Computer-aided Materials Characterisation of the Solid Boosters for the Redox Flow Batteries

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Redox flow batteries (RFBs) are a promising alternative for stationary energy storage and present advantages such as high safety, stability, flexibility, and scalability. However, the low energy density limited by the solubility of the redox active species, hinders RFBs from gaining ground in the market of stationary energy storage. An emerging concept for improving the energy storage capacity of RFBs is the use of Solid Booster (SB), i.e. redox solid storage material in the tanks [1].

While the thermodynamics of RFBs with SB have been comprehensively detailed in regards with their techno-economic design, little efforts have been devoted to the storage rate or kinetics of such systems for now. Although the cell kinetics is very similar to that of conventional RFBs, one should also consider the charge transfer kinetics between the solid and the electrolyte in the tank, which remains challenging to probe experimentally due to the intricate nature of the reaction involving biphasic and interfacial chemistry and mass transfer. That creates a necessity for the development of the electrochemical characterisation methods combined with the theoretical description and numerical simulation of the behaviour of this type of materials.

This work focuses on the mathematical model of the Scanning Electrochemical Microscopy (SECM), used for the characterisation of the SB materials. The 2D-axisimetrical model is developed and implemented in COMSOL Multiphysics software [2], in order to describe the system, where the microelectrode is placed over a particle of the hexacyanoferrate SB material deposited on indium tin oxide substrate immersed in the KNO_3 solution containing TEMPTMA (N,N,N-2,2,6,6-heptamethyl piperidinyl oxy-4-ammonium chloride) redox species.

The computer-aided SECM is combined with optical microscopy [3], in order to investigate the charging/discharging of a single redox solid particle by a liquid phase redox mediator. The tip of the SECM is used to trigger locally the electrochemical charge/discharge of a single SB particle, while, it is imaged by optical microscopy. Such techniques have proved to be efficient to image operando the dynamics of ion transport within individual battery particles [4]. A methodology is described to estimate local conversion rates of the particle during oxidation/reduction cycles along with the local amount of charge stored within the particle. The combination of experimental methods with Multiphysics modelling shows that the conversion rate, and its local distribution, is associated to local porosity of the particle.

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