

High Voltage, High Capacity, Room Temperature Sodium Flow Batteries

Leon L. Shaw^{1,2} & Vincent L. Sprenkle³

¹ Wagner Institute for Sustainable Energy Research

² Department of Mechanical, Materials and Aerospace Engineering

Illinois Institute of Technology, Chicago, Illinois 60616

³ Energy Storage and Conversion Energy Materials

Pacific Northwest National Laboratory, Richland, WA 99352

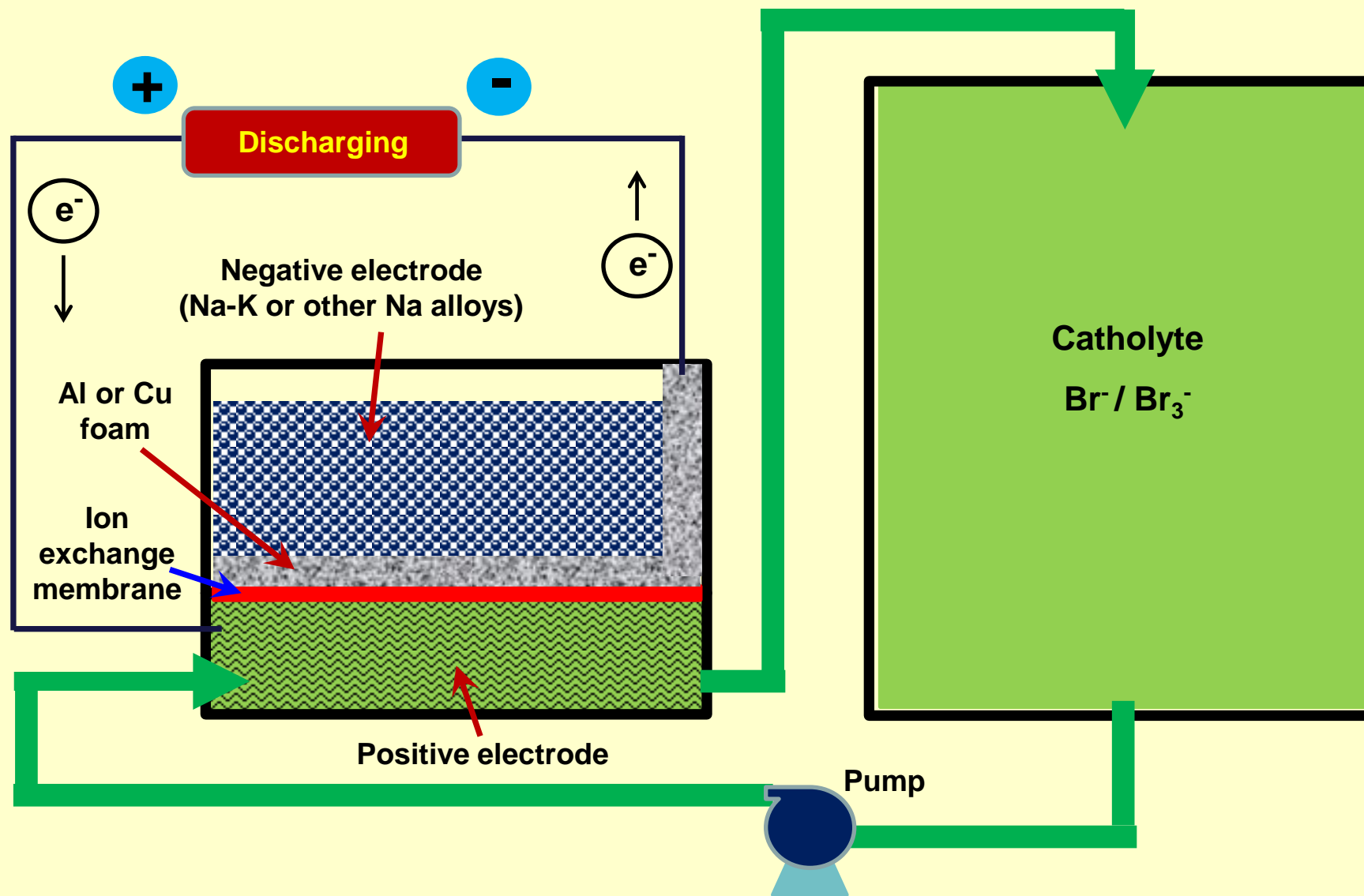
Sponsor: DOE Office of Electricity Delivery and Energy Reliability (OE) Energy Storage Program

Purpose of the Project

The objective of this project is to investigate and create a complete new family of high voltage, high capacity, room temperature, hybrid sodium-based flow batteries (hereafter termed as HNFBs) that will possess ultrahigh energy densities with specific energies approaching 400 Wh/kg or higher. We envision that such unparalleled flow batteries will revolutionize the energy storage technology and offer enormous impacts on smart cities, smart grids and renewable energy integration.

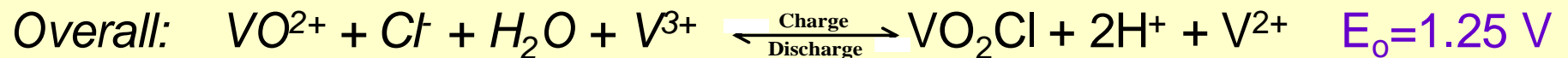
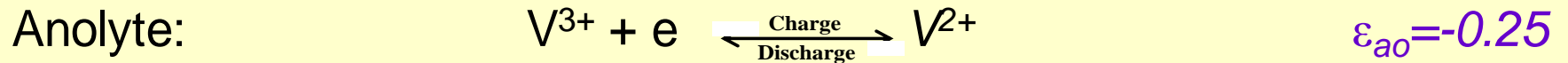
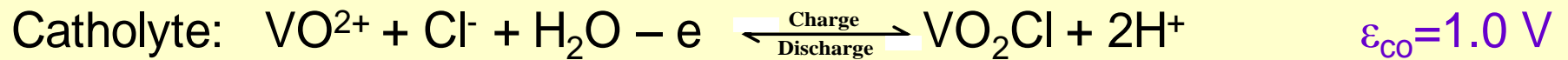


Concept of High Voltage, High Capacity, Room Temperature, Hybrid NFBs



* L. Shaw and J. Shamie, "Sodium Based Hybrid Flow Batteries with Ultrahigh Energy Densities," US Patent Application # 14/157,180.

The state-of-the-art vanadium redox flow battery



- ❑ Cell voltage ~1 V, one electron transfer redox reaction per active ion, and specific energy only ~35 Wh/kg

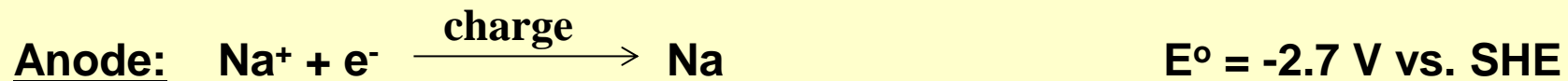
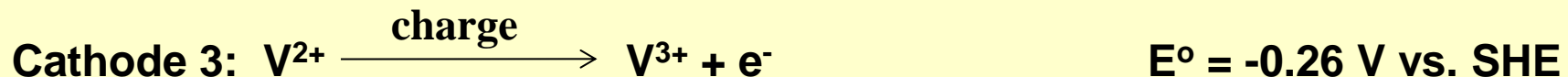
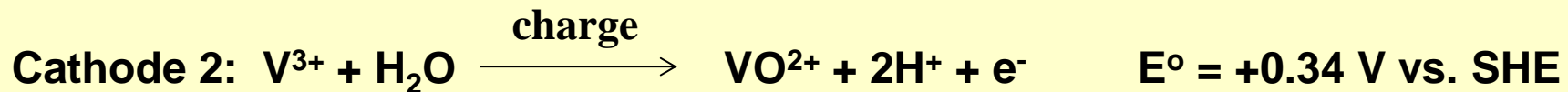
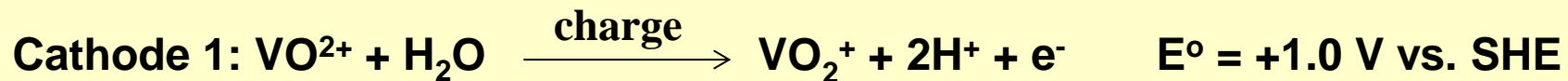
* Li, et al, Advanced Energy Materials, 1, 394, 2011.

The high voltage, high capacity, hybrid sodium-ion flow batteries have several unprecedented advantages:

- ❑ High cell voltage (> 3 V)
- ❑ Multiple electron transfer redox reactions per active ion
- ❑ Ultrahigh energy densities (> 500 Wh/kg & > 600 Wh/L)
- ❑ Low costs (avoid the use of expansive Nafion membranes, reduction in the amount of catholytes used, reduction in the use of storage materials and space, no pumping energy consumption in the anode)

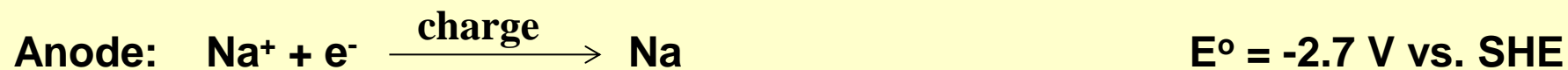
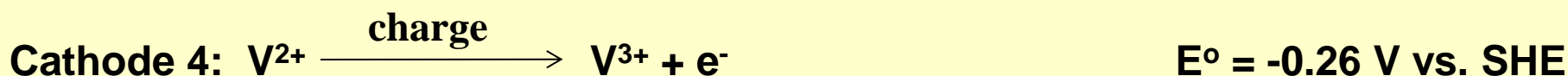
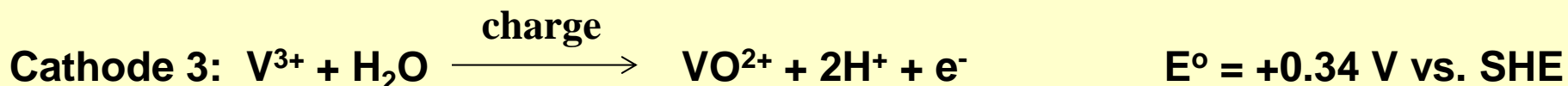
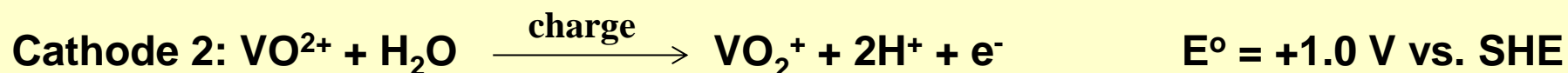
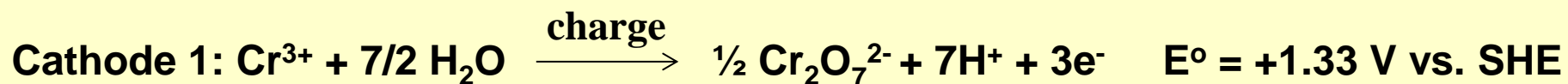
Chemistries for High Voltage, High Capacity Sodium-Ion Flow Batteries (1)

The sodium/vanadium system:



- ❑ **Three electron transfer** redox reaction per vanadium ion.
- ❑ Theoretic specific energy for a 2.5M V^{2+} aqueous solution is **483.7 Wh/kg**, which is the sum of redox 1 (195 Wh/kg), redox 2 (160 Wh/kg), and redox 3 (128.7 Wh/kg) reactions.
- ❑ This specific energy (480 Wh/kg) is **1280%** of the specific energy provided by the state-of-the-art all vanadium flow batteries (~35 Wh/kg).
- ❑ Space and container material usage is reduced by **~20 times** (including both catholyte and anolyte tanks), whereas the electrolyte solution is reduced by **~24 times**.

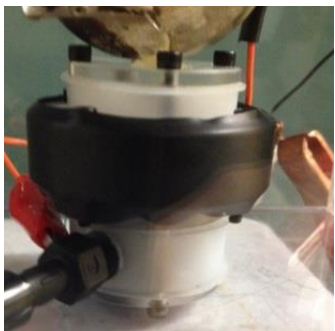
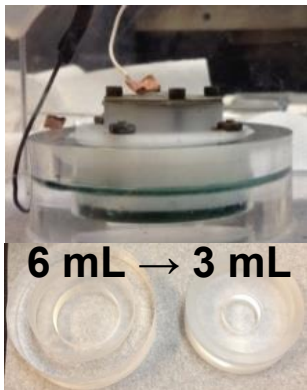


Chemistries for High Voltage, High Capacity Sodium-Ion Flow Batteries (2)



- ❑ Theoretic specific energy for a 2.5M V^{2+} plus 3M Cr^{2+} aqueous solution is an unprecedented **1,312 Wh/kg**, which is the sum of redox 1 (697 Wh/kg), redox 2 (195 Wh/kg), redox 3 (160 Wh/kg), redox 4 (128 Wh/kg), and redox 5 (131 Wh/kg) reactions.
- ❑ This specific energy (1,312 Wh/kg) is **36,486%** of the specific energy provided by the state-of-the-art all vanadium flow batteries (~35 Wh/kg).

Project Progress to Date 1:

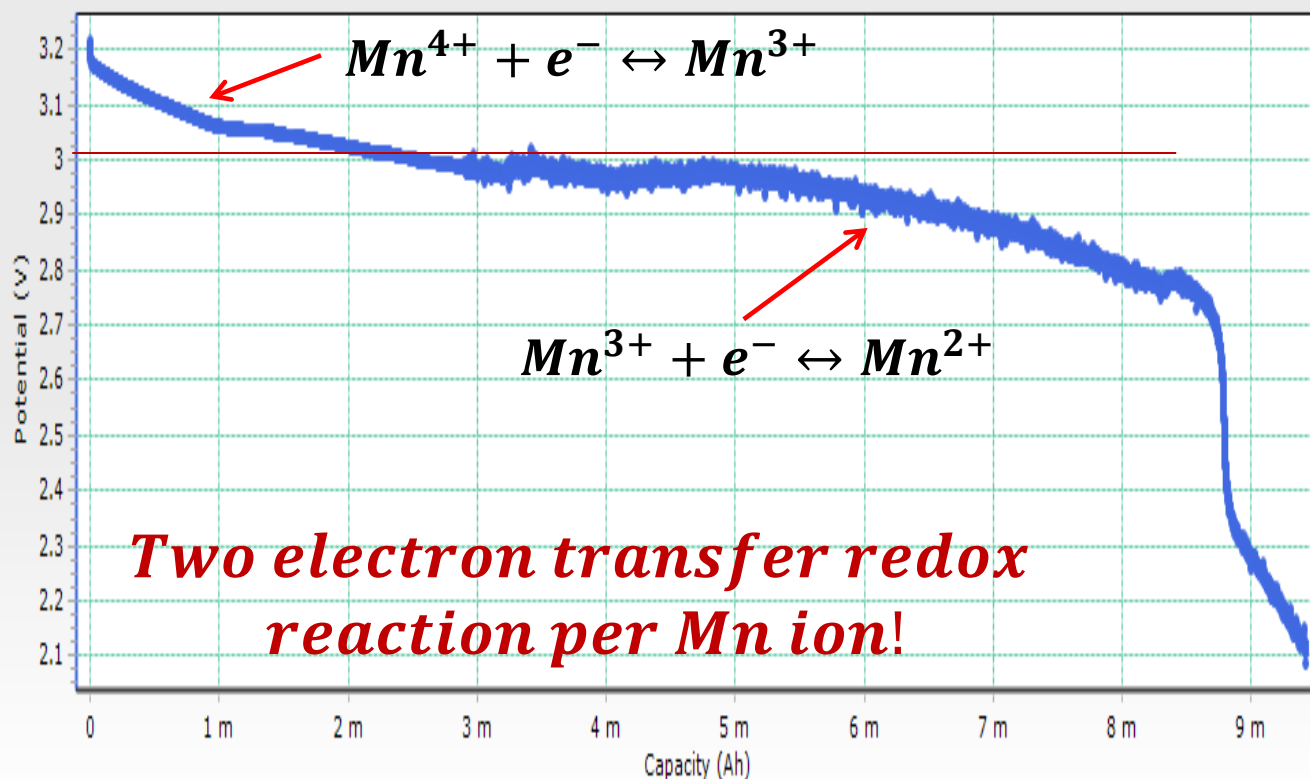
Cell Designs for HNFBs

Cell ID	I	IIa	IIb	III
Cell design				
Flowing or stirring of catholyte	Stirring	Stirring	Stirring	Flowing
Cell materials	Acrylic / polypropylene / polyethylene for acidic aqueous catholytes ; Polypropylene / polyethylene for non-aqueous catholytes			
Minimum volume of catholyte (mL)	~12	~6	~3	~10

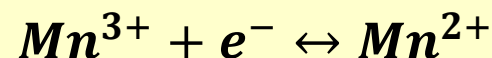
Project Progress to Date 2: HNFBs with the Catholyte Made of $\text{Mn}(\text{acac})_3$ in Acetonitrile

Experimental Conditions:

- ❑ Anode: A solid Na chunk floating on top of an ionic liquid with 0.1M sodium trifluoromethylsulfonyl imide (NaTFSI) salt
- ❑ Cathode: 0.025M $\text{Mn}(\text{acac})_3$ and 0.1M NaClO_4 dissolved in acetonitrile (CH_3CN) with a Pt wire current collector
- ❑ Ion exchange membrane and temperature: $\beta''\text{-Al}_2\text{O}_3$ tube and 25°C

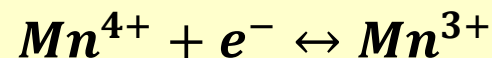


Cathode Rx 1:



$$E^0 = 0.4 \text{ V vs. SHE}$$

Cathode Rx 2:



$$E^0 = 1.5 \text{ V vs. SHE}$$

Anode:

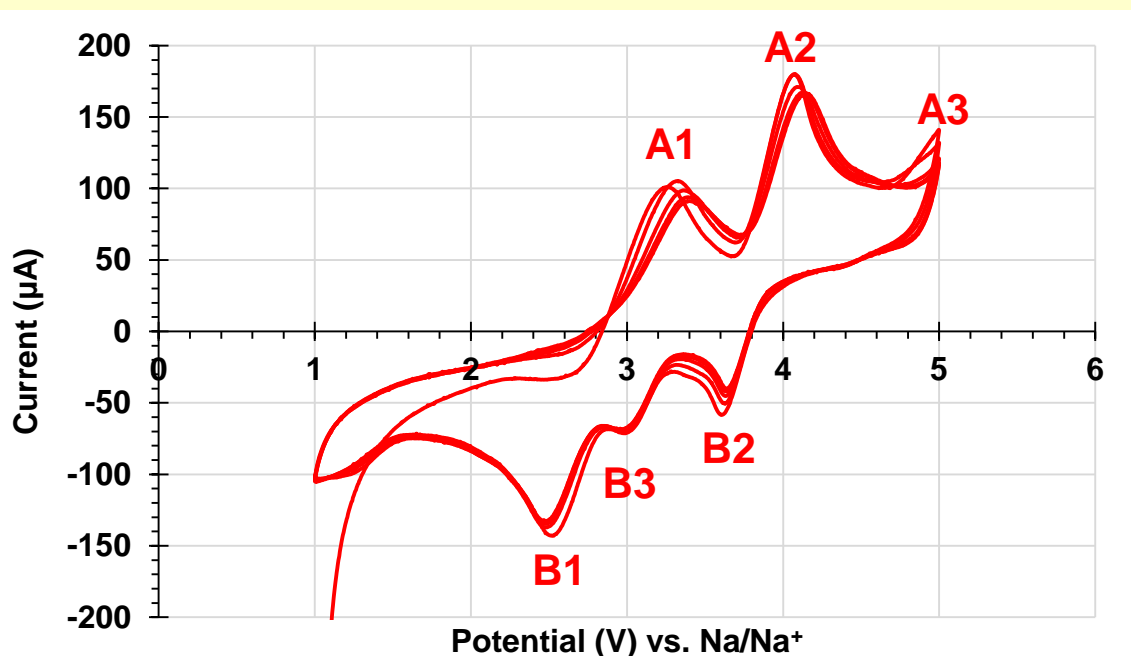


$$E^0 = -2.7 \text{ V vs. SHE}$$

Project Progress to Date 3: CV of the Catholyte Made of $\text{Mn}(\text{acac})_3$ in Acetonitrile

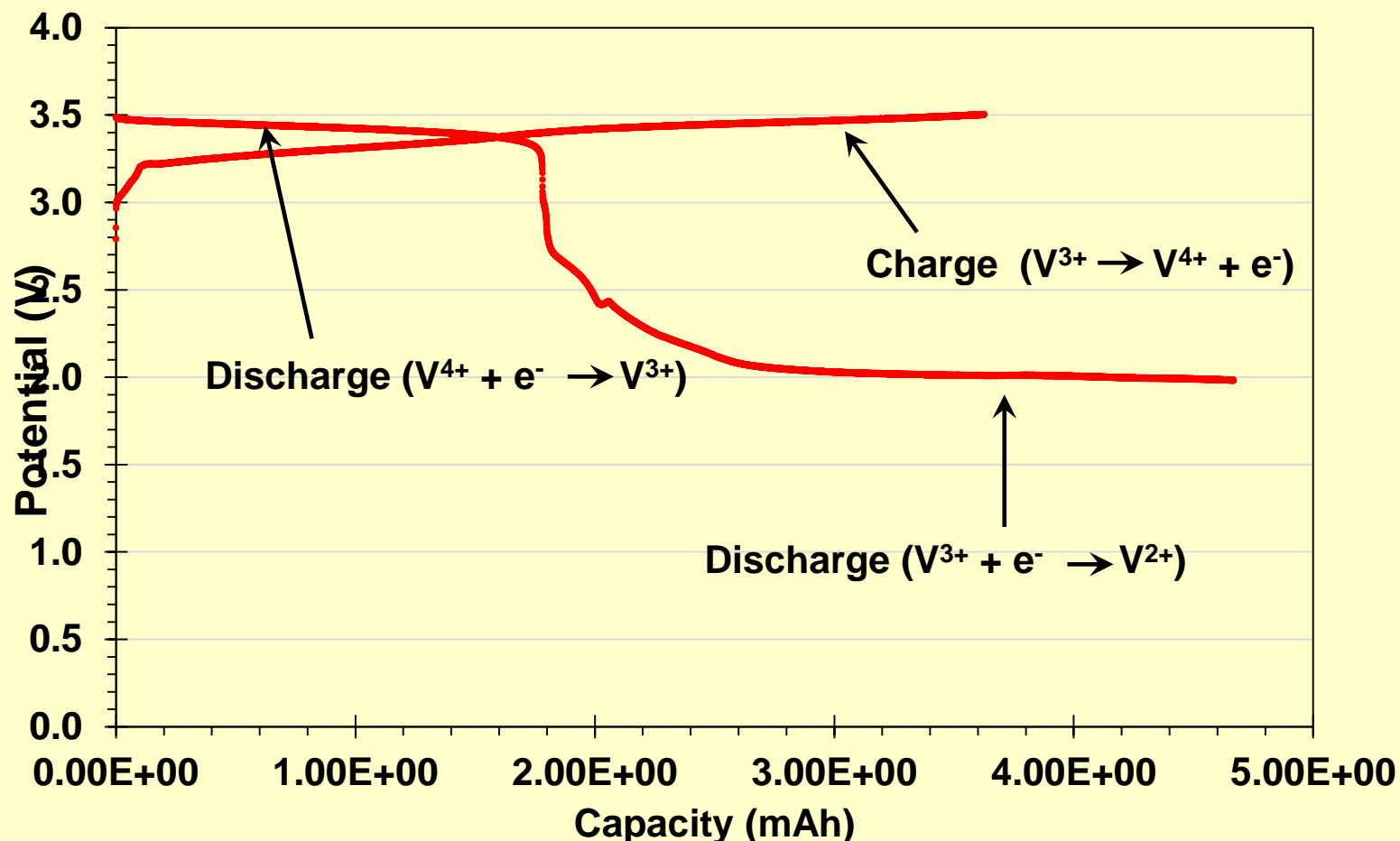
Experimental Conditions:

- ❑ Cyclic voltammetry (CV) with a 3-electrode setup
- ❑ Working electrode: a gold wire
- ❑ Reference electrode: a Na inside a $\beta''\text{-Al}_2\text{O}_3$ tube (Na^+/Na)
- ❑ Counter electrode: a tinned copper wire
- ❑ Electrolyte: 0.05M $\text{Mn}(\text{acac})_3$ in acetonitrile
- ❑ Scan rate: 250 mV/s
- ❑ Three oxidation peaks, A1, A2 and A3, are observed in the anodic scan.
- ❑ A1 peak (3.37 V vs Na/Na^+) is oxidation of Mn^{2+} to Mn^{3+} , A2 (4.1 V) is oxidation of Mn^{3+} to Mn^{4+} and A3 (~5.0 V) is oxidation of acetonitrile.
- ❑ Both A1 and A2 oxidations are reversible in the cathodic scan (B1 and B2 peaks). B3 is due to residual H_2O in the electrolyte.



Project Progress to Date 4: HNFBs with Catholyte Made of $V(acac)_3$ in Acetonitrile

- ❑ Anode: A solid Na chunk floating on top of an ionic liquid with 1 M sodium trifluoromethylsulfonyl imide (NaTFSI) salt in 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (PyrrTFSI)
- ❑ Catholyte: 0.025M $V(acac)_3$ dissolved in acetonitrile (CH_3CN) with 0.1M $NaClO_4$ supporting electrolyte and a graphite foam current collector
- ❑ Ion exchange membrane & temperature: β'' - Al_2O_3 tube and 25°C
- ❑ OCV: 2.52 V



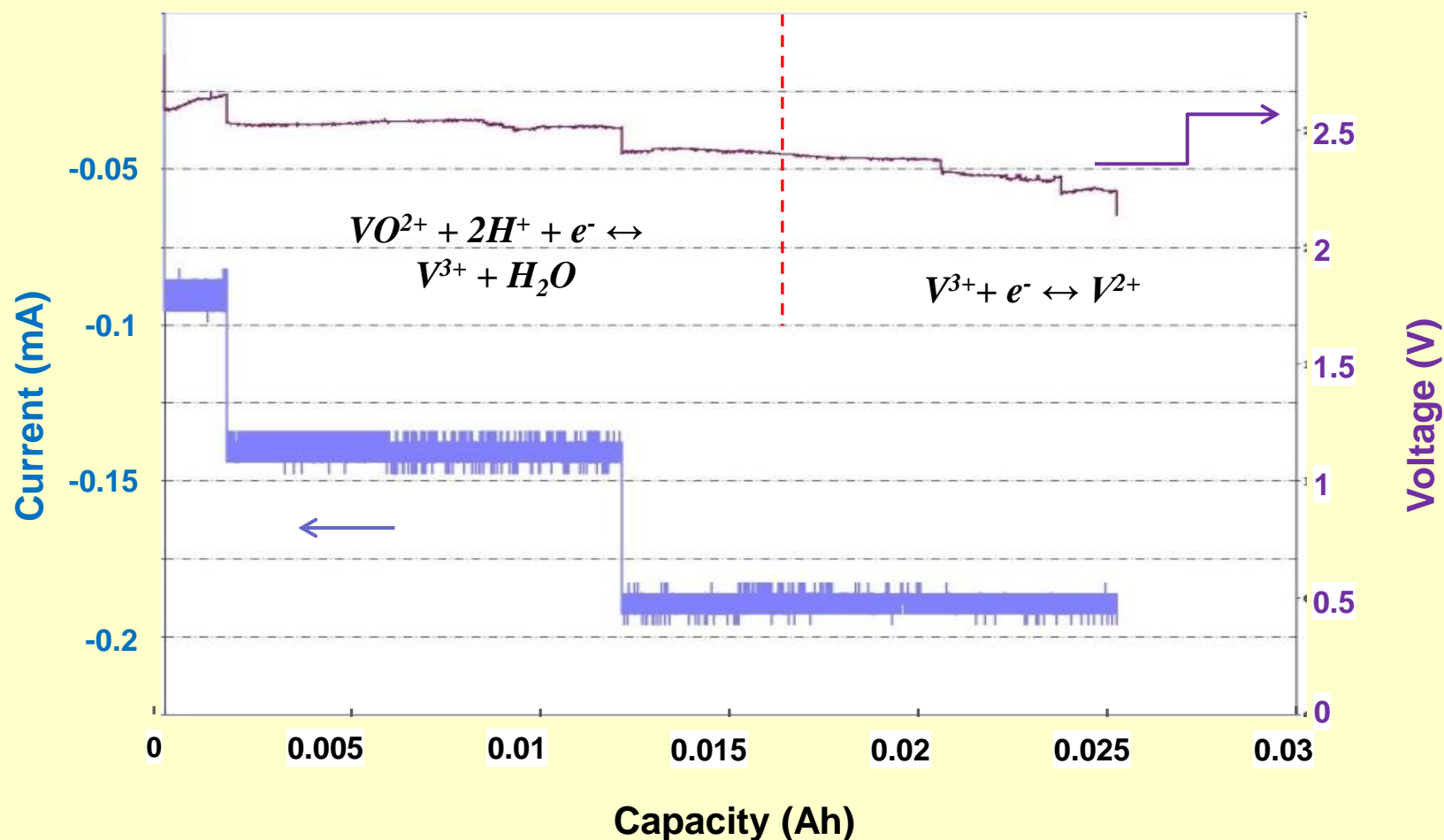
Project Progress to Date 5: Discharge Profile of Vanadium-Based Aqueous Catholytes

Cell conditions:

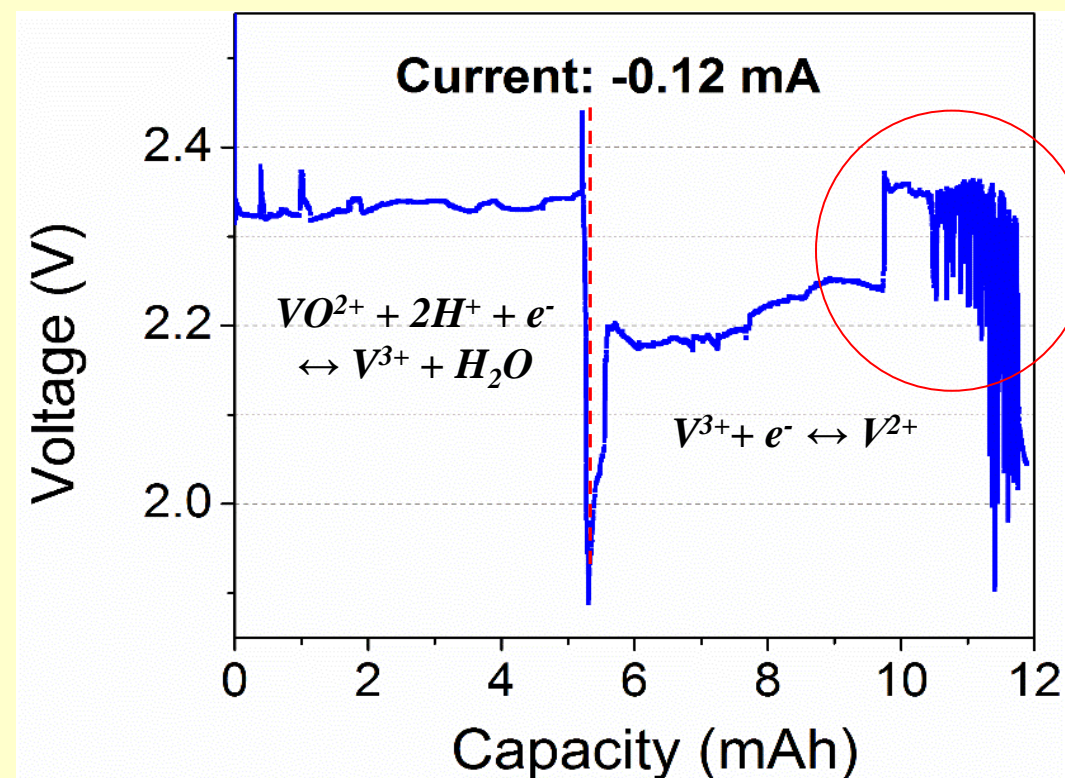
Catholyte: 0.05 M VOSO_4 + 0.1 M Na_2SO_4 + 1.5 M HCl

Anode: $\text{Na}_{37}\text{Cs}_{63}$

Membrane: $\beta''\text{-Al}_2\text{O}_3$ disc with Au coating



Project Progress to Date 6: Discharge Profile of Vanadium-Based Aqueous Catholytes

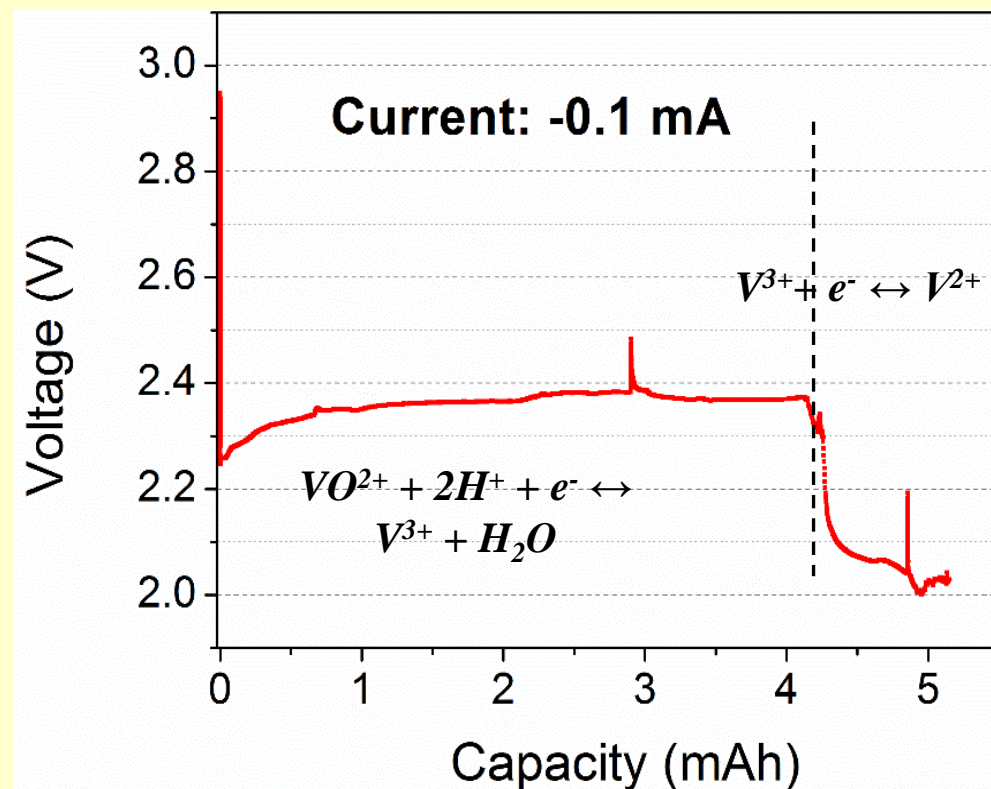


Cell conditions:

Catholyte: 0.025 M $VOSO_4$ + 0.1 M Na_2SO_4 + 1.5 M HCl

Anode: $Na_{37}Cs_{63}$

Membrane: β'' - Al_2O_3 disc with Au coating



Cell conditions:

Catholyte: 0.025 M $VOSO_4$ + 0.1 M Na_2SO_4 + 1.5 M HCl

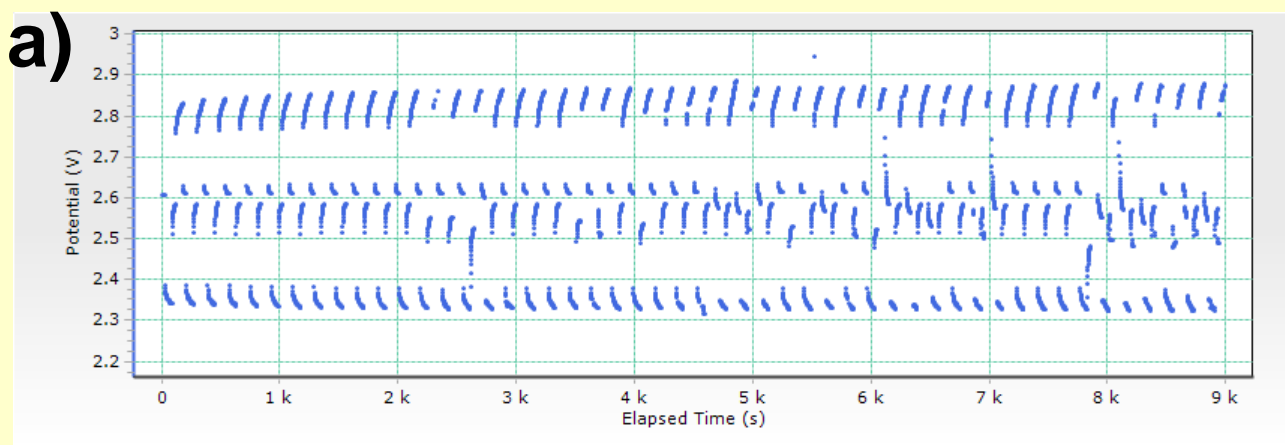
Anode: Na + 0.2 M NaTSFI/Pyrr TSFI

Membrane: β'' - Al_2O_3 disc w/o Au coating

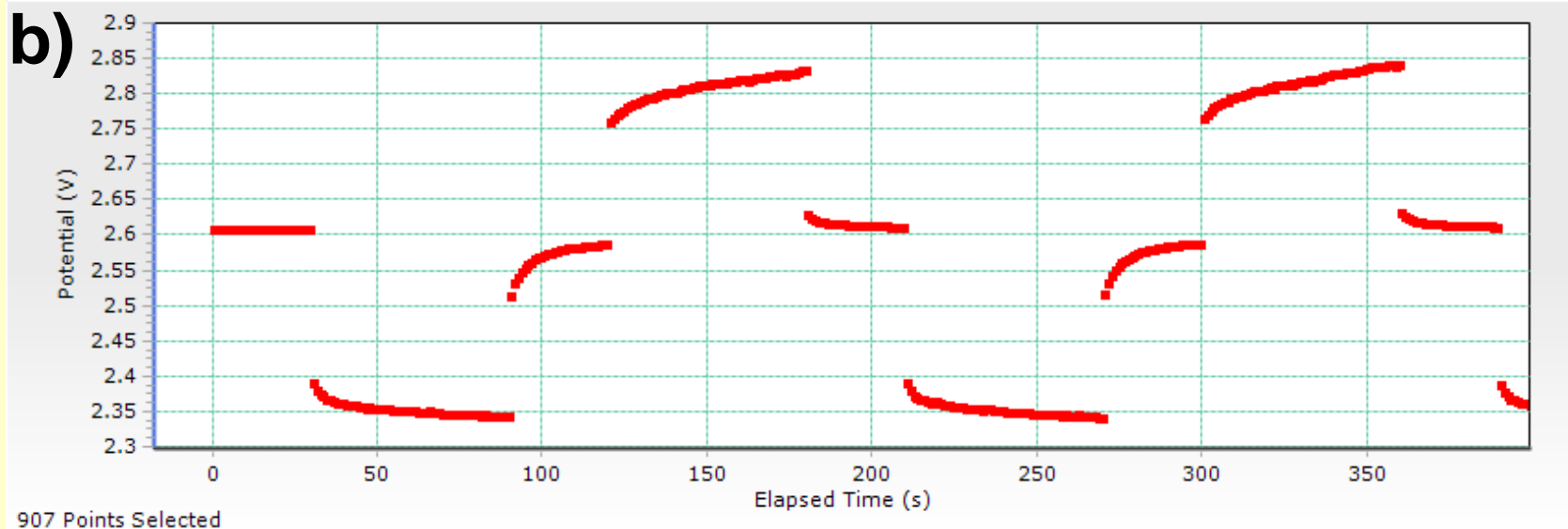
Project Progress to Date 7: Cycling Stabilities of HNFBs with Catholyte Made of $\text{Mn}(\text{acac})_3$ in Acetonitrile

Experimental Conditions:

- ❑ Anode: A solid Na chunk floating on top of an ionic liquid with 0.1M sodium trifluoromethylsulfonyl imide (NaTFSI) salt
- ❑ Cathode: 0.05M $\text{Mn}(\text{acac})_3$ dissolved in acetonitrile (CH_3CN) with a **tinned Cu wire** current collector with mechanical stirring
- ❑ Ion exchange membrane & temperature: $\beta''\text{-Al}_2\text{O}_3$ tube and 25°C

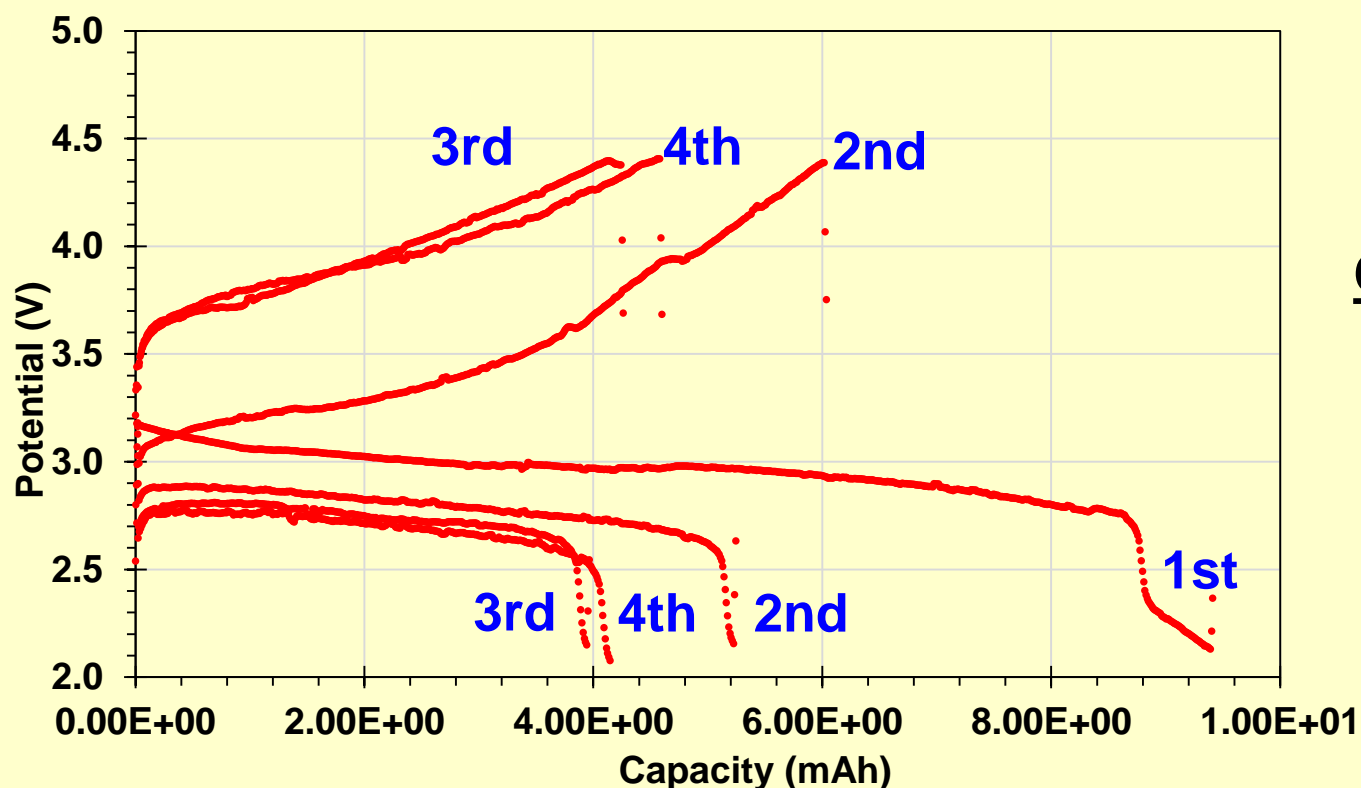


- a) 50 cycles of charge /rest/discharge/rest.
b) A close view of the 50 cycles.



Project Progress to Date 8: Cycling Behavior of HNFBS with Catholyte Made of $\text{Mn}(\text{acac})_3$ in Acetonitrile

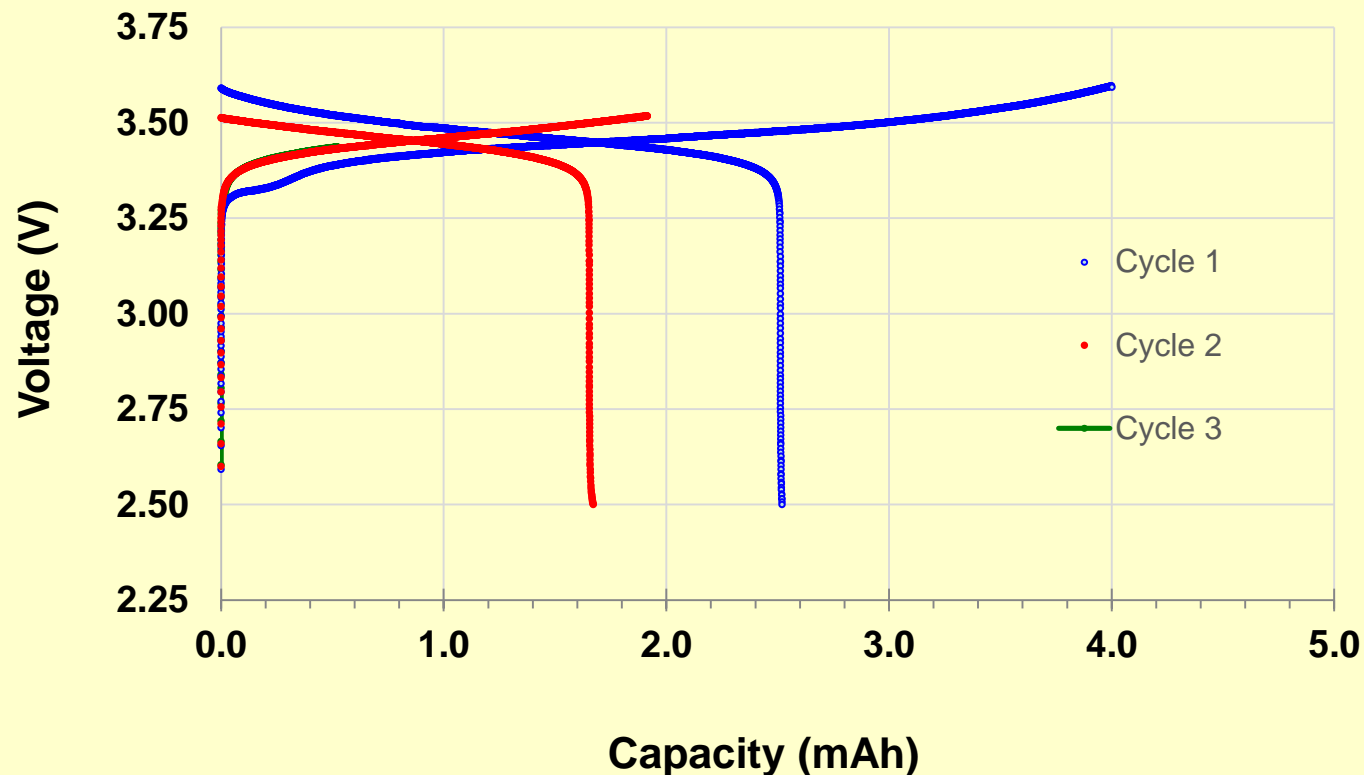
- ❑ Anode: A solid Na chuck floating on top of an ionic liquid with 0.1M sodium trifluoromethylsulfonyl imide (NaTFSI) salt
- ❑ Cathode: 0.025M $\text{Mn}(\text{acac})_3$ and 0.1M NaClO_4 dissolved in acetonitrile (CH_3CN) with a carbon foam as the current collector with mechanical stirring
- ❑ Ion exchange membrane & temperature: $\beta''\text{-Al}_2\text{O}_3$ tube and 25°C
- ❑ After charging for 36 h at 0.25 mA and resting for 43 h, the cell was discharged for 4 times and charged for 3 times at 0.05 mA with the cutoff voltage at 2.1 V for discharge and 4.4 V for charge.



Coulombic Efficiency

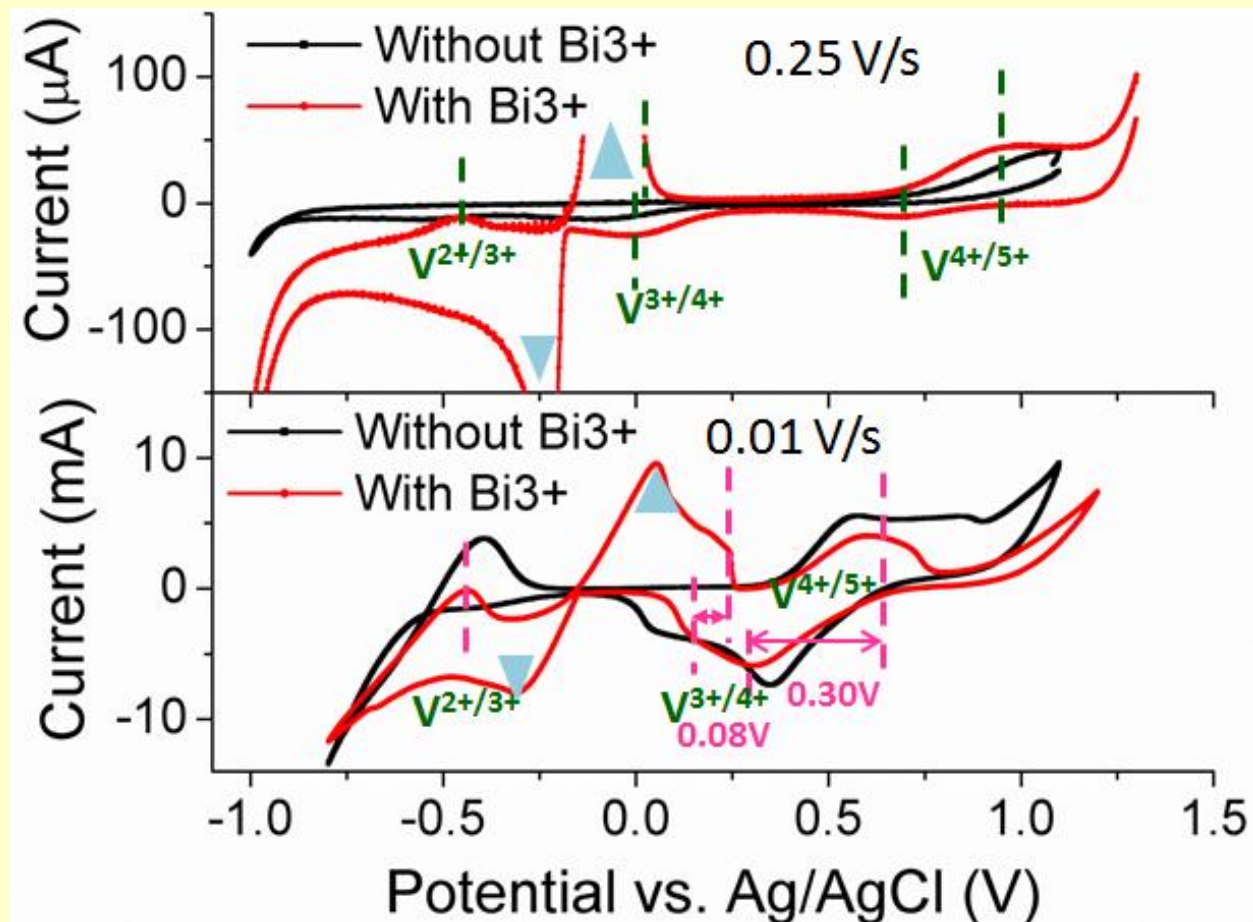
2nd discharge: 87.0%
3rd discharge: 93.2%
4th discharge: 90.2%

Project Progress to Date 9: Cycling Behavior of HNFBS with Catholyte Made of $V(acac)_3$ in Acetonitrile



Charge-discharge profile of 0.005M $V(III)(acac)_3$ with saturated $NaPF_6$ in acetonitrile as the catholyte. The anode was NaCs. The current collector was carbon foam with apparent area of 0.1 x 0.1 inch. The solution was stirred at 600 RPM during the test. The cutoff voltage is set as 2.5 V for discharge and 3.5-3.6 V for charge.

Project Progress to Date 10: Cathode Catalysts to Improve Cycling Stability of HNFBs



CV recorded for a catholyte with 0.02 M VOSO_4 - 0.1 M Na_2SO_4 - 1.0 M HCl - 0.002M BiCl_3 , in which glassy carbon (GC) (top) or C foam (bottom), Ag/AgCl, Pt wire were used as working, reference, and counter electrodes, respectively. The blue solid triangles (\blacktriangledown and \blacktriangle) indicate Bi^{3+}/Bi redox reaction peaks. Clearly, the reversibility of all these V ion redox reactions are significantly improved after adding BiCl_3 into the catholyte.

Plans for the Next Year

- ❑ Investigate the mechanisms of cyclic instability of two and three electron transfer redox reactions per V ion in HNFBs, including electrochemical tests under a controlled atmosphere and spectroscopy analysis to identify chemical species at different charge/discharge states.
- ❑ Demonstrate cyclic stability of two electron transfer redox reactions per V ion in HNFBs.
- ❑ Study the stability and electrochemical performance of various anode/anolyte candidates.
- ❑ Optimize the battery performance from the aspects of cell design, anode/cathode compositions, electrode modification, and test parameter setting.