-1600mV(SCE) bring as a consequence the formation of a film of different nature judging by the obtained capacitive values. Data indicate a charge transfer process that might involve localized corrosion (Fig.5a).

An increase of lithium in solution (0.05M Li₂CO₃) at the same potential improves the quality of the film with probably more incorporated lithium and the absence of localized corrosion (Fig.5b). SEM observation of tested samples confirmed it.

For 0.05M Li₂CO₃, an increase in potential give an AC response that evidenced the formation of a film, a charge transfer process and also diffusion at low frequencies.

The quantification of Li profiles using RBS and other techniques is under way in order to characterized film composition under potentiostatic control.
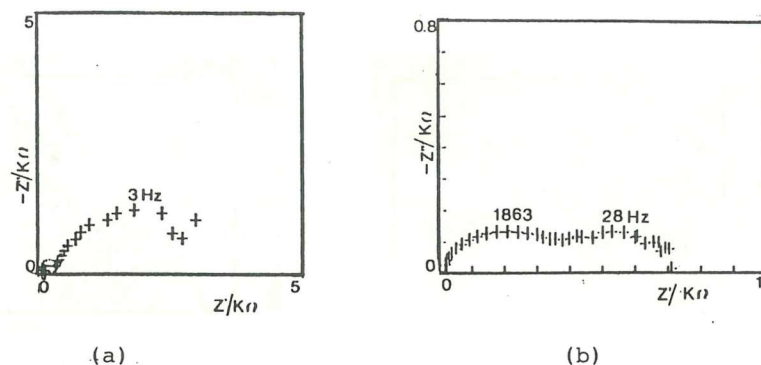

(a)   (b)

Fig.5. AC Impedance diagrams for Al 99.999% in Lithium containing solutions at 1.60V(SCE)
0.01M Li₂CO₃ (a)
0.05M Li₂CO₃ (b).

STUDIES ON ALUMINIUM CORROSION IN HYDROCHLORIC ACID SOLUTION

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Corrosion of aluminium usually results in the formation of a porous or barrier type oxide film on its surface [1]. The film can be formed anodically, except at low pH, or cathodically even at low pH due to local pH increase at the aluminium surface associated with hydrogen evolution. The corrosion rate is enhanced by the presence of chloride ion in solution through a pitting mechanism, procedure employed in the etching of aluminium by hydrochloric acid for use in dielectric capacitors [2].

The corrosion behaviour of aluminium in 0.1M HCl has been studied in this work by three techniques. A cylinder of pure aluminium, diameter 0.5cm, was encased in Teflon and made into the form of a rotating disc electrode. Experiments were conducted with and without electrode rotation, and in aerated and de-aerated solution. Firstly, the variation of corrosion potential, E_{corr}, with time was measured for freshly polished smooth and deliberately roughened aluminium. Secondly, the polarization resistance, R_p, of the aluminium/solution interface was measured using small amplitude cyclic voltammetry at slow scan rate at potentials within 20mV of the corrosion potential. Thirdly, impedance spectra were recorded over a frequency range of $10^{-2} \rightarrow 10^{4}$Hz at a variety of applied dc potentials using a 5mV rms

sinusoidal potential perturbation from a Solartron 1250 Frequency Response Analyser with 1286 Electrochemical Interface. With all techniques the effect of cycling the potential from E_{corr} to 0V vs SCE and back, which activates pitting corrosion [3], was studied.

Corrosion potential measurements gave initial values of around -0.70V vs SCE which became gradually more negative during 4 hours in stationary solution, the final, equilibrium value being approximately -0.91V. At the same time a film of aluminium oxide was formed on the surface. Activating the surface to pitting by potential cycling caused the stable value of E_{corr} to descend to -0.95V. The explanation for the change on activation lies in the increased anodic partial current. Rotating the electrode decreased the time necessary to reach an equilibrium value of -0.87V to 1 hour. This more positive value is because electrode movement causes solution renewal and the pH at the electrode surface remains lower; this explanation is supported by the fact that E_{corr} is almost independent of rotation speed. De-aeration increased the time necessary to reach equilibrium, but not the potentials.

Small amplitude cyclic voltammetry is a convenient method for determining the polarisation resistance of corroding interfaces [4]. It was found that a scan rate value of 0.1mV s^{-1} was necessary to avoid hysteresis and led to R_P = 3.8kΩ, showing the existence of an oxide film. Variation in R_P values according to the different experimental conditions described earlier is small. This value of R_P is not very high, suggesting a porous film or one across which transport is fairly easy.

Complex plane impedance plots obtained at two dc potentials are shown in Fig.1. The shape of the plots is indicative of a multistep
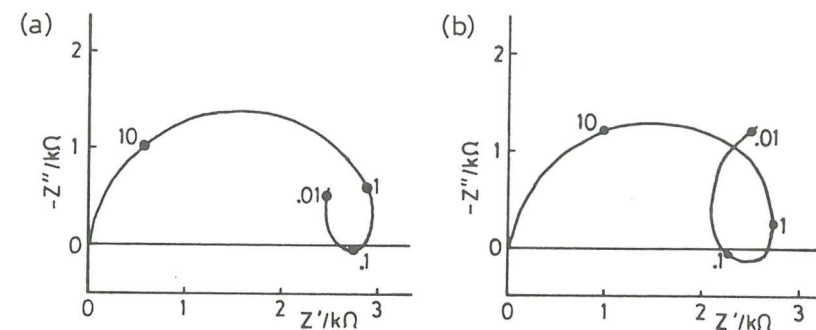
Fig.1 Impedance plot for Al in 0.1M HCl stationary solution after pitting activation. E_{corr} = -0.95V; dc polarisation (a) -0.93V and (b) -0.80V vs SCE. Frequencies in Hz.

corrosion mechanism and contains two semicircles centred below the real axis. The polarisation resistance corresponds to the real axis intercept of the low frequency semicircle, but is difficult to determine accurately by impedance measurements owing to noisy signals at very low frequencies. This illustrates the advantage of determining R_P by small amplitude cyclic voltammetry. It is found that deaeration of the solution and rotating the aluminium electrode do not affect the shape of the impedance plots. Interfacial capacitances calculated from the higher frequency semicircle are of the order of 100μF cm^{-2}. A full interpretation of the impedance spectra requires an electrical analogue model, probably in terms of transmission lines, for the interface, for which further experiments are necessary.

The experimental results obtained can be examined in the light of a mechanism proposed for corrosion in neutral solution [5] in which Al$^+$ is formed at the Al/Al$_2$O$_3$ interface, the Al$^+$ then migrating through the oxide film (which has a high electric field) to the oxide/solution interface where oxidation to Al(III) occurs. The results obtained in 0.1M HCl appear to agree with this model. More work is under way to

establish this conclusion and to enable the quantitative determination of corrosion rate kinetic parameters.

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ELECTROCHEMICAL BEHAVIOUR OF THE BASAL PLATINUM (110) SINGLE CRYSTAL IN 0.1 M NaOH.

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INTRODUCTION:

Whereas the electrochemical behaviour of the platinum electrode has been extensively studied in acid media, mainly due to its use as electrolyte in fuel cells, only a few studies have been made in of platinum in an alkaline solution [1-5], because this electrolyte suffer from progressive carbonation during the oxidation of organic molecules. In spite of this, it is interesting to study the adsorption of hydrogen and oxygen in an alkaline electrolyte and to compare it with that in acid media.

EXPERIMENTAL:

The electrolyte was an 0.1M sodium hydroxide (P.A. Merck) solution and the water used for its preparation was from a Millipore- Milli Q system. A Pt counter electrode was used and all potentials are referred to the reference hydrogen electrode in the same solution (RHE).

The cyclic voltammograms were recorded at room temperature at a sweep rate of 50 mV/s, starting in the negative sense from an initial potential of 0.7V.

The single crystal electrode, kindly prepared by J.Clavilier, was thermically treated before each experience using the customary experimental procedure developed by J.Clavilier [6].

RESULTS AND DISCUSSION:

After treatment in flame and after cooling, the surface