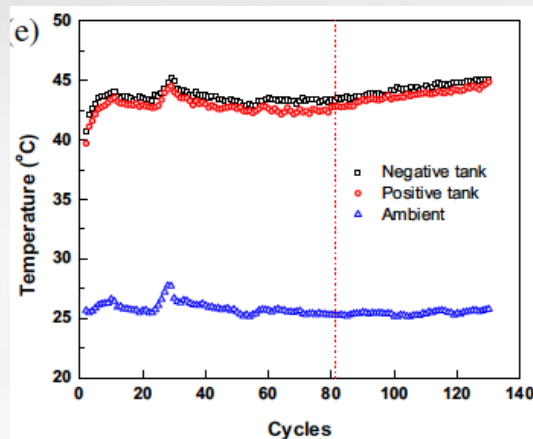
Problem of tradition VRB electrolyte

V concentration < 1.5M

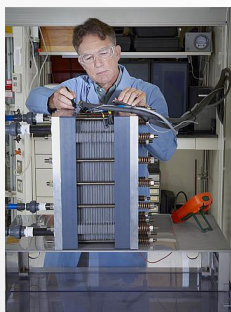
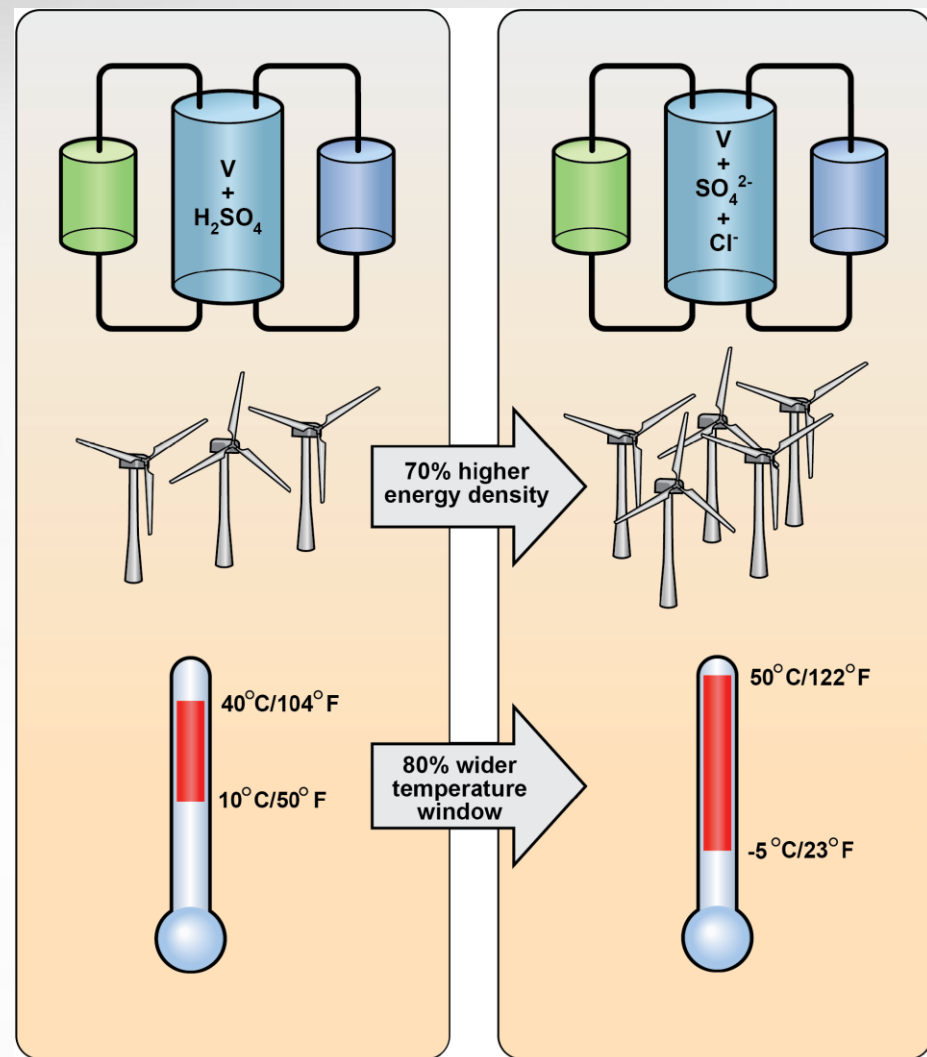
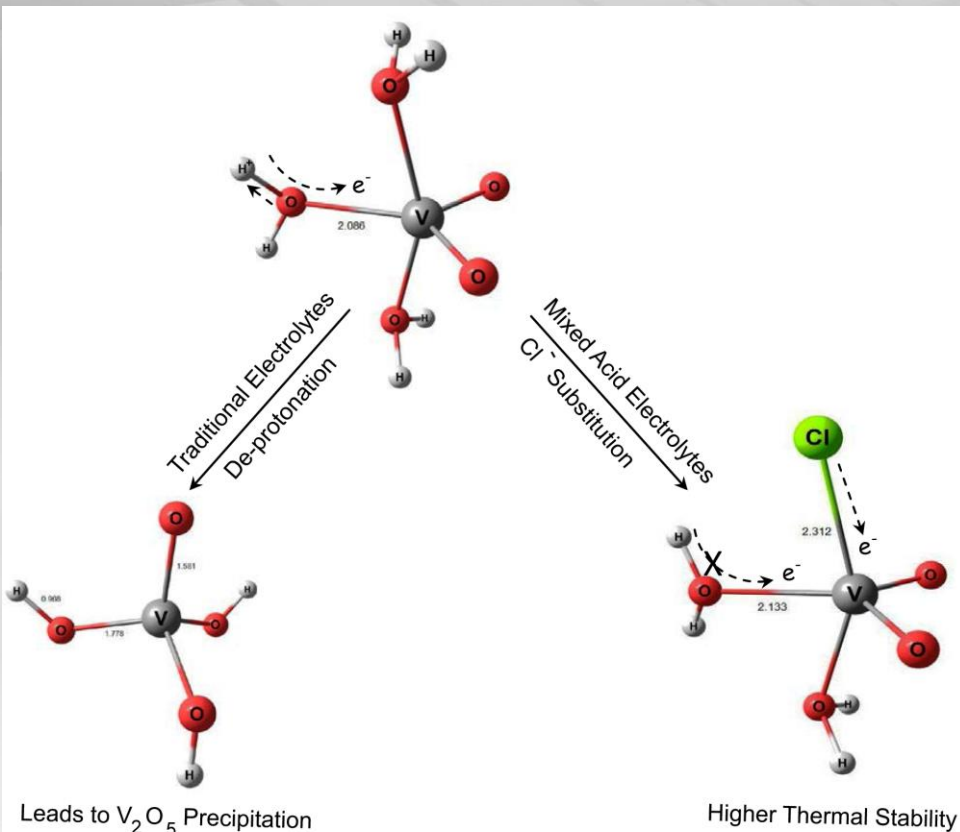
Temperature window 10~40°C

V specie	-5°C	25°C	40°C
	sulfate	sulfate	sulfate
V ²⁺	2M (419 h)*	2M	2M
V ³⁺	2M (634 h)	2M	2M
V ⁴⁺ (VO ₂ ⁺)	2M (18 h)	2M (95 h)	2M
V ⁵⁺ (VO ₂ ⁺)	2M	2M	2.0M (95 h)

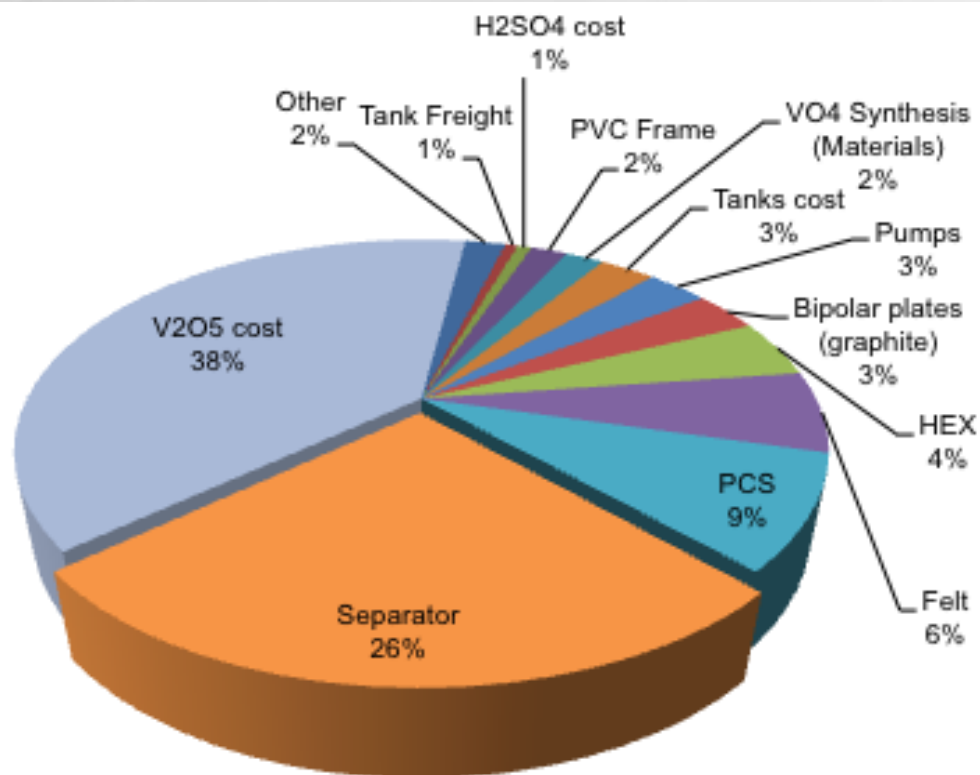
V⁵⁺ precipitation (1.5M @ ~43°C)



Solution Chemistry of the Electrolyte



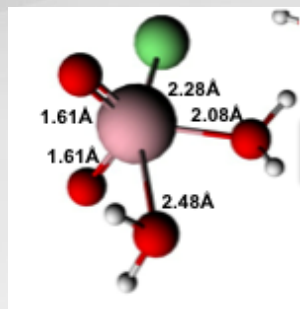
Redox Flow Battery Cost Projection



**Gen 2 V-V 1 MW /4 MWh
At 80 mA/cm2**

Redox Flow Battery Objectives

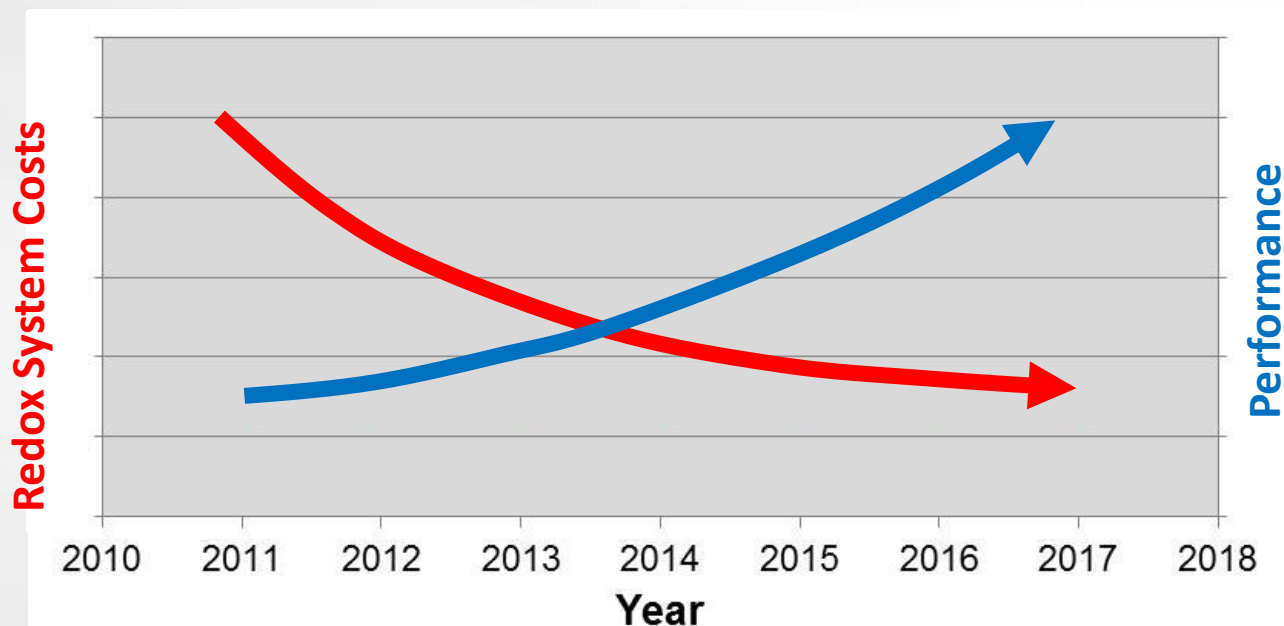
Develop the technologies, tools, and system understanding required to move the mixed acid electrolyte chemistry from basic chemistry to cost effective system solution.



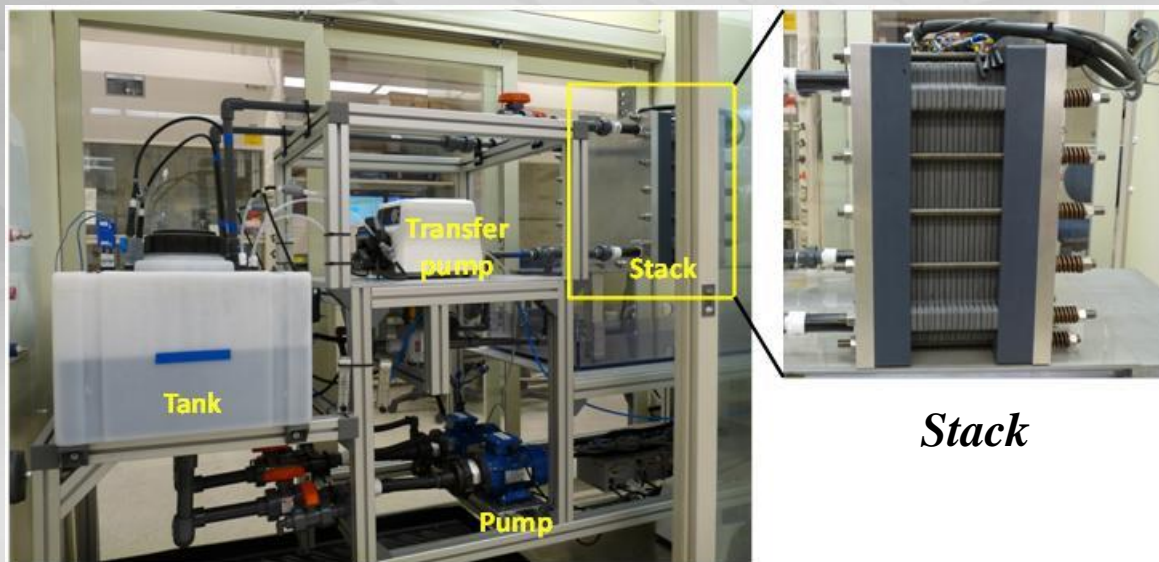
Basic Chemistry



Applied Systems



VRFB kW scale Stack Parameters



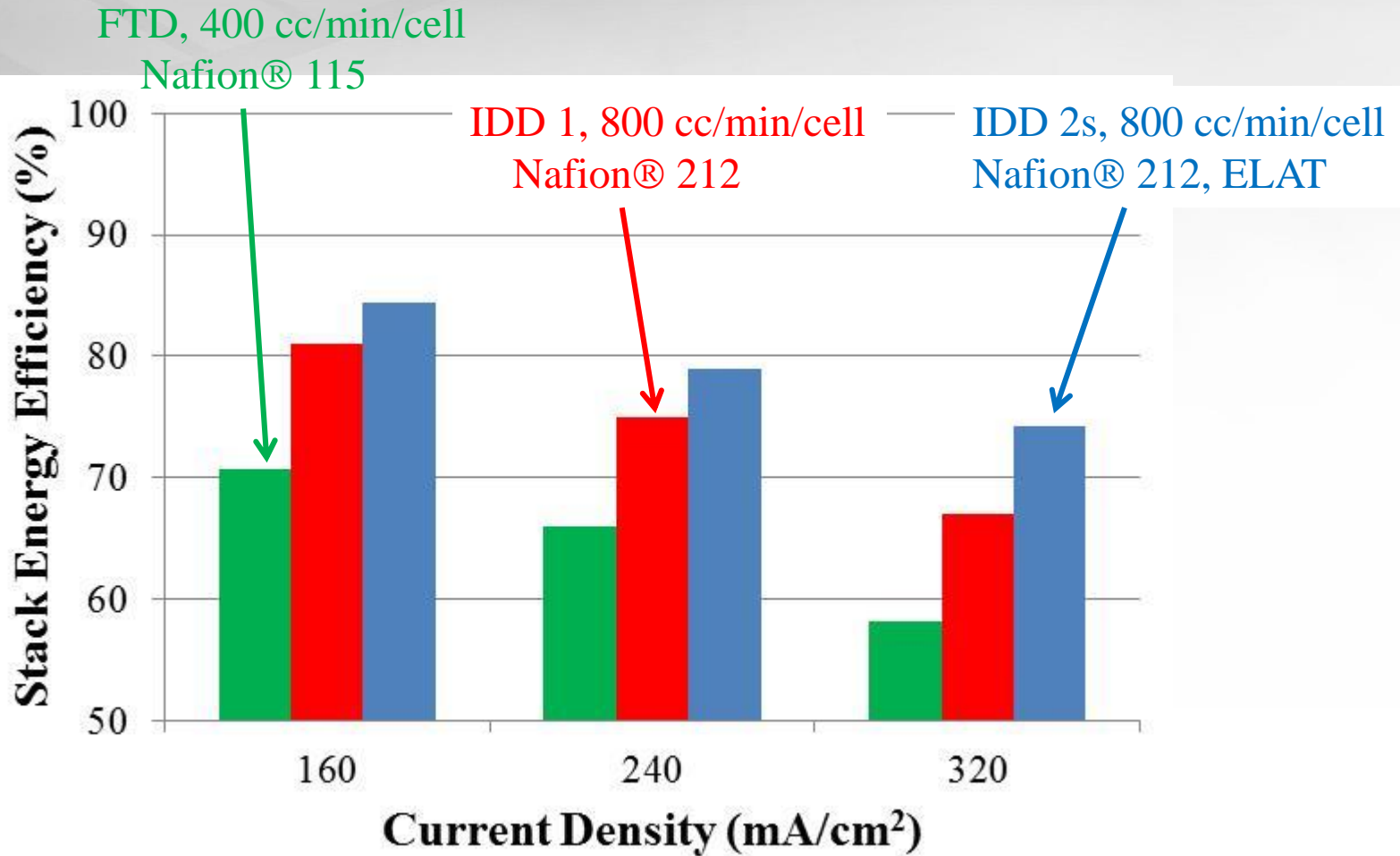
Stack



Test Parameters

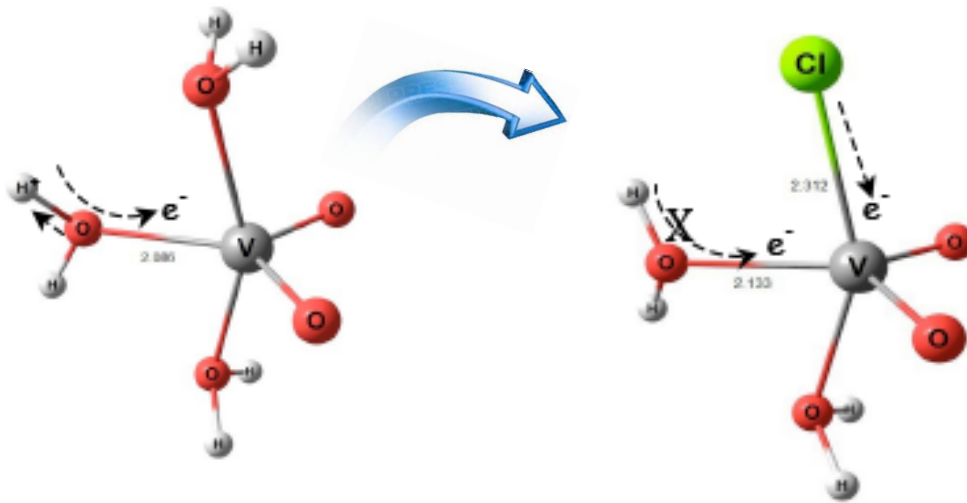
- 780 cm^2
- 1-20 cell stacks
- 15-85% SOC
- Mixed acid electrolyte
 - 2M V, 2M S, 2M Cl
- Nafion[®] membrane
 - 212 (~ 2 mil)
 - $j = 80 - 320 \text{ mA/cm}^2$
- Modified interdigitated flow design
- 1-5 KW stack
- Chillers to control temperature

20-cell Stack Performance



Mixed-acid VRB Development

Collaboration with
EMSL/FCSD on
standard sulfuric
electrolyte:
deprotonation leads
to precipitation at
elevated
temperatures



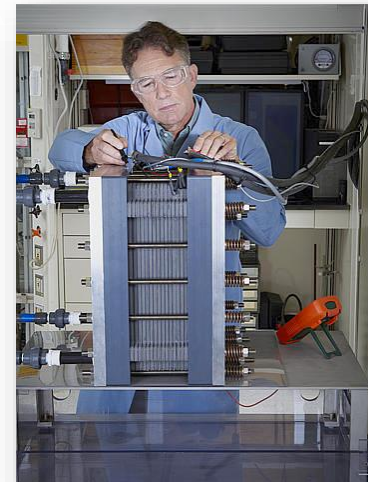
HCl addition prevents
deprotonation increasing
temperature stability by 80%
and energy density by 70%



Avista/UniEnergy 1 MW/4 MWh
System installation February 2015,
commissioned in June.



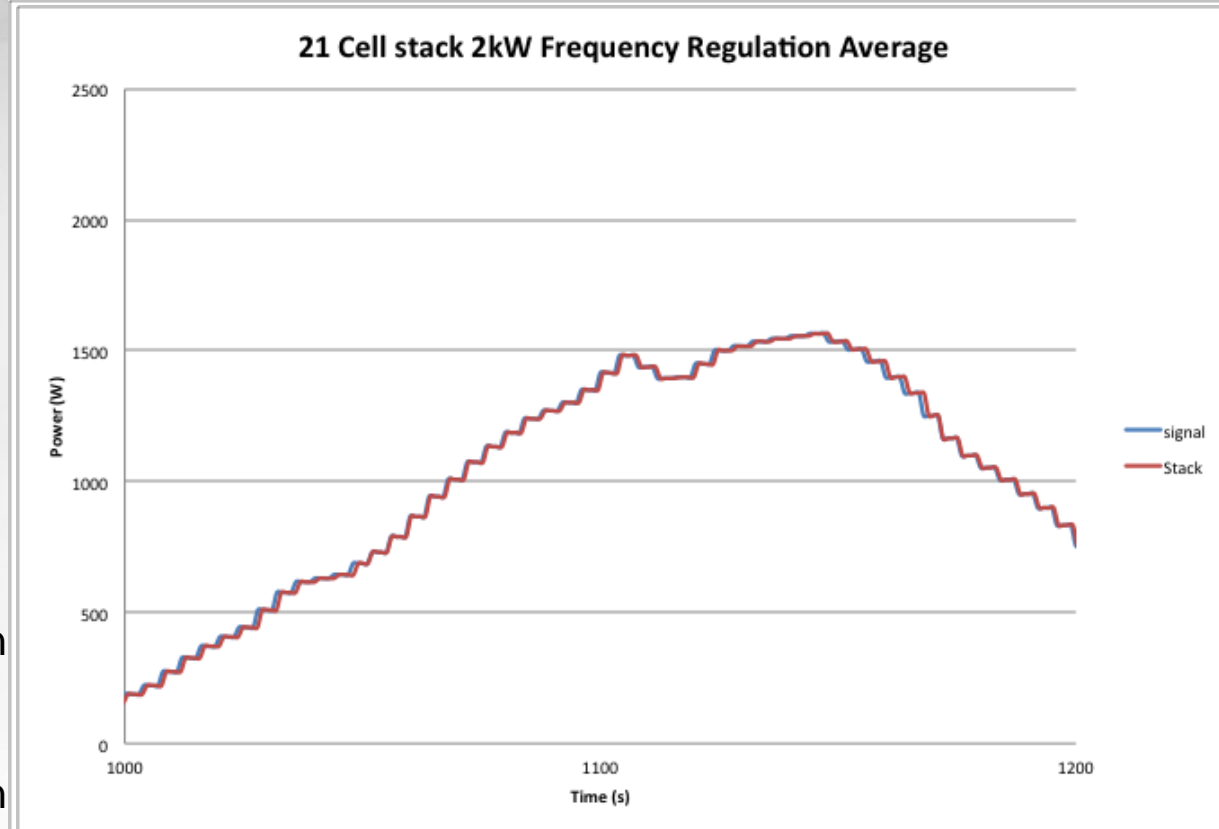
WA Governor Jay Inslee,
UniEnergy CEO Gary Yang,
OE Asst. Sec. Pat Hoffman at
CEF kickoff June 2014



PNNL kW lab scale
demonstration of technology

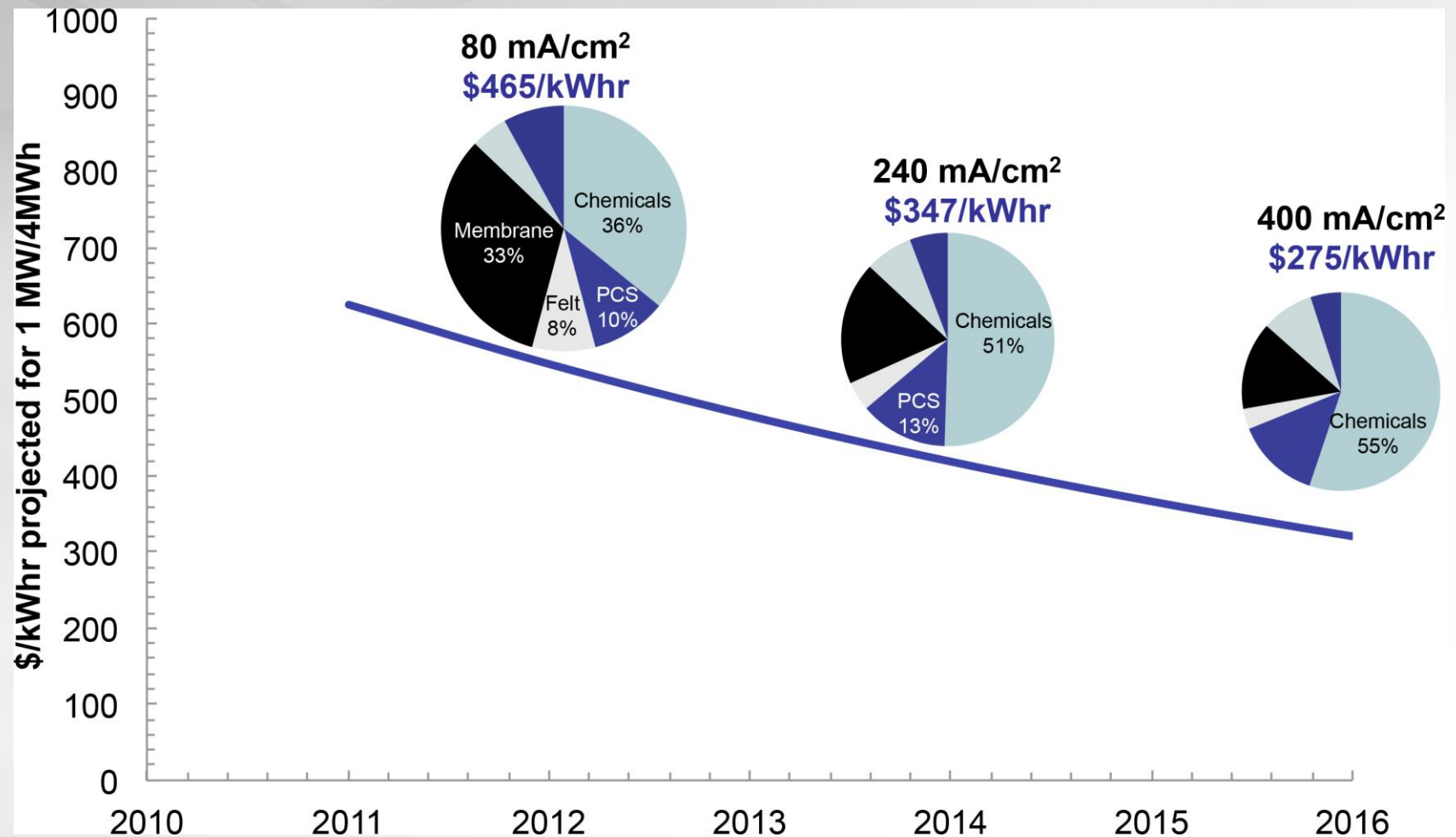
21 cell VRFB stack under Frequency Regulation protocol

- FR duty cycle determined from PJM balancing signal for year 2011
- Signals grouped into low, average and high standard deviations
- Representative 2-hour intervals with average standard deviation and 2-hour intervals with high standard deviation chosen
 - each being energy neutral
- Duty cycle consisted of three 2-hour average standard deviation (SD) signals followed by one 2-hour high SD signals, three 2-hour average standard deviation (SD) signals followed by one 2-hour high SD signals and four 2-hour average SD signals

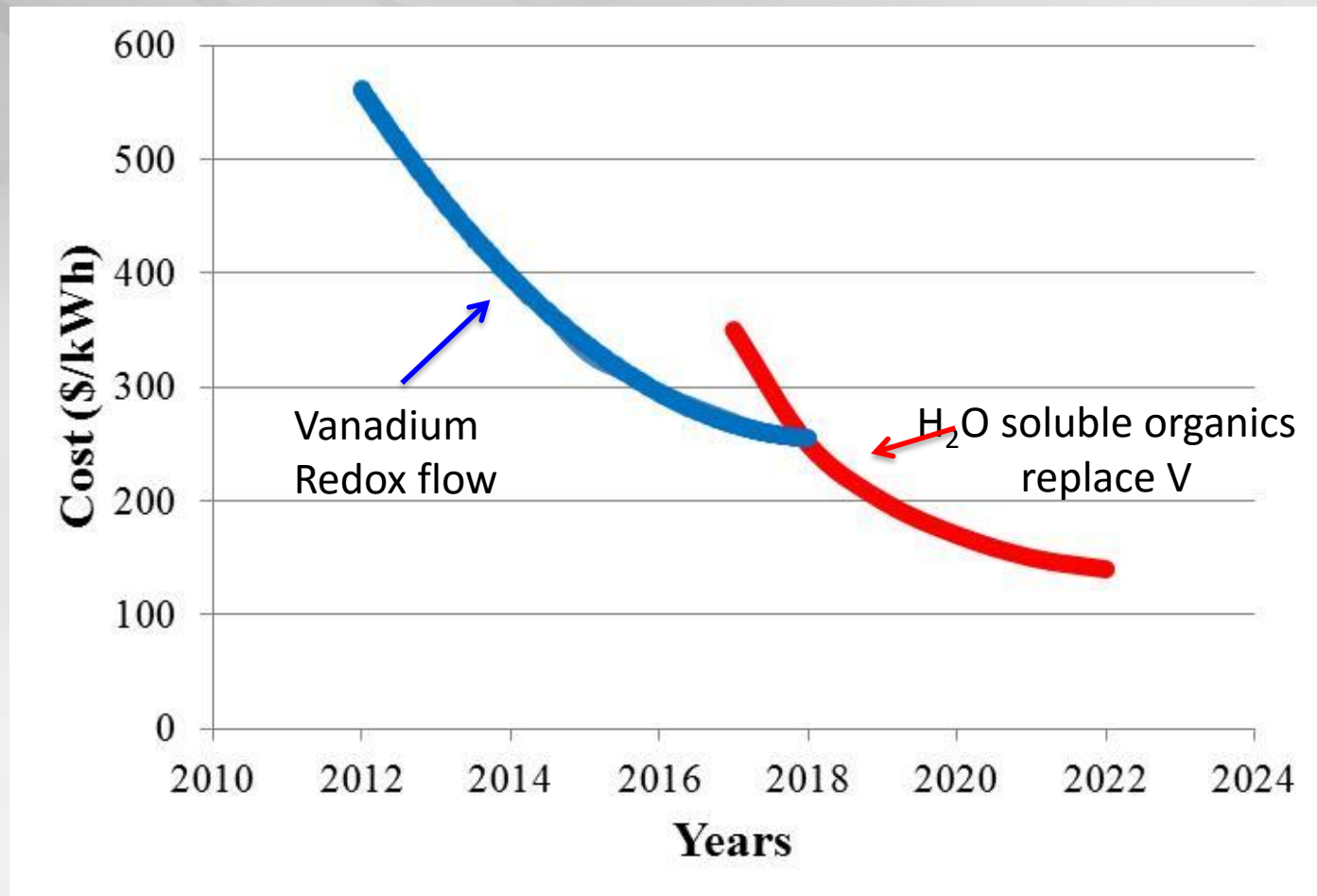


*DC only

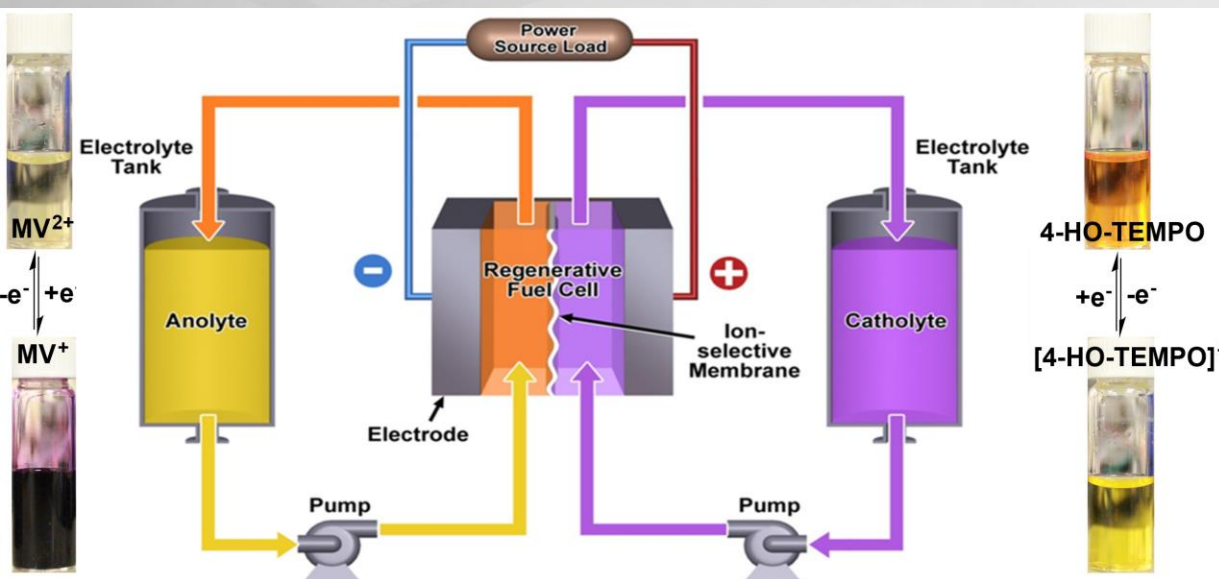
Remaining Challenges - Cost Reduction



Next Generation Redox Battery Development



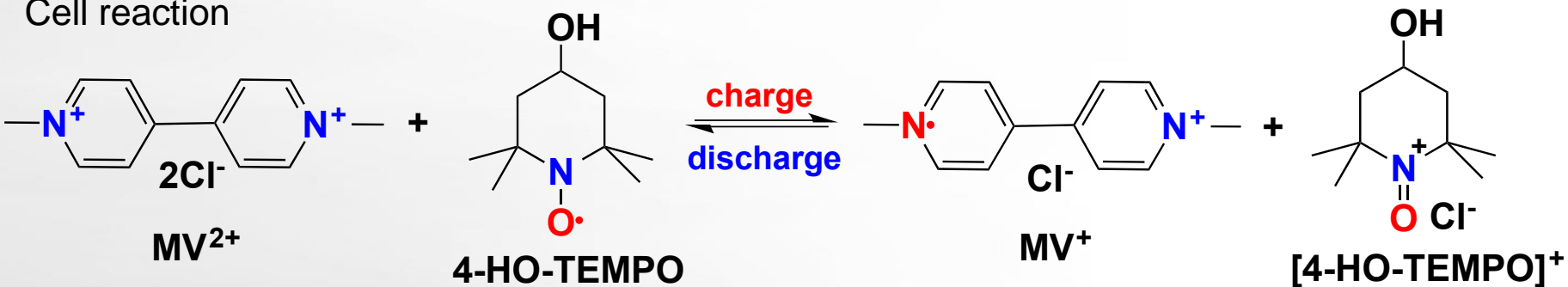
Low-cost aqueous organic RFBs



Advantage:

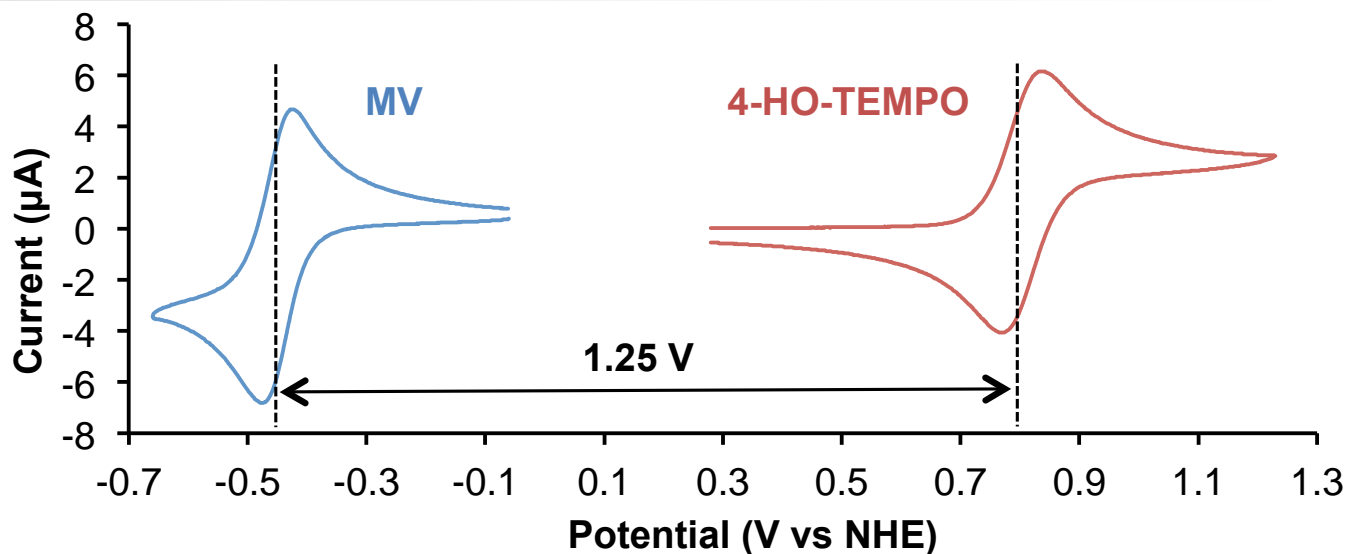
- ◆ Low-cost redox couple;
- ◆ Low-cost supporting electrolyte;
- ◆ No resource constraints;
- ◆ Less corrosive and toxic.

Cell reaction



Voltage of Aqueous Redox Flow Battery

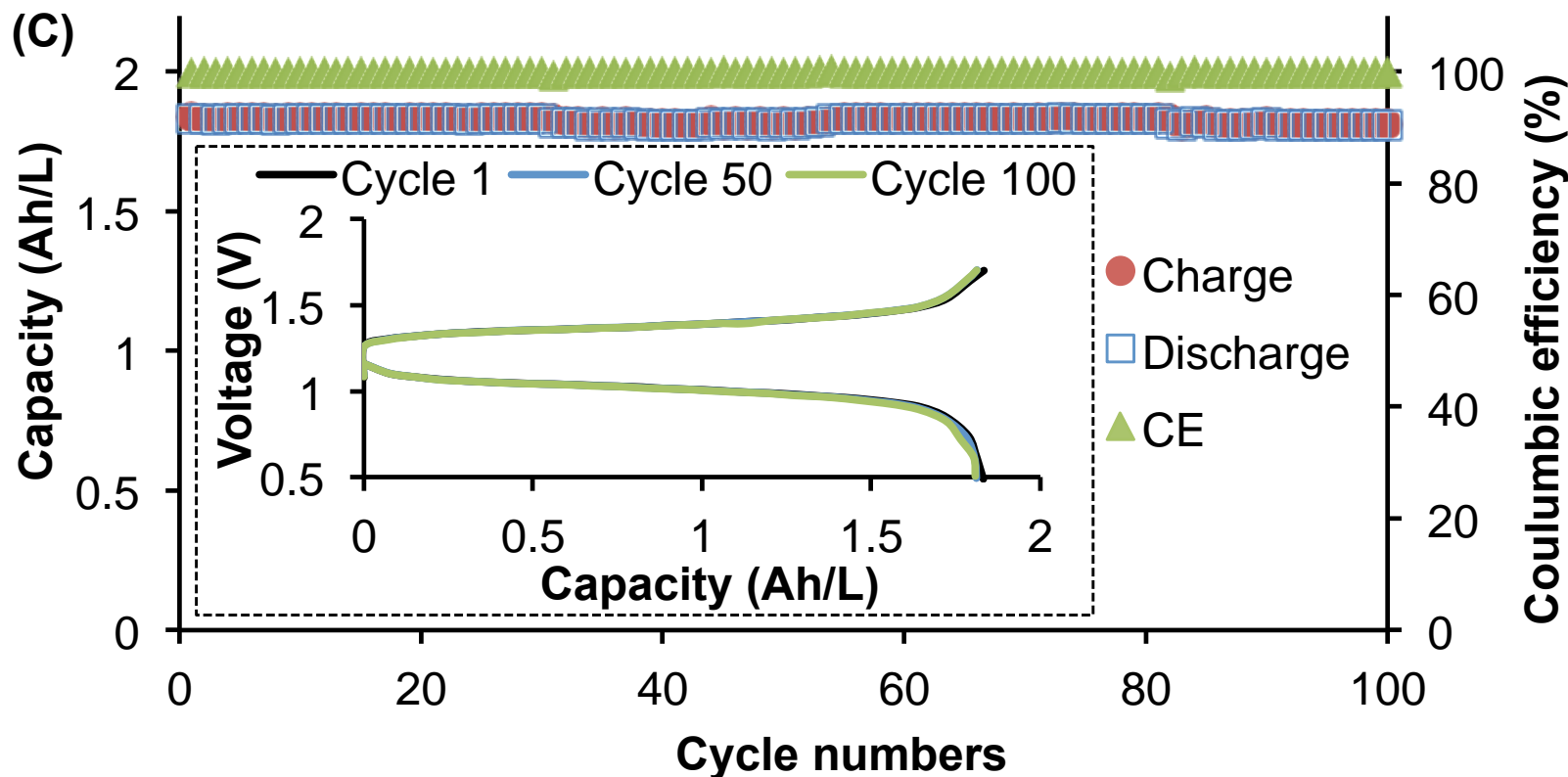
ARFBs (anolyte/catholyte)	Cell voltage (V)	Current density (mA/cm ²)	Supporting electrolytes	Membrane
PbSO ₄ /BQDS	1.07	10	H ₂ SO ₄	Nafion 115
AQDS/Br ₂	0.96	500	H ₂ SO ₄ and HBr	Nafion 117
AQDS/BQDS	0.76	8	H ₂ SO ₄	Nafion 112
MV/4-HO-TEMPO	1.25	60	NaCl	AME



Solubility in water:

MV > 3.0M

4-HO-TEMPO: >2.1M



Capacity and coulombic efficiency vs cycling numbers of the cell at 40 mA/cm². Conditions: anolyte, 0.1 M **MV** in 1.0 M NaCl aqueous solution; catholyte, 0.1 M **4-HO-TEMPO** in 1.0 M NaCl aqueous solution; flow rate, 20 mL/min; AMV anion membrane. No remixing.

Redox flow battery with high energy density



120MWh system, peak power ~15MW.
Each tank holds 1800m³ of electrolyte.

- Large form factor/footprint
- Limited application

$$E = \frac{NC_a FV}{n}$$

E , system energy density

N , the number of electrons transferred

F , Faraday constant (26.8 Ah mol⁻¹)

C_a , Max concentration of active redox species

V , Voltage of the cell

n , number of electrolyte tanks

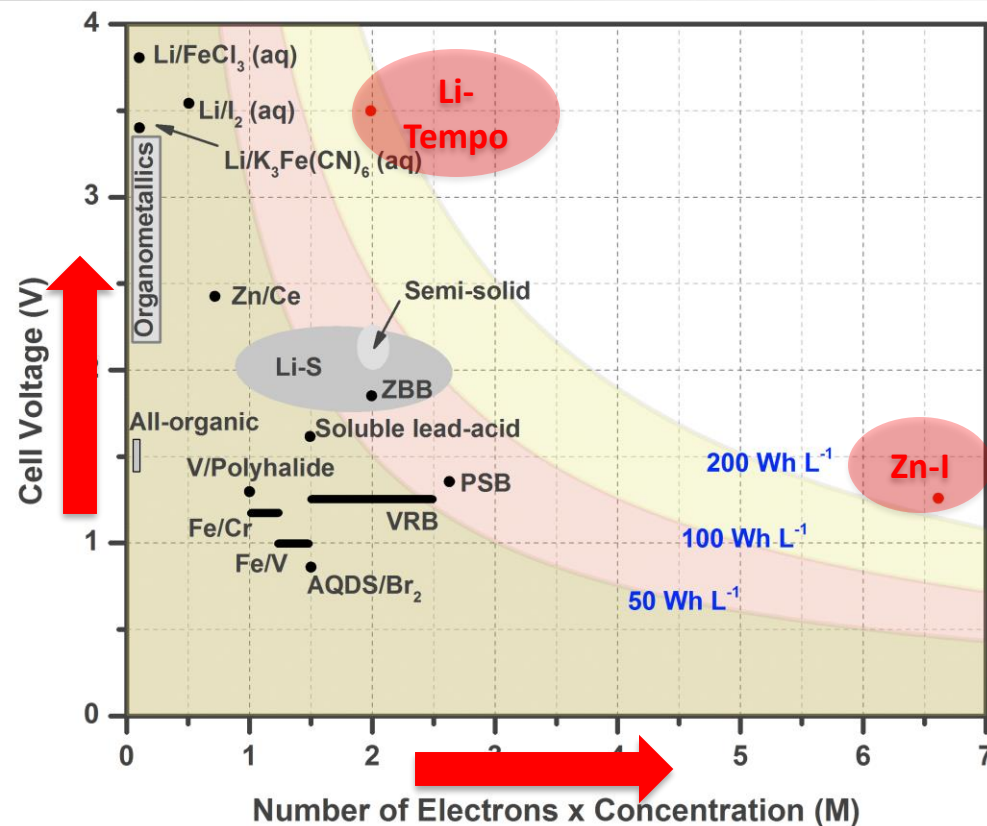
➤ Hybrid flow battery design

➤ Ambipolar electrolyte

Both anion and cation are active species.

➤ Bifunctional electrolyte

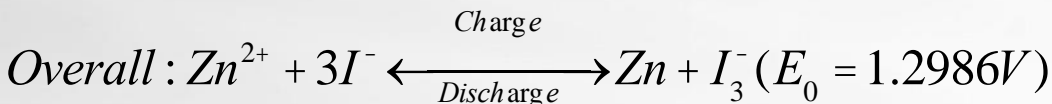
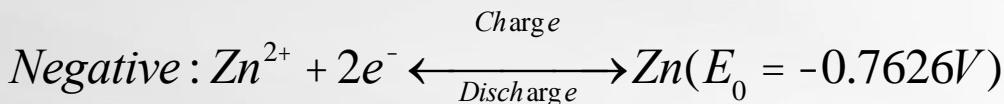
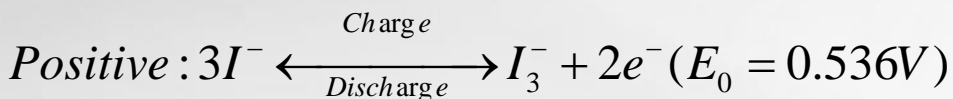
Active species can act as charge carrier.



High energy density Zn-Polyiodide aqueous RFB

Solubility of ZnI_2 is 7M in water \rightarrow theoretical energy density $\sim 322\text{Wh/L}$

Identify high solubility redox active species

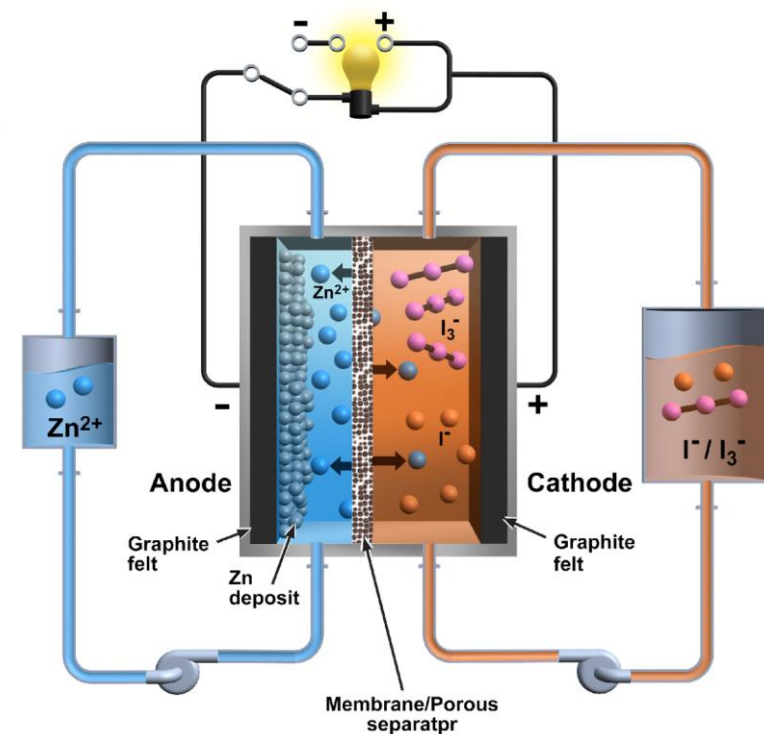


Characteristics of the Zn-I_x RFB

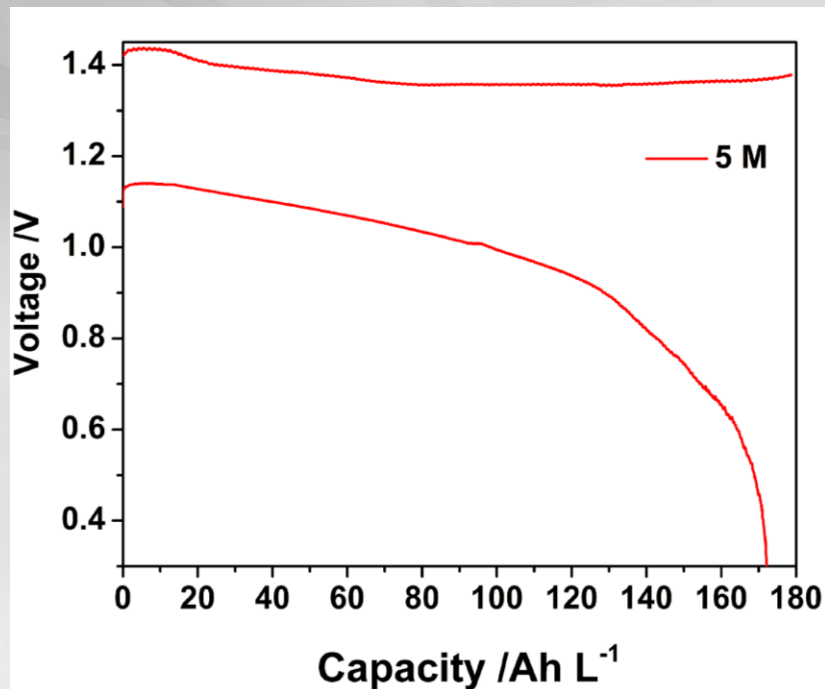
- Ambipolar electrolyte
- Bifunctional electrolyte
- High energy density
- High safety: PH value: 3~4

No strong acid

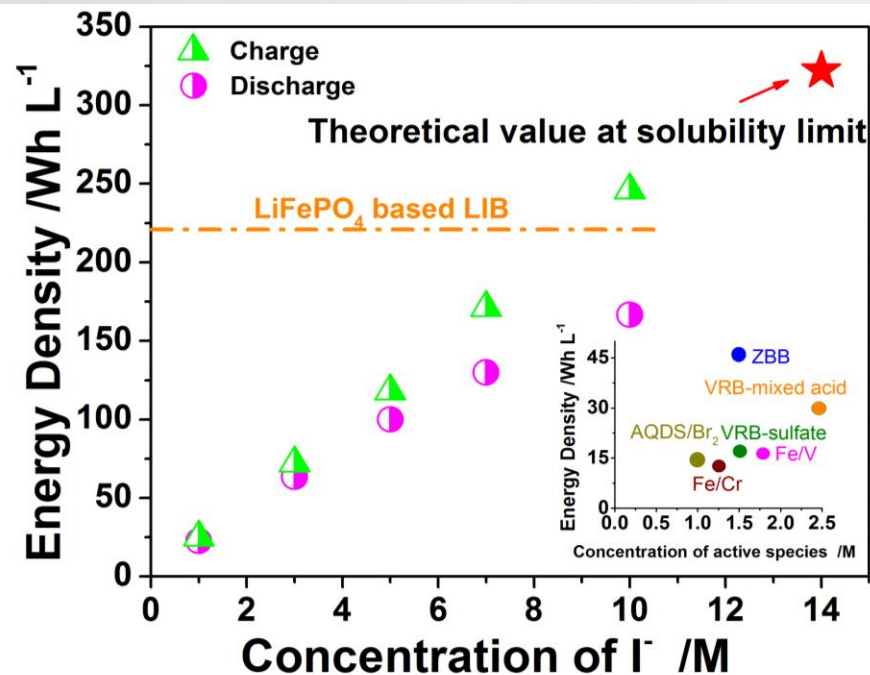
No hazardous materials



Electrochemical performance

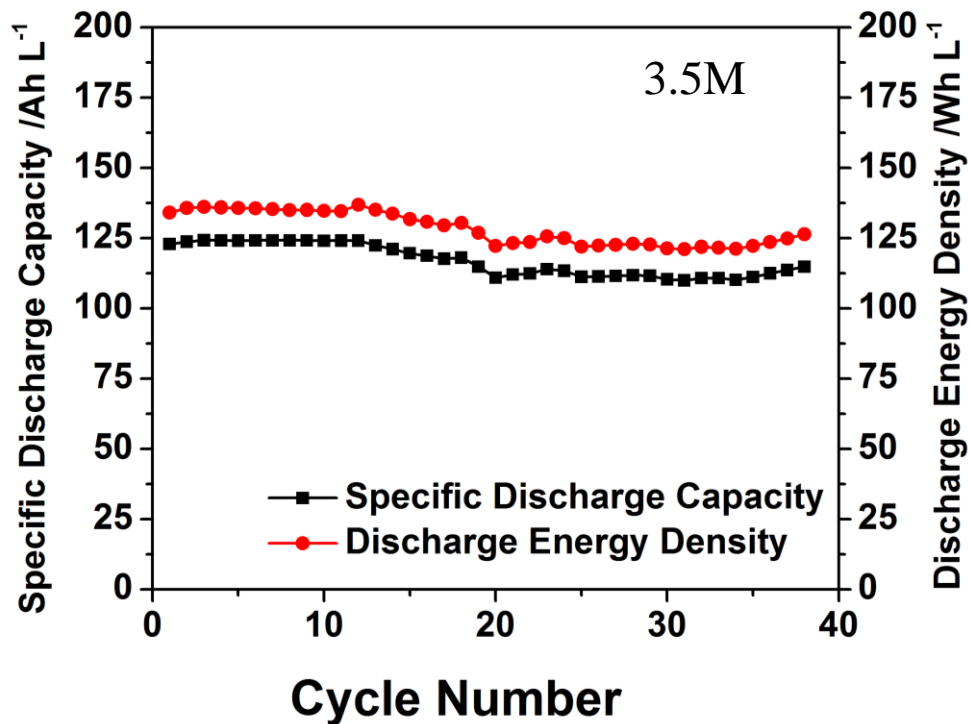


Charge/discharge curves for the cell with 5.0 M ZnI_2 and Nafion 115 as membranes operated at the current density of 5 mA cm^{-2} .

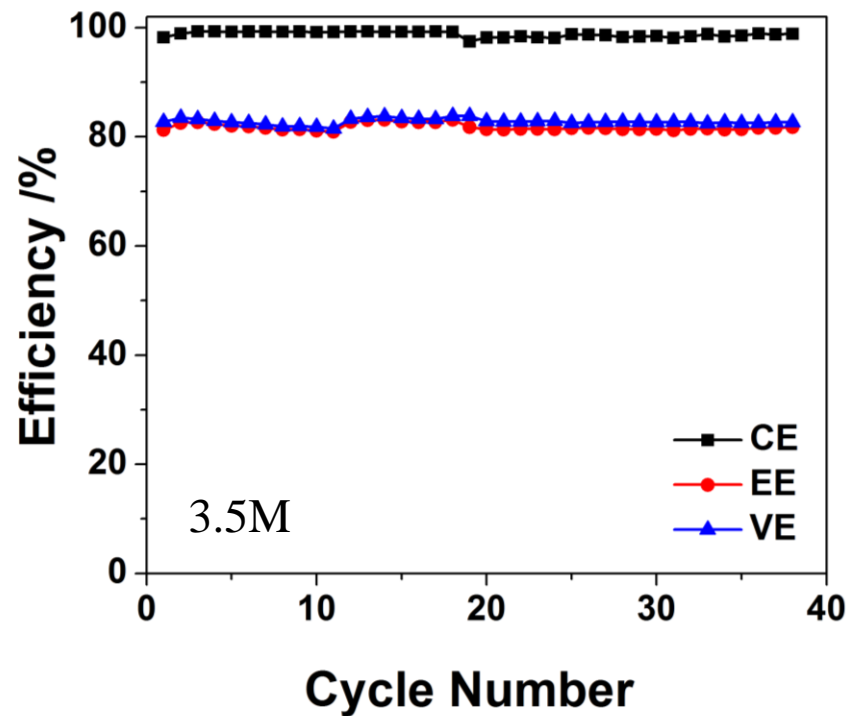


The charge and discharge energy density as a function of the concentration of I⁻. The inset lists concentration vs. energy density of several current aqueous redox flow battery chemistries for comparison.

Cycling performance



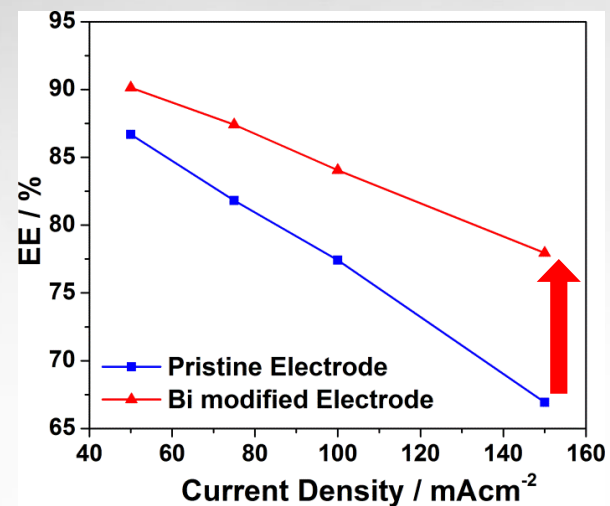
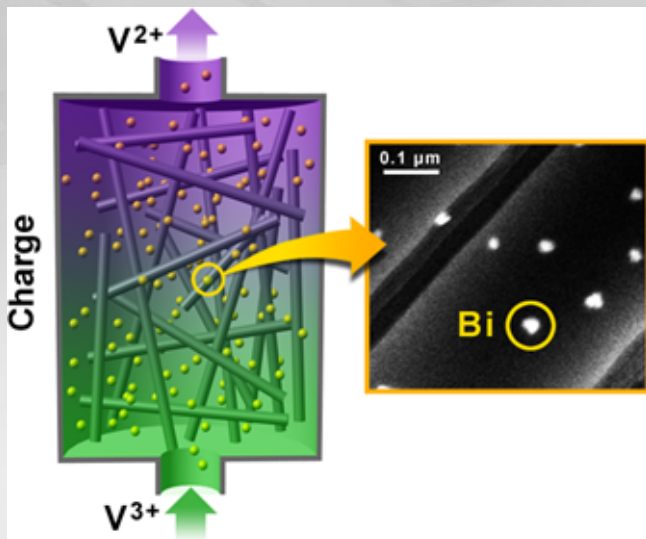
Capacities and energy density of the cell with 3.5 M ZnI₂ and Nafion 115 as membranes under the current density of 10 mA cm⁻².



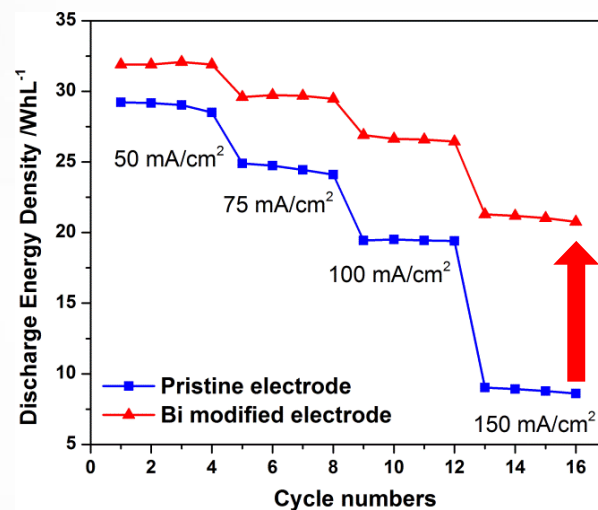
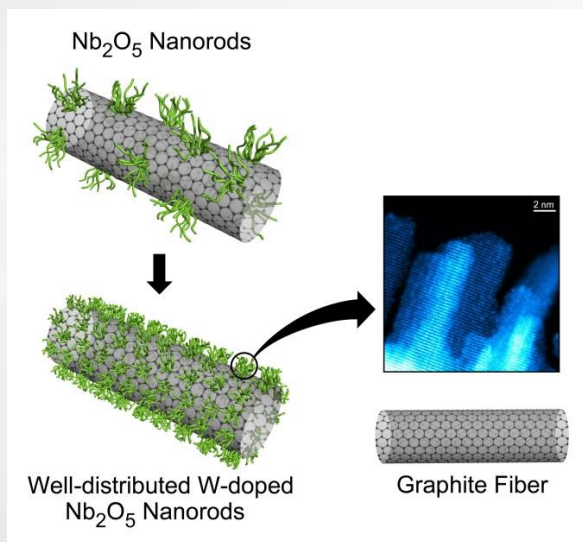
Efficiencies of the cell with 3.5 M ZnI₂ and Nafion 115 as membranes under the current density of 10 mA cm⁻².

Development in other areas – Advanced electrodes

Bismuth nanoparticles

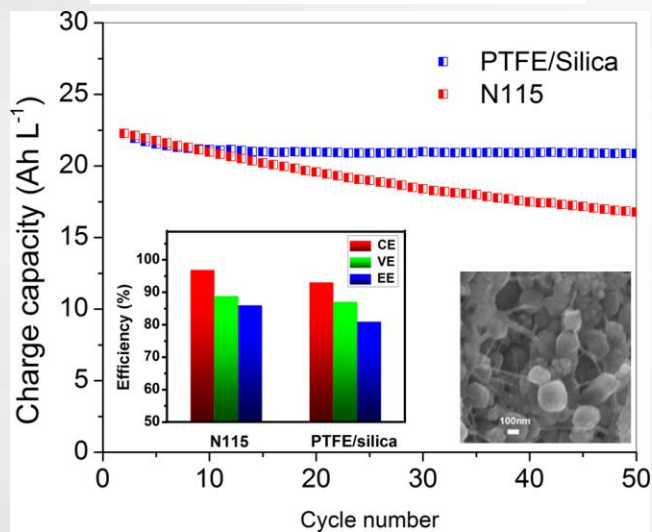
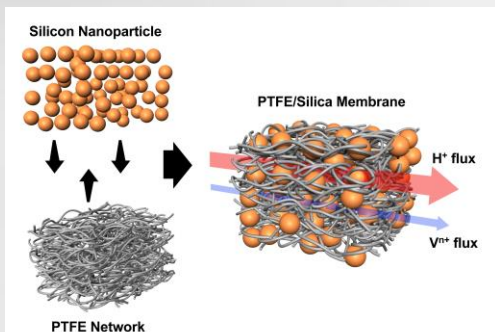


W-doped Nb₂O₅ nanorods

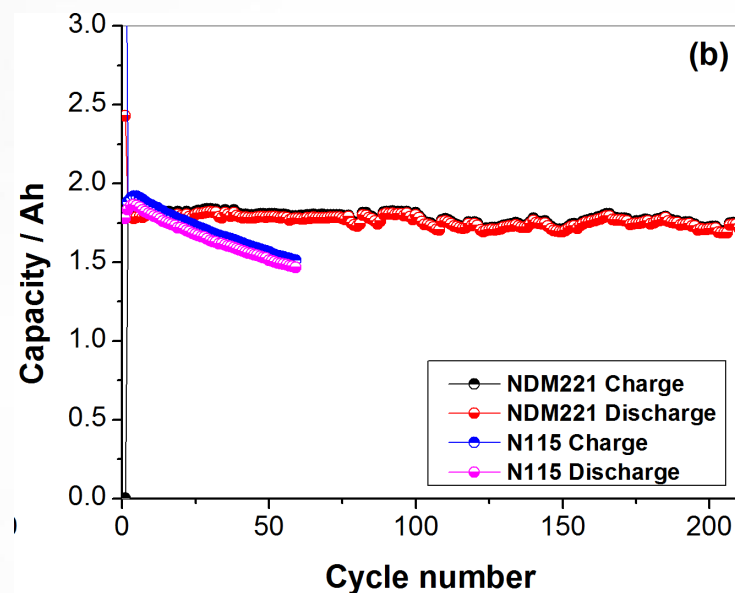
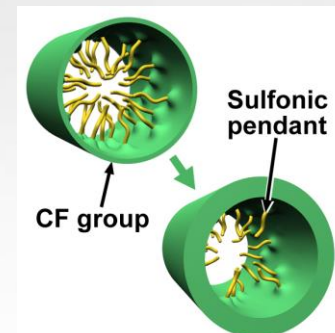


PNNL PTFE/SiO₂ separator

- Comparable efficiency
- Proven chemical stability
- No capacity decay
- Low cost (<5% of Nafion price)



Development of high selective PFSA membrane with Dupont



Acknowledgements

- ▶ Support from US DOE Office of Electricity Delivery & Energy Reliability - Dr. Imre Gyuk, Energy Storage Program Manager
- ▶ Pacific Northwest National Laboratory is a multi-program national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC05-76RL01830.
- ▶ External collaborators
 - Sandia National Laboratory
 - Oak Ridge National Laboratory
 - Chemours (Formerly Dupont)

Contact Info

CESA Project Director:

Todd Olinsky-Paul

(Todd@cleanegroup.org)

Sandia Project Director:

Dan Borneo

(drborne@sandia.gov)

Webinar Archive: www.cesa.org/webinars

ESTAP Website: bit.ly/CESA-ESTAP

ESTAP Listserv: bit.ly/EnergyStorageList



Upcoming Webinar

- What are flow batteries and how can they improve resiliency, continuity and safety in urban installations? March 24, 1-2 pm ET

More information at www.cesa.org/webinars