Materials Science, Vol. 20, No. 1, 2002

Electrochemical redox reactions in solvated silica sol–gel glass*

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The studies of the electrochemical redox reactions in solvated silica sol–gel glass were reviewed. The methodology of the experiments with emphasis on the direct preparation of the solid electrolyte and the application ultramicroelectrodes was described. Generally, the level of the electrochemical signal is not much below that observed in liquid electrolyte. The current depends on time elapsed after gelation, namely the longer time, the smaller current. The differences between electrochemical behaviour of the redox couples in monoliths and thin layers were described.

Key words: sol–gel, solid electrolyte, electrode reaction, redox reaction, diffusion coefficient, ultramicroelectrode

1. Introduction

Inorganic materials obtained in a mild reaction conditions, i.e. by sol–gel method [1], emerged recently as versatile matrices for preparation of solid electrolytes suitable for use at ambient temperatures [2]. These materials offer several advantages over organic polymers including physical rigidity, chemical inertness, negligible swelling in aqueous or organic solutions, photochemical and thermal stability and optical transparency [3]. The presence of some amount of mobile ions within the matrix is required for the future application of these materials in electrochemical devices. Therefore they cannot be used in the form of xerogels – thoroughly dried gels, where mobility of species is heavily restricted, because of the small volume of solvent (typically water) left after aging and drying. The use of wet or – in another words – solvated gels seems to be a better strategy.

Application of these materials as electrolytes in amperometric sensors, electrochemiluminescent or electrochromic devices often requires the presence of redox-active ions or molecules within the matrix. These species are able to exchange elec-

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[*] The paper presented at the International Conference on Sol–Gel Materials, SGM 2001, Rokosowo, Poland.

trons with the electrode without the mass transfer across the electrode/electrolyte interface. Before practical application the knowledge about electrochemical redox reactions at the electrode/silica matrix interface seems to be indispensable. On the other hand, the electrochemical methodology using redox probes provides a promising approach for characterisation of inorganic materials.

The sol–gel chemistry received attention of electrochemists quite recently (see [2] and refs. therein). Here, the first attempts to study electrochemical redox reactions in solvated silica sol–gel glass will be presented and summarized. This review will be restricted to the systems without macroscopically liquid phase. Therefore, the electrochemical processes at silica-matrix modified electrodes immersed into the liquid electrolyte will not be taken into account.

2. Methodology

Most of the electrochemical studies were carried out during tens of days starting from the sol preparation for aging process. In this way all changes in gel structure during formation and aging can be followed. The sol was usually placed into a small covered vial made of organic polymer (polyethylene, polypropylene or polystyrene) (Fig. 1). The working, reference and (sometimes) counter electrodes in a form of glass embedded discs or metal wires were immersed into the sol and fixed in the cap [4–19]. Fortunately, due too poor affinity of silicate matrix towards the organic polymer walls the shrinking gel pulls away only from the walls and the bottom of the cell. After few days it is held only by the electrodes, especially when they consist of glass body.

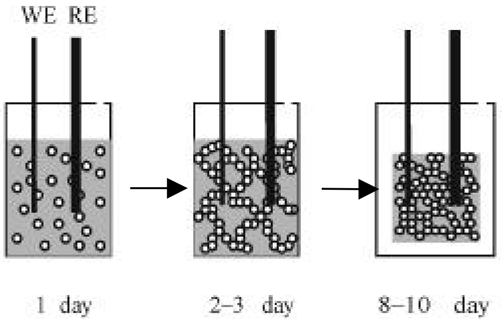

Fig. 1. Scheme of the electrochemical cell used in experiments with solvated sol–gel glass blocks;
WE – working microdisc electrode, RE – reference electrode

This methodology seems to be superior, because the electrical contact between the electrodes and solid electrolyte is not affected by the gelation and aging. However, it makes the working electrode vulnerable on the fouling processes. The latter include adsorption of impurities or uncontrolled potential step far beyond the potential window. This in turn affects the reproducibility of electrochemical experiments, because the working electrode cannot be removed from the electrolyte for polishing without destroying the gel. This problem can be eventually avoided by gentle pressing the electrode towards the wall of the gel. Until now such methodology was used only for impedance spectroscopy studies, where the sample was held between two spring loaded electrodes [20–26]. The electrode assembly embedded on the flat support covered by sol–gel film [10, 15, 27–31] (Fig. 2) also may suffer from uncontrolled fouling. Additionally, the properties of the thin layer of the sol–gel electrolyte usually differ from those of gel monolith [10, 18]. However, from the point of view of application in electrochemical device, this configuration seems to be superior.

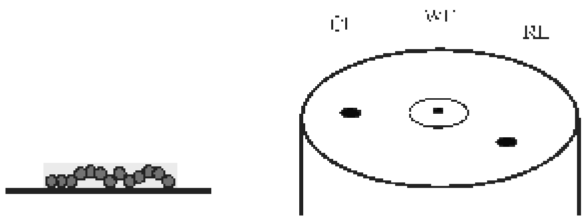

Fig. 2. Scheme of the electrochemical cell used in experiments with solvated sol–gel glass blocks; WE – working microdisc electrode, CE – counter electrode and RE – reference electrode

Almost all studies of the electrochemical redox reactions in silica sol–gel glass have been done with ultramicroelectrodes – electrodes of dimensions in the range of micrometers [32]. This is because of the relatively large resistance of the sol–gel electrolyte and large signal to noise ratio. The current obtained with a standard disc ultramicroelectrode, of diameter of about 10 μm, is in the nanoampers range. Therefore, the effect of the electrolyte resistance, proportional to the product of current and resistance (so-called ohmic or IR drop [33]), is minor. It has to be emphasized that the measurement of such low current no longer remains a problem. Eventually its magnitude can be increased by application of interdigitated microelectrodes (IMES) without loosing most of the features of the single ultramicroelectrode [27]. Also the application of the ultramicroelectrodes enables one independent estimation of the diffusion coefficient and concentration of the redox probe. This is because of two different transport regimes, namely, hemispherical and semiinfinite diffusion, which can be observed in a single experiment at long- and short-time scales [34].

3. Sol–gel electrolyte composition

Until now most of the studies were done in acid catalysed gel obtained from tetramethoxysilicate (TMOS) or tetraethoxysilicate (TEOS) precursor. The redox probe was dissolved in the sol. The mobility of the substrate is essential to obtain measurable current. Therefore, the drying rate was carefully controlled by making small hole(s) in the cap of the electrochemical cell. Although there are reports about electrochemical studies in liquid without so-called supporting electrolyte, only the presence of the excess of ions allows to obtain results which can be analysed in a straightforward manner [33]. Therefore, in almost all studies the salt was added to the sol before the gel formation. Its presence does not affect the stability of the gel. The addition of ionomer like Nafion® which results in formation of polymer–silica composite material represents an alternative approach (see [12] and refs. therein).

In order to introduce reactant insoluble in water, we added it as its solution in organic solvents like PC [10, 16], sulfolane (TMS) [16–18] or dimethylsulphoxide (DMSO) [19] directly to the sol. Such a way of preparation of sol–gel organic solid electrolyte was originally proposed by Wu et al. [20] for the prospective application in batteries. A concentrated lithium salt solution in ethylene carbonate and propylene carbonate mixture was directly added to an aqueous TMOS sol. The gel formation rate and material stability depend on the sol to organic solvent ratio. The gel obtained with a small amount of organic electrolyte was not transparent and susceptible to fracturing, whereas a large excess of the organic electrolyte resulted in a very soft, wet material [20]. We observed that addition of organic solvent increased gelation time in comparison to hydrated gel and it depended on the properties of the solvent and salt. After addition of PC or TMS solution it increases from few hours to 1–3 days [16–18], whereas DMSO extends gelation time to more than 20 days [19]. For lithium perchlorate solution in PC it occurs within 12 hours, however, it takes 2 days to obtain gel containing tetraalkylammonium salts. The replacement of PC with TMS also similarly extends the time of gelation.

The exchange of an organic electrolyte with liquid already present within silicate matrix as an effect of hydrolysis and gelation represents another possibility of silica sol–gel glass modification [21–26]. Like as in the case described previously [20] the solid electrolyte with conductivity not much below of the liquid one was obtained. It has to be emphasized that during both procedures few percent of strongly solvating water is left within matrix [26].

The value of isoelectric point of silica sol–gel glass equal to 2 [35] indicates quite large concentration of protons in the matrix. This may be enough to provide ionic budget for electrochemical experiments. Indeed, it is possible to obtain a cyclic voltammogram with the features similar to that obtained in a liquid in the absence of salt added [19]. This was done in sol–gel glass with ferrocene (Fc) solution in organic aprotic solvent: propylene carbonate (PC) without any salt present and it indicates the important role of protonic conduction of the wet sol–gel silica matrix.

4. Electrode reactions and transport rate

The electrochemical behaviour of the redox-active ions and molecules in a gel monolith is not much different from that in an electrolyte solution [4–19]. The shape of the cyclic voltammograms corresponding to simple redox reaction:

$$\mathrm{Ox}_{\mathrm{(electrolyte)}} + \mathrm{e}_{\mathrm{(electrode)}} \leftrightarrow \mathrm{Red}_{\mathrm{(electrode)}} \tag{1}$$

obtained at slow and fast scan rate is similar for all systems studied within tens of days after aging. This indicates the stability of the electrode/sol–gel electrolyte interface under slow and fast polarisation conditions and it looks promising from the point of view of the prospective applications. Contrary to the gel solvated with organic solvent some deterioration of fast scan cyclic voltammetry curve was reported for hydrated gels [8]. This may be caused by gel shrinking and pore collapse. It has been observed that during 20–50 days the hydrated gel shrinks by about 30%, whereas that containing organic solvent shrinks only by about 10%. For all cases studied the rate of electrode reaction is controlled by the reactant transport. The magnitude of the plateau or peak current decreases with time, however for a given time the magnitude of decrease depends on the system. We have found that even after one year after gelation of the gel modified with organic solvent, it is possible to obtain relatively well developed voltammetric curve.

Some shift of the redox potential ($E°$), which can be considered the measure of the difference in interactions of Ox and Red with surrounding environment, was observed during gel aging [7, 10, 13, 16]. However, there exists the problem of the stability of the reference electrode potential. It has to be emphasized that the effect on silica matrix on the surface of metals, their oxides or salts is unknown. Therefore it is better to use reference electrode separated from the gel. With this methodology small shift of $E°$ by no more than 0.04 V [13] was observed in hydrated gel 30 days after gelation. This indicates small change in interactions between redox probe and surrounding media after gelation. Its degree and direction depends on the redox couple.

The fact that the presence of the silica matrix does not substantially affect the heterogeneous electron transfer rate enables us to determine the rate of the redox probe motion in terms of apparent diffusion coefficient (D_{app}). This parameter should be called "apparent" because it is not always clear whether the concentration of redox species is equal to that in the sol and also it may depend on time passed after gelation [9].

It is quite general that the value of D_{app} is smaller than that for an analogous liquid electrolyte. However, for some systems shortly after gel point it is larger than in the sol [16, 18]. The degree of D_{app} decrease depends on the redox probe, salt and organic solvent additives [4, 5, 7, 10, 16–19]. For the systems where this effect is substantial (2–4 times), it is most pronounced during the first few days elapsed after gelation. At longer time it is not significant. The D_{app} decrease correlates with the mass decrease during aging and drying [13]. For positively charged and neutral probes in hydrated gels or in gels solvated by organic solvents the decrease is substantial [4, 5, 7, 10, 16–19]. On contrary, D_{app} of the negatively charged reactants in hydrated gels is almost time-independent [7, 13].

The decrease of D_{app} seems to be caused by the fact that within a silicate matrix at some positions redox probes ions cannot move in every direction. Their motion is restricted by the size and geometry of the pores. This of course depends on the degree of polycondensation which still occurs, especially just after gel point and on aging of the gel. Unfortunately, there is no efficient direct method of the pore size of a wet gel estimation. The diameter of pores in TMOS acid-catalysed xerogel obtained in the presence of surfactant is in the range of 10 nm [1]. The minor shrinking of the wet gel indicates that they are much larger than pores in an analogous xerogel. Therefore, they are expected to be one or two orders of magnitude larger than the typical diameter of the redox probe equal about 1 nm. The correlation between D_{app} and sample mass decrease may indicate the evaporation of the liquid volume within the matrix [13]. This should eventually affect the concentration of the redox probes. The concentration increase in aging hydrated gel was claimed [7]. For gels solvated with organic solvents this effect is not important [16, 18].

There are many observations indicating that the interactions between the silicate matrix and the redox probes are minor, such as the correlation between the value of D_{app}, the size of the reactant and viscosity of the solvent predominatly present in the matrix [16–18], as results from the Nernst–Einstein equation valid for liquids. Also a similar activation energy (E_a) of the reactant transport in the matrix and analogous liquid electrolyte supports this view [18]. However, more pronounced temporal dependence of the rate transport of the positively charged or neutral probes [4, 5, 7, 10, 16–19] indicates that situation is not so simple. The surface of the pore walls of silica sol–gel glass is covered by a number of functional groups: siloxane (SiOSi), silanol (SiOH), siloxide (SiO^-) and unreacted alkoxide groups. The interactions between matrix charged substituents bearing electric charge or oxygen atoms having free electron pair (oxygen) with molecules and ions present in the pores may occur. This may be the reason of the different temporal dependences of the apparent diffusion coefficient. Organic additives may also affect the process of the gel formation. It is already known that addition of organic substances, usually surfactants, causes the increase of the xerogel pores (see [36] and refs. therein). The minor shrinking of the gel modified with organic solvents and D_{app} increase in the presence of large tetraalkylammonium cations in the gel [16–19] indicates that this is the case. One may also conclude that the addition of organic solvent or surfactant eventually allows one to increase the reactant transport by manipulation with the pore size.

The electrochemical behaviour of insoluble redox probes encapsulated into silica sol–gel glass and their action as electron mediators was also reported [9, 15]. The precursors of the redox active solids were incorporated directly into the sol. The formation of mixed valence ruthenium oxide with cyano cross links [9] or colloidal Prussian Blue occurs during sol–gel transistion. Their electrochemical behaviour was not very far from that observed in contact with liquid electrolyte. This is because the hydrated gel provided mobile ions and their motion limits the electron hopping rate [9, 15].

The generation of light using electrochemical redox reaction represents another interesting aspect of sol–gel electrochemistry with prospective application in chemical analysis or electrochemiluminescent displays. It is possible to generate light within hydrated sol–gel glass monolith of ruthenium(II) tris(bipyridine) $(Ru(bpy)_3)^{2+}$ at the presence of oxalate or tertiary amines as reducing agents [8, 11]. The electrogenerated chemiluminescence (ecl) process can be described as follows:

$$\mathrm{Ru}\left(\mathrm{bpy}\right)^{2+}_{3\,(\mathrm{electrolyte})} - \mathrm{e}_{(\mathrm{electrolyte})} \leftrightarrow \mathrm{Ru}\left(\mathrm{bpy}\right)^{3+}_{3\,(\mathrm{electrolyte})} \tag{2a}$$

$$\mathrm{Ru}\left(\mathrm{bpy}\right)^{2+}_{3\,(\mathrm{electrolyte})} + \text{reducing agent}_{(\mathrm{electrolyte})} \rightarrow \mathrm{Ru}\left(\mathrm{bpy}\right)^{+*}_{3\,(\mathrm{electrolyte})} \tag{2b}$$

$$\mathrm{Ru}\left(\mathrm{bpy}\right)^{2+*}_{3\,(\mathrm{electrolyte})} + \rightarrow \mathrm{Ru}\left(\mathrm{bpy}\right)^{2+}_{3\,(\mathrm{electrolyte})} + \text{light} \tag{2c}$$

However, the intensity of electrogenerated light was smaller than that in the absence of the sol–gel matrix. Ecl was found to be stable for 10 days [11].

5. Thin films

There is no electrochemical study comparing the electrochemical behaviour of the same system in hydrated gel. This, however, has been done for sol–gel glass with gel solvated by organic solvent [10, 16]. For gel made from TEOS, the magnitude of the current connected with electrooxidation of ferrocene is similar for thin film and monolith [16], whereas in the case of TMOS precursor the former is few times smaller [10]. Unfortunately, the signal disappears few days after gel formation.

The sol–gel approach has also been used by Cox group for generation of thin films of electrolytes containing catalyst for prospective use in amperometric sensors [27–29, 31]. The conductivity of the sol–gel matrix filled with concentrated acid, concentrated salt solution or redox catalyst is large enough that device can work in the absence of liquid electrolyte. They can be used for determination of gaseous substrates: NH_3 [27], CO [28], H_2O_2 [29] or monomethyl hydrazine [31]. These compounds are extracted into sol–gel film and electrochemically oxidised. Their electrode reaction involves nonmediated or mediated electrooxidation with mechanism more complicated than Eq. (1). It has to be emphasized that in one case the signal was claimed to be independent on humidity of the air [28] what is exciting in terms of application to gas sensors.

6. Conclusions

The electrochemical studies in silica sol–gel glass represent an example of the electrochemistry without the liquid electrolyte while preserving characteristic features known from the experiments in liquid media. Although quite consistent view emerges from the papers reviewed, there are many things to be done. At first sight the course of the electrochemical redox reactions in solvated silica sol–gel glass seems to be not very far from that observed in liquid electrolytes. However, the knowledge about interactions between matrix and solvent or solute except the restrain of redox probe motion is very modest. Obviously more systems have to be studied. Also the careful studies of the gelation effect on the redox potential are highly desirable.

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