

# Electrochemistry: An Important Tool To Study and Create New Sol–Gel-Derived Materials

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## ABSTRACT

Electrochemical methods can be used to study the structure and properties of sol–gel-derived materials. In addition, they can be used to create new materials and nanostructures. In this Account, these methods and the resulting information and materials obtained from them are described.

## I. Introduction

Electrochemistry plays an important role in sol–gel-based research.<sup>1–4</sup> In chemical sensor development, an electrode has often been used as the transducer to record the flow of electrons when an analyte or reagent gets oxidized/reduced. A well-known example is the preparation of a glucose sensor where glucose oxidase is trapped in a sol–gel-derived thin film. Glucose in solution diffuses into the film to react with entrapped glucose oxidase to generate hydrogen peroxide, which is then electrochemically oxidized.<sup>5</sup> The current flowing through the electrode relates to the concentration of glucose in solution. Electrochemistry is also the driving force behind the development of alternative energy devices. A specific unique example involves the development of 3-D batteries by merging sol–gel chemistry, templating, and electrochemistry.<sup>6–8</sup> In the reverse case, sol–gel chemistry has been invaluable to electrochemists because it provides a simple means to fabricate stable, reusable electrodes for electroanalytical applications.<sup>9–11</sup> In a specific example, Lev and coworkers prepared a viscous carbon powder sol packed in a glass tube and polished flat to yield an electrode with better properties than many traditional electrodes.<sup>10,11</sup> A number of recent reviews on the cross-section of electrochemistry and sol–gel chemistry can be found in the literature.<sup>1–4</sup> Here, the focal point will be on how electrochemistry can be used to *study and create* new sol–gel-based materials. The specific focus will be on recent electrochemical studies that aim to (1) understand and control diffusion in sol–gel-derived gels and (2)

understand how the “ancient” technique of electrodeposition can be used to create new sol–gel-based materials.

## II. Electrochemical Characterization

**A. Historical Perspective.** Sol–gel-derived materials have been around for more than a century.<sup>12</sup> In the mid 1980s, it was shown that molecules can be entrapped in the porous framework by simply doping them into a sol prior to its gelation.<sup>13</sup> The retained molecule was shown to have many of the same properties that it did when it was in a solution.<sup>14</sup> Since this time, the field of sol–gel chemistry has exploded with numerous studies on understanding the structure and gelation of these porous hosts, as well as their applications in the areas of chemical sensors, catalysis, and solid-state electrochemical devices.<sup>14–21</sup>

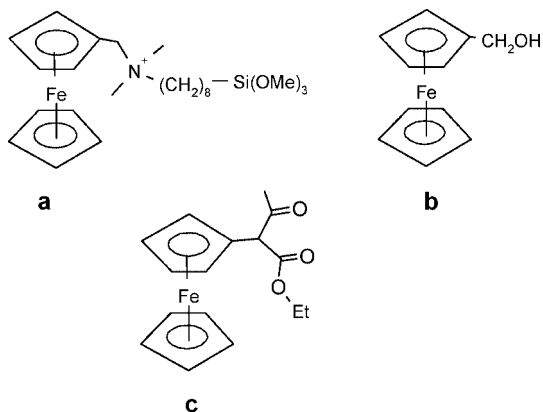
A number of different electrochemical methods have been used to obtain information about the gelation process and the mobility and reactivity of entrapped reagents including cyclic voltammetry (CV) and chronoamperometry (CA),<sup>22–32</sup> ac impedance,<sup>33</sup> and electrogenerated chemiluminescence (ECL).<sup>34–36</sup> In many of these studies, the hydrated gel serves as a “solid electrolyte” allowing ions to freely move to and from the electrode surface. By eye, these materials look like solids in that when they are tilted or turned up side down, they retain their original shape. However, microscopically, they behave as an open liquid. Murray and Zhang were among the first to study the gelation process by inserting a 2-mm diameter glassy carbon electrode into a sol containing a redox active reagent (ferrocenylmethyltrimethylammonium ion) and measuring the current that flowed before, during, and after gelation.<sup>37</sup> They used fluoride as the catalyst (which results in fast gelation) and were able to show that the current drops by a factor of  $\sim 2$  near gelation and then reaches a steady state, followed by a further small drop. The total time frame of the experiment was a few days. Audebert and coworkers performed similar studies around that same time in silica and titania gels.<sup>22,23</sup> In their work, they also inserted an electrode assembly into a sol and recorded the oxidation/reduction of ferrocene derivatives throughout gelation and drying. Examples of redox probes used in these studies included one that would not interact strongly with the matrix (ferrocene methanol, **b**), one that could be hydrolyzed and condensed with the alkoxide precursors (ferrocene trimethoxysilyl derivative, **a**), and one that could coordinate with the forming network (ferrocene–acetylacetonate (acac), **c**).<sup>23</sup>

One inherent disadvantage (or complication) with many of these studies is that a conventional-sized electrode (metal diam  $\geq \sim 1$  mm, electrode diam  $\sim 3$ – $5$  mm when encased in plastic), along with a conventional-sized reference ( $> 1$  mm) and auxiliary electrode ( $\sim 1$  mm), was used. The length of time that the gel can be dried was limited because the gel cracked, separated, or both from

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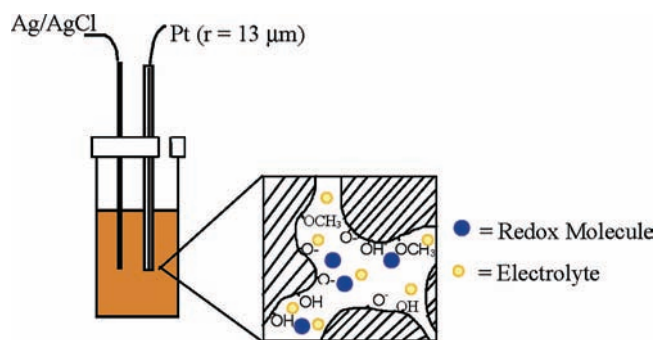
these rather large electrodes. Furthermore, the measurement of a diffusion coefficient independent of concentration, which becomes very important at long drying times because of volume changes, cannot easily be done with conventional-sized electrodes. The use of ultramicroelectrodes solved many of these problems.



### B. Ultramicroelectrode Electrochemistry: An Introduction.

Electrochemistry with ultramicroelectrodes provides an enormously powerful way to measure the diffusion coefficients of redox molecules in “nontraditional” environments.<sup>38</sup> With regard to sol–gel materials, the use of ultramicroelectrodes (micrometer dimensions) has a number of important advantages not found in conventionally sized electrodes: (1) the diffusion coefficient ( $D$ ) of an entrapped redox molecule can be measured without having to know the concentration (important since concentration changes during long-term drying); (2) their small size (metal diam  $<0.05$  mm, electrode size with insulation  $\sim 0.1$ – $1$  mm) minimizes gel cracking during drying (important because the gels are rigid, unlike those formed from organic polymers); (3) their reduced double-layer capacitance enables high sweep rates to be utilized (important to verify the integrity of the gel–electrode interface); (4) reduced ohmic drop (reduces the need to add supporting electrolyte to the sol–gel); (5) a two-electrode geometry can be used (ultramicroelectrode and reference (diam  $< 1$  mm), which also helps minimize gel cracking).

The Collinson group<sup>24–26,28,29</sup> has predominately utilized ultramicroelectrode electrochemistry to understand how entrapped reagents diffuse and interact with the complex surface of channels and pores in gels. The goals have been to understand diffusion in constrained, hydrated solids and to develop ways to control it. Diffusion in sol–gel-derived gels can be more complex than that in fluids. Factors that can influence diffusion in these solids include pore size, pore size distribution, tortuosity and connectivity, and the type and extent of surface interactions the entrapped molecules have with the walls of the silica host.<sup>28,29,39–43</sup> The manner in which entrapped reagents move, interact with pore walls, and react with other analytes is of utmost importance to their application in chemical sensor development or as solid-state electrochemical devices.



**FIGURE 1.** Schematic representation of the electrochemical cell and an enlargement of a fluid-filled pore in the gel. Not drawn to scale. The channels in the gel are much larger than the dimensions of the ions and molecules.

**C. Characterization of Dopant Mobility.** In this electrochemical system, the sol–gel containing an immobilized ultramicroelectrode (typically Pt, radius =  $13 \mu\text{m}$  or smaller) and a reference electrode (typically AgCl-precoated Ag wire, radius  $< 0.5$  mm) serves as the electrochemical cell. Supporting electrolyte (i.e., KCl) and a redox probe (ideally a substance that is chemically and electrochemically reversible) are added to the sol along with the electrodes prior to its gelation. Figure 1 shows a simplified view of the electrochemical cell used in these experiments.

Cyclic voltammetric (CV) and chronoamperometric (CA) curves are collected hourly or daily while it is still a sol and then after gelation and during drying. Figure 2 shows slow scan CV curves and a corresponding normalized CA graph for gel-entrapped cobalt(II) tris(bipyridine).<sup>28</sup> From the electrochemical data, the diffusion coefficient of the entrapped redox probe can be obtained. Specifically, cyclic voltammetry at slow scan rates ( $< 10$  mV/s) provides the steady-state limiting current ( $i_{\text{ss}}$ ). The CA response when normalized by the steady-state current and fit to an appropriate equation<sup>44</sup> provides  $D$ ,

$$i_{\text{ss}} = 4nFrCD \quad (1)$$

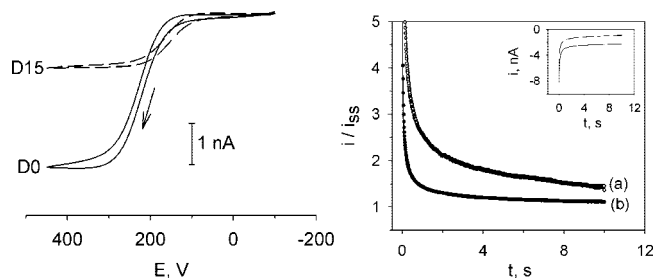
$$\frac{i_{\text{CA}}}{i_{\text{ss}}} = \frac{\pi}{4} + \frac{\pi^{1/2}}{4} \left( \frac{Dt}{r^2} \right)^{-1/2} + \left( 1 - \frac{\pi}{4} \right) \exp \left( -\frac{\pi^{1/2} - 8\pi^{-3/2}}{4 - \pi} \left( \frac{Dt}{r^2} \right)^{-1/2} \right) \quad (2)$$

$$\frac{i_{\text{CA}}}{i_{\text{ss}}} = 0.7854 + 0.4431 \left( \frac{Dt}{r^2} \right)^{-1/2} + 0.2146 \exp \left( -0.3911 \left( \frac{Dt}{r^2} \right)^{-1/2} \right) \quad (3)$$

where  $F$  is Faraday’s constant,  $C$  is concentration,  $r$  is electrode radius,  $n$  is the number of electrons, and  $t$  is time. Equations 2 and 3 are different forms of the same equation. Either the data can be fit to eq 2 (or 3) or the method of Bard and coworkers<sup>45</sup> can be used whereby eqs 1 and 2 are combined to yield eq 4 after simplifying assumptions are made (valid at long times):

$$\frac{i_{\text{CA}}}{i_{\text{ss}}} = 1 + \left( \frac{2r}{\pi^{3/2}} \right) (Dt)^{-1/2} \quad (4)$$

A plot of  $i_{\text{CA}}/i_{\text{ss}}$  vs  $t^{-1/2}$  yields a straight line with a slope related to  $D$  and an intercept of 1. If the electrode starts

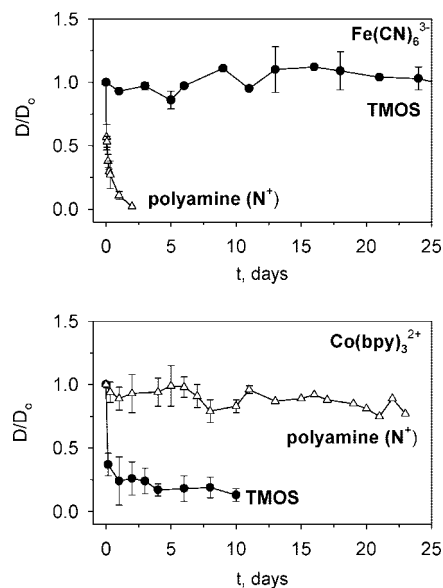


**FIGURE 2.** Cyclic voltammograms (2 mV/s) and normalized amperometric response for cobalt(II) tris(bipyridine) encapsulated in a sol-gel prepared from tetramethoxysilane using NaF as the catalyst. The walls of the silica matrix will be negatively charged under these conditions ( $\text{pH} > 3$ ). Left panel: (D0) just prior to gelation, (D15) 15 days after gelation and subsequent slow drying under a high humidity environment ( $\sim 70\%$  RH). Right panel: (a) 2 hours and (b) 24 days after gelation and subsequent drying. The inset shows the original current-time (CA) transients. Solid lines represent nonlinear regression fit to the experimental data (points),  $R^2 = 0.98$ .

separating from the gel, the intercept in eq 4 starts deviating from unity and the regression coefficient obtained by fitting the data to eq 2 will be less than the expected value of one (i.e., 0.95–0.97). By measuring the diffusion coefficient of redox molecules with differing size and charge and during different stages of drying, significant information can be obtained about the importance of size and charge on the diffusion of reagents in gels.

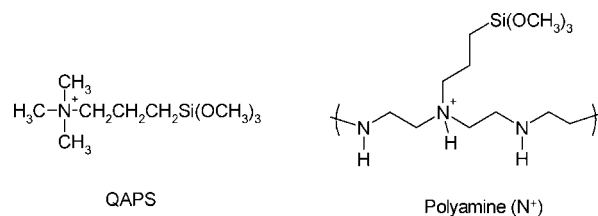
Examples of redox probes utilized by Collinson and coworkers can be broken up into three main categories: (1) those that are positively charged, (2) those that are negatively charged, and (3) those that are neutral but able to hydrogen bond with the matrix.<sup>25</sup> Those that proved to be the most interesting from a sol-gel perspective were those molecules that were negatively charged, that is, potassium ferricyanide ( $\text{Fe}(\text{CN})_6^{3-}$ ) and potassium octacyanomolybdate(IV) ( $\text{Mo}(\text{CN})_8^{4-}$ ).<sup>24,25</sup> When these were doped in a matrix formed from tetramethoxysilane (TMOS), the diffusion coefficient was found to be the same as it was in solution, and furthermore, it did not change at all through a 20–40 day drying period (slow drying under high humidity).<sup>24,25</sup> In contrast, cationic redox molecules showed a  $\frac{1}{2}$  to 1 order of magnitude drop in their apparent diffusion coefficient under a similar (or shorter) drying period. These results suggest that diffusion is governed by interactions between the entrapped cationic guest and the negatively charged walls of the sol-gel host. Specifically, negatively charged molecules will reside in the center of the fluid-filled pore and move at rates similar to the rates at which they move in solution. Positively charged molecules, however, will electrostatically interact with the walls of the matrix (silica has a  $pI$  of  $\sim 2$  and therefore the walls will be negatively charged under these conditions) and not move as rapidly.<sup>25</sup> Diffusional rates will slow down as the gel dries and shrinks because the entrapped reagents will be closer to the pore walls.

This hypothesis was supported by strategically modifying the walls of the silica host with organoalkoxysilanes.<sup>26</sup> The most convincing evidence came from hybrid gels prepared using *N*-trimethoxysilylpropyl-*N,N,N*-trimethyl-



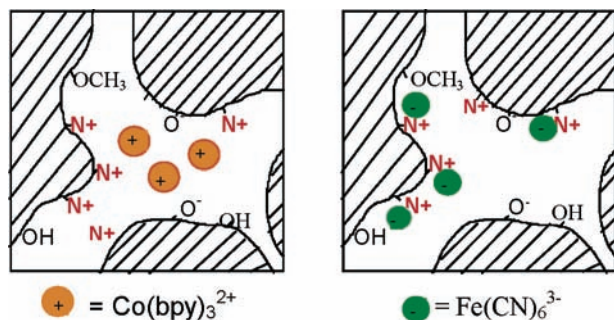
**FIGURE 3.** Normalized diffusion coefficients ( $D/D_0$ ) as a function of drying time for gel-encapsulated  $\text{Fe}(\text{CN})_6^{3-}$  (top) or  $\text{Co}(\text{bpy})_3^{2+}$  (bottom). The gels were prepared from either TMOS only or a mixture of polyamine ( $\text{N}^+$ )/TMOS.  $D_0$  is the diffusion coefficient of the redox probe obtained within the first hour after the sol was made. The error bars represent the standard deviations in  $D$  for three to six gels. Lines have been added to guide the eye.

ammonium chloride (QAPS) or a polyamine ( $\text{N}^+$ ) polymer.<sup>29</sup> In these gels, it was shown that  $\text{Co}(\text{bpy})_3^{2+}$ , a large positively charged molecule, diffused at the same rate as it did in the sol and maintained that rate during a 3-week drying period. In contrast,  $\text{Fe}(\text{CN})_6^{3-}$  showed an order of magnitude drop in its apparent diffusion coefficient during a few day drying period.<sup>29</sup> Figure 3 shows normalized diffusional rates of  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Co}(\text{bpy})_3^{2+}$  in negatively charged gels prepared from TMOS and positively charged gels prepared in part from a polyamine ( $\text{N}^+$ ) precursor. Figure 4 depicts a simple model that explains these observations.



### III. Electrodeposition: An Old Route To Form New Materials

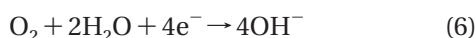
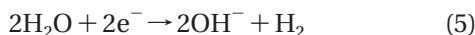
**A. Historical Perspective and Background.** Electrodeposition (or electrolytic deposition) is a popular method to produce metallic coatings on metal surfaces via application of a sufficiently negative (or positive) potential to a conductor immersed in a suitable bath.<sup>46</sup> Developed in the early 19th century, electrodeposition has been widely used to impart corrosion resistance, to improve frictional wear, and to increase the decorative properties of various materials including those used in automobile parts, integrated circuits, and common house-



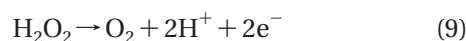
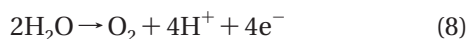
**FIGURE 4.** Simplified representation of fluid-filled ammonium-ion-modified pores.  $\text{Co}(\text{bpy})_3^{2+}$  diffuses in the center of the pore at a rate similar to what it does in the sol, whereas  $\text{Fe}(\text{CN})_6^{3-}$  is attracted to the surface and diffuses at an order-of-magnitude slower rate. Just the opposite is observed for gels prepared from TMOS only. Not drawn to scale.

hold items.<sup>46</sup> Electrodeposition has also seen increased use as a means to prepare inorganic coatings primarily because it is extremely versatile and relatively inexpensive compared with modern lithographic methods. This method has been used to fabricate thin films for chemical sensor applications, materials for solid oxide fuel cells, biocompatible coatings, nanorods, and other nanostructured materials.<sup>47–49</sup>

One of the most common methods for the preparation of materials using electrodeposition involves the application of sufficiently negative potentials to generate hydroxide ions at the electrode surface. This leads to an increase in pH at the electrode surface, which hydrolyzes metal salts or precursors yielding colloidal particles that coalesce to form the solid oxide.<sup>47,48</sup> The properties of the deposit depend on a number of variables including the current density, the composition of the precursor solution, concentration of the precursor, and the cleanliness and surface composition of the electrode.<sup>47–49</sup> Below are relevant electrochemical reactions that lead to the production of hydroxide ions. In addition to these reactions, it may also be possible to form hydroxide ions through the reduction of nitrate or perchlorate ions.<sup>47,48</sup>



In addition to cathodic electrodeposition, the application of positive potentials to *decrease* the pH at the electrode surface to cause the coalescence of colloidal particles to yield solid oxide structures has also been reported, albeit less frequently.<sup>47,48</sup> The relevant electrochemical reactions are given below. In addition to these, it is also possible to decrease the pH at the interface through the oxidation of ascorbic acid or another proton-producing substance.

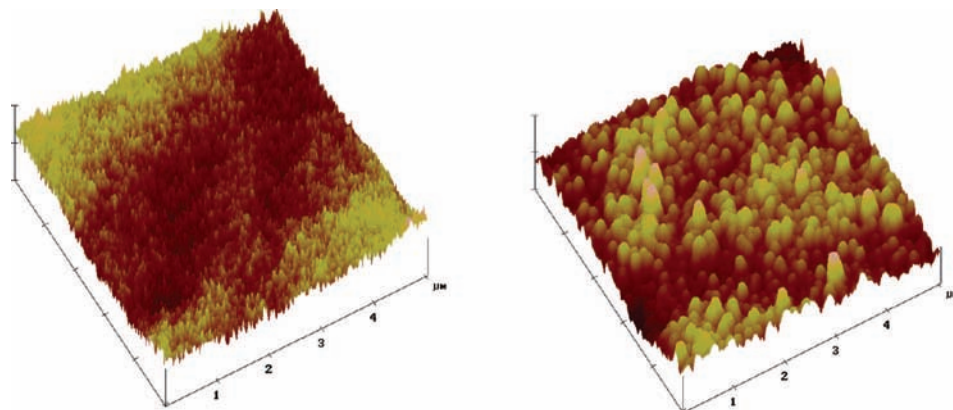


It is important to note that the pH at the electrode–solution interface will be considerably different compared with the bulk solution pH.<sup>47,48</sup> In electrochemistry, all the “action” happens at the electrode–solution interface and extends into solution at a distance defined by the diffusion layer thickness (i.e.,  $(Dt)^{1/2}$ ). In the case where hydroxide ions are electrochemically generated at the electrode, the pH at the interface can be high ( $\gg 8$ ), while the bulk solution is quite acidic ( $< 4$ ). Another point to consider is the product that is formed at the other electrode (i.e., the anode) and how it may impact electrodeposition at the first (i.e., cathode). Often, a divided cell is used so that the product of one electrode does not interfere with the reaction occurring at the other.<sup>49</sup> This is especially important if the electrodeposition times are long or the solutions are stirred or both. When using a divided cell containing a frit, however, caution needs to be used to ensure that the frit does not clog due to condensation of the alkoxy silanes in the pores.

Electrodeposition has been used to form films and nanostructures starting with silicon, titanium, and zirconium precursors, as well as other precursors containing Ce, Al, Cr, Pb, etc.<sup>47–49</sup> The field is too broad for the context of this Account to discuss all the literature. Instead the focus will just be on studies dealing with the cathodic/anodic electrodeposition of silicon alkoxydes and the interested reader can refer to other reviews and articles for more information on titanium and zirconia alkoxydes and the other precursors.<sup>1,47–51</sup>

**B. Electrodeposition of Silica-Based Films.** Silica thin films are traditionally formed via spin coating, dip coating, or spray coating a sol on a flat surface.<sup>12,52,53</sup> In 1999, Mandler and coworkers showed that it is possible to use electrodeposition to create sol–gel-based silica thin films on a conducting surface.<sup>54</sup> In this example, the film was prepared from a pre-hydrolyzed sol of methyltrimethoxysilane. Hydroxide ions were formed by application of a sufficiently negative potential to form methylated films ranging in thickness from nanometers to micrometers. The thickness of the films depended on the magnitude of the applied potential and the nature of the electrode surface. These authors showed that the formation of these films was not “driven by an electrophoretic mechanism”, but rather due to an “enhancement in sol–gel condensation” via electrogeneration of hydroxide.<sup>54</sup> In 2003, Collinson and coworkers used electrodeposition to create thin silica films on glassy carbon electrodes from sols prepared solely from tetramethoxysilane.<sup>55</sup> They also showed that it was possible to trap reagents in the materials by simply adding the reagent to the sol prior to film formation.<sup>55</sup> At the same time, Walcarius and coworkers showed that electrodeposited films on gold can be prepared using a sol containing mercaptopropyltrimethoxysilane.<sup>56</sup>

Since this time, a number of other papers have been published.<sup>57–61</sup> Films prepared by sols that contain a number of different alkoxy silanes including phenyltrimethoxysilane, 3-aminopropyltrimethoxysilane, mercaptopropyltrimethoxysilane, and a pyridine alkoxy silane precursor have been reported. Examples of conducting



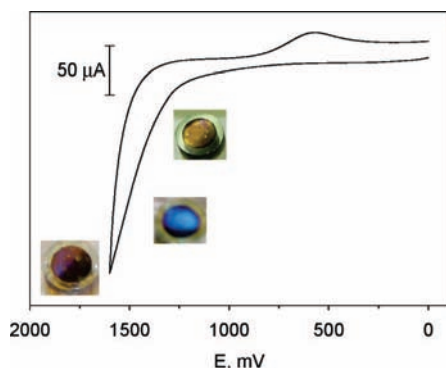
**FIGURE 5.** AFM images ( $5 \times 5 \mu\text{m}^2$ ) of a film spin cast at 7000 rpm on glassy carbon from a base-catalyzed sol (left) and an electrodeposited film on glassy carbon (right). The Z-scale of the spin cast film is 20 nm and that of the electrodeposited film is 100 nm.

surfaces (electrodes) that have been used include glassy carbon, gold, indium tin oxide (ITO), and aluminum. To form adherent films on gold, a molecular “glue” must be used to attach the growing silica to the gold surface.<sup>56,57,61</sup> The “glue” Walcarius and coworkers used was mercaptopropyltrimethoxysilane: the thiol strongly adsorbs to the gold whereas the hydrolyzed alkoxy groups (i.e., silanols) react with the growing silica network. The growth of the films can be followed using the quartz crystal microbalance, while the surface microstructure can be examined using optical microscopy, scanning electron microscopy, or atomic force microscopy. These sol-gel-based films have been used as corrosion protectors,<sup>59</sup> to preconcentrate Cr(VI) for electrochemical detection,<sup>57</sup> to selectively determine cytidine,<sup>60</sup> and to detect mercury.<sup>56</sup> Electrodeposition of tetraethoxysilane in the 20-nm diameter channels of anodic aluminum oxide membranes to form solid silica nanorods or tubular structures depending on the applied potential has also been recently described.<sup>62</sup>

This “old” but “new” material preparation technique has received such interest because it offers a number of appealing attributes. It is versatile: films can be easily formed on any *conducting* surface from sols that contain an alkoxy silane, an organoalkoxy silane, or both. The concentration of the alkoxy silane in the sol can be as low as 1 mM, which can be attractive for biomolecule encapsulation. The films prepared can be potentially more porous than those prepared from spin coating. During spin coating, gelation and evaporation occur almost simultaneously in a very short period of time (seconds).<sup>12,52,53</sup> In electrodeposition, gelation and evaporation are separated in time.<sup>55</sup> The film forms first over a few seconds to a 60 min or more time period, and then it is removed to dry. Also, condensation (and hydrolysis, in some cases) is base-catalyzed thereby yielding films that are more “colloidal” like and subsequently more porous. Figure 5 shows an AFM image of the surface of a film formed by spin casting a TMOS-based sol on glassy carbon and another of a film formed via electrodeposition.<sup>55</sup> The “colloidal nature” of the electrodeposited film can be clearly observed. The thickness of the films, their porosity, and the rate they are formed can be controlled by (1) the

magnitude of the electrode potential, (2) the time the potential is applied, (3) the concentration of alkoxy silane in the sol, and (4) the nature and type of the electrode surface.<sup>54,55,61</sup> Finally, patterning is possible because the film will only form on conducting surfaces and not adjacent insulating surfaces,<sup>54</sup> providing that the diffusion layer distance (which is time dependent) does not significantly overlap with the insulating surface.

Most of the studies to date have focused on the cathodic generation of hydroxide ions to cause the alkoxy silane to immediately condense on the electrode surface. The reason that electrodeposition works so well is that the rate of condensation of silanols is fast under basic conditions and slow under acidic conditions.<sup>12</sup> That is why at the electrode interface a gel forms while the bulk solution is still a sol. Hydronium ions can be electrochemically generated as described earlier through the oxidation of water. However, sols containing TMOS generally do not produce films<sup>55</sup> on the conducting surfaces, likely because the condensation rate is very slow under acidic conditions.<sup>12</sup> One exception to this was recently shown by Collinson and coworkers.<sup>63</sup> Instead of starting with a sol containing an alkoxy silane, a sol containing colloidal particles stabilized under basic conditions (i.e., Ludox colloidal silica or Stober silica) was used. Application of a sufficiently positive potential to electrochemically generate protons decreases the pH of the sol at the electrode surface. As a result, the surface  $\text{SiO}^-$  on the Ludox particles become neutralized, leading to coagulation and condensation of the surface  $\text{SiOH}$  groups resulting in film formation. At the interface, a thin film is formed, while the bulk solution is still a sol. Films prepared in this fashion can be used to ion-exchange cations from solution and appear to have more surface porosity than those prepared from the traditional alkoxy silanes.<sup>63</sup> In a more recent example, electrodeposited thin films on glassy carbon electrodes were prepared from a pre-hydrolyzed/partially condensed sol containing methyltrimethoxysilane (MTMOS) via application of sufficiently positive potentials.<sup>64</sup> Figure 6 shows a representative CV at a glassy carbon electrode and pictures of the



**FIGURE 6.** Cyclic voltammogram at a glassy carbon electrode in a MTMOS sol (MTMOS, ethanol, H<sub>2</sub>O, KCl (0.1 M), HF (few drops, concentrated)) just prior to electrodeposition. Scan rate: 100 mV/s. The top brown film was formed at ~1.2 V, the blue at ~1.4 V, and the purple at ~1.8 V with respect to a silver chloride precoated silver wire reference. A 2 mm graphite rod was used as the counter electrode.

films that formed on it upon application of the given potential for 30 min in an unstirred solution.

Another rather unique example where electrochemistry has been used to form thin sol-gel-based films dates back to the late 1970s and early 1980s.<sup>65,66</sup> In this method, more recently termed “electrochemically assisted polymerization”,<sup>67</sup> a certain reagent (i.e., methylene blue or viologen) known to precipitate on an electrode surface upon reduction is first modified to contain silicon alkoxide functionalities.<sup>67,68</sup> When reduced, the derivative and its hydrolyzed or oligomerized forms precipitate on the electrode surface. The locally high concentration of trimethoxysilyl groups effectively accelerates condensation and cross-linking to produce an “exceptionally insoluble film”.<sup>68</sup>

#### IV. Conclusions

Sol-gel-derived materials, while generally easy to make, are complex both in terms of how the individual precursors hydrolyze and condense and also in terms of their molecular-scale structure. When alkoxysilanes are mixed with organoalkoxysilanes, the chemistry becomes even more complex. Electroanalytical techniques have provided an important, relatively inexpensive means to unravel some of this complexity. More information is now known about how reagents trapped within this complicated framework move and react with each other and how diffusional rates can be manipulated. There is still much to learn, however, about the reactions and formation of the gel structure, as well as about other gels besides those made out of silica. Electrodeposition, as it pertains to the formation of films from alkoxysilanes, is still in its infancy and provides an interesting, versatile way to create materials on conducting surfaces. Patterning and the creation of new composite materials and structures is possible. There is still much to learn, however, about how the films form, how reagents can be incorporated in the materials, whether those entrapped reagents have the same properties as they do in solution, and how these materials can be applied to sensing and other related applications.

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