

Highly Concentrated Iodine/Iodide Redox Electrolytes for Efficient Charge Propagation and Storage

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There has been also growing interest in the systems capable of fast charge propagation not only with respect to efficient electrochemical charging and discharging of redox flow batteries but also fast charge mediation in solar cells and sensors. The redox flow batteries (RFBs) utilize as energy storage systems the appropriate electroactive species dissolved in externally flowing electrolytes which are ready to accumulate all (or part) of the charge. Among important issues is the search for highly efficient (i.e., capable of fast electron transfers) electroactive systems that would yield high power and energy densities during the systems' operation. Here we concentrate on utilization of highly concentrated iodine/iodide redox systems and on their possibility to exhibit high rates of charge propagation. In practical terms, iodine/iodide can be combined with ZnI_2 , or other zinc salt, containing electrolyte. The iodine/iodide redox system has so far been the most commonly and most successfully used as a charge relay (mediator) in dye sensitized solar cells (DSSCs).

The increase of current density (e.g. in RFBs) could be achieved not only by reducing the viscosity of the electrolyte, thus accelerating charge-carrier transport, but also – by referencing to my 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 redox species as well as by accelerating the interfacial kinetics at electrodes. This can be realized by choosing appropriate electrode materials and through their 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. In the presentation, we are going to explore the respective interfacial (electrocatalytic) phenomena on nanostructured metal oxides (e.g. zirconia), in addition to traces of expensive

platinum or palladium nanoparticles (provided that catalytic centers are three-dimensionally distributed in the electrolyte phase), and we will utilize them to enhance iodine/iodide electron transfers to develop a new generation of redox mediators or ultra-fast components of redox electrolytes. Our results show that the catalyzed iodine/iodide system can reach extremely high electron transfer rates, namely on the level of 10^9 – 10^{10} mol⁻¹ dm³ s⁻¹.

The redox electrolyte plays a very important role in the DSSC performance, and its usefulness largely depends on dynamics of both interfacial electron transfers and bulk charge propagation within the system. For example, the triiodide/iodide redox couple has been considered here together with ionic liquids. Room-temperature ionic liquids (e.g., those with 1,3-dialkylimidazolium cations) exhibit such important features as negligible vapor pressure, high ionic conductivity and thermal stability, fairly wide electrochemical window, and ability to dissolve organic and inorganic solutes. The resulting redox-conducting electrolytes have several advantages: high conductivity, low vapor pressure, high iodide concentration and good electrochemical stability. Among disadvantages is their high viscosity that certainly contributes to the low mass transport coefficient of the triiodide/iodide redox couple, not only if the charge transport mechanism is predominantly physical (at low concentrations) but also when the Grotthus exchange mechanism is operative at high concentrations of the redox system. Using the microelectrode-based and sandwich-type electroanalytical methodologies of solid-state electrochemistry, we address here the charge transport dynamics within the semi-solid triiodide/iodide ionic-liquid electrolyte admixed with noble metal or carbon nanostructures. We will comment on the charge propagation enhancement effects as well as on reasonably high power conversion efficiencies of DSCs utilizing such electrolytes.
