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CHEMISTRY & CHEMICAL BIOLOGY



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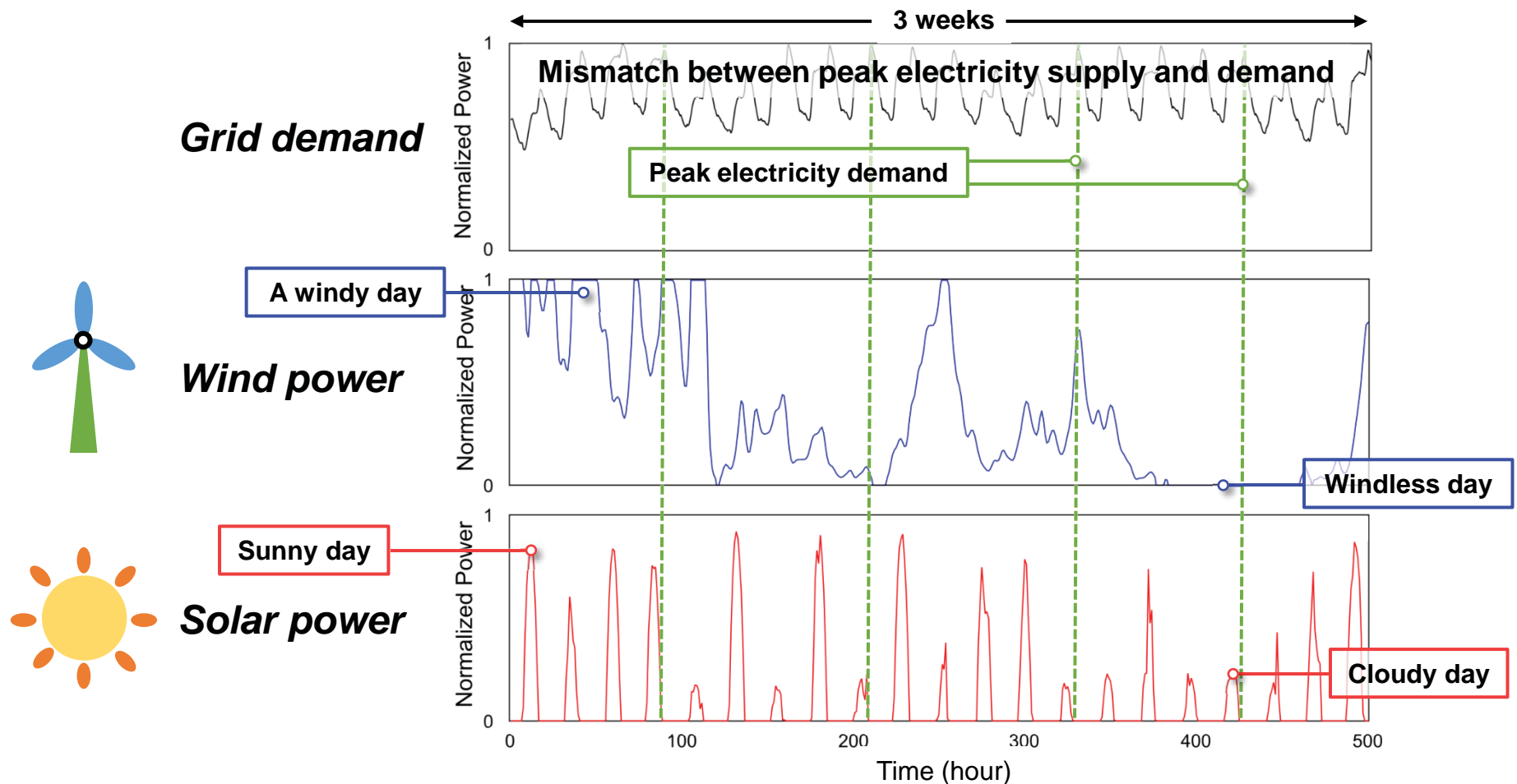
250<sup>th</sup> American Chemical Society National Meeting & Exposition

# High-performance Aqueous Redox Flow Battery (ARFB)

Kaixiang Lin, Qing Chen, Louise Eisenach, Alvaro Valle,  
Roy G. Gordon, Michael J. Aziz, Michael P. Marshak

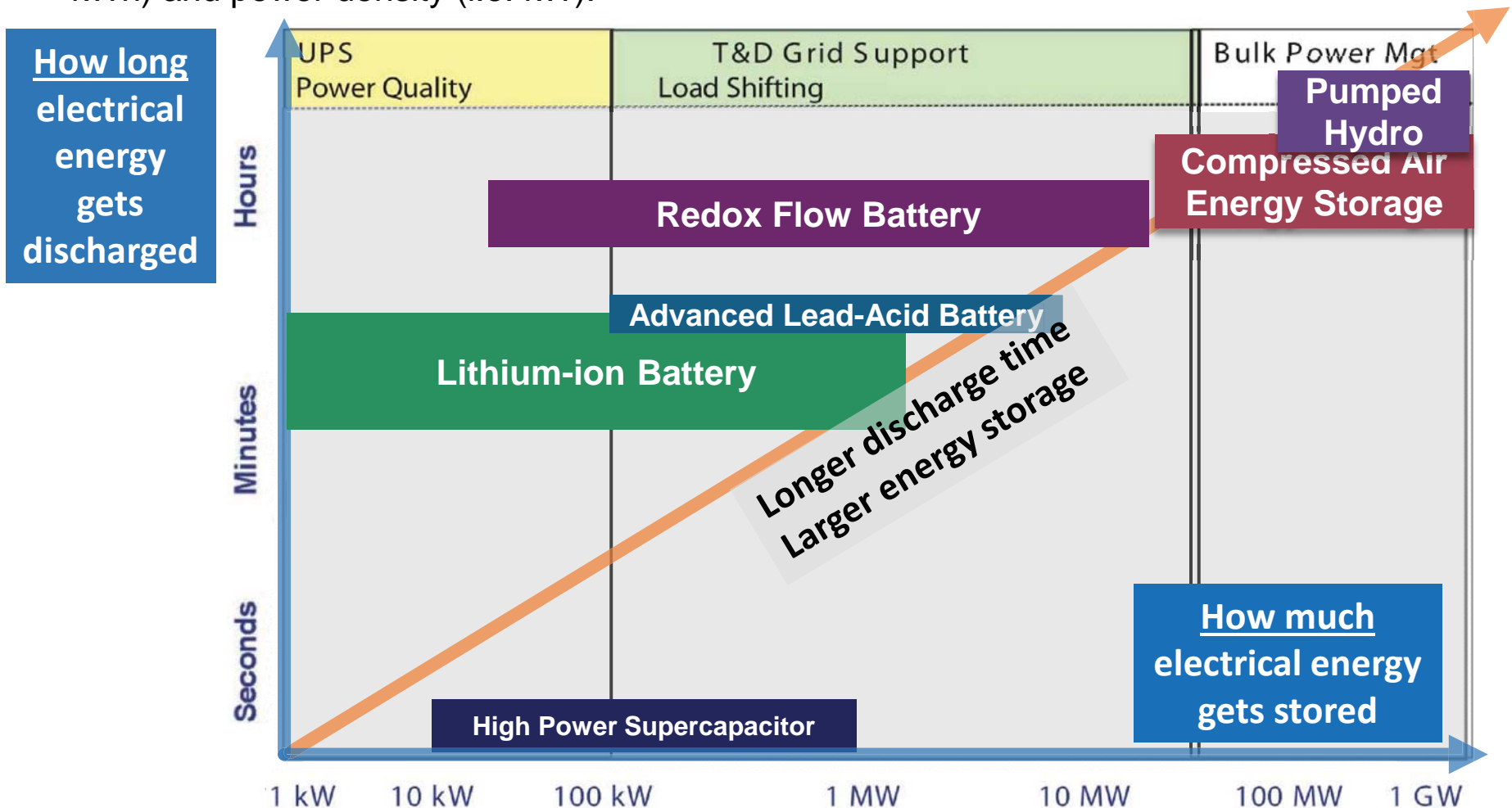
# Motivation

- **Wind** and **solar energy** are widely and increasingly used for electricity generation
- Their **intermittency** leads to mismatch of peak energy production and demand
- Need a **cheap** and **scalable** method to capture intermittent energy and reuse it when wind stops and sun sets.



# Existing Energy Storage Technology

- **Pumped hydro** and compressed air energy storage (**CAES**) require special geology & have high environmental costs.
- **Solid-state battery systems** have low discharge time due to coupled energy density (i.e. kWh) and power density (i.e. kW).





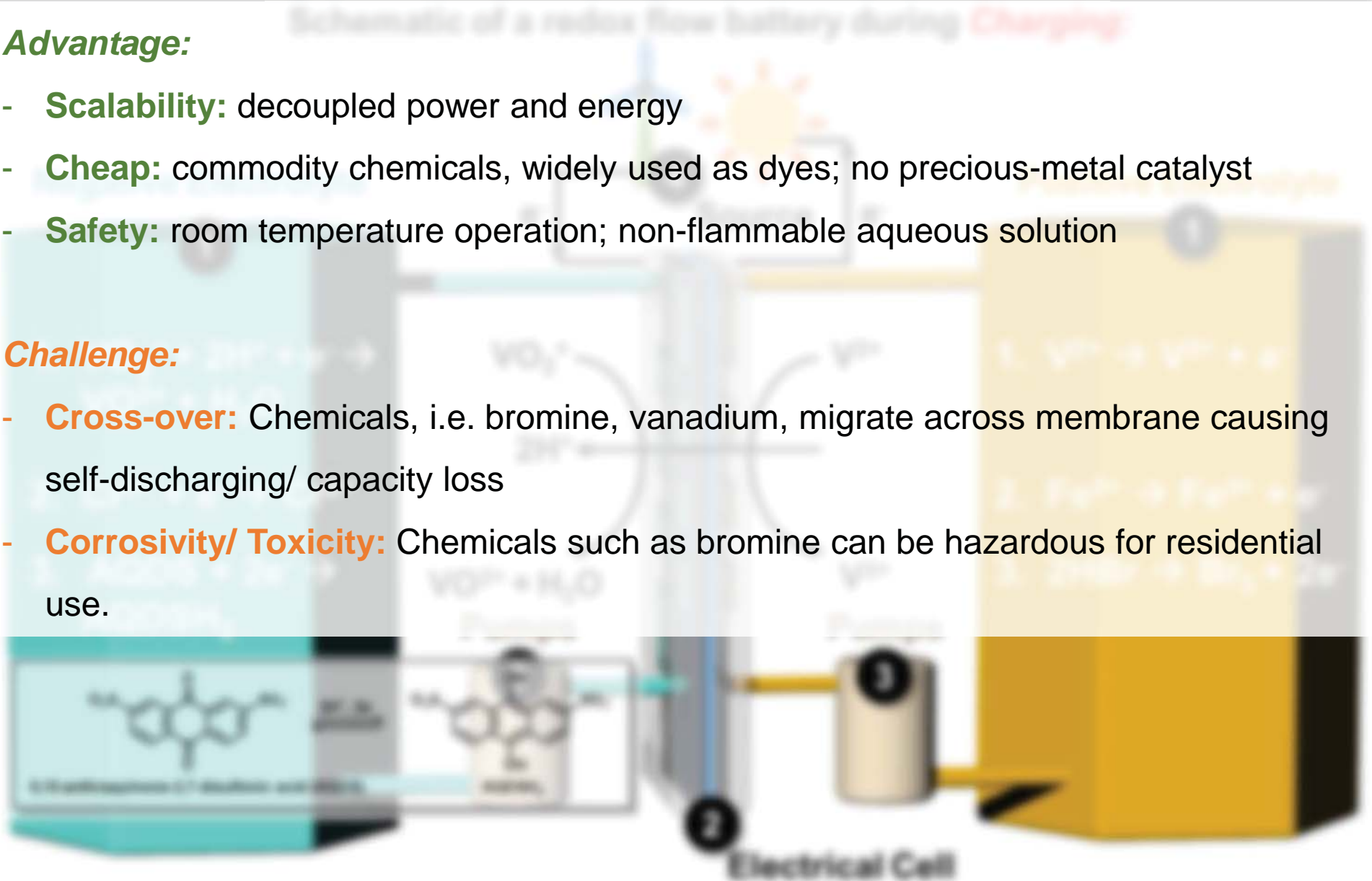
# Aqueous Redox Flow Battery

## Advantage:

- **Scalability:** decoupled power and energy
- **Cheap:** commodity chemicals, widely used as dyes; no precious-metal catalyst
- **Safety:** room temperature operation; non-flammable aqueous solution

## Challenge:

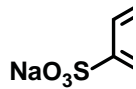
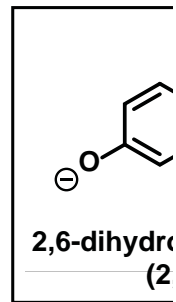
- **Cross-over:** Chemicals, i.e. bromine, vanadium, migrate across membrane causing self-discharging/ capacity loss
- **Corrosivity/ Toxicity:** Chemicals such as bromine can be hazardous for residential use.



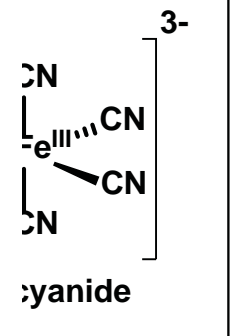
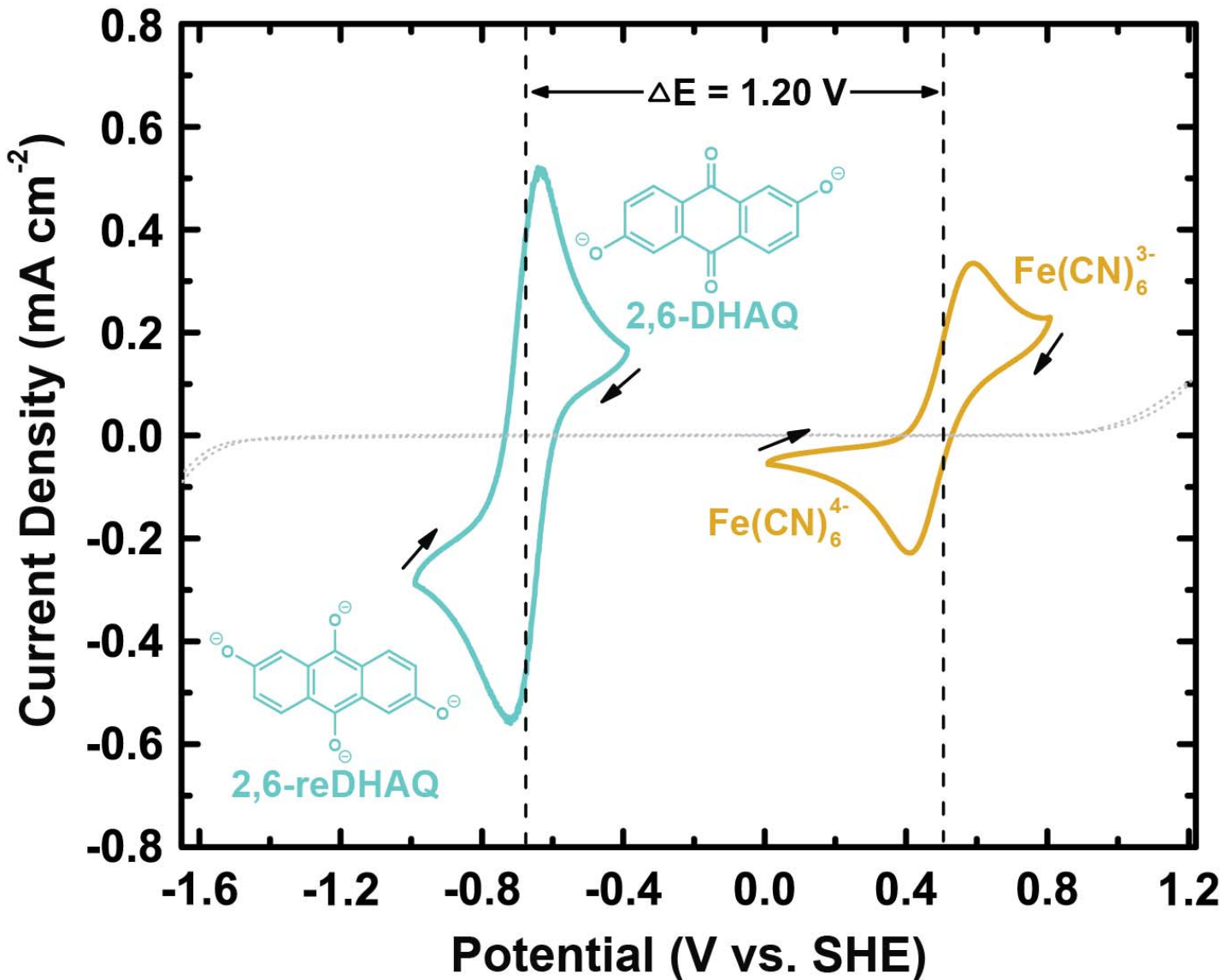
# Quinone/Ferrocyanide Redox Flow Battery

Negative Electrolyte

Positive Electrolyte



- Synthesis
- chemical
- $E_{eq} =$
- solution
- 2,6-D
- M KC



- de hybrid
- gent<sup>2</sup>
- ie solution
- alkaline
- H
- battery
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Expert  
9," Wild Hlth Org.  
tion, 1974).

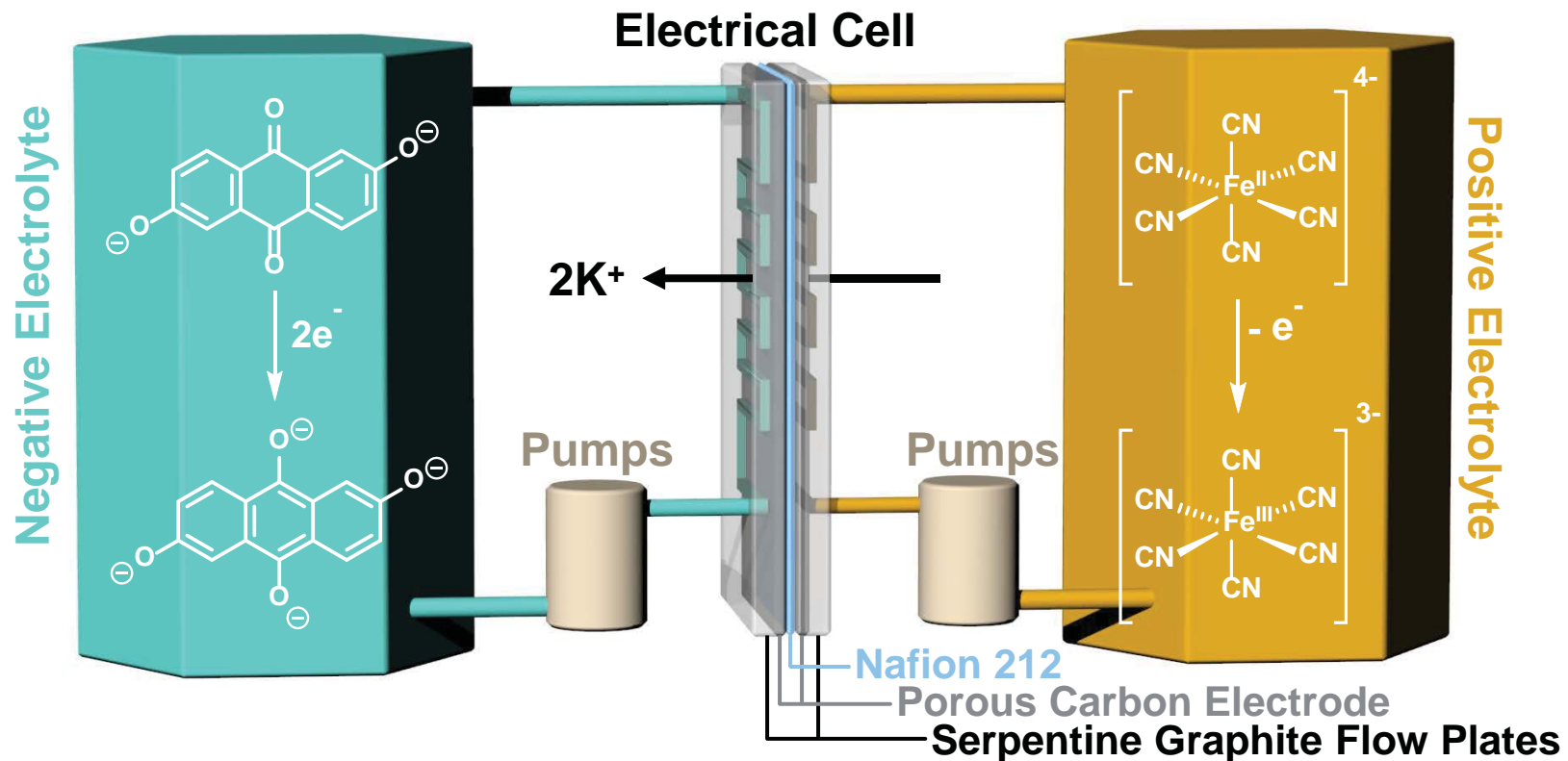
# Cell Performance – Setup

## Cell Configuration:

- Graphite plates with **serpentine** flow pattern
- Pretreated SGL **porous carbon** electrodes
- Pretreated **Nafion 212** membrane
- Gear Pump

## Electrolyte Composition:

- Positive:** 0.4 M ferricyanide at r.t. and 0.8 M at 45 °C both in 1 M KOH
- Negative:** 0.5 M K<sup>+</sup> salt of 2,6-DHAQ and 1 M K<sup>+</sup> salt of 2,6-DHAQ at 45 °C both in 1 M KOH



# Cell Performance – Power Density

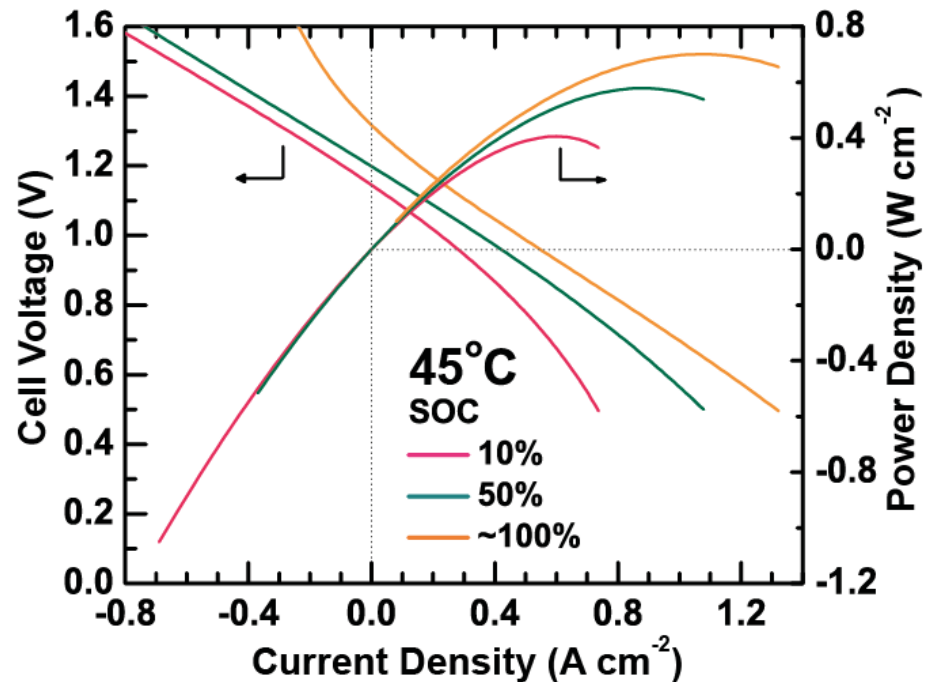
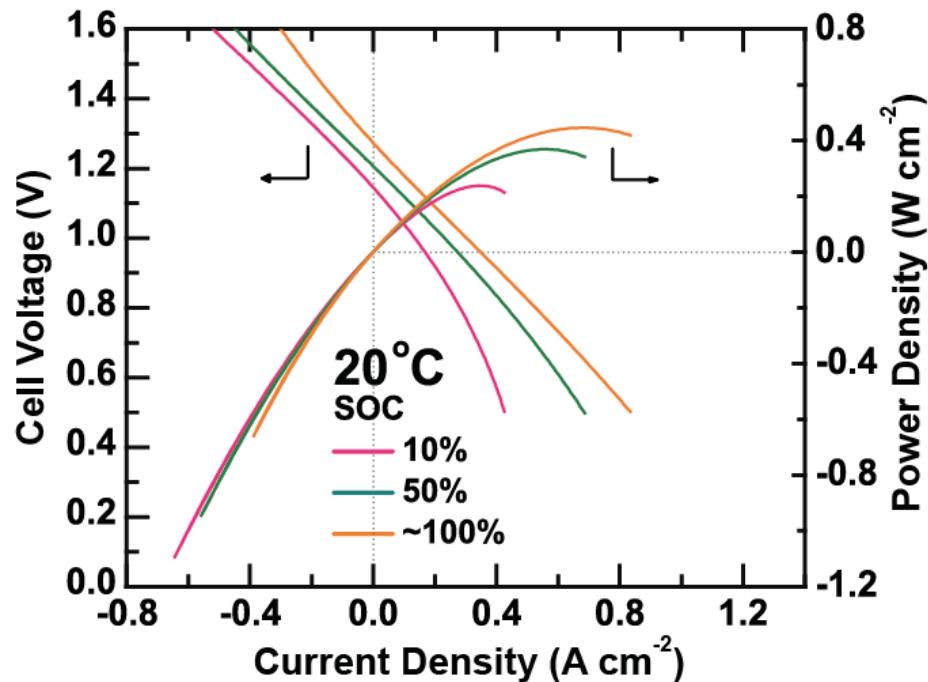
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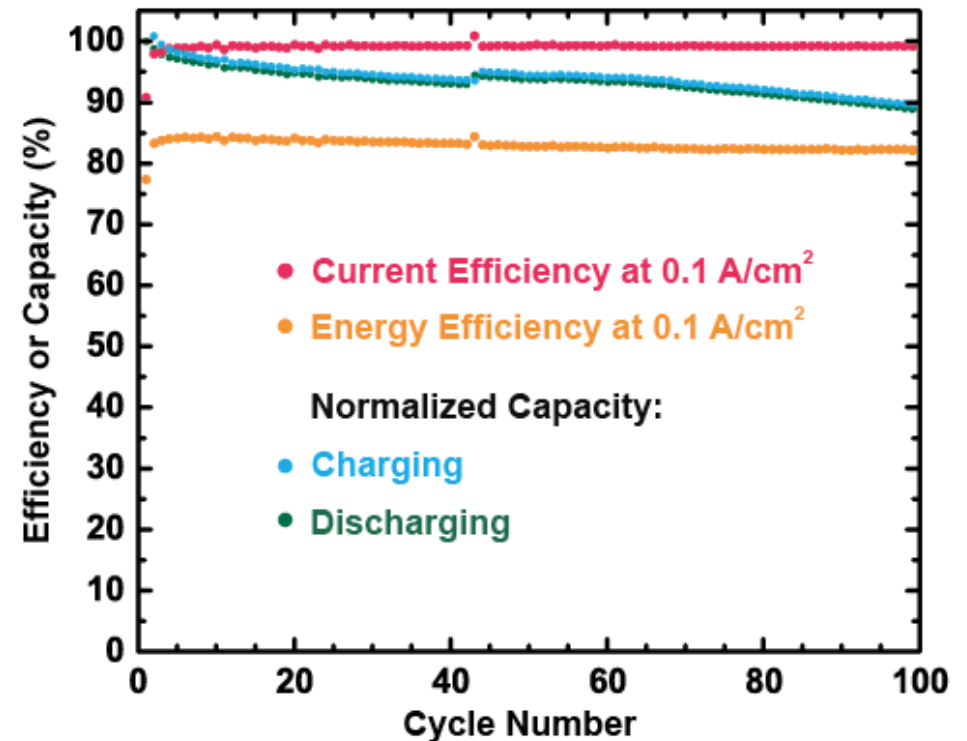
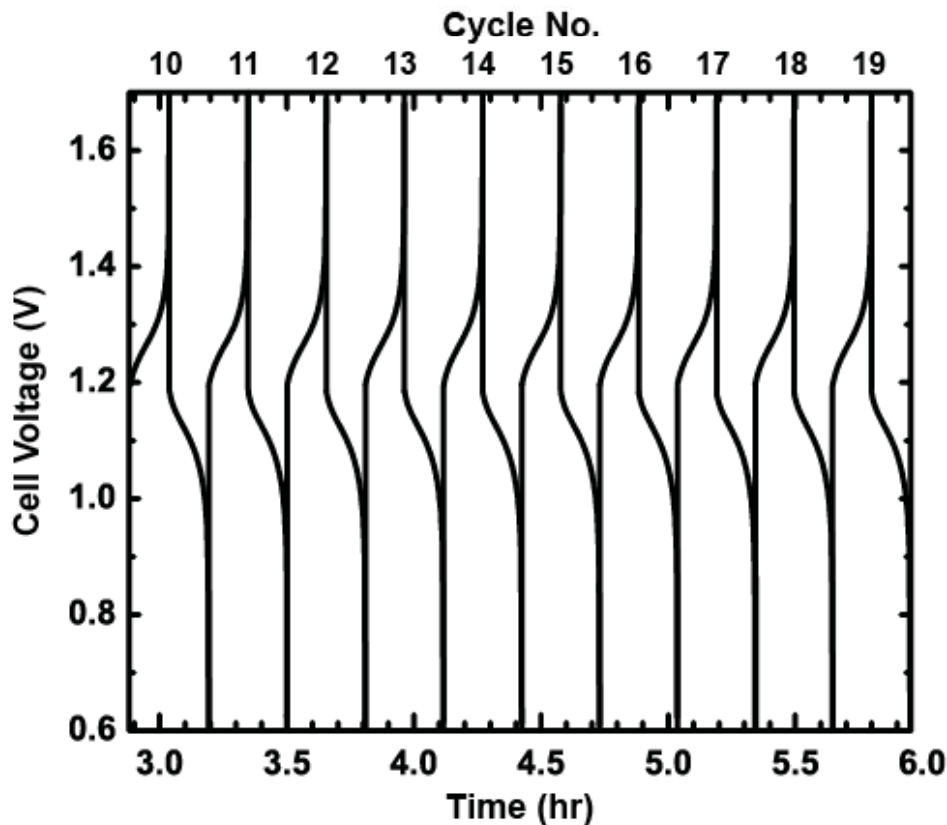
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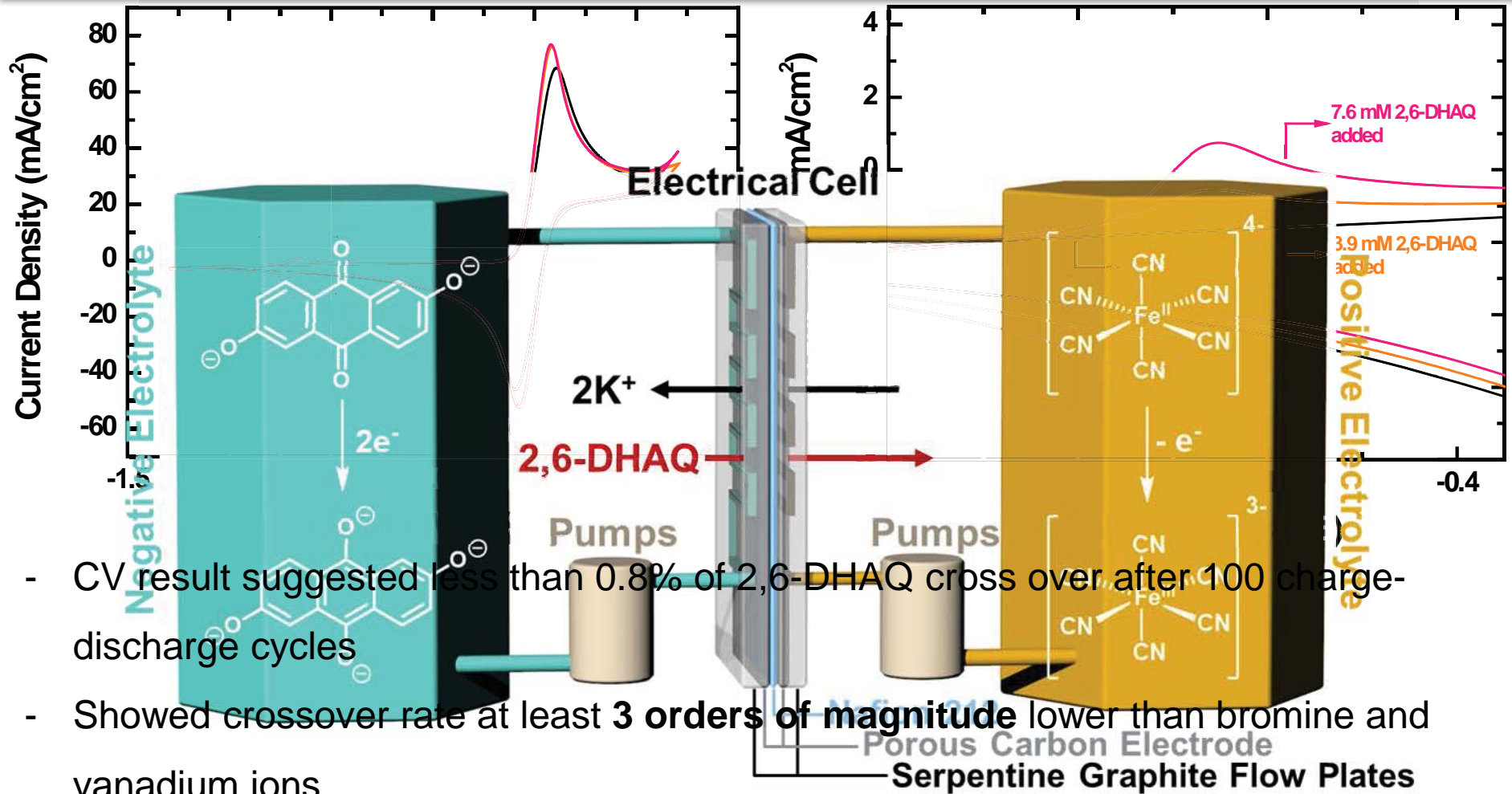


# Cell Performance – Cycling, Capacity Retention and Efficiency



- Average **current** and **energy efficiency** over 100 cycles is **> 99%** and **84%** respectively.
- Cell showed **~ 0.1% → 0.067% capacity loss per cycle**; this is mainly due to electrolyte leakage

# Cell Performance – Membrane Crossover

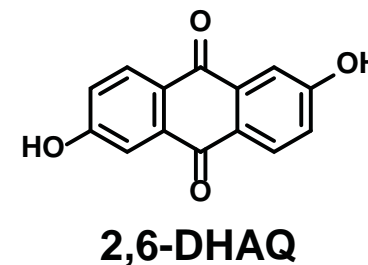


- CV result suggested less than 0.8% of 2,6-DHAQ cross over after 100 charge-discharge cycles
- Showed crossover rate at least **3 orders of magnitude** lower than bromine and vanadium ions
- The result showed possibility of using cheaper membrane or even separator for future batteries

M. C. Tucker, et al. Impact of membrane characteristics on the performance and cycling of the Br<sub>2</sub>-H<sub>2</sub> redox flow cell. *Journal of Power Sources*. **284**, 212–221 (2015).; S. Jeong, et al. Effect of nafion membrane thickness on performance of vanadium redox flow battery. *Korean Journal of Chemical Engineering*. **31**, 2081–2087 (2014).

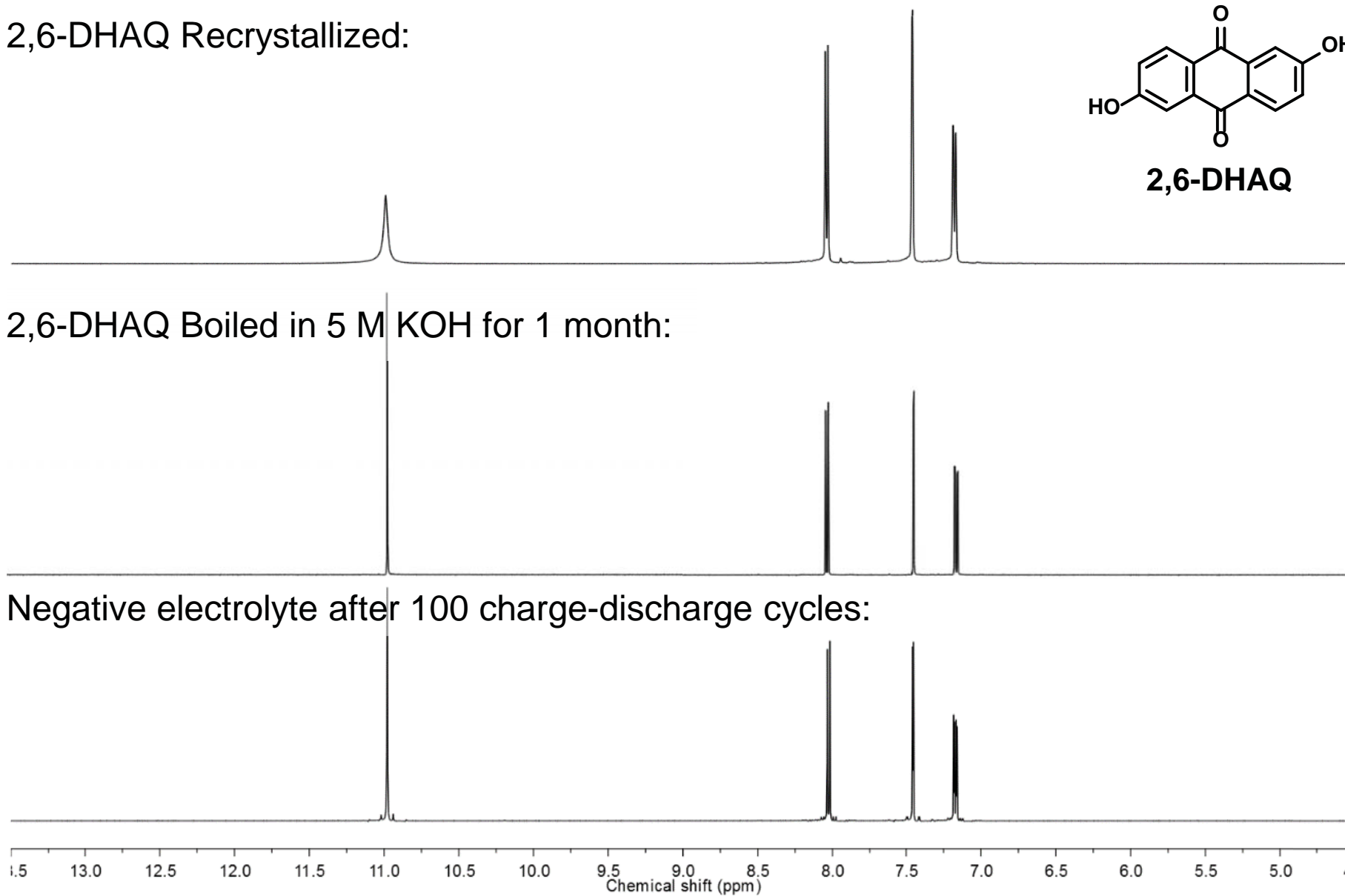
# Chemical and Electrochemical Stability of 2,6-DHAQ

2,6-DHAQ Recrystallized:

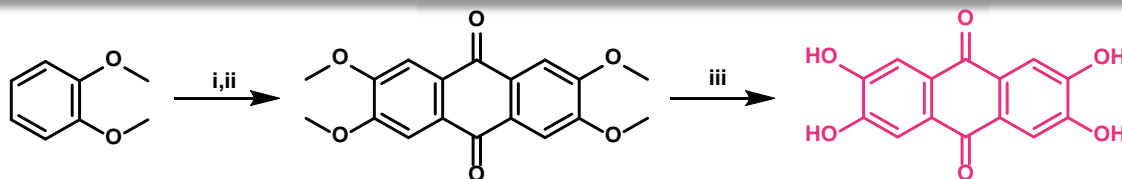


2,6-DHAQ Boiled in 5 M KOH for 1 month:

Negative electrolyte after 100 charge-discharge cycles:



# Future Work



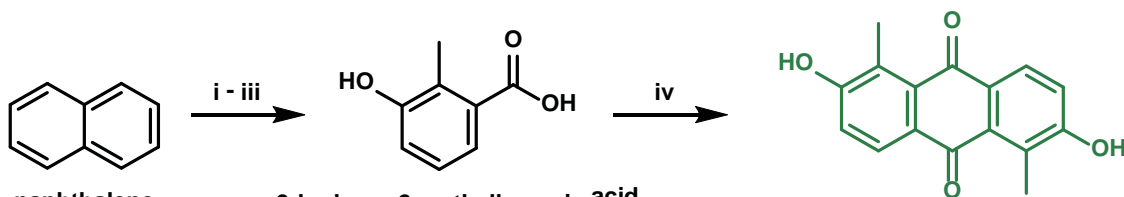
1,2-dimethoxybenzene

2,3,6,7-tetramethoxyanthraquinone

2,3,6,7-tetrahydroxyanthraquinone

- T. S. Balaban, et al. *Helv. Chim. Acta.* **89**, 333–351 (2006)

i. condensation with acetaldehyde; ii. oxidation by  $\text{Na}_2\text{Cr}_2\text{O}_7$ ; iii. Hydrolysis by HBr



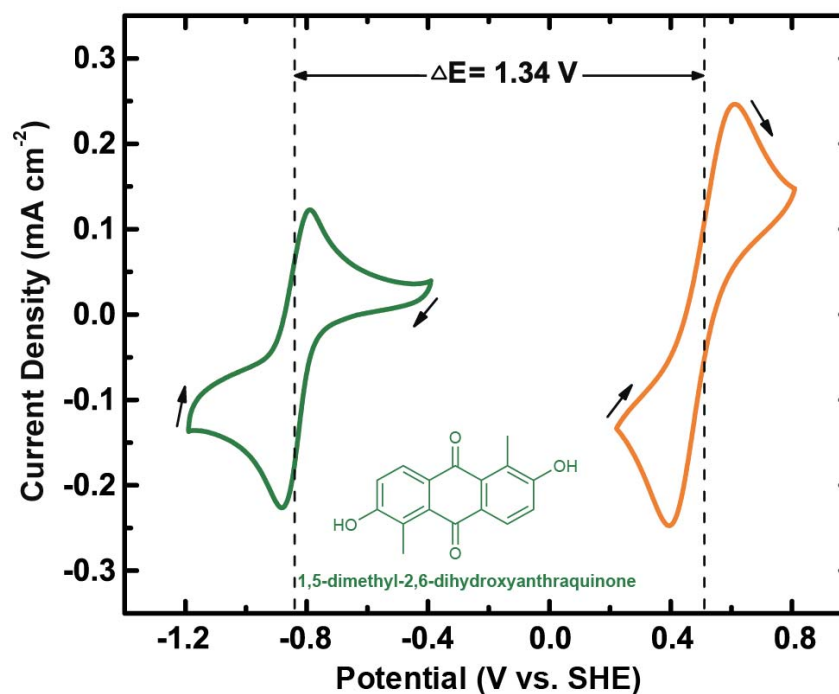
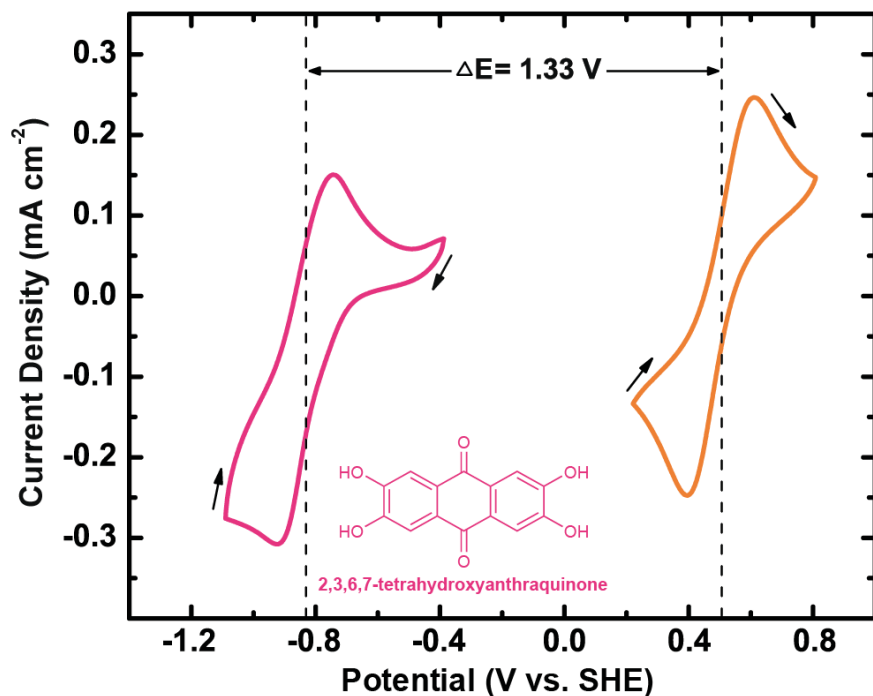
naphthalene

3-hydroxy-2-methylbenzoic acid

1,5-dimethyldihydroxyanthraquinone

- H. Behre, F. et al. Method for producing 3-hydroxy-2-methylbenzoic acid (2004), WO2003080542A3.

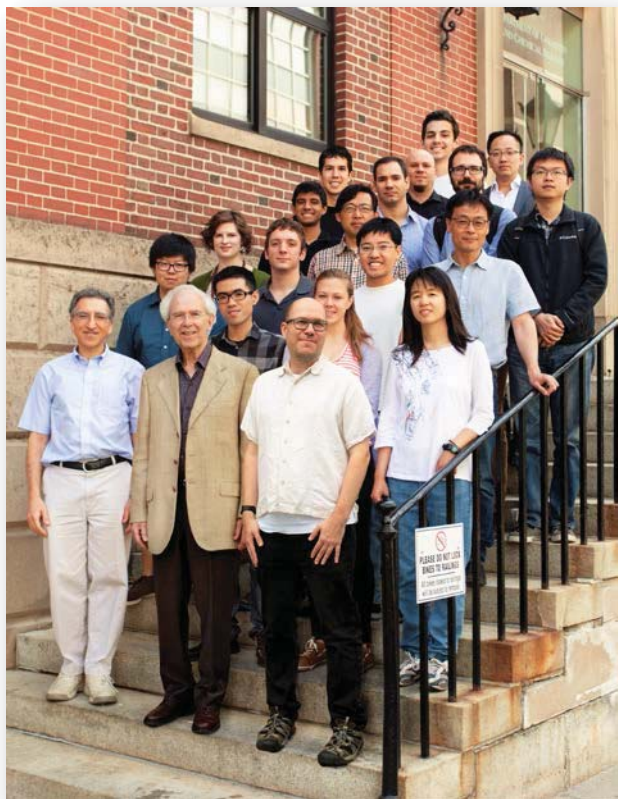
i-iii. Sulfonate followed by hydrolysis iv. Dimerization in  $\text{AlCl}_3:\text{NaCl}$  molten salt



# Conclusion and Acknowledgement

## Conclusion

- Quinone molecules can be utilized in both acidic and alkaline flow batteries
- Non-toxic and low corrosive electrolyte
- High cell voltage and peak power density
- High current and energy efficiency and small capacity loss
- Low membrane crossover rate
- High chemical and electrochemical stability
- Explore new hydroxylated anthraquinones to achieve higher cell performance



## Acknowledgement

- I want to specially thank Prof. Michael Aziz, Prof. Roy Gordon and Prof. Alan Aspuru-Guzik (1st row from left to right respectively) for their inspiration and guidance to move this project forward and Dr. Qing Chen (2<sup>nd</sup> row next to me) for helping with electrochemical analysis and cell cycling experiment.
- Finally I want to thank the entire team and financial support from ARPA-E.

