Multi-phase electrolytes for redox flow batteries

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MINISTRY OF EDUCATION, YOUTH AND SPORTS

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Introduction

Organic Electrolytes:

- Domestically producible
- Highly tunable
- **Low solubility in aqueous environment ➡ MICROEMULSIONS**

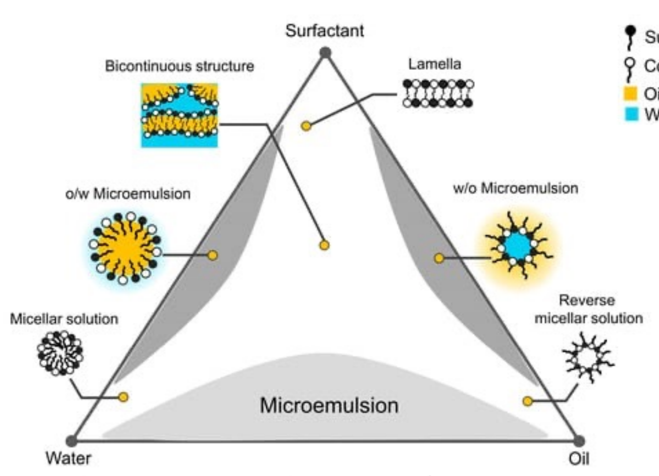

Fig. 1. Ternary diagram of structures In microemulsion solutions [1]

- Great solvent
- Non viscous
- Conductive
- Non-flammable
- Spontaneously formin

Table 1. Composition of used microemulsion

	Aqueous	Oil	Surfactant	Co-surfactant
substance	Water	Toluene	SDS	Butanol
wt.%	40	31	9,7	19,3

Aim

- Identify suitable redox active species based on primary screening experiments such as solubility tests and cyclic/linear sweep voltammetry
- Carry out stability tests of identified species in charge-discharge cycling tests

Disk Electrode experiments

RDE analysis of redox active species at glassy carbon to validate usability in RFBs

- reaction reversibility, kinetic constant, diffusivity, concentration analysis
- Promising candidates to be used in cycling tests

Solvent Impact

- MEs offer wider electrochemical window hindering H_2 evolution
- No evident impact on reaction reversibility ➡ MEs viable for RFB use
- **Increased dissolution of O_2** in MEs oil phase
  - Remove How? N_2 purge, sonication

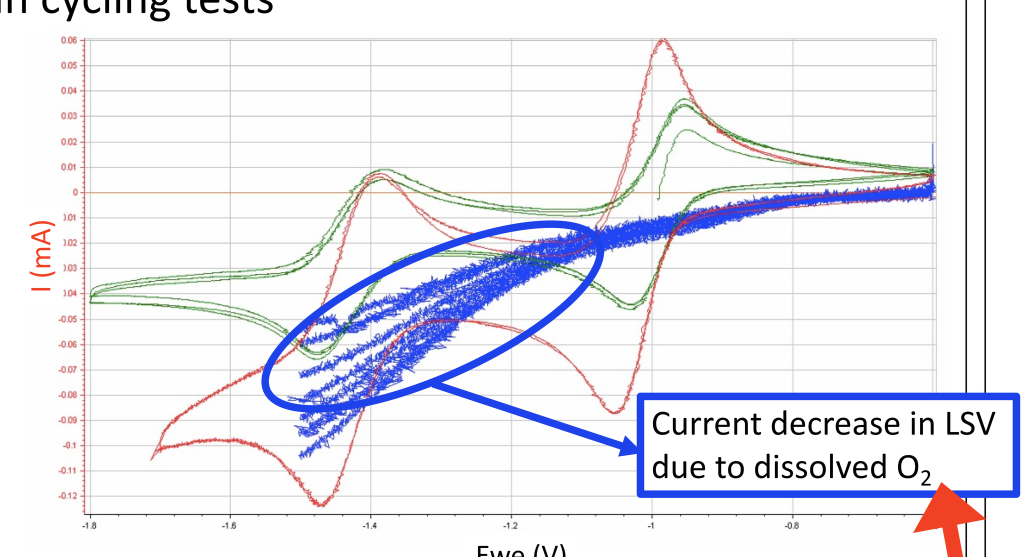

Fig. 2. Cyclic voltammogram of 10 mM *sulpho-propyl viologen* in 1M NaCl (red), ME (green) and linear sweep voltammogram of *blank ME* (blue), glassy carbon. 10 mV/s 20 °C, N_2 purged, mercury sulphate reference

Redox active species identification

- From non-aqueous literature
- First sieve solubility in toluene
  Negolyte: *1,4-p-napthoquinone*
  - Toluene solubility *0.54* mol/l
  - *1.08* mol/l of electrons
- **Posilyte**: *ferrocene*
  - Toluene solubility *0.87* mol/l
  - *0.87* mol/l of electrons

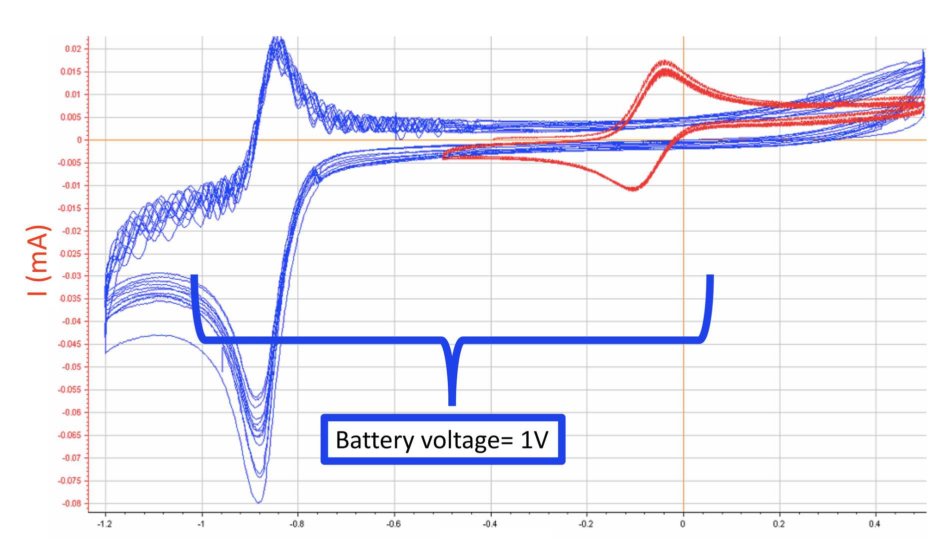

Fig. 3. CV of 1mM *1,4-p-napthoquinone* (blue) and 1 mM *ferrocene* (red) at glassy carbon, 10 mV/s, 20 °C, N_2 purged, mercury sulphate reference

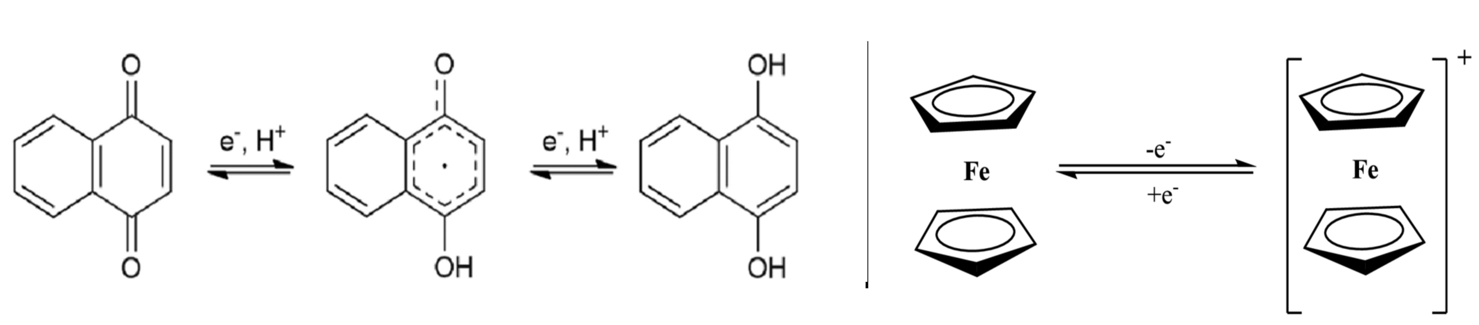

Fig. 4. redox reactions of *1,4-p-napthoquinone* and *ferrocene*

Cycling tests

- Mid-term low concentration stability cycling tests of *1,4-p-napthoquinone* (-) and *ferrocene* (+) in a laboratory single cell

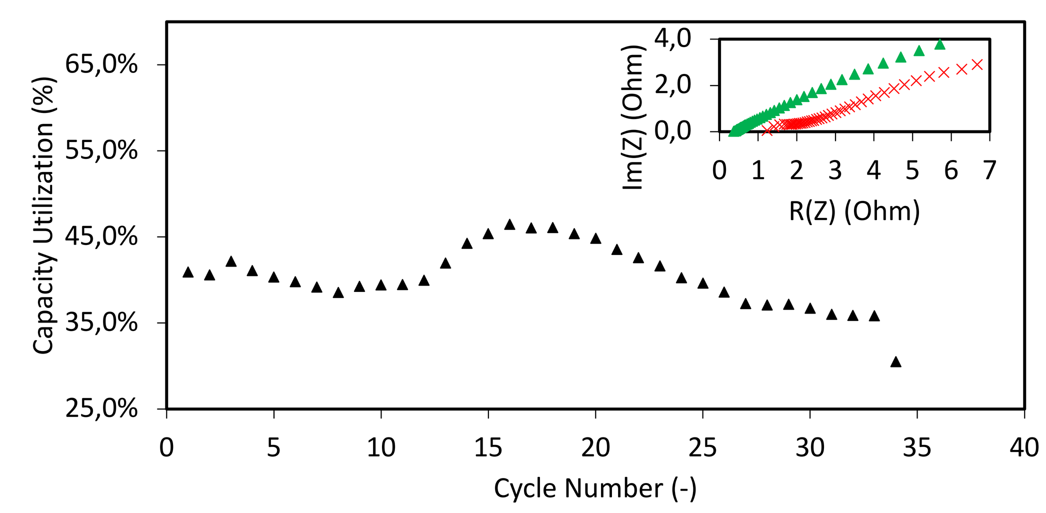

Fig. 5. Charge discharge cycling test of 25mM *1,4-p-naphtoquinone* and 50mM *ferrocene* in ME, CC *100* mA/cm², half-cll voltage controlled, catex F930rfd, graphite felt electrodes. Inset: Nyquist spectra before (green) and after the cycling load (red)

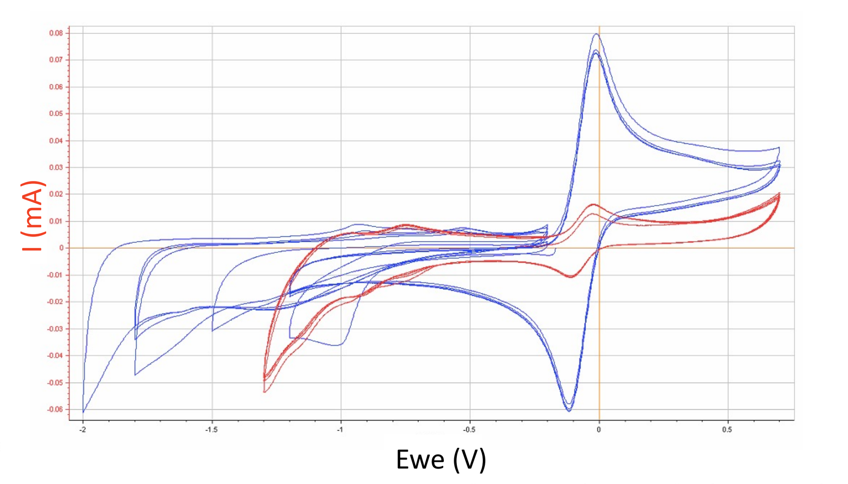

Fig. 6. Post-mortem CV after cycling of the anolyte (red) and *catholyte* (blue) diluted to *100* ml, at glassy carbon, 10 mV/s, 20 °C, N_2 purged, mercury sulphate reference

Problem:

Low capacity utilization

- **No *1,4-naphtoquinone* during post-mortem RDE**
- *CU(max)=46%*
- *CU(end)=35%*

Ohmic resistence Increase

- *rOhm(start)=1.48* ohm·cm²
- *rOhm(end)=4.92* ohm·cm²

Electrolyte evaporation

- *-50* % volumetric loss in both electrolytes

Solution

- Change controlling side
- **Use AQDS in 1M NaCl as anolyte**
- Operate in glove box to avoid oxygen discharge

- Change catex membrane
- Use an anex membrane
  - *rOhm=120* ohm·cm²
- Use $Na4[Fe(CN)_6]$ as catholyte: ***ferrocene* membrane fouling**

- Use all-teflon tubing
- Go from peristaltic to diaphragm pumps
  - **Still observing *20* % decrease after 24 hrs**

Oxygen is 37 times more soluble in toluene than in water at ambient conditions!

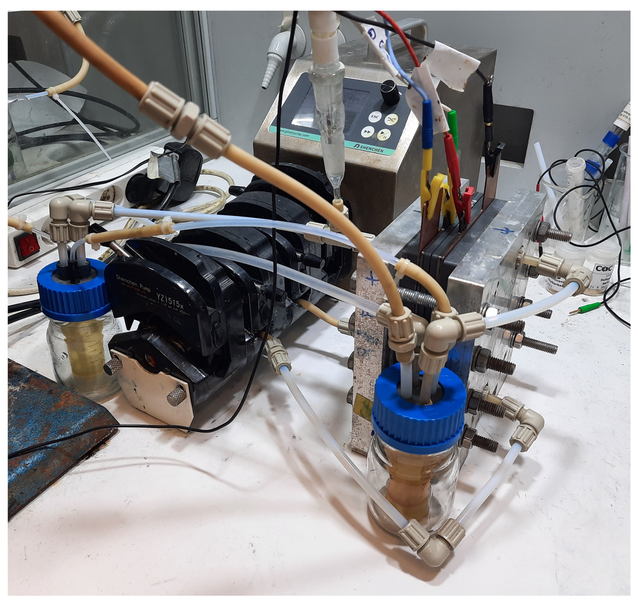

Fig. 7. Laboratory single cell testing set-up

Microemulsion (in)compatibility

- Toluene incompatible with number of typically used components

Membrane fouling physically fragile + resistence increase

Tubing degradation and evaporation through

Classic polymer distribution frames unusable, opt for teflon

Conclusion

- *1,4-naphtoquinone* unstable and undergoes degredation when submitted to charge-discharge cycling
- *Ferrocene* causes increase in the ohmic resistance up to an extent of *1000%* and permeates through catex membrane
- Anex membranes unusable due to ohmic resistance
- O_2 dissolved in MEs causes self discharge and strongly complicates low concentration tests both in the cell and at the RDE
- Experimental aperture optimization to withstand toluene environment

References

1. Leanpolchareanchai, J.; Teeranachaideekul, V., Topical Microemulsions: Skin Irritation Potential and Anti-Inflammatory Effects of Herbal Substances. *Pharmaceuticals* **2023**, 16 (7), 999.

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