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Surface resistivity studies on leached E-glass fabric

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The direct-current resistivity of leached E-glass fabric was measured. The surface resistivity of the fabric increased on removing the alkali ions. The removal of the ions depended on the concentration of the acid and the leaching time. The surface resistivity of the fabric increased as the post heat-treatment temperature increased. However, on exposure to the atmosphere the surface resistivity decreased. The re-adsorption of water and the decrease in surface resistivity were found to be reduced in fabrics which were heated to higher temperatures. The residual alkali ions and the protons (of H_2O) were the conducting species.

1. Introduction

Oxide glasses are widely used as insulators in the form of substrates and vacuum envelopes because of their high electrical resistance and chemical inertness. For these uses, surface resistance is an important property requiring study [1, 2]. The inherent electrical resistance of the surface is very high but if there is any ionic contamination on the surface it can conduct current in humid air. The physically adsorbed water reacts with the contaminating ions to give mobile ions. Monovalent cations present in the glass can react with water by ion exchange forming metallic hydroxides on their surfaces. These hydroxides further react with water forming mobile ions on the surface [3].

In the present work E-glass fabrics were soaked in different concentrations of hydrochloric acid for varying intervals of time to remove non-siliceous ions including alkali ions. The effect of the removal of alkali ions, in particular, on surface resistivity was studied, in conjunction with the independent effects of concentration of the leaching acid and time of leaching. The removal of ions from the network makes it susceptible to water absorption. The effect of moisture on surface resistivity was also studied. The effect of post heat treatment and subsequent moisture absorption on surface resistivity were studied separately.

2. Experimental procedure

E-glass fabric with the composition as given in Table I was used as the starting material throughout the experiment. The fabric was 0.4 cm thick and made of fibres 10 μm in diameter. The fabric sample, 7 to 8 g in weight, was refluxed in 800 to 900 ml hydrochloric acid solution. The concentration of the solution was varied from 0.5 to 0.4 N and the time of treatment from 0.5 to 6 h. After the treatment, the fabrics were washed in water and ammonia solution to remove all the acid. They were subsequently heated to different temperatures (100 to 600° C) for 4 h. The resistivity measurements were made by measuring the direct current (d.c.) potential across the sample in a high resistance ohm-meter. Special stainless steel jigs were used according to the ASTM specification D257- 66 [4] (at 60% r.h.). In this test a strip electrode was used and the voltage applied over the surface. The resistance, R_s, was noted and using the perimeter, P, of the rectangular sample and guard distance, g ($g = 2.5$ cm), the surface resistivity, ρ_s (Ω), could be calculated using

TABLE I Chemical composition (wt%) of the E-glass fabric used as starting material

SiO_2	Al_2O_3	CaO	MgO	B_2O_3	Fe_2O_3	$Na_2O + K_2O$
54.2	14.0	19.8	2.2	8.2	0.3	0.6

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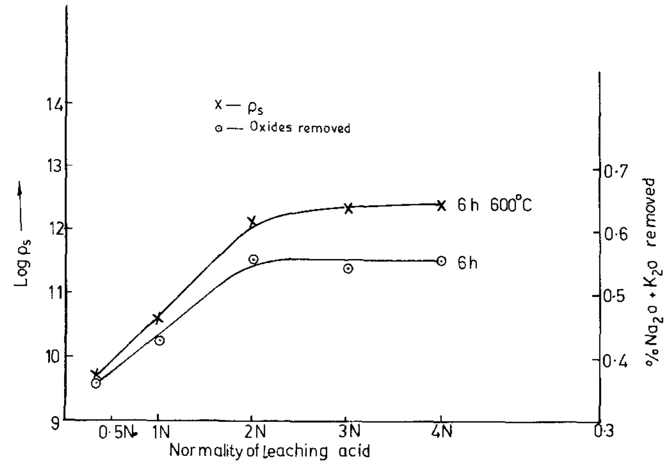

Figure 1 Variation of surface resistivity with normality of the leaching acid. Leaching time 6 h, post heat-treatment temperature 600° C. A plot of alkali ions removed against the concentration of the acid is also shown.

$$\rho_s = \frac{P}{g} R_s$$

$$= \frac{2W}{g} R_s . \quad (1)$$

For thin samples, the perimeter can be assumed to be twice the width, W, of the test sample [4]. The fabric was also exposed to humid atmospheres for different intervals of time and the surface resistivity was measured to determine the effect of such exposure to moisture.

3. Results and discussion

Pure silica in the form of quartz has a volume resistivity of the order of $10^{18}\,\Omega$ cm. Addition of other ions such as Na^+ and Ca^{2+} etc. to silica decreases the volume resistivity. For example, soda-lime silicate glass has a volume resistivity of $10^{12}\,\Omega$ cm. The removal of these ions increases the volume resistivity of the glass [5]. Similarly the presence of alkali ions in particular alters the surface resistivity of the glass. E-glass which has 0.6% alkali oxide ions shows an increase in surface resistivity on removing these ions. It is well known that an addition of Na^+ ions (of the order ppm) is sufficient to drastically decrease the resistance of fused silica and conduction is directly related to the alkali ion content [6, 7]. The removal of non-siliceous ions from E-glass can be achieved by soaking the glass in mineral caids like hydrochloric acid. The removal works on the principle of ion exchange [8] which can be expressed by

$$\equiv\text{Si–O–}M + H^+ \rightleftharpoons \equiv\text{Si–OH} + M^+, \quad (2)$$

where M^+ represents cations such as Na^+, Ca^{2+} etc. and H^+ represents the hydrogen ion from the acid.

During ion exchange, as the cations are removed from the glass, in order to maintain electrical neutrality, H^+ ions diffuse into the glass network. The H^+ ions form silanol groups. These groups can be dehydrated according to

$$2(\text{Si–OH}) \xrightleftharpoons{\text{heating}} \equiv\text{Si–O–Si}\equiv + H_2O. \quad (3)$$

As a result of the removal of cations (non-siliceous ions) from the glass, pores are introduced in the network. In the process of post heat treatment water is removed and the pore size distribution is also altered either by shrinkage or by closing of the pores. These pores make the material susceptible to water absorption which effects the surface resistivity.

3.1. Effect of acid concentration

Fabrics were refluxed in different acid concentrations (0.5 to 4.0 N) for 6 h. The fabrics were then washed and heated to 600° C for 4 h and surface resistivity was measured at different voltages. The results are plotted in Fig. 1. The surface resistivity increased sharply during the initial stages of leaching and then the increase became very marginal. The surface resistivity values did not alter much with the various test voltages (100 to 500 V). The weight percentage of alkali oxides removed during the treatment at different normalities is also plotted in Fig. 1. The pattern is almost the same as that for surface resistivity values plotted against the acid concentrations. This indicates that alkali ion removal affects the surface resistivity in particular. The weight percentage of other oxides removed with different normalities of acid for various periods of time are given in Table II.

TABLE II Weight percentage of oxides removed from the E-glass fabric with respect to normality and time

Time (h)	Al_2O_3 (wt%)				CaO (wt%)				$Na_2O + K_2O$ (wt%)			
	0.5N	1N	2N	4N	0.5N	1N	2N	4N	0.5N	1N	2N	4N
0.5	2.8	2.9	6.1	12.31	3.6	5.8	11.5	15.0	0.16	0.31	0.42	0.50
1.0	3.6	5.2	9.4	12.46	4.4	8.3	13.6	18.2	0.21	0.316	0.46	0.51
4.0	5.48	7.3	10.5	12.38	6.1	9.0	15.6	18.3	0.295	0.40	0.52	0.56
6.0	7.3	8.1	12.3	11.39	9.9	11.7	17.4	18.7	0.378	0.42	0.56	0.55

3.2. Effect of leaching time

Experiments were carried out to determine the effect of leaching time on the surface resistivity. The fabrics were soaked in 4N hydrochloric acid for various periods of time (0.5 to 6 h) and their surface resistivity was measured. The weight percentage of alkali oxides removed with leaching time is plotted in Fig. 2 along with surface resistivity values. This also shows that ion removal, which in turn depends on leaching time, does effect the surface resistivity values. The steep increase in the surface resistivity at the initial stages may be due to the bulk removal of alkali ions which becomes marginal in the later stages. By removing the alkali ions an increase in the surface resistivity, of several hundred times, has been observed in high alkali glass [9].

3.3. Effect of post heat-treatment temperature

During the removal of non-siliceous ions from the glass network by ion exchange, H^+ ions diffuse into the network to maintain electrical neutrality and form a silanol group (–Si–OH). The presence of –OH groups on the silica surface makes it hydrophilic, since they can hydrogen bond with water to form a multimolecular layer of adsorbate over the surface [10]. Infra-red spectroscopic analysis has shown the presence of –Si–OH groups and free water over the surface of acid-leached fabric [11]. The film of water over the surface can form the conducting film. The application of a d.c. potential, polarizes the adsorbed water, induces the dissociation of water and thereby increases the ionic mobility. During the post heat treatment, two adjacent silanol groups come together and stable Si–O–Si linkages are formed causing dehydration (as shown in Equation 3). From Equation 3, it is clear that as the post heat treatment temperature increases, more and more stable ≡Si–O–Si≡ linkages are formed decreasing the concentration of conducting ions. This effect is clearly seen in Fig. 3 where surface resistivity values increase with increase in post heat-treatment temperatures. The diffusion of water into silica has been explained by a lattice breaking model [12] and a diffusion and reaction of molecular water model [13]. From Fig. 3 it is also seen that the fabrics treated with lower concentrations of the acid have lower surface resistivity because of the partial removel of alkali ions.

3.4. Effect of moisture, adsorption on surface resistivity

As explained earlier, during post heat treatment silanol groups become dehydrated to form stable

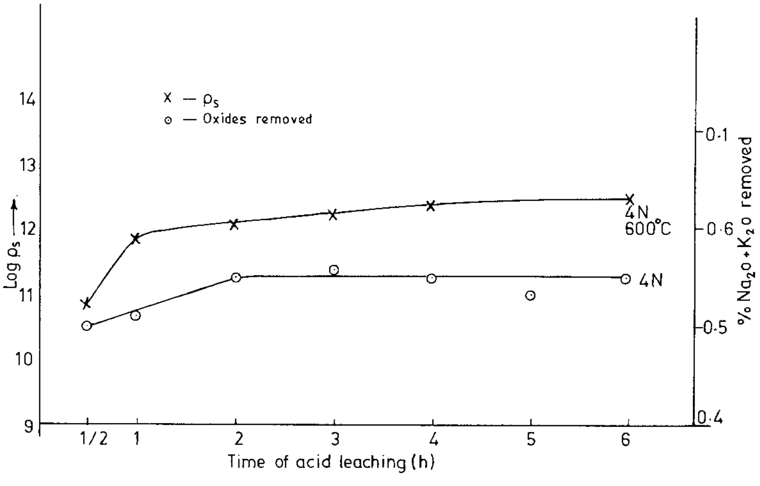

Figure 2 Variation of surface resistivity with leaching time. The normality of the leaching acid is 4N and post heat-treatment temperature 600°C. A plot of alkali ions removed against time is also shown.

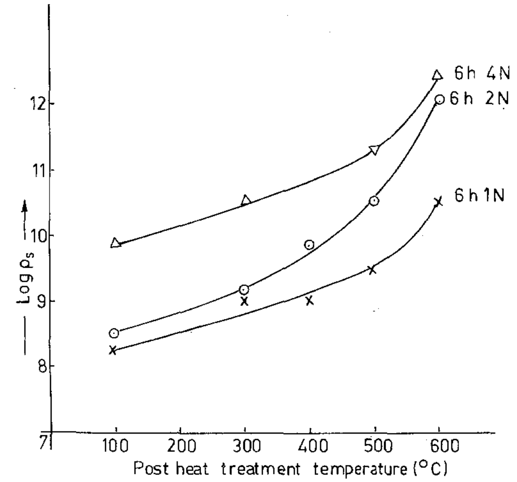

Figure 3 Variation of surface resistivity with post heat treatment temperature. Fabrics leached in 4N, 2N and 1N acids for 6 h.

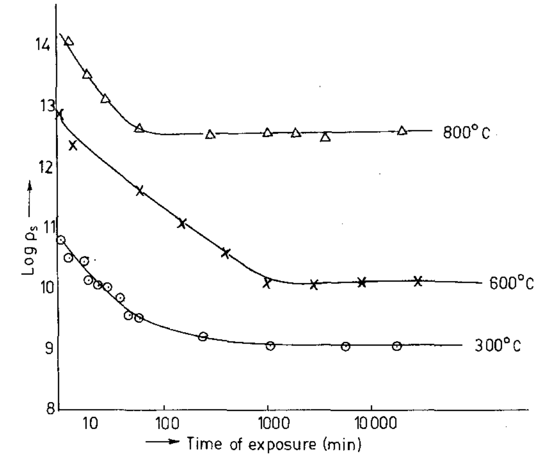

Figure 4 Change in the surface resistivity with time of exposure for heat treated fabrics.

Si–O–Si linkages. It has also been found that with an increase in the post heat treatment temperature, the surface resistivity increased because of the dehydration. Surface area measurements were made on the fabrics before and after leaching, using nitrogen (BET method) as adsorbant. The results indicate that leached fibres have 100 times more surface area than the untreated ones. The acid treatment introduces porosity into the structure because bulkier ions are removed by ion exchange and small protons (H^+) are introduced. Porosity can be decreased by heat treatment. To evaluate the effect of porosity on the adsorption of moisture and on the mobility of residual alkali ions, the fabrics were leached in 4N acids for 6 h, to keep the residual alkali ion concentration constant, and then given post heat treatment at 300, 600 and 800° C, in an oxidizing atmosphere. They were removed from the furnace and cooled to room temperature in a desiccator and then exposed to atmosphere for the resistivity measurements. The change in surface resistivity with time was recorded and is plotted in Fig. 4. The decrease in surface resistivity is not as steep in the case of fabrics which were heated to higher temperatures as those heated to lower temperatures. The final equilibrium surface resistivity increases with increase in the post heat treatment temperature. The higher value of surface resistivity at higher post heat treatment temperature is due to removal of water and the formation of Si–O–Si linkages. At higher post heat treatment temperatures subsequent water adsorption becomes difficult. After heating to 800° C and above the silica surface will not absorb water without special treatment to reform a hydroxylated surface [14]. Further, with an increase in post heat treatment temperature the porosity decreases. This makes it difficult for the residual alkali ions present in the fabric to move out to the aqueous layer to form a conducting film [15].

4. Conclusion

Non-siliceous ions can be removed from E-glass by hydrochloric acid leaching. The removal of alkali ions in particular increases the surface resistivity of the glass fabric. The percentage removal of ions depends on the normality of the acid and time of leaching. The increase in the post heat treatment temperature increases the surface resistivity of the fabric. The removal of ions makes it porous and susceptible to moisture adsorption. This decreases the surface resistivity of the fabric on exposure to the atmosphere. The increase in the post curing temperature decreases water adsorption, due to the closure of pores resulting in an increase in equilibrium surface resistivity. The phenomenon of the increase in the conductivity by water adsorption can be explained by polarization of the water and formation of protons which act as the conducting species. Residual alkali ions present also affect the surface resistivity.

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