

Proton diffusion in crystalline ruthenium dioxide

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Porous powder electrodes of ruthenium dioxide (RuO_2) with varying chlorine contents were prepared. A potential-step technique was used to measure the chemical diffusion coefficient for protons in these RuO_2 powders and the results were correlated with published data on proton diffusion in thin films of RuO_2 .

1. Introduction

Dimensionally stable anodes [1] consisting of films of microcrystalline ruthenium dioxide (RuO_2), formed by the thermal decomposition of ruthenium trichloride (RuCl_3) on a titanium substrate, are well-known electrocatalysts for the production of chlorine. Although the large current densities produced on these electrodes during cyclic voltammetry between the hydrogen and oxygen evolution potentials, in both acidic and basic electrolytes, are well known [2–4], there is conflicting evidence on the mechanism of this large charge transfer. Galizzioli *et al.* [2] and Arikado *et al.* [3] consider that the mechanism is the modification of the bulk of the electrode by the insertion or removal of protons in the RuO_2 lattice while Burke *et al.* [4] account for the charge transfer in terms of surface redox reactions.

In order to examine further the behaviour of crystalline RuO_2 , measurements of the chemical diffusion coefficient for protons in powders prepared by the thermal decomposition of RuCl_3 have been attempted using electrochemical methods at ambient temperatures.

2. Experimental techniques

Two types of RuO_2 powder were examined. Powder A was prepared by heating 'Specpure' $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Johnson Matthey) in a platinum crucible for 3 h at 700°C . Guinier X-ray powder analysis revealed only diffraction lines for RuO_2 and BET analysis gave the surface area of the

powder as $3.5\text{ m}^2\text{g}^{-1}$. Powder B consisted of 'Specpure' $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ which had been heated to 450°C for 2 h in a platinum crucible. X-ray analysis revealed diffraction lines for RuO_2 and also faint lines indicating a trace of RuCl_3 . It is probable that this material also contained a significant amount of chlorine dissolved in the RuO_2 lattice as this has been found in similar materials by chemical analysis [5] and secondary ion mass spectrometry [3]. The BET surface area of this powder was $9.3\text{ m}^2\text{g}^{-1}$.

Porous pellets (6 mm diameter) of these powders were prepared by cold-pressing at approximately 300 MN m^{-2} . The electrode pellet was placed between perforated gold electrodes in a perspex holder which allowed free access of electrolyte to the powder electrode. The electrochemical cell had a gold counter electrode and a reference hydrogen electrode in a separate compartment connected to the main cell compartment by a Luggin capillary. Thus the hydrogen electrode was in the same electrolyte solution as the working and counter electrodes. The electrolyte was nitrogen-purged 1.2 N HCl ($\text{pH} = 0.35$) and the cell assembly was thermostatted at $30.0 \pm 0.5^\circ\text{C}$.

The electrode was initially allowed to stabilize at open circuit for several days. The standing potential for both materials was approximately 850 mV versus RHE. During the experiments, the electrode potential was controlled using an Amel 551 potentiostat which was used to apply small potential steps ($\leq \pm 5\text{ mV}$) to the electrode. The current passing between the counter and working electrodes after such a potential step was measured

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as a function of time. The electrode was allowed to recover at open circuit for at least 24 h between experiments.

3. Results and discussion

Figs. 1 and 2 show typical current versus time curves for the two types of electrode after anodic or cathodic steps of 5 mV. Powder A (Fig. 1) always behaved symmetrically, i.e. the anodic and cathodic decay curves were virtually identical in every case. This indicates that proton diffusion into the bulk of the electrode is the dominant process for small changes in the electrode potential. This is so as any reaction such as the formation of RuO_4^- ions would occur at a faster rate than the reverse reaction due to the relatively low product ion (e.g. RuO_4^-) concentration in the electrolyte. Although powder B (Fig. 2) did not produce symmetrical decay curves, the time scale of the decay was the same for anodic and cathodic potential steps and the current (A g^{-1}) for the anodic step was always approximately 40 per cent greater than that for the corresponding cathodic step after the same time interval, for times up to approximately 30 min. This suggests that the same

process, i.e. proton diffusion into the bulk is responsible for the charge transfer in both cases but that the available surface area of electrode is lower for the cathodic than for the anodic charge transfer. It is possible that surface ruthenium ions co-ordinated by chlorine block the injection of protons into the material but will allow the removal of protons from the RuO_2 lattice. In this case the relatively high chlorine content of powder B (which is implied by X-ray analysis) would cause the assymetry of the anodic/cathodic decay curves.

Current versus time curves for potential steps of ± 5 mV, ± 4 mV and ± 3 mV for both types of electrode were analysed on the basis of a model proposed by Valand [6]. This model treats the powder electrode as being composed of a large number of spheres and by considering diffusion into a sphere obtains the following approximate relationship:

$$I = 8\pi F D r m (C_0 - C_1) \exp(-D\pi^2 t/r^2) \quad (1)$$

where I is the current per gram of electrode, D is the diffusion coefficient of solute, r is the radius of sphere, m is the number of spheres per gram of electrode, C_0 is the equilibrium concentration of

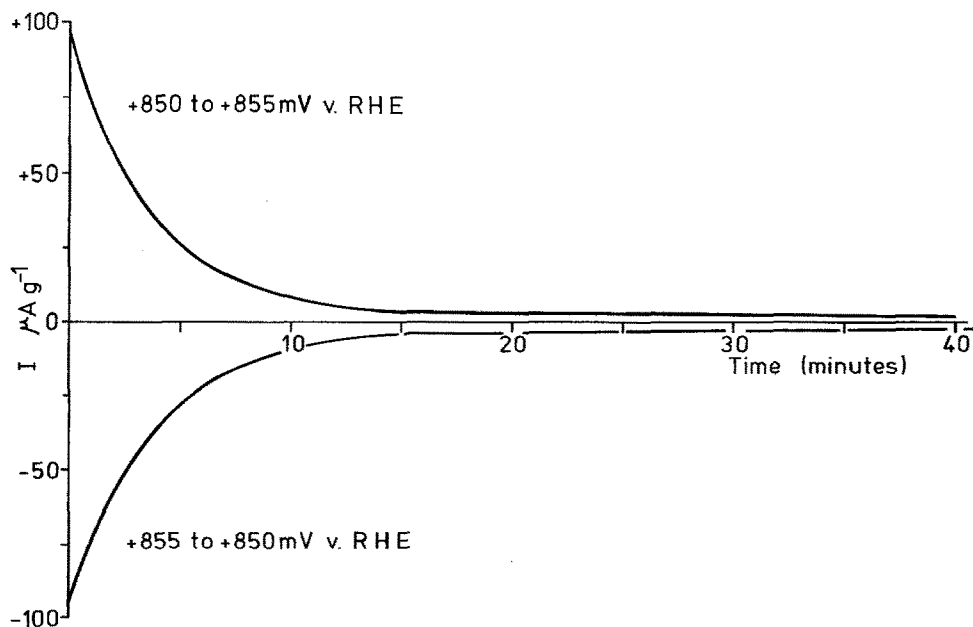


Fig. 1. Potentiostatic current versus time decay curves for RuO_2 powder A electrode (prepared at 700°C) after potential step of ± 5 mV, 30°C .

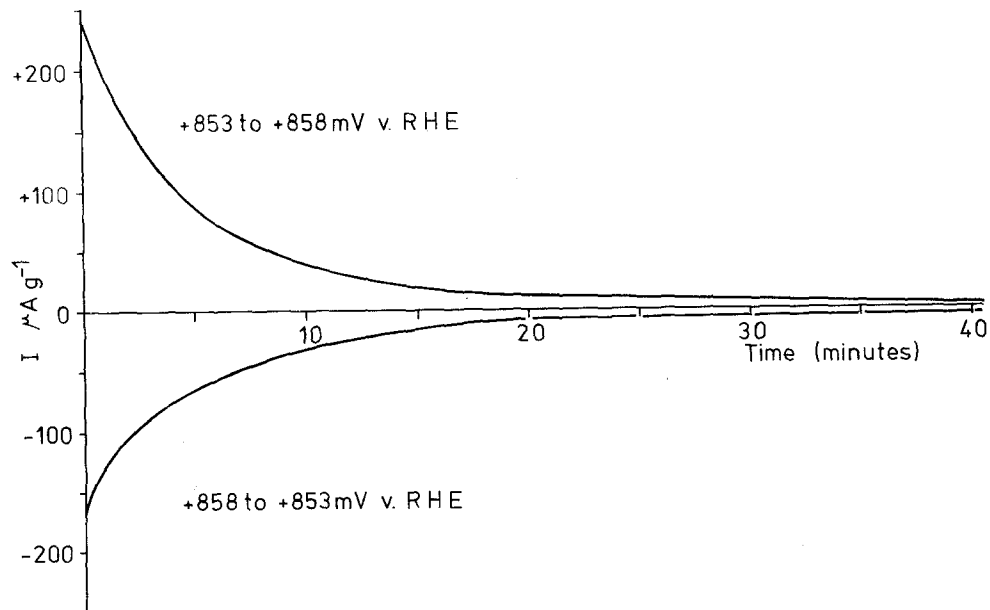


Fig. 2. Potentiostatic current versus time decay curves for RuO₂ powder B electrode (prepared at 450° C) after potential step of ± 5 mV, 30° C.

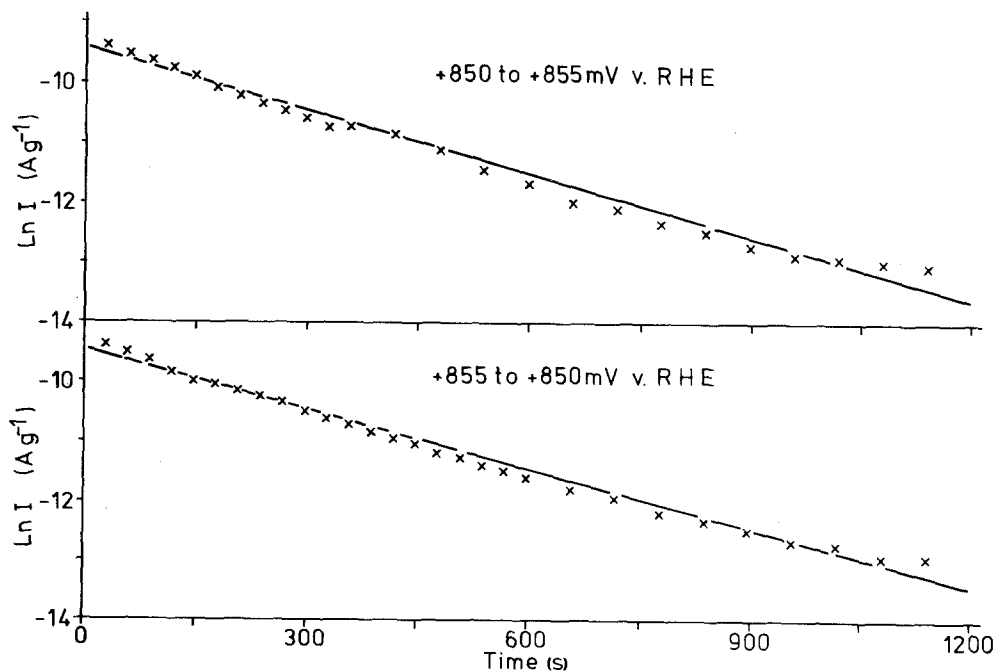


Fig. 3. Ln current versus time for RuO₂ powder A electrode, as Fig. 1; x experimental result, — least squares straight line.

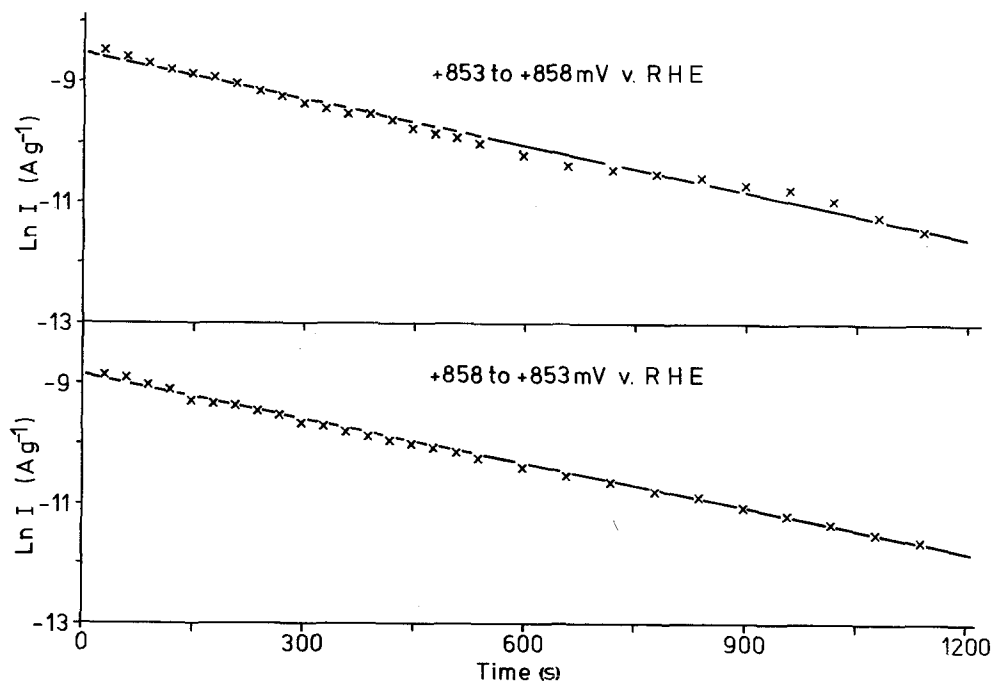


Fig. 4. $\ln I$ versus time for RuO_2 powder B electrode, as Fig. 2; \times experimental result, — least squares straight line.

solute, C_1 is the surface concentration of solute, and t is the time after potential step. The error in the use of this approximate formula is < 0.25 per cent if:

$$t > \frac{2r^2}{D\pi^2} \quad (2)$$

Graphs were plotted of $\ln I$ versus t for each case and typical examples are shown in Figs. 3 and 4. The slopes obtained from a least squares fit are shown in Table 1. By assuming the electrode powder to consist of equally sized spherical par-

Table 1

Powder code	Preparation temperature ($^{\circ}\text{C}$)	Potential step (mV)	Slope $\ln I$ versus t ($-\tilde{D}_{\text{H}^+}\pi^2/r^2$) ($\text{s}^{-1} \times 10^{-3}$)	Average particle radius (r) (m)	\tilde{D}_{H^+} ($\text{m}^2 \text{s}^{-1}$)
A	700	+5	-3.55	1.2×10^{-7}	5.0×10^{-18}
		-5	-3.37		
		+4	-3.54		
		-4	-3.28		
		+3	-3.19		
		-3	-3.62		
B	450	+5	-2.54	4.6×10^{-8}	5.2×10^{-19}
		-5	-2.44		
		+4	-2.38		
		-4	-2.54		
		+3	-2.44		
		-3	-2.27		
		+3	-2.47		
		-3	-2.46		

ticles, an average particle diameter could be calculated for each powder from the BET surface area. This enabled a value for the chemical diffusion coefficient of protons (\tilde{D}_{H^+}) in the material to be obtained (Table 1). This value is related to the self-diffusion coefficient ($D_{\text{H}^+}^*$) via the relation

$$\tilde{D}_{\text{H}^+} = D_{\text{H}^+}^* \frac{d \ln a_{\text{H}^+}}{d \ln C_{\text{H}^+}} \quad (3)$$

where $a_{\text{H}^+}(C_{\text{H}^+})$ is the activity (concentration) of protons in the RuO_2 lattice.

Comparison of \tilde{D}_{H^+} for powders A and B suggests that the presence of chlorine in the RuO_2 lattice reduces the rate of proton diffusion. It is significant that the value obtained for \tilde{D}_{H^+} for powder B is consistent with the results of Arikado *et al.* [3], which were obtained using RuO_2 films prepared by the thermal decomposition of RuCl_3 at 450°C , if it is assumed that these films consisted of crystallites of RuO_2 with a particle size of the order of 20 nm. Particle sizes similar to this have been found in RuO_2 films prepared under similar conditions [5, 7].

It should be noted that the $\ln I$ versus t plots

did not show large deviations from linearity at very short times as expected by the theoretical model [6]. This may indicate that some process other than proton diffusion in the bulk is rate controlling at very short times, when the proton diffusion rate would be relatively high.

Acknowledgements

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