Studies of changes of pH, H^+ ion limiting current, conductivity and temperature during sol–gel processes in a TMOS system [1]

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Abstract

Two gas-tight cells with appropriate electrodes were constructed of transparent polypropylene and kept at constant temperature in a water bath. Simultaneous measurements of pH, conductivity and temperature as a function of time were carried out in the first cell containing a solution with the molar ratio (TMOS:H_2O:HCl) of 1:4:10^{-3} or 1:4:10^{-4}. The H^+ ion limiting current was periodically determined by linear voltammetry on a Pt microelectrode in the second cell with the same solution. The measurements were made in deoxygenated solutions, at 25°C, 40°C or 50°C and extended to a point after gelation until the contact between the respective electrode and the gel broke down. A significant temperature change was found to occur in the first 20 min after mixing. Strong fluctuations of pH and conductivity were observed in this period. The subsequent changes with time of temperature, pH, conductivity and limiting current were small. The results are discussed in relation to other studies. © 1997 Elsevier Science S.A.

Keywords: Sol-gel; Conductivity; Temperature; pH Electrode; Microelectrode

1. Introduction

Ion transport in sol–gel materials has been of interest for various reasons [1]: preparation of precursor materials for glasses and ceramics [2]; production of gels and xerogels as electrode materials [3] or ionically conducting glasses [4]; and application of doped gels as chemical and biochemical sensors [5]. The ability to dope sol–gel matrices with a variety of molecules has provided researchers with electrochemical [6–8] and optical [9–11] methods for studying transport processes in these matrices. It has been demonstrated [7,8] that molecules which are not connected to large polymers diffuse freely towards an electrode in the liquid part of the gel. The same value of the diffusion coefficient was measured for various compounds in the sol and gel states. Silica, zirconium and titanium gels were used. Recently, tests were made [12] to see if chemical and structural changes which occur during the sol–gel transition can be probed by impedance spectroscopy. The results in the tetra-methoxy-silane (TMOS) system indicated, in agreement with the study by electrochemical probes [7,8],

that ionic transport took place within the solvent phase. Proton transport was considered responsible for the observed behaviour at pH values below about 2.

Microelectrodes which proved useful [13–16] for cyclic voltammetry in media of low conductivity were employed in the previous work [6–8]. The components of suitable redox systems were added for this purpose. In contrast, electrochemical investigations involving the inherent H^+ ions are described here. A Pt microelectrode was employed for the measurement of the H^+ limiting current which is observable [17] during the transition of the H_2 evolution from acid to alkaline solutions. The surface of this Pt electrode had to be polished repeatedly to obtain reproducible results. The use of polarographic methods with a mercury electrode, which operates well [18,19] even in the presence of dispersed particles, would have been preferable because its surface can be easily renewed. However, such an electrode does not allow the sol–gel transition to be followed.

An attempt was made to monitor continuously the changes in pH, H^+ ion limiting current (I_{l}), conductivity (σ) and temperature (T) after the mixing of TMOS with H_2O + HCl solutions and to see if information about the sol–gel processes may be obtained in this way. If measurable by a glass electrode, the pH will supply information

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about the activity of the H^+ ions. The limiting current is proportional to the product of diffusion coefficient and concentration of the H^+ ions if diffusion is the controlling transport process. The conductivity is determined by the mobility and concentration of the conducting species. The measurement of the temperature is important because a significant temperature increase occurs during the hydrolysis of TMOS. The values of pH, H^+ limiting current and conductivity are affected by the increase and subsequent decrease in temperature within a certain time.

2. Experimental

Two transparent cells (cells 1 and 2) were constructed of polypropylene. The transparency was required for a visual observation of the gelation point. Nitrogen could be bubbled through each of these cells to remove molecular oxygen from the solution. If it is not removed thoroughly, the oxygen reduction, which also occurs [16] in media of low conductivity, interferes in a critical fashion and does not allow the determination of the H^+ limiting current. In the beginning the cells were filled by 20.25 ml of TMOS which was stirred by nitrogen for 45 min before adding the appropriate $H_2O + HCl$ solution from a separate glass vessel by gas pressure through a plastic tube. The latter solution (9.75 ml) was also deoxygenated by a 45 min stirring with N_2 before the mixing. Since the specific density of TMOS is relatively high, a magnetic stirring rod was operated at the bottom of the cell to improve the mixing. The cell and the glass vessel were in a water bath. Initially the experiments were carried out at 25°C. In order to record a complete run during 1 day, the bath temperature was increased to 40°C or 50°C. This allowed the point of gelation to be reached in a reasonable time. The cell was located in a flat part of the bath so that the magnetic stirring rod could be activated through the bottom of the bath and the glass vessel from the outside.

Two platinum wires, to which rectangular Pt foils (1 cm × 1 cm) were spot welded, served as the leads for the conductivity measurements in cell 1. These leads were cemented at a distance of 1 cm from each other into the plastic lid which was tightly attached to the cell body by screws. The Pt foils were parallel to each other. The calibration of the conductivity cell was done by standard solutions before the experiments with sol–gels and yielded a value close to 1 for the calibration constant, as was to be expected from the geometry.

The pH glass electrode (Mikro-pH-Einstabsmesskette NG6000 A, Schott) was of the smallest size (outer diameter of 0.35 cm) which is commercially available here. It was cemented into the lid on the right side of the conductivity cell. According to the operating instructions the interior of the pH electrode was filled by a mixture of 2 parts CH_3OH and 8 parts internal filling solution. The operation of the pH electrode in solutions, containing

different amounts of CH_3OH, had been checked previously [12]. $CH_3OH + H_2O + HCl$ solutions with different ratios of $CH_3OH:H_2O$ (3:4 to 3:1) and the same amount of HCl were prepared. The experimental pH values differed only by about 0.2 (compare the respective data in fig. 6 of [12]).

A direct failure of the glass electrode is easily discovered by checking the functioning of the glass electrode periodically in a standard solution. It was found in this way that the glass electrode appeared to work for a certain number of experiments (at least 3–5 runs) in the TMOS sols and gels. It had to be replaced by a new one when it no longer showed the proper pH values during the check in the standard solution before the start of the sol–gel experiment. Usually the preceding run had to be discarded if the pH electrode displayed a malfunction.

A thermocouple was located at the bottom of a closed-end tubing of polyethylene. The outer diameter of the tubing was 0.6 cm. It was located on the left side of the conductivity cell and allowed to monitor the temperature. The thermocouple, the end of the glass electrode and the Pt foils for the conductivity measurement were at nearly equal distances from the bottom of the polypropylene vessel.

The second cell was of a similar construction to the first cell. It contained a microelectrode (Pt wire of 0.01 cm diameter in glass capillary of 0.15 cm outer diameter), a Pt foil as counter electrode, an Ag|AgCl reference electrode and the thermocouple. The reference electrode consisted of a silver wire in a glass tubing with the lower end protruding. A film of silver chloride had been formed anodically with 12 mA/cm^2 for 20 min in 1 M HCl on the lower part of the wire. This procedure yielded reproducible reference electrodes. The measurements of the H^+ ion limiting current were made by applying a single negative sweep to −1.2 V at 100 mV/s and recording the current–potential curve (I–E curve) by an X–Y recorder. The sweep was applied at certain intervals and started close to the potential of the hydrogen electrode in the given solution. The nitrogen bubbling and the magnetic stirrer were interrupted briefly during this measurement to reduce the effect of current oscillations.

For comparison, the H^+ ion limiting current was also determined in two reference solutions with the molar ratio ($CH_3OH:H_2O:HCl$) of 4:2:10^{-3} or 4:2:10^{-4}. Such ratios are expected if the net reaction:

$$n Si(OCH_3)_4 + m H_2O$$

$$= SiO_2 + 4n CH_3OH + (m - 2n) H_2O \qquad (1)$$
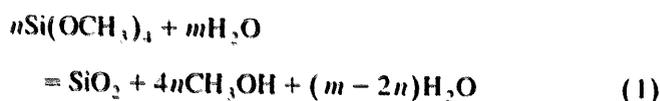
is completed for the TMOS solutions used in this work.

Attempts to employ a microelectrode with the smaller diameter of 0.005 cm were not successful. Initial measurements with this electrode showed that the Pt surface was blocked by a film, probably SiO_2, after applying a few sweeps. Finally, it should be mentioned that the use of
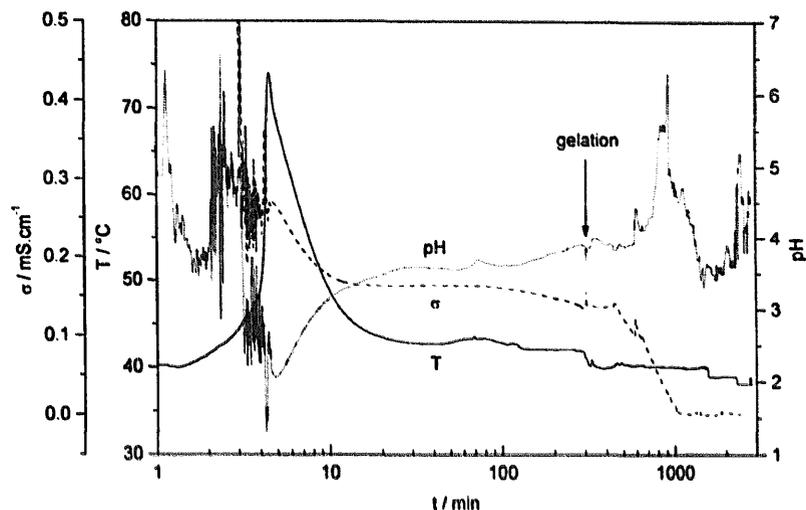
Fig. 1. Time dependence of temperature, pH and conductivity during and after mixing the solution with the molar ratio 1:4:10⁻⁴. Bath temperature: 40°C.

only one cell for all the electrochemical techniques was not feasible because of an electronic interference between the instruments for the measurements of pH and limiting current.

It should be pointed out that the regions which determine the experimental values of pH, conductivity, H^+ ion limiting current and temperature vary considerably in size. Average values over relatively large volumes are obtained in the measurement of conductivity and temperature. In contrast, small dimensions are involved with the microelectrode. Finally, the concentration of H^+ ions in the vicinity of the active part of the relatively large surface at the bottom of the glass electrode controls the pH. Thus the different types of measurements are expected to reflect the same trends in the chemical processes, leading from a sol to a gel. However, a proportionality between the hydrogen ion concentration, obtained from the pH, and the H^+ ion limiting current need not be observed.

The external outputs of the pH meter, the thermocouple meter and the conductivity meter, operating at a frequency of 5 kHz, were used for the transfer of these data by 3 channels of a digital recorder, which was scanned periodically, to the interface of a PC/286. The scanning rate could be varied. The data of the measurements in cell 1 were stored on disk for further processing on a PC/486. The single sweep experiments in cell 2 were activated manually using a PAR programmer and potentiostat. Since a graphical determination of the limiting current was employed, the recording of the cathodic current–potential curves by an X–Y recorder proved to be efficient.

3. Results

A plot of pH, conductivity and temperature versus the logarithm of time, obtained after mixing TMOS with acidified H_2O in the molar ratio $1:4:10^{-3}$ at 40°C, is shown in

Fig. 1 as an example. The conductivity data are reproduced in such a way that the fluctuations are clearly visible. Similar plots resulted at the other temperatures and the second composition of the sol. The maximum of the temperature–time curve appeared at shorter times at the higher temperatures since the hydrolysis reaction was more rapid. The increase in the HCl concentration had a similar effect. The point of gelation, determined by visual observation, is marked by an arrow.

A cathodic current–potential curve, taken in the solution with the molar ratio $1:4:10^{-3}$ at a sweep rate of 100 mV/s, is plotted in Fig. 2 as an example. The graphical determination of the H^+ limiting current is illustrated. An attempt was made to increase the pH range of the measure-
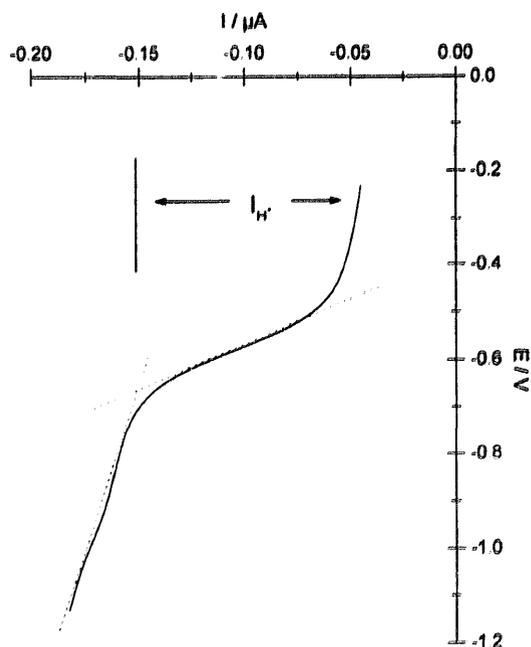

Fig. 2. Current–potential curve at 100 mV/s in the solution with the molar ratio $1:4:10^{-3}$ at 25°C.
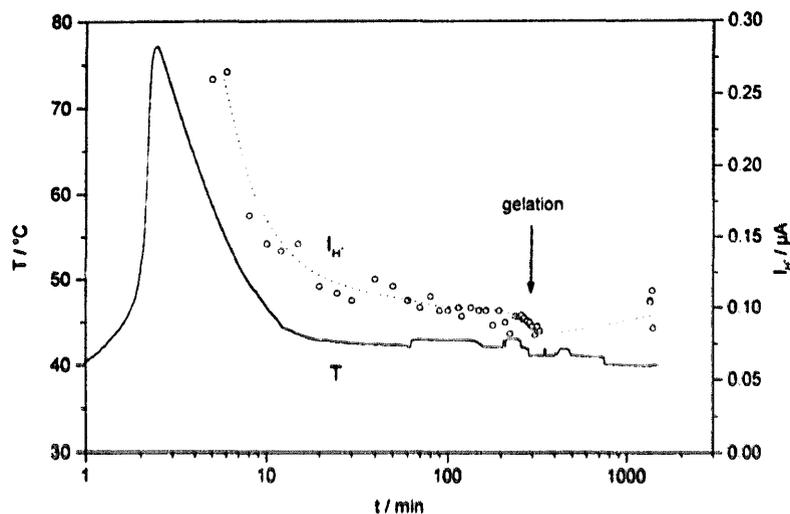
Fig. 3. Time dependence of temperature and limiting current in the solution with the molar ratio 1:4:10⁻³. Bath temperature 40°C.

ments of the limiting current. However, there are limits at both sides of this range. The formation of hydrogen bubbles occurs at greater H⁺ ion concentrations because the cathodic currents become large. Bubble formation leads to extensive current fluctuations. Since the electrode surface area is very small, even small bubbles exert great influence on the current. At lower concentrations, the limiting current becomes too small to be determined with accuracy. Another observation is briefly mentioned here. If the sweep was extended above about −1.2 V, the behaviour of the Pt surface was changed considerably, probably by the formation of a SiO₂ film. The alkaline vicinity of the electrode seems to favour the production of such a film.

The short-term behaviour of the H⁺ ion limiting current and of the temperature at 40°C are presented in Fig. 3 for 10⁻³ M HCl. The measurement of the limiting current had to be interrupted about 1 h after reaching the point of gelation in the evening. As indicated by a dashed line, it was continued the next morning. Sometimes the limiting current could be measured but in other cases this could not be done. A closer examination revealed that a measurement is feasible whenever numerous cracks are formed. In the latter case the values of the limiting current scattered considerably but were close to those obtained before gelation occurred.

4. Discussion

The measurements display a considerable rise in the solution temperature, caused by the exothermic hydrolysis of TMOS. Most of the temperature rise and fall occurs within about 15 min in our set-up at 25°C, 40°C and 50°C (Fig. 1). However, the solution temperature is still about 5°C higher than that of the bath after 15 min and approaches the bath temperature very gradually (Fig. 1). The measurements of pH, conductivity and H⁺ limiting current

are affected under the present conditions by the temperature changes at times smaller than 15 min. However, this result is not particularly restrictive since large fluctuations in pH and conductivity during the relatively slow mixing make it difficult to advance an interpretation of the time dependence for this region. In contrast, the gradual temperature decrease after 15 min does not seem to exert a noticeable influence on the experimental values of pH and conductivity.

The time dependence of pH and σ of Fig. 1 demonstrates a slight increase in pH when the point of gelation is approached. This increase is paralleled by a small decrease in the conductivity. A small decrease in the proton concentration is considered responsible for this behaviour in the system studied here. Since both curves in Fig. 1 display small peaks in the opposite direction up to about 580 min, it is concluded that correct values are obtained for pH and σ for about 300 min after gelation. Over longer periods of time the contact between electrodes and gel degenerates, leading to large fluctuations in the pH values and to a strong decrease in conductivity with time (Fig. 1). The preceding statements can be made only if the measurement of the two parameters is carried out continuously in a system where possible changes occur relatively fast. The previous studies [6–8,12] of the transition from sol to gel were done point by point in systems with slow changes and therefore yielded the information that the transport processes remain unchanged to a first approximation.

When gelation is approached, the rotations of the magnetic stirring rod become slower and finally stop. This process occurs within 10 min and allows an accurate determination of the gelation point by visual observation. Fig. 1 demonstrates that there is a slight increase in pH during the approach to the gelation point. The occurrence of gelation is indicated by spikes in the pH–t curve and the σ–t curve. The T–t curve displays a spike, followed by a narrow minimum. The spikes appear at the same time in the three curves.

The beginning part of the E–I curve in Fig. 2 reflects a strong increase in potential with current. The hydrogen overvoltage is relatively large in contrast [17] to the behaviour of a Pt electrode, pretreated anodically. It is suggested that the electrode surface is poisoned, possibly by SiO_2 particles. When mass transport of H^+ ions becomes rate determining at larger overvoltages, the limiting current I_H, is observed. Afterwards there is a rapid increase in E with I, due to the transition of H_2 evolution from acid to alkaline media.

The limiting current of H^+ ions is shown as a function of the logarithm of time in Fig. 3. The I_H,–t curve does not contain a maximum like the T–t curve in Fig. 1. However, the first two values of I_H, are sometimes smaller than the next ones. This indicates that the I_H,–t curve has a shape which is similar to that of the T–t curve. It is suggested that the temperature rise and fall are responsible for the initial part of the I_H,–t curve.

In Fig. 3 the limiting current decreases slightly between 100 and 300 min. The decrease is the strongest close to the point of gelation. This result is in agreement with the data for the said time interval in Fig. 1. The interpretation, a slight decrease in the proton concentration, was already advanced in the discussion of the data of Fig. 1.

As stated in Section 1, a detailed interpretation of the behaviour of the diffusion coefficient of free species of a suitable redox system has been given in [7,8] for different sols and gels. It was overlooked there that migration should be considered in addition to diffusion, since an excess of foreign electrolyte was not present. However, it is very likely that the general conclusions in [7,8] remain valid for the following reasons:

(1) early work, comparing diffusion in the presence of an excess of foreign electrolyte with combined diffusion and migration in the absence of foreign electrolyte at the same concentration of H^+ ions, demonstrated [17] that the product $I\tau^{1/2}$ was independent of I for both cases. Here, I designates the cathodic current and τ the transition time during galvanostatic measurements of the transition of H_2 evolution from acid to alkaline solution. The relative increase in the product $I\tau^{1/2}$ from diffusion in the presence of an excess of foreign electrolyte to combined diffusion and migration in the absence of foreign electrolyte was found [17] to be somewhat larger than $\sqrt{2}$ in a linear geometry.

(2) ratios of diffusion coefficients, computed for spherical geometry, were considered in [7,8].

Another effect has to be included besides the combined diffusion and migration for the interpretation of I_H, in the present work. This became evident from the measurements in the reference solutions. When computing a diffusion coefficient according to the equation for a microelectrode, it turned out to be a factor of about 10 larger than D_H, (about 10^{-4} cm^2 s^{-1}). Such a factor is too large to be

explained by the contribution of migration. The other effect which has not to be considered for redox systems which do not involve the production of gas is the transport of H_2 by bubbles. Bubble formation becomes noticeable [20] at active Pt electrodes at cathodic current densities above about 10 mA cm^{-2}. It becomes effective at smaller current densities when the electrodes are not activated by anodic pretreatment, as in the present work. The bubble formation in the present studies produces convection of the solution in the vicinity of the electrode. Therefore it is not possible to give a more detailed discussion of the mass transport processes here. A linear dependence of the limiting current upon the concentration of H^+ is not observable because the effect of bubble formation becomes earlier noticeable when the pH decreases.

Acknowledgements

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