High Voltage, High Capacity, Room Temperature Sodium Flow Batteries

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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

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

Catholyte: \[ \text{VO}^{2+} + \text{Cl}^- + \text{H}_2\text{O} - \text{e} \xleftrightarrow{\text{Charge/Discharge}} \text{VO}_2\text{Cl} + 2\text{H}^+ \]
\[ \varepsilon_{\text{co}} = 1.0 \text{ V} \]

Anolyte: \[ \text{V}^{3+} + \text{e} \xleftrightarrow{\text{Charge/Discharge}} \text{V}^{2+} \]
\[ \varepsilon_{\text{ao}} = -0.25 \text{ V} \]

Overall: \[ \text{VO}^{2+} + \text{Cl}^- + \text{H}_2\text{O} + \text{V}^{3+} \xleftrightarrow{\text{Charge/Discharge}} \text{VO}_2\text{Cl} + 2\text{H}^+ + \text{V}^{2+} \]
\[ E_0 = 1.25 \text{ V} \]

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


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:

Cathode 1: \( \text{VO}^{2+} + \text{H}_2\text{O} \xrightarrow{\text{charge}} \text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \) \( E^o = +1.0 \text{ V vs. SHE} \)

Cathode 2: \( \text{V}^{3+} + \text{H}_2\text{O} \xrightarrow{\text{charge}} \text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \) \( E^o = +0.34 \text{ V vs. SHE} \)

Cathode 3: \( \text{V}^{2+} \xrightarrow{\text{charge}} \text{V}^{3+} + \text{e}^- \) \( E^o = -0.26 \text{ V vs. SHE} \)

Anode: \( \text{Na}^+ + \text{e}^- \xrightarrow{\text{charge}} \text{Na} \) \( E^o = -2.7 \text{ V vs. SHE} \)

- 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)

Cathode 1: \( \text{Cr}^{3+} + \frac{7}{2} \text{H}_2\text{O} \xrightarrow{\text{charge}} \frac{1}{2} \text{Cr}_2\text{O}_7^{2-} + 7\text{H}^+ + 3\text{e}^- \) \( E^o = +1.33 \text{ V vs. SHE} \)

Cathode 2: \( \text{VO}^{2+} + \text{H}_2\text{O} \xrightarrow{\text{charge}} \text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \) \( E^o = +1.0 \text{ V vs. SHE} \)

Cathode 3: \( \text{V}^{3+} + \text{H}_2\text{O} \xrightarrow{\text{charge}} \text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \) \( E^o = +0.34 \text{ V vs. SHE} \)

Cathode 4: \( \text{V}^{2+} \xrightarrow{\text{charge}} \text{V}^{3+} + \text{e}^- \) \( E^o = -0.26 \text{ V vs. SHE} \)

Cathode 5: \( \text{Cr}^{2+} \xrightarrow{\text{charge}} \text{Cr}^{3+} + \text{e}^- \) \( E^o = -0.42 \text{ V vs. SHE} \)

Anode: \( \text{Na}^+ + \text{e}^- \xrightarrow{\text{charge}} \text{Na} \) \( E^o = -2.7 \text{ V vs. SHE} \)

- Theoretic specific energy for a 2.5M \( \text{V}^{2+} \) plus 3M \( \text{Cr}^{2+} \) 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

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<th>IIb</th>
<th>III</th>
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<td>~3</td>
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Project Progress to Date 2: HNFBs with the Catholyte Made of Mn(acac)\textsubscript{3} in Acetonitrile

**Experimental Conditions:**

- **Anode:** A solid Na chuck floating on top of an ionic liquid with 0.1M sodium trifluoromethylsulfonyl imide (NaTFSI) salt
- **Cathode:** 0.025M Mn(acac)\textsubscript{3} and 0.1M NaClO\textsubscript{4} dissolved in acetonitrile (CH\textsubscript{3}CN) with a Pt wire current collector
- **Ion exchange membrane and temperature:** $\beta''$-Al\textsubscript{2}O\textsubscript{3} tube and 25°C

**Cathode Rx 1:**

\[
Mn^{3+} + e^- \leftrightarrow Mn^{2+}
\]

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

**Cathode Rx 2:**

\[
Mn^{4+} + e^- \leftrightarrow Mn^{3+}
\]

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

**Anode:**

\[
Na \leftrightarrow Na^+ + e^-
\]

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

**Two electron transfer redox reaction per Mn ion!**
Project Progress to Date 3: CV of the Catholyte Made of Mn(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 $\beta''$-Al$_2$O$_3$ tube (Na$^+/Na$)
- Counter electrode: a tinned copper wire
- Electrolyte: 0.05M Mn(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$_2$O in the electrolyte.
Project Progress to Date 4: HNFBs with Catholyte Made of V(acac)$_3$ in Acetonitrile

- **Anode:** A solid Na chuck 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$_3$CN) with 0.1M NaClO$_4$ supporting electrolyte and a graphite foam current collector
- **Ion exchange membrane & temperature:** $\beta''$-Al$_2$O$_3$ 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 VOSO₄ + 0.1 M Na₂SO₄ + 1.5 M HCl
Anode: Na₃⁷Cs₆³
Membrane: β”-Al₂O₃ disc with Au coating

VO²⁺ + 2H⁺ + e⁻ ↔ V³⁺ + H₂O

V³⁺ + e⁻ ↔ V²⁺
Project Progress to Date 6: Discharge Profile of Vanadium-Based Aqueous Catholytes

Cell conditions:
Catholyte: 0.025 M VOSO$_4$ + 0.1 M Na$_2$SO$_4$ + 1.5 M HCl
Anode: Na$_{37}$Cs$_{63}$
Membrane: $\beta''$-Al$_2$O$_3$ disc with Au coating

Cell conditions:
Catholyte: 0.025 M VOSO$_4$ + 0.1 M Na$_2$SO$_4$ + 1.5 M HCl
Anode: Na + 0.2 M NaTSFI/Pyrr TSFI
Membrane: $\beta''$-Al$_2$O$_3$ disc w/o Au coating
Experimental Conditions:

- **Anode:** A solid Na chuck floating on top of an ionic liquid with 0.1M sodium trifluoromethylsulfonyl imide (NaTFSI) salt
- **Cathode:** 0.05M Mn(acac)$_3$ dissolved in acetonitrile (CH$_3$CN) with a tinned Cu wire current collector with mechanical stirring
- **Ion exchange membrane & temperature:** β”-Al$_2$O$_3$ tube and 25°C

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

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 Mn(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 Mn(acac)$_3$ and 0.1M NaClO$_4$ dissolved in acetonitrile (CH$_3$CN) with a carbon foam as the current collector with mechanical stirring
- **Ion exchange membrane & temperature:** β''-Al$_2$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
- 2$^{nd}$ discharge: 87.0%
- 3$^{rd}$ discharge: 93.2%
- 4$^{th}$ discharge: 90.2%
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.
CV recorded for a catholyte with 0.02 M VOSO$_4$ - 0.1 M Na$_2$SO$_4$ -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 (▼ and ▲) 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.