Ultramicroelectrode Based Approaches to Diagnose Utility of Redox Electrolytes in Flow Batteries

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The proposed redox electrolyte system, concentrated solutions of Keggin type silicotungstic acid ($H_4SiW_{12}O_{40}$), have been tested using the microelectrode methodology to determine mass-transport (effectively diffusional) coefficients for charge propagation and homogeneous (electron self-exchange) rates of electron transfers. Silicotungstic acid acts as proton conductors, 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 ultramicrodisk electrodes have been adapted to characterization of redox electrolytes.

Introduction

Redox flow batteries have been recognized as an important perspective technology for stationary energy storage, including grid-scale energy storage (1) thanks to their high power performance, flexible design, and ease of scaling-up. The flow-based electrochemical energy storage systems utilize the appropriate electroactive species dissolved in externally flowing electrolytes which are ready to accumulate all (or part) of the charge and, unlike traditional batteries, they can separate the energy storage and power generation. The redox electrolytes (that is, the anolyte and catholyte) are typically stored in separate reservoirs and circulated through the system during charging and discharging steps. The actual redox processes, which are responsible for the reversible conversion of chemical energy directly to electricity, occur at surfaces of the oppositely charged electrodes, and they are maintained within the redox electrolyte phases (2-4). The present state of the art is represented by the all-vanadium redox flow batteries, even though they are still relatively expensive (5) and are characterized by a limited volumetric energy density. Many inorganic and organic electroactive systems have been proposed as alternatives (6-11) to vanadium species in redox flow batteries. Ideally, there is a need to develop or identify robust organic, inorganic or hybrid compounds that could function as reversible redox species in a rechargeable battery under flow conditions.

Progress in the area depends on identification, synthesis, modification, characterization, and deep understanding of the operation of novel redox active compounds of potential utility to redox flow rechargeable batteries. As the choice of redox-active charge-storage material has a significant impact on performance of the flow battery, care

must be exercised to develop systems characterized by fast charge propagation (including electron self-exchange and unimpeded counterion displacements) and fast electron-transfers at the interfaces formed with electrode materials (12-18). While the kinetics 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. In this respect, fundamental electroanalytical approaches utilizing ultramicrodisk electrodes and/or interdigitated should be considered with the ultimate goal of preliminary evaluation of the proposed materials.

Among representative systems of potential interest to the area, highly concentrated solutions of the polyoxometallates of molybdenum and tungsten could serve as examples of multi-electron systems for all-liquid redox flow batteries and related fundamental investigations. Polyoxometallates, are polynuclear inorganic materials with well-defined multi-electron reversible electrochemistry and electrocatalytic properties (19). Among other important characteristics of heteropolyacids are that 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 (20). In addition, by changing their chemical composition the acid base and redox behavior can be modified and adjusted to a desired level. This fact makes heteropolyacids of molybdenum or tungsten (or their salts) attractive components of redox catalysts in electrochemical processes (21-23).

From the viewpoint of applicability of concentrated solutions of redox electrolytes in redox flow batteries, the important parameters to be considered include diffusion (mass transport) coefficients, rates of electron transfer kinetics and electrochemical potentials at which reactions proceed (25-32). In the case of *all-liquid systems*, the mass transport parameter can be considered as physical-diffusion-type and, thus, it determines the overall charge propagation within the electrolyte phase. Electron hopping (self-exchange), when is sufficiently fast (as in the case of redox reactions of heteropolytungstates), may contribute to the overall charge propagation in solutions at concentrations higher than 0.2 mol dm^{-3}. Electron transfers would also reflect the surrounding environment of the redox molecules (e.g. a choice of solvent, pH, ionic strength, total concentration, etc. In the present study, we consider a series of highly concentrated solutions of a model Keggin-type polyoxomettalate, such as silicododecatungstic acid (32).

Experimental

All chemicals were analytical grade materials and were used as received. Solutions were prepared from the deionized (Millipore Milli-Q) water. They were deoxygenated by bubbling with ultrahigh purified argon. Experiments were carried out at room temperature (22 ± 2 °C).

Chemical reagents were analytical grade materials. Silicotungstic acid hydrate was obtained from Sigma-Aldrich and sulfuric acid from POCh (Gliwice, Poland).

All electrochemical measurements were performed using a CH Instruments (Austin, TX, USA) Model 660 workstation in three electrodes configuration. A conventional glassy carbon working electrode was in a form of the disk of geometric area, 0.071 cm^2. The reference electrode was the calomel electrode, and the platinum rod was used as the counter electrode. An ultramicroelectrode was in a form of the Au disk having diameter of 10 µm).

All potentials reported here were recalculated and expressed vs. RHE.

Results and Discussion

Fundamental considerations

Depending on the experimental conditions (e.g. type of the system, nature and concentration of redox centers, mobility and availability of counterions), the overall transport process can be controlled by variety of phenomena such as electron hopping rate, counterion migration and ion-pairing, coupling of physical diffusion, and electron hopping (15,18). Regardless the actual mechanism, the situation is advantageous when the overall rate of charge transport in the investigated material obeys Fick's law of diffusion; then it can be characterized by an observable parameter defined as the apparent or effective diffusion coefficient, D_{app} or D_{eff}. When the electron self-exchange rate, rather than the mobility of charge-compensation ions, is kinetically limiting factor, it is plausible to describe currents arising from electron hopping in term of a Fickian model with equivalent electron diffusion coefficient, D_e. Several theoretical treatments have related such a macroscopic property as D_e to site-to-site electron exchange rate constant (k_{ex});

$$D_e = \theta k_{ex} \delta^2 C_T \qquad [1]$$

where C_T is the total concentration of redox sites, θ stands for a geometric factor that in the case of three-dimensional electron hopping becomes equal to 1/6, and δ is the distance between the redox sites at the time of electron transfer that is usually estimated as the average intersite distance, $(C_T N_A)^{-1/3}$, with N_A as Avogadro's number. It comes from Eq. [1] that both the population of the redox centers (C_T) and the rate constant for electron self-exchange (k_{ex}) must be large enough to develop a diffusion-controlled current. For concentrated redox electrolytes (between 0.5 and 4.5 mol dm^{-3}), the average site spacings (δ's) are from 0.4 to 1.8 nm. These facts can be kept in mind when developing new redox systems for fast charge propagation. Concentrated solutions of nodel inorganic mixed-valence polynuclear materials, such as heteropolytungstes, are applicable in this respect.

The coupling of physical diffusion and electron self-exchange was initially developed to describe electron self-exchange reactions in solutions of redox ions (15,18). The experimental diffusion rate, D_{app}, was found to be dependent on the physical diffusion rate, D_{phys}. Our experiments with highly concentrated solutions of iodine/iodides and Keggin-type heteropolytungstic acids imply that contribution originating from self-exchange could be significant enough to increase sizeably the effective charge transport coefficients. Indeed, in such systems the k_{ex} electron self-exchange values reach the exceptionally high level of 10^9 to 10^{10} mol^{-1} dm^3 s^{-1}. Such observations are of primary importance to the development of highly effective redox conducting electrolytes. Though separating electron and diffusion rates is not generally straightforward, certain experimental approaches for redox monomers have been described (15-18). They rely on the so-called Dahms-Ruff relation, which in its corrected form (15,18) is as follows:

$$D_{app} = D_{phys} + D_e = D_{phys} + k_{ex} \delta^2 C_T / 6 \qquad [2]$$

It should be remembered that, the mixed-valence sits typically differ in oxidation state by one electron, therefore at least one state must be ionic. To preserve electroneutrality, the electron transport must be accompanied by the unimpeded motion of charge-compensating, structural, or interstitial counterions. Their population must be high, and they must have good diffusive mobility within the investigated systems. In many cases, the overall kinetics might be controlled by counterion diffusion rather than by electron motion or mass transport. Then, it is more appropriate to describe diffusional charge transport in terms of D_{eff} or D_{app} instead of D_e. The ideal systems are the highly concentrated redox electrolytes in which D_{phys} and k_{ex} are maximized.

To execute the above mentioned analysis, ultramicroelectrode-based methodology involving cyclic voltammetry and potential step techniques (chronocoulometry) (15-18) will be considered here.

Diagnosis with ultramicroelectrodes

An example of the measurement result permitting diagnosis of the Keggin-type silicotiungstic acid redox electrolyte with use ultramicorelectrode-based probe is illustrated in Figure 1. The experiments can be performed in two diffusional regimes: (A) radial, and (B) linear. The data implies not only the well-behaved character of the system but also permits absolute electroanalytical determination of the concentration of redox centers and effective (apparent) diffusion coefficient in a manner described earlier (18,32). The informative dependence of the current on the square-root of scan rate – which is consistent with effectively diffusional charge propagation is also provided.

Conclusions

Acknowledgments

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