Exploring iron multivalency for symmetric aqueous redox flow batteries

João Guilherme Machado de Carvalho,*[a] Ting-Yi Chen[a]
[a]Litricity GmbH, Schulstrasse 56, Germany. E-mail: joao.decarvalho@litricity.de

Introduction.

Symmetric redox flow batteries employ the same redox-active species in both reservoirs, intrinsically mitigating cross-contamination, pH and osmotic imbalances. However, this concept requires a species that can access at least three stable oxidation states within the aqueous electrochemical window.

Fe-clathrochelate & electrochemistry

Cyclic voltammetry of a water-soluble iron(IV) clathrochelate complex reveals two accessible and reversible one-electron redox processes, tentatively assigned to Fe. The ca. 1.0 V separation between both events provides the thermodynamic basis for a symmetric flow battery design.

One iron complex. Both electrolytes.

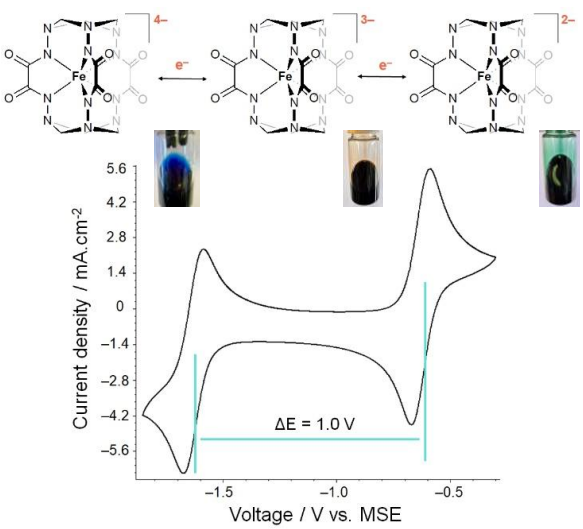

Figure 1. Cyclic voltammogram of 25 mM $[FeL]^{2-}$ (pH 9) at 100 mV·s^{-1} scan rate.

Electrochemical Highlights:

- Two reversible 1e$^-$ processes;
- Both stable over 500+ cycles;
- ΔE = 1.0 V between redox couples;
- Alkaline conditions (pH 9);
- No metal plating;
- Fast electron transfer kinetics.

Symmetric cell design and cycling.

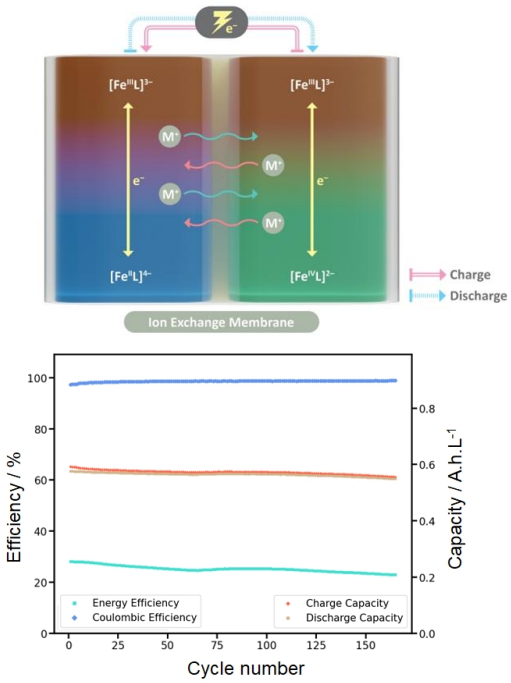

Figure 2. The working principle (top) and performance (bottom) of the all-iron RFB based on $[Fe^{IV}L]^{2-}$. In the discharge process: anodic reaction: Fe(II) → Fe(III), cathodic reaction: Fe(IV) → Fe(III). M^+ represents a cation within Na^+, K^+, NH_4^+, NMe_4^+, NEt_4^+.

Proof-of-concept cell

- Stable cycling for 150+ cycles;
- CE ≈ 99%;
- Low parasitic hydrogen evolution.

Conclusion

Multivalent molecular iron chemistry enabled a symmetric aqueous RFB architecture, combining iron sustainability with crossover tolerance and mild alkaline working conditions.

References

1. G. L. Soloveichik, Chem. Rev., **2015**, 115, 11533–11558.
2. J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager and U. S. Schubert, Angew. Chem., Int. Ed., **2017**, 56, 686–711.
3. S. Tomyn, S. I. Shylin, D. Bykov, V. Ksenofontov, E. Gumienna-Kontecka, V. Bon and I. O. Fritsky, Nat. Commun., **2017**, 8, 14099.