Available online at www.sciencedirect.com

SCIENCE DIRECT®

Analytica Chimica Acta 575 (2006) 144–150

ANALYTICA CHIMICA ACTA

www.elsevier.com/locate/aca

Analysis of charge transport in gels containing polyoxometallates using methods of different sensitivity to migration

Karolina Caban[a], Adam Lewera[a], Grazyna Z. Zukowska[b], Pawel J. Kulesza[a],
Zbigniew Stojek[a,*], Kenneth R. Jeffrey[c]

[a] Department of Chemistry, Warsaw University, ul. Pasteura 1, 02-093 Warsaw, Poland
[b] Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, PL-00-664 Warsaw, Poland
[c] Physics Department, The Guelph-Waterloo Physics Institute, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Received 23 February 2006; received in revised form 18 May 2006; accepted 22 May 2006
Available online 27 May 2006

Abstract

Two methods have been used for examination of transport of charge in gels soaked with DMF and containing dissolved polyoxometallates. The first method is based on the analysis of both Cottrellian and steady-state currents and therefore is capable of giving the concentration of the electroactive redox centres and their transport (diffusion-type) coefficient. The second method provides the real diffusion coefficients, i.e. transport coefficients free of migrational influence, for both the substrate and the product of the electrode reaction. Several gels based on poly(methyl methacrylate), with charged (addition of 1-acrylamido-2-methyl-2-propanesulphonic acid to the polymerization mixture) and uncharged chains, have been used in the investigation. The ratio obtained for the diffusion coefficient (second method) and transport coefficient (first method) was smaller for the gels containing charged polymer chains than for the gels with uncharged chains. In part these changes could be explained by the contribution of migration to the transport of polyoxomatallates in the gels. However, the impact of the changes in the polymer-channel capacity at the electrode surface while the electrode process proceeds was also considered. These structural changes should affect differently the methods based on different time domains.

Keywords: Polymer gel; Solid-state electroanalysis; Migration; Diffusion coefficient; Concentration of redox sites

1. Introduction

In true solid-state voltammetry, there is no contact between the solid reaction medium and liquid electrolyte solution. Under such circumstances, a material to be investigated serves as both electrolyte medium and electroactive species. This is due to the presence of mobile charge-balancing ions in its structure and highly concentrated immobile redox centres. Since the redox centres are macroscopically fixed, the transport of electrons between them is based on the hopping (self-exchange) process. In order to maintain electroneutrality at each point in the solid lattice, electron hopping is accompanied by the displacement of appropriate counterions, intrinsically present in the redox material. "Ionic budgets" of such solid materials may differ much. Various aspects of solid-state voltammetry have been discussed in some reviews [1–4].

The materials investigated by solid-state electrochemistry can be classified into different categories, according to their chemical composition, structure, and charge propagation mode. Mixed-valence inorganic materials are the first important category of solid-state electroactive systems. They include e.g. solids of Prussian Blue type, inorganic oxides like WO_3 and single crystals of heteropolyacids like $H_3PW_{12}O_{40}{\cdot}29H_2O$. The second group includes polymeric systems, in which the polymer is electroinactive (e.g. polyethylene oxide) and soaked with a solvent, and plays the role of an inert matrix containing immobilised or dispersed redox species (e.g. ferrocene, metalotetraphenyl-porphyrins). The third group consists of redox polymers, in which electroactive groups (such as e.g. poly-Ru(vinylbipyridine)) are chemically bound to polymer chains. These systems comprise mixed-valence films.

---

[*] Corresponding author. Tel.: +48 22 822 4889; fax: +48 22 822 4889.
E-mail address: stojek@chem.uw.edu.pl (Z. Stojek).

0003-2670/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2006.05.070

It often happens that the overall charge propagation within the solid phase obeys Fick's law of diffusion. Then, from appropriate voltammetric investigations, the apparent diffusion coefficient, $D_{\mathrm{s\,app}}$, can be estimated. The rate-determining step in the hopping transport process can be either slow electron hopping or slow counterion mobility. In the former case, the so-called diffusion coefficient of electron, D_{e}, is commonly defined. Another possibility is that the kinetics of charge transport is controlled by the flux of charge-compensating ions and then can be described quantitatively by D_{phys} (physical diffusion). The extent to which each of two components contributes to the total charge propagation is not easy to be determined. However, they are interrelated according to the Dahms–Ruff relation [2,3]:

$$D_{\mathrm{app}} = D_{\mathrm{phys}} + D_{\mathrm{e}} = D_{\mathrm{phys}} + \tfrac{1}{6} k_{\mathrm{ex}} \delta^2 C_0 \tag{1}$$

where 1/6 is a geometric factor for the three-dimensional electron hopping, k_{ex} the rate constant for the electron self-exchange, C_0 the concentration of redox sites, and δ denotes average distance between the redox centres, usually estimated as $(C_0 N_{\mathrm{A}})^{-1/3}$.

Regarding the size of the diffusive space, in solid-state voltammetry two ultimate cases can be identified: semi-infinite diffusion and thin-layer behaviour. The concentration profiles developed within the electrolysed solid material depend on the parameter Dt/d^2, where t is a given experimental time, and d is the thickness of the investigated material. Semi-infinite diffusion and bulk behaviour are observed when $\sqrt{Dt} \ll d$, namely, when the diffusion layer is much thinner than the investigated material. Then, peak-shaped current–potential responses are obtained and the peak current magnitude depends linearly on the square root of scan rate, as the appropriately adapted Randles–Sevcik equation predicts:

$$I_{\mathrm{p}} = 2.69 \times 10^5 n^{3/2} A D_{\mathrm{app}}^{1/2} C_0 v^{1/2} \tag{2}$$

A linear I_{p} versus $v^{1/2}$ dependence is a popular diagnostic criterion of diffusive mass transport in the system and allows excluding, e.g. adsorption of the participating species and limited diffusion space.

A significant improvement in the quality of solid-state voltammetric responses has been achieved with ultramicroelectrodes. Their application in this field opens also new diagnostic and analytical possibilities. An important feature of microelectrodes, of distinct consequences in solid-state voltammetry and chronoamperometry, is their compact size and utility in characterisation of small samples. Moreover, they provide low capacitance currents even at large scan rates and their responses are much less affected by uncompensated resistance [5–7]. At microelectrodes, it is easy to switch from long to short time domains by applying either slow or high potential scan rates (or either long or short polarisation times), which leads to the development of either spherical or linear diffusion fields, respectively. In spherical diffusion regime, sigmoidal wave-shaped voltammograms are formed instead of the peak-shaped ones. The *plateau* current obtained at a sufficiently small disc microelectrode does not depend on scan rate and is described as

$$I_{\mathrm{ss}} = 4 n r_0 F D_{\mathrm{app}} C_0 \tag{3}$$

By performing cyclic voltammetric measurements at a microelectrode in two different time regimes, i.e. under conditions of linear and spherical diffusion, it is possible to determine both D_{app} and C_0. An equivalent situation will appear for a combination of long pulse chronoamperometry and high scan rate cyclic voltammetry, and, optionally, for long pulse chronoamperometry and short-pulse chronocoulometry [8]. The system of Cottrell and Randles–Sevcik equations is rather easy to be solved analytically and thus has become popular [9–12]. Even when one of the limiting cases cannot be achieved, very good results are also obtained by the iterative (successive approximations) method [13]. The latter approach requires numerical solving of the combination of two equations in which the first one describes the current (or charge) in a well-defined diffusional regime and the second general equation refers to chronoamperometric current under mixed (linear–spherical) conditions.

Yet, the above approaches are not free from some limitations. For example, possible inhomogeneities of the investigated bulk material may affect the diffusion process and, as a result, Eqs. (2) and (3) may be no longer applicable. A relatively low concentration of the inert electrolyte, compared to that of the redox centres (insufficient ionic support), is another challenge. A good question is whether migration contributes to the charge transport in the examined solid material. The answer to this question may be obtained by employing a method that can be called the removal-of-migrational-bias approach. This new method allows the determination of real diffusion coefficients of both substrate and product and is based on the analysis of the transient currents in a double potential step chronoamperometric experiment (DPSC). Since it eliminates the influence of migration, it can be used at any level of the ionic support [14]. Diffusivities of the substrate (D_{s}) and the product (D_{p}) are obtained by incorporating either the slope, a, or the intercept, b, of the appropriate linear plots: $I^{\mathrm{L}}(\xi,t)/I^{\mathrm{L}}(\xi,t_g)$ versus $1/\sqrt{t}$ for the first-step chronoamperometric current and $I_{\mathrm{r}}(\xi,t)/I^{\mathrm{L}}(\xi,t_{\mathrm{g}})$ versus $1/\sqrt{t-t_{\mathrm{g}}}$ for the second-step chronoamperometric current, where ξ is the support ratio, t_{g} is the length of the first pulse, and I_{r} is the current measured in the second pulse. The formulas obtained from the expressions for the slopes of the first- and second-pulse plots can be written as

$$D_{\mathrm{s}} = \frac{4 r_0^2}{\pi^3} \left(\frac{1}{a} - \frac{1}{\sqrt{t_{\mathrm{g}}}} \right)^2 \tag{4}$$

and

$$D_{\mathrm{p}} = \frac{1}{a^2} \left(\frac{\pi\sqrt{\pi}}{2 r_0^2} + \frac{1}{\sqrt{D_{\mathrm{s}} t_{\mathrm{g}}}} \right)^{-2} \tag{5}$$

respectively, where r_0 is the microelectrode radius. Please note that to use Eqs. (4) and (5) we do not need to know the electroactive species concentration. The discussed method can be used when there is no contribution of electron hopping to the transport.