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Application of electrochemical impedance spectroscopy (EIS) for in situ study of glass alteration

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Abstract

In situ continuous recording of glass alteration is a difficult experimental problem. In this paper, an electrochemical method is proposed for monitoring the concentrations of dissolved ions in the altering solution. This method was tested in a real case (alteration of a binary glass in water at room temperature). The possibility to measure local concentrations in the vicinity of the glass/solution interface is an interesting prospective of the method. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Many experimental studies have been devoted to the problem of glass alteration in water during the last 20 years. The main mechanisms involved in this process are now well known. Glass alteration results from two different pH-dependent processes known as interdiffusion and dissolution of the glassy network [1–5]. Two types of informations are important for alteration studies:

1. evolution of the glass surface properties (morphology, texture, composition, etc.
2. evolution of the chemical composition of the altering solution.

Monitoring the solution composition during glass alteration allows one to make a solid/liquid mass transfer balance and to measure the glass dissolution rate [6].

Usually solution sampling at different times is used for monitoring the solution composition. This procedure is not completely satisfactory for the following reasons:

1. short-time phenomena cannot be detected;
2. sampling data do not reflect the local chemistry of the altering solution in the vicinity of the glass/liquid interface;
3. perturbations of the experimental conditions due to sampling are possible.

In this paper, electrochemical impedance spectroscopy (EIS) is proposed for in situ continuous monitoring of glass alteration in water. This technique is well-adapted for qualitative recording, and in some cases quantitative results can be obtained (evolution of the dissolved ions concentrations). It provides the following advantages in respect to alteration studies:

1. no contamination of the solution during measurements;
2. good reproducibility of experimental data;
3. measurements can be provided in media with very low electrical conductivity (such as deionized water), contrarily to stationary electrochemical methods.

In the first part of this paper, the principle of EIS and its application to the study of glass alteration are presented. In the second part, an example of a concrete utilization is given (continuous recording of pH and sodium concentration during the alteration of a binary glass in water). The possible application of EIS for measuring local concentrations near the glass/solution interface is also discussed.

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2. Application of EIS to the monitoring of glass alteration in water

2.1. Principle and impedance module measurements

EIS is widely used for studying electrochemical reactions and the structure of polarized interfaces [7,8]. The method consists in measuring the impedance of an electrode system in contact with the electrolyte solution. Impedance (Z) is defined as a proportionality coefficient between alternating potential $U(t) = U_0 \cos(\omega t)$ which is applied to the electrodes and alternating current $I(t) = I_0 \cos(\omega t + \theta)$ which passes in the electrochemical system. Impedance is expressed by means of a complex number $Z = |Z|e^{i\theta}$ where the impedance module: $|Z| = U_0/I_0$. The argument of impedance θ (phase angle) is expressed in degrees. Both impedance module ($|Z|$) and phase angle (θ) depend on the frequency of the electrical perturbation ω.

In general, the total impedance of the system is the sum of the electrical resistance of the solution and the impedances of the electrode/solution interfaces. The electrical resistance of the solution (R) can be expressed as a function of the dissolved ions concentrations, according to the following equations [9,10]:

$$R = \frac{A}{\chi}, \tag{1}$$

$$\chi = \sum_i D_i n_i^2 C_i, \tag{2}$$

where A is a constant geometrical factor, D_i, n_i, C_i are respectively the diffusion coefficient in water, the electrical charge and the molar concentration of each dissolved ion. Electrical resistance measurements can be used to monitor the variations of the solution composition. For example, the durabilities of different glasses can be compared by this method. Furthermore, our experiments showed that phase angle measurements are useful for identification and separate quantification of ions [11].

2.2. Influence of sodium and calcium ions on phase angle measurements

The influence of these two ions on the phase angle value was studied in an experimental way, using different ionic compounds (sodium carbonate, sodium sulphate, sodium chloride and calcium carbonate). In each case, 2 g of powdered material were dissolved in deionized water at room temperature (20 ± 2°C). For each salt, impedance measurements were recorded at different times during dissolution. The experimental setup corresponds to Fig. 1. The impedancemeter was a Solartron 1280, which allows the scanning of a frequency range up to 20 000 Hz. For our experiments, measurements were recorded in the [0.1 Hz; 10 000 Hz] frequency range. Results are reported on graphs which represent the variation of the impedance module and phase angle with frequency at different reaction times (Fig. 2).

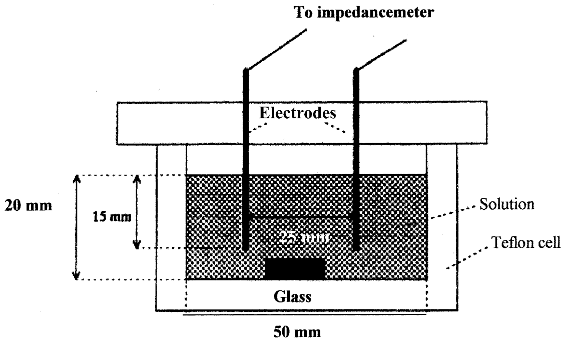

Fig. 1. Schema of the experimental setup.

The evolution of the phase angle value during the dissolution of salts was rather different for sodic compounds and for calcium carbonate. In the first case, the phase angle value increased at all frequencies between 0.1 and 20 000 Hz. In the second case, this increase was limited to low (<1 Hz) and high (>10 000 Hz) frequency ranges. So, calcium ions at low concentration [2] have no sensible influence at medium frequencies.

The variation of the phase angle value versus the sodium concentration was studied experimentally in the [1000 Hz; 10 000 Hz] frequency range (Fig. 3). For this purpose, measurements were recorded on titrated sodium carbonate solutions with concentrations (in mol l^{-1} of Na_2CO_3) from 10^{-3} to 10^{-1}. In the $[10^{-3}; 7 \times 10^{-3}]$ and $[10^{-2}; 10^{-1}]$ concentration ranges, the variation of the phase angle versus the sodium concentration is linear for all tested frequencies (1000, 2000, 5000, 10 000 Hz). In the $[7 \times 10^{-3}; 10^{-2}]$ concentration range, the variation of the phase angle is nonlinear. A maximum of θ is noticed for concentrations about 8×10^{-3} mol l^{-1}. So, as shown by Fig. 3, quantification of sodium ions by means of phase angle measurements is possible in the following concentration ranges (in mol l^{-1} of Na_2CO_3): $[10^{-3}; 5.2 \times 10^{-3}]$ and $[1.5 \times 10^{-2}; 10^{-1}]$. Outside these two ranges, precise quantification is not possible because the $\theta = f([Na_2CO_3])$ relation is not bijective. In this case, only a concentration interval can be associated to a measured phase angle value.

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[2] Solubility of calcium carbonate in water at 25°C: 1.40 mg $CaCO_3$ per 100 ml [12]. The $[Ca^{2+}]$ concentration at equilibrium is, thus, equal to 1.40×10^{-4} mol l^{-1}. As calcium carbonate is only partly dissolved this concentration is independant from the calcium carbonate weight introduced in the solution.

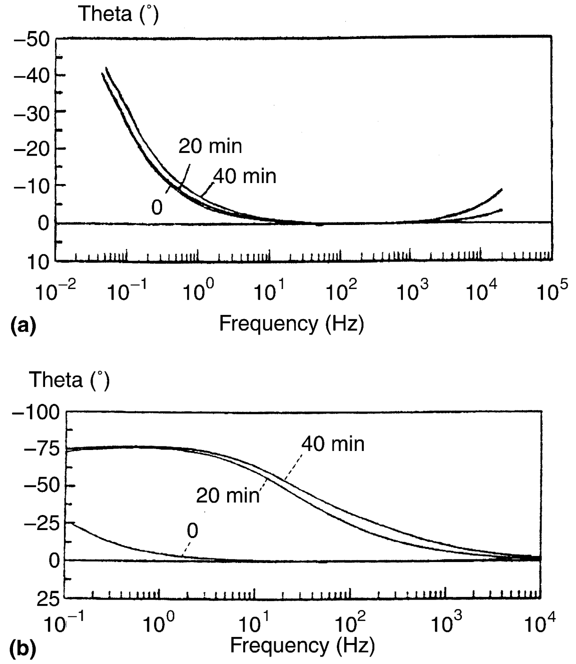

Fig. 2. Evolution of the phase angle value during the dissolution of calcium carbonate (a) and sodium carbonate (b) in deionized water at room temperature.

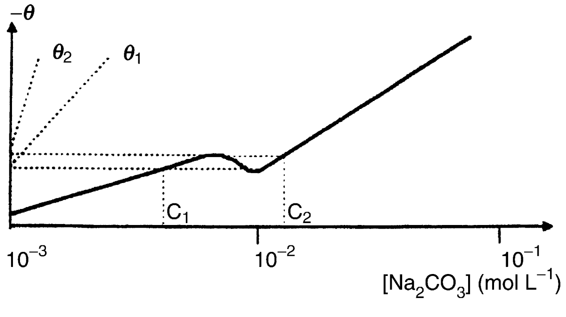

Fig. 3. Relation between the phase angle value and the sodium concentration in the [1000 Hz; 10 000 Hz] frequency range.

As a conclusion, phase angle measurements may allow one to quantify separately sodium ions when they co-exist with calcium ions at low concentration.

2.3. Application to the monitoring of glass alteration

Alteration manifests itself by a mass transfer between the glass and the surrounding solution. In the present study, the solution pH is always less than 9.6. Under this pH value, dissolved silica is mainly represented by the neutral complex $Si(OH)_4$, which is not detected by impedancemetry.

2.3.1. Alteration of a binary glass in pure water

In a first step, a CO_2-free altering solution, containing only H^+, OH^- and H_2O, is considered (later, the influence of dissolved carbon dioxide will be taken into account). Let us consider the alteration of a binary glass, for example Na_2O–SiO_2. At each time, the solution contains only three types of ions (Na^+, H^+, OH^-). The concentrations of these species vary with time, due to the glass/solution interdiffusion process. The sodium concentration $[Na^+]$, which is near zero at initial time, increases with time, whereas $[H^+]$ decreases. As a result, $[OH^-]$ also changes according to Eq. (4a). At each time, the following relations can be used to determine ion concentrations:

$$[H^+]\cdot[OH^-] = 10^{-14} \quad \text{(Dissociation constant of water at 25°C)}, \tag{3}$$

$$[H^+] + [Na^+] = [OH^-] \quad \text{(Electroneutrality of the bulk solution)}, \tag{4a}$$

$$\frac{A}{R} = D_{H^+}[H^+] + D_{OH^-}[OH^-] + D_{Na^+}[Na^+] \quad \text{(Combination of Eqs. (1) and (2))}. \tag{5a}$$

Combination of Eqs. (3)–(5b) allows one to determine three concentrations $([H^+], [OH^-], [Na^+])$ from electrical resistance measurements. The geometrical coefficient A (see Eqs. (1) and (5a)) depends on the geometry of the electrodes system. This coefficient can be experimentally determined by means of electrical resistance measurements on titrated solutions [11]. So, electrical resistance measurements allow one to monitor the evolution of pH and sodium concentration during the alteration of binary glasses in pure water.

2.3.2. Alteration of a ternary glass in pure water

Let us now consider the alteration of a ternary glass, for example $Na_2O/CaO/SiO_2$, in pure water. In comparison with binary glasses, one more concentration $([Ca^{2+}])$ must be monitored. Thus, Eqs. (4a), (4b), (5a) and (5b) become

$$[H^+] + [Na^+] + [Ca^{2+}] = [OH^-] \tag{4b}$$

$$\frac{A}{R} = D_{H^+}[H^+] + D_{OH^-}[OH^-] + D_{Na^+}[Na^+] + D_{Ca^{2+}}[Ca^{2+}]. \tag{5b}$$

In this case (three equations, four unknown concentrations), electrical resistance measurements are not sufficient for quantitative monitoring. Nevertheless, in some cases [3] phase angle measurements can be used to determine the sodium concentration (see Section 2.2). Then, the other concentrations can be obtained by

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[3] Only for limited range of composition.

means of electrical resistance measurements (Eqs. (3), (4b), (5b)).

2.3.3. Influence of dissolved CO_2

In real conditions, the altering solution is not pure water. At least, the influence of dissolved carbon dioxide should be taken into account, so Eqs. (4a),(4b),(5a) and (5b) need to be modified. If the solution pH does not increase to very basic values, the following approximations can be made:

1. dissolved CO_2 is mainly represented by HCO_3^- ions,
2. the $[HCO_3^-]$ concentration is not strongly modified by glass alteration and can be considered as constant. In this situation, $[HCO_3^-]$ can be determined by measuring simultaneously the solution pH and electrical conductivity at initial time. Then, the value of $[HCO_3^-]$ is reported in Eqs. (4a)–(5b) In the next example (see Section 3), the presence of dissolved carbon dioxide is taken into account in data interpretation.

3. Example of application

In the following example, EIS is used for monitoring pH and sodium concentration during the alteration of a binary (Na_2O–SiO_2) glass. Experiments were conducted in deionized water (initial pH: 5.9), at room temperature (20 ± 2°C). The experimental setup corresponds to Fig. 1. Both impedance module and phase angle were measured every 5 min, up to 150 min. The glass sample was a small block with polished faces (surface about 2 cm^2), the S/V ratio was about 0.1 cm^{-1}. The glass, with molecular composition of about $20Na_2O, 80SiO_2$, was synthesized at 1200°C from silica powder and hydrated sodium carbonate.

For each time, both sodium concentration and pH were determined using the method presented in Section 2.3. The presence of dissolved carbon dioxide was taken into account: the $[HCO_3^-]$ concentration was determined from initial pH measurement.

Results were compared to these obtained by other methods (pH-metry and ICP–AES analysis) for similar experimental conditions (Table 1). The qualitative evolution of pH and sodium concentration is the same for EIS and other methods, but impedance measurements give slightly higher pH values and slightly lower sodium concentration values.

The evolution of pH determined by EIS (Fig. 4) shows a very fast increase in the first 5 min of glass alteration. From 5 to 150 min, the pH evolution is much lower and decreases with time. The evolution of $[Na^+]$ determined by EIS presents four steps (Fig. 5):

- at 5 min, the increasing of $[Na^+]$ is very fast;
- between 5 and 30 min, a quite linear evolution can be noticed;
- between 30 and 120 min, the evolution is also quite linear but with a higher slope;
- after 120 min, the evolution rate of $[Na^+]$ decreases.

It should be noticed that the evolution of the sodium concentration deduced from continuous impedance measurements is not in complete agreement with classical models of interdiffusion [13], where sodium extraction is described by a $t^{1/2}$ rate law. Nevertheless, the general evolution and order of magnitude of calculated

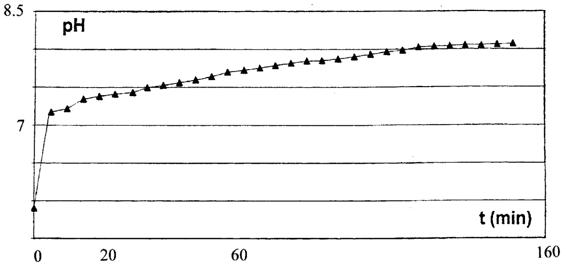

Fig. 4. Continuous recording of glass alteration by EIS: monitoring of pH (binary glass).

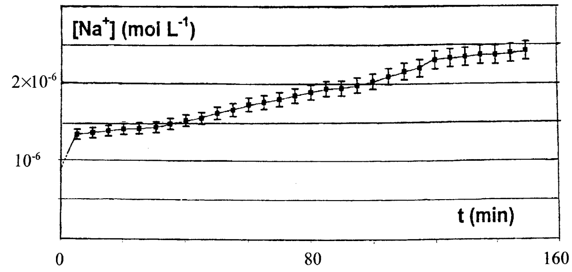

Fig. 5. Continuous recording of glass alteration by EIS: monitoring of sodium concentration.

Table 1
Comparison of results obtained by EIS and other methods (pH-metry, ICP–AES)

Time (min)	60	120	150
Measured pH	7.33 ± 0.01	7.50 ± 0.01	7.56 ± 0.01
Calculated pH (EIS)	7.70 ± 0.05	8.03 ± 0.05	8.10 ± 0.05
Measured $[Na^+]^a$	2.3 ± 0.1	2.9 ± 0.1	3.1 ± 0.1
Calculated $[Na^+]^a$(EIS)	1.7 ± 0.1	2.3 ± 0.1	2.4 ± 0.1

[a] Data in 10^{-6} mol l^{-1}.

values are realistic in comparison with the results of other methods. A possible explanation is that concentrations determined by EIS are not equal to the bulk ones but correspond to local conditions in the vicinity of the electrodes.

4. Conclusion

This paper shows that EIS is a powerful method with respect to alteration studies. It is well-adapted for in situ continuous monitoring of the alteration process for ‘simple’ glasses alteration (compositions with two or three components, including silica). At the present time, applications mainly concern fundamental research (understanding of glass alteration mechanisms). The possible applications of EIS for studying the alteration of complex industrial glasses need further developments of this method. An important advantage of EIS in respect to alteration studies is the possibility to measure local concentrations, which allows one to investigate local conditions near the glass surface. This information is very important for understanding of the glass/solution interface evolution. For this purpose, experiments are presently conducted with an electrode system in the vicinity of the glass surface (1 mm).

References

[1] R.H. Doremus, J. Non-Cryst. Solids 19 (1975) 137.
[2] H. Scholze, J. Non-Cryst. Solids 52 (1982) 91.
[3] L.L. Hench, J. Phys. 12 (9) (1982) 625.
[4] B.C. Bunker, G.W. Arnold, E.K. Beauchamp, D.E. Day, J. Non-Cryst. Solids 58 (1983) 295.
[5] M. Schreiner, J. Am. Ceram. Soc. 72 (9) (1989) 1713.
[6] R.W. Douglas, J.O. Isard, J. Soc. Glass Tech. 33 (1949) 289.
[7] D.D. Macdonald, Transient Techniques in Electrochemistry, Plenum, New York, 1977.
[8] Z.B. Stoynov, B.M. Grafov, B.S. Savova-Stoynov, V.V. Elkin, Electrochemical Impedance, Nauka, Moscow, 1991.
[9] V.G. Levich, Physicochemical Hydrodynamics, Prentice-Hall, Englewood Cliffs, NJ, 1962.
[10] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980.
[11] D. Chaulet, S. Martemianov, J.H. Thomassin, in: Mallinson (Ed.), Ageing Studies and Lifetime Extension of Materials, Kluwer Academic/Plenum, New York, 2001, p. 367.
[12] CRC Handbook of Chemistry and Physics, 75th Ed., CRC, London, 1994/95.
[13] A. Paul, Chemistry of Glasses, Chapman and Hall, London, 1982.