

Behaviour of silicate and borosilicate glasses in contact with metallic sodium.

Part 1. Sodium silicate glasses

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When sodium silicate glasses were heat treated in contact with metallic sodium at temperatures between 300 and 400°C, glasses containing less than 70 mol% SiO₂ developed a coloured region, and glasses containing more than 70 mol% SiO₂ developed a sodium metasilicate crystal layer. The glasses which exhibited coloration were characterised by low levels of sodium absorption. The glasses which crystallised to sodium metasilicate had a high level of sodium absorption. Both the thickness of the coloured region and the thickness of the crystal layer increased proportional to the square root of time, as expected for a process which involves sodium transport through a glass or crystal layer. When heated in vacuum, the glasses which coloured lost weight, indicating that the sodium absorption process is reversible. It was decided that the occurrence of colour is preferable to crystallisation in a glass selected for sealing sodium-sulphur battery components.

The development of the sodium-sulphur battery system has created a need for a sealing glass resistant to attack by the metallic sodium environment encountered within the battery. The sealing glass must remain intact during long exposures to metallic sodium at battery operating temperatures of 300 to 350°C. In a recent review⁽¹⁾ of the effect of metallic sodium on a variety of glass compositions, no single mechanism has been assigned which describes well all of the experimental results. It has been suggested that atomic sodium can, under certain conditions, diffuse into glass without reacting with components in the glass structure⁽²⁾ while, under other conditions, a chemical reaction between the absorbed sodium and the glass takes place.^(3,4)

One of two effects is commonly observed in glasses after heat treatment in contact with metallic sodium. One which several authors⁽²⁻⁶⁾ have observed is a yellow or black coloration of glass. The coloured region of the glass has been described as advancing into the glass with, in some cases, a sharp boundary⁽³⁾ and, in other cases, with a sodium profile ahead of the

coloured region that can be fitted to an error function solution.⁽⁵⁾

In most of the studies where glasses developed a coloured region, the optical absorption of exposed glasses varied with the square root of time. This implies that the coloration process is diffusion-controlled.^(1,2) In only one investigation did the optical absorption vary linearly with time, and in this case the coloration may not be a case of simple diffusion.⁽³⁾ Over a narrow range of temperatures, the reported values of the apparent activation energy associated with the coloration process vary from 90 to 130 kJ/mole.⁽¹⁾ There is a tendency to assign an ionic diffusion mechanism to the low values and an atomic sodium diffusion mechanism to the high values.

In one investigation of a borate solder glass,⁽⁴⁾ it was reported that the electrical resistivity was lower in the coloured region by 2 to 3 orders of magnitude. This indicated that the sodium present in the coloured region was easily dissociated to an ion and an electron. Yet it was possible subsequently to volatilise most of the absorbed sodium, which made it appear that the sodium was not strongly bound to the glass structure as by a reduction reaction.

In contrast to the appearance of a coloured region, the second effect commonly reported in silicate glasses is that contact with metallic sodium produces a sodium metasilicate layer at the sodium-glass interface.⁽⁶⁾ This crystal layer is often accompanied by a black scale as a result of the reduction of silica to silicon. It has been shown that this process becomes energetically more favoured in silicate glasses as the silica content of the glasses is increased.

The effects of contact with metallic sodium have been studied primarily in glasses used for lamp envelopes. The two effects commonly reported are the appearance of a coloured region and the growth of a crystal layer. The mechanisms for these processes are in general not well understood. Therefore, this study has been undertaken to investigate the nature of the sodium-glass interaction. The initial study has been performed on three sodium silicate glasses whose designations, glass 60, glass 70, and glass 75 refer to the nominal silica content in mol%. The ultimate goal

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of this investigation is the selection of a sealing glass for a sodium-sulphur battery application.

Experimental procedures

Thoroughly mixed reagent grade Na_2CO_3 and SiO_2 powders were melted in 99.9% fused quartz crucibles in a gas-fired furnace until an optically homogeneous glass was obtained. Cylindrical rods averaging 5–7 mm in diameter were drawn from the melt and annealed. The compositions of the glasses were analysed for Na and Si by atomic absorption spectrometry and the results are listed in Table 1.

Table 1. Compositions investigated experimentally

	Glass 60		70		75	
	(mol%)	(wt%)	(mol%)	(wt%)	(mol%)	(wt%)
Na_2O	41.8	42.6	29.9	30.6	25.4	26.0
SiO_2	58.2	57.4	70.1	69.4	74.6	74.0

Sections of the glass rods, 5 cm long, were encapsulated with metallic sodium in stainless steel (Swagelok) reaction vessels under a flowing helium atmosphere. Care was taken to ensure that the glass specimens were completely surrounded by metallic sodium and free from surface water. The samples were heat treated isothermally at temperatures ranging from about 300 to 400°C for various periods of time, and then quenched to room temperature.

After the heat treatments the recovered glasses were sectioned perpendicular to the long axis, polished with oil-based diamond abrasives, and stored in a desiccator. Using an SEM equipped with an energy dispersive spectrometer, sodium concentration profiles were determined. In samples which became coloured, corresponding optical densities were measured with a microphotometer. For samples which developed a crystal layer, crystal growth measurements were made from SEM photomicrographs and crystalline phases were identified by x-ray diffraction analysis.

Experimental results

As a result of the heat treatments with metallic sodium one of two effects was observed, a reddish-orange coloration and crystallisation. In glasses 60 and 70, a uniformly coloured region with a sharp boundary advanced from the reaction surface toward the interior of the sample; the general appearance of a coloured region is shown in Figure 1. In glass 75, the colour effect was absent; instead a black crystalline product layer was observed at the sodium-glass interface and this is shown in Figure 2.

In the glasses that show the colour effect, sodium concentrations were measured radially across the sodium-glass interface. Optical density measurements were performed as well. Typical concentration profiles are shown in Figure 3 for glass 60 and in Figure 4 for glass 70 (filled circles), along with their corresponding optical density measurements (open circles).

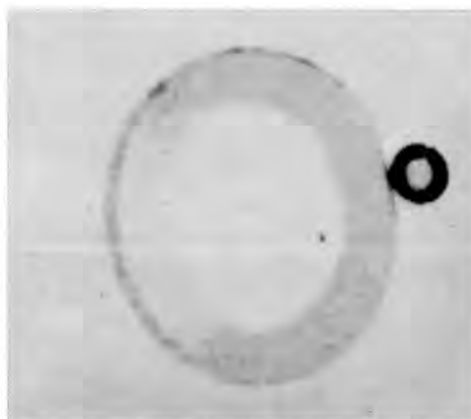


Figure 1. Section of glass 60 after heat treatment for 12 days at 300°C in metallic sodium

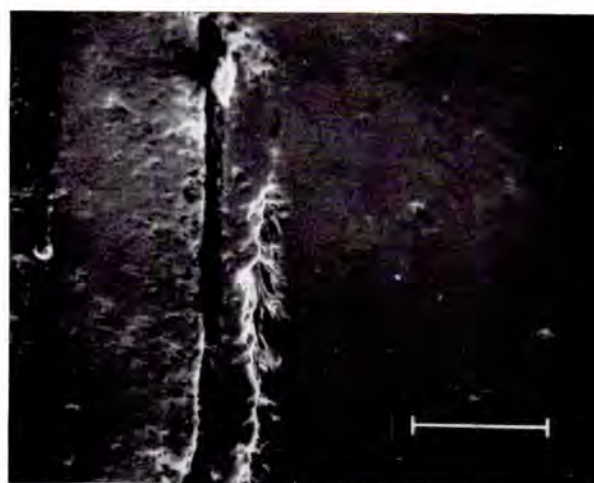


Figure 2. Section of glass 75 after heat treatment for 17 days at 375°C in metallic sodium (bar = 0.1 mm)

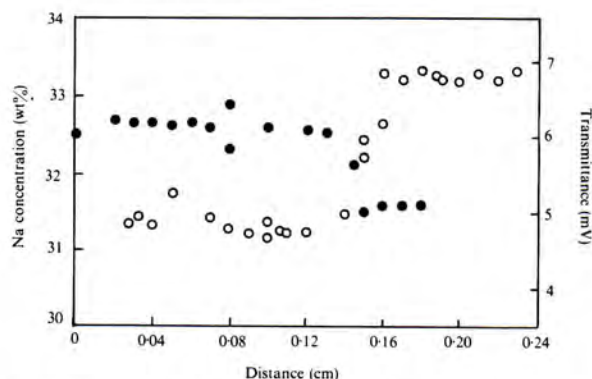


Figure 3. Variation of sodium content (●) and transmittance (○) with depth in glass 60 after heat treatment for 7 days at 325°C

As shown in Figure 3, the coloured region of glass 60 corresponds to a uniform addition of 1.1 wt% sodium to the bulk glass composition. The position of the colour front, approximately 1.6 mm from the reaction surface, is characterised by a sharp increase in optical transmission along with a sharp decrease in sodium concentration. As shown in Figure 4, the coloured region of glass 70 has a higher optical density

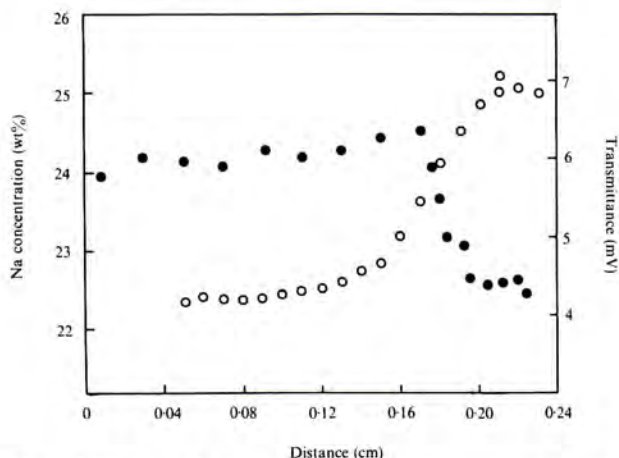


Figure 4. Variation of sodium content (●) and transmittance (○) with depth in glass 70 after heat treatment for 7 days at 325°C

and corresponds to a uniform addition of approximately 1.5 wt% sodium to the bulk glass composition. The position of the colour front is again characterised by a sharp increase in optical transmission along with a sharp decrease in sodium concentration.

In the glasses that show the colour effect, the position of the colour front was measured as a function of time at each reaction temperature. The results of these measurements are shown in Figure 5 for glass 60 and in Figure 6 for glass 70. In each case the square of the boundary position is plotted against reaction time for the various temperatures. The linear relationship which exists is indicative of a diffusion-controlled process as described by a parabolic rate law.

A comparison of measurements for a series of times at a given temperature indicate that there is a characteristic sodium absorption level and corresponding optical density for each glass composition. The position of the colour front advances with time and the rate of advance increases with increased temperature, while the sodium absorption level remains independent of time and temperature for each glass composition.

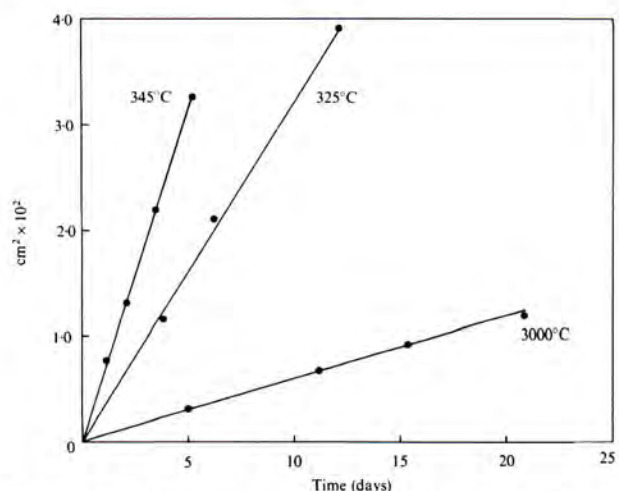


Figure 5. Time dependence for advancement of colour front in glass 60

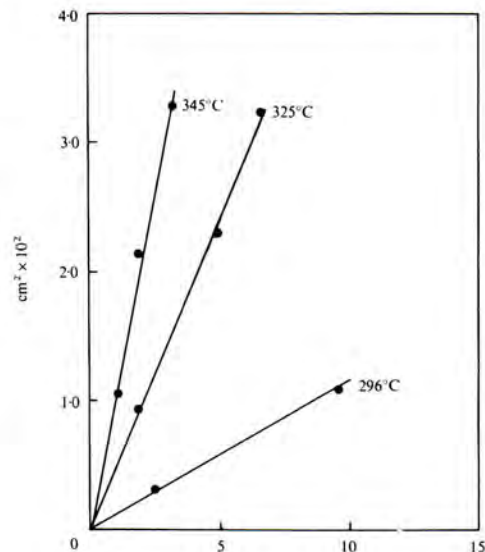


Figure 6. Time dependence for advancement of colour front in glass 70

In glass 75, which developed a black crystalline product layer, the sodium concentration was measured radially across the reacted sample from crystal layer, across the interface, into the bulk glass. The results of these measurements are shown in Figure 7. There is a high level of sodium present in the product layer and a sharp drop in sodium concentration at the product layer–glass interface. The sodium content measured at the product layer–glass interface is approximately that of sodium metasilicate, the major crystalline phase identified by x-ray diffraction analysis.

The discontinuity observed in the sodium concentration indicates that the formation of sodium metasilicate at the crystal–glass interface is more rapid than the transport of sodium through the product layer. When this is the case, the product layer is expected to grow at a rate proportional to the square root of time. A typical plot of product layer thickness against square root of time is shown in Figure 8 for glass 75.

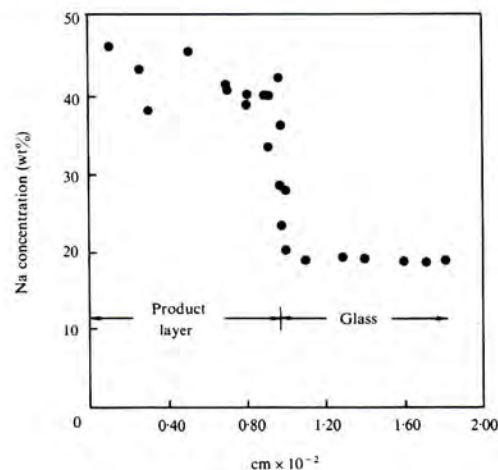


Figure 7. Variation of sodium content with depth in glass 75 after heat treatment for 17 days at 375°C in metallic sodium

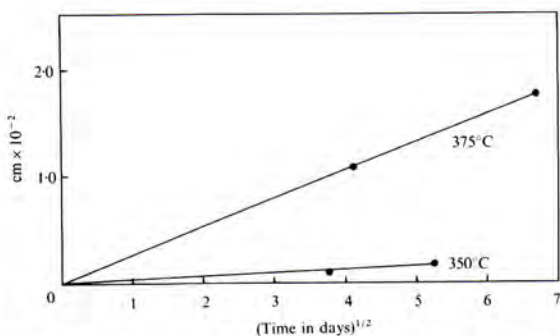


Figure 8. Layer thickness as a function of $(\text{time})^{1/2}$ for glass 75

Discussion

Coloration

For most diffusion-like processes, an apparent activation energy can be determined. Using the slopes in $\text{cm}^2 \text{s}^{-1}$ of the plots in Figures 5 and 6, values for the apparent activation energy for glasses 60 and 70 were calculated. The values for the temperature range 300–400°C are 142 kJ/mole for composition 60 and 121 kJ/mole for composition 70. These values are close to values of apparent activation energies predicted by a model for atomic sodium diffusion⁽⁷⁾ and are higher than values predicted for ionic sodium diffusion.^(8,9) In this model for atomic diffusion⁽⁷⁾ it is found that the square root of the apparent activation energy is proportional to the molecular diameter of the diffusing specie. In fused silica, an activation energy of 121 kJ/mole represents a diffusing specie with a molecular diameter of about 3.4 Å, which has been suggested as an approximate value for the molecular diameter of gaseous sodium metal.

Modifier additions to fused silica are expected to increase the activation energy for molecular diffusion. A value of 142 kJ/mole seems reasonable for atomic sodium diffusion in glass 60 which contains over 40 mol% modifier, while an activation energy value of 121 kJ/mole seems somewhat low for glass 70 which contains about 30 mol% modifier. In a study of atomic sodium diffusion in a borosilicate glass,⁽⁵⁾ a value of 121 kJ/mole was also obtained for about 30 mol% modifier addition, which may indicate that the value obtained in this study for the silicate glass containing 30 mol% modifier is likewise reasonable.

The optical transmission spectra of glasses 60 (barred circles) and 70 (filled circles) are shown in Figure 9 along with that of a sodium borosilicate glass⁽¹⁰⁾ (open circles) for comparison. In the borosilicate glass it was possible to identify by electron diffraction the nature of small crystals of metallic sodium in a glass sample reacted under similar conditions to the present investigation. The similarities in optical transmission of the glasses suggest that crystalline metallic sodium is present in all three and contributes to the generation of colour in the silicate glasses.

Coloured glass samples when heated to 400°C in high vacuum gradually lose weight. This is possibly due to sodium volatilisation, which has been observed in alkali borate glasses.⁽⁴⁾ This implies that the absor-

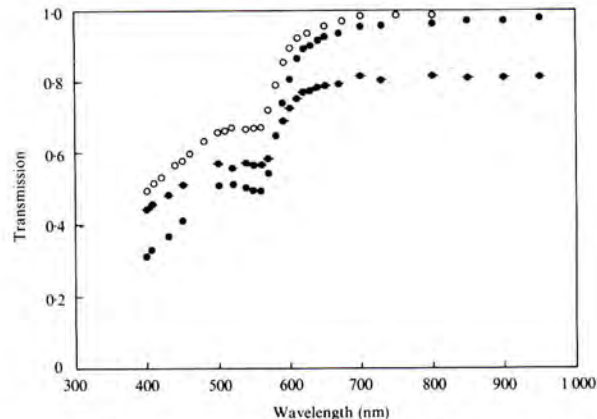


Figure 9. Comparison of spectral transmission for glass 60 (●), 70 (●), and a sodium borosilicate glass with 12.5 mol% alumina (○) after heat treatment with metallic sodium

bed sodium does not react chemically with the glass network as in a reduction reaction and that the absorption process is reversible.

In summary, the advance of colour in glasses 60 and 70 appears to be diffusion-controlled. The values of apparent activation energies for this process correspond to a mechanism involving atomic sodium diffusion. From comparisons of the optical transmission spectra of the coloured silicate with those of a glass containing atomic sodium, it appears that crystalline sodium is the colour centre. Finally, weight loss in vacuum suggests that the coloration process is at least partially reversible.

Crystallisation

It appears from the present investigation that a critical level of SiO_2 is necessary to favour the formation of sodium metasilicate. This can be seen from the fact that glass 75 always exhibited crystallisation while glass 70 always exhibited coloration when heated in contact with metallic sodium. Yet the difference in silica content between the two glasses is only 4.5 mol%. This follows the predictions of Elyard & Rawson⁽⁶⁾ that from a thermodynamic standpoint the reduction of silica by metallic sodium becomes more favoured in sodium silicate glasses as the silica content of the glass is increased. Though the free energy of formation of SiO_2 is approximately -770 kJ/mole and that for $2\text{Na}_2\text{O}$ is -648 kJ/mole, it is possible that the reaction $4\text{Na} + 3\text{Na}_2\text{O} + 6\text{SiO}_2 \rightarrow 5\text{Na}_2\text{SiO}_3 + \text{Si}$ occurs. The free energy of formation of Na_2SiO_3 is approximately -1435 kJ/mole, and the free energy change for the overall reaction at 400°C is approximately -1583 kJ/mole.

In the glass with the highest silica content where the thermodynamics indicate that the reduction of SiO_2 by the sodium metal is possible, the growth of sodium metasilicate crystals is observed. The rate at which the crystals grow into the sample is proportional to the square root of time, indicating diffusion-controlled growth. The concentration profiles of sodium across the crystal-glass interface (Figure 7) lend support to a diffusion-controlled mechanism that involves the

transport of sodium through the crystal layer and some reduction of silica at the crystal-glass interface. At all temperatures investigated, the interface is essentially flat. Only when a mixed alkali glass is heat treated in contact with metallic sodium does the interface breakdown into cells.⁽¹⁰⁾ The crystalline phase which appears in these glasses is always sodium metasilicate with minor amounts of silicon detectable by x-ray diffraction analysis.

Conclusions

When sodium silicate glasses are heat treated in contact with metallic sodium at temperatures between 300 and 400°C, two phenomena are observed, the first is characterised by low levels of sodium absorption resulting in a coloration of the glass and the second is characterised by a high concentration of sodium and a layer of sodium metasilicate crystals at the glass – metallic sodium contact surface. Both processes appear to be diffusion-controlled.

The coloration effect was observed at all temperatures investigated in glasses 60 and 70, each of which exhibited a characteristic sodium absorption level which was independent of reaction time and temperature. The sodium absorption level was lower in glass 60 which has a higher modifier content than glass 70. The apparent activation energy for the rate of advancement of the colour front was higher in glass 60 than in glass 70; this supports a diffusion mechanism for this process which involves transport of atomic sodium through the sodium silicate glass.

A crystalline layer formed at the glass – metallic sodium contact surface over the temperature range

investigated in glass 75 which had the highest silica content. The thickness of the layer increased in proportion to the square root of time. This supports a diffusion mechanism for this process which involves transport of sodium through the crystalline layer along with a reduction of some of the silica. The crystalline layer has been identified as sodium metasilicate and there is evidence for the presence of silicon metal in the crystalline layer.

Based on the results of this study, it is concluded that crystallisation is undesirable in glasses used for sealing sodium-sulphur battery components; the development of a crystalline layer indicates a high level of sodium absorption. Use of a glass which shows a coloration is recommended because the coloration indicates a low level of sodium absorption. Further study of this behaviour has led to the development of glasses which show this coloration and have thermal expansions compatible with those of other battery components.⁽¹⁰⁾

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