

## SHORT COMMUNICATION

## HYDROGEN EVOLUTION ON PLATINUM ELECTRODES DURING THE ELECTROLYSIS OF MOLTEN POTASSIUM BISULPHATE\*

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HYDROGEN is practically the only product formed on a platinum cathode when molten potassium bisulphate is electrolysed at low voltages.<sup>1,2</sup> It seemed worthwhile to attempt the study of the kinetics of the electrochemical reaction on platinum cathodes at temperatures ranging from 250 to 440°C.

We have measured voltage/current curves and the potential decay after the interruption of electrolysis. The electrode potential was measured against a silver/silver-ion reference electrode placed in a container ending in a capillary tip. The ohmic or pseudo-ohmic overpotential was obtained directly by photographing the instantaneous drop of potential at a set current density on the oscilloscope screen.

The relationship between the overpotential and the current density referred to the apparent electrode area, within the range 0.50–230 mA/cm<sup>2</sup>, fits into a Tafel line  $\eta = a + b \log i$  as previously found.<sup>2</sup> The cathodic overpotential,  $\eta$ , was calculated from

$$\eta = E_T - E_r - \eta_{\Omega}, \quad (1)$$

where  $E_T$  is the electrode potential at current density  $i$ ,  $\eta_{\Omega}$  the ohmic overpotential, and  $E_r$  the potential of the residual reversible cell formed after current interruption. The results obtained from Tafel plots are assembled in Table 1.  $b$  is the slope of the  $\eta$  vs  $\log i$  plot and  $a = -b \log i_0$ , where  $i_0$  is the exchange current density.

TABLE 1

$T$ °C	$b$ mV	$i_0$ A/cm <sup>2</sup>
<i>Bright platinum</i>		
246	206 ± 10	2.3 × 10 <sup>-6</sup>
260	212	2.0 × 10 <sup>-6</sup>
330	239	1.6 × 10 <sup>-5</sup>
440	283	5.2 × 10 <sup>-4</sup>
<i>Black platinum</i>		
263	54 ± 5	1.1 × 10 <sup>-3</sup>
263	54 ± 5	0.8 × 10 <sup>-3</sup>

TABLE 2

$T$ °C	$i$ mA/cm <sup>2</sup>	$(b)_{dec.}$ mV
<i>Bright platinum</i>		
260	28.0	228 ± 5
260	98.7	236
330	32.5	214
330	115.0	222
<i>Black platinum</i>		
263	51.4	54 ± 5
243	38.6	53

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A linear plot of  $\eta$  vs  $\log t$  was obtained for the decay of the cathodic overpotential  $\eta$ ,  $t$  being the time elapsed after the current was switched off. Tafel slopes obtained from decay curves at different temperatures are listed in Table 2, where the cathodic current densities  $i$  employed in each of the previous electrolysis are also included.

These results indicate that the most likely value of Tafel slope for hydrogen evolution on bright platinum electrodes during the electrolysis of molten potassium bisulphate is  $2RT/F$  and for platinum-black electrodes  $RT/2F$ , both independent of current density and temperature in the range considered.

Consequently, assuming a mechanism of consecutive reactions for the cathodic evolution of hydrogen on platinum electrodes, the above mentioned Tafel slopes should be related, in the first case, to a rate-determining step involving the discharge of a hydrogen ion on an available active site of the electrode surface,<sup>3</sup> and the reaction may be treated similarly to hydrogen-ion discharge from acid aqueous solutions on inactive platinum surfaces.<sup>4</sup> In our case the heat of activation at the reversible potential, deduced from the dependence of the exchange current density on temperature, is  $17.0 \pm 1.5$  Kcal/mole, in remarkable agreement with the theoretical value calculated by Parsons and Bockris.<sup>5</sup>

On the other hand, the results obtained for the hydrogen-evolution reaction on black-platinum electrodes are satisfactorily explained assuming that the recombination of hydrogen atoms on the electrode surface is the rate-determining step, as in hydrogen-ion discharge on black-platinum electrodes in aqueous solutions.<sup>6</sup>

It is interesting to emphasize that a very reproducible hydrogen electrode is formed on black-platinum electrodes after current interruption, when they have been previously employed as cathodes during the electrolysis of molten potassium bisulphate.

A detailed description of these experiments will be published in the near future.

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