Optimization and Diagnosis of Electrochemical Charging/Discharging Capabilities of Polytungstate-Based Semi-Solid/Semi-Liquid Solutions

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Concentrated solutions of Keggin-type silicotungstic acid, as well as the system's single crystals ($H_4SiW_{12}O_{40}$*$31H_2O$) and their colloidal suspensions have been tested using the microelectrode methodology to determine mass-transport, electron self-exchange and apparent (effective) diffusion-type coefficients for charge propagation and homogeneous (electron self-exchange) rates of electron transfers. Silicotungstic acid facilitates proton conductivity, and undergoes fast, reversible, multi-electron electron transfers leading to the formation of highly conducting, mixed-valence (tungsten(VI,V) heteropoly blue) compounds. To develop useful electroanalytical diagnostic criteria, electroanalytical approaches utilizing microdisk electrodes have been adapted to characterize redox transitions of the system and to determine kinetic parameters. Combination of micoroelectrode-based experiments performed in two distinct diffusional regimes: radial (long-term experiment; e.g., slow scan rate voltammetry or long-pulse chronoamperometry) and linear (short-term experiment; e.g., fast scan rate voltammetry or short-pulse chronocoulometry) permits absolute determination of such parameters as effective concentration of redox centers (C_0) and apparent transport (diffusion) coefficient (D_{app}). The knowledge of these parameters, in particular of [$D_{app}{}^{1/2}C_0$] seems to be of importance to the evaluation of utility of redox electrolytes for charge storage.

While current densities which reflect dynamics of electrochemical processes have an influence on the systems' current densities, the viscosity of the electrolyte and the mass transport dynamics are also affected by the nature of the redox-active material and its concentration. Trying to develop useful electroanalytical diagnostic approaches, we have successfully utilized microelectrode-based probes, as well as the historical concepts of charge propagation in semi-solid or semi-liquid systems developed for mixed-valence polynuclear materials in order to characterize concentrated redox electrolytes. Among important parameters are concentration of redox centers (C_0) and apparent transport (diffusion) coefficient (D_{app}). The knowledge of these parameters and, in particular of [$D_{app}{}^{1/2}C_0$], are crucial when it comes to evaluation of the diffusional-type charge propagation dynamics in the concentrated electrolyte which may reflect both physical mass transport and electron self-exchange (electron-hopping) contributions. Both potential-step (chronocoulometry, chronoamperometry) and cyclic voltammetric experiments utilizing microdisk electrodes have been adapted to characterization (identification of redox transitions and determination of kinetic parameters) of

model inorganic redox electrolytes, namely highly-concentrated solutions or colloidal suspensions of Keggin-type polyoxometallate, silicotungstic acid.
