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Silicate solvated by an organic solvent as electrolyte or electrode material

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Preparation and properties of silicate gels solvated by organic solvents as electrolytes or electrode materials were summarised. A silicate matrix based on tetraalkoxysilane, trialkoxysilane modified with organic groups or a mixture of these two, modified by organic solvents or solutions is the principal component of all the systems studied. The material used as the electrolyte is filled with a salt solution in an organic polar solvent or in the case of hybrid organic-inorganic silicate matrix it is functionalised with tetraalkylammonium groups with a pure solvent. The electrodes are made of a composite material consisting of graphite particles, silicate matrix functionalised with methyl groups and filled with a pure or diluted redox liquid.

Key words: *sol-gel; solid electrolyte; electrode; silicate; redox liquid; ion transfer*

1. Introduction

Typically, the synthesis of silicate glass based on the sol-gel process and performed at ambient conditions is aimed at preparation of xerogels with the amount of liquid left reduced to minimum [1]. However, the impregnation of a silicate matrix or composite material with silicate glass as one of the components, with carefully selected organic liquid, may result in a solid material having some properties of the latter. Among them is high mobility of molecules or ions dissolved in impregnating liquid. This is because the pore diameter of sol-gel silicate glass is in the range of several to several hundred nanometres [1]. Its comparison with the size of typical molecules or ions shows that at least a single molecule or ion with its solvation shell is able to move along the pores.

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In the paper, the results of the research on preparation and properties of solid electrolytes or modified electrodes based on this concept are summarised, also in relation to those already published. The paper is restricted to silicate matrices solvated by solutions of substances in organic solvents or pure organic solvents. This approach can be considered as a variant of the popular modification of glass by organic substances by sol doping [2] or covalent bonding [3]. It has to be emphasized that it is not restricted to electrochemistry. Silica sol-gel glasses with embedded organic liquids can be used as containers for oil solutions of flavours or fragrances [4]. This is because encapsulated substances offer greater convenience, improved storage stability and possibility of their controlled release [4]. Electrochemical redox reactions in solid electrolytes based on the solvated silica sol-gel glass were recently reviewed [5].

2. Solid electrolytes based on solvated silicate gels

Solvated gels acting as solid electrolytes consist of silicate matrices impregnated by ionic solutions in organic solvents. They are based on unmodified or modified silicates. Tetramethoxysilicate (TMOS) or tetraethoxysilicate (TEOS)-based matrix solvated by salt solutions in viscous organic polar solvents like ethylene carbonate (EC), propylene carbonate (PC) or sulpholane (TMS) [6–16] belong to the first group. Other are based on hybrid organic-inorganic matrices [17–19].

The matrix composed of silicate and hydrocarbon-based chain elements and filled with Li^+ solution in a polar organic solvent mixture [17] was applied as the electrolyte in lithium secondary batteries [18]. The presence of short alkyl chains makes the matrix flexible and reduces the number of unreacted hydrophilic groups OH bonded to Si atoms. Recently, our group prepared a solid electrolyte consisting of a hybrid organic-inorganic silicate matrix functionalised with tetraalkylammonium groups solvated by a viscous organic polar solvent [19]. It was obtained from the mixture of trimethoxysilane functionalised with alkyl-N,N,N,-trialkylammonium group and TMOS with the excess of the latter component. It has to be emphasized that analogous matrices based on unmodified or modified alkoxysilanes filled with an aqueous solution of a salt were also proposed as media for electrode reactions [20–22].

There are two strategies for silicate matrix modification by organic solution. It may be added directly to the sol before the sol-gel transition occurs [7, 11–19] or exchanged with the liquid left after the sol-gel process [6, 8–10]. The loss of mass accompanying gelation and ageing during the first procedure indicates that almost all alcohol produced during hydrolysis of tetraalkoxysilane is removed [16]. If the sol-gel process is not carried out in a humidity-free environment [6], some amount of water is left in organic solvent-modified silicate as is confirmed by differential scanning calorimetry, thermogravimetry, IR spectroscopy [16, 19] and electrochemical experiments [13].

The time of gelation (t_{gel}) of the sol-gel electrolyte impregnated with organic solution in an acid-catalysed process depends on the precursor, the solvent and the salt dissolved [13, 16, 19]. t_{gel} is always longer than that of the material prepared in the absence of organic solvent. Obviously, the presence of organic solvent decreases water activity in all systems leading to slower hydrolysis. Typically, t_{gel} of a PC -solvated TMOS-based gel equals 1–4 days, whereas the formation of an analogous TEOS-based material occurs after 25–30 days [13]. The addition of more viscous solvents extends the time of gelation because higher viscosity is expected to slow down all steps of the sol-gel process. The replacement of ‘structure making’ Li^+ ions by ‘structure breaking’ tetraalkylammonium cations also slows down the sol-gel formation. This can be explained by their influence on the structure of hydrogen bonds and thereby affecting pH of the sol. The rate of formation of a solid electrolyte functionalised with tetraalkylammonium groups depends on the ratio of precursors [19].

The structure of a wet gel seems to be dramatically affected by the presence of an organic solvent. It shrinks by about 10–20% in comparison to 80–90% observed for the unmodified material. Interestingly, the syneresis of an analogous TMOS-based silicate matrix filled with an aqueous salt solution is larger being equal to about 40% [21]. As revealed by IR spectra, some OH groups of the TMOS-based gel solvated by the tetraalkylammonium (TAA^+) salt solution in PC or TMS remain unreacted [16]. For a TAA^+ functionalised material, the number of these groups is much lower [19]. The formation of this electrolyte seems to be complete, because no NMR signal of organic substituent can be found in the solution used for the extraction of crushed material [19].

Unfortunately, no convenient method for determination of the porosity and internal area of wet gels is available. However, it is reasonable to assume that the size of pores is larger than in dry or calcined material. The results based on the BET method indicate that the pore size depends on the organic modifier and precursor being in the range of 5–15 nm [16, 19].

The electrical conductivity (σ) of TMOS-based solvated gels is typically one order of magnitude smaller than that of an analogous liquid electrolyte [7–10, 16]. For the material solvated by PC solution, it is close to 10^{-3} $S \times cm^{-1}$ [16]. The value of σ of the electrolyte functionalised with tetraalkylammonium groups is at least one order of magnitude smaller [19, 20], yet still larger than that of the silicate matrix modified with the pure solvent [16]. The value of this parameter depends on the time elapsed after gelation. A most substantial decrease is observed during first 10 days after gelation correlating with the mass loss [16, 19]. A similar dependence is observed for the diffusion coefficients of neutral or ionic species obtained from the voltammetric and chronoamperometric experiments [11–15, 19]. This is connected with the development of the silicate network, affecting the mobility of ions. Interestingly, the temperature dependence and thereby activation energy of the conductivity and diffusion coefficients are not much affected by the presence of the silicate matrix [15, 16]. This indicates weak interactions between neutral or ionic species and the silicate matrix. It has to be emphasized that a similar temporal dependence of the diffusion coefficients of the redox probes was observed in the silicate matrix solvated by an aqueous salt solution [20–22].

3. Composite electrodes based on solvated gels

Despite its insulating properties, the silicate matrix can be used as a component for the composite electrode preparation. Lev et al. opened the way to a new family of electrode materials showing that a conductive porous material can be obtained by the sol-gel method from the mixture of carbon (graphite) particles and an alkoxysilane-based sol [24, 25]. The ratio of these two components affects both the electrical conductivity and mechanical stability of carbon ceramic electrodes (CCE) [25]. The optimised amount of carbon particles depends also on the their type and size [25].

Typical application of modified electrodes requires the presence of a redox component which is absent in unmodified material except some amount of quinone functionalities present on the graphite particle surface. The redox active groups can be introduced by (i) sol doping, (ii) covalent bonding to the silicate matrix (iii) covalent bonding to the surface of graphite particles and (iv) adsorption on the electrode surface (see ref. [25] for a recent review on CCE).

Recently, our group put forward another method of modification of CCE [26, 27]. This approach was inspired by the electroactivity of redox molecules dissolved in a drop or a thin film of a hydrophobic polar solvent like nitrobenzene (NB) or benzonitrile (BN) placed on the surface of the electrode made of hydrophobised graphite, pyrolytic graphite or glassy carbon [28–31]. An analogous approach was used for the modification of the electrode with droplets of the so-called redox liquid. It can be defined as a redox active compound being liquid at ambient conditions [32]. Tetraalkyl-*p*-phenylenediamines or butyloferrocene are the examples reported in the literature [33, 34]. One can manipulate the hydrophobic properties of such molecules by changing the number, length and shape of alkyl substituents connected to the redox active core. The mechanism of the electrode processes on the electrodes described above, immersed into an aqueous electrolyte which does not contain any redox active compounds involves electron transfer from/to the redox probe followed by a counter -ion transfer from the aqueous phase or a charged product ejection to the aqueous phase [31, 33, 34].

Our strategy was based on a strong affinity of hydrophobic organic solvents towards the hydrophobic silicate matrix. We have shown that CCE obtained from the organically modified precursor methyltrimethoxysilane (MTMOS) can be impregnated with the redox probe solution in a hydrophobic solvent or a pure redox liquid. The properties of these electrodes made of hydrophobic matrices are similar to those of redox polymer electrodes [35, 36] in the sense that the electron exchange between highly concentrated redox centres dissolved in a hydrophobic solvent and an electronic conductor is the source of the measured current. However, they exhibit some specific features, which are connected with the anion transfer through the hydrophobic sol-gel glass-supported liquid–liquid interface.

The following solvents were used for the CCE modification: chain hydrocarbons, toluene, nitrobenzene and *o*-nitrophenylether [14, 26, 27, 37–39]. The electrodes modified with a hydrophobic redox probe solution – decamethyloferrocene in hydrocarbons resemble electroactive carbon paste electrodes, having been widely used for almost 40 years [40–42]. These are made of a mixture of graphite particles with the redox probe solution in a viscous oil like Nujol, silicone oil or hexadecane. The use of rigid silicate matrix extends the range of solvents to less viscous ones, enhancing the mobility of the redox probe and leading to the increase of the current. Even redox probe solution in a solvent as volatile as hexane can be used for electrode modification [37].

Electrochemical studies of CCE electrodes modified with organic solvents were performed with an aqueous salt solution without any redox probe dissolved. The shape of the voltammogram and the current magnitude observed under linear polarisation conditions is proportional to the concentration of the redox probe in the modifying solution with the largest value for the pure redox liquid [37–39]. In the latter case, the current density is similar to that observed with the redox polymer-modified electrodes [35–36]. This is not surprising since in a redox liquid, the concentration of redox groups is equal to about 4 mol×dm^{-3}. Interestingly, the dependence of current vs. redox probe concentration indicates some matrix effect.

The linear relationship between the current and the concentration of ions is a specific feature of the CCE modified with organic liquid containing redox active molecules [37–39]. This is observed for the electrodes modified with a pure redox liquid – *t*-butyloferrocene (BuFc) or its solution in nitrobenzene. This effect is absent in the electrodes modified with the redox probe solution in hydrocarbons. Like in the case of the redox liquid-modified electrodes this can be explained by the participation of counterions in the electrode process – insertion in an organic solvent or ejection of the charged redox probe to aqueous solution in order to provide the charge balance for electrogenerated ions. Despite some loss of the electroactive substance, a stable electrode response can be maintained [39]. This is because the hydrophobic silicate matrix serves as a reservoir of the redox liquid enabling its continuous supply to the organic aqueous interface.

The effect of the ion concentration on the amperometric response of CCE modified with undiluted or diluted redox liquid is quite unusual and almost not observed for the electrodes modified with thin films of redox or other conductive polymers [43–45]. This is probably because the polymer films are porous and ions can interact with charged redox groups without transfer to a different phase. On the other hand, the current proportional to nonelectroactive ion concentration can be generated at unsupported or supported liquid–liquid interface where ion transfer is generated by applying a potential difference [47–49]. After optimisation, the CCE-modified with organic liquids can be eventually applied as amperometric nonelectroactive anion sensors based on different phenomena – electrogeneration of ions near the liquid –liquid interface.

We were also able to observe the effect of electrode morphology on the amperometric response. One can imagine a composite material as interconnected network of large (diameter equal to tens of micrometers) conducting particles immersed in a porous matrix with the pore size of about three orders of magnitude smaller [46]. Hydrophobic liquid fills the matrix pores and they can be easily penetrated by individual redox molecules or tBuFc$^+$ cations having the size smaller than 1 nm. Eventually, the hydrophobic liquid covers the rough surface of the sol-gel material facing the aqueous phase as well as the surface of the most outer graphite particles not covered by the silicate matrix. We proved that the electrode process occurs at a three-phase junction formed by the wall of graphite particles, organic solvent and aqueous phase [37–39].

Although we did not yet study systematically the effect of the silicate matrix on the electrochemical behaviour of the CCE-modified organic liquid it is clear that some interactions with reactant of the electrode process exist. We have shown a stabilising effect of the matrix towards formation of butyloferrocene cation within CCE body [38]. This was explained by a likely coordination of electrogenerated cation to oxygens bridging silicon atoms.

4. Conclusions

The modification of silicate or silicate-based composites by selected organic liquids enables us to obtain solid materials while preserving some properties of liquids. Their electrochemical properties are sometimes unusual, like these of impregnated carbon ceramic electrodes because of the ability of hydrophobic silicate-based material to support liquid–liquid interface. One can envisage their future use in electrochemical devices after optimisation and improvement of their long-term stability.

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