Titanium organometallic complex as a promising redox mediator for producing hydrogen in redox flow batteries

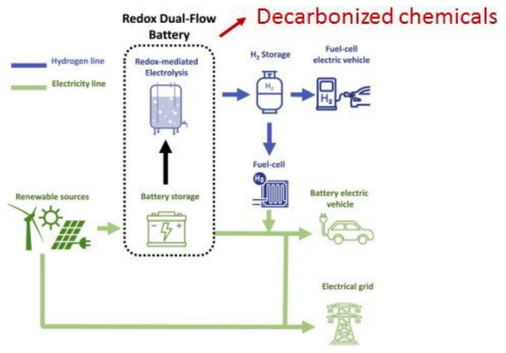
Mikhail Petrov, Albert O.E. Honh, Mohammad Rahimi, Anders Bentien
Department of biological and chemical engineering, Aarhus University, Aarhus, Denmark
mikhail.petrov@bce.au.dk

Introduction

Dual redox flow battery (**DRFB**) combines concepts of energy storage and energy conversion – producing hydrogen and other chemicals [1,2].

This can be achieved by using mediator compounds to be reversibly oxidized/reduced in **RFB** cell and then transferred to a separate reactor to participate in a chemical reaction.

A mediator should demonstrate suitable potentials, long-term stability, and fast kinetics or reactions involved – both heterogeneous and homogeneous.

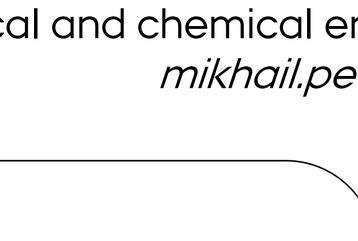


Redox-mediator

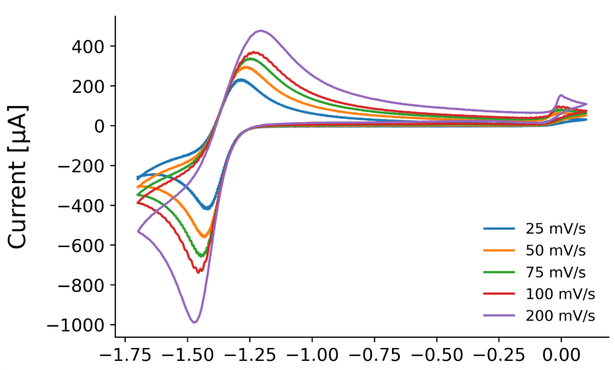
This work focuses on the negative side of where hydrogen evolution reaction (**HER**) occurs, mediated by the Ti complex with an organic chelating agent – **catechol**.

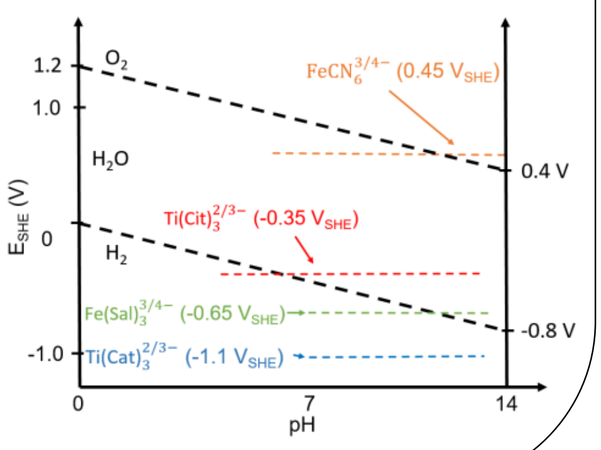
TiCat has a standard potential of 1.1 V vs. SHE allowing the reduced form of the complex to mediate **HER** at alkaline pH.

Cyclic voltammetry (71 mM **TiCat**, pH 10.7, glassy carbon electrode) illustrated the reversibility of ongoing redox reactions.



$$Ti(Cat)_3^{2-} + e^- \leftrightarrow Ti(Cat)_3^{3-}$$





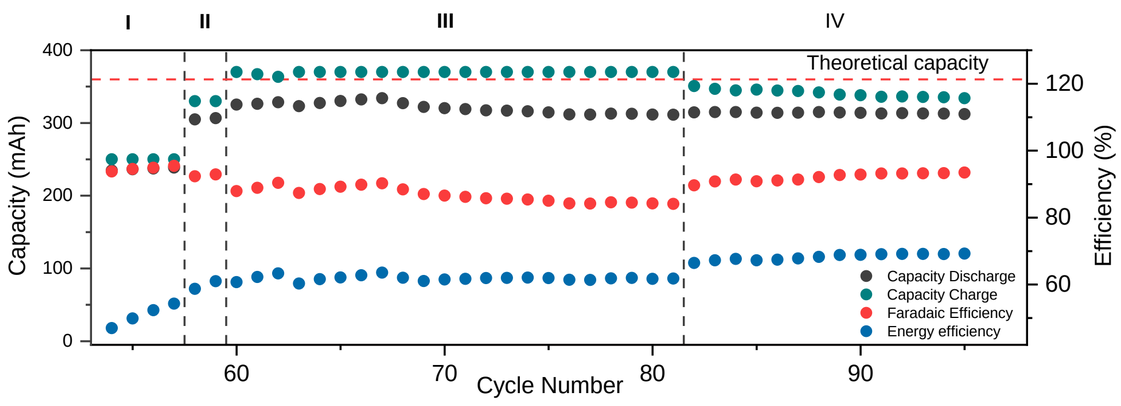
RFB cycling

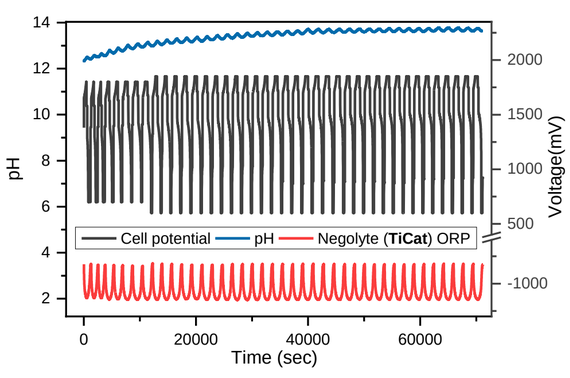
To show the possibility of usage **TiCat** as an electroactive component of aqueous alkaline negolytes, we tested it vs. ferrocyanide $\mathbf{Fe(CN)_6^{4-}}$ acting as a posolyte

By exhibiting faradaic efficiency, energy efficiency and capacity utilization up to 96, 70 and 90 %, respectively tested RFB confirmed the feasibility of using TiCat

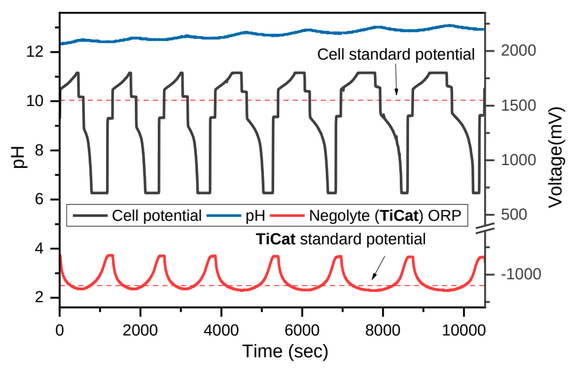
positive half−cell: $Fe(CN)_6^{4-} \leftrightarrow Fe(CN)_6^{3-} + e^-$ $\quad E_0 = 0.51$ V vs SHE

negative half−cell: $Ti(Cat)_3^{2-} + e^- \leftrightarrow Ti(Cat)_3^{3-}$ $\quad E_0 = 1.10$ V vs SHE





Negolyte – 0.28 M **TiCat**
Posolyte – 0.5 M **FeCN**
Cell 25 cm^2 Membrane: Fumasep E610
Electrode: GFD4.6 (activated)



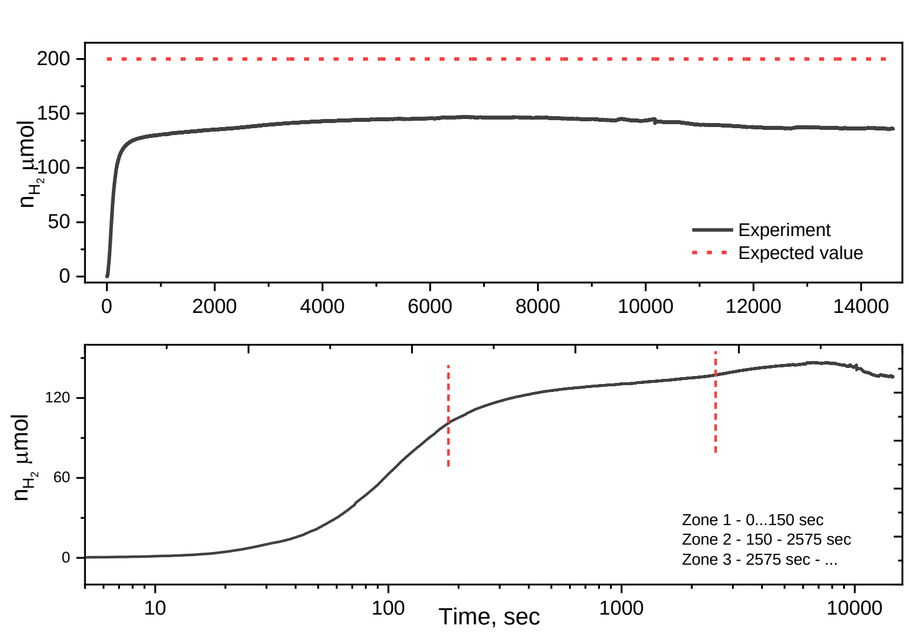
Constant current-constant voltage charge-discharge
Voltage limit: 1850 mV, **Current**: 1.25 A, **Current limit**: 200 mA , **Capacity limit**: 250 mAh (Zone I), 330 mAh (II), 370 mAh (III), No limits (IV)

Batch-mode experiments

Even the RFB experiments evidence the HER proceeding without any catalysts (decrease of pH during the cycling).

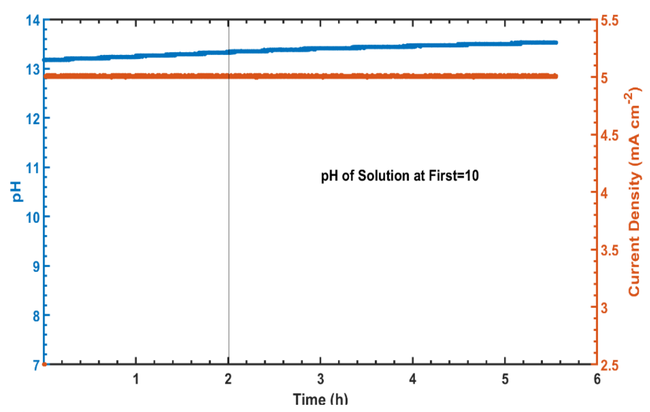
To further test the feasibility of using **TiCat** to provoke **HER** we made a trial experiment. Reduced **TiCat** (formula, 5 mL of 0.28 M solution) was added into a bottle with $\mathbf{H_2SO_4}$ (pH 5) and Ni foam (5 g in total, cut by peace 1*1 cm).

Immediately gas bubbles appeared. Concertation of $\mathbf{H_2}$ was accessed using a pressure sensor amounted at the outlet. Most of the reaction goes within the 100-second interval.



$$Ti(Cat)_3^{3-} + 2H^+ \rightarrow Ti(Cat)_3^{2-} + H_2$$

Flow-mode experiments



We tested a setup with the RFB cell and reactor working simultaneously under constant flow conditions

Posolyte: 0.5M NaOH; **Cathode**: Stainless steel
Negolyte: 0.28M **Ti(Cat)**, aqueous solutions; **Anode**: GFD 4.6 (activated); Ni foam was placed to negolyte tank

Under applying constant current (5 mA cm^{-2}) system reached steady-state conditions: cell voltage, pH, and anode polarization were the same for 6 hours. It means that **Ti(Cat)** reduction reaction that goes inside the discharge cell was balanced by **HER** occurring inside the negolyte tank

positive half−cell: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

negative half−cell: $Ti(Cat)_3^{2-} + e^- \leftrightarrow Ti(Cat)_3^{3-}$

chemical reaction inside the negolyte tank: $Ti(Cat)_3^{3-} + 2H^+ \rightarrow Ti(Cat)_3^{2-}$

Conclusions, Acknowledgments, References

- Titanium catechol complex **Ti(Cat)** demonstrates a reversible redox behaviour with E_o = 1.1 V vs SHE and can be used as an electroactive compound of RFB negolyte.
- **Ti(Cat)-FeCN** RFB demonstrated the following key characteristics: energy efficiency of up to 70 %, coulombic efficiency – of up to 96 %, and capacity utilization of up to 90 %.
- Experiments carried out both in batch and flow regimes showed that Ti(Cat) can act as a redox mediator for HER in the presence of **Ni foam** playing the role of a catalyst

The research was carried out as part of the program **HORIZON**-EIC-2021-PATHFINDERCHALLENGES-01

[1] Gentil, S., Reynard, D., & Girault, H. H. (**2020**). Aqueous organic and redox-mediated redox flow batteries: A review. *Current Opinion in Electrochemistry*, *21*, 7-13.
[2] Piwek, J., Dennison, C., Frackowiak, E., Girault, H., & Battistel, A. (**2019**). Vanadium-oxygen cell for positive electrolyte discharge in dual-circuit vanadium redox flow battery. *Journal of Power Sources*, *439*, 227075.