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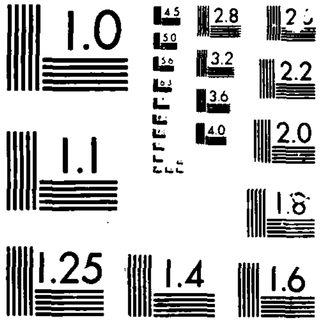
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A Study into the Effect of Humidity on $(PEO)_a.LiCF_3SO_3$ Solid Polymer Electrolyte

by

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A STUDY INTO THE EFFECT OF HUMIDITY ON (PEO)$_8$.LiCF$_3$SO$_3$ SOLID POLYMER ELECTROLYTE

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ABSTRACT

Ac impedance measurements have been made on a number of (PEO)$_8$.LiCF$_3$SO$_3$ polymeric electrolytes subjected to different levels of humidity stored up to 5 days. Arrhenius plots indicate that there is a decrease in the conductivity with increasing levels of humidity. However this effect appears to be reversible and the material can regain its original conductivity somewhat upon heating.

1. INTRODUCTION

The work of Fenton et al. (1] showed that polyethylene oxide (PEO) and various alkali metal salts form complexes with high ionic conductivities. This was followed by Armand's proposal for an all solid-state lithium battery (2). Since then much interest has been stimulated in the application of this polymeric solid electrolyte.

It is widely known that these polymeric solid electrolytes must be protected from water vapour during the manufacture of the electrolyte and the cell assembly. This is partly because lithium appears to have a stronger affinity for water than the other alkali metals (3,4). A number of studies have been made concerning the detrimental effect of water vapour on the conductivity of the electrolyte. However the results seem to contradict one another. Weston and Steele (5) demonstrated that water in the original constitutents and preparatory solvents could change the properties of the cast electrolyte films. Farrington et al (6,7) have shown that electrolyte films that had been exposed to moisture increased in conductivity. However vacuum drying at elevated temperatures results in a return of the original conductivity. The salts they investigated were $LiCF_3COO.(PEO)_5$ and $PbBr_2.(PEO)_8$. Armstrong et al. (8) showed that exposure to trace moisture resulted in a decrease in the conductivity value.

Passivation studies of the $Li/(PEO)n.LiCF_3SO_3$ interface indicate the presence of an LiF film formed by the electrochemical reaction of $LiCF_3SO_3$ (9). The electrolyte in this case is claimed to be water free. However, apart from this result, there is little quantitative data reported on the level of water contained in these polymer electrolytes after preparation. Despite the differing results, it is clear that water must be eliminated from these electrolytes if they are going to be used in any alkali-metal anode batteries.

Previous work on sodium-β-alumina electrolyte exposed to water suggested the absorption of water through the micropores and surface defects resulting in rapid saturation followed by the slower process of hydronium ion exchange of the sodium ions (10). These results were later confirmed somewhat by Armstrong et al. (4) who studied the quantitative effect of water vapour on sodium-β-alumina. Similar mechanism of hydronium exchange may apply to the lithium ion conducting electrolytes especially since both (PEO) and $LiCF_3SO_3$ are readily soluble in water.

In the present work the authors have employed a complex plane a.c. impedance technique to determine the resistance change as a function of water content of these polymeric materials.

Armstrong and Archer (11) have shown that for any number of charged species in the electrolyte with completely blocking electrodes, the equivalent circuit and impedance spectra predicted by Macdonald (12) could be represented by Figure 1. This applies to the case where there is no specific adsorption by the charged species at the electrodes. If specific adsorption do occur by one of the mobile species, the resultant spectra consist of a second semi-circle due to the charge transfer resistance arising at the electrode/electrolyte interface (11).

In the present study stainless-steel blocking electrodes were used to determine the conductivity change of the electrolytes as a function of time and temperature at different levels of water vapour exposure. The variation in the activation energies should provide us with a measure of the electrical breakdown. Measurements were made on several films cast from the same composition. In addition, films exposed to varying degrees of water vapour were analyzed for water content using the Karl-Fisher method and by infra-red technique to determine any structural changes occurring as a result of the presence of water.

2. EXPERIMENTAL

Polymer films were prepared as follows: $LiCF_3SO_3$ (Fluorad, 3M) was dissolved in acetonitrile (American Scientific Product, U.V. grade) followed by addition of the required amount of PEO(M.W. 5×10^6, Polysciences, Inc.) with constant stirring to give an O:Li ratio of 8:1 and a 4% solution. This was carefully sealed and stored in a sample bottle at 50°C overnight to homogenize. Films of about 20-40μm were cast onto Halar sheets in a fumehood and then air-dried in a dry room (relative humidity 0.5%) for 3 days.

Studies were made under four types of condition. The relative humidity was measured using a Veekay VK-35 hygrometer.

(a) Dry - The sample was placed in a vacuum dessicator containing P_2O_5 as the dessicant and was equilibriated for five days at 50°C. The relative humidity was <<0.01%.

(b) Dry room atmosphere - The sample was placed in the dry room and equilibriated at 22°C for five days prior to analysis. The relative humidity in this case was 0.5%.

(c) Saturated vapour pressure - The sample was placed in a sealed dessicator containing 250 mls of water and equilibriated for five days. The relative humidity was assumed to be 100% at 22°C.

(d) Saturated vapour pressure and elevated temperature - The sample was equilibriated for five days in a sealed dessicator containing 250 mls of water, at a temperature of 50°C. The humidity was assumed to be 100% at 50°C.

A.c. conductivity measurements were made using the Hewlett Packard 4192 HPLF impedance measurement analyser in conjunction with a Hewlett Packard 2623A terminal and a 7225A plotter. Measurements were made between 1 Hz and 13MHz and from room temperature to 120°C on cells of the type:

stainless steel|polymer electrolyte|stainless steel

The sample was sandwiched between polished stainless steel electrodes kept under pressure by a spring loaded holder encased in a glass cell design. This was placed in a small tube furnace controlled by a variac. The temperature was monitored (to ± 0.2°C) by a chromel-alumel thermocouple placed adjacent to the sample. Measurements were made under vacuum (<20μm) after a sufficient time had been allowed for temperature equilibriation. The thickness of the sample exhibited a decrease of about 5% after the experiment which eventually turned out to be insignificant compared to the overall change.

Impedance measurements were also performed on the "dry" sample (a) under vacuum at room temperature, with subsequent measurements being made every thirty minutes under normal lab air.

The water content of the various samples were analyzed using the Karl-Fisher method. This part of the work was extremely difficult to conduct since the weighings and subsequent manipulations of the samples were carried out in the dry room (relative humidity $< 1\%$) which could have a significant water pick-up on the driest sample.

Infra-red analyses were made using the Perkin Elmer 1710 FTIR infrared analyzer. Samples were sandwiched between KBr discs and sealed in a Teflon holder prior to measurement.

3. RESULTS AND DISCUSSIONS

Figures 2 and 3 show the complex plane impedance plots obtained at various temperatures for the "dry" sample (a) and the "wet" sample (d) stored in a 50°C, 100% humid environment, respectively. Similar responses were also obtained for conditions (b) and (c). Below 50°C, the shape of the spectrum was part of a semi-circle for all samples. Above 50°C, the response was a familiar semi-circle and a capacitance line and can be interpreted in terms of an equivalent circuit (Figure 1) involving the series combination of two double layer capacitances (arising at the electrode/electrolyte interface) and a resistance proportional to the conductivity of the electrolyte in parallel with the geometric capacitance of the cell C_g. The parameter ω, the frequency at the maximum of the semi-circle is related to C_g and R_b by

$$\omega = (R_b C_g)^{-1} \qquad (1)$$

The figures indicate that there is considerable deviation from ideality of the capacitance line and this is interpreted as due to possible non-uniformity of the film thickness.

A typical computer simulated spectra (a-d) at 80°C normalized for a 35μm film thickness is shown in Figure 4. This clearly shows the variation in the bulk resistance with varying exposure to water vapour. Figure 5 shows an Arrhenius plot of the conductivity of each sample under investigation upon heating. This demonstrates the usual Arrhenius behaviour above 70°C and below 55°C. This is consistent with the generalized view that the material consists of three phases below 60°C, viz., the pure PEO crystals, the salt rich stoichiometric complex and the amorphous phase. Upon heating the crystals start dissolving in the elastomeric phase, thus giving arise to a sudden conductivity transition around 60°C. It is clearly seen from this figure that the effect of moisture has a significant effect in decreasing the overall conductivity of the electrolyte. The effect appears to be more so below 55°C where there is a 1-1.5 order of magnitude decrease in the conductivity between the "dry" sample (a) and the "wet" sample (d). It appears too from the figure that once the sample has been sufficiently saturated (as in the case of c), there is little change in the conductivity (cf. d). Furthermore above 140°C, the plots seem to converge to a common value. This suggests that water is continuously being lost from the samples.

Table 1 summarizes the activation energies of the various samples above and below the conductivity transition. The result indicates that when the samples are stored in an increasingly more humid environment, the activation energy progressively increases. This is the result of the ion-exchange of Li^+ ions by the hydronium ion. The effect appears to be greater in the low temperature region than in the high temperature region. This may be explained by the fact that at temperatures of 70°C and above, water begins to exit from the material and the conductivity returns to a value quite close to the original value. This reversibility was demonstrated by measuring the impedance of sample (d) during the cooling cycle (Figure 5). The result was a partial confirmation of the work by Farrington et al.(6).

Conductivity measurements were also made at varying time intervals on the dry sample (a) exposed to normal laboratory air (R.H. ~ 50%). Figure 6 shows the resistance rise with time at room temperature as a result of the moisture pick-up. Although there is quite a scatter in the experimental points, the result does show a significant difference from the first to the final measurement. Armstrong and Clarke (8) found similar behaviour as expected and our result seems to be in good correlation with theirs in that the resistance increases rather than decreases as shown by other workers (6,13).

Table 2 summarizes the Karl-Fisher analysis of the water content in our samples. It shows that the driest material analyzed

TABLE 1
Activation Energies for the Samples under Investigation

Sample	Activation Energy in eV between +25°C and +55°C	 between +75°C and +120°C
#1 "Dry," R.H. <<0.01%	0.99	0.64
#2 Dryroom R.H. 0.5%	1.15	0.64
#3 R.H. 100% @ 22°C	1.20	0.77
#4 "Wet," R.H. 100% @ 50°C	1.42	0.80
#4 After heating	1.08	0.64

TABLE 2
Karl-Fisher Analysis of the Water Content
in the Polymer Electrolytes

Sample	% Water
#1 "Dry," R.H. <<0.01%	< 0.03
#2 Dryroom R.H. 0.5%	0.1 - 0.2
#3 R.H. 100% @ 22°C	2.5 - 2.8
#4 "Wet," R.H. 100% @ 50°C	6.5 - 7.0
#4 After heating	0.1 - 0.15

may still have several hundred ppm of water. As mentioned earlier, it was very difficult to get an accurate analysis done on these electrolytes mainly because of the various manipulations that are required during the analysis. Therefore the actual figures might be considerably less than those given in the table.

Infra-red analysis of the various samples showed that the water observed in the electrolyte did not break down the characteristic structure of the complex (Figure 7). The figure shown for samples (a) and (d) for comparison indicate that between 3000 and 450 cm^{-1} the peaks and their shape are the same. This indicates that the basic structure of the complex is the same. However at about 3450 cm^{-1} there is a broad absorption peak in sample (d) resulting from the water absorbed into the PEO and subsequent ion exchange of Li^+ by H_3O^+. Infra-red spectra for samples (b) and (c) (not shown) were similar and no further information could be obtained from them.

4. SUMMARY

Polymer electrolytes based on $(PEO)_8.LiCF_3SO_3$ are susceptible to moisture attack and undergo a decrease in the conductivity with increasing humidity. However this effect is reversible and the material regains its original conductivity somewhat upon heating. Upon storage in a humid environment there is a progressive increase in the resistivity of the material with time. This indicates that these materials must be protected from water at all times if they are to be used in alkali-metal anode batteries. Infra-red spectroscopy could not shed further light as to the form of the attacking species and it appears that this is due to a large amount of water absorption by the PEO masking these effects or actually causing the resistance increase.

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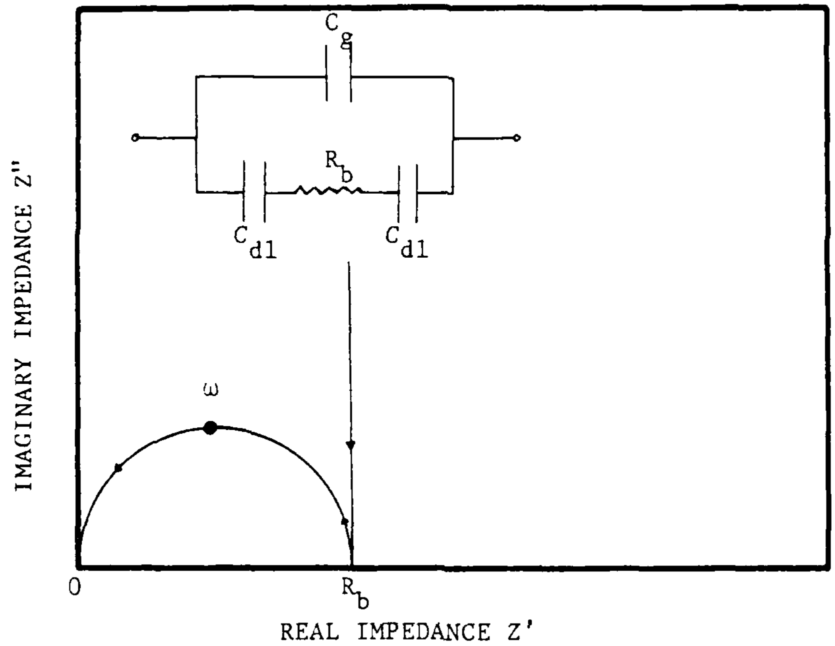

Figure 1. Equivalent circuit and predicted complex-plane impedance spectrum for the case of complete blocking. (The arrows indicate the direction of increasing frequency).

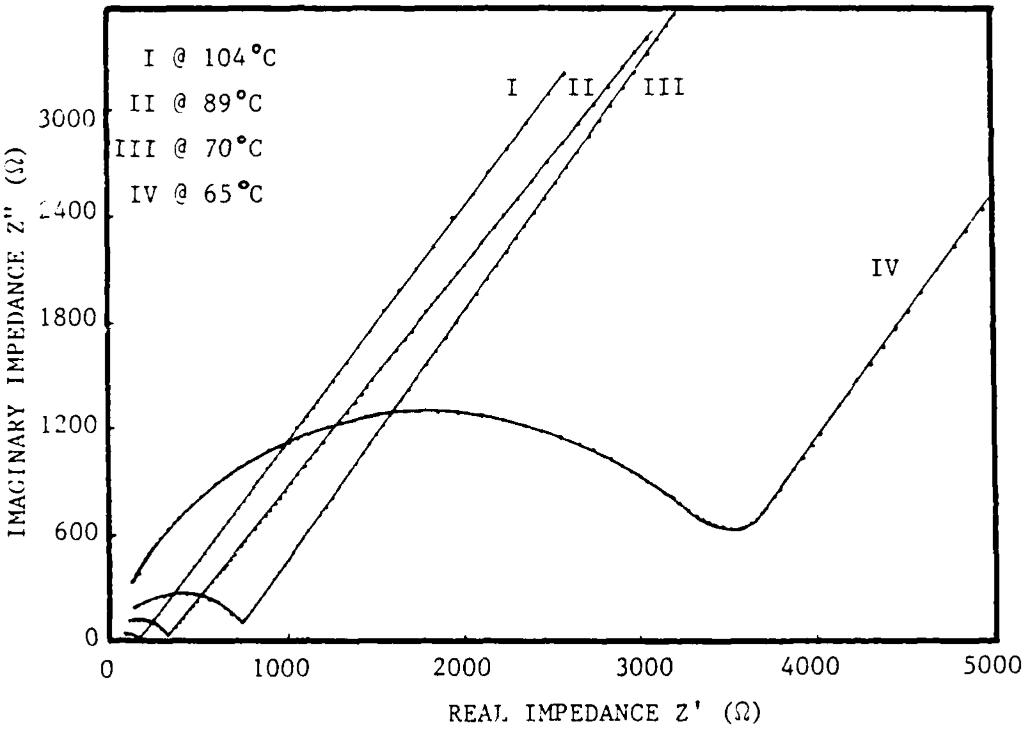

Figure 2. Complex plane plots for sample (a) between 60°C and 110°C (relative humidity <0.01%).

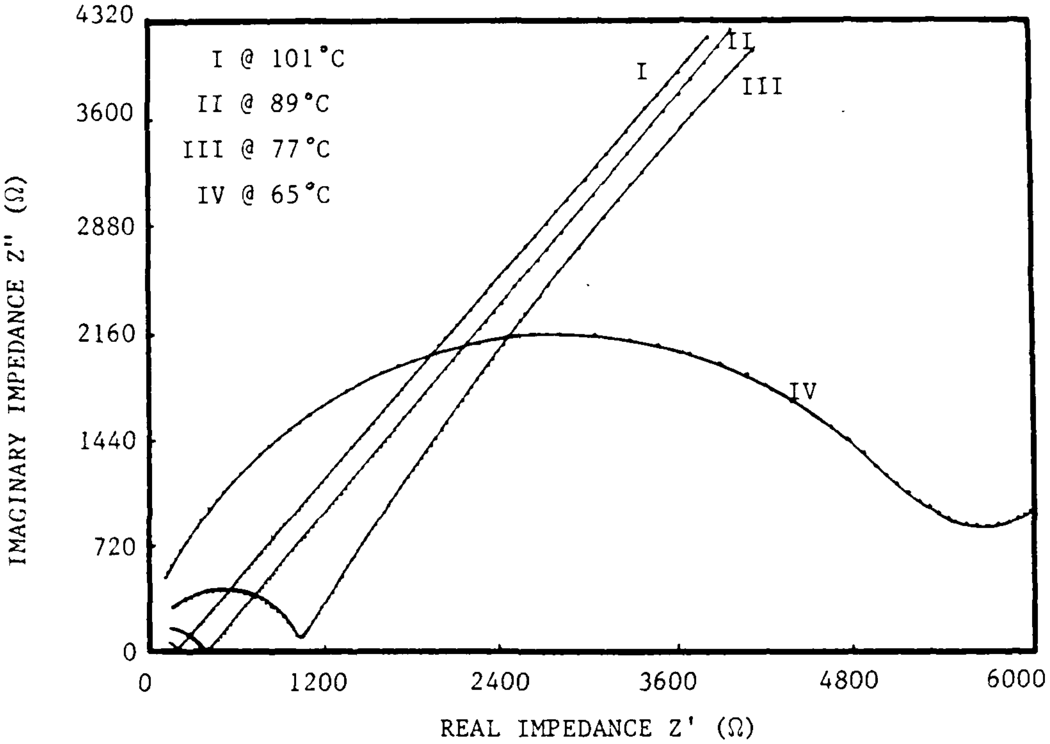

Figure 3. Complex plane plots for sample (d) between 60°C and 110°C (relative humidity of 100% @ 50°C, "wet").

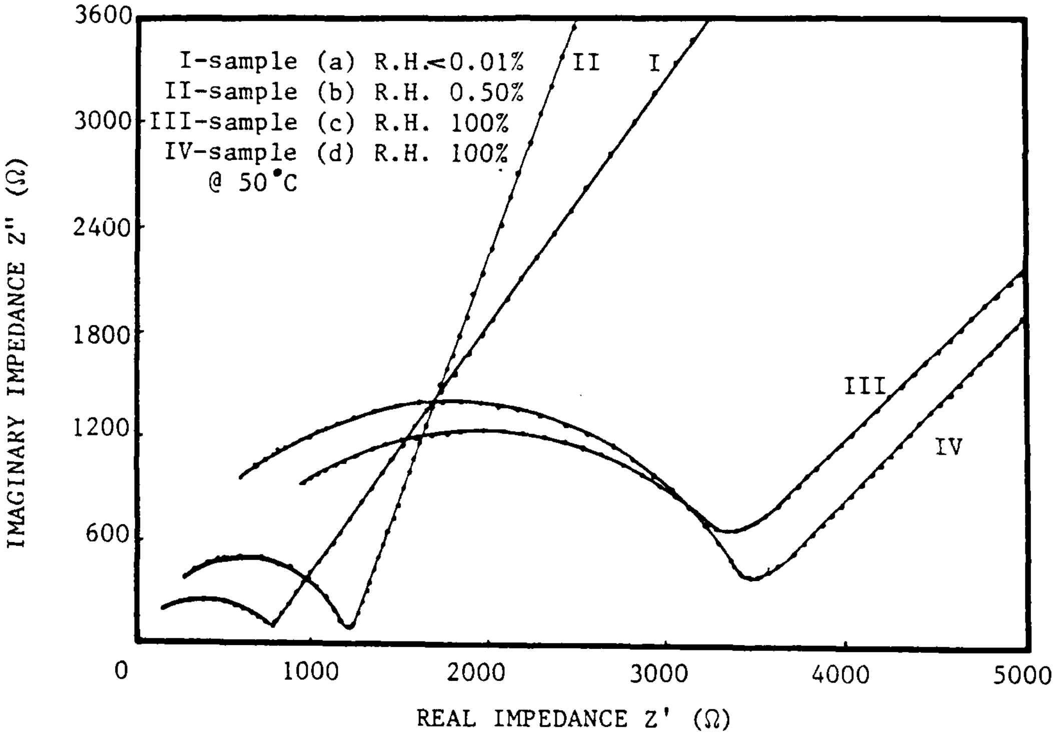

Figure 4. Computer simulated plots for samples (a - d) @ 80°C, normalized for a 35μm film thickness

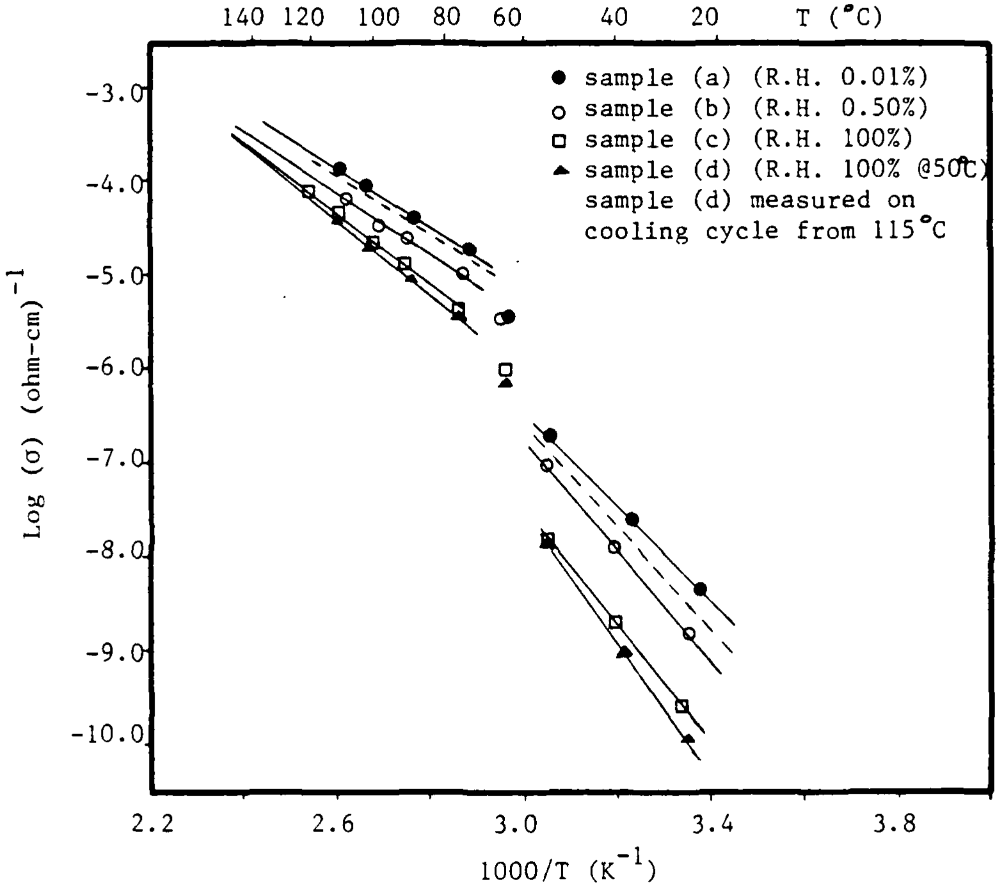

Figure 5. Conductivity vs temperature plots for samples (a - d) between 20°C and 120°C.

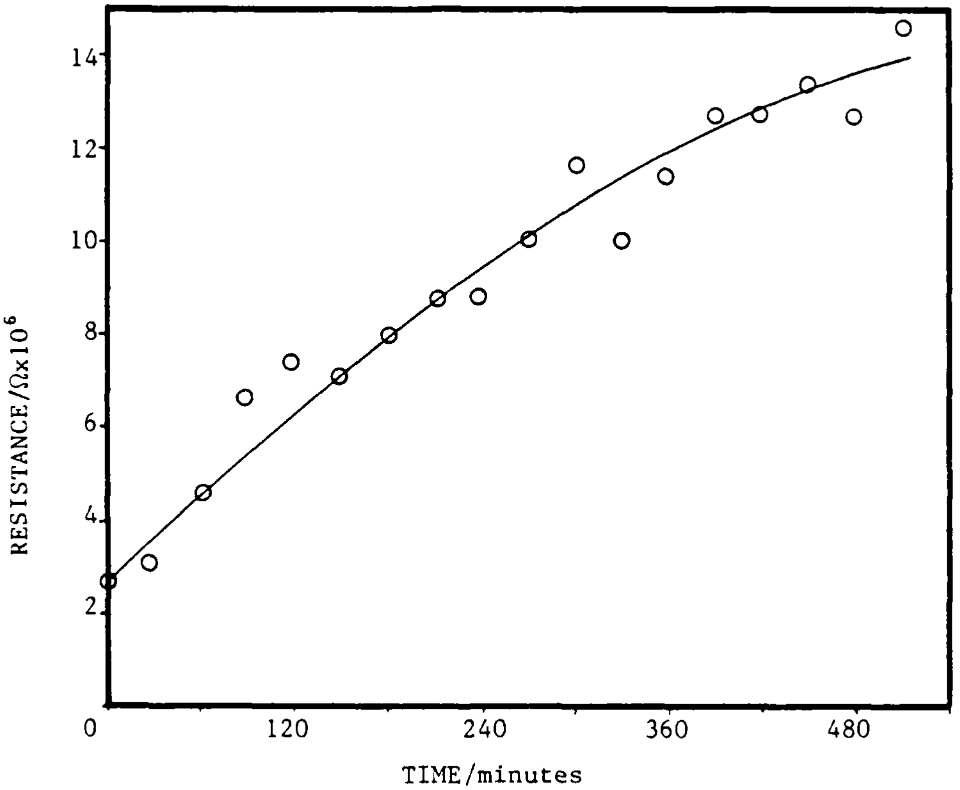

Figure 6. Variation of the total resistance of sample (a) with time under normal laboratory atmosphere.

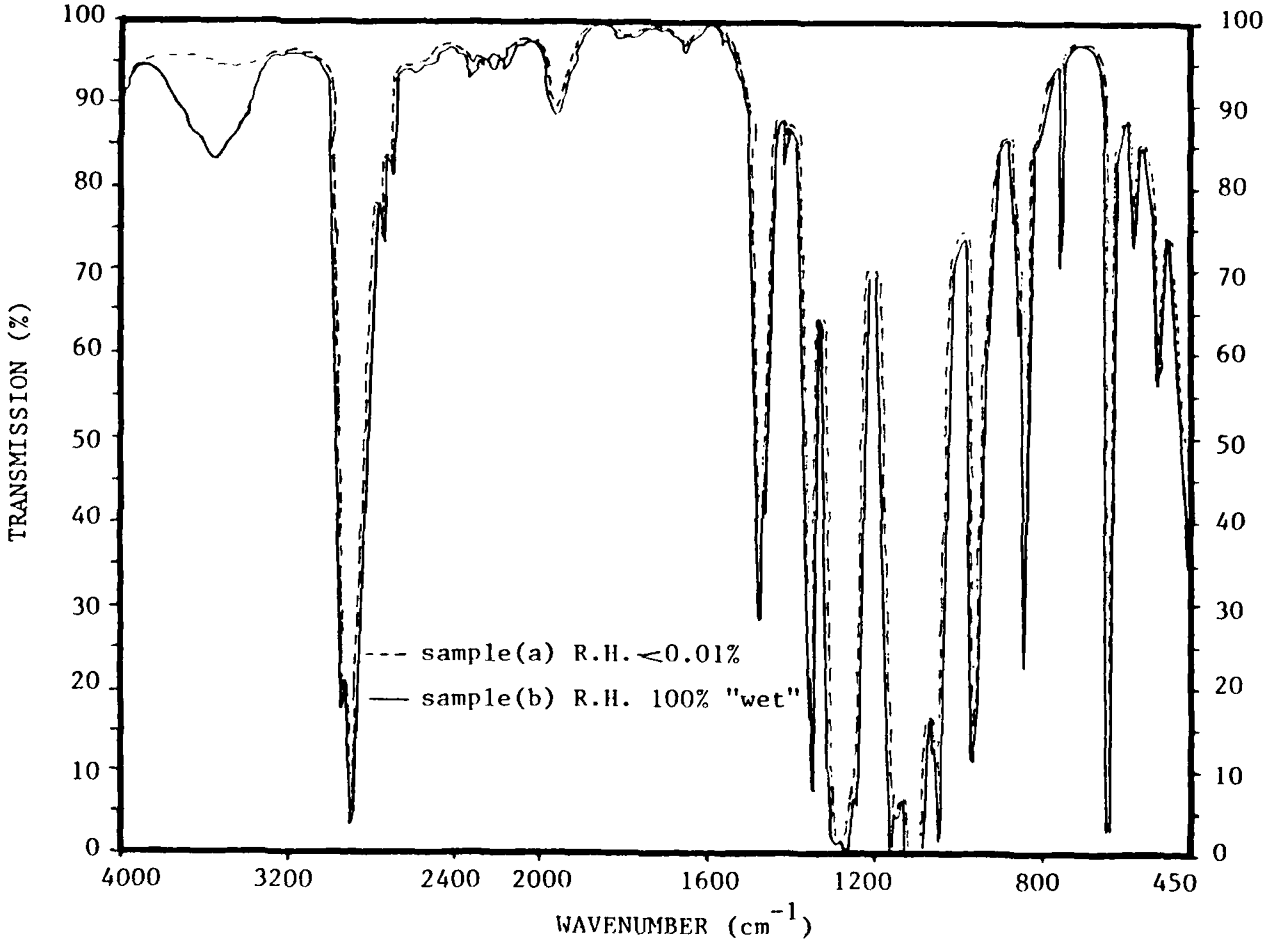

Figure 7. Infrared spectra of samples (a) and (d) recorded between $4000cm^{-1}$ and $450cm^{-1}$

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