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Solid-state electrochemistry of silicotungstic acid immobilized by sol-gel chemistry

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Abstract Voltammetry of silicotungstic acid (STA), $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, that was encapsulated in silica was performed in the absence of a contacting liquid phase. Two one-electron reductions that are separated by 200 mV were observed, which is the same behavior as in aqueous solution. At scan rates, ν , below 10 mV s^{-1} with a $10 \mu\text{m}$ dia. carbon fiber indicator electrode, plateaus with limiting currents which are independent of ν were observed, which is indicative of spherical diffusion from a field that is much larger than the electrode area. At $\nu > 20 \text{ V s}^{-1}$, peaks were observed with currents directly proportional to $\nu^{1/2}$. For a gel aged for 2 days, an effective diffusion coefficient, D_{eff} , of $3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ was estimated by voltammetry and chronoamperometry; the concentration of the redox sites thereby determined was about 0.5 M. The D_{eff} values that were obtained in this study were larger than expected for a solid electrolyte, which suggests an important role of residual water. In support of this model, gels that were aged in a humidistat at 33% humidity at room temperature for 2 and 5 days lost 16% and 13%, respectively, of their mass when dried at 120° .

Key words Silica · Voltammetry · Polyoxometalate · Diffusion · Solids

Introduction

The redox chemistry of heteropolyacids has been studied by voltammetry of these species as solutes in aqueous

solution, as components of films on electrodes in contact with a liquid phase, and as single crystals that are not in contact with a bulk liquid phase. The voltammetry of phosphotungstate or tungstosilicate as solutes in acidic solution produces three reversible reduction peaks corresponding to two one-electron steps followed by an additional two-electron process [1, 2]. Similar results were obtained when these substances were immobilized in composite films with organic polymers on glassy carbon electrodes [2].

Previous solid-state electrochemical studies of these heteropolyacids have been performed on single crystals. In this regard, these Keggin-type heteropolyanions have chemistry that is particularly well suited to interrogation by solid-state voltammetry. They have a rigid structure with twelve WO_3 groups around a central, usually non-electroactive, heteroatom in an oxidized form (e.g., phosphate, silicate). Partial reduction of W^{VI} sites produces a mixed-valence ($\text{W}^{\text{VI,V}}$) microstructure, through which fast electron transfer is possible. Moreover, they have a secondary “pseudo-liquid” structure containing exceptionally mobile protons [1]; this network is important in retaining electroneutrality during redox transitions.

Kulesza and Faulkner described application of various electroanalytical techniques for kinetic (heterogeneous rate constant for electron transfer) and analytical (redox centers concentration and effective diffusion coefficient) characterization of silicotungstic acid (STA) single crystals in the absence of a bulk liquid [3, 4]. Phosphotungstic acid (PTA) single crystals were studied in a similar manner by Kulesza and Karwowska [5]. The general voltammetric results were the same as those observed in liquid-phase experiments, namely the reductions proceed in reversible steps that are well separated. An important finding was that these single crystals have large $\text{W}^{\text{VI,V}}$ mixed-valence redox center populations and high effective diffusion coefficients; for example, with PTA, the values are 1.45 M and $4.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively. The corresponding results for STA were 1.5 M and $2.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

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The above-cited results suggest that these heteropolyanions are suited for mediating electrochemical reductions. Indeed, in the liquid phase, the presence of a heteropolytungstate in which a tungsten atom replaces an iron atom, $\text{FeSiW}_{12}\text{O}_{39}^{5-}$, promotes the electrochemical reduction of nitrite, nitric oxide, and hydrogen peroxide [6–8].

The electrocatalysis of the reduction of bromate with $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ as a solid electrolyte is described by Kulesza and Faulkner [9]. This report, along with the demonstration by Karwowska and Kulesza [10] that $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ and STA single crystals are structurally and electrochemically similar, suggests that heteropolyacids could serve as electrocatalysts in solid-state voltammetry. This supposition is tested in the present study where the heteropolyacids are encapsulated in solids prepared by sol-gel chemistry. These solids often are termed “xerogels” when, as in this study, they are dried under ambient laboratory conditions. As defined, the term usually is a misnomer in that various forms of water remain in the resulting solid [11].

As detailed in a recent review [12], gels, xerogels and related solids that are prepared by sol-gel chemistry have been investigated as cathodes for batteries and fuel cells; however, they have been the subject of only a few studies where they host substances to be studied by voltammetry in the absence of a contacting liquid phase. Such applications require the product of sol-gel chemistry, which in the case of dried gels includes pore water, to serve as the electrolyte. Perhaps the first report on analytical voltammetry in inorganic gels was by Oliver et al. [13]. The cyclic voltammetry of ferrocene was followed as silica was formed by gelation of tetraethyl orthosilicate. Over a wide time window, during which the water content was steadily decreasing, the peak currents remained constant [13].

We investigated the utility of dried gels of vanadium pentoxide as solid electrolytes for voltammetry in the absence of a contacting liquid phase [14]. The cell consisted of an interdigitated microelectrode array (IME) that was coated with vanadium pentoxide which, in turn, hosted $\text{Fe}(\text{phen})_3^{3+}$, where phen is 1,10-phenanthroline. Cyclic voltammograms of $\text{Fe}(\text{phen})_3^{3+}$ that were obtained with the cell placed in an argon atmosphere were virtually identical to those obtained for $\text{Fe}(\text{phen})_3^{3+}$ in aqueous solution [14]. The currents were independent of the water content of the solid over a wide range; however, the driest solids yielded lower currents than those which contained intentionally added water. When the Pt indicator electrode of the IME was modified with a mixed-valence ruthenium oxide film, this system served as an amperometric sensor for gaseous ammonia with the current presumably developed from the oxidation of ammonia [15].

The present study was initiated primarily to determine whether the attractive electrochemical characteristics of silicotungstic acid in the form of a single crystal are retained in a solid matrix prepared by sol-gel chemistry. Presumably, the porosity of these solids

makes them more suited than a single crystal for application to amperometric sensors for gas-phase analytes. Secondly, from our previous work and a review of the literature, we have hypothesized that silica prepared by sol-gel chemistry with drying under ambient conditions results in a rigid matrix that serves as a water-like system in terms of voltammetry of hosted materials. This study tests this suggestion as well.

Experimental

Except as noted, all chemicals were ACS Reagent Grade and were used without further purification. Silicotungstic acid (STA, analyzed reagent) was from Fluka, and tetramethyl orthosilicate (TMOS, 98% purity) was from Aldrich. Solutions were prepared from house-distilled water that was further purified with a Barnstead NANOpure II system.

The silica monoliths were prepared from a mixture containing 0.5 mL of TMOS, 0.5 mL of CH_3OH , 0.5 mL of 0.1 M STA in 0.1 M HCl, and 0.5 mL of 0.2 M KCl. Blanks were prepared in the same manner except that STA was absent. The mixtures were stirred for 2 h in a fume hood, after which they were in the form of a viscous liquid. An assembly holding a glassy carbon counter and an Ag/AgCl reference electrode (Fig. 1) was covered with 400 μL of this liquid. By drying for at least 24 h at room temperature in a 33% humidity atmosphere, the coating was converted into a solid. This procedure produces cylindrical monoliths with an estimated volume of $9 \times 10^{-5} \text{ dm}^3$ (5 mm dia.).

The electrochemical measurements were performed at a 10- μm dia. Bioanalytical Systems (BAS) carbon fiber that was pressed against the outer layer of the semi-rigid cylinder (Fig. 1). In all cases where the gel was dried as described previously for more than 5 days, the material was too rigid for reliable contact with the fiber electrode. In these cases 5 μL of water was spotted on the silica, the fiber was pressed onto the softened material, and the system was permitted to re-equilibrate for 1 h prior to initiating experiments. During this time, the excess water either evaporated or soaked into

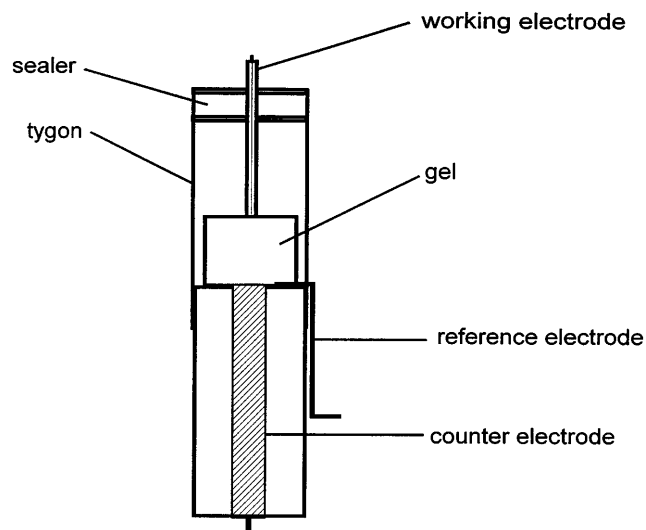


Fig. 1 Design of the electrochemical cell. Working electrode, 10 μm -dia. carbon fiber disk; reference electrode, AgCl-coated Ag wire; counter electrode, 3-mm dia. glassy carbon on which the silica is deposited. The silica monolith is a ca. $9 \times 10^{-5} \text{ dm}^3$ cylinder with a diameter of 5 mm

the silica. Microscopic interrogation revealed that the original gels and those to which water was added were homogeneous; there was no evidence of a residual layer of water when the observation was made 1 h after the addition of 5 μL of water.

The electrochemical experiments were performed with a Model 750 Electrochemical Workstation (CH Instruments). Liquid-phase experiments were performed in a three-electrode cell with an Ag/AgCl/3 M NaCl reference electrode (BAS) and 3-mm diameter glassy carbon working electrode (BAS). Solid state experiments were performed with the cell depicted in Fig. 1. Electrodes were polished before use with 0.3- μm alumina with water as the lubricant. The thermogravimetric analysis measurements were made with a Perkin Elmer TGA 7 system. All chemical and electrochemical procedures were performed at room temperature, 20 ± 2 $^{\circ}\text{C}$.

Results and discussion

Preliminary cyclic voltammetry (CV) experiments were performed to establish that silicotungstic acid (STA) that is incorporated in a silica matrix is electroactive and to compare the general redox behavior to that observed in aqueous solution. In 0.1 M HCl, CV of 10 mM STA at 50 mVs^{-1} (Fig. 2A) produced two well-defined, reversible peaks on a 3-mm dia. glassy carbon electrode, which agreed with the voltammetry reported previously [2]. Peak currents for both reductions were the same, and the potential difference between the peaks was 236 mV. With STA in silica as the sample, CV at 5 mVs^{-1} with a 10- μm dia electrode yielded plateaus rather than peaks (Fig. 2B); however, at 30 Vs^{-1} , the CV was nearly identical to that in aqueous solution (Fig. 2C). At 30 Vs^{-1} , the two reduction steps, which appear to be reversible, were separated by 200 mV and had the same limiting currents. The actual potentials of the processes in Fig. 2A and C cannot be compared because of the difference in the reference electrodes.

The shape of the voltammogram in Fig. 2B is characteristic of cases where the diffusional field is much larger than size of electrode, and hemispherical flux of redox species to the planar electrode is observed. In such cases, the dimensionless parameter, τ , is much larger than 1, where $\tau = 4D_{\text{eff}}t/r^2$ (where D_{eff} is an effective diffusion coefficient, t time; and r the electrode radius) [16, 17]. As a first step in testing this mass transport model, the influence of scan rate, ν , on the current in the first reduction step was examined (Fig. 3). Consistent with this model, with $\nu < 10 \text{ mVs}^{-1}$ the limiting current was independent of ν .

At $\nu > 20 \text{ Vs}^{-1}$, voltammetric peaks rather than plateaus are developed, which demonstrates that the condition $\tau \gg 1$ no longer applies. The shape of the plot in Fig. 3 is indicative of a transition from a regime where the above-described spherical field is important to one where the flux from a cylinder perpendicular to the disk electrode is dominant (semi-infinite linear diffusion). In the latter case, the peak current, i_p , is directly proportional to $\nu^{1/2}$. Evaluation of the data at $\nu > 20 \text{ Vs}^{-1}$ (5 points) by a linear-least-squares fit of i_p to $\nu^{1/2}$ yields a slope of $1.47 \pm 0.07 \text{ nA} \cdot \text{s}^{1/2} \cdot \text{mV}^{-1/2}$ and a correlation

coefficient of 0.995. The intercept is 3% of the current developed at 50 Vs^{-1} .

The steady-state voltammograms developed at slow scan rates were analyzed by plotting $\log[(i_l - i)/i]$ vs E , where i_l is the limiting current and E represents potential values on the rising portion of the voltammogram in Fig. 2B. A 58-mV per decade slope was obtained, which is consistent with that for a Nernstian, one-electron reduction. From comparison of limiting currents, it is surmised that the second reduction step also is a one-electron step. These results, along with the difference between the potentials of the two processes, demonstrate that the voltammetry of STA is the same in the silica as

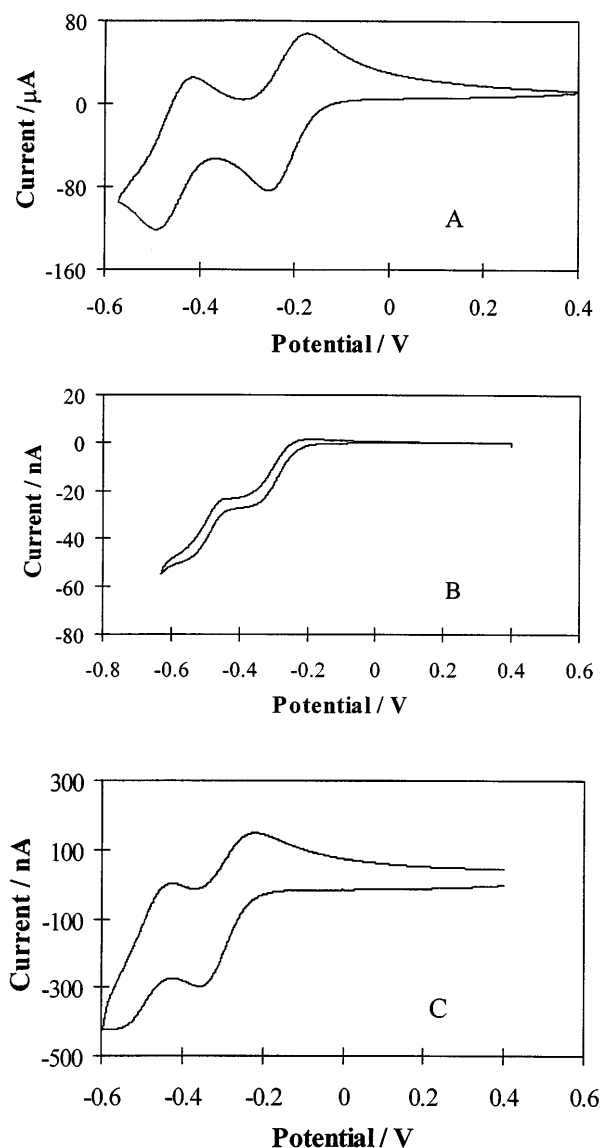


Fig. 2A–C Cyclic voltammetry of **A** 10 mM STA in 0.1 M HCl at a glassy carbon disk electrode (dia. = 3 mm) in a liquid phase system with $\nu = 50 \text{ mVs}^{-1}$; **B** ca. 0.5 mol dm^{-3} STA in a silica monolith at a carbon fiber electrode (dia. = 10 μm) with $\nu = 5 \text{ mVs}^{-1}$; and **C** same as **B** except $\nu = 30 \text{ Vs}^{-1}$

in aqueous acidic solution. In this regard, it should be noted that the silica is formed by an acid-catalyzed reaction, so the environment of the monolith, which includes residual water, is probably acidic as well.

As detailed above, increasing v to values above 20 Vs^{-1} results in a transition from spherical diffusion with $\tau \gg 1$ to a time domain that is sufficiently short to allow the semi-infinite linear diffusion model of flux to the disk electrode to be followed. When these two limiting cases can be observed, the determination of D_{eff} and of C_0 , the apparent concentration of the redox sites, can be made readily [18]. The limiting (steady-state) current, i_l , which is developed at slow scan rates is described by Eq. 1:

$$i_l = 4nFD_{\text{eff}}C_0r \quad (1)$$

with two unknown variables, C_0 and D_{eff} .

As the scan rate is increased, peaks (Fig. 2C) rather than the steady-state currents of Fig. 2B are observed. As detailed above, the peak currents, i_p , approach proportionality to $v^{1/2}$. Moreover, the position of the peaks on the potential axis is nearly independent of scan rate. Regarding the latter, at scan rates over the range $20\text{--}50 \text{ Vs}^{-1}$, the potential of the first cathodic peak varies by only 18 mV, and the difference in potential between that peak and the corresponding anodic peak of Fig. 2C changes by only 26 mV. At a scan rate of 30 Vs^{-1} , the ratio of the anodic-to-cathodic currents for the one-electron reduction step is 1.0. These data demonstrate that the first reduction step approaches a reversible process with a current limited by D_{eff} , and, therefore, are predicted by the Randles-Sevcik equation (Eq. 2)

$$i_p = (2.69 \times 10^5)n^{3/2}\pi r^2 D_{\text{eff}}^{1/2} v^{1/2} C_0 \quad (2)$$

where π , F , r , n , and v are known constants or measured parameters. Solution of this pair of equations yields [18]:

$$C_0 = (4Fi_p^2)/[i_l v n^2 (2.69 \times 10^5)^2 \pi^2 r^3] \quad (3)$$

$$D_{\text{eff}} = [nv(2.69 \times 10^5)^2 \pi^2 r^2 i_p^2]/(16F^2 i_p^2) \quad (4)$$

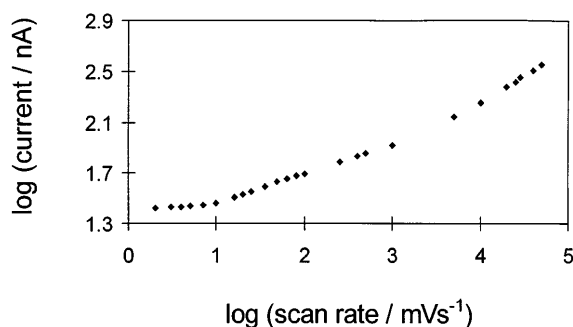


Fig. 3 Influence of scan rate effect on the cyclic voltammetric current for the reduction of STA incorporated in a silica monolith. The general conditions are those in Fig. 2B

With the gel that was aged for 2 days, the values of D_{eff} and C_0 that were obtained were $3.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and 0.4 M, respectively (Table 1). For comparison, D_{eff} was $2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for a measurement on 10 mM STA in 0.1 M HCl (Fig. 2A).

The general results obtained by cyclic voltammetry were confirmed by chronoamperometry. The chronoamperometry experiments were performed with the potential stepped from 0.0 to -0.41 V . The electrolysis potential, -0.41 V , is approximately 50 mV more negative than the first reduction peak and 150 mV more positive than the second reduction peak, so a one-electron transfer to STA will occur. The data were analyzed by a curve-fitting procedure that was first described by Shoup and Szabo [19] and was applied to solid-state electrochemistry by Cox and Gorski [20]. The current-time decay in the range 1.2 ms to 5 s was fitted to the expression (80-point fit):

$$i/4nFD_{\text{eff}}C_0r = 0.7854 + 0.8862\tau^{-1/2} + 0.2146 \exp(-0.7823\tau^{-1/2}) \quad (5)$$

The values of D_{eff} and C_0 thereby obtained were $2.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and 0.6 M (Table 1).

A second chronoamperometric data analysis procedure also was used. At short times ($t < 36 \text{ ms}$), the current-time decay obeyed the Cottrell Equation:

$$i_d = nF\pi^{1/2}r^2 D_{\text{eff}}^{1/2} C_0 t^{-1/2} \quad (6)$$

At $t \geq 30 \text{ s}$, a steady state current, i_{ss} , was obtained (Fig. 4). Here, i_{ss} obeys the same expression as i_l in Eq. 1. By solving Eqs. 1 (except using i_{ss}) and 6, the following expressions are obtained:

$$D_{\text{eff}} = i_{\text{ss}}^2 \pi r^2 / (16a^2) \quad (7)$$

$$C_0 = 4a^2 / (i_{\text{ss}} n F \pi r^3) \quad (8)$$

where a is $nF\pi^{1/2}r^2 D_{\text{eff}}^{1/2} C_0$, the slope of the plot of i_d vs $t^{-1/2}$ in Eq. 6. By solving Eqs. 7 and 8, values for D_{eff} and C_0 of $2.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and 0.5 M, respectively, were obtained (Table 1).

Table 1 Influence of aging on the voltammetry of silicotungstic acid in silica

Analysis by:	Age/days	Wt% water	$D_{\text{eff}} \times 10^7 / \text{cm}^2 \text{ s}^{-1}$	$C_0 / \text{mol dm}^{-3}$
Eqs. 3,4	2	16	3.2	0.4
Eqs. 7,8			2.6	0.5
Eq. 5			2.7	0.6
Eqs. 3,4	3	14	3.5	0.6
Eqs. 7,8			3.6	0.6
Eq. 5			2.7	0.7
Eqs. 3,4	4	13	4.0	0.6
Eqs. 7,8			4.2	0.6
Eq. 5			2.8	1.0
Eqs. 3,4	5	13	3.7	0.5
Eqs. 7,8			3.8	0.6
Eq. 5			2.8	0.8

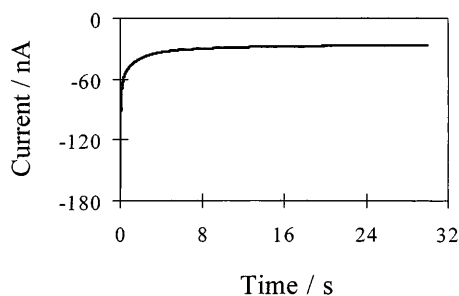


Fig. 4 Long-pulse (30 s) chronoamperometry of STA encapsulated in silica. The cell is that shown in Fig. 1. The potential step was from 0.00 V to -0.41 V

The value of D_{eff} obtained with the gel is higher than expected for that of a solid-state electrolyte. For example, solid-state voltammetry of Prussian Blue films yields D_{eff} in the range of 10^{-8} – 10^{-9} $\text{cm}^2 \text{s}^{-1}$ [21]. The higher value in the gel suggests that the solid, although rigid and visually dry, contains sufficient water and electrolyte (e.g., residual acid) to support facile mobility of the charge carrier (presumably proton). To test this interpretation, thermogravimetric analysis was performed on a gel that was aged for 2 days under the same conditions as employed for preparing the silica electrolyte. Heating at 120 °C caused a 16% loss of mass (Table 1), which supports the model that this gel can be considered “rigid water” in terms of its role as a supporting electrolyte. This does not suggest that STA is mobile within the matrix; that is, D_{eff} is not the physical diffusion coefficient of STA in silica, but rather it is a term that is related to electron self-exchange supported by proton mobility [4, 5] with perhaps some contribution from physical diffusion.

Additional evidence that physical diffusion in the silica was limited was obtained by performing a test of whether the heteropolyacid is leached from silica when it is contacted to a liquid. A silica monolith was prepared as described in the Experimental section, except that electrode contact was not made. It was dried for 3 days at 33% humidity (using a saturated MgCl_2 solution as a chemical humidistat) and removed from the mold. The monolith was placed in contact with 10 mL of deionized water. After leaching for 2 h, the liquid was analyzed by argon inductively coupled plasma atomic emission spectrometry; the heteropolyacid therein was quantified by a calibration curve. A quantity corresponding to less than 4% leaching was obtained. Considering that contact with an external aqueous solution will hydrolyze the surface Si–O bonds, thereby releasing a portion of an encapsulated material, this low value supports the suggestion that the physical diffusion of STA in silica is limited. However, as stated above, some contribution of physical diffusion to D_{eff} is undoubtedly occurring, in that the water content of the silica gel used in these experiments is rather high.

The influence of age of the silica on the voltammetry, on its water content, and on the values of D_{eff} and C_0 for

STA encapsulated therein was investigated. The results are summarized in Table 1. The results are constant over the period of 2–5 days; however, from cyclic voltammetry, it is apparent that the physical nature of the gel has changed. For example, cyclic voltammograms obtained under the Fig. 2 conditions with the carbon fiber indicator electrode simply pressed against the gel that was aged for 5 days yielded peaks rather than plateaus at 5 mVs^{-1} , and resolution of the first two-electron reduction steps was not observed at $\nu > 10 \text{ Vs}^{-1}$. Moreover, the required limiting conditions at short and long times in chronoamperometry are not attained. Hence, the data cannot be analyzed for D_{eff} and C_0 .

The problem of obtaining sufficient contact to make measurements at fast scan rates is corrected by spotting $5 \mu\text{L}$ of water on the gel, pressing the fiber electrode into the “softened” portion of gel, and allowing the added water to disperse into the gel and/or to evaporate. Under microscopic interrogation, the gel appears homogeneous; there is no evidence that the added water remains as a separate phase after 1 h. The quantity of the added water is negligible in comparison to the overall solvent content of these gels, so even the portion that does not evaporate is not expected to perturb the electrochemical behavior.

The veracity of the above procedure for contacting the carbon fiber electrode to the gel was supported by a set of measurements on a gel that was aged for 2 days. Measurements of D_{eff} and C_0 by CV (Eqs. 3 and 4) and chronoamperometry (Eqs. 7 and 8) yielded results that are consistent with those obtained without addition of water when gels were studied both without addition of water and with addition of $5 \mu\text{L}$ of water but waiting for 15 min and for 1 h prior to obtaining data. With addition of water as described above, the following values for D_{eff} (and C_0) were obtained: 15-min delay, $5.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (0.4 M); 1 h delay, $6.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (0.4 M). A direct measurement prior to adding water yielded D_{eff} and C_0 results of $3.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and 0.5 M, respectively, when cyclic voltammetry was the measurement technique.

The above series of D_{eff} values are essentially equivalent. With the measurement techniques that are used, it is important to note that these results are, in fact, estimates. The active electrode area is the source of the greatest uncertainty. Not only can the area be altered by pretreatment steps, but also the silica backbone may block an unknown fraction of the surface. It is unlikely that these factors cause a systematic error of more than 10–20% given the consistency of the results over a several-month study during which several electrodes were used and the agreement of calculations based on an intermediate time regime (using Eq. 5) with those based on limiting behavior at long and short time regimes. Second, the experimental procedure (whether added water is necessary or not to make contact) required to obtain useful data is dependent on the procedure for preparing the gels. In this regard, preliminary studies (not reported) suggest that gels

based on hydrolysis of tetraethyl orthosilicate are more suited than those used in the present study for long term studies without use of water to assure contact. Yet, the parameters for STA that are obtained are consistent with those in this report. A study of electrochemical behavior as a function of gel preparation will be the topic of a future report.

Conclusion

This study has demonstrated that silica prepared by sol-gel chemistry with drying at room temperature for up to 5 days retains sufficient moisture to cause the voltammetry of materials hosted therein to have effective diffusion coefficients nearly as high as in the liquid phase. Yet, these materials have general physical properties of solids, e.g. a tendency to fracture and the capability to be formed in a variety of shapes. Silicotungstic acid that is encapsulated in silica retains the redox characteristics that it has in a liquid phase.

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