Effect of temperature on the impedance response of coated metals

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ABSTRACT

This work tested painted steel panels in chloride solutions at 50 °C using electrochemical impedance spectroscopy (EIS) and compared performance with tests at room temperature. EIS spectra were measured over a range of temperature while the samples cooled and activation energies for ion migration in the coating and the corrosion reaction at the interface were determined by analysis based on fitting to model circuits. The significance of the activation energies was explored from examination of transient behaviour after a sudden temperature change.

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1. Introduction

Our previous papers [1,2] demonstrated for painted steel samples that if the separate resistances for the coating and the coating-metal interface could be resolved from EIS spectra, then Arrhenius plots of $\log R$ vs. $1/T$ from change of resistance with temperature yielded larger activation energies for the corrosion reaction than for ion transport in the coating, showing that the film resistance (as measured) could not be responsible for controlling the corrosion rate. Here further coatings, including a full 3-coat system with an inhibitive primer have been studied. In order to separate the true activation energy for ion transport from temperature dependence of the coating properties (from e.g. water uptake) some tests included a sudden temperature change with the impedance measured at intervals to follow subsequent changes with time (for both coatings on steel and a free film). The aim was to better understand the mode by which coatings protect the metal substrate.

2. Experimental

A commercial polyamide adduct cured epoxy-phenolic paint with 150 μm (1-coat) or 250 μm (2-coat) thickness were tested. Coatings were applied to grit-blasted mild steel panels by air spraying. Further tests were conducted on a full anti-corrosive system consisting of a zinc–phosphate-pigmented 2-component epoxy primer (50 μm), a low-VOC high-solid high-build epoxy barrier coat pigmented with micaceous iron oxide (180 μm) and a 2-component acrylic–urethane topcoat (60 μm). A commercial 2-pack epoxy paint (150 μm), prepared and applied similarly, was also tested. The edges of all panels were protected with a thick high-performance epoxy coating. Free films of the epoxy-phenolic paint (150 μm thick) were prepared by casting onto a degreased sheet of thick silicone rubber using a draw-down bar. Adhesion to the rubber was poor and coatings could be easily peeled off. For measurements on these free-standing films the sample was clamped between silicone rubber gaskets in a two-compartment cell exposing 7.06 cm². For EIS tests on free films a two-electrode arrangement was used, with one Ag/AgCl electrode acting as both counter electrode and reference electrode and the other as working electrode. For coated panels the electrochemical measurements were made using a three-electrode cell with a vertical working electrode of area 40 cm². The reference electrode was a saturated calomel electrode (SCE) and the counter electrode a platinised titanium electrode of area 9 cm². The samples were exposed in hot 3% NaCl solution (800 cm³), made from analytical grade chemicals and deionised water, held at constant temperature in a water bath (then slowly cooled in an insulated box to study change with temperature) and also at room temperature. One set of tests was made in 3% KCl solution to examine how ion mobility affected coating deterioration and activation energy for ion transport. All tests were conducted in duplicate.

Impedance measurements were taken at the free corrosion potential (or zero voltage offset for free films) using a Gill AC (ACM Instruments) computer-controlled potentiostat with a high-impedance paint buffer. The tests used a 20 mV sine amplitude and a frequency range from 0.1 Hz to 30 kHz. Samples were cooled

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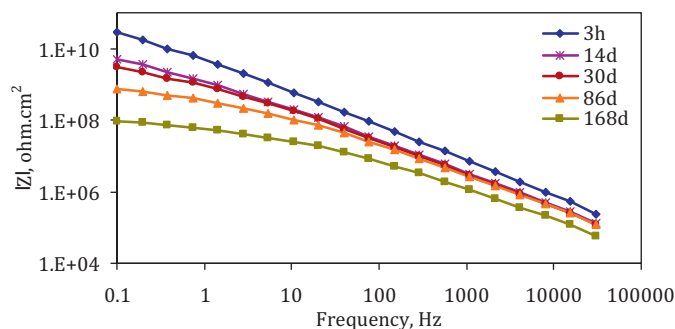*E-mail addresses:* john.sykes@materials.ox.ac.uk, johnsykes.sykes@gmail.com (J.M. Sykes).

Fig. 1. Bode plot for 2-coat epoxy-phenolic, in 3% NaCl at 21 °C after various periods.

Fig. 3. Two-coat epoxy-phenolic after 1 day at 50 °C in 3% NaCl: Nyquist plot showing effect of temperature on impedance.

from 50 °C down to ambient in an insulated container after removal from the water bath over (typically) 4 h. After the samples had been tested, the cell was replaced in the hot water bath and kept at 50 °C until the next measurement. Results were fitted to a suitable model circuit using ZsimpWin software.

To study transient behaviour, samples of the single coat epoxy phenolic (coated on steel and free films) were exposed in 3% NaCl at room temperature (21 °C), transferred to a beaker of the same solution at 50 °C in a hot water bath for a time then transferred quickly back to the cold solution. A series of EIS tests were made over the course of the experiment.

3. Results

3.1. Tests with epoxy phenolic paint

Fig. 1 shows results for tests in NaCl at 21 °C for the 2-coat epoxy-phenolic sample; the impedance remained high for several months. On the other hand results for the same coating tested at 50 °C (Fig. 2) show Z falling below $1 M\Omega\,cm^{-2}$ in 30 days. However it should be noted (Fig. 3) that although the impedance after 1 day is low at 50 °C, it becomes much higher when the sample is cooled back to 25 °C before measurement. For a meaningful comparison between exposure tests at different temperatures, we need to make measurements at the same temperature. Results for a single coat of the same epoxy-phenolic were published previously [2]; in that case two well defined time constants could be resolved so that an activation energy could be deduced from the variation in coating resistance with temperature ($32 \pm 4\,kJ\,mol^{-1}$), while that from the charge transfer resistance at the coating-metal interface yielded a much higher value of $61 \pm 4\,kJ\,mol^{-1}$. In this experiment with two coats of epoxy-phenolic paint only one time constant is
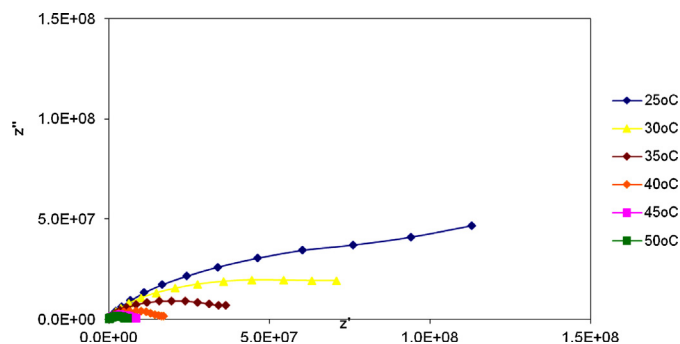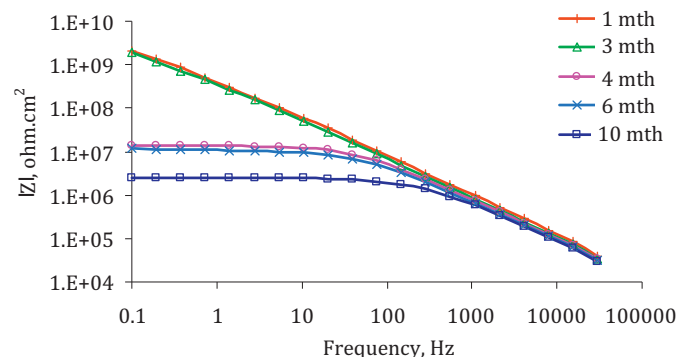

Fig. 4. Full scheme: bode plot for tests in 3% NaCl at 21° C after various periods.

seen, so that separate impedance contributions from the coating and the coating-metal interface cannot be distinguished; however taking the change in impedance modulus, |Z|, at 0.1 Hz between the two temperature extremes estimates an activation energy of about $60\,kJ\,mol^{-1}$, similar to that for the interface alone in the one coat measurement, rather than that for the coating resistance, though it seems most likely that the coating resistance is the main component.

3.2. Tests on full system

Like the thick 2-coat epoxy-phenolic paint, this system maintained a high impedance for several months in tests at 21 °C (Fig. 4), however at 50 °C impedance at the lowest frequency was down to $1 M\Omega\,cm^{-2}$ after 30 days (Fig. 5). However, if we again examine how impedance changes with temperature (Fig. 6), it can be seen that
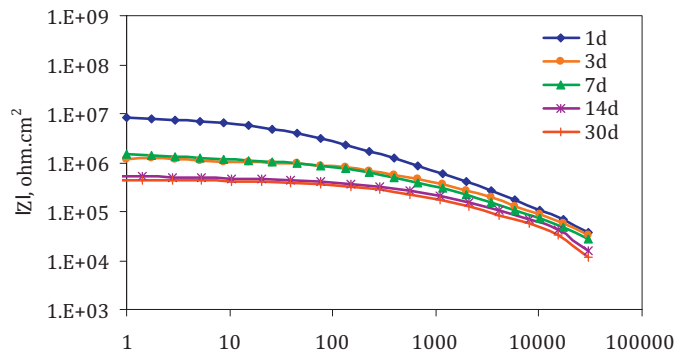

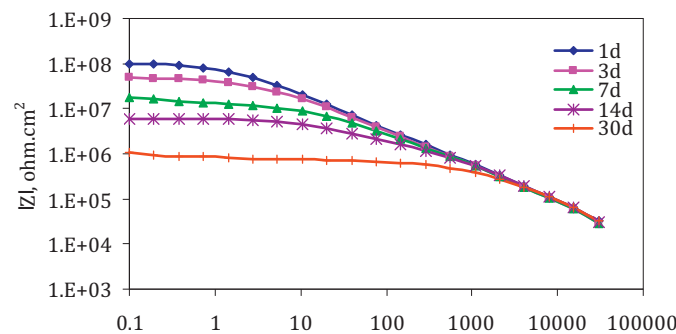**Fig. 2.** Bode plot for 2-coat epoxy-phenolic, in 3% NaCl at 50 °C after various periods.

Fig. 5. Full scheme: bode plot for tests in 3% NaCl at 50° after various periods.
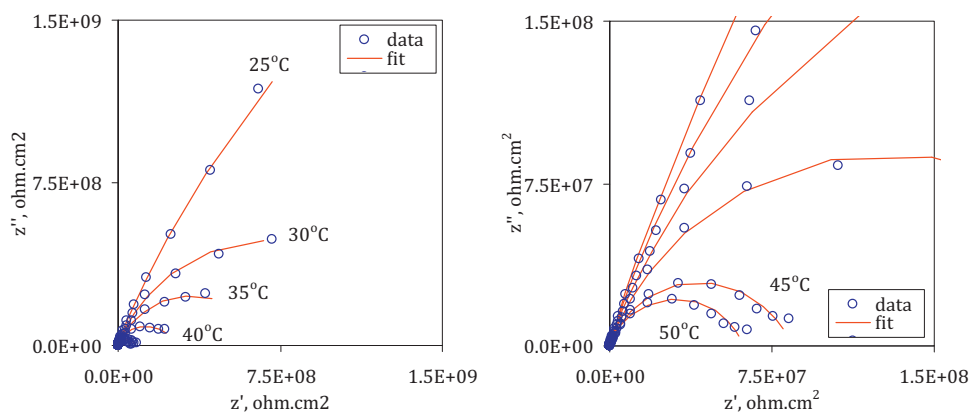
Fig. 6. Full scheme: Nyquist plot showing variation of impedance with temperature (plus expanded view for 45 and 50 °C), with calculated fits to model circuit shown.
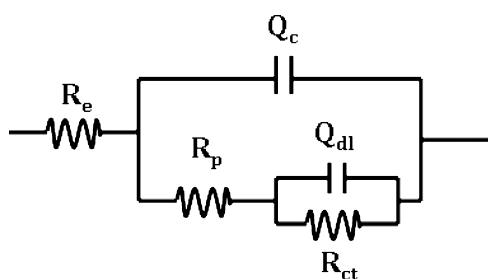

Fig. 7. Model circuit for coated steel.

the impedance modulus increases by about two orders of magnitude on cooling to room temperature, so that the low impedance at 50 °C is not really a good indicator of coating condition. Even after 30 days this system still shows a single semi-circle in Nyquist plots, and although the best fit is obtained by using a four-component model (shown in Fig. 7), the "R_p" value is extremely small and the "R_{ct}" value essentially corresponds to the semicircle diameter. Here it does not appear to be possible to separate coating resistance from interface impedance with certainty, so the activation energies calculated from "R_{ct}" in the Arrhenius plots (Fig. 8), which is likely that of the film (R_p is far too small), cannot be ascribed for sure to any particular process. The values show a broadly decreasing trend: 191 ± 2, 194 ± 3, 124 ± 3, 96 ± 6, 44 ± 2 and 50 ± 3 kJ mol^{-1} after 7, 14, 30, 46 and 180 days. Initially they gave similar high values of activation energy to those reported by Ochs and Vogelsang [5] for

thick coatings. It seems highly possible that this resistance is simply that of the coating, with the interface response unable to be detected in the absence of measurements at even lower frequencies.

3.3. Two-pack epoxy

Results for the two-pack epoxy coating on steel show little difference between exposure to KCl or NaCl; in both cases impedance dropped quickly at 50 °C, with little difference between them (Fig. 9). The relative changes in film resistance (first semi-circle) and charge transfer resistance (second semi-circle) with temperature are apparent in the Nyquist plots (Figs. 10 and 11). When component values were determined by least squares fitting to the same model circuit and an Arrhenius plot made for the coating and charge transfer resistances a significant difference was observed (Fig. 12). From the coating resistance KCl gave an activation energy of only 9 ± 1.8 kJ mol^{-1}, whereas NaCl gave 18 ± 1.5 kJ mol^{-1}. The charge transfer resistances gave 10 ± 1.3 kJ mol^{-1} and 5 ± 0.5 kJ mol^{-1} for KCl and NaCl respectively. In the case of KCl both are low (not dissimilar to that for conduction in aqueous solution), so the heavily blistered coating may contain defects that perhaps short circuit the coating. On the other hand for NaCl it is clear that the corrosion process is not controlled by the coating resistance, as the temperature dependence is quite different, with in this case lower activation energy for the corrosion process than for conduction in the paint. In our previous work [1,2] the reverse was true with the activation energy lower for conduction than for the corrosion process.
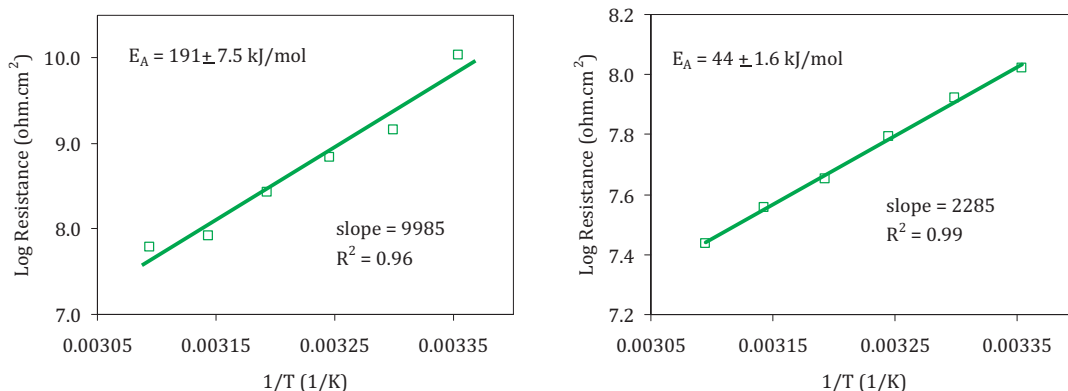

Fig. 8. Arrhenius plots of log R_{ct} vs. $1/T$ after 7 days and 70 days exposure of full scheme to 3% NaCl.
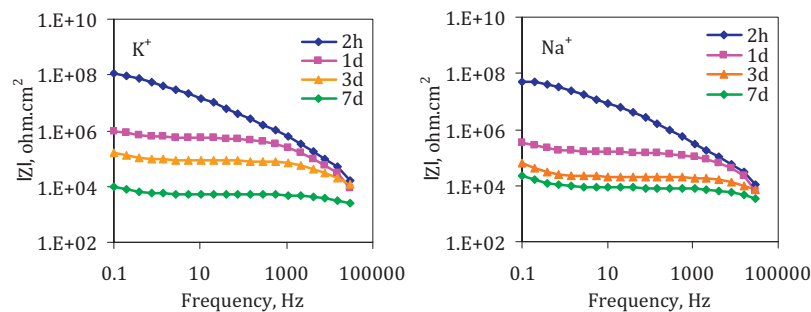
Fig. 9. Bode plots for 2-pack epoxy (75 μm) on steel in alkali metal chlorides (3%) at 50° C: effect of ion mobility.
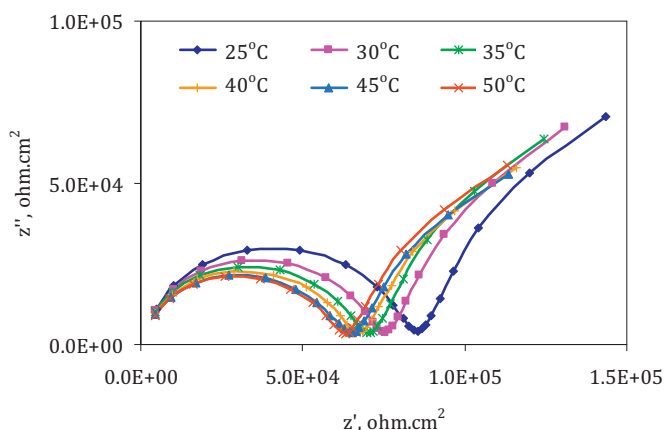

Fig. 10. Bode plot for 2-pack epoxy after 7 days exposure in 3% KCl at 50 °C: effect of temperature on impedance.
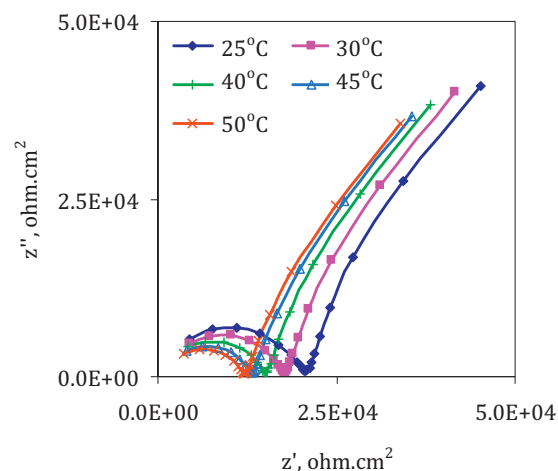
Fig. 11. Bode plot for 2-pack epoxy after 7 days exposure to 3% NaCl at 50 °C: effect of temperature on impedance.

3.4. Significance of activation energy for conduction

The linear dependence of log(film resistance) plotted with reciprocal temperature was first noted by Mayne and Mills [3], and from the slope an "activation energy of conduction" was calculated. Two types of behaviour were seen depending on whether the samples showed D type behaviour (resistance decreases if salt concentration in the test solution is increased) or I type behaviour (resistance increases if salt concentration is increased). D behaviour is believed to arise when ions from the solution pass through the coating; for I behaviour conduction within the paint is controlled by water activity in the tests solution, which regulates water uptake. Activation

energies were higher for I type films (155–250 kJ mol^{-1}) and significantly lower for D type films (20–45 kJ mol^{-1}). This dependence has been observed frequently by other workers [1,2,4,5]. Because ion migration in the coating is a "rate process" regulated by an activation barrier (energy, E_M) the conductivity ($1/R_f$) will obey the Arrhenius equation [6]:

$$\frac{1}{R_f} = A \ \exp\left[-\frac{E_M}{RT}\right] \tag{1}$$

The term A is a property of the coating which will depend upon factors such as water uptake and concentration of mobile ions and
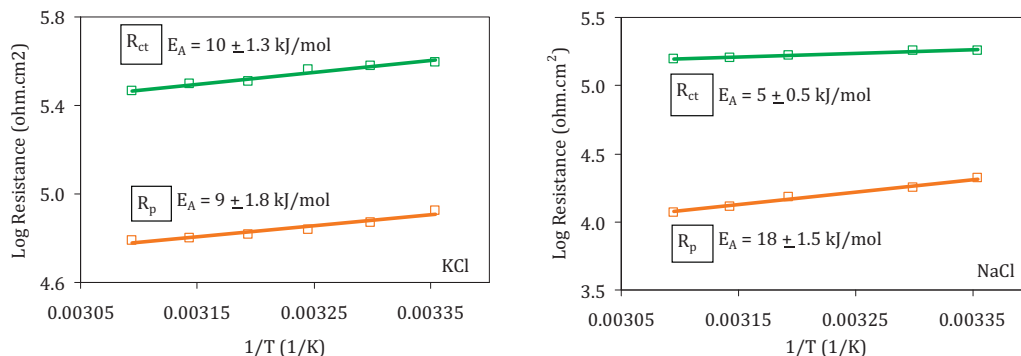

Fig. 12. Arrhenius plots for 2-pack epoxy after 3 days in 3% KCl and NaCl at 50 °C.
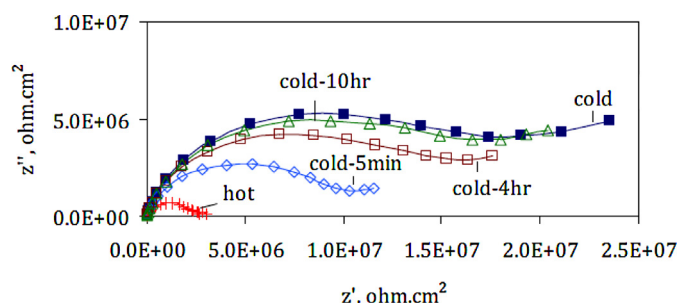
Fig. 13. Nyquist plot for epoxy-phenolic (150 μm) showing slow recovery in impedance after rapid transfer from 3% NaCl at 50 °C to 3% NaCl at 21 °C.

will, therefore, also depend upon temperature. Indeed in the same paper Mayne and Mills [3] observed an Arrhenius relationship for water uptake in their films; on this basis it seems reasonable to express this constant as a function of temperature:

$$A(T) = B \exp \left[-\frac{E_f}{RT} \right] \tag{2}$$

where E_f is an enthalpy change associated with the uptake of water and/or ions into the film depending upon the I or D character of the coating. Indeed the Gibbs–Helmholtz equation leads to a similar relationship for the dependence of an equilibrium constant (between bound and free ions in the film say, or for ions within and outside the coating) with temperature [6].

If we substitute the expression in [2] for A in [1] we obtain an equation that describes the empirical relationship between R_f and T:

$$\frac{1}{R_f} = B \exp \left[-\frac{E_M + E_f}{RT} \right] \tag{3}$$

Thus we see that the empirical activation energy for conduction is the sum of two terms, one associated with migration of ions in the paint (E_M) and the other that arises from the temperature dependence of coating properties (E_f).

The effect of temperature change on ion migration will be instantaneous following a sudden cooling of the sample, but the film properties will respond more slowly as, for instance, the coating takes up (or loses) water and ions by diffusion. (For a sample of 40 cm², even an I type paint will be expected to contain D areas that will, because of their lower resistance, dominate the panel response. This means that we expect equilibrium of ions with the outside solution, to change the resistance, rather than equilibration of water.)

To test this, samples of the single coat epoxy phenolic were tested in 3% NaCl at room temperature, transferred to a beaker of solution in a water bath at 50 °C and EIS measurements made before transferring back to the cold solution. The Nyquist plots in Fig. 13 show a marked reduction in impedance from 21° to 50 °C (cold → hot) as expected, but over the sequence of measurements after sudden cooling at 5 min, 4 h, and 10 h the semi-circle changes quickly at first but only returns slowly to its original size. The total activation energy calculated from the transition cold to hot (after fitting to the same model circuit) gives an estimate 56.6 kJ mol⁻¹, whereas the resistance increase after 5 min recovery following the transition hot to cold (where migration of ions will slow down at once but re-equilibration will be slow) yields only 7.9 kJ mol⁻¹ as an estimate of the activation energy for ion migration. This experiment suggests that most of the activation energy relates to changes in the film with temperature, rather than the size of the energy barrier for migration of ions between sites in the paint. A further test on a free film of the epoxy-phenolic coating (Fig. 14) showed similar behaviour with a massive reduction in impedance on rapid heating to 50 °C, but only slow recovery after a rapid initial change when

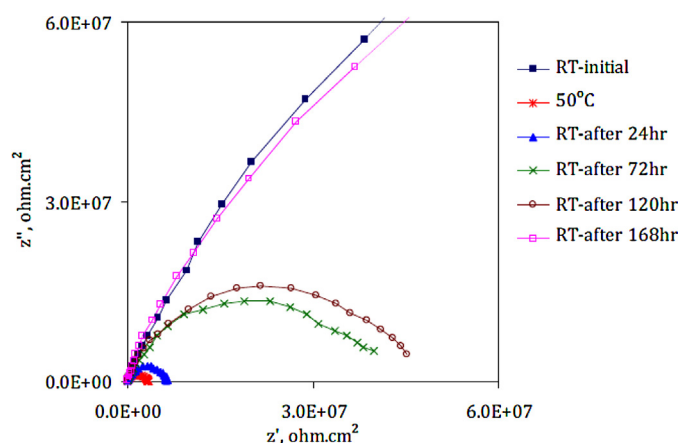**Fig. 14.** Nyquist plot showing for epoxy-phenolic free film (150 μm) slow recovery in impedance after rapid transfer from 3% NaCl at 50 °C to 3% NaCl at 21 °C.

transferred back to the cold solution (taking 168 h to return to the original value).

4. Discussion

In the present work temperature was always maintained below 50 °C in order to avoid exceeding the glass transition temperature, where diffusion and ion conduction will proceed more rapidly. The results did not show any discontinuity in the Arrhenius plots [3] suggesting that samples were never exposed above this critical temperature.

The panels with two coats of epoxy-phenolic paint and those with the full anti-corrosive system performed well at 21 °C, but increasing temperature to 50 °C gave much faster degradation. Blisters became apparent on the samples within 30 days. In both cases the stage had not been reached where well defined responses from coating and substrate could be distinguished, so that their separate temperature response could not be determined, however Z at the lowest frequency gives about 60 kJ mol⁻¹ for the 2-coat epoxy-phenolic and R_{ct} for the full system (which is most likely the coating resistance) gave a high value (191 ± 7.5 kJ mol⁻¹) at first which fell over time. We now argue that these values consist of the sum of two components, an activation energy for migration of ions in the paint and another energy arising from the temperature dependence of film properties, but at the moment we do not know for these coatings which part changes most with time.

Unfortunately because the coating-metal impedance response could not be resolved for the full system, we were unable to test the influence of inhibitive pigment in the primer coat on the corrosion reaction, though it may have influenced coating deterioration.

The results with 2-pack epoxy show different activation energies for conduction in KCl and NaCl. We would expect the smaller hydrated K⁺ ion to migrate more easily through the film, yielding a lower activation energy, as is observed; the low activation energy for corrosion may indicate coating damage in KCl. In the case of NaCl the difference between the activation energies for ion migration (from film resistance) and corrosion are sufficiently great to suggest that the corrosion process is not controlled by the coating resistance. In this case the fact that the corrosion reaction shows less temperature dependence than conduction in the coating must mean that the corrosion current cannot be passing through the coating. If the local anode and cathodes are inside blisters (which have been observed) connected by the ionic pathway of the blister solution then this would explain the lower temperature dependence.

In our previous work we found a much higher activation energy for the charge transfer resistance than for ion transport in the paint, which challenges the idea that conduction of ions through the coating regulates the corrosion rate, however if we suppose that the conduction path between anode and cathode includes a low resistance region (at the anode say) connected in series with a higher resistance region (in this case at the cathode) then the higher resistance would control the corrosion current. Because the two regions are coupled in parallel for the EIS measurement, only the lower resistance can be measured. If conduction in the low resistance region exhibits a low activation energy, but the high resistance region has a higher activation energy, then the corrosion current would give the same higher activation energy, different from the activation energy calculated from the measured conductivity of the coating. This offers an alternative explanation for these results, but we should keep in mind that other work on a model system concluded that much of the available driving force for the corrosion process can be taken up in electrode polarisation, rather than driving current through the coating [7,8], and this could well apply here too.

The results for rapid changes in temperature make it clear that measured activation energies for ion migration in coatings consist of two parts: one from the energy barrier to ion migration and the other arising from slower changes in the paint.

5. Conclusions

Testing at elevated temperature can be used to produce more rapid failure, but for meaningful comparison with room temperature tests impedance need to be measured at the same temperature.

The variation of coating resistance with temperature gave an activation energy of $60 \, kJ \, mol^{-1}$ for the 2-coat epoxy-phenolic coating, but a much higher early value for the full system with an anti-corrosive primer ($191 \pm 7.5 \, kJ \, mol^{-1}$) which dropped considerably with time.

Tests using sudden temperature changes revealed that activation energy calculated from temperature dependence of coating resistance consists of two parts, the energy barrier for ion migration and an enthalpy change term that controls the number of mobile ions and possibly their mobility in the film through change in water uptake.

In tests with thicker coatings it was not possible to distinguish coating resistance from charge transfer resistance.

Tests with 2-pack epoxy in NaCl showed different activation energies for conduction in the paint and the corrosion process, possibly because an ionic pathway exists within blisters that links anodic and cathodic sites.

Again we conclude that if the rate of corrosion is controlled by the paint resistance, then the EIS method will tell us nothing about the part of the ion pathway which potentially controls the corrosion rate.

The possibility that polarisation of the electrode reactions could be the controlling factor [7,8] may also apply here.

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