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A note on the impedance of reduced PbO_2 layers on some lead alloys in sulphuric acid

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The impedances of reduced layers of PbO_2 in sulphuric acid are measured at potentials in the range between initial discharge and complete reduction to lead. The electrode behaviour is fairly polarizable when the electrode is remote from the $PbSO_4/Pb$ potential. Near the reversible potential the electrode behaves as a porous electrode under charge-transfer and diffusion control.

1. Introduction

In the preceding paper [1] we discussed our measurements of the impedance of films of PbO_2 formed on various lead alloys and showed how, as the electrode was reduced in sulphuric acid, the structure of the consequential lead sulphate film could be deduced from impedance plots.

In this note we wish to present some further impedance data obtained as the electrode film is progressively transformed to lead.

2. Experimental

The experimental details are exactly the same as in the previous paper [1]. Care was taken to ensure that the current flowing across the electrode was zero when the measurements were obtained, i.e., that a true steady-state had been achieved. Measurements on a series of alloys were taken at 700 mV[†], 400 mV, 0 mV and − 970 mV, the latter corresponding to the completely reduced electrode, i.e. $PbSO_4/Pb$.

3. Results and discussion

Fig. 1 shows the impedance plot for the reduced PbO_2 formed on antimonial lead at 700 mV to be a distorted semicircle leading to a rising portion; this is the only system which showed a well-defined high-frequency shape. Other systems, see, for example, Figs. 2 and 3, showed curving high-frequency regions, but these deteriorated tangentially into rising lines whose dihedral angle generally exceeded 45°. It can be concluded that whereas the films on the other alloys at 700 mV form fairly passive layers that on antimonial lead does not.

Fig. 4 shows that at 400 mV the impedance spectrum of the Pb–Sb alloy is a rising line which shows some curvature; this is typical of all the alloys and the most curvature is again observed with the antimonial alloy. At 0.0 mV the impedance spectra for all the alloys are lines (Figs. 5 and 6) with concavity towards the real axis at the higher frequencies, degenerating into straight lines whose slopes exceed 45° at lower frequency. This behaviour indicates that the electrodes are passive and relatively polarizable being covered with a layer of $PbSO_4$ which seals off the surface almost completely.

When the electrode is fully reduced the impedance plots are shown in Figs. 7–10. Here the high-frequency semicircle is well defined and comes away from the real axis at the highest frequency at ~ 90°, as expected by theory [2]. As the frequency is reduced the complex-plane plot becomes an elongated semicircle, the tail coming away from the resistance axis at approximately

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[†] All potential measurements were made using an Hg_2SO_4/Hg electrode in the same solution.

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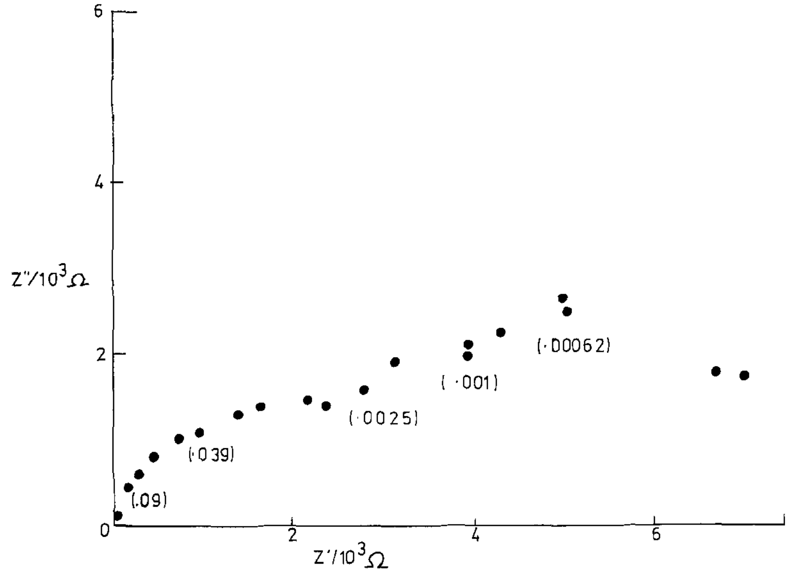

Fig. 1. Sluyter plot for Pb–Sb(5.15%) in 5 M H_2SO_4 at 23° C. $E = 700$ mV; $\phi = 0.071$ cm^2. Frequencies in kilohertz in parentheses.

22.5°, as required for a porous electrode. In certain alloys (e.g. Bi 0.26%; Pb 99.74%) this was very well developed; however, with pure lead this region was not really observed in the experimental frequency range. The high-frequency part, moreover, rises at 45° from the real axis. This shape can be transformed to the simple charge-transfer and diffusion model behaviour by squaring [3]. Furthermore, the Randles plots for these curves when treated in this manner behave similarly to those already discussed [1], i.e., they show the correct variation with frequency. We can conclude from this that the porous nature of the product lead is sufficiently well developed to cause the electrode to behave as a porous one at a sufficiently low frequency.

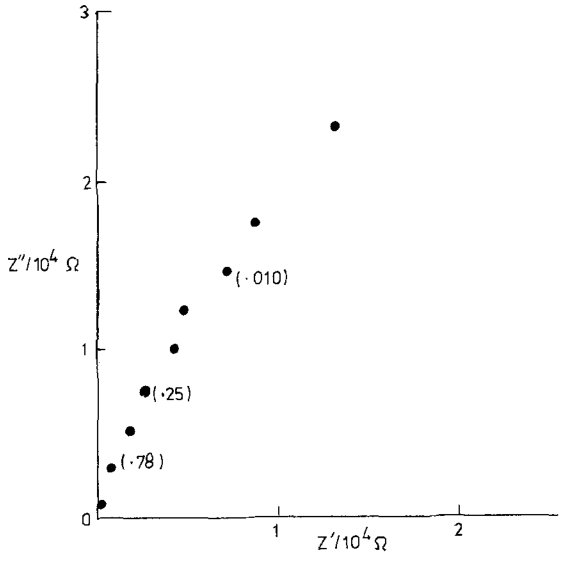

Fig. 2. Details as Fig. 1, but for pure lead.

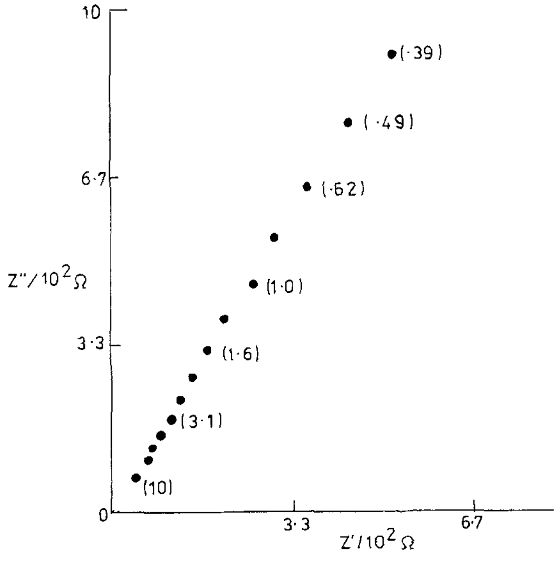

Fig. 3. Details as Fig. 1, but for Pb–Bi(0.13%).

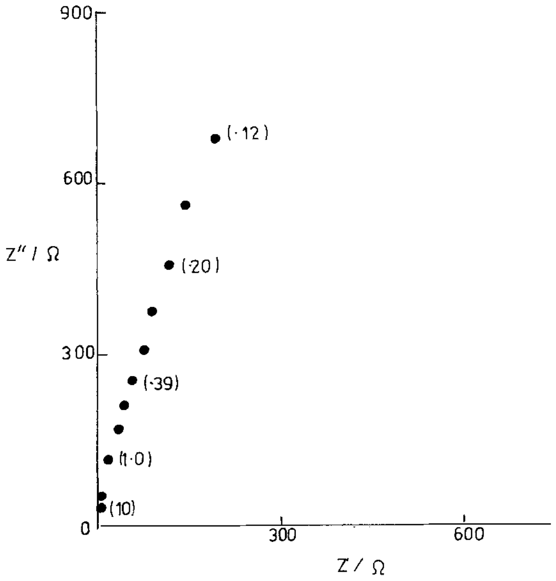

Fig. 4. Details as Fig. 1, but for Pb–Sb at 400 mV.

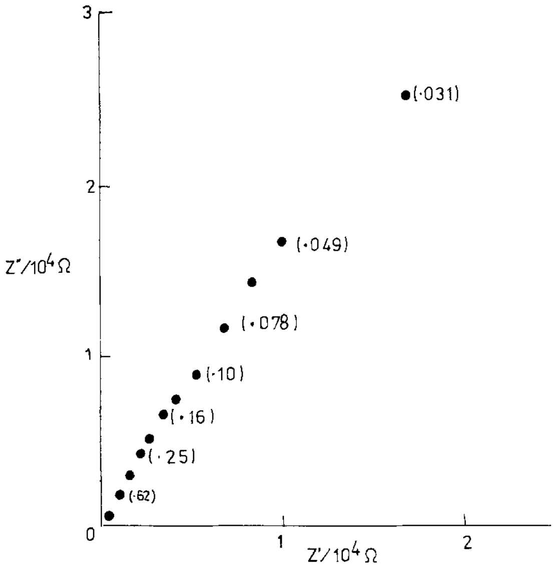

Fig. 5. Details as Fig. 1, but for pure Pb at 0.0 mV.

With antimonial lead these features were very obvious and in fact at high frequency a small inductive semicircle indicates that porosity is sufficiently well defined to cause a phase delay due to the porous structure of the electrode. These features were absent in all the other cases except the antimonial alloy.

These results indicate that the nominally porous lead dioxide electrode for which pososity in the sense of de Levie [4, 5] is absent becomes effectively porous in the electrochemical sense when reduced to lead. Thus the 'halving' of the time dependencies observed by us [6] in the case of porous negative electrodes would be expected to be absent in the case of the similarly porous positive electrode produced electrochemically from similar starting materials. The reason for this lies in the high conductivity and high exchange current for lead in sulphuric acid compared with these same parameters in the case of lead dioxide.

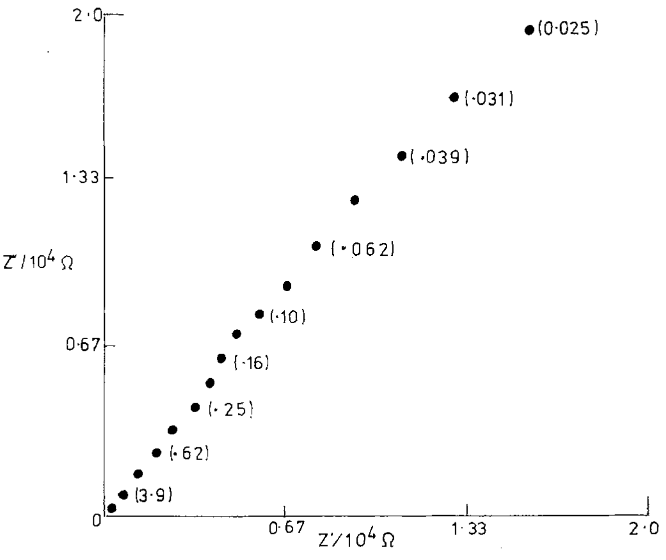

Fig. 6. Details as Fig. 1, but for pure Pb(0.13%) at 0.0 mV.

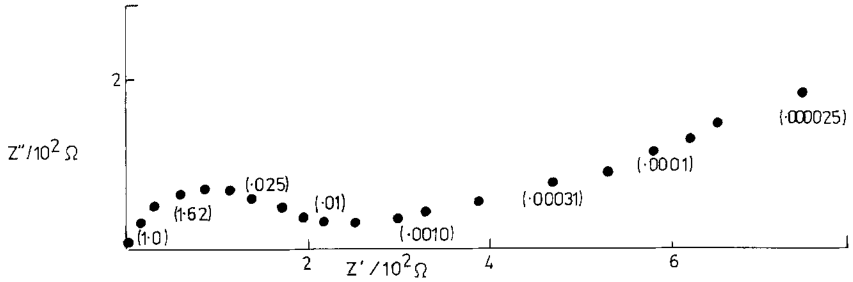

Fig. 7. Sluyters plot for pure lead electrode in 5 M H_2SO_4 at 23° C. $E = -970$ mV; $\phi = 0.071$ cm^2.

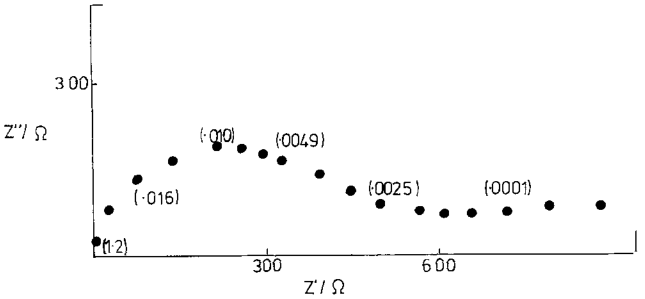

Fig. 8. Details as in Fig. 7, but for Pb–Sb.

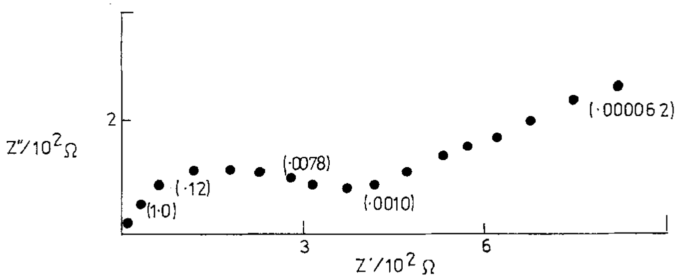

Fig. 9. Details as in Fig. 7, but for Pb–Bi (0.26%).

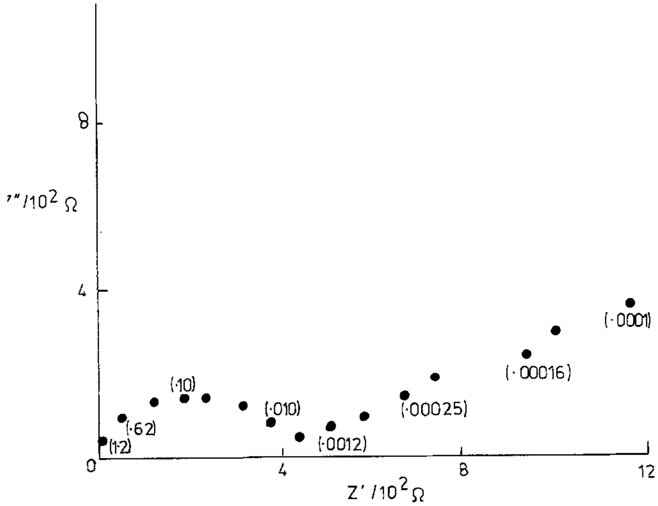

Fig. 10. Details as in Fig. 7, but for Pb–Ca (0.09%)–Sn(0.66%)–Bi(0.15%).

Acknowledgement

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