Non-functionalized TEMPO-based Aqueous Catholyte for High Capacity Aqueous Redox Flow Batteries

Paula Navalpotro[1*], Eduardo Pedraza[1], Carlos de la Cruz[1], Andreas Mavrandonakis[1], Edgar Ventosa[2], Rubén Rubio-Presa[2], Roberto Sanz[2], S.T. Shentilkumar[1], Rebeca Marcilla[1*]

1 Electrochemical Processes Unit, IMDEA Energy
2 Department of Chemistry, University of Burgos, Burgos, Spain.
Avda. Ramón de La Sagra, 3, 28935 Móstoles, Spain
paula.navalpotro@imdea.org; rebeca.marcilla@imdea.org

The implementation of renewable energies (solar, wind, etc) is driven the development of new energy storage systems that can mitigate their inherent intermittency solving the mismatch between the energy demand and production. Specifically, Redox Flow Batteries (RFB) are an unique type of battery able to decouple energy and power densities making them promising candidates for large-scale energy storage applications. In the last years, Aqueous Organic Redox Flow Batteries (AORFB) containing organic molecules that replace the problematic vanadium redox compounds, have triggered the interest in this technology. Significant synthetic efforts have been made on the functionalization of organic molecules (eg, TEMPO, phenazynes, quinones, etc) to get higher solubility and suitable electrochemical performance. TEMPO- derivatives (nitroxyl radicals) constitute one of the most widely investigated catholytes for pH-neutral AORFB.[1-3] Unfortunately, despite the robust and highly reversible redox activity of pristine TEMPO their application in aqueous RFBs has been hindered to date due to the low solubility of the non-functionalized TEMPO in water (≈70 mM). In this talk, we present a simple approach to solubilize non-functionalized and commercially available TEMPO in aqueous solution reaching an unprecedented solubility (up to 5.6 M in presence of supporting electrolyte). Our approach, corroborated by computations chemistry, consists on modifying the properties of the electrolyte to promote intimate interaction between the anion of the supporting electrolyte and pristine TEMPO. TEMPO-based catholytes were tested showing an excellent electrochemical performance with fast kinetics (k^0 = 0.018 cm/s) and impressive long-term stability in symmetric flow cell configuration (0.552%/day). This new TEMPO catholyte was paired with a sulfonated viologen anolyte resulting in a AORFB with an open-circuit voltage of 1.08 V, and demonstrating a robust performance with low capacity fading over cycling (0.60%/day and 0.048%/cycle)[4].

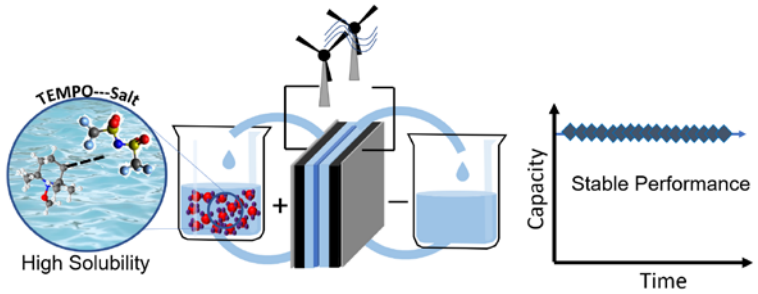

Figure 1. Schematic representation of a high capacity aqueous redox flow battery with proposed TEMPO catholyte

References

[1] W. Wang et al , *Adv. Energy Mater.* **2016**, *6*, 1501449

[2] T. Janoschka, N. Martin, M. D. Hager, U. S. Schubert, *Angew. Chemie - Int. Ed.* **2016**, *55*, 14427

[3] Y. Liu, et al, *Chem* **2019**, *5*, 1861.

[4] R. Marcilla et al, *Submitted to Advanced Energy Materials*, 2023