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High-performance Aqueous Redox Flow Battery (ARFB)

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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.

Grid demand

Wind power

Solar power

Mismatch between peak electricity supply and demand

Time (hour)

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).

Adapted from Dunn, B. et al., *Science* 334, 928 (2011)
Aqueous Redox Flow Battery

Schematic of a redox flow battery during **Charging**:

1. **VO₂⁺ + 2H⁺ + e⁻ → VO²⁺ + H₂O**
2. **Cr³⁺ + e⁻ → Cr²⁺**
3. **AQDS + 2e⁻ → AQDSH₂**

**Negative Electrolyte**

**Positive Electrolyte**

1. **V²⁺ → V³⁺ + e⁻**
2. **Fe²⁺ → Fe³⁺ + e⁻**
3. **2HBr → Br₂ + 2e⁻**

9,10-anthraquinone-2,7-disulfonic acid (AQDS)
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.
2,6-dihydroxyanthraquinone (2,6-DHAQ) - Synthesized from cheap commodity chemical - $E_{eq} = -680$ mV vs. SHE (in alkaline solution) - 2,6-DHAQ potassium salt solubility in 1 M KOH 0.6 M at r.t. and > 1 M at 40 ºC - First used in Zinc/ferricyanide hybrid flow battery in 1985 - Food additive, anti-caking agent - Soluble and stable in alkaline solution - $E_{eq} = 500$ mV vs. SHE (in alkaline solution); independent of pH

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 ºC both in 1 M KOH
Negative: 0.5 M K⁺ salt of 2,6-DHAQ and 1 M K⁺ salt of 2,6-DHAQ at 45 ºC both in 1 M KOH
Cell Performance – Power Density

Cell Configuration:
- Graphite plates with \textit{serpentine} flow pattern
- Pretreated SGL \textit{porous carbon} electrodes
- Pretreated \textit{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\textsuperscript+ salt of 2,6-DHAQ and 1 M K\textsuperscript+ salt of 2,6-DHAQ at 45 °C both in 1 M KOH

![Graph showing cell voltage and power density at 20 °C and 45 °C](image)
- Average current and energy efficiency over 100 cycles is > 99% and 84% respectively.

- Cell showed ~ 0.1% $\Rightarrow$ 0.067% capacity loss per cycle; this is mainly due to electrolyte leakage.
- 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

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

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


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

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

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