

Nanoelectrochemistry as a Tool to Interrogate Solid/Liquid Interface Reactions in Mediated Flow Batteries

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Redox flow batteries (RFBs) are promising stationary energy storage technologies due to their high flexibility in their scalability, which allows the flexible design of power and energy densities independently. However, the advantageous scalability is counterbalanced by the limitation of increasing the energy density. This factor is more pronounced in the aqueous RFB system with the water electrolysis voltage limitation and low redox species solubility. Hence, solid materials were proposed in the flow cell system as a strategy to increase the energy density of the rechargeable battery.^[1,2] Instead of the soluble species being the primary energy storage system, they mediate the energy carrying from the high energy density solid material to the current collector. Recently, this powerful strategy was combined with the possibility of storing the solid material in an external compartment to the redox-mediated flow battery^[1,3,4]. Finding candidates of SB and soluble redox species is based on thermodynamics parameters, such as the reversibility and spontaneity of charge transfer reaction occurring between them. The study of the system gains complexity with the reaction reversibility (kinetics) dependence on the state of charge (SOC). As pointed out before, the evaluation of the reaction between SB and soluble species by common techniques is hard, in the example, the use of cyclic voltammograms concluded as a non-reversible system due to the limitations on mass transport and low kinetics.^[4] Here we demonstrate

the use of nano-electrochemistry as a methodology to evaluate the spontaneous reaction between the SB and the soluble RM. Due to an effective mass transfer of the soluble species, the use of a nanoelectrode enabled us to interrogate the rate of the spontaneous reaction, avoiding the diffusion limitation. Therefore, as a proof-of-concept, Prussian-blue (FeIII/II) complex was employed as a precursor SB and confined in a recessed carbon nanoelectrode (CNE), while I₃/I⁻ reversible redox species was employed as dissolved specie. The conversion rate of the soluble redox species on the active SB (A-SB) was evaluated by following the period of achieving the equilibrium open circuit potential (OCP) at different soluble redox species concentrations. The OCP values were correlated to the SOC, and the period to reach the equilibrium was used to estimate the rate of reaction. We showed a methodology based on nano-electrochemistry to deconvolute the complexity in accessing the kinetics between the solid and soluble materials, which will shed light on better finding alternative chemistries for redox flow batteries.

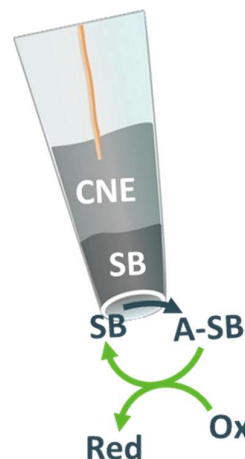


Figure 1. Schematic image of the carbon nanoelectrode tip and the feedback reaction between the solid booster (SB) and the soluble redox mediator (Ox-Red).

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