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Solid-State Electroanalysis of Silicotungstic Acid Single Crystals at an Ultramicrodisk Electrode

Pawel J. Kulesza[†] and Larry R. Faulkner[*,‡]

Contribution from the Department of Chemistry, University of Illinois, 1209 West California Street, Urbana, Illinois 61801, and Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland

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Abstract: An electroanalytical approach for the quantitative and qualitative characterization of certain fast redox-conducting molecular solids is proposed here. The method utilizes ultramicroelectrodes within a three-electrode solid-state electrochemical cell and is based on a set of potential step and cyclic voltammetry experiments. Such measurements permit the determination of the following parameters: the concentration of mixed-valence redox sites (C_o) that are electrochemically accessible in the system, the effective diffusion coefficient for charge propagation (D_{eff}), the standard heterogeneous rate constant for electron transfer between the working ultramicroelectrode and the electroactive sites (k^o), and the formal potentials ($E^{o\prime}$) for solid-state redox reactions. For a well-defined 12-tungstosilicic acid tetragonal single crystal ($H_4SiW_{12}O_{40}{\cdot}31H_2O$), the obtained values are $C_o = 1.5 \pm 0.1$ M, $D_{eff} = 2.8 \pm 0.3 \times 10^{-7}\ \text{cm}^2\ \text{s}^{-1}$, and $k^o = (7\text{–}13) \times 10^{-2}\ \text{cm s}^{-1}$ for the most positive redox transition at $E^{o\prime} = -0.225$ V versus gel-filled Ag/AgCl (3 M NaCl/agar) reference. This approach can be extended to the characterization of other ionically-conducting solids that contain fixed mixed-valence redox sites on the conditions that (1) the overall charge propagation mechanism can be described in terms of bulk diffusion, (2) the electron transfer between the working electrode and the electroactive sites is not rate-limiting in potential step experiments, and (3) the structural counterions are available in large numbers and are sufficiently mobile to minimize ohmic effects and to support fast diffusive mass transport of electrons. In this context, silicotungstic acid, which shows facile redox processes and hosts large amounts of easily accessible mobile protons, is a model system.

Introduction

Recently, we have demonstrated that the tetragonal silicotungstic acid single crystal $H_4SiW_{12}O_{40}{\cdot}31H_2O$, a protonically conducting,[1] well-defined molecular material,[2] is an attractive bulk system for solid-state electrochemical studies.[3] The present study aims at extending electroanalytical methodology to the quantitative characterization of certain ionically-conducting mixed-valence bulk materials.

Such a heteropoly 12-tungstate system as silicotungstic acid possesses a rigid Keggin-type anionic primary structure in which all 12 tungsten atoms are fixed and structurally equivalent.[4–6] The Si heteroatom, which is nonelectroactive, sits in the center of the polynuclear system and has a stabilizing effect on its structure. The polytungstate array has various accessible oxidation states and, while in the mixed-valence W(VI,V) state, remains capable of fast electron transfer between the redox sites.[7] The solid also hosts exceptionally mobile protons within the hydrated three-dimensional "pseudoliquid" secondary structure.[4b,6] The hydrated protons are believed to be transported through the hydrogen-bonded network almost as quickly as in the aqueous phase,[1,6] so that the sizeable population of these structural protons in the crystal can serve the same purpose as the supporting electrolytes in conventional electrochemistry.[8] This ionic budget of protons permits the electron transfer to be readily coupled to the counterion displacement, thus providing electroneutrality and making solid-state redox transitions feasible.[9,10] Partial reduction (i.e., addition of one to four electrons to the heteropoly 12-tungstate

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[*] To whom correspondence should be addressed.

[†] University of Warsaw.

[‡] University of Illinois.

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anion) yields a dark blue mixed-valence microstructure, hetero polyblue,[4,7] in which the added "blue" electrons undergo delocalization over all 12 W atoms[11a] at a rapid rate on the ESR and NMR time scales.[4b,11] The reduction process is electrochemically well-defined and reversible,[3,4,12] and the heteropoly blue redox transitions do not lead to any significant structural changes.[11a] In conclusion, the 12-tungstosilicic acid single crystal seems to be a perfect model material for fundamental electrochemical characterization in the solid state.

By analogy to hydrogen bronzes[13] (i.e., nonstoichiometric infinite oxides, such as H_xWO_3, where $0 < x < 1$), the Keggin-type heteropoly blue anions[4,7] ($H_zSiW_{12}O_{40}{}^{4-}$, where z is 1, 2, or 4) contain interstitial hydrogen of high reducing power. These materials are able to facilitate formal transfers of oxygen or hydrogen during chemical reactions. Heteropoly complexes are finding increasing use as catalysts and specialized, electrochromic, redox reagents.[4-6,14] In this context, practical evaluation of these materials requires knowledge of charge propagation dynamics and information concerning the concentration of reactive sites available during redox reactions.

We have shown in our previous communication[3a] that conventional electroanalytical techniques, utilizing a special three-electrode cell, can provide basic information about thermodynamics and reversibility of redox transitions in a single crystal. In this report, we demonstrate that application of ultramicroelectrodes[15] leads to an improvement in the quality of solid-state electrochemical data and provides new diagnostic and analytical possibilities. Ultramicroelectrodes have been widely studied not only because of their compact size and utility in characterization of small samples but also because of such physical characteristics as the small electrode surface area and the related small double-layer capacitance. Of primary importance to solid-state investigations is that the small currents make ohmic drops negligible.

Finally, we demonstrate that potential step experiments utilizing an ultramicrodisk electrode permit estimation of both the effective diffusion coefficient and the concentration of redox sites in the material. This benefit arises because the potential step experiment can be performed in two time regimes related to the application of short and long potential pulses. Since two distinct mass-transfer patterns (linear and spherical) apply in the different regimes, one has two different equations that can be solved simultaneously for two unknowns, the concentration and the effective diffusion coefficient. Fast-scan cyclic voltammetry at an ultramicroelectrode also permits estimation, via the Nicholson method,[8] of a heterogeneous (intrinsic) rate of electron transfer between a carbon ultramicroelectrode and the electroactive W(VI,V) redox sites in the silicotungstic acid single crystal. The physicochemical meaning of these parameters, as well as the reliability of such determinations and their potential utility to other solid systems, will also be addressed here.

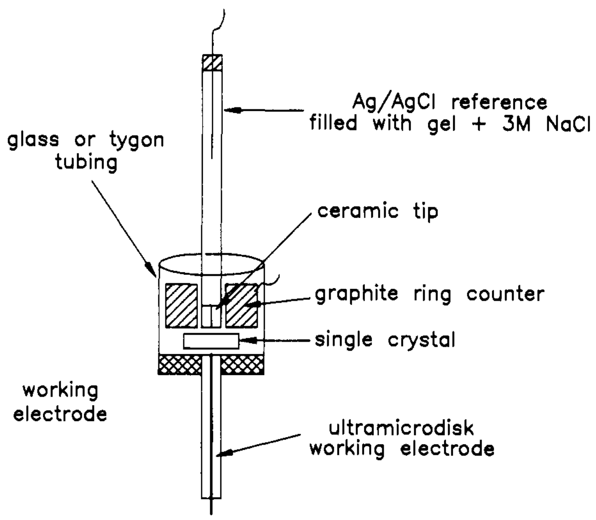

Figure 1. Cross sectional view of the three-electrode solid-state electrochemical cell utilizing an ultramicroelectrode.

Experimental Section

The three-electrode cell used for the solid-state electrochemical investigations of bulk materials (Figure 1) is analogous to that described by us in the preliminary report,[3a] except that an ultramicroelectrode (Bioanalytical Systems), a 10-μm diameter carbon fiber disk, was used as the working electrode. This electrode was positioned opposite the gel-type reference electrode (Bioanalytical Systems), which itself was surrounded by a relatively large graphite ring, as a counter electrode. To assure good contact between the working electrode and the crystal, a brass weight (ca. 20 g) was attached to the ultramicroelectrode. The electrochemical responses were not dependent on additional hand pressure as long as the single crystal was not destroyed.

The reference electrode was manufactured with a conducting gel (3 M NaCl/agar) electrolyte. A dry contact with the silicotungstic acid single crystal was provided through the reference electrode's ion-permeable ceramic tip. This type of reference electrode works reproducibly, is virtually noncontaminating, and serves as a potential standard (offset 0.197 V vs SHE). Between measurements, the reference electrode was stored in aqueous 3 M NaCl. Before each use, it was dipped into a gel prepared by heating 5 g of agar in 100 mL of 3 M NaCl solution. The excess gel was removed with a Kimwipe.

The single crystal was positioned in the center of the cell, and the cell was then enclosed in transparent Tygon tubing. To protect the crystal from partial dehydration, which would lead to the loss of its well-defined crystalline character, the assembly was sealed with parafilm or Teflon tape where necessary.

Electrochemical measurements were performed with a BAS Model 100C electrochemical analyzer (Bioanalytical Systems). Carbon electrodes were activated in a manner reported elsewhere.[13e] All experiments were conducted at room temperature, 20 ± 2 °C.

All chemicals were of highest available purity, ACS reagent grade or Puratronic. Single crystals of silicotungstic acid were grown at ambient temperature by slow evaporation of a saturated solution prepared by dissolution of 10 g of the commercially available 12-tungstosilicic acid (Fluka) in 5 mL of Millipore deionized water. Typically crystals appeared after 2 days of growth.

Results and Discussion

Qualitative Characterization. Cyclic voltammetric responses at conventional-size electrodes are very similar for a silicotungstic acid single crystal in a cell of our original design[3a] (Figure 2, curve A) and for a solution of silicotungstic acid (Figure 2, curve B). In the potential range from 0.5 to −0.65 V, both systems exhibit three sets of well-defined and reversible voltammetric peaks at comparable potentials. The peak potentials have been measured and reported in the respective solid-state and solution experiments versus two different references, gel-type Ag/AgCl and SCE. Therefore, curve A is shifted about 40 mV toward more positive potentials in comparison to curve B. The principal difference in character is that the first two sets of peaks, appearing

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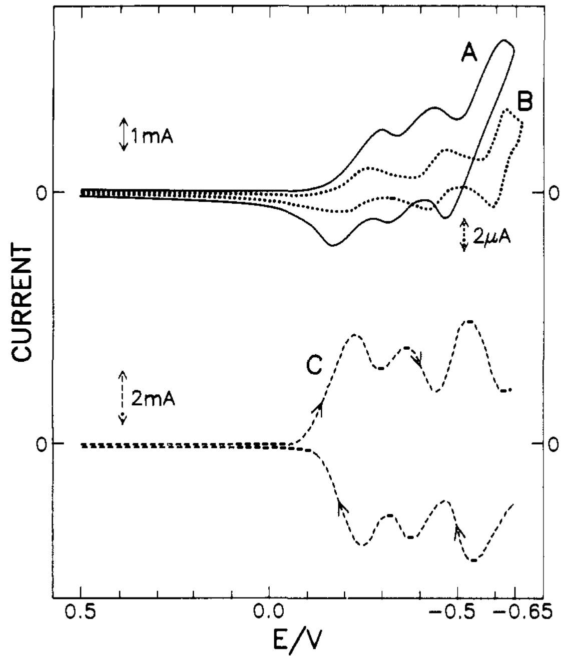

Figure 2. Cyclic voltammetry of silicotungstic acid recorded at a conventional-size glassy carbon disk electrode: (A) at 50 mV s^{-1} with a single crystal sample; (B) at 100 mV s^{-1} in 0.5 M H_2SO_4 solution containing 4 mM $H_4SiW_{12}O_{40}$; and (C) with a single-crystal sample but in the differential pulse mode (pulse amplitude 50 mV; pulse width 50 ms; pulse period 200 ms; scan rate 10 mV s^{-1}). The reverse scan shows currents of the opposite (negative) sign; electrode surface areas: ca. 0.3 cm^2 for (A) and (C) and 0.07 cm^2 for (B). Positive currents are cathodic.

at the most positive potentials, are better separated in the solution experiment (Figure 2, curve B) than in the solid-state measurement (Figure 2, curve A). The latter behavior seems to be characteristic of silicotungstates, given that it was also observed in conventional voltammetric studies utilizing electrodes modified with thin solid films of silicotungstates.[12d,e] Nevertheless, the first two most positive silicotungstic acid single-crystal redox transitions are distinct, and their separate nature is clearly apparent when the solid-state electrochemical experiment is repeated using differential pulse voltammetry (Figure 2, curve C), which is known to provide good resolution for electrochemically reversible systems.

Both solution and solid-state voltammetric peaks (Figure 2) have height ratios 1:1:2, as expected from the literature[4,7] for Keggin-type heteropoly 12-tungstates. This behavior is consistent with the view that, depending on the applied potential, one, two, or four electrons are added and delocalized over the rigid silicotungstate anion, the crystal's primary structure.[4,6] Statistically, one, two, or four out of the 12 hexavalent tungsten atoms in the lattice are transformed into the pentavalent state, and the material becomes truly mixed-valence. The redox processes taking place in the rigid polyanion are reversible and can be described as follows:[3a,4,7,12d]

$$SiW_{12}O_{40}^{4-} + ze + zH^+ \rightarrow H_zSiW_{12}O_{40}^{4-} \qquad (1)$$

where z can have values equal to 1, 2, and 4. Protons that participate directly in reaction 1 and provide charge balance during electron transfer are present in large numbers in the secondary (hydrated) structure of the crystal.[6]

During the operation of the three-electrode solid-state electrochemical cell, a current flows between the working and counter electrodes and produces changes at the counter electrode. The anodic reaction there presumably involves oxidation of the crystal's structural water to oxygen, coupled with the release of protons. Although no direct effect of this side reaction has been found during 20 consecutive potential cycles using a conventional electrode,[3a] the reaction products may eventually interfere. The problem would be practically eliminated with the use of smaller current densities, which one can readily achieve by coupling an ultramicrodisk working electrode with a large surface area counter electrode. We propose this solution in our new design (Figure 1) to make the measurement approach truly nondestructive.

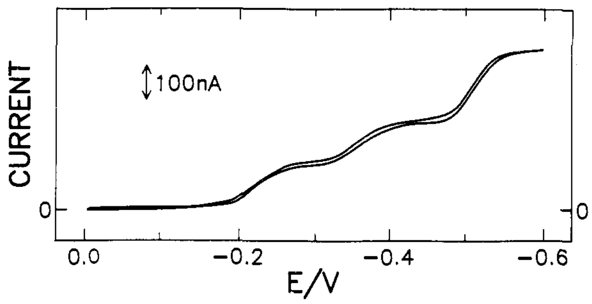

Figure 3. Solid-state cyclic voltammetry of a silicotungstic acid single crystal using an ultramicroelectrode (r_0 = 5 μm); scan rate 5 mV s^{-1}.

Another issue is the long-term durability of the investigated crystal. We found that application of 50 voltammetric cycles within the potential limits of Figure 2, curve A, but with a conventional-size (surface area ca. 0.3–0.4 cm^2) working electrode turns the single crystal blue. Although the crystal can be slowly reoxidized by oxygen from the air, the coloring process is irreversible, at least on the time scale of a typical electrochemical experiment. At first sight, this observation may seem to be in contradiction to our voltammetric diagnostic experiments (Figure 2), which are consistent with the reversibility of electron transfer. Careful examination of the data shown in Figure 2, curve A, particularly at potentials more negative than −0.35 V, shows that the cyclic voltammogram is not perfectly symmetrical around the zero current axis and that the reduction currents, relative to the oxidation currents, are somewhat higher. The difference in currents may originate from the catalytic discharge of protons and the evolution of hydrogen within the solid phase, as seen in the photochemistry of polytungstates.[4c] Silicotungstates, by analogy to the related tungsten oxides, can be expected to turn blue upon absorbing hydrogen,[4a,13a] thereby supporting our hypothesis.

The bulk coloring effect has been practically eliminated with the change to the ultramicroelectrode-based cell arrangement (Figure 1). The whole approach is virtually nondestructive, as during electrolysis only the population of redox sites within a very small geometric area and distance from the surface of an ultramicrodisk electrode is perturbed. The resulting three voltammetric waves (Figure 3) reflect three distinct redox transitions in the silicotungstic acid single crystal, as discussed earlier. The response is in the form of steady-state plateau currents, which are consistent with the predominantly spherical mass transport to the electrode surface. The experiment is, in practice, indefinitely reproducible. When the direction of the potential sweep was reversed, the current essentially retraced the initial scan since the products of electrolysis diffused away from the electrode. At an electrode of larger size, this type of effect cannot be observed (Figure 2, curve A) because the scan rate must be very slow for spherical diffusion to contribute appreciably to the current.

The separate nature of the three redox transitions (Figure 3; eq 1) was clearly marked in the experiments involving the application of small-amplitude controlled-potential wave forms (Figure 4), characteristic of such techniques as differential pulse voltammetry (curve A) and alternating current voltammetry (curve B),[8] to an ultramicrodisk electrode. These techniques improve upon standard cyclic voltammetry at the ultramicroelectrode by providing peak-type responses with clear resolution and by subtracting out a large portion of the background current. The ac voltammetry data illustrated in Figure 4, curve B, are also consistent with fast electrode kinetics of the redox reactions

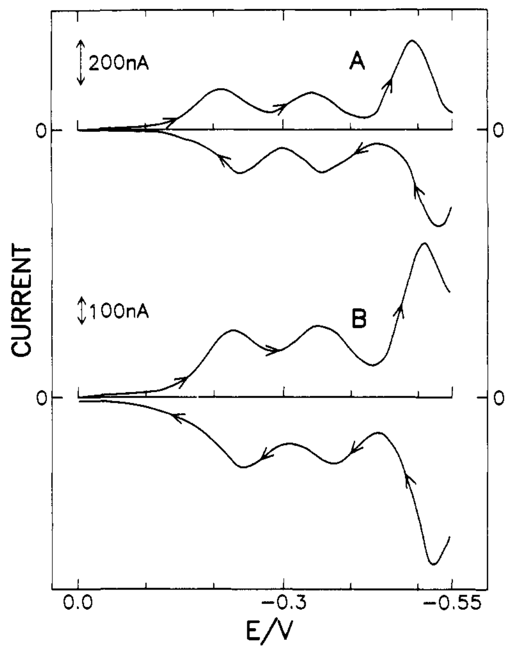

Figure 4. Differential pulse voltammetry (curve A) and ac voltammetry (curve B) of a silicotungstic acid single crystal recorded with the use of an ultramicroelectrode. Parameters for (A) are the same as for Figure 2C; parameters for (B): frequency 50 Hz; ac amplitude 25 mV; scan rate 4 mV s^{-1}. The reverse currents have the opposite (negative) sign.

expressed in eq 1. The fact that the differential pulse and ac voltammetric peaks (Figures 2, curve C, and 4) for positive-going scans appear at more negative (30–80 mV) potentials than the respective peaks for negative-going scans may reflect a slight change in the reaction thermodynamics as a result of hydrogen formation in the crystal's phase (chemical reaction) following the system's reduction (electron transfer). However, exactly this effect is expected as an artifact of the differential pulse method.[8] Our preliminary results show that the ultramicroelectrode-based differential pulse and ac voltammetric approaches are useful diagnostic tools in the electrochemical characterization of various redox-conducting solids. Further research is in progress along this line.

Model of Mass Transport. For simplicity, the present study concentrates mainly on the first redox transition which appears at the most positive formal potential of ca. –0.225 V (Figures 2, curve A, and 3) and involves a single electron transfer. It is generally accepted that this electrode reaction is very fast in all Keggin-type heteropoly 12-tungstates.[4,7] Our previous electrochemical studies, performed in various media and under different conditions,[3a,12e] are consistent with this statement. For example, cyclic voltammetry (in 1 M H_2SO_4),[12e] utilizing a conventional glassy carbon electrode covered with approximately a monolayer of silicotungstates, yielded corresponding peak currents proportional to the scan rate up to 40 V s^{-1}. In addition, the peak potentials were largely independent of the scan rate, and the difference between them did not exceed 30–40 mV.[12e] These data imply that the silicotungstate surface electrode reaction involves a fast electron transfer. In the solid-state voltammetry of a silicotungstic acid single crystal at a conventional size electrode, the cathodic peak current of the first (most positive) reduction peak was found to be proportional to the square root of the scan rate up to 1000 mV s^{-1} and had zero intercept,[3a] as expected for a diffusional process. In the comparable solution experiment in which silicotungstate was dissolved at 2 mM in 1 M H_2SO_4, the effect of the scan rate (up to 1000 mV s^{-1}) on the peak current also met the diagnostic criteria for a diffusion-controlled process. In both cases, the electron transfer is not a limiting factor, but the mechanism of charge propagation must be different in the solid-state experiment and in the solution electrochemical measurement.

In a conventional solution experiment, the silicotungstate redox species diffuse to the electrode surface where they undergo fast partial reduction on the condition that a sufficiently negative potential is applied. According to eq 1, the actual electron-transfer step takes place at one of the 12 structurally equivalent hexavalent tungsten atoms and involves a proton from the acid electrolyte. In the case of a bulk solid, such as the silicotungstic acid single crystal, the tungsten redox sites are fixed and therefore diffusively immobile. To show solid-state redox transitions under the potential bias, the system must be capable of generating chemically identifiable redox sites, e.g., the electron donor W(V) and the electron acceptor W(VI), between which fast electron hopping (self-exchange) is feasible. To preserve electroneutrality, the electron transport must be accompanied by the unimpeded motion of structural protons. If this ionic motion were not operative, the material would behave as a Robin and Day mixed-valence semiconductor or semimetal[7] and would provide an ohmic (linear) response. Our solid-state electrochemical experiments[3a] show, however, that potentials applied to the crystal produce voltammetric patterns consistent with the development of diffusional concentration gradients in the material. The "ionic budget" of mobile protons in the crystal's secondary structure is apparently extensive enough to support difffusive mass transport of electrons and to minimize ohmic effects. Formally, the overall mechanism of charge propagation can be made equivalent to the "diffusion" of the immobile redox centers with the same effective diffusion coefficient for both oxidized and reduced states.

Determination of the Effective Diffusion Coefficient and Population of Redox Sites. An important feature of the potential step chronocoulometry or chronoamperometry experiment, utilizing an ultramicrodisk electrode, is that the nature of mass transport depends on the time t domain,[16] or more precisely, on the value of the dimensionless time parameter $\tau = 4Dt/r_0^2$, where r_0 stands for the electrode radius and D is the diffusion coefficient. In the short-pulse experiment, for $\tau \ll 1$, when the diffusion field is small compared to the electrode radius, the linear flux of electroactive species perpendicular to the electrode predominates. On the other hand, large values of τ correspond to the long-pulse experiment, in which the spherical diffusion layer greatly exceeds the size of the electrode, and spherical (nonlinear) diffusion becomes predominant. In a few published papers, authors have utilized the distinctive current transients in the potential step experiments at ultramicroelectrodes for the absolute determination of the diffusion coefficient and concentrations of the electroactive species in solution.[17]

In the solid-state electrochemistry of the silicotungstic acid single crystal, the W(VI,V) redox sites are immobile but the mechanism for charge propagation meets the diagnostic criteria of a diffusional process. Thus, the respective solid-state experiment utilizing ultramicroelectrodes would produce concentration gradients that, upon application of a sufficiently short pulse or a long pulse, could formally manifest either linear or spherical diffusion of the redox sites in the single crystal.

For simplicity of calculations and interpretations, we performed the short-pulse (36 ms) and long-pulse (30 s) solid-state experiments in the chronocoulometric and chronoamperometric modes, respectively. In both cases, the step potential was to –0.300 V, i.e., to the potential that is approximately 70 mV more negative than the first reduction peak in Figures 2, curve A, and 4. Chronocoulometry gives the cumulative charge Q passed in

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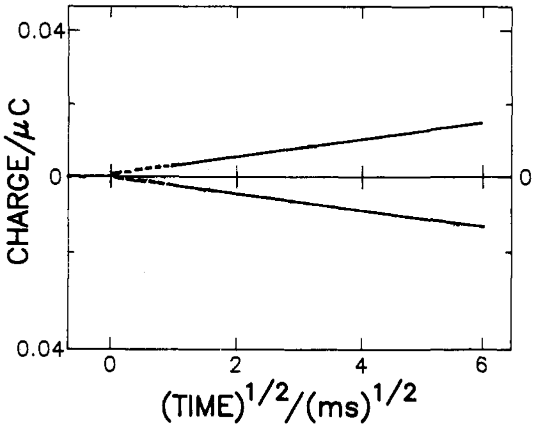

Figure 5. Anson plot for short-pulse (36 ms) solid-state chronocoulometry of the crystal using an ultramicroelectrode; forward potential step from 0.1 to −0.3 V. Dashed segments are extrapolated.

reducing silicotungstate molecules that are effectively transported to the ultramicroelectrode by linear diffusion along the concentration gradient within the crystal. The dependence can be described in terms of an integrated Cottrell equation:[8]

$$Q = 2nF\pi^{1/2}r_0^{\,2}D_{\text{eff}}^{\,1/2}C_0t^{1/2} \tag{2}$$

where the parameters either have been discussed above or have the usual significance. As the experimental time scale increases, spherical diffusion predominates and a steady-state plateau current is produced, as expected for chronoamperometry at an ultramicroelectrode.[15] The steady state current is described as follows:

$$i_{\text{ss}} = 4nFD_{\text{eff}}C_0r_0 \tag{3}$$

As a result, we have a system of two equations that can be solved for two variables, C_0 and D_{eff}, because all other parameters are known (n, F, and r_0) or can be measured (Q and i_{ss}). The solution is as follows:

$$C_0 = (Q/t^{1/2})^2/nF\pi r_0^{\,3}i_{\text{ss}} \tag{4}$$

and

$$D_{\text{eff}} = i_{\text{ss}}^{\,2}\pi r_0^{\,2}/4(Q/t^{1/2})^2 \tag{5}$$

This approach permits the absolute determination of the concentration of the redox sites (C_0) as well as the effective diffusion coefficient for charge propagation (D_{eff}) in the crystal.

Chronocoulometry experiments with a short pulse width (36 ms) produced the dependency of Q versus $t^{1/2}$ (Anson plot) shown in Figure 5. These data were reproducible during at least 20 consecutive measurements. As expected for a process controlled by linear diffusion, the plot in Figure 5 is linear and characterized by a near-unit correlation coefficient, 0.9978 ± 0.0012. The slope is 2.3 ± 0.2 nC ms$^{-1/2}$. Further, the dependence showed effectively a zero intercept, namely −0.3 ± 0.2 nC. The error bars are standard deviations based on the data from 10 independent experiments. It is interesting to note that the linear characteristics and the slope of the backward response are comparable to those in the forward experiment and imply that the pulse experiment was fast enough that the electrolysis products were not able to escape from communication with the electrode surface by semiinfinite linear diffusion.

On the whole, the results of Figure 5 are consistent with (1) absence of ohmic/migration effects, (2) no limitation caused by slow electron transfer between the working electrode and the electroactive sites, and (3) linear diffusion as a predominant mass-transport mechanism. If there were any ohmic or kinetic limitations or any significant contribution from radial diffusion, a sizeable negative intercept and a positive deviation from linearity would be observed. The characteristics of silicotungstic acid single crystals, particularly fast electron hopping and good ionic conductivity of abundant protons, seem to rule out the ohmic and kinetic limitations. The successful chronocoulometry experiment requires application of the shortest reasonable pulse (36 ms). An increase of the pulse width in the order: 49, 64, 100, 400, and 900 ms produced more negative intercepts, −0.5, −1.2, −2.0, −11.2, and −56.1 nC, as the radial contributions to diffusion became more significant and produced more "parabolic" Anson plots.

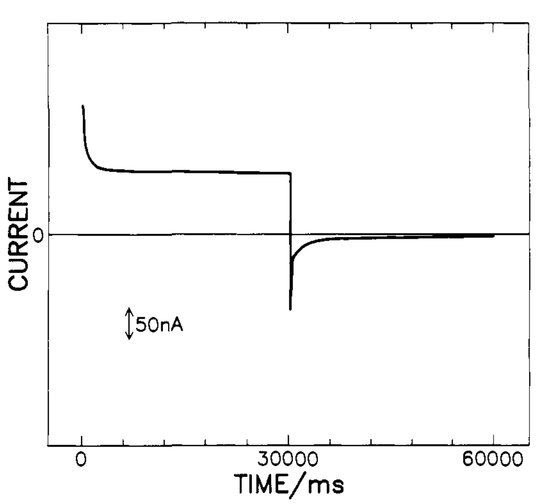

Figure 6. Long-pulse (30 s) solid-state chronoamperometry of the crystal using an ultramicroelectrode; forward potential step from 0.1 to −0.3 V.

The 36-ms potential pulse from 0.1 to −0.3 V is equivalent to a scan rate on the order of 1 V s^{-1} in cyclic voltammetry. The latter technique provides an additional means of diagnosing whether any kinetic or ohmic limitations exist in short-time experiments. We found that cyclic voltammetry at 8.5 V s^{-1} of the crystal produced well-developed peaks that were proportional to the square root of the scan rate up to at least 34 V s^{-1}. Furthermore, the separation between the reduction and oxidation peaks was ca. 60 mV at 8.5 V s^{-1} for the first (most positive) redox process. As the reaction involves one electron, the results are again consistent with a fast reversible transfer of an electron and imply a negligible ohmic drop.[8]

The long-pulse chronoamperometry experiment (30-s pulse width) featured a steady-state current response (Figure 6), as expected from the predominantly nonlinear mass-transport mechanism. The response was unchanged during at least 20 consecutive measurements. The mean value of the steady-state current, based on 10 independent experiments, was 83 ± 5 nA. During the reverse pulse, the current decayed to zero, thus implying that the time scale of the measurement was long enough for the electrolysis products to diffuse away from the surface of the ultramicrodisk electrode.

Equations 4 and 5 yield $D_{\text{eff}} = (2.8 \pm 0.3) \times 10^{-7}$ cm^2 s^{-1} and $C_0 = 1.5 \pm 0.1$ M where the error bars are standard deviations, as discussed above. The concentration of redox sites (C_0) is large; hence, no preamplifier was necessary in the electrochemical measurements utilizing ultramicroelectrodes. The high value of the effective diffusion coefficient for charge propagation (D_{eff}) is consistent with the knowledge that heteropoly 12-tungstates have very good (pseudometallic) electronic conductivity (when partially reduced to heteropoly blues)[4] and exceptionally high proton conductivity (on the level (1–2) x 10^{-1} ohm^{-1} cm^{-1})[1a] in the solid state.

The value of $C_0 = 1.5$ M expresses the population of W(VI,V) mixed-valence sites, or pentavalent W atoms, that would be generated upon supplying one electron to one hexavalent W statistically in each heteropoly 12-tungstate molecule in the crystal. Thus, C_0 is formally equivalent to a macroscopic concentration of silicotungstate units in the crystal. Since the system is well-defined and its molecular weight is known (3401 g mol^{-1} with water of hydration), the knowledge of C_0 has allowed us to estimate indirectly the crystal's density as 5.1 g cm^{-3}. Further, assuming the ideal cubic symmetry and using Avogadro's number, we obtain the unit cell parameter 1.1 nm. The values for density and cell parameter are in agreement with those reported in literature[2,5e–g] (density 5–6 g cm^{-3}, depending on the degree of hydration; unit cell parameter 1.2 nm) for Keggin-type heteropoly 12-tungstates having P, Si, or B as heteroatoms.

Injection of one, two, or four electrons into the transition-metal cluster is reversible and produces a partially reduced heteropoly blue species that possesses largely unchanged primary and secondary structures of the parent system. Electrochemical experiments utilizing ultramicroelectrodes are virtually nondestructive and are not expected to alter the population and mobility of the charge-compensating and rate-controlling protons. Thus, it is possible to extend the analysis used above to all three redox transitions appearing in the potential range from 0 to –0.6 V (Figures 2–4). Short-pulse (36 ms) chronocoulometry, employing potential steps from 0 to –0.310, –0.470, and –0.590 V, yielded linear responses as in Figure 5, characterized by effectively zero intercepts and slopes of 2.3 ± 0.2, 4.7 ± 0.3, and 9.3 ± 0.5 nC ms$^{-1/2}$. These numbers are clearly proportional to the number of electrons transferred (one, two, and four)/whole silicotungstate unit. Long-pulse (30 s) chronoamperometry, utilizing the same potential steps as above, yielded steady-state currents (as in Figure 6) having the values 83 ± 5, 167 ± 5, and 335 ± 4 nA. The plateau currents were also proportional to the number of electrons transferred (n = 1, 2, or 4). For all three redox transitions, eqs 4 and 5 for $D_{\rm eff}$ and $C_{\rm o}$ led to almost identical values ranging from 3×10^{-7} to 4×10^{-7} cm^2 s^{-1} and from 1.5 to 1.7 M, respectively.

Since only one electron is involved in the formation of a mixed-valence W(VI,V) site within a silicotungstate unit, the concentrations of the local sites generated in each of the first two one-electron redox reactions (at the formal potentials of –0.225 and –0.370 V in Figure 4) are equal to ca. 1.5 M, as estimated above. The most negative process (at about –0.520 V) is known from solution electrochemistry to be a two-electron reduction per silicotungstate unit; more precisely, it should be viewed as two simultaneous one-electron reductions involving W(VI) local sites and leading to two W(V), rather than to one W(IV).[4]

Estimation of Heterogeneous Rate Constants for Electron Transfer at the Crystal/Electrode Interface. Cyclic voltammetry can be used to estimate standard (intrinsic) heterogeneous rate constants for quasi-reversible reactions by determining the variation of the difference between the cathodic and anodic peaks with the scan rate.[8] One must apply sufficiently fast scan rates to make the reversible, diffusion-controlled electrode reactions show some irreversibility, in the form of increased peak separation due to the finite rates of electron transfer. With this approach, one must be sure that the uncompensated resistance is sufficiently small to make the voltage drops negligible. The development of ultramicrodisk electrodes has made possible fast voltammetric measurements because of the smaller cell time constants associated with these electrodes.[15] The voltammetry at fast scan rates follows the behavior predicted for linear diffusion as long as $D_{\rm eff}t/r_{\rm o}^2 \ll 1$. In the case of the respective solid-state voltammetry of a single crystal, in which $D_{\rm eff} = 3 \times 10^{-7}$ cm^2 s^{-1} and $r_{\rm o} = 5 \times 10^{-4}$ cm, the time for the scan over the voltammetric wave (t) should be less than 100 ms. In other words, the scan rates should exceed ca. 2 V s^{-1}. Figure 7 shows that useful peak potentials can be obtained for all three silicotungstate redox transitions at 34 V s^{-1}. At this compromise scan rate, the overlap among peaks was not significant yet the respective pairs of cathodic and anodic peaks could be identified and were separated by more than 70 mV, permitting reliable calculation of the rate constant using the Nicholson method.[8] In the range of scan rates, from 4 to 34 V s^{-1}, the peak currents in cyclic voltammograms were proportional to the square root of the scan rate, as expected for linear diffusion to the planar electrode. Below 20 V s^{-1}, the peak separations were too close to the reversible value to allow for estimation of the rate constant. No background current correction (Figure 7) was necessary, as faradaic currents in the electrochemistry of silicotungstic acid single crystals were relatively high.

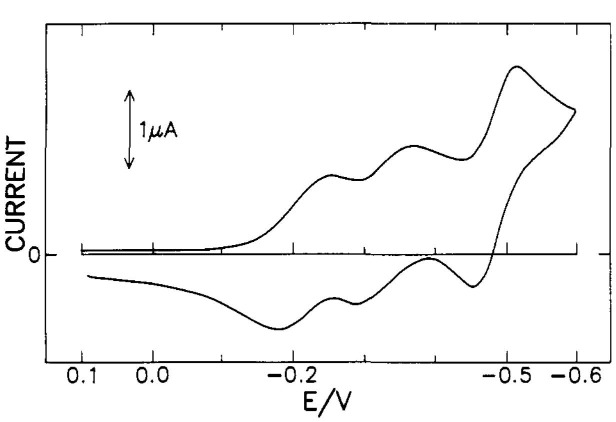

Figure 7. Fast-scan (34 V s^{-1}) solid-state cyclic voltammetry of the crystal at an ultramicroelectrode.

The basic kinetic equation in the Nicholson method[8] correlates a peak-separation-dependent kinetic parameter (ψ) with the standard heterogeneous rate constant k°,

$$\psi = (D_{\rm O}/D_{\rm R})^{\alpha/2}k_{\rm o}/[D_{\rm O}\pi v(nF/RT)]^{1/2} \qquad (6)$$

This relation takes a simplified form in solid-state voltammetry,

$$\psi = k_{\rm o}/[D_{\rm eff}\pi v(nF/RT)]^{1/2} \qquad (7)$$

because the effective diffusion coefficent ($D_{\rm eff}$) has the same value for the oxidized ($D_{\rm O}$) and reduced species ($D_{\rm R}$) and the transfer coefficient α disappears. The dependence of the kinetic parameter on the peak separation is tabulated elsewhere.[8] Although the nature of charge propagation in solid-state electrochemistry is different than that in solution electrochemistry, the solid-state voltammetric data meet all diagnostic criteria[8] for reversible (at slow scan rates) or quasi-reversible (at faster scan rates) processes. Thus, the use of the Nicholson method[8] is justified.

Special attention was paid to the ohmic drop, which in cyclic voltammetry increases the separation of the reduction and oxidation peaks in a similar way to that of slow heterogeneous kinetics.[8] The uncompensated resistance R in voltammetry at a disk-shaped ultramicroelectrode is dominated by the resistance near the electrode surface and is inversely proportional to the radius $r_{\rm o}$:

$$R = \rho/4\pi r_{\rm o} \qquad (8)$$

where ρ is the specific resistance of the solution in ohm cm. This equation was derived with an assumption of isotropy of the medium, which is expected to hold for the voltammetry of a single crystal with an ultramicroelectrode at a fast scan rate. The system is characterized by a very small diffusion layer and a large reference and working electrode separation ($>10r_{\rm o}$). Using the literature value for specific conductivity, reported to be ca. (1–2) $\times 10^{-1}$ ohm^{-1} cm^{-1} for Keggin-type heteropolyacids,[1a] the crystal's resistance is expected to be on the level 1 K ohm. This value is fairly low and is in agreement with the uncompensated resistance, typically not exceeding 5 K ohm, that was determined instrumentally with the BAS-100C analyzer. Under the conditions of cyclic voltammetry shown in Figure 7, the ohmic drop is not significant and is expected to increase the peak separation between the pairs of cathodic and anodic peaks by less than 5 mV.

To perform the kinetic analysis of the three silicotungstate redox transitions (Figure 7) using eq 7, the peak separation data were determined from the cyclic voltammograms recorded at scan rates in the range from 20 to 34 V s^{-1}. The experiments were typically repeated 10 times on independent crystal samples. For the optimum scan rate, 34 V s^{-1}, the following peak separations were obtained, 73, 79, and 49 mV (standard deviation ±3 mV) for the three redox transitions (starting from the most positive one). The k° values determined were in the ranges: (7–13) $\times 10^{-2}$, (5–8) $\times 10^{-2}$, and (2–3) $\times 10^{-2}$ cm s^{-1} for these redox reactions, taking n = 1, 1, and 2 for the three processes, respectively, in eq 7. Within experimental precision, the same values were obtained when the kinetic analysis was performed at other scan rates in the range 20–34 V s^{-1}. The upper limits for the rate constants account for the ohmic drop correction discussed above. The data are consistent with the fairly fast electron transfers in W(VI)/W(V) pairs in the crystal and the nonblocking character of the ultramicroelectrode/crystal interface. Injection of the first electron, at the most positive formal potential of –0.225 V, to the silicotungstic acid molecule is kinetically the fastest, while the last reaction, involving simultaneous injection of 2 electrons/silicotungstate molecule at the formal potential of –0.490 V, is somewhat slower.

Conclusions

We have demonstrated that potential step techniques and cyclic voltammetry at ultramicroelectrodes permit the determination of thermodynamic, kinetic, structural, and mass-transfer parameters in silicotungstic acid single crystals. This quantitative electroanalytical approach can be extended to the investigation of other ionically-conducting mixed-valence bulk materials. They must be characterized by a diffusive mechanism of charge propagation and negligible or correctable uncompensated resistance as well as by fast (i.e., not rate-limiting in the potential step experiments) electron transfer at the interface formed by the electrode surface and the electroactive sites in the crystal. These criteria require the presence of mobile structural counterions in large numbers in the solid, fast electron transfer between the redox sites, and good, reproducible contact between the working ultramicrodisk electrode and the material. Otherwise, the short-pulse experiment at an ultramicroelectrode would not produce a linear response in Q versus $t^{1/2}$ with a zero intercept. The pulse must be short enough to assure linear diffusion transport to a planar ultramicrodisk electrode but not so short as to introduce any kinetic limitations to the electron transfer.

A successful long-pulse chronoamperometric experiment requires development of a steady-state current, characteristic of spherical diffusion to ultramicroelectrodes. Slow effective diffusion may not allow establishment of the steady-state response, as recently reported for solid Prussian blue.[19] In the case of materials characterized by low diffusion coefficients ($D_{\text{eff}} < 10^{-10}$ cm^2 s^{-1}), fairly long pulses (even larger than 100 s with a 10-μm diameter ultramicroelectrode) would have to be applied to meet the requirement $4D_{\text{eff}}t/r_o^2 > 1$.

The relatively small currents that occur at ultramicroelectrodes facilitate their use for cyclic voltammetry at fast scan rates. As long as the charge propagation mechanism is described in terms of semiinfinite linear diffusion, the well-defined voltammetric peaks develop, and their separation increases with the scan rate, the Nicholson method[8] can be used to determine the heterogeneous rate constant for electron transfer between the mixed-valence redox sites and the electrode. This is the case for the silicotungstic acid single crystal.

The proposed approaches are designed for bulk materials. This fact imposes a certain requirement on the thickness of the material. For a given experimental time t, this thickness must exceed[8] the diffusion layer thickness $(2D_{\text{eff}}t)^{1/2}$. Such limitation applies, for example, to thin solid films of transition-metal hexacyanoferrates.[19]

The results were reproducible and this means that full contact must have always been achieved between the ultramicrodisk electrode and the crystal. As long as the crystal was not destroyed, the results were not dependent on the applied hand pressure to the electrode. None of the solid-state electroanalytical experiments required any background correction because faradaic currents, originating from highly abundant W(VI,V) redox sites, made background (adsorption and double-layer charging) responses relatively negligible.

Solid-state electronalysis seems to provide reliable information about the dynamics of charge propagation, the heterogeneous kinetics of electron transfer, and the concentration of mixed-valence redox sites in the silicotungstic acid single crystal. An important and perhaps surprising point is that the obtained values of effective diffusion coefficients are virtually the same for all three silicotungstate redox reactions (D_{eff} = (3–4) $\times 10^{-7}$ cm^2 s^{-1}). Moreover, the heterogeneous rate constants k° were not much dependent on the actual redox reaction.

It is worthwhile to keep these points in mind as one considers the mechanism by which charge can diffuse in the crystal. We can imagine several different possibilities: (a) the electron exchange among sites might be fast enough to make the motion of protons the limiting element; (b) the kinetics of intersite electron transfer might be limiting; and (c) the motion of charge might not involve an electron transfer at all but might be based on the displacement of monoatomic hydrogen resulting from the existence of (H^+ + e) pairs in the system, as has been postulated for hydrogen tungsten oxide bronzes, analogues of heteropoly blues.[4] A starting point for distinguishing these cases is to examine the relationship between diffusivity and conductivity.

If case (a) applies, the measured D_{eff} should be the diffusivity of protons in the lattice, and one ought to be able to project the ionic conductivity of the crystal from it. Upon consideration of (1) the Nernst–Einstein relation[20] between the diffusion coefficient and the molar ion conductivity λ,

$$\lambda = (z^2F^2/RT)D_{\text{eff}} \tag{8}$$

where z stands for the charge of an ion (z = 1); (2) the structural concentration of protons C_{H^+} in $H_4SiW_{12}O_{40}\cdot 31H_2O$, which is four times larger than the concentration of silicotungstate units (C_{H^+} = 6 M); and (3) the dependence between λ and the specific conductivity κ,

$$\lambda = \kappa/C_{H^+} \tag{9}$$

one obtains $\kappa = 1 \times 10^{-2}$ ohm^{-1} cm^{-1}, which is ca. 1 order of magnitude lower than the literature value for the analogous heteropoly 12-tungstate and molybdate acids ((1–2) $\times 10^{-1}$ ohm^{-1} cm^{-1}). Thus, the diffusion of protons is clearly not the limiting factor.

Apparently, charge propagation in the silicotungstate crystal is controlled either by the kinetics of electron hopping between the mixed-valence W(VI,V) sites or by the transfer of hydrogen atoms among silicotungstate units. The consistency in the value of D_{eff} for the different redox transitions makes the latter possibility attractive, but further research is necessary to establish the exact nature of this mechanism.

Our study shows that silicotungstic acid crystals are characterized by a fairly large population of redox sites and a high effective diffusion coefficient for mass transfer and therefore are potentially applicable as charge mediators in batteries, photoelectrochemical cells, solid-state sensors, and electrochromic devices.

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