Catalysis of Electrolytic Hydrogen Evolution at Lead by *Absorbed* Atomic Hydrogen

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Summary Both the capacity and the potential of a lead cathode increase linearly with the logarithm of the charge passed (10 to 600 C cm^{-2}) in prolonged cathodisation, suggesting that the rate of charge transfer increases linearly with the bulk hydrogen content of the metal.

IVES and Smith[1] found that the cathodic hydrogen overpotential ($-\eta$) at lead cathodes in acid solution decreased linearly with log ($-Q$), where $-Q$ is the total charge passed during extended cathodic electrolysis. No similar observations had previously been made with any metal; it was proposed[1] that H atoms were being continuously *absorbed* by the lead and that in some way these catalysed the hydronium ion discharge step [equation (1)].

$$H_3O^+_{aq} + e^- + Pb = H_2O + Pb\text{–}H_{ads} \qquad (1)$$

Wells and Roberts[2] had shown that evaporated and sintered lead films take up gas phase H atoms to a maximum bulk composition $PbH_{0\cdot19}$ at room temperature. We recently confirmed by electrochemical and radiochemical experiments[3] that hydrogen and tritium atoms, generated electrochemically at the cathode face, diffuse through a lead foil with a diffusivity comparable in magnitude to that of H in Pd. Calculated H atom concentrations were *ca.* 10^{-6} g atom cm^{-2}, much lower than Wells and Roberts' figure,[2] which has recently been confirmed.[4] Our data refer without doubt to bulk Pb but may be too *low* by one or more orders of magnitude, because of the experimental difficulty of excluding O_2 completely.

We now report that, using experimental conditions like those of ref. 1, the electrode capacity, C, of a lead cathode in 1M $HClO_4$ has been found to increase with time of electrolysis, following an analogous law for $10 < -Q < 600C\,cm^{-2}$ (Figure 1) to that previously noted for th overpotential decrease. Capacity measurements were made by observing the rapid open-circuit decay of overpotential ($-\eta$) on an oscilloscope, a standard technique,[5] which has been improved.[6] The relation $C = i(dt/d\eta)_{t=0}$ applies, where $-i$ is the cathodic current density and t the time elapsed after the current interruption. For particular values of η between -950 mV and -1250 mV, C increased with $-Q$ in all satisfactory[1] experiments in which, *e.g.* Tafel slopes[7] close to $4{\cdot}6RT/F$ were observed. The increase of C with $-Q$ is attributed to growth of an adsorption pseudocapacity component, arising from a growing hydrogen surface coverage (θ_H) of the electrode. Thus, initial C values were close to those of the double layer alone (*ca.* $20\,\mu F\,cm^{-2}$)[7] and consistent with an initial θ_H *ca.* 0.[8] On this basis and assuming a pseudocapacity of $1500\,\mu F\,cm^{-2}$ to correspond to a monolayer, θ_H rose in about one week of cathodisation to 0·005—0·0075 in two experiments with 2—3 mm diameter Pb rods and to ca. 0·05 in an experiment with a 0·25 mm thick Pb foil.

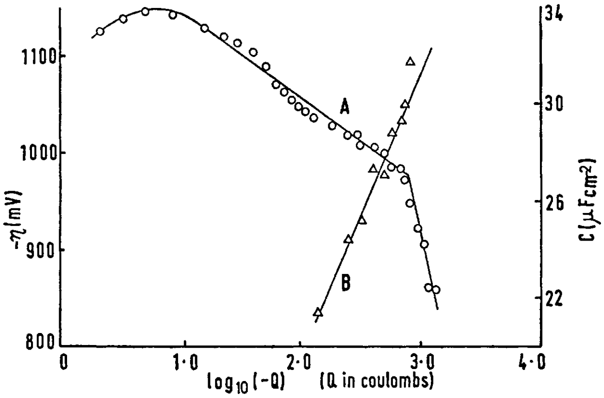

FIGURE 1. *Typical linear relationships between hydrogen overpotential ($-\eta$) at constant i ($= -$ 0·65 mA cm^{-2}) and $\log_{10}$ ($-$Q) and between electrode capacity (C) at constant η ($= -$ 1100 mV) and $\log_{10}$ ($-Q$) for the same lead rod (Expt.* C *see Figure* 2) *electrode in* 1M $HClO_4$. *$-Q$ is the total number of coulombs passed cathodically from the commencement of the electrolysis.*

Plots of C (at constant η) versus η (at constant i) for different experiments, for $-Q > 10$ C, proved to be linear, with identical slopes of $7{\cdot}5 \pm 0{\cdot}2$ mV $cm^2\,\mu F^{-1}$. Since the observed decrease of $-\eta$ (at constant i) is equivalent to an increase of $\log_{10}$ ($-i$) (at constant η) as $-Q$ increases, measured C values were plotted against $\log_{10}$ ($-i$) calculated from the measured η and the Tafel equation, $-\eta = a - b \log_{10} (-i)$, using experimental values of the constants a and b. As Figure 2 shows, the growth of C and of $\log_{10}$ ($-i$) (both at constant η) with $-Q$ are parallel phenomena, the data from four separate experiments being remarkably conformable. We interpret this to mean that the increase of cathodic current occurs because of changes occurring in the electrode material, which we deduce to be bulk changes for the following reasons: (i) A *linear* growth of $-i$ with C, if it had occurred, *might be attributed* to increases in rate of the reaction, equation (2), with θ_H (concentration of

$$H_3O^+_{aq} + Pb{-}H_{ads} + e^- = H_2O + H_2 + Pb \qquad (2)$$

$Pb{-}H_{ads}$), if this were the rate-limiting step in H_2 evolution at lead; this step is not, however, generally considered to be rate-limiting at lead.[8] Furthermore, $-i$ depends *exponentially* on C, not linearly, so that this explanation is not adequate. (ii) Since H_3O^+ discharge is thought to be rate-limiting at lead,[8] the observed decrease of $-\eta$ (or equivalent increase in $-i$) must be due to catalysis of this reaction step. Increase of θ_H at constant η might, however, be expected to *diminish* the rate of this step, which would be expected to fall as the density of unoccupied surface sites is decreased, if this were the only factor at work. (iii) Since experiments were conducted at constant i, the flux of H atoms diffusing inwards might be expected to be essentially constant, because of the reasonable constancy of the H atom concentration gradient from the interface into the centre of the metal (where C_H *ca.* 0 throughout). Then, the mean concentration of H atoms taken up (C_H) will be directly proportional to $-Q$. If the surface coverage θ_H and the bulk concentration C_H are exponentially related, *i.e.* $C_H \propto e^{\,\theta_H}$, as Breger and Gileadi found with palladium,[9] the observed increase of C with the logarithm of $-Q$ (Figure 1) is only to be expected. (iv) From Figure 1, $-\eta \propto \log_{10}$ ($-Q$) over a wide range of Q, ignoring initial deviations. The constant of proportionality has a range of values, as reported previously[1], a steeper slope generally being found at high values of $-Q$. Focussing attention on the middle region of Figure 1, in which both η and C vary

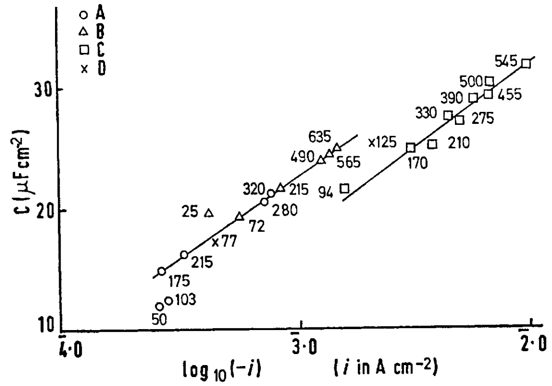

FIGURE 2 *Relationship between the growth of $\log_{10}$ ($-$i) and of C with $-Q$ (values indicated by numerals are $-Q$ in C cm^{-2}) at constant overpotentials. Expt.* A, *lead foil, $\eta = -$ 800 mV; expt.* B, *lead rod, $\eta = -$ 950 mV; expt.* C, *lead rod, $\eta = -$ 1100 mV; expt.* D, *lead rod, $\eta = -$ 1000 mV. Non-coincidence of points at equal $-Q$ is to be expected because of differing constants η's.*

linearly with $\log_{10}(-Q)$ and expressing η in terms of the Tafel equation, $-i$ (at constant η) must increase linearly with $-Q$. This simple relationship is intelligible if the catalysis of H_3O^+ discharge is directly proportional to the bulk H atom concentration, C_H, which, it is argued above, will itself be directly proportional to $-Q$.

This catalytic effect appears to operate through donation of electrons to the metallic conduction band by the dissolved H atoms, as earlier postulated.[1] The effect is by no means negligible, increases of electrode activity of 10^2 to 10^3 fold having been observed repeatedly,[1,10] under sufficiently stringent experimental conditions.

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