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High Voltage, High Capacity, Room Temperature Sodium Flow Batteries

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

Concept and Merits of Hybrid NFBs

- **Traditional vanadium redox flow battery**

Catholyte: $VO^{2+} + Cl^- + H_2O - e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^+$ ε_{co}=1.0 V

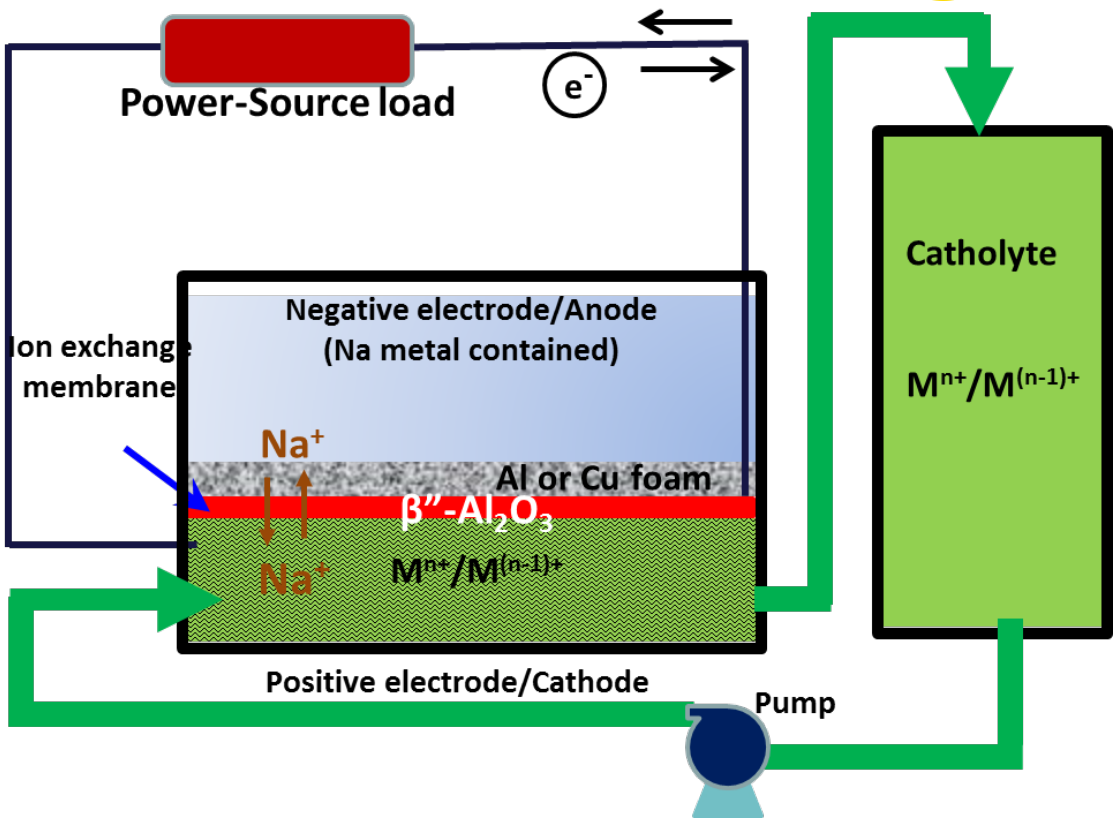
Anolyte: $V^{3+} + e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+}$ ε_{ao}=-0.25

Overall: $VO^{2+} + Cl^- + H_2O + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^+ + V^{2+}$ E_o=1.25 V

- 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.

- **Novel Hybrid NFBs: Concept**

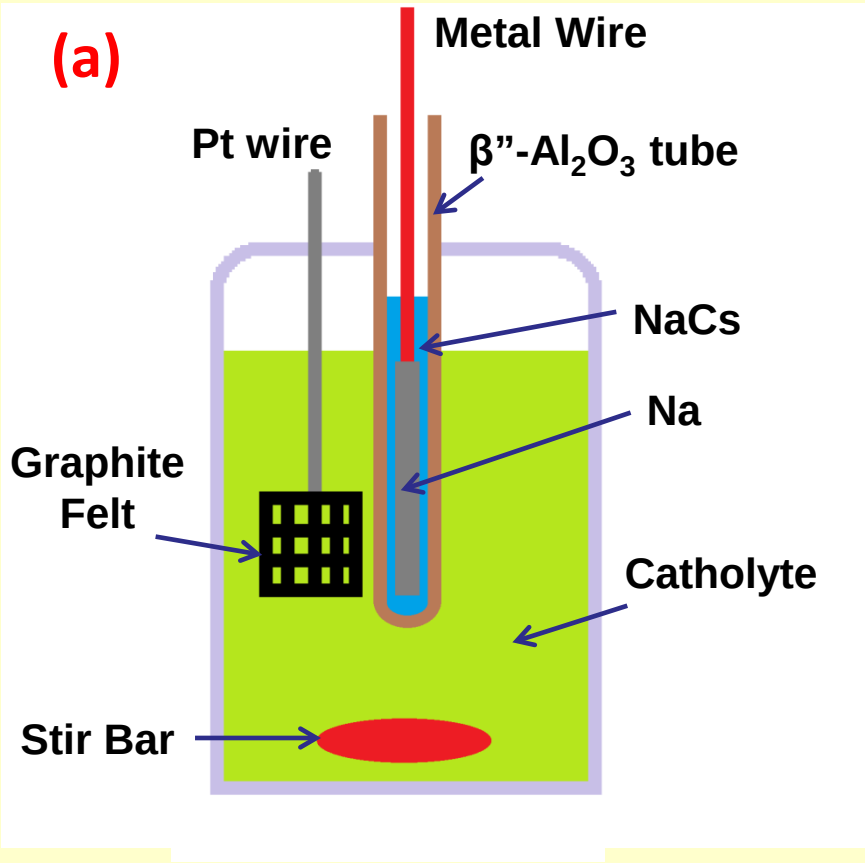


- **Novel Hybrid NFBs: unprecedented advantages**

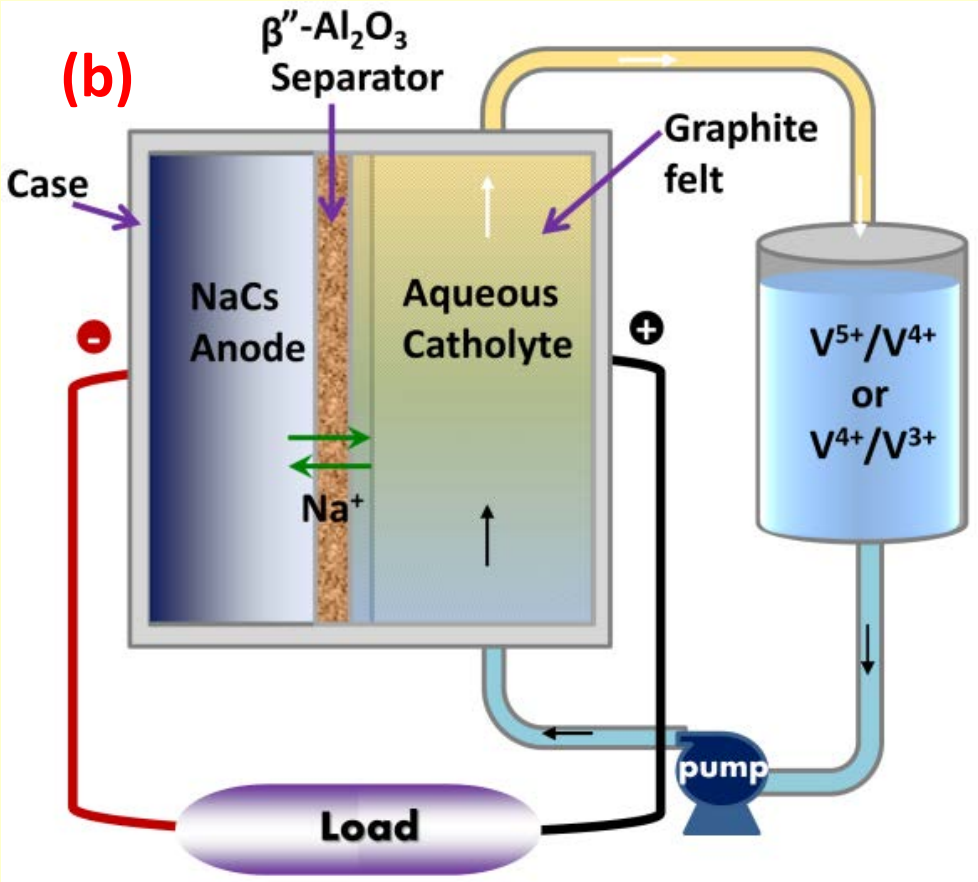
- High cell voltage (> 3 V)
- Multiple electron transfer redox reactions per active ion
- Ultrahigh energy densities (> 500 Wh/kg & > 600 Wh/L)
- Low costs (avoid the use of expansive Nafion membranes, reduction in the amount of anolytes used, reduction in the use of storage materials and space, no pumping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

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

Room temperature hybrid cell design



Na| β”-Al_2O_3 |**Non-aqueous** catholyte



Na| β”-Al_2O_3 |**Aqueous** catholyte

Cathode:

a) $V(acac)_3$- $NaPF_6$ or $V(acac)_3$ – $NaClO_4$ in acetonitrile

b) $Mn(acac)_3$- $NaClO_4$ in Acetonitrile

c) Tempo-$NaPF_6$ in acetonitrile or PC

Anode: Na_xCs_{1-x} (0.1<x< 0.37), heat to 200 ◦C before test

Beta”-Al_2O_3 tube: 0.5 mm thick, 3.5 cm^2 effective area

Solution stirred during cycling

Anode:

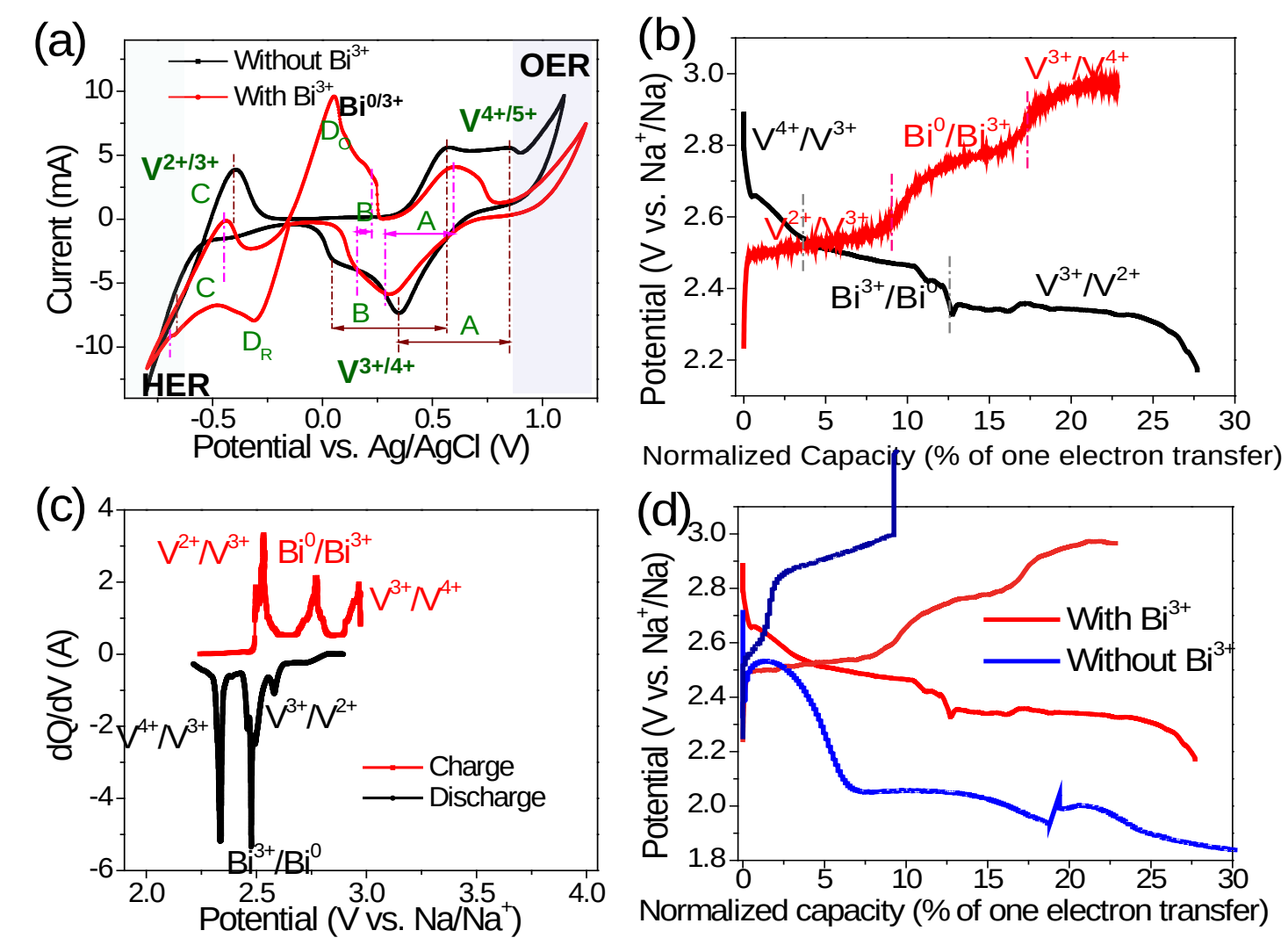
a) NaCs: Na(at.)%=< 37% (heat to 90 ◦C before test)

b) Al or Cu foam-Na/NaTFSI-IL;

Cathode: $VOSO_4$- Na_2SO_4- HCl ($BiCl_3$)

Beta”-Al_2O_3 membrane: 1.4-1.5 mm thick, 1” dia disc

Multiple electron transfer redox in aqueous catholyte based HNFBs



Cell components:

Catholyte: 0.01 M $VOSO_4$ + 0.05 M Na_2SO_4 + 1.5 M HCl+ 0.002 M $BiCl_3$

Anode: Na/ NaTFSI/ BMPyrrTFSI

Membrane: β"-Al_2O_3 disc (water resistable)

Catholyte just stirred, not flowing

CV test:

Working: Carbon foam

Counter: Pt wire

Ref.: Ag/AgCl

Electrolyte: same as catholyte

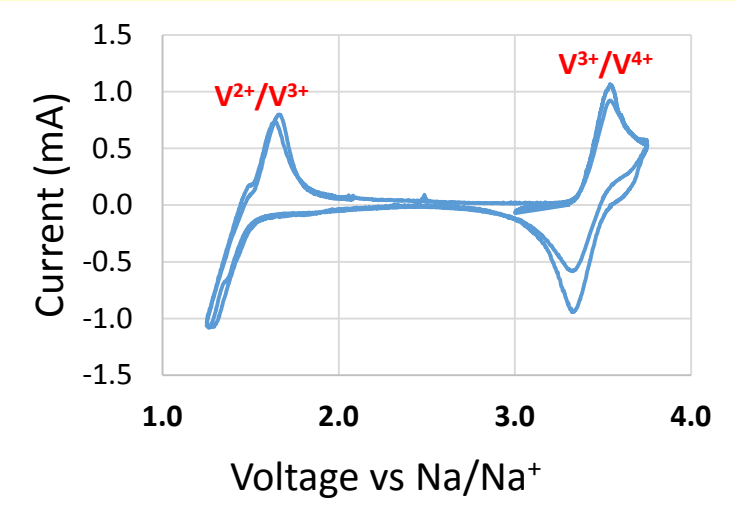
Scan rate: 10 mV/s

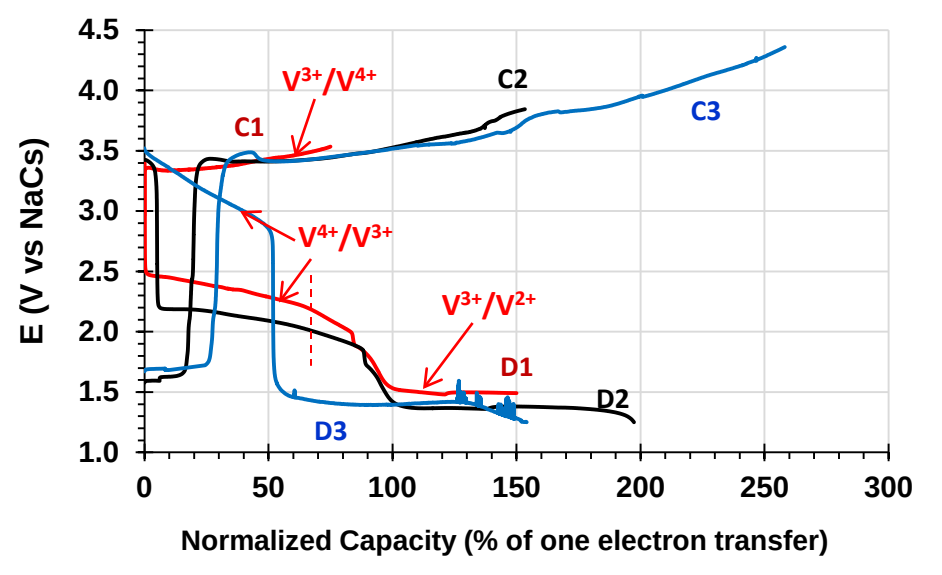
L. Shaw, et al., Scientific Reports, 5:11215, 2015, DOI:10.1038/srep11215

- **2 electron transfer for V ions**
- **2 species multiple electron transfer**
- **V is the main reactive species, Bi is the catalyst (Nano Lett., 2013, 13, 1330)**
- **The low ratio to the theoretical capacity mainly due to the bad mass transportation**

Multiple electron transfer redox in non-aqueous catholyte based HNFBs

- **Na- $V(acac)_3$**

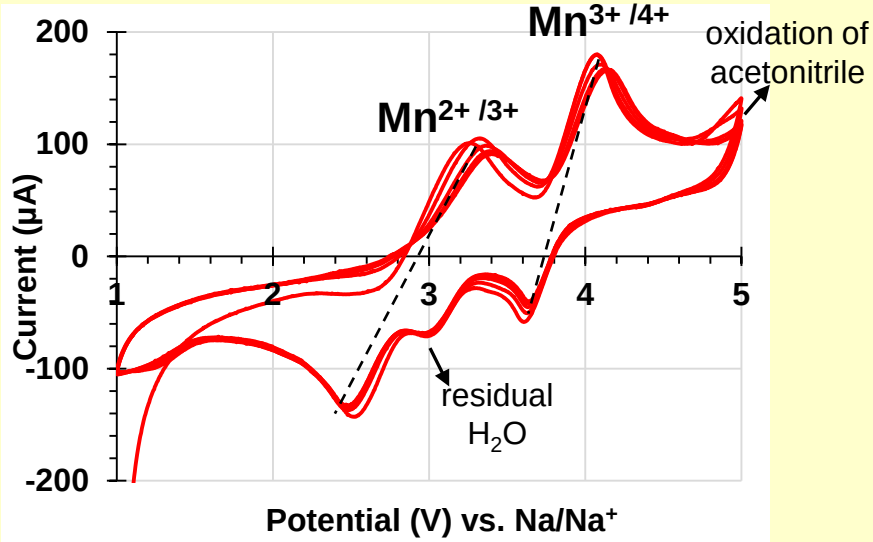


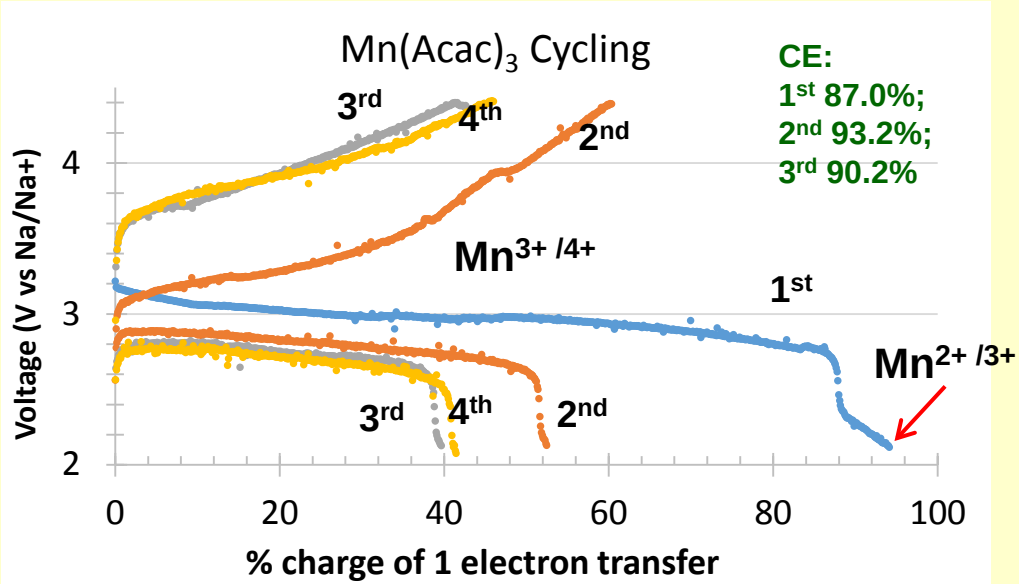


Cell components:

- $V(acac)_3$- $NaPF_6$ in CH3CN
- $Na_{10}Cs_{90}$ Anode
- Solution unstirred for CV test
- Scan rate: 25 mV/s
- Capacities of redox reaction invloved in CV test reach the ~75% of theoretical value.

- **Na- $Mn(acac)_3$**



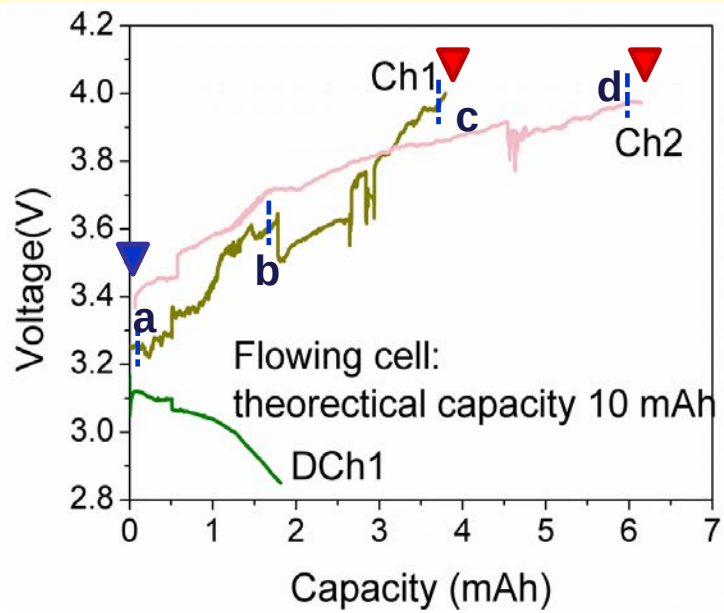


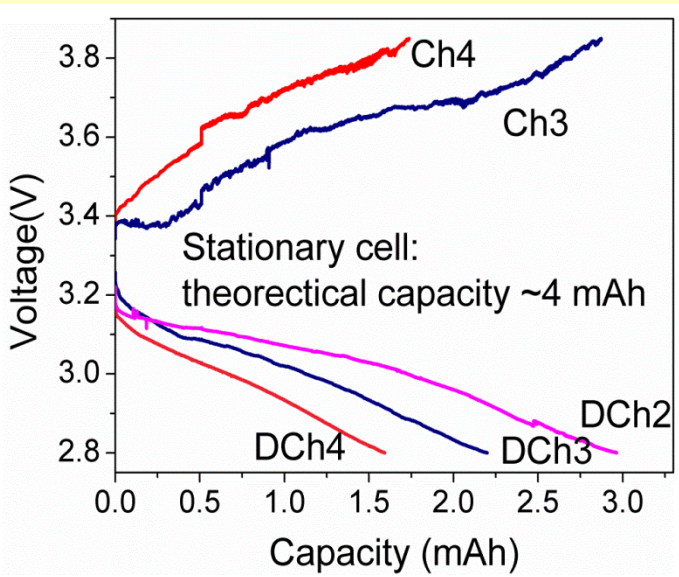
- **Anode:** Na/ 0.1M NaTFSI; **Cathode:** Mn(acac)3 -NaClO4 in CH3CN

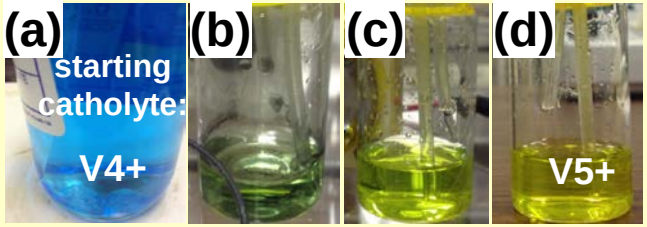
CV with a 3-electrode setup
Electrolyte: 0.05 M $Mn(acac)_3$ in acetonitrile
WE: Au; RE: Na in b"-Al2O3 tube; CE: tinned copper wire
Scan rate: 250 mV/s

Cycling performance of Na-V aqueous (V4+/V5+ redox)

- **Room Temp**



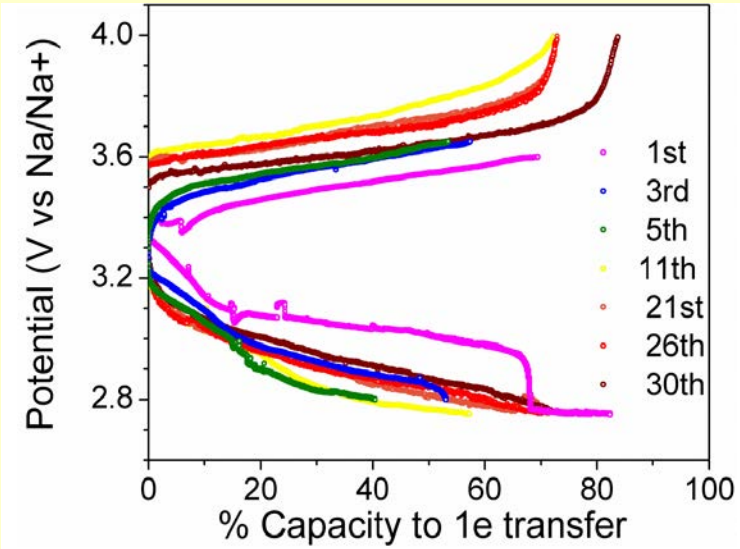


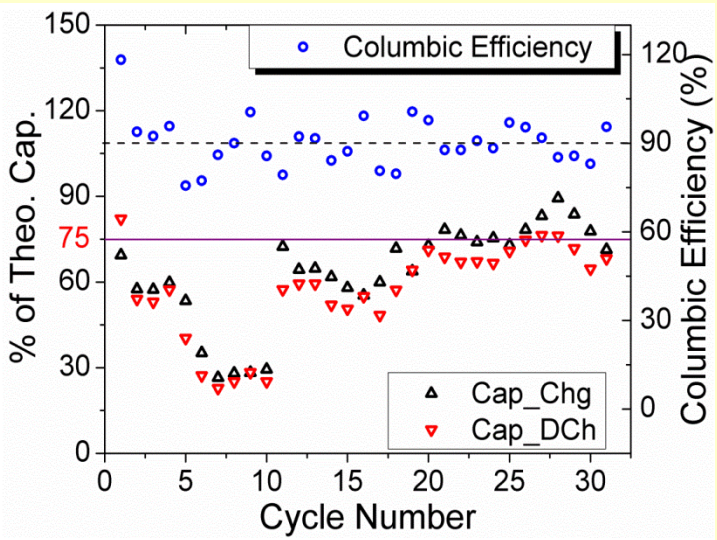


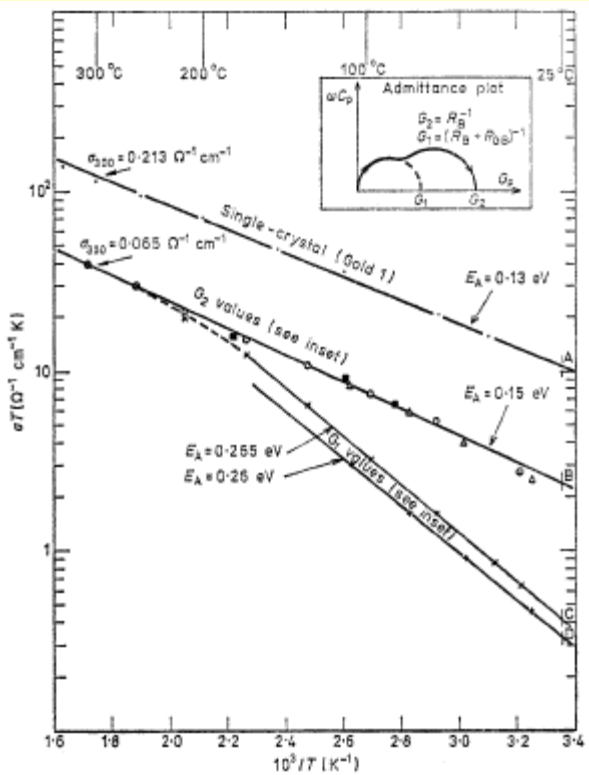
SOC: 0%, 20%, 40%, > 60%

red triangle: pump-head tube failure the cathode was blue triangle: refill catholyte, blue dash line: the corresponding photo-taken time/points.

- **50 ◦C**



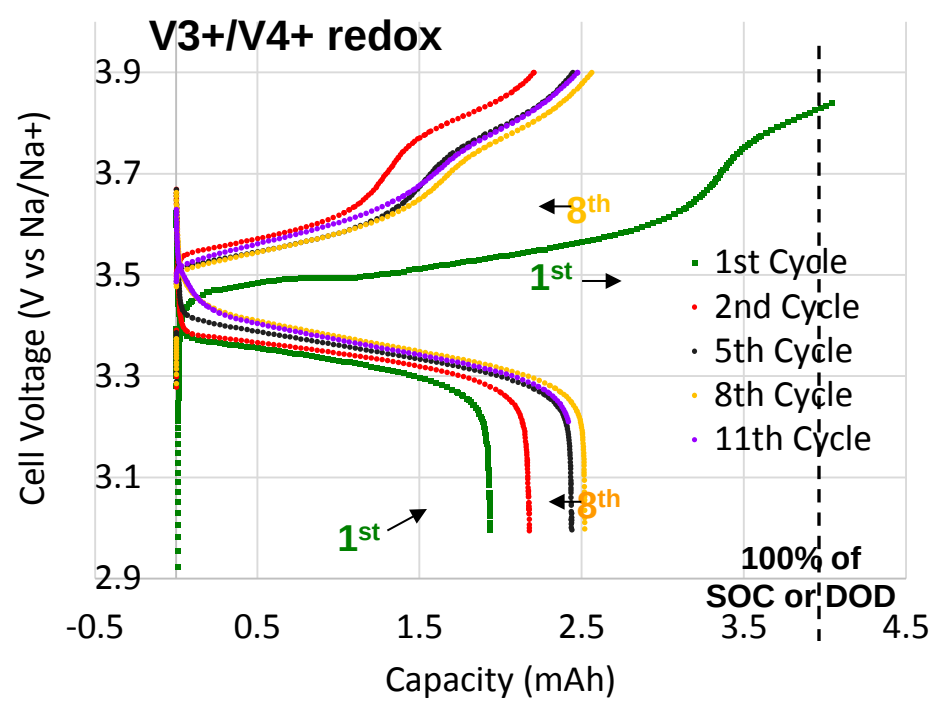




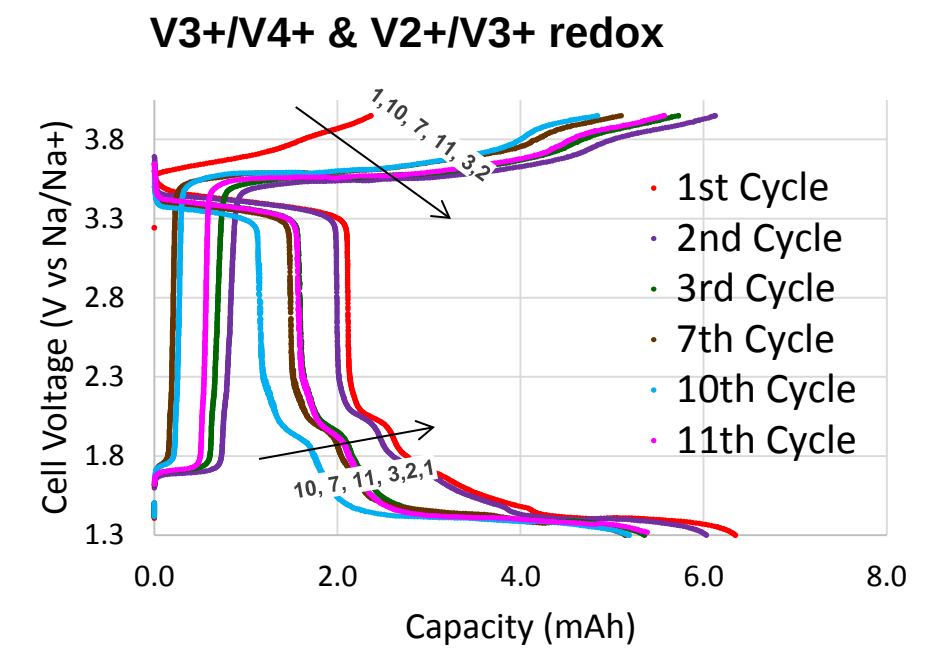
J. Phys. D: Appl. Phys., Vol. 10, 1487 (1977).

- ❑ **Color change observed, indicating efficient redox reactions;**
- ❑ **Cycling performance dramatically improved at 50 C**
- ❑ **The conductivity of β”-Al_2O_3 membrane significant affect the cell performance**

Cycling performance of Na-V nonaqueous

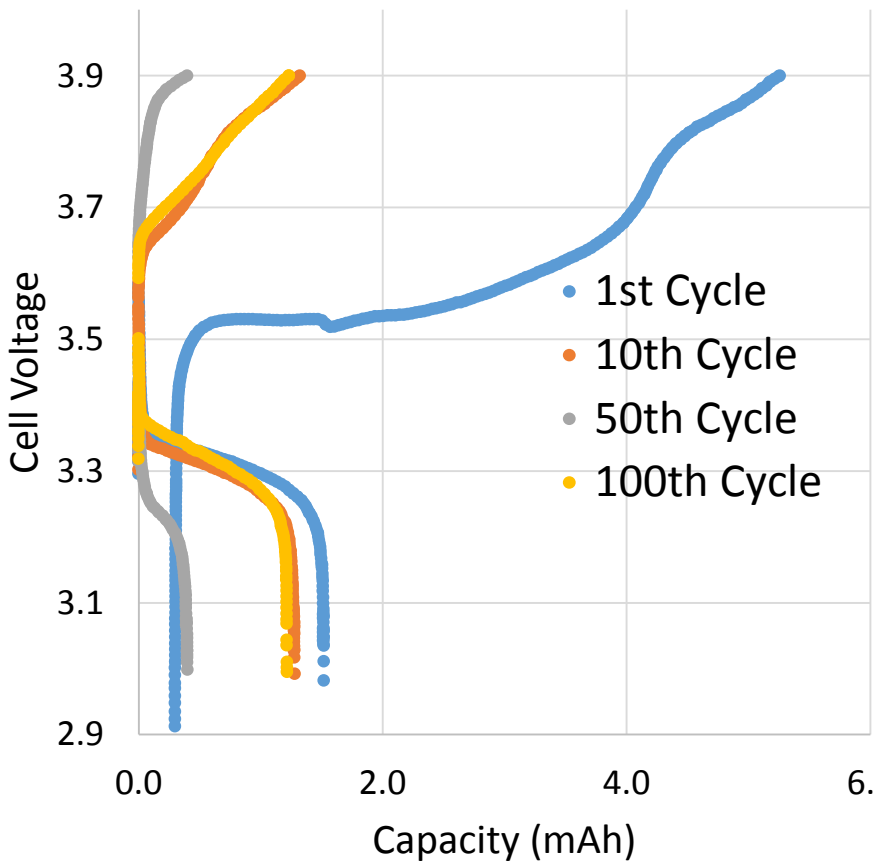


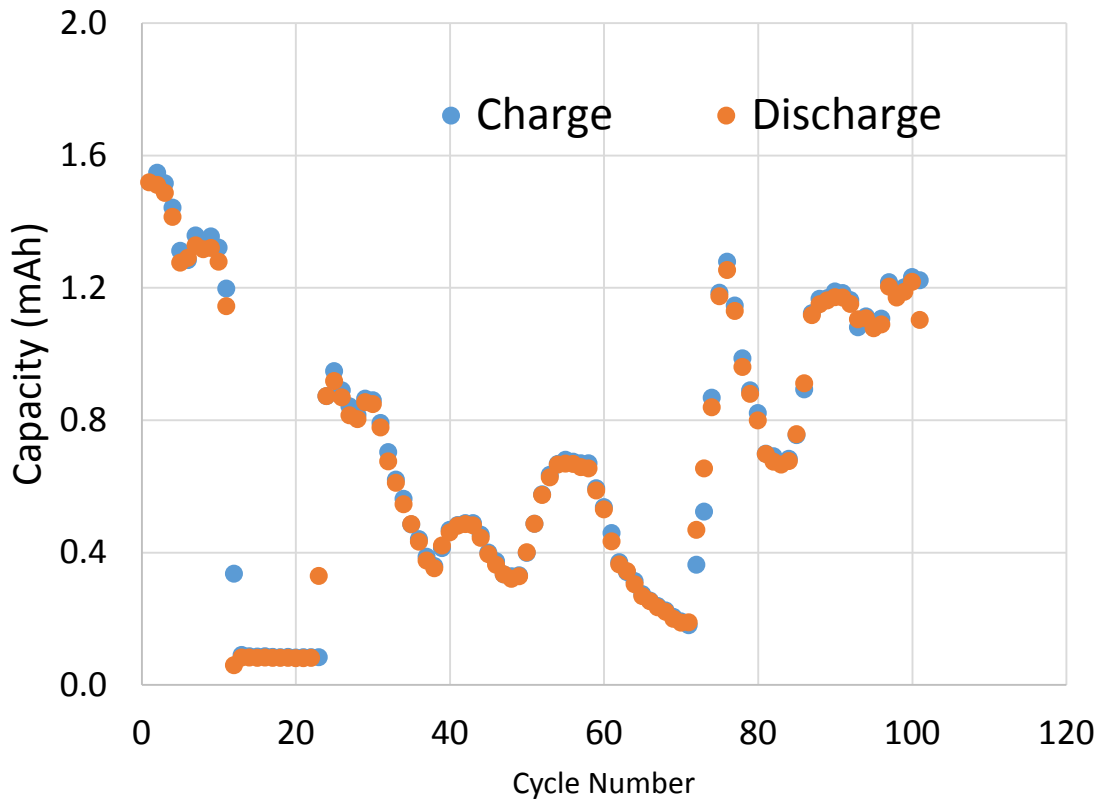
- Voltage range: 3.9V to 3V
- Current: 1 mA
- Initial Cycle: Highest charge capacity/ lowest discharge
- Capacity increased initially before decreasing
- 2 Plateaus on charge
  - Possible second reaction



- Voltage range: 3.9V to 1.25V
- Current: 1mA
- Initial charge at higher voltage
- 3 redox peaks on discharge
- Redox at ~1.5V limited in reversibility
- Capacity fade issues
  - 11th cycle shows recovery?

Cycling performance of Na-V nonaqueous: 100 cycles

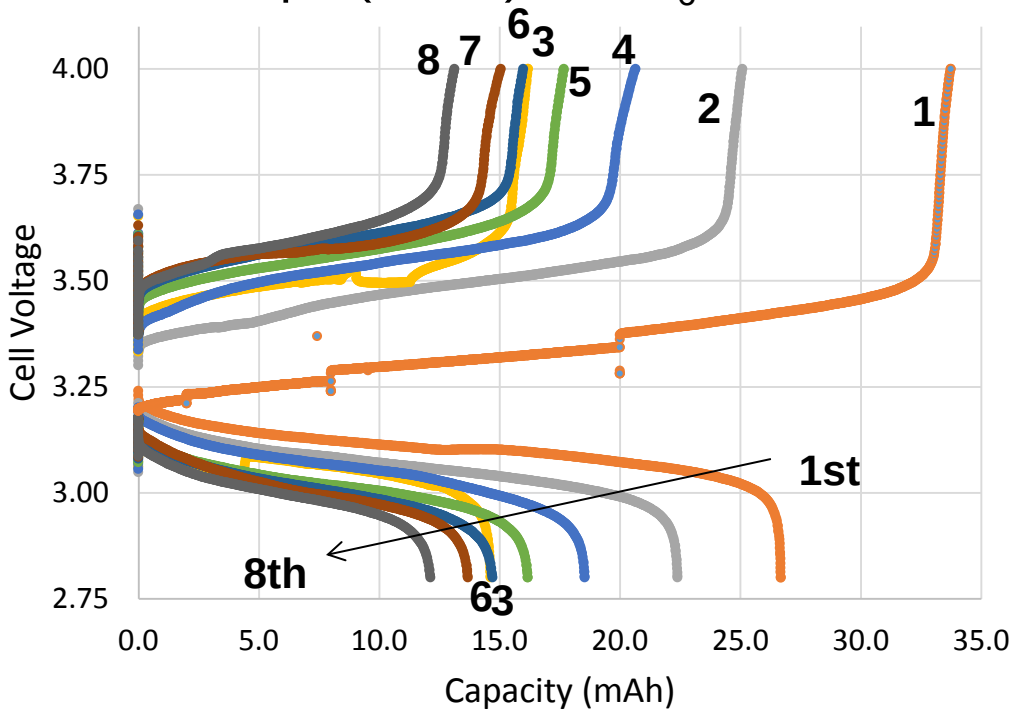




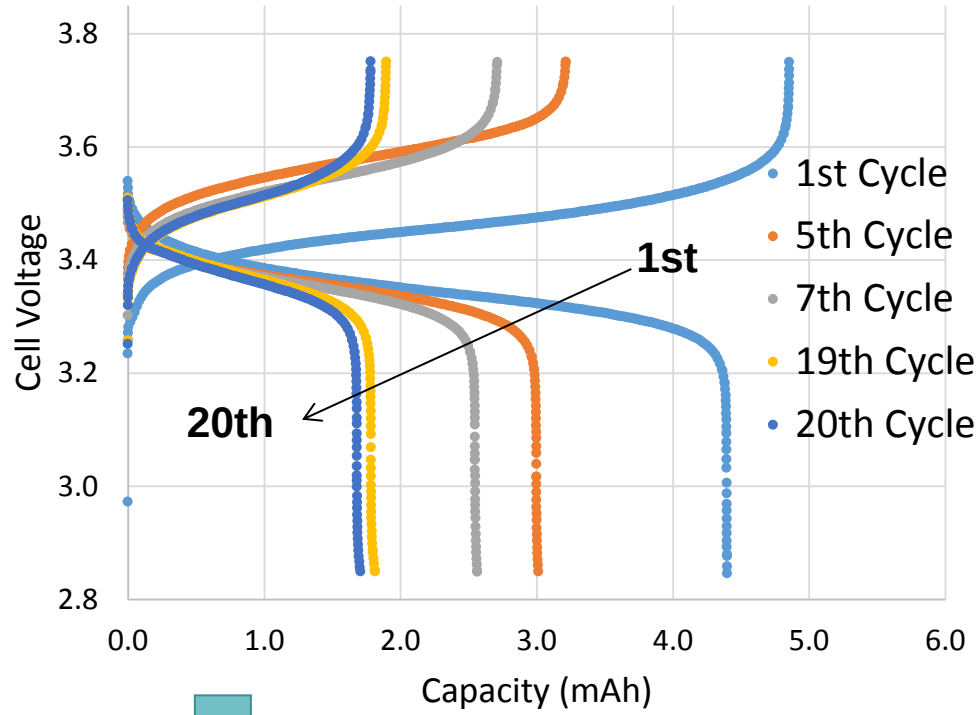
- In the 3.9 to 1.25V window there appears to be 3 voltage plateaus:
  - Charging: 1.65V, 3.5V, 3.8V
  - Discharging: 3.3V, 1.9V, 1.36V
- In the 3.9 to 3V window there is only one plateau per segment
  - 3.75V charge, 3.3V discharge

Na-Tempo Batteries

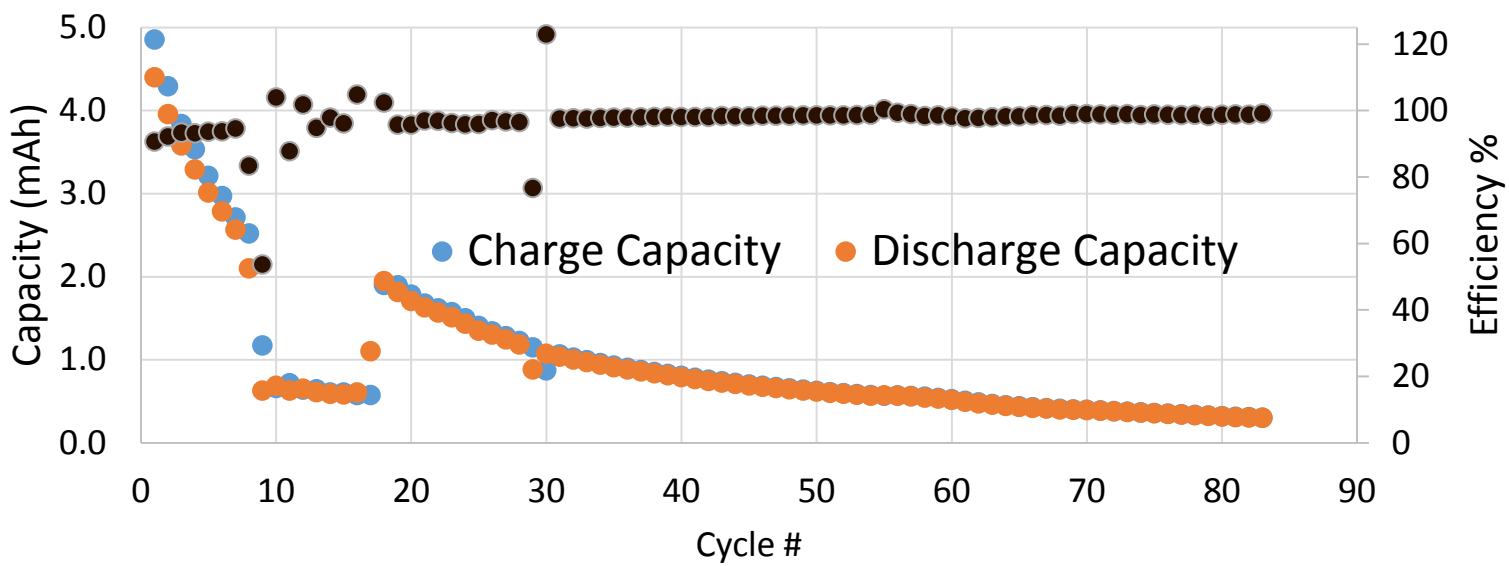
Tempo (0.1 M)-$NaPF_6$ in PC

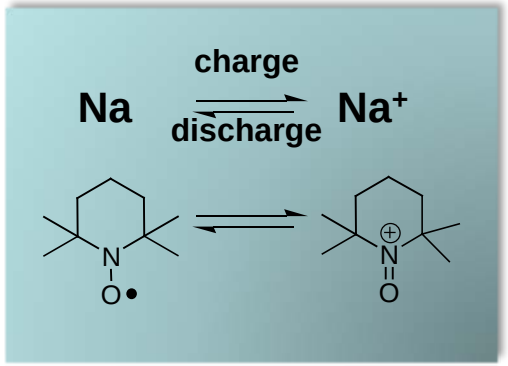


Tempo (0.01 M)-$NaPF_6$ in ACN



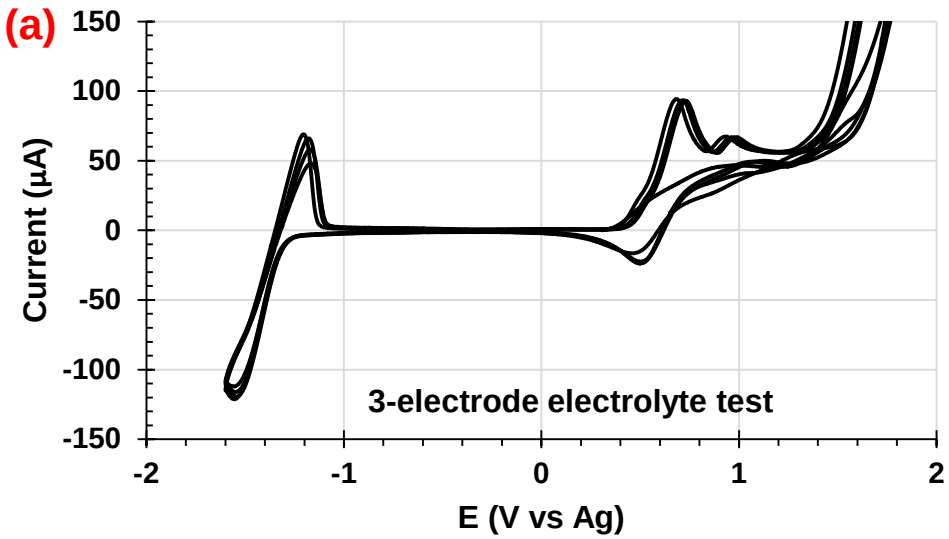
Na- Tempo (0.01M) Cycle Data

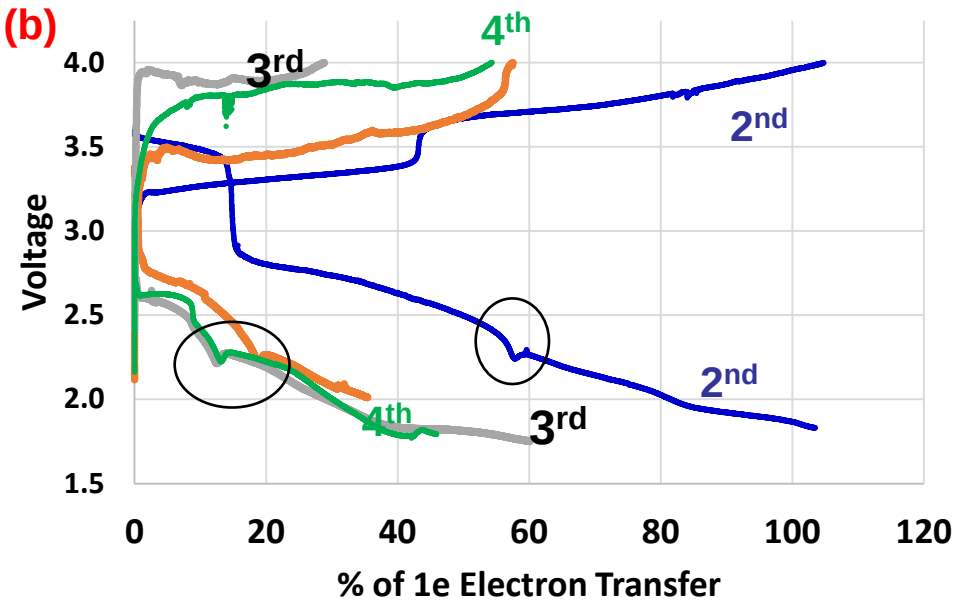




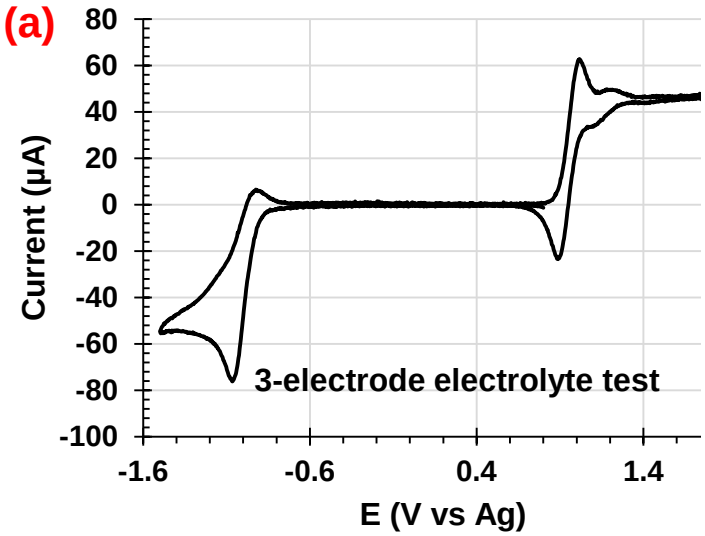
The effect of supporting electrolyte (nonaqueous)

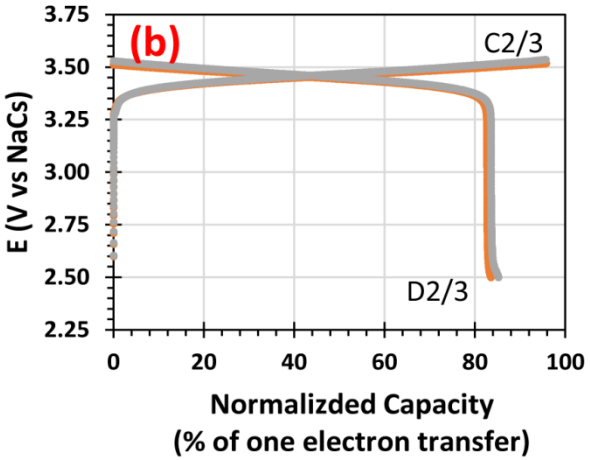
- $V(acac)_3$ - $NaClO_4$ in CH_3CN

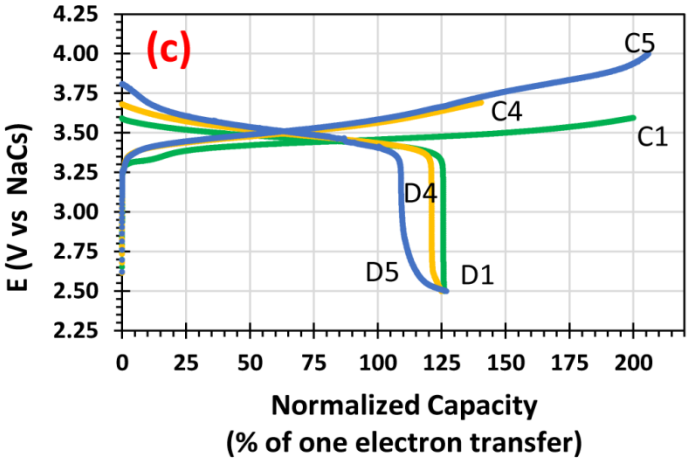




- $V(acac)_3$ - $NaPF_6$ in CH_3CN

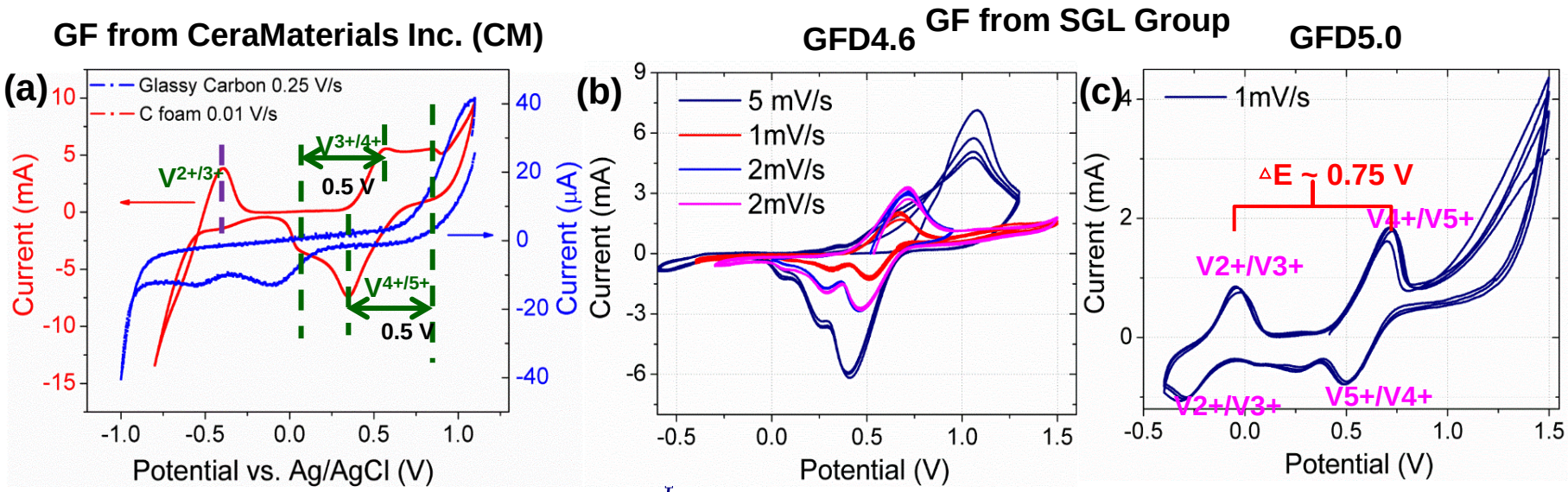


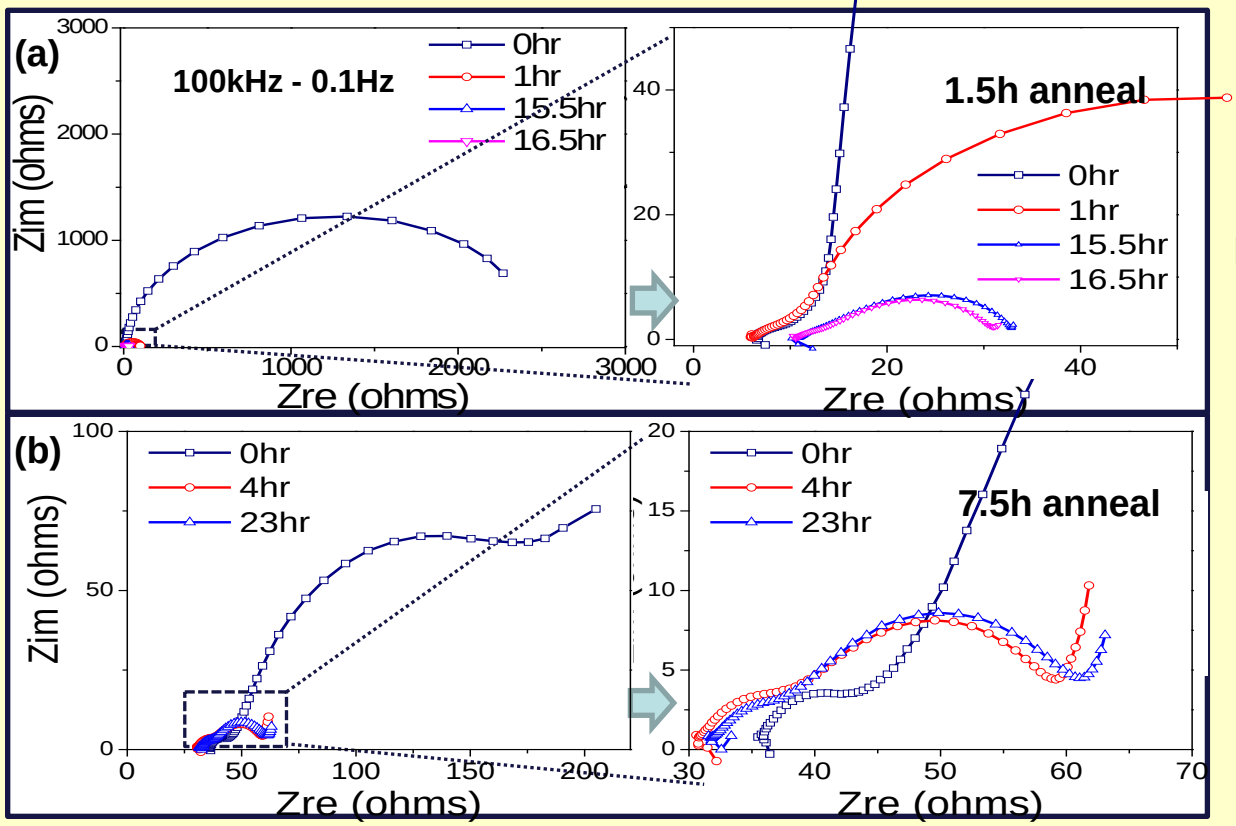




The effect of cathode electrode: graphite felts (aqueous)

❑ Different GF



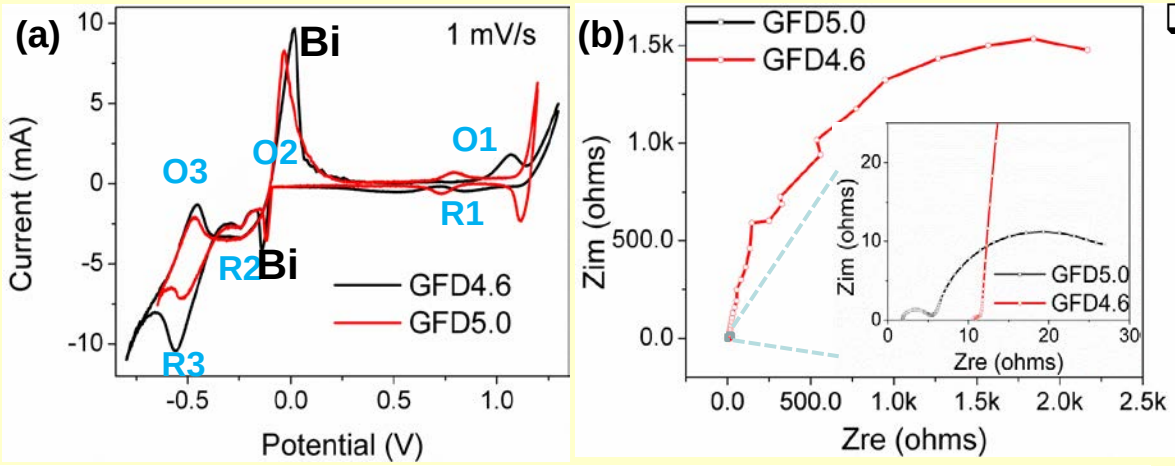


CV of $VOSO_4$-Na_2SO_4 electrolyte using different GF working electrode: (a) glassy carbon and GF (C foam) from Ceramaterials; (b) GFD4.6 and (c) GFD5.0 from SGL group. Ag/AgCl, Pt wire are used as reference and counter electrode, respectively.

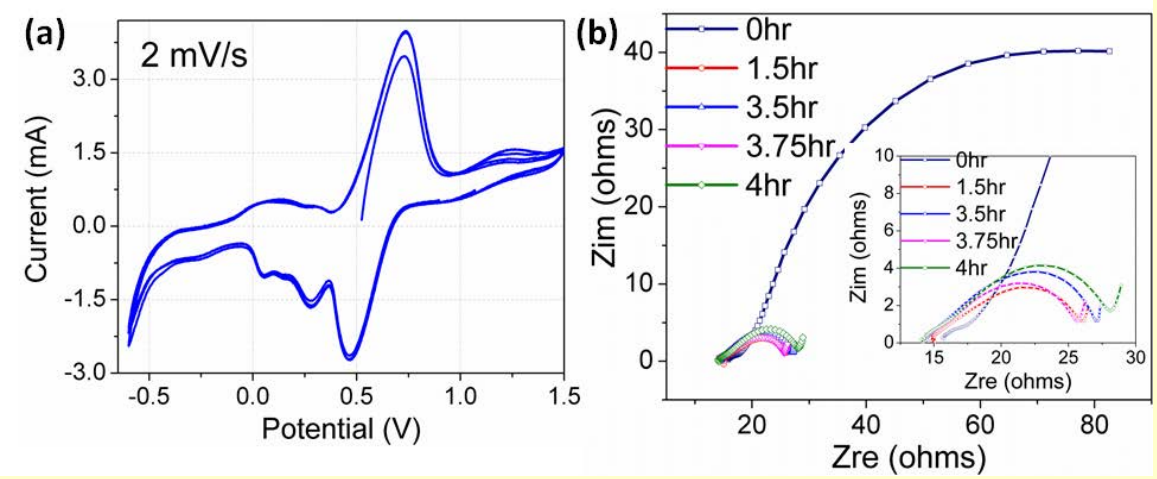
❑ Different annealing condition

- working electrodes: graphite felt GFD4.6 after annealed in air for 1.5 hours (a) and 7.5 hours (b).
- Nyquist plots for electrolyte 0.05M VOSO4- 0.1M Na2SO4.
- EIS were performed at OCV of the cell from 3-electrode setup

Catalytic activity on different graphite felts (aqueous)



- **Catalyst: BiCl3**
  - 0.05M $VOSO_4$- 0.1M Na_2SO_4- 0.002 M $BiCl_3$– 1.5M HCl electrolyte.
  - 3-electrode setup, in which GF, Ag/AgCl, and Pt wire were WE, RE, CE, respectively.
  - The EIS were recorded after the electrodes soaked in solution for *ca* 4.5 hours.

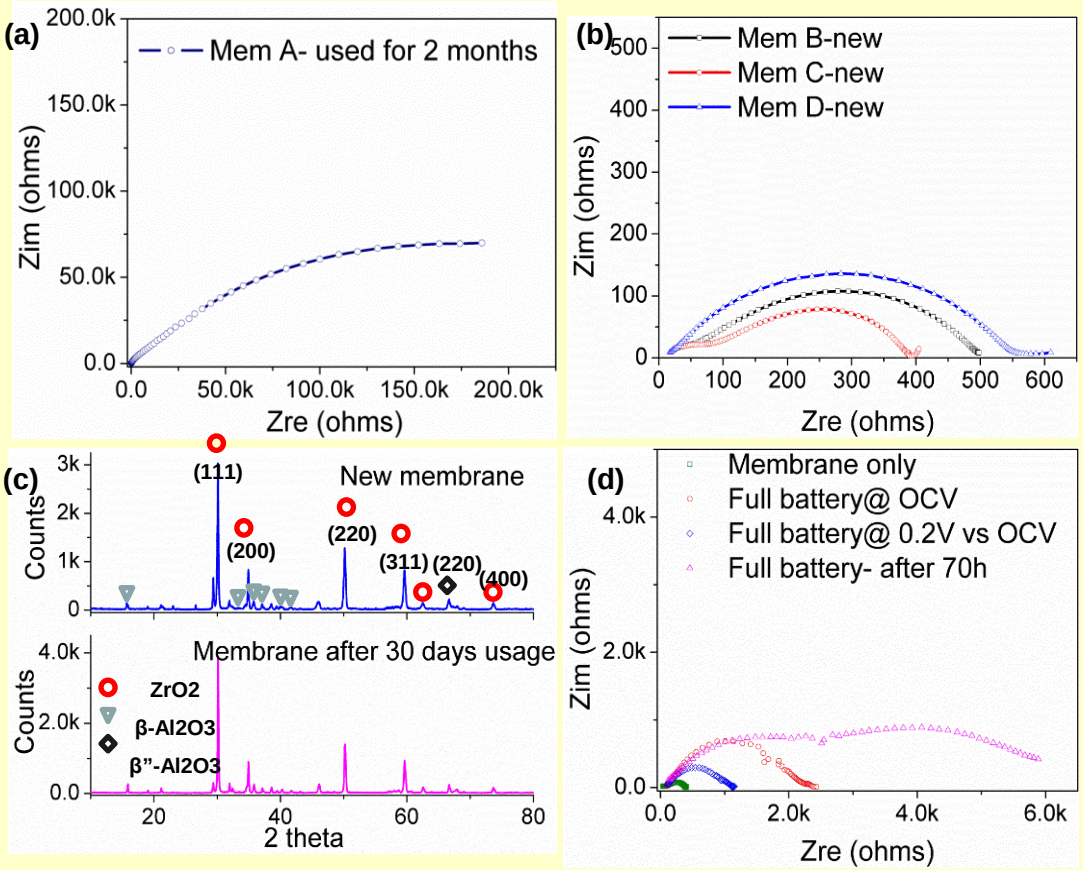


- **Catalyst: WO_3-AC**
  - 0.05M VOSO4- 0.1M Na2SO4 electrolyte.
  - WO3-AC nanoparticle coated graphite felts (GFD4.6) served as WE in a 3-eletrode setup.
  - EIS frequency 100 kHz to 0.1 Hz, under OCV.

EIS equivalent circuit fitting for some of the Nyquist plots by circuit R(QR)(QR)W

	GFD4.6_annealed 1.5 hr			GFD4.6_annealed 7.5hr		GFD5.0_annealed 7.5hr		GFD4.6 (1.5hr anneal)_WO3-AC	
Test time after immersion	0hr	1hr	16.5hr	0hr	4hr	5.8hr	5.9hr	1.5hr	3.5hr
R_e (Ω)	6.45	5.71	10.17	35.33	30.66	33.03	35.07	14.72	12.75
R_{ct} (Ω)	6.32	8.51	12.20	9.50	14.89	4.59	10.36	5.83	9.82
R_{int} (Ω)	2452	78.79	8.36	97.87	10.17	18.62	2.09	5.05	4.88

Membrane RT conductivity and stability (for aqueous)



Equivalent circuit simulation results for β"-Al_2O_3 membranes in which circuit R(Q(R(Q(R(CR))))) was utilized.

Samples	Mem C only	Fresh full battery (flowing)	Charged 70h_stopped flowing	Charged 70h_reflowing
R_e (Ω)	10.05	81.3	30.64	29.6
R_{ct} (Ω)	84.3	205.7	433.1	258.6
R_{gb} (Ω)	228.4	1711	1981	2018
R_{int} (Ω)	74.0	364.8	4734	4026

Equivalent circuit simulation results in which circuit R(Q(R(Q(R(CR))))) was utilized.

Samples	Mem A (2 months)	Mem B (new)	Mem C (new)	Mem D (new)
R_e (Ω)	30.41	5.855	10.05	6.43
R_{ct} (Ω)	875.9	64.97	84.3	59.6
R_{gb} (Ω)	1601	374.4	228.4	501.1
R_{int} (Ω)	344.1k	56.34	74.0	1.001
σ (S/cm, based on R_{gb})	**2.30×10^{-5}**	**9.84×10^{-5}**	**1.61×10^{-4}**	**7.35×10^{-5}**

Challenges

Better Sodium-Ion Exchange Membranes

- ✓ **Mechanically Robust and thin β"-Al_2O_3 membrane**
- ✓ **Water Resistant and long life β"-Al_2O_3 membrane**
- ✓ **High ionic conductivity Na ion based solid eletrolyte**

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Progress to Date

- Demonstrate feasibility of two electron transfer redox reactions per V ion in HNFBs with aqueous and nonaqueous catholytes.
- Good cyclic stability for Na-V aqueous over 1e transfer, > 30 cycles
- Good cyclic stability for Na-V, Na-Mn, and Na-Tempo nonaqueous batteries , 100 cycles achieved
- High performance of Na-V nonaqueous battery with two V redox reactions.
- Optimize the battery performance from the aspects of electrode materials and modification (catalysts deposition), electrolyte composition, membrane surface coating, etc..

Ongoing and Future work

- Identify the active species in Na-V nonaqueous battery
- Suppress the capacity decay in Na-V and Na-Tempo nonaqueous battery
- Develop new Na-I_2 batteries with NaSICON membrane

Acknowledgements

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