Improve the Kinetics of the Ketone-based Aqueous Organic Redox Flow Batteries

Presentation # 603

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Low-carbon electricity system
With renewable energy

>20% of renewable energy in grid, energy storage system is needed for grid stabilization

Fluctuation of solar and wind resources
Miss match of supply and demand

Modular structure

- fluidic electrolyte
- spatial separation of energy storage and power generation
- individually tuning of energy capacity and power capability
NASA Redox Storage System Development Project

ESS inc. iron flow battery

Nat. Rev. Chem. 2022, 6, 524–543.
Vanadium redox flow battery cost

Benefits of Organic Materials
- lower material cost on large scale
- **tunability** of electrolyte
- multi-electron transfer redox events

50 mA/cm² $615/kWh
240 mA/cm² $350/kWh
400 mA/cm² $290/kWh
Material driven approach: tunability of organic molecule

Parameters of redox-active materials

- Materials cost
- Stability
- Solubility
- Reaction kinetics
- Redox potential

Redox potential / Solubility

Stability

Vanadium species
- Other inorganic species
- Organic species (aqueous)
- Organic species (non-aqueous)
- New redox species

References:

- Material driven approach: tunability of organic molecule
Activate reversibility with molecular engineer

Ketone hydrogenation in water

Activate reversibility with functional groups

comproportionation

disproportionation

coupled chemical electrochemical process

**FL kinetics comparing to other organic systems**

DHPS 75 Ah/L

[Chemical structure of DHPS]

4C7SFL 73 Ah/L

[Chemical structure of 4C7SFL]

(SPr)$_2$V 13.4 Ah/L

[Chemical structure of (SPr)$_2$V]

*Alkaline system* | *Alkaline system* | *neutral system*

*Nat. Energy* 2018, 3 (6), 508-514.

In redox flow battery
For a fixed material, tune kinetics?

Electrode modification with metal/metal oxide electrocatalyst

Additives in electrolyte leading to electrode modification


Nano Lett. 2013, 13, 1330–1335
For fluorenone: mechanism-informed approach

On discharge accelerate the radical anion supply

Chronocoulometry in H-cell potential held at -0.65V vs Hg/HgO

Unpublished result
Battery validation: current response test

Objective:
Battery electrode potential being held at certain potential against selected reference
Check the discharge current
Higher the current, faster the kinetics

Method: Dynamic Hydrogen Reference Electrode

\[ \text{Pt wires with straight (||) or curved (\(\sim\)) shape inserted into the membranes of a RFB} \]
Battery validation: current response test

Objective:
Battery electrode potential being held at certain potential against selected reference
Check the discharge current
Higher the current, faster the kinetics

Method: **Dynamic Hydrogen Reference Electrode**

- **Charge**
  - CC at 20 mA/cm² until 0 V cutoff
  - CP at -50 mV vs DHE until 1 mA/cm²

- **Discharge**
  - CP at -0.55 V vs DHE until 10% DOD

- alkaline condition
- reference electrode potential drift

Unpublished result
Battery validation: current response test

Objective:
Battery electrode potential being held at certain potential against selected reference
Check the discharge current
Higher the current, faster the kinetics

Method: pseudo reference
Battery assembled with large excess catholyte, catholyte solution SOC maintained minimal fluctuation during tests, battery discharge at held voltage against catholyte, similar effect to anode held at fixed potential against reference

Charge
CP at 1.4 V until desired SOC

Discharge
CP at 0.9 V, recording the current response

Unpublished result
first: viscosity influence on flow battery

J. Power Sources 2018, 399, 133-143

Unpublished result
Battery performance

- Net positive effect
- *Kinetic enhancement* outcompete *viscosity negative impact*
- Optimal ratio
**Summary**

**Parameters of redox-active materials**

- **Materials cost**
- **Stability**
- **Solubility**
- **Reaction kinetics**
- **Redox potential**

**Vanadium species**
- Other inorganic species
- Organic species (aqueous)
- Organic species (non-aqueous)
- New redox species


- **molecular engineer**
  - **activate** traditionally considered redox-inactive material
  - coupled chemical reaction electrochemical process
  - taking advantage of highly stable organic molecule core

- **electrolyte design**
  - higher battery power capability
  - One-step closer to practical application

- **Ground-breaking approach for kinetic enhancement**
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