



**Half day GDR dedicated to
Aqueous organic redox flow batteries**

1st July 2021

Program

14h00-15h00: Recent Progress in Anthraquinone-Based Flow Batteries,
Michael J. Aziz

15h00-15h15: Quantitative thermodynamics of solubilization of pH-sensitive, redox-flow battery relevant anthraquinones, *Théophile Gaudin*

15h15-15h30: The role of thermodynamics in cell-scale modelling of aqueous organic flow batteries, *Gaël Mourouga*

Break

15h45-16h00: A new dihydroxylated anthraquinone as negolyte for AORFB,
Solène Guihéneuf

16h00-16h15: Study of aqueous organic electrolytes on microelectrodes, *Ranine El Hage*

16h15-16h30: Addition of weak acids in electrolytes as a strategy to prevent osmosis in AORFBs, *Jean-Marie Fontmorin*

16h30-17h30: GDR discussion

Recent Progress in Anthraquinone-Based Flow Batteries

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The ability to store large amounts of electrical energy is of increasing importance with the growing fraction of electricity generation from intermittent renewable sources such as wind and solar. We have developed an approach to electricity storage in flow batteries using the aqueous redox chemistry of small, potentially inexpensive organic molecules exemplified by the anthraquinone family. The primary challenges of making such chemistries suitable for practical deployment are cell-level performance, molecular lifetime and mass-production cost. I will report our recent progress in these directions.

Quantitative thermodynamics of solubilization of pH-sensitive, redox-flow battery relevant anthraquinones

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Redox flow batteries (RFBs) are secondary batteries in which the energy conversions are based on the reversible electrochemical reactions of two redox couples¹. RFBs are ideally suited for relatively large stationary applications (capacities of 1 kWh to 10 MWh)², among which is the highly relevant energy storage from intermittent sources such as solar or wind power³. The understanding of dissolution of renewable battery electrolytes, such as those based on anthraquinone skeletons which are generally sparingly soluble in water and have acido-basic activity⁴, is of critical importance. Indeed, in order for battery electrolytes to be operated properly, a high solubility of both their oxidized and reduced forms should be guaranteed in their entire operation. In addition, the achievable cell potentials should be maximized in order to optimize the energy density of the RFB, and this is usually done by tuning the pH, leading to potential precipitation of the electrolyte with the counter-ion of the involved base, acid and/or buffer.

The impact of pH on the solubility is relevant in a variety of areas. For example, it has been studied in the pharmaceutical industry, where, it has been found relevant for the preparation or administration of pH-sensitive drugs⁵. In addition, it is exploited to selectively precipitate inorganic anions such as Zn²⁺ or Cd²⁺⁶. However, in the first case, generally, the solubility of ion forms is neglected as it is assumed much greater than that of the neutral form, and in the second case, the solubility of the neutral form is not considered as its presence is negligible and only a few different ion dissociation equilibria are compared. Yet, as RFB electrolytes may be sparingly soluble in both neutral and salt forms, both solubility of neutral forms and solubility products of ionic forms are important to consider. To the best of our knowledge, no research has been focused on analyzing all above equilibria simultaneously, notably in the context of RFB electrolytes.

In this contribution, we interpret solubility-pH diagrams in terms of acid-base and dissolution phenomena, using a novel self-consistent algorithm. A surprising diversity of behaviors originates from moderate changes in the pKa, pKs and solubilities. In addition, the precipitate that is formed upon addition of appropriate equivalents of a strong acid or base may not be the one suggested by chemical intuition. We propose rules of thumb to anticipate solubility issues in redox-flow batteries as a function of the thermodynamic understanding provided by our self-consistent algorithm. From a purely predictive standpoint, nowadays, some methods exist to estimate pKa and solubility of neutral compounds. However, the ab-initio prediction of solubility products is still slightly out of reach in present time due to the difficulty of predicting the packing of organic salts into the solid phase. Nevertheless, our self-consistent algorithm

paves the way to quantitatively predict solubility-pH curves for any molecule of interest, fully ab-initio, as soon as the solubility product becomes predictable.

This work was financially supported by the Agence Nationale de Recherche (Grant number: ANR-19-CE05-0012), and has been partially funded by the CNRS Energy unit (Cellule Energie) through the project PEPS-Catether.

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- (2) Service, R. F., Advances in flow batteries promise cheap backup power. *Science* **2018**, 362 (6414), 508.
- (3) Wang, W.; Sprenkle, V., Redox flow batteries go organic. *Nature Chem.* **2016**, 8 (3), 204-206.
- (4) Huskinson, B.; Marshak, M. P.; Suh, C.; Er, S.; Gerhardt, M. R.; Galvin, C. J.; Chen, X.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J., A metal-free organic-inorganic aqueous flow battery. *Nature* **2014**, 505 (7482), 195-198.
- (5) Avdeef, A., Solubility of sparingly-soluble ionizable drugs. *Advanced Drug Delivery Reviews* **2007**, 59 (7), 568-590.
- (6) Burgot, J. L., Solubility and pH. In *Ionic Equilibria in Analytical Chemistry*, Springer: New York City, 2012; pp 633-658.

The role of thermodynamics in cell-scale modelling of aqueous organic flow batteries

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Cell-scale modelling of aqueous flow batteries focuses on predicting current/voltage relationships of the battery as a function of many parameters, including: State-of-Charge, number of cycles, temperature, flow rate, etc...

Physics-based models (as opposed to empirical equivalent circuit models) make use of equations (e.g. Nernst, Fick) classically used within the dilute solution hypothesis which neglects interactions between species that are mixing. While this hypothesis is acceptable in the context of cyclic voltammetry or rotating disk electrodes experiments, where typical concentrations are in the millimolar range, it becomes somewhat debatable in flow batteries, where typical concentrations are in the molar range.

This communication will focus on introducing a concentrated solution framework to take in account non-idealities of mixing (e.g activity coefficients, enthalpy of mixing) and discuss their impact on cell-scale modelling in aqueous organic redox-flow batteries.

This framework is currently being applied to the aqueous organic TEMPTMA / Methyl Viologen system in collaboration with the German start-up JenaBatteries GmbH.

A new dihydroxylated anthraquinone as negolyte for AORFB

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Among current negolytes described for AORFBs, functionalized anthraquinones seem to be very promising as their properties match the application in term of solubility and potential (1). Previous reported results showed that hydroxyl groups allow more negative potentials and, depending on the substituted position, can favor solubilization in alkaline aqueous media (2). Several commercially available dihydroxyanthraquinones (DHAQs) have been used as negolyte as the 1,8-DHAQ which solubility was improved by adding choline hydroxide as a hydrotropic agent (3). 2,6-DHAQ was first reported by Aziz and coworkers in alkaline medium with potassium ferrocyanide as a posolyte (4) and more studies followed focusing on its stability under cycling conditions (5).

We prepared the 2,3-DHAQ, also known as hystazarin, and evaluated its performances in a redox flow battery. This compound exhibited a good solubility in alkaline aqueous solutions (0.7 M in aqueous KOH at pH above 13.5) and a suitable potential (-0.87 V in aqueous KOH vs Ag/AgCl) leading to a 1.13 V theoretical open-circuit cell voltage at 50% SOC with potassium ferrocyanide as posolyte. We experimented this compounds in a 25cm² cell for 180 cycles and obtained a capacity fading of 0.022% per cycle, a CE higher than 99.8% and the initial energy density was 17 Wh.L⁻¹ (7.7Wh.L⁻¹ when both posolyte and negolyte volumes are considered). This molecule exhibited a good chemical stability compare to other DHAQ (2,6-DHAQ -0.1%/cycle; AQ18OH -0.12%/cycle) (6). We were also able to perform more than 3000 cycles and after analysis, 2,3-DHAQ was the main product observed.

- (1) Chai *et al.* *ACS Symposium Series* **2020**, 1364, 1; Li *et al.* *Advanced Materials* **2020**, 32 (47), 2002132.
- (2) Wedege *et al.* *Scientific Reports* **2016**, 6, 39101; Ding *et al.* *Chem Soc Rev* **2018**, 47, 69.
- (3) Cao *et al.* *Journal of Power Sources* **2018**, 386, 40.
- (4) Lin *et al.* *Science* **2015**, 349 (6255), 1529.
- (5) Goulet *et al.* *Journal of the Electrochemical Society* **2018**, 165 (7), A1466; Goulet *et al.* *Journal of the American Chemical Society* **2019**, 141, 8014.
- (6) Kwabi *et al.* *Chemical Reviews* **2020**, 120 (14), 6467.

Study of aqueous organic electrolytes on microelectrodes

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Keywords: organic aqueous electrolyte, ferrocyanide, TEMPO, microelectrodes, redox flow batteries

The redox systems that are growing in interest for redox flow battery applications are the ones that have fast kinetics such as Ferrocyanide and TEMPO derivatives as posolyte, allowing to reduce the problems related to the reactivity of the active species and their affinity to the graphite felt used as working electrode.

Fundamental kinetics studies of these systems are of great importance for the determination of kinetic constants and for a better understanding of the overall electrochemical behavior. In fact, it allows to show possible improvements in the reaction kinetics and performances, when the electrode properties (activation, deterioration, *etc.*) or the bipolar plate constituents and geometry are modified. Therefore, a first approach for this study is using graphite felt electrodes, in diluted (10^{-4} M) Ferrocyanide and TEMPO solutions, performing cyclic voltammetry and impedance spectroscopy. However, due to the porous texture of the felt and its high specific surface, the obtained results do not allow a clear distinction between an activated and a non-activated felt as well as an accurate determination of the corresponding kinetic constants.

Hence, another system is introduced, allowing to shift from the macro to the micro scale: microelectrodes prepared from fibers extracted from the corresponding graphite porous felt [1-2]. These microelectrodes allow the qualitative study of solutions at higher concentrations (up to 0.5 M in $K_4[Fe(CN)_6]$) and a quantitative analysis through EIS for solutions at 10^{-2} M with the determination of kinetic constants on activated and non-activated single fibers.

[1] L. Landon-Lane, A. T. Marshall, D. A. Harrington, EIS at carbon fiber cylindrical microelectrodes, *Electrochemistry Communications*, 109 (2019) 106566

[2] L. Landon-Lane, A. J. Downard, A. T. Marshall, Single fibre electrode measurements – A versatile strategy for assessing the non-uniform kinetics at carbon felt electrodes, *Electrochimica Acta*, 354 (2020) 136709

Addition of weak acids in electrolytes as a strategy to prevent osmosis in AORFBs

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Ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}$ is widely used as a positive active material in neutral and alkaline Aqueous Organic Redox Flow Batteries (AORFBs) (Páez et al., 2020). In addition to being a food additive that is non-toxic to human body, it offers excellent redox reactivity and fast electron transfer kinetics (Lee et al., 2020). However the utilisation of $[\text{Fe}(\text{CN})_6]^{4-}$ in AORFB electrolytes inevitably implies the addition of four molar equivalents of a counter-ion, usually K^+ or Na^+ (*i.e.* $\text{K}_4[\text{Fe}(\text{CN})_6]$ or $\text{Na}_4[\text{Fe}(\text{CN})_6]$). In addition, $[\text{Fe}(\text{CN})_6]^{4-}$ is involved in a one-electron process while the redox reaction involving most negative active materials such as anthraquinones implies two electrons, thus requiring two equivalents of $[\text{Fe}(\text{CN})_6]^{4-}$ in a battery. Therefore, the corresponding posolyte usually results in a much higher ionic strength compared to that of the negolyte, thermodynamically leading to severe water transfers between both tanks. Although the utilisation of positive and negative electrolytes with dissymmetric volumes and concentrations can limit osmosis, this bottleneck specifically associated with the utilisation of $[\text{Fe}(\text{CN})_6]^{4-}$ remains overlooked. In this work, we propose a simple strategy based on the addition of weak acids such as aspartic acid ($\text{C}_4\text{H}_7\text{NO}_4$) in the negolyte to prevent osmosis in AORFBs. The addition of acid aspartic as well as strong bases such as KOH, NaOH or LiOH to reach the complete deprotonation of the acid and the desired pH contributes to balancing the cations total concentration of both compartments. Battery cycling experiments were carried out with negolyte and posolyte composed of 0.2 – 0.3 M anthraquinone-2,7-disulfonic acid disodium salt (AQDS) and 0.4 – 0.6 M $[\text{Fe}(\text{CN})_6]^{4-}$ as active materials, respectively. When no weak acid was used, osmosis quickly leading to a shortage of negative electrolyte was observed, while in presence of aspartic acid both electrolyte volumes remained unchanged during the time of experiment. This simple yet effective strategy is promising to develop AORFBs with symmetric electrolyte tanks at higher scale.

Lee, W., Park, G., Kwon, Y., 2020. Alkaline aqueous organic redox flow batteries of high energy and power densities using mixed naphthoquinone derivatives. *Chem. Eng. J.* 386, 123985. <https://doi.org/10.1016/j.cej.2019.123985>

Páez, T., Martínez-Cuezva, A., Palma, J., Ventosa, E., 2020. Revisiting the cycling stability of ferrocyanide in alkaline media for redox flow batteries. *J. Power Sources* 471, 228453. <https://doi.org/10.1016/j.jpowsour.2020.228453>