

Microelectrode-Based Characterization of Concentrated Redox Electrolytes for Charge Storage Applications in Flow Batteries

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Redox flow batteries are of potential importance to both large scale energy storage and powering the electrical vehicle. Among critical challenges are low volumetric energy density of redox electrolytes, high cost and the maintenance limitations that greatly impede the wide application of conventional flow batteries. In this respect, the redox-active charge-storage material has a significant impact on the performance of a flow battery. The concentration of redox centers and their reaction kinetics have an influence on the available current densities and, thus, the power of the device.

Many inorganic and organic electroactive systems have been proposed as alternatives to vanadium species in redox flow batteries. In the study, we explore the concept of highly concentrated solutions of such redox systems as iodine/iodide and poloxometallates of molybdenum and tungsten, and the possibility of optimizing their performance to exhibit high rates of charge propagation. While the iodine/iodide system can be prepared at high concentrations, the polyoxometallates of molybdenum and tungsten can serve as model examples of multi-electron systems for all-liquid redox flow batteries and related fundamental investigations. Reactions in the zinc/iodine (polyiodide) redox flow battery are as follows: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ ($E = -0.76$ V vs SHE) at the negative electrode (anode), and $3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^-$ ($E = 0.54$ V vs SHE) at the positive electrode (cathode) thus yielding a total theoretical potential output as high as ~ 1.3 V. The increase of current density could be achieved not only by reducing the viscosity of the electrolyte, thus accelerating charge-carrier transport, but also – by referencing to our experience with the iodine/iodide couple as charge relay for dye-sensitized solar cells – through improvement of the dynamics of charge propagation in highly concentrated iodine/iodide solution via the catalyzed enhancement of rates of electron self-exchange (hopping) between iodine/iodide (polyiodide) redox species as well as by accelerating the interfacial kinetics at electrodes. This can be realized by choosing appropriate electrode materials and through their activation or modification. The electrochemical activities of the redox couples are usually significantly increased through application of nanostructured functionalized carbons. While dispersed in solutions they can improve electron transfers to the redox sites. The proposed chemistry has been first tested using the microelectrode methodology to determine mass-transport (effectively diffusional) coefficients for charge propagation, heterogeneous and homogeneous (electron self-exchange) rates of electron transfers. Unless catalyzed, both interfacial and bulk (self-exchange) electron transfers involving the iodine/iodide redox system are somewhat complicated; there is a need to break the I-I bond in the I_3^- or I_2 molecule; it has also been well-established that platinum (e.g. when deposited on the counter electrode) induces electron transfers within the iodine/iodide redox system. As far as heteropolyacids are concerned, they exhibit very strong Brønsted acidity, act as proton conductors, and undergo fast, reversible, multi-electron electron transfers leading to the formation of highly conducting, mixed-valence (e.g. tungsten(VI,V) or molybdenum(VI,V) heteropoly blue) compounds. The polyoxometallate-based redox electrolytes have different chemical identities, and they could be considered as anolytes or catholytes, depending on their redox potentials but, typically, their use would require formation of an asymmetric system with different-type redox species.

While dynamics of electrochemical processes has an influence on the systems' current densities, the viscosity of the electrolyte and the mass transport dynamics are also affected by the choice of the redox-active material and its concentration. Trying to develop useful electroanalytical diagnostic criteria, we are going to extend the historical concepts of charge propagation in semi-solid or semi-liquid systems developed for mixed-valence redox polymers and polynuclear materials to the development of redox electrolytes. Fundamental electroanalytical approaches utilizing ultramicrodisk electrodes and interdigitated arrays will be adapted to characterization of redox electrolytes.