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SHORT COMMUNICATION

# *Impedance measurements on platinum in sulphuric acid solutions*

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## 1. Introduction

In the development of the methanol–air fuel cell, the performance of electro-oxidation catalysts has been reported to fall-off with increasing sulphuric acid electrolyte concentration. The results were consistent with the assumption that the catalyst surface is poisoned by adsorbed sulphuric acid species [1]. In an attempt to verify this conclusion, it was decided to investigate the electrode impedance on platinum over a large range of sulphuric acid concentrations. This investigation would provide complementary data to the LSV measurements already reported [1].

The double layer on platinum has been investigated by many workers [2, 3]. Bockris [4, 5] has shown that in perchloric acid solutions of low concentration, the pzc (as identified by the diffuse layer capacitance minimum) varied with concentration according to

$$V_{\mathrm{pzc}} = 0{\cdot}56 - 2{\cdot}3(RT/F)\,\mathrm{pH} \qquad (1)$$

and accordingly, the pH dependence of $V_{\mathrm{pzc}}$ could not be associated with adsorbed hydrogen. Labrovskaya, Luk'yanycheva and Bagotskii [6] using normal sulphuric acid electrolytes showed that $HSO_4^-$ adsorption passed through a maximum at ~ 0·7 V NHE and concluded that the univalent ion occupies two oxygen adsorption sites.

In this communication we present impedance data for platinum in sulphuric acid solutions up to a concentration of 6 M $H_2SO_4$. These solutions are of practical importance with regard to fuel cell technology.

## 2. Experimental

For the estimation of the electrode impedance of platinum and the measurement of steady-state polarization curves, the apparatus described previously [7] was used.

For these experiments the electrolyte was subjected to continuous purification by the adsorption of impurities onto activated charcoal. Impedance measurements attained a consistent value after prolonged solution cleaning; the magnitudes of the values were considered satisfactory when they were constant and not less than those of previous work [7]. The time taken to clean the electrolyte sufficiently was approximately three days.

The platinum electrode ($\phi$ = 3 mm) was mounted in soda glass and polished on successive grades of abrasive down to 0·25 $\mu$m diamond. The electrode was etched in $H_2SO_4$ (98%) for 30 min and washed in bidistilled water. Before any measurements were made, the electrode was allowed to come into equilibrium for 30 min with the experimental solution under nitrogen.

## 3. Results and discussion

Fig. 1 shows a typical faradaic current v. bias potential curve for Pt in 1 M sulphuric acid. In dilute sulphuric acid a potential region of ~ 1·3 V. was observed in which the electrode was experimentally polarizable. In concentrated solutions (>3 M) there existed no region of ideal polarizability. However, measurements could be made

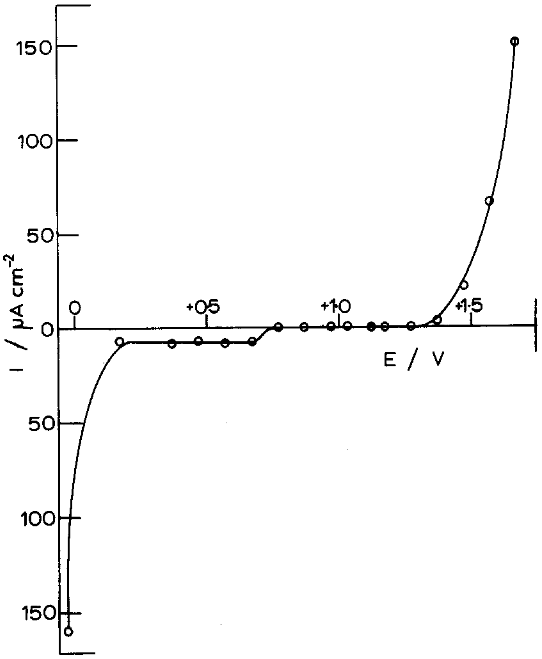

Fig. 1. Faradaic current v. bias potential for Pt in 1 M $H_2SO_4$.

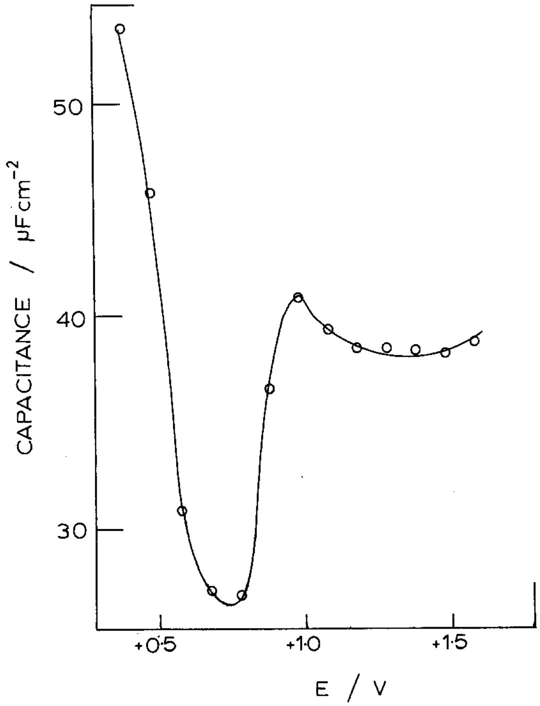

Fig. 2. Electrode capacitance curve for Pt in 6 M $H_2SO_4$.

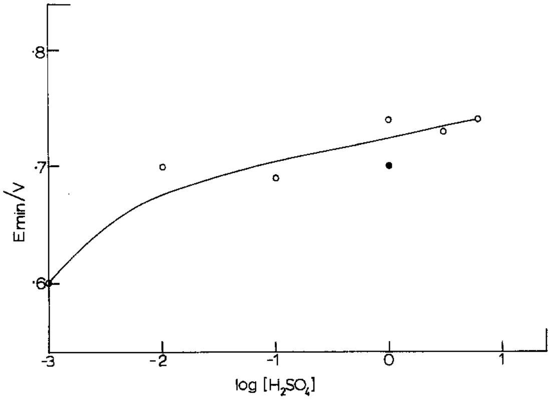

Fig. 3. Plot of potential of electrode capacitance minima v. log [$H_2SO_4$]; ○ our data; ● Rosen *et al.* [7].

in the range 0·2 to 1·4 V NHE* without an undue flow of d.c., (< 20 μA cm$^{-2}$, which is well below the level required to affect the results through diffusion processes).

The form of the capacitance curve in the most dilute solutions was identical with those found by Bockris and co-workers [4], and showed a well-defined minimum at a potential somewhat more positive than the generally accepted value of the pzc. This would be expected in view of the well-established adsorption of $HSO_4^-$ on platinum [6]. In the absence of specific adsorption, the diffuse layer minimum should be progressively removed by increasing the electrolyte concentration, to conform with the Stern theory. In the present experiments a capacitance trough was observed at all concentrations giving strong evidence for adsorption at the electrode. Fig. 2 shows a typical electrode impedance curve for Pt in 6 M $H_2SO_4$. A well defined capacitance hollow is observed extending over a range of about 300 mV. The breadth of the capacitance hollow increased with acid concentration from about 140 mV in 0·1 M acid to 300 mV in 6 M $H_2SO_4$. This suggests an increasing adsorption of neutral sulphuric acid molecules.

Fig. 3 shows a plot of the capacitance minimum versus log [$H_2SO_4$]. The single point available from the work of Rosen *et al.* [8] is included. This curve shows that the minimum is shifted to more anodic potentials as the concentration is increased. In the case of a non-specifically adsorbed electrolyte the locus of the capacitance

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* All measurements were made with reference to the $HgSO_4$/Hg electrode, corrections to NHE being made by calculation.

minimum should describe a straight line with a slope of 60 mV per concentration decade (in accordance with Equation 1). In our curve the gradient exceeds this value at low acid concentrations owing to the presence of adsorbed $HSO_4^-$ ions at the electrode. (At these potentials $SO_4{}^{2-}$ is unlikely to be adsorbed.) At high sulphuric acid concentrations the slope decreases to about 20 mV/decade. This behaviour would be expected if the adsorption of neutral molecules of $H_2SO_4$ (which displace adsorbed $HSO_4^-$ ions from the electrode) occurred.

These observations confirm previous work [1] and show that adsorption of neutral molecules is significant.

## Acknowledgement

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