Original Paper

Transient ionic conductivity in fused silica

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Transient currents in doped and commercial type-I fused silica glasses were monitored by electrolyzing alkali ions (Na^+, Li^+ and K^+) through a sample disk in a U-tube dc non-blocking conductivity cell until steady state was achieved. The experiments were carried out either at 600 or 650 °C. Approach to steady state varied from sample to sample depending not only on the electrolyzing ion but also on the alumina/alkali ratio and the concentration of Li^+ and Na^+ impurity level in the silica.

Results indicated that the transient behavior (current versus time) at a particular temperature was best expressed as a lg – lg plot showing two linear regions. The initial slope was attributed to the flushing of more mobile species and the final slope to the disappearance of interdiffusional coupling effects. The nature of the interdiffusional coupling, in some cases, was typical of the mixed-alkali effect in silicate glasses containing much higher levels of mixed alkali.

Instationäre Ionenleitfähigkeit von Kieselglas

Mit der Alkaliionenelektrolyse (Na^+-, Li^+- und K^+-Ionen) wurden in dotierten und handelsüblichen Kieselgläsern des Typs I instationäre elektrische Ströme bis zum Erreichen der stationären Leitfähigkeit verfolgt. Die Messungen wurden an scheibenförmigen Proben in einer U-rohrförmigen Leitfähigkeitszelle mit nicht-blockierenden Elektroden bei 600 oder 650 °C durchgeführt. Das Erreichen der stationären Leitfähigkeit änderte sich von Probe zu Probe und hing einmal von der Art des elektrolysierten Ions ab, zum anderen vom Verhältnis Aluminiumoxid/Alkalioxid sowie von der Verunreinigungskonzentration der Li^+- und Na^+-Ionen in Kieselglas.

Die Ergebnisse zeigten, daß das instationäre Verhalten (Strom in Abhängigkeit von der Zeit) bei einer bestimmten Temperatur am besten mit Hilfe einer doppeltlogarithmischen Auftragung, die zwei lineare Bereiche aufwies, beschrieben werden konnte. Dabei konnte die Anfangssteigung der Geraden dem Fluten mit den beweglicheren Ionen zugeordnet werden und die Endsteigung dem Verschwinden von Interdiffusionskoppelungeffekten. Die Art dieser Koppelungseffekte war in einigen Fällen typisch für den Mischalkalieffekt in Silicatgläsern mit wesentlich höherem Anteil an Mischalkalien.

1. Introduction

When an electric field is applied across a sample in non-blocking mode, the cations are flushed out of the sample at the cathode and are replaced by the electrolyzing ions at the anode. The magnitude of the current through the sample as a function of time depends upon several factors. Some of the well-known factors that determine the nature of transient current are: the concentration of charge carriers in the glass, and the difference in the size of charge carriers in the glass and the electrolyzing ion. An increase (or decrease) in current as a function of time would be observed if the electrolyzing ion has a higher (or lower) mobility compared to the ions in the glass. Thus, depending upon the ratio of the mobilities of the anode electrolyte ion to the ions in the glass, different alkali ions in the glass would contribute to the conduction at different times. This, in turn, would determine the time to attain a steady state, e.g. when the parent ions in the glass have been flushed out to the extent that the current no longer appears to change significantly with time.

Even if the glass contained a single alkali ion at the beginning of the electrolysis, it could become a "mixed-alkali glass" during the transient conduction stage depending upon the ionic mobilities. The effect of one alkali ion upon the other's mobility is well-known as the "mixed-alkali effect" [1]. An analysis of the transient behavior could be used to gain a better insight into the mixed-alkali effect.

If the ions present in the glass differ in size compared to the electrolyzing ion, then stresses may develop in the glass. The magnitude of the stresses so developed depends on the concentration of cations in the glass. The higher the alkali ion concentration, the higher the stress. Failure occurs when the stresses developed during electrolysis exceed the engineering strength of the glass. Abou-El-leil and Cooper [2] and Shaisha and Cooper [3] have attempted to analyze the stress profiles in a field-assisted ion exchange process in high alkali silicate glasses. In their experiments, the electrolysis could not be carried out to completion: specimens fractured due to generation of high stresses when the diffusion depth exceeded ≈ 500 μm. On the

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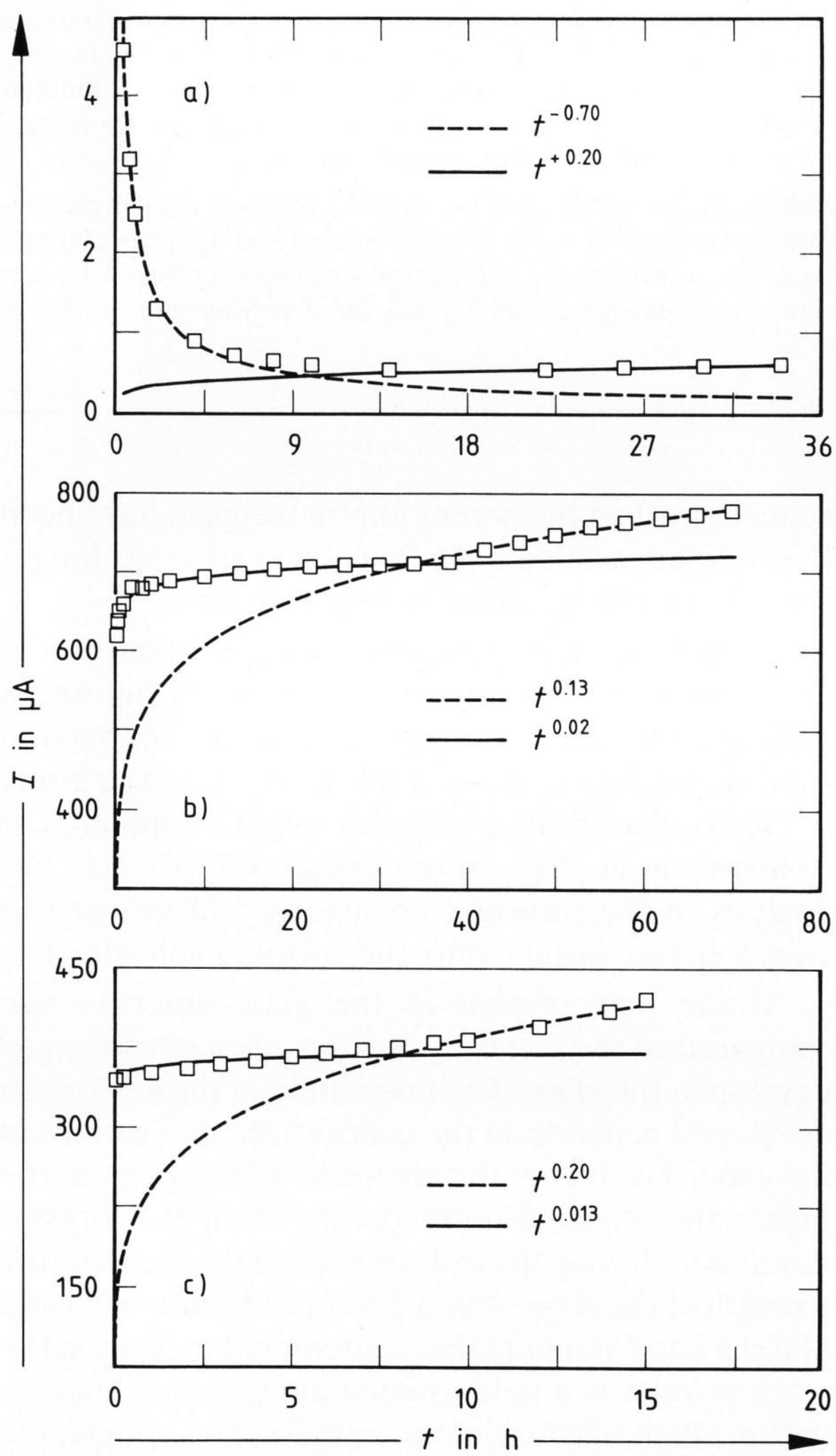
Table 1. Impurity content of doped and commercial type-I fused silica

sample	impurity content in ppm					Al_2O_3/M_2O
	Al_2O_3	Na_2O	Li_2O	K_2O	M_2O[3])	
ME 25	48.2	57.8	5.6	< 1.5	63.4	0.8
ME 24	24.9	14.9	3.9	< 1.5	18.8	1.3
ME 11	29.1	14.2	3.5	< 1.5	17.7	1.6
ME 27	25.1	5.6	2.6	< 1.5	8.2	3.1
ME 18	79.0	16.9	2.2	3.8	19.1	3.5
ME 10	24.9	1.6	4.8	< 1.5	6.4	3.9
ME 26	73.3	8.5	3.0	< 1.5	11.5	6.4
ME 19	141.0	15.9	2.6	< 1.5	18.5	7.6
ME 20	138.0	9.1	1.7	< 1.5	10.8	12.8
ME 21	61.0	1.0	3.0	< 1.5	4.0	15.2
ME 16	351.0	5.1	4.3	< 1.5	9.4	37.3
GE 124	22.3	1.8	4.3	< 1.5	6.1	3.6
GE 214	22.3	1.8	4.3	< 1.5	6.1	3.6
GE 510	22.3	1.8	4.3	< 1.5	6.1	3.6

[3]) $M_2O = Li_2O + Na_2O$.



Figures 2a to c. Electrolysis by a) K^+ ions in sample ME 27 at 650 °C, b) Li^+ ions in sample ME 11 at 600 °C, c) Na^+ ions in sample ME 21 at 650 °C.

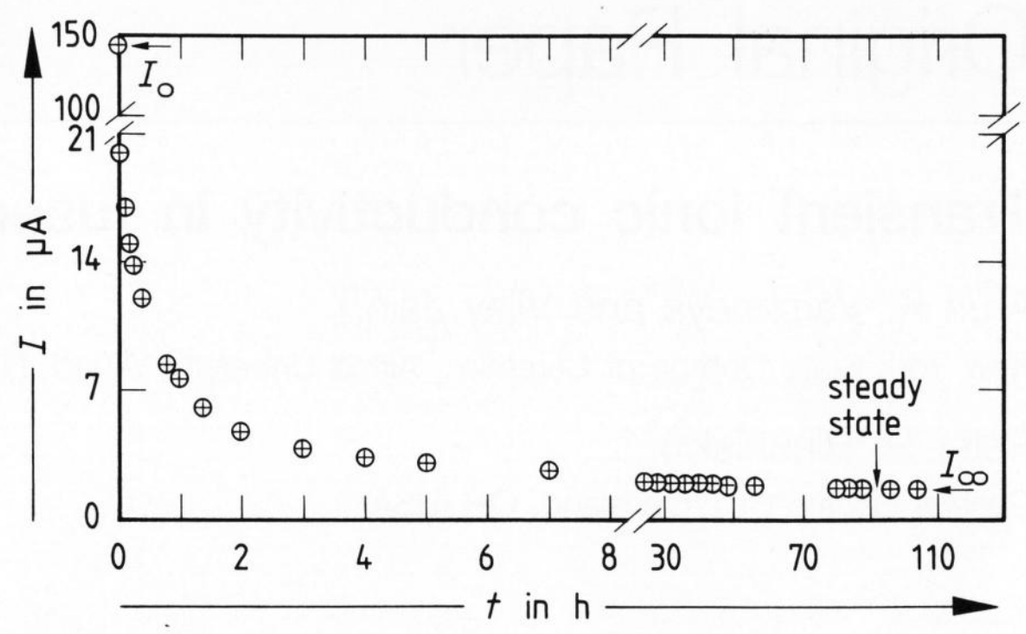


Figure 1. Electrolysis by K^+ ions in sample GE 124 at 650 °C.

other hand, since doped fused silicas contain only trace level concentrations of alkali ions, the electrolysis in doped fused silicas can be carried out to reveal the transient behavior until a steady state is reached. It is an interesting question, indeed, whether or not the transient conduction in doped fused silicas displays attributes typical of glasses containing much higher concentrations of mixed alkalis. The primary objective of this study was to answer this question.

The transient currents in doped and commercial type-I fused silica glasses were monitored by electrolyzing alkali ions (Na^+, Li^+ and K^+) through a sample disk in a U-tube type dc non-blocking conductivity cell until steady state was achieved [4]. The experiments were carried out either at 600 or 650 °C. Table 1 lists the chemical analysis of the doped fused silica glasses.

2. Results and discussion

Figures 1 and 2a to c represent trends typically observed for K^+, Na^+ and Li^+ ion transient conduction in doped and commercial fused silica samples at 650 or 600 °C. In most cases, the variation of current, I, with time, t, appeared to be given by two piecewise smooth functions (drawn in the figures) rather than a single monotonically decreasing or increasing function.

According to Doremus [5], the electrolysis of fused silica by low mobility cation such as K^+ causes the alkali ions to move in the form of bands or layers. This is schematically shown in figure 3. The net resistance in such a case is a series resistance, i.e.

$$\frac{1}{I} = \frac{R_1 + R_2}{V} = \frac{1}{VA}\left[\frac{l_1}{\sigma_1} + \frac{l_2}{\sigma_2}\right] \quad (1)$$

where I = current, V = voltage, A = cross-sectional area; l_1, l_2 = widths of the bands of exiting ions "1" and entering ions "2" having conductivities σ_1 and σ_2, respectively, R_1 and R_2 = resistances of the bands l_1 and l_2.

Differentiating with respect to time, t, one gets

$$-\frac{1}{I^2}\frac{\mathrm{d}I}{\mathrm{d}t} = \frac{1}{V\,A}\left[\frac{1}{\sigma_1} - \frac{1}{\sigma_2}\right]\frac{\mathrm{d}l_1}{\mathrm{d}t} \tag{2}$$

where Doremus assumed σ_1 and σ_2 to be independent of time displaying no interdiffusional coupling effects. In other words, the glass was merely a layered composite of single alkali glasses. From charge conservation, the flux J is given by

$$J = -C_0\frac{\mathrm{d}l_1}{\mathrm{d}t} = \frac{+I}{A\,F} \tag{3}$$

where C_0 = number of exchangeable ionic sites/volume and F = Faraday constant.

Substitution of $\mathrm{d}l_1/\mathrm{d}t$ from equation (3) in equation (2) gives

$$\frac{+1}{I^3}\frac{\mathrm{d}I}{\mathrm{d}t} = \frac{1}{C_0\,A^2\,V\,F}\left[\frac{1}{\sigma_1} - \frac{1}{\sigma_2}\right]. \tag{4}$$

After integration, one gets

$$\frac{1}{I^2} - \frac{1}{I_0^2} = \frac{1}{C_0\,A^2\,V\,F}\left[\frac{1}{\sigma_1} - \frac{1}{\sigma_2}\right]t \tag{5}$$

where I_0 is the current at $t = 0$. Doremus [5] analyzed the transient conduction data obtained for K^+ electrolysis in GE 204 fused silica over 5 h and failed to get a linear dependence of $1/I^2$ upon t beyond ≈3 h. This deviation was ascribed to the cylindrical shape of the fused silica specimen. A similar plot for electrolysis by Li^+ ions in Spectrosil silica (Thermal Syndicate Ltd., Wallsend, Northumberland (Great Britain)) which contained Na^+ ions initially was not linear even for the first hour of electrolysis. This was attributed by Doremus to a non-homogeneous distribution of Na^+ ions in Spectrosil. The K^+ electrolysis transient conduction data do not show a linear fit either when replotted as $1/I^2$ versus t (figure 4). Now, equation (4) can be rewritten as

$$\int_{I_0}^{I_t}\frac{\mathrm{d}I}{I^2} = \frac{1}{V\,C_0\,A^2\,F}\left[\frac{1}{\sigma_1} - \frac{1}{\sigma_2}\right]\int_0^t I\,\mathrm{d}t\,. \tag{6}$$

Hence

$$\int_0^t I\,\mathrm{d}t = V\,C_0\,A^2\,F\frac{\left[\frac{1}{I_0} - \frac{1}{I_t}\right]}{\left[\frac{1}{\sigma_1} - \frac{1}{\sigma_2}\right]} \tag{7}$$

and since $I_0 = V/R_1 = \sigma_1\,V\,A/L$ and $I_\infty = V/R_2 = \sigma_2\,V\,A/L$,

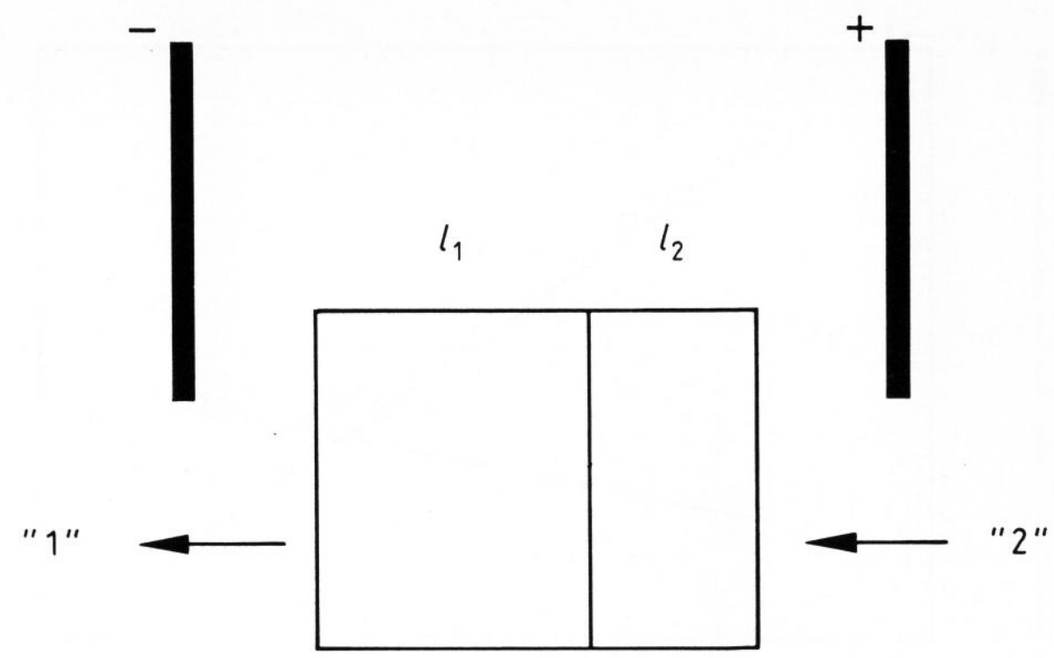


Figure 3. Doremus' [5] analysis of electrolysis by slow mobility ions. l_1, l_2 = widths of the bands of exiting ions "1" and entering ions "2".

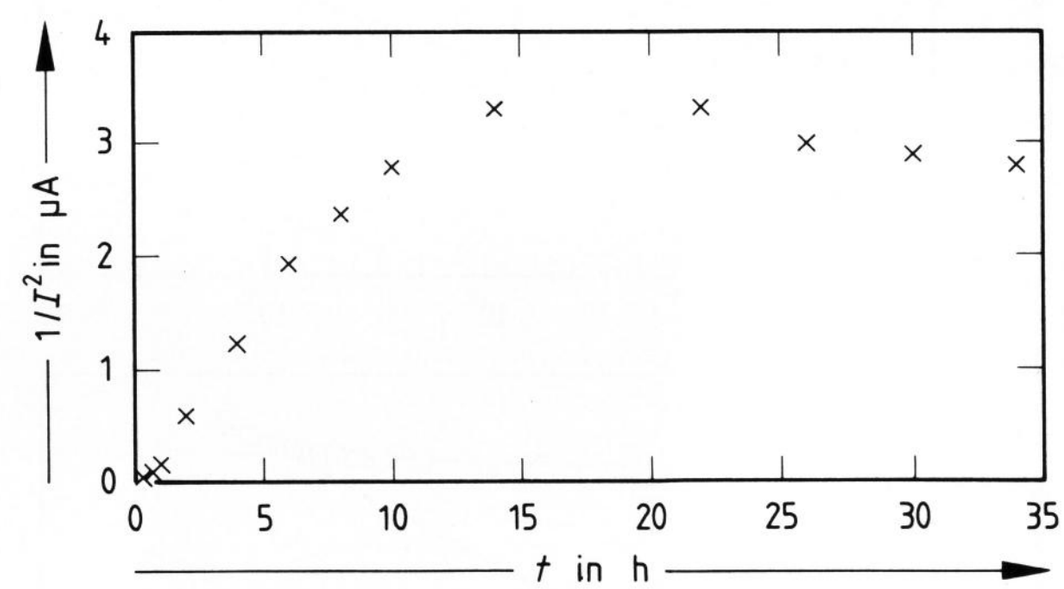


Figure 4. Replot of the K^+ ion current in sample ME 27 at 650 °C as $1/I^2$ versus t.

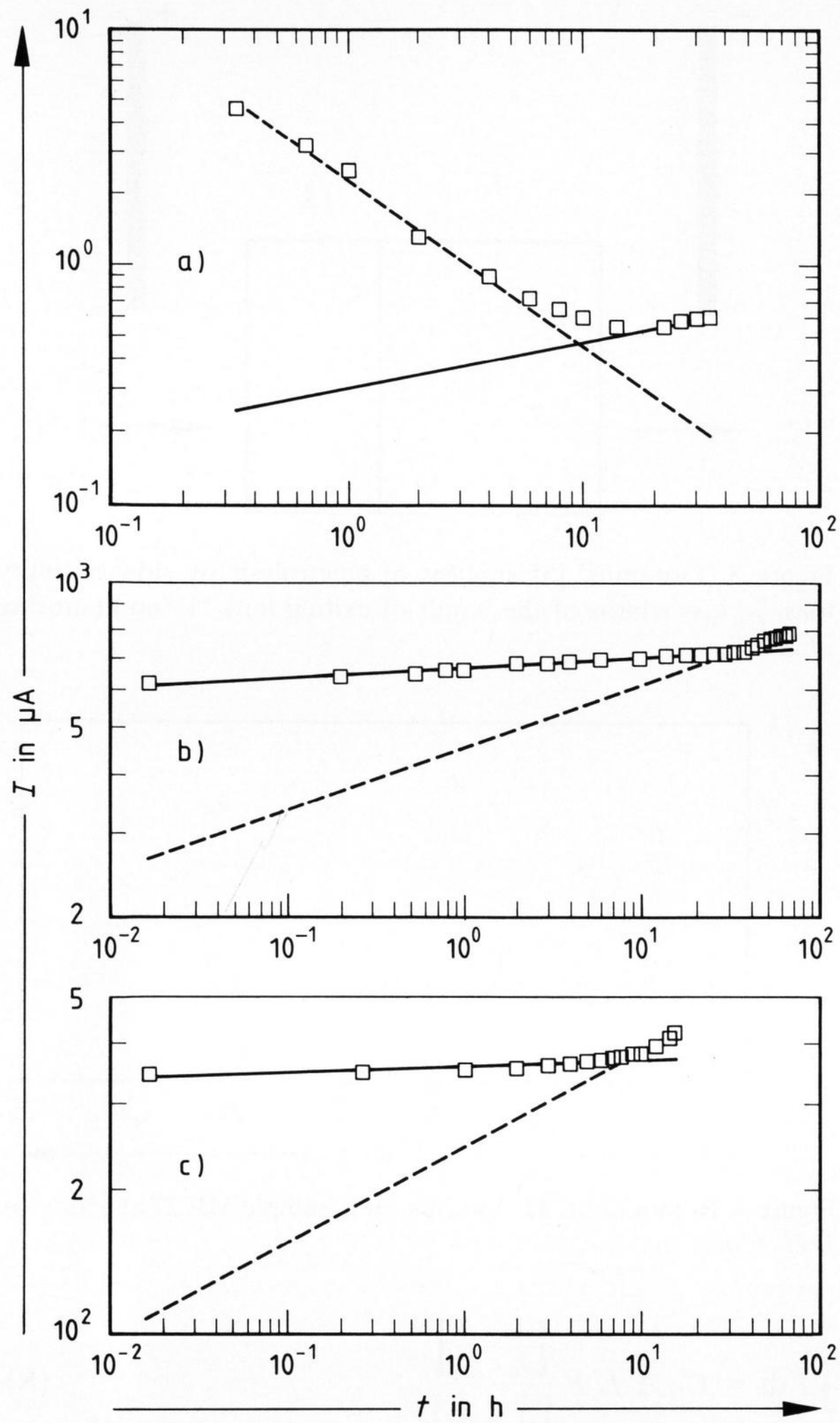
$$\int_0^t I\,\mathrm{d}t = C_0\,A\,L\,F\frac{\left[\frac{1}{I_0} - \frac{1}{I_t}\right]}{\left[\frac{1}{I_0} - \frac{1}{I_\infty}\right]}. \tag{8}$$

The left hand side represents the total charge transferred upto time t. Clearly as $t \to \infty$,

$$\int_0^t I\,\mathrm{d}t \to C_0\,A\,L\,F$$

which is essentially the charge corresponding to the total number of mobile alkali ions contained in the volume initially. For the GE124 specimen of figure 1, $C_0 = 3.4 \cdot 10^{17}/\mathrm{cm}^3$, $A = 2.14\ \mathrm{cm}^2$ and $L = 0.284$ cm. Hence $C_0\,A\,L\,F = 0.033$ C. This corresponds to the integral over the first 15 min on the $I - t$ curve. The steady state is clearly not reached by then, implying that some higher mobility Na^+ and Li^+ ions were yet to be flushed out. In fact, the attainment of an apparent steady state (time = t_s) occurs as much as ≈90 h later, at which point the area integral under the $I - t$ curve corresponds to roughly 25 times the number of ions contained initially. Yet another issue is the implication of

$$\int_0^{t_s}(I - I_\infty)\,\mathrm{d}t$$



Figures 5a to c. Replot of a) K^+ ion current in sample ME 27 at 650 °C (figure 2a), b) Li^+ ion current in sample ME 11 at 600 °C (figure 2b), c) Na^+ ion current in sample ME 21 at 650 °C (figure 2c) as lg I versus lg t.

which is the area integral above the steady state value. Since the mobility of the K^+ ion is much lower compared to that of the Na^+ or Li^+ ion, this area should correspond to the number of ($Na^+ + Li^+$) ions. Again, for figure 1,

$$\int_0^{90\,\mathrm{h}} (I - 1.8\ \mu\mathrm{A})\ \mathrm{d}t \approx 0.22\ \mathrm{C}$$

of charge which corresponds to $1.2 \cdot 10^{18}$ ions. This is roughly three times the sum of Na^+ and Li^+ ions present initially ($4.4 \cdot 10^{17}$). The observation that it took as much as 25 times the initial concentration of ions before a steady state was reached implies that many higher mobility ions are "leftover", presumably in deep potential wells. In other words, the trailing band (layer l_2) cannot be pure "2" ions, but must be a mixed-alkali layer, designated more appropriately as layer $l_{1,2}$. The discrepancy of the area integral above the steady state value can be readily resolved if it is assumed, contrary to Doremus' notion, that the conductivity $\sigma_{1,2}$ of the layer $l_{1,2}$ varies with time: the initial value is higher than that towards later stages of electrolysis. This is reminiscent of an interdiffusional coupling during ion exchange where the interdiffusion coefficient $\bar{D}$ is given by the Nernst-Planck equation $\bar{D} = D_1 D_2/(N_1 D_1 + N_2 D_2)$, where D_i and N_i are the self-diffusion coefficient and the mole fraction, respectively, of the ion i. The conductivity $\sigma_{1,2}$ depends upon the mixed-alkali ratio in addition to σ_1 and σ_2. With time, the layer l_1 shrinks to zero, and the continued electrolysis with ions "2" gradually drives $l_{1,2}$ to become purer in "2". When a few leftover ions "1" are in apparent equilibrium at the temperature of electrolysis, a seemingly steady state is achieved. Since the concentration of the deep potential wells is expected to be governed by a Boltzmann probability, it may be concluded that the higher the temperature, the lesser the leftover concentration of "1" ions. It is clear that this notion together with the act of stopping the electrolysis when no measurable change occurs in practical times leads to the observation of "conduction history" effects reported in the earlier publication [6]. The "steady state" resistance would depend upon which ions were electrolyzed, in which sequence, and at what temperatures.

The situation must be different when a fast moving cation "1" such as Na^+ or Li^+ is introduced into a glass containing lower mobility cations "2" such as K^+. As Abou-el-leil and Cooper [2] point out, the ionic distribution profiles are no longer "stable" (with respect to some frame) – the electric field itself acts to enhance mixing of the mobile species. In other words, one can no longer consider the glass to comprise of distinct layers l_2, $l_{1,2}$, etc.

In principle, as noted by Abou-el-leil and Cooper [2], a concentration distribution of the fast moving species "1" is established through the entire specimen thickness soon after the application of the field. The net conduction would, therefore, proceed as additive contributions of the individual conductances Λ rather than additive resistances, i.e.

$$\Lambda_{\mathrm{total}} = \Lambda_1 + \Lambda_{1,2} + \Lambda_2$$

where Λ_i is the conductance due to ions i if ions i exchange with themselves to transport the charge, and $\Lambda_{i,j}$ is the conductance of the mixed-alkali pairs.

To rationalize the opportunities for mixed-alkali interactions in doped fused silica, one need to examine the interstitial structure of silica. It was suggested in [4] that the mobilities of the alkali ions in vitreous silica depend upon the relative concentration of the SiO^- and the AlO_4^- groups in addition to the concentration of the alkalis. Unlike the alkali-aluminosilicates with inceasing alumina content, the non-bridging oxygens (i.e. the SiO^- groups) do not vanish at alumina/alkali ratio of ≈ 1. Rather, they decrease slowly to alumina/alkali ratio of ≈ 8 at

Table 2. Slope n of lg I versus lg t plots for K^+ ion transient current

sample	value of slope n in		t in h at the end of	
	region I	region II	region I	region II
ME 27	− 0.70	0.20	10.0	34.0
ME 10	− 0.57	0.37	8.0	95.0
ME 11	− 0.46	− 0.050	18.0	60.0
ME 18	− 0.69	− 0.060	12.0	24.0
ME 21	− 0.44	− 0.23	4.0	136.0
ME 16	− 0.50	− 0.18	6.0	70.0
GE 124	− 0.47	− 0.17	10.0	90.0
GE 510	− 0.58	− 0.21	4.0	68.0
GE 214	− 0.27	–	100.0	–
ME 19	− 0.56	–	20.0	–
ME 20	− 0.60	–	16.0	–

which point they reach some low value. Since the non-bridging oxygens generally are expected to occur in pairs, one may argue that the probability of mixed-alkali interactions is high when either the concentrations of the alkalis are comparable or the alumina/alkali ratio is low.

The relative concentrations and the mobilities of the alkali ions, and the influence of alumina/alkali ratio make the analysis of transients in vitreous silica far more complex than that presented by Doremus [5]. It is no surprise, then, that the $I - t$ data even for the simpler case of electrolysis by K^+ ions cannot be fitted to the Doremus analysis (equation (5)). Empirically, a better fit to the data is obtained using the following equation

$$\lg (I/I_0) = n \lg (t/t_0),$$

for $t > 0$ i.e.

$$I = I_0 (t/t_0)^n \tag{9}$$

where I_0 and t_0 are normalizing parameters with n as exponent index. Replots of the figures 2a to c data on lg I versus lg t scale are shown in figures 5a to c. As may be noted, two regions of linear behavior are apparent. These can be tentatively identified as region I where the resistance is $R_1 + R_{1,2}$ with the layer $l_{1,2}$ gradually growing (and l_1 shrinking), and region II where the layer l_1 has vanished, the resistance is $R_{1,2}$, but now the mixed-alkali ratio is changing such that $R_{1,2}$ is gradually approaching R_2 (within the measurement period). The end of region II marks the achievement of the apparent steady state.

Calculated values of the slope n in the two regions for all the transient conduction curves as well as the times to reach steady state are listed in tables 2 to 4. In table 2, the slightly positive values of n in region II for glasses ME 27 and ME 10 suggest that the conductivity actually increases as the mixed alkali composition gets richer in K^+ ions – a true mixed-alkali behavior observed in mixed-alkali silicate glasses with much higher total alkali content [7].

Table 3. Slope n of lg I versus lg t plots for Li^+ ion transient conduction in fused silica

sample	value of slope n in		t in h at the end of	
	region I	region II	region I	region II
ME 25	0.008	–	45.0	–
ME 11	0.019	0.13	33.0	70.0
ME 27	0.024	0.13	26.0	60.0
ME 18	0.014	0.12	18.0	80.0
ME 10	0.023	0.38	10.0	70.0
ME 19	0.013	0.13	22.0	60.0
ME 20	0.008	–	3.0	–
ME 21	0.042	0.46	13.0	80.0
GE 214	0.015	0.46	18.0	50.0
GE 510	0.002	0.42	12.0	35.0

Table 4. Slope n of lg I versus lg t plots for Na^+ ion transient conduction in fused silica

sample	value of slope n in		t in h at the end of	
	region I	region II	region I	region II
ME 25	0.003	–	1.0	–
ME 10	0.045	–	20.0	–
ME 19	0.005	–	10.0	–
ME 20	0.003	–	4.0	–
ME 18	0.001	0.011	6.0	22.0
ME 21	0.013	0.12	7.5	15.0
GE 124	0.180	0.13	9.0	28.0
GE 214	0.032	0.18	9.0	22.0
GE 510	− 0.022	− 0.066	10.0	27.0
ME 16	− 0.003	0.048	5.0	24.0
ME 11	− 0.015	0.065	13.0	36.0
ME 27	− 0.003	0.027	8.0	22.0

The negative and positive n values in region I for Na^+ ions shown in table 4 are indicative of the relative mobilities of Li^+ and Na^+ ions in the various glasses. The region II slopes for Na^+ and Li^+ electrolyses are mostly positive (with one exception for glass GE 510 in table 4). This, again, is consistent with the notion that region II comprises the gradual flushing of the lower mobility mixed-alkali pairs by the higher mobility anode electrolyte ion.

It must be emphasized that equation (9) can only be an approximate representation of the transient behavior, particularly for the more complex case of electrolysis by faster moving ions. An accurate description would require a careful chemical analysis of either the glass or the salt baths at various stages of electrolysis which was not performed during this study, and the solution to electrodiffusion equations using numerical methods [8].

3. Conclusions

The following conclusions regarding transient ionic conduction in fused silica may be drawn from this study:

First, the relationship of the current I and the time t is best approximated by $I = I_0 (t/t_0)^n$ where the exponent index n may be positive or negative depending upon the relative mobilities of the various ions which take part in the conduction.

Second, two regions of behavior were apparent in the $I - t$ curves before an apparent steady state was achieved: the earlier (region I) could be attributed to the flushing of the more mobile species, whereas the later (region II) was presumably due to the disappearance of interdiffusional coupling.

Third, there was some evidence that the interdiffusional coupling in some specimens was similar to the mixed-alkali effect observed in silicate glasses with much higher alkali content.

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