

# HYDROGEN ADSORPTION ON SILVER CATHODES IN PERCHLORIC ACID SOLUTIONS

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## Abstract

In this paper studies of overvoltage and capacitance measurements at silver cathodes in aqueous perchloric acid at room temperature are described. Capacitances were deduced from open-circuit potential decay measurements. The increase of overvoltage and the growth of the measured capacitances in the course of electrolysis are attributed to a growing pseudocapacitance component. This is analysed in terms of an increasing coverage,  $\Delta\theta_H$ , of the cathode by adsorbed hydrogen atoms. The increase in surface coverage from the beginning up to several days of cathodisation ranged up to 2% of a monolayer for silver in  $0.1 \text{ mol l}^{-1} \text{ HClO}_4$  and up to 0.9% of a monolayer in  $1 \text{ mol l}^{-1} \text{ HClO}_4$ . The increase in overvoltage at constant current density and the increase in electrode capacitance at constant overvoltage with the logarithm of the cathodic charge ( $-Q$ ) were linear up to  $Q$  values of about  $-60^\circ \text{ C cm}^{-2}$ . This increase in overvoltage and pseudocapacitance might be attributed to the adsorption and absorption of hydrogen atoms by silver cathodes.

## Theoretical Considerations

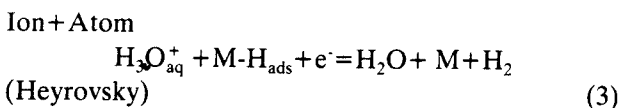
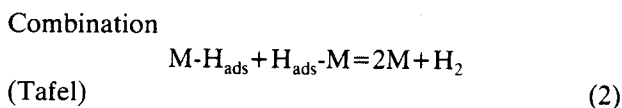
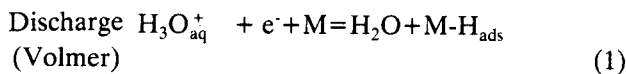
Theoretical considerations contain three different sections:

- A. Hydrogen Overvoltage.
- B. Adsorption Pseudocapacitance.
- C. Determination of Adsorption Pseudocapacitance Involving Open Circuit Decay.

### A. Hydrogen Overvoltage

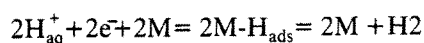
There is a long history to the study of the hydrogen evolution reaction (h.e.r.) on metals dating from the beginning of this century. Many reaction steps have been proposed as part of the overall process. However,

only two reaction paths involving three possible steps are regarded as likely. The principal steps of the h.e.r. in acid solution probably occur through the following partial reactions:



The overall reaction may be completed by two

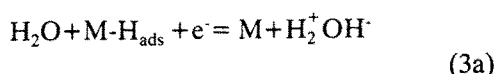
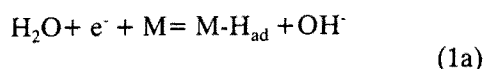
routes which are (1) followed by (2):



or (1) followed by (3):



In solutions of  $\text{pH} \geq 8$ , reactions analogous to reaction (1) and (3) occur, but with  $\text{H}_2\text{O}$  as the main proton source, i.e.



### Types of Overvoltage

It is well known that the hydrogen overvoltage depends on electrode material as first shown experimentally at the beginning of this century by Tafel [1]. The relationship between overvoltage and cathodic current density could be satisfactorily expressed in the form:

$$-\eta = a - b \log_{10} (-i)$$

where the hydrogen overvoltage,  $-\eta$ , is the difference of electrical potential between the working cathode and a reversible hydrogen electrode in the same solution, and  $-i$  is cathodic current density (current density is defined as c.d.), with  $a$  and  $b$  constants.

Overvoltage may arise from a number of causes, each of which may effect a retardation of the overall process. Depending on the origin, overvoltage can be divided into a number of additive parts (2).

#### (a) Charge-Transfer Overvoltage

The charge-transfer overvoltage,  $\eta_t$ , arises from a barrier to charge transfer across the electrode-electrolyte interface, e.g. reactions (1) or (3). Charge-transfer reactions are of fundamental importance in the h.e.r., since they are the only reactions directly affected by the electrode potential.

The charge-transfer overvoltage is frequently called activation overvoltage. However, this expression is ambiguous as noted by Vetter [2], because partial control of an electrode process by a chemical reaction also corresponds to an activation process associated with a significant activation energy.

#### (b) Reaction Overvoltage

Reaction overvoltage,  $\eta_r$ , arises from a slow chemical reaction, e.g. reaction (2), producing a reactant or removing a product of the charge-transfer step, which is indirectly retarded because of depletion or accumulation of reactants or products.

#### (c) Mass-Transport or Diffusion Overvoltage

Mass-transport overvoltage,  $\eta_m$ , arises when a slow transport process is responsible for the depletion or accumulation of reactants or products, respectively, once again resulting in the indirect retardation of charge transfer, e.g.

$\text{H}_3\text{O}_{\text{aq}}^+$  (bulk solution)  $\xrightarrow{\text{slow}}$   $\text{H}_3\text{O}_{\text{aq}}^+$  (interface) and  $\text{H}_{2\text{aq}}$  (interface)  $\xrightarrow{\text{slow}}$   $\text{H}_{2\text{aq}}$  (bulk solution).

Mass-transport processes play an important role in the h.e.r. of catalytically active metals such as Pt, Ir, Rh and Pd [3] where the rate of hydrogen ion discharge, i.e. reaction 1, or of hydrogen generation, i.e. reaction 2 and 3, can be significantly greater than the rate at which  $\text{H}_2$  is transported to or from the interface.

The transport of  $\text{H}_3\text{O}_{\text{aq}}^+$  ions from the bulk solution to the solution electrode interface may be rate determining at  $\text{pH} \geq 3$  at quite small cathodic currents and at lower pH at sufficiently high cathodic currents. However, calculated values of  $\eta_m$  [4] in 0.1 and 1 mol l<sup>-1</sup> acid solutions bubbled rapidly by gas are less than 4 mV up to  $i = -50 \text{ mA cm}^{-2}$ . Even though it does not seem possible to eliminate  $\eta_m$  entirely by extremely vigorous stirring of the catholyte, it seems that the contribution of  $\eta_m$  to the total apparent overvoltage can be made very small in stirred solution. To diminish it still further one would have to use a rotating disc electrode or similar mechanical device.

#### (d) IR Drop Overvoltage, $\eta_\Omega$

Another contribution to the experimentally observed overvoltage is due to a potential drop between working and reference electrodes. This is not caused by any slow process in the overall reaction but is a function of the effective electrical resistance between the reference electrode and the cathode, and of the current flowing between the cathode and the anode during electrolysis. Attempts are made to minimize the effect of this potential drop in practice by placing the reference electrode (or generally the tip of a connection to it,

designated a luggin capillary) close to the cathode or using oscilloscopic techniques to measure the open circuit electrode potential immediately subsequent to the interruption of the current flow. The measured overvoltage will be exclusive of  $\eta_{\Omega}$ . Thus the total measured overvoltage,  $\eta_{meas}$ , is the sum of individual overvoltages, i.e.

$$\eta_{meas} = \eta_t + \eta_r + \eta_m^+ \eta_{\Omega}$$

### B. The Adsorption Pseudocapacitance

It is generally accepted that the adsorbed hydrogen produced during the discharge of  $H_3O_{aq}^+$  ions or the ionisation of  $H_2$  molecules by metals during the h.e.r. is chemisorbed on the metal electrodes. The study of hydrogen adsorption is helpful in the elucidation of the mechanism of the h.e.r. During the h.e.r., adsorbed H atoms are produced and consumed. The surface concentration of adsorbed hydrogen is thought to be potential dependent. Information concerning the adsorption of hydrogen atoms on the surface of an electrode can be obtained from suitable kinetic studies involving measurements of the electrode capacitance or surface coverage of the electrode by adsorbed hydrogen.

Early investigations of the h.e.r. revealed [5] the presence of  $H_{ads}$  atoms, but the existence of an adsorption pseudocapacitance,  $C_{ps}$ , due to adsorbed hydrogen atoms was first predicted and demonstrated by Eucken and Weblus [6]. The term pseudocapacitance was introduced by Grahame [7] to distinguish the capacitance arising in a reaction such as (1) or (3) which is associated with charge transfer across the interface from the strictly non-faradaic capacitance associated with the dependence of ionic and electronic charge in

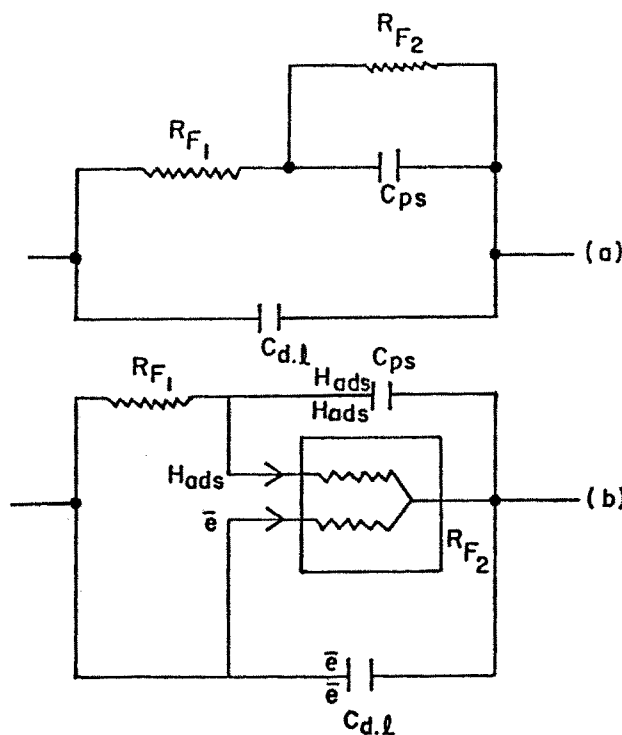


Fig.1 Equivalent circuit for system exhibiting an adsorption pseudocapacitance.

(a) Volmer discharge with Tafel desorption step.

(b) Volmer discharge with Heyrovsky desorption step.

R-reaction resistance:  $R_{F1}$  for charging step and  $R_{F2}$  for desorption step, respectively.

the double layer on potential. The prefix «pseudo» is used because  $C_{ps}$  refers to a leaky capacitor, that cannot exist unless the interphase leaks that is, unless charge is transferred across it [8].

Since, however, electron transfer is an essential requirement for the formation of adsorbed hydrogen atoms, the presence of these adsorbed intermediates on

Table 1. Experimental capacitances of a silver electrode B1 in  $1 \text{ mol l}^{-1} \text{ HClO}_4$  during passage of  $-192^\circ \text{C cm}^2$  at  $i = -0.231 \text{ mA cm}^{-2}$  and at the higher current densities of the capacitance measurements.

Total	1.16		5.78		11.56		18.50		27.75		34.68	
cathodic charge passed	$-n/C_{expt}$		$-n/C_{expt}$		$-n/C_{expt}/$		$-n/C_{expt}/$		$-n/C_{expt}$		$-n/C_{expt}$	
$-Q/C \text{ cm}^2$	mV	$\mu\text{F cm}^{-2}$	mV	$\mu\text{F cm}^{-2}$	mV	$\mu\text{F cm}^{-2}$	mV	$\mu\text{F cm}^{-2}$	mV	$\mu\text{F cm}^{-2}$	mV	$\mu\text{F cm}^{-2}$
2	250	54.3	320	70.5	347	76.6	358	80.6	367	85.4	376	95.4
46	279	59.6	324	75.1	339	81.8	351	90.0	361	101.8	367	111.6
97	279	66.0	323	77.7	350	86.1	360	96.7	370	107.5	380	117.0
143	279	68.4	329	79.0	347	81.8	360	96.7	378	109.5	385	117.0
192	277	68.4	329	80.3	346	86.5	362	104.6	376	111.6	386	117.0

the surface is equivalent to the storage of electricity in the interface as in a condenser and the corresponding capacitance,  $C_{ps}$  behaves like an ordinary capacitance except that it may vary to a much greater extent (relative to the double layer capacitance) with potential and frequency.

The electrochemical behaviour of the electrode-electrolyte interface can be represented by the electrical behaviour of equivalent circuit elements [8,9,10]. So long as an ideal polarised electrode is considered and no faradaic charge-transfer is involved, the capacitance representation of the double layer is adequate. When a charge-transfer process can occur at a rate depending on the electrode potential, representation as a pure capacitance is inadequate. In this case the adsorption pseudocapacitance plays an important role in the total measured electrode capacitance. The adsorption pseudocapacitance must be charged through the non-ohmic resistance,  $R_{F1}$ , corresponding (at a given potential) to the reciprocal of the rate of the  $H_3O_{aq}^+$  ion discharge step producing  $H_{ads}$ . The series combination of  $C_{ps}$  and  $R_{F1}$  must be in parallel with the electrical double-layer capacitance,  $C_{dl}$ , since it provides a leakage path across the double layer [8,9,10]. Then, if hydrogen recombination is the desorption step in the h.e.r.,  $C_{ps}$  is also short-circuited by a second non-ohmic resistive component,  $R_{F2}$ , which is the reciprocal of the rate of recombination. The representation is hence as shown in figure 1a. The whole of the combination of  $R_{F1}$ ,  $C_{ps}$  and  $R_{F2}$  is in parallel across  $C_{dl}$  in the case of a non-ideally polarisable electrode.

When desorption is by an electrochemical step, i.e. atom + ion desorption (3), a special representation is required as shown in figure 1b, where the non-ohmic resistance,  $R_{F2}$ , corresponding to the reciprocal rate of the Heyrovsky atom + ion desorption step is drawn with two parallel input channels, one for electrons and  $H_3O_{aq}^+$  ions and the other for the  $H_{ads}$  atoms removed as equivalent charge form  $C_{ps}$ .

### C. Determination of Adsorption Pseudocapacitance Involving Open-Circuit Decay

Methods for determination of the capacitance-potential relationship have been based on (a) the geometrical differentiation of d.c. galvanostatic charging curves, e.g. the double-charging method of Devanathan, Bockris and Mehl [11], or of open-circuit decay curves by Conway and Gileadi [12], (b) direct a.c. bridge capacitance studies [6] or (c) direct differentia-

tion of charging or decay curves [13]. The interpretation of results for  $C_{ps}$  values from the a.c. capacitance studies is complicated by the large frequency dependence of the capacitance which was still observed down to very low frequencies. The methods involving geometric differentiation rely on rather unsatisfactory manual procedures and the rise time dependence of the capacitance makes it rather difficult to interpret the results for  $C_{ps}$  values obtained by these methods. Direct differentiation of the open-circuit decay curve is free from some of these disadvantages.

The direct differential galvanostatic method was developed by Angerstein Kozłowska and Conway [13] and later Conway, Gileadi and Angerstein-Kozłowska [14] pointed out that any method based on the rate of decay of potential on an open-circuit following steady-state polarisation will represent a true equilibrium pseudocapacitance, i.e. the value corresponding to an infinitely low frequency using the a.c. bridge method, and is therefore to be preferred. The direct differential galvanostatic method (rapid open circuit decay) is most suitable for studies of the potential dependence of adsorption pseudocapacitances. This method is based on the assumption that the faradaic process taking place during steady-state polarisation, continues on open circuit by a self-discharge\* process which momentarily, at the beginning of the open-circuit transient, has the same rate as that corresponding to the initial steady-state polarisation current density at the instant of current interruption.

The electrode capacitance,  $C_{expt}$ , can be calculated from the initial rate of decay  $(\frac{dn}{dt})_{t=0}$  using the following equation

$$C_{expt} = \frac{-i}{(\frac{dn}{dt})_{t=0}} \quad (4)$$

Where  $-i$  is the steady-state cathodic current density at the time of current interruption,  $t = 0$  ( $t$  is the time elapsed after the current interruption) and  $C_{expt} = C_{dl} + C_{ps}$  (because  $C_{ps}$  is in parallel with  $C_{dl}$ , see figure 1). If  $C_{ps} \ll C_{dl}$  at very small values of cathodic charge passed,  $-Q$ , then it can be assumed that  $C_{expt} = C_{dl}$ . at this value of  $-Q$  and the increase of  $C_{expt}$  with  $-Q$  can be

\* For instance, in the h.e.r. involving steps (1) and (3), the open-circuit discharge of the adsorption pseudocapacitance occurs by continuing desorption of  $H_{ads}$  by step (3) with reverse of step (1) providing the electrons for step (3).

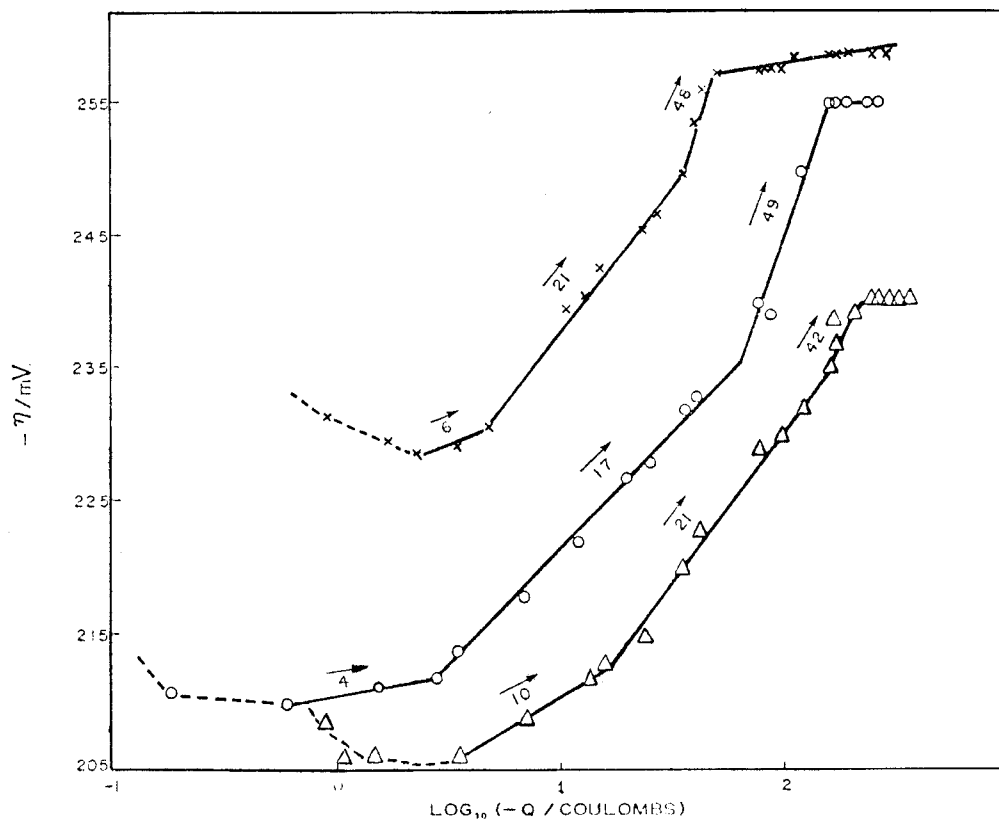


Fig.2 Semilogarithmic plot of overvoltage versus total charge passed at constant 1.16 mA cm<sup>-2</sup> for electrode A3, ○; for electrode A2, △; for electrode A1, X; numbers on each curve are slopes in mV.

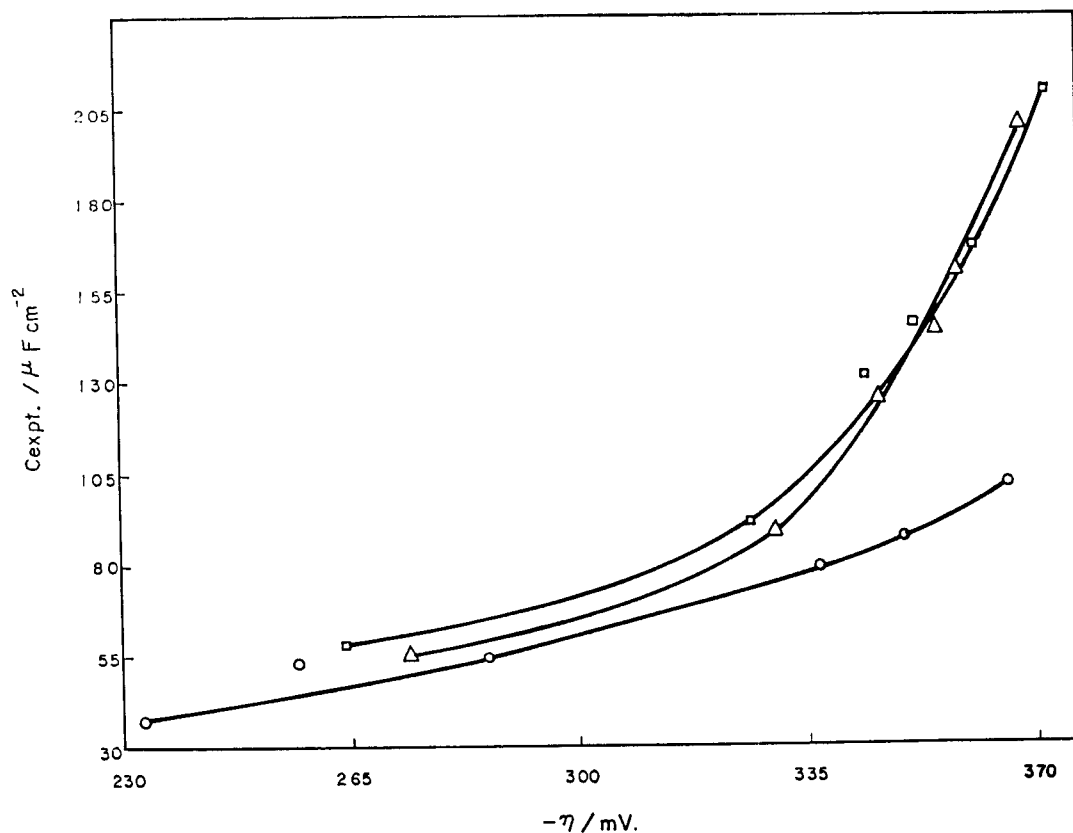
used to evaluate  $C_{ps}$ , i.e.,  $C_{ps} = (C_{expt} - C_{d.l.})$ ; otherwise we must be content with  $\Delta C_{ps}$  that is the increase of pseudocapacitance with  $-Q$ . By polarising the electrode at various current densities  $i$  and recording  $-\eta$  at the instant of interruption of current, followed by open-circuit decay,  $C_p$ , or rather  $\Delta C_p$ , can be obtained as a function of overvoltage.

### Introduction

A rapid technique of measuring hydrogen overvoltage was used by Azzam et.al [15] for silver cathodes in acidic solutions. Reproducible results were obtained when solutions were adequately purified by pre-electrolysis.

Table 2. Experimental capacitances of a silver electrode B2 in 0.1 mol l<sup>-1</sup> HClO<sub>4</sub> during passage of -293 C cm<sup>-2</sup> at  $i = -1.16$  mA cm<sup>-2</sup> and at the higher current densities of the capacitance measurements.

Total cathodic charge passed	Cathodic current density $i$ / mA cm <sup>-2</sup>											
	1.16		5.78		11.56		17.34		23.12		34.68	
	$-n/C_{expt}/$ mV	$\mu F cm^{-2}$	$-n/C_{expt}/$ mV	$\mu F cm^{-2}$	$-n/C_{expt}/$ mV	$\mu F cm^{-2}$	$-n/C_{expt}/$ mV	$\mu F cm^{-2}$	$-n/C_{expt}/$ mV	$\mu F cm^{-2}$	$-n/C_{expt}/$ mV	$\mu F cm^{-2}$
19	233	37	292	53.3	321	53.9	337	78.7	350	86.4	366	102
183	274	54.3	330	88.1	346	123.8	355	143.2	358	160.8	368	201
293	264	57.7	327	92.0	344	130.9	352	146	362	166.3	372	209.5



**Fig. 3** Variation of electrode capacitance with overvoltage and total charge  $Q$  for electrode B1 during continuous polarisation at  $i = -0.231 \text{ mA cm}^{-2}$  in  $1 \text{ mol l}^{-1} \text{ HClO}_4$ ,  $\circ$ ,  $-Q = 2 \text{ C cm}^{-2}$ ;  $\Delta$ ,  $-Q = 97 \text{ C cm}^{-2}$ ;  $\square$ ,  $-Q = 191 \text{ C cm}^{-2}$ .

Various studies of  $C_{\text{d.l.}}$  of silver in aqueous solutions have been carried out [11,16-18]. The agreement among the values of the capacitance observed in these studies is very poor. Bystrov and Krishtalik [17] studied the behaviour of silver cathodes in  $0.05 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ . The slopes of the overvoltage decay after the interruption of the cathodic current were used to measure the capacitances, all of which lay in the range  $60\text{-}80 \mu\text{F cm}^{-2}$ . Bockris et al [19] studied the structure of the electrical double layer on a silver electrode in very dilute,  $10^{-3} \text{ mol l}^{-1}$ ,  $\text{HClO}_4$  in charcoal-cleaned by the alternative current method. They found  $C_{\text{d.l.}} = 20\text{-}21 \mu\text{F cm}^{-2}$  in the cathodic potential range  $-100$  up to  $-150 \text{ mV}$ .

There is no indication recorded, of previous measurements of hydrogen coverage,  $\theta_{\text{H}}$ , at silver cathodes in acidic solutions, although the capacitance of silver electrodes in acidic solutions has been reported [16-19].

### Experimental Section

Perchloric acid solutions were prepared by dilution

of B.D.H. Aristar reagents with triple-distilled water. Matheson 99.999% ultra pure hydrogen was deoxygenated further by B.A.S.F.BTS catalyst at  $140^\circ\text{C}$ , trapped at  $-180^\circ\text{C}$ , supplied through copper and pyrex tubing and presaturated with triple-distilled water. Gas lines were free from potential air leaks or grease contamination. Charcoal was prepared from sucrose (Fisher Scientific Co.) and concentrated sulphuric acid.

99.99% pure silver foils, 0.1 mm in thickness (processed by Goodfellow Metals) were used. Pre-electrolytic purification was used to deposit impurities of  $\text{HClO}_4$  on the cathode under a hydrogen atmosphere for a sufficiently long time so that impurities were essentially eliminated. Cathodic polarisation is ineffective in removing surface-active non-electrolytes, because such substances are unlikely to be adsorbed at a strongly polarised electrode, as normally used in pre-electrolysis. It is, therefore, useful to supplement pre-electrolysis by use of some unpolarised adsorbing medium. This can be achieved by means of adsorptive cleaning of the cell solution with activated charcoal [20,21]. Silver foils were initially degreased in refluxing

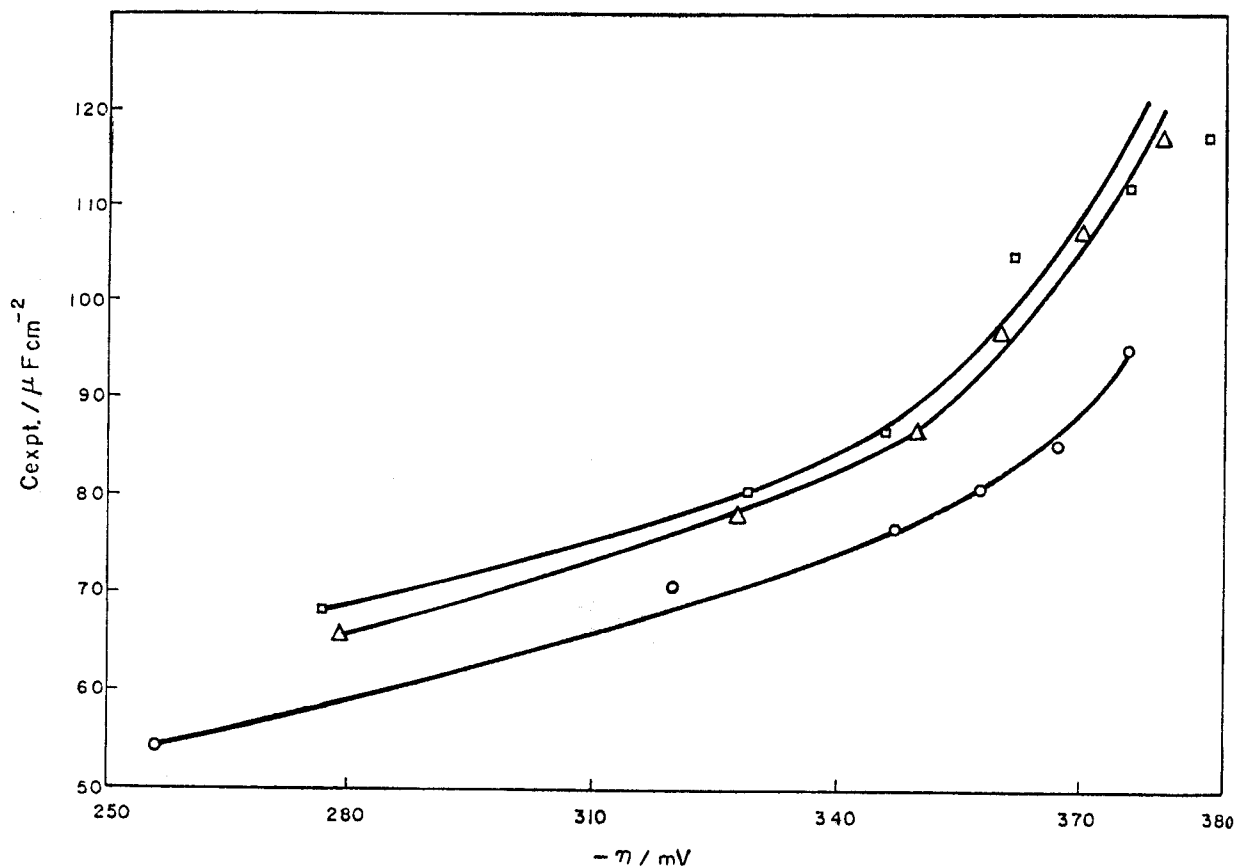


Fig. 4 Variation of electrode capacitance with overvoltage and total charge  $Q$  for electrode B2 during continuous polarisation at  $i = -1.16 \text{ mA cm}^{-2}$  in  $0.1 \text{ mol l}^{-1} \text{ HClO}_4$ ,  $\circ$ ,  $-Q = 19 \text{ C cm}^{-2}$ ;  $\Delta$ ,  $-Q = 183 \text{ C cm}^{-2}$ ;  $\square$ ,  $-Q = 293 \text{ C cm}^{-2}$ .

with xylene for 8-12 hours. They were then washed with ethanol and triple-distilled water and then subjected to chemical polishing and electropolishing [20,22]. After electropolishing, the mirror-bright electrode was thoroughly washed with nitrogen-saturated triple-distilled water and mounted in the cell as quickly as possible.

Experiments A1 to A3 were to investigate the variation of overvoltage on a silver cathode with time at constant cathodic current density. Experiment A1 was carried out using pre-electrolysed  $1 \text{ mol l}^{-1} \text{ HClO}_4$ , while experiments A2 and A3 was studied charcoal-cleaned pre-electrolysed  $0.1 \text{ mol l}^{-1} \text{ HClO}_4$ .

Experiments B1 and B2 involved the measurements of hydrogen overvoltage as well as electrode capacitance at a silver cathode using charcoal-cleaned pre-electrolysed 1 and  $0.1 \text{ mol l}^{-1} \text{ HClO}_4$ , respectively.

Electrode capacitance measurements were made by observing the rapid open circuit decay on an oscilloscope (13). The voltage decay and its derivative were measured with a microswitch in combination with

a differentiating circuit. In capacitance measurements, the silver electrodes of  $0.1 \text{ mm}$  thickness were cathodised galvanostatically (initially at  $30 \mu\text{A}$  to  $1 \text{ mA}$ ). Capacitance measurements were begun after passage of cathodic current for about 1 to 2 h. Then, the overvoltage decay and its derivative were photographed. Also,  $-\eta$  corresponding to the cathodic current density,  $-i$ , at the time of the current interruption,  $t = 0$ , was recorded. Thus, the calculated  $C_{\text{expt.}}$  using measured  $(\frac{dn}{dt})_{t=0}$  and  $-i$  with equation (4) correspond to  $-\eta$  recorded at  $t = 0$ . Later, the steady-state current density was increased to other values in a step-wise manner and kept constant at the new current density for a predetermined time (which ranged from 3 to 8 minutes). At the end of the predetermined time, open-circuit decays were followed from each polarisation current. The overvoltages at the instant of current interruption, at each current, were also recorded. Thereby,  $C_{\text{expt.}}$  was calculated at different  $-\eta$ . This sequence of measurements was repeated up to 5 consecutive days.

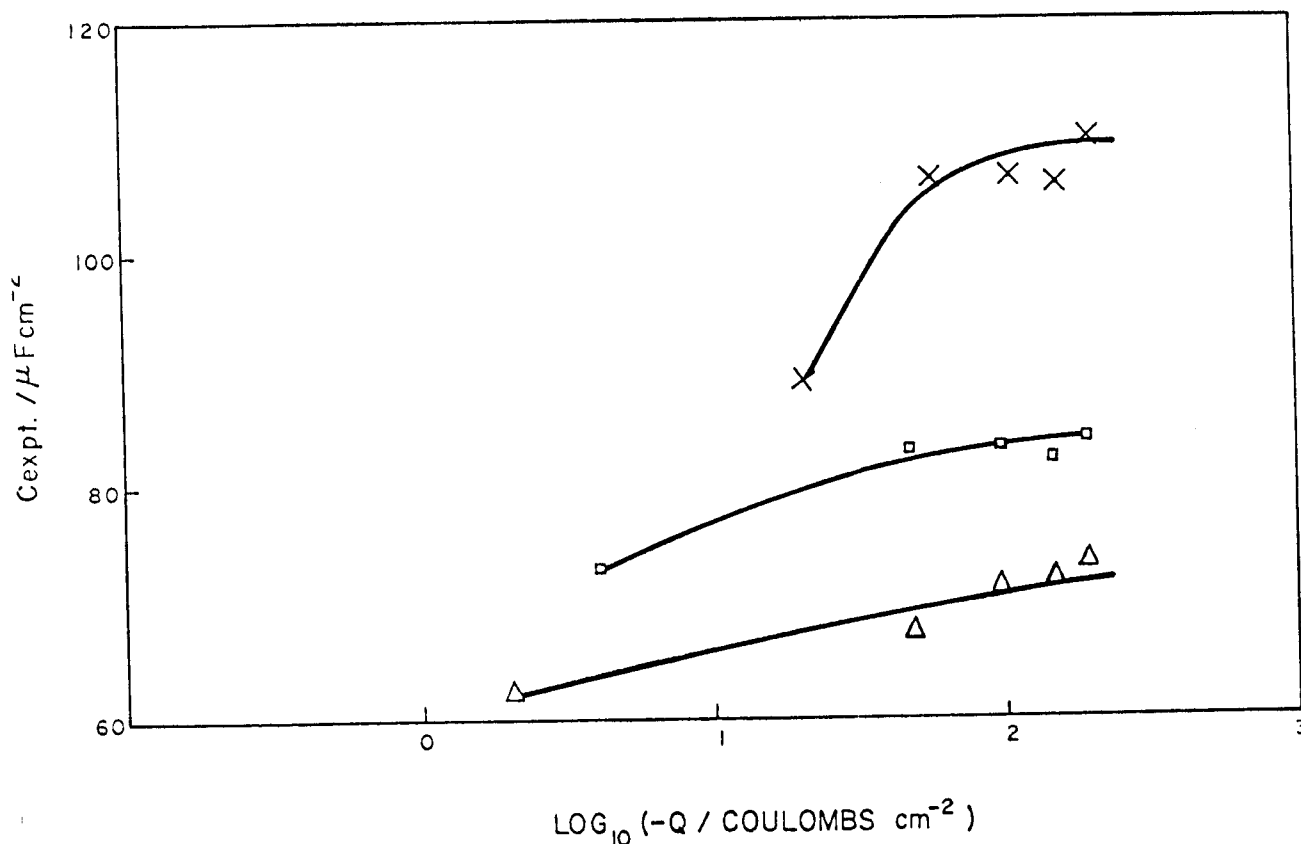


Fig.5 Relationship between electrode capacitance at constant  $-\eta$ 's ( $\Delta$  300 mV,  $\square$ , 340 mV;  $\times$ , 370 mV) and  $\log_{10}(-Q)$  for electrode B1.

## Results

### (a). Hydrogen Overvoltage Measurements at a Silver Cathode

In an attempt to clarify the relationship between overvoltage and the quantity of charge passed cathodically, a number of experiments were carried out in which the cathodic current was kept constant. Variation of  $-\eta$  with  $\log_{10}(-Q)$  is shown in figure 2 which indicates that the overvoltage at  $-1.16 \text{ mA cm}^{-2}$  initially fell, as had been observed by Gossner and Mansfeld [23], then rose continuously with  $-Q$  and finally reached a plateau. The same trend was also observed by Antoniou and Wetmore [24]. The initial fall, could be associated with the removal of oxygen from the solution. It is apparent from figure 2 that the initial overvoltage for electrode A1, i.e. 233 mV is greater than that for electrodes A2 and A3, i.e.  $206 \pm 1 \text{ mV}$ . It may be due to the fact that experiment A1 was studied in  $1 \text{ mol l}^{-1} \text{ HClO}_4$  that had been pre-electrolysed for 3 days at current density of  $10\text{-}20 \text{ mA cm}^{-2}$ , while the  $0.1 \text{ mol l}^{-1}$  solution used for A2

and A3 experiments had been electrolysed for longer periods (4 days) at a current density of  $10\text{-}20$  and  $10\text{-}30 \text{ mA cm}^{-2}$ , respectively. The initial overvoltages for electrodes A2 and A3 (the expt. in which activated charcoal was also used) are identical within experimental error but after the passage of some 37 coulombs, the overvoltages had increased by different amounts (13 mV and 23 mV), respectively, for electrodes A2 and A3. A larger difference is observed for the final overvoltages of these two electrodes after the same amount of charging ( $276 \pm 1$  coulombs). The larger increase of overvoltage for the same amount of charging could be because of the use of either higher purity of silver or activated charcoal, or both in experiment A3. It is obvious from figure 2 that a similar but not identical increase of  $-\eta$  with  $-Q$  occurred in each experiment and the slopes of  $-\eta$  versus  $\log_{10}(-Q)$  range from 4-10 mV, obtained for small amounts of charge, and from 17 to 49 mV for larger amounts of charge. Moreover, the slopes in figure 2 for the same range of  $-Q$  for different experiments are almost the same. This suggests that the



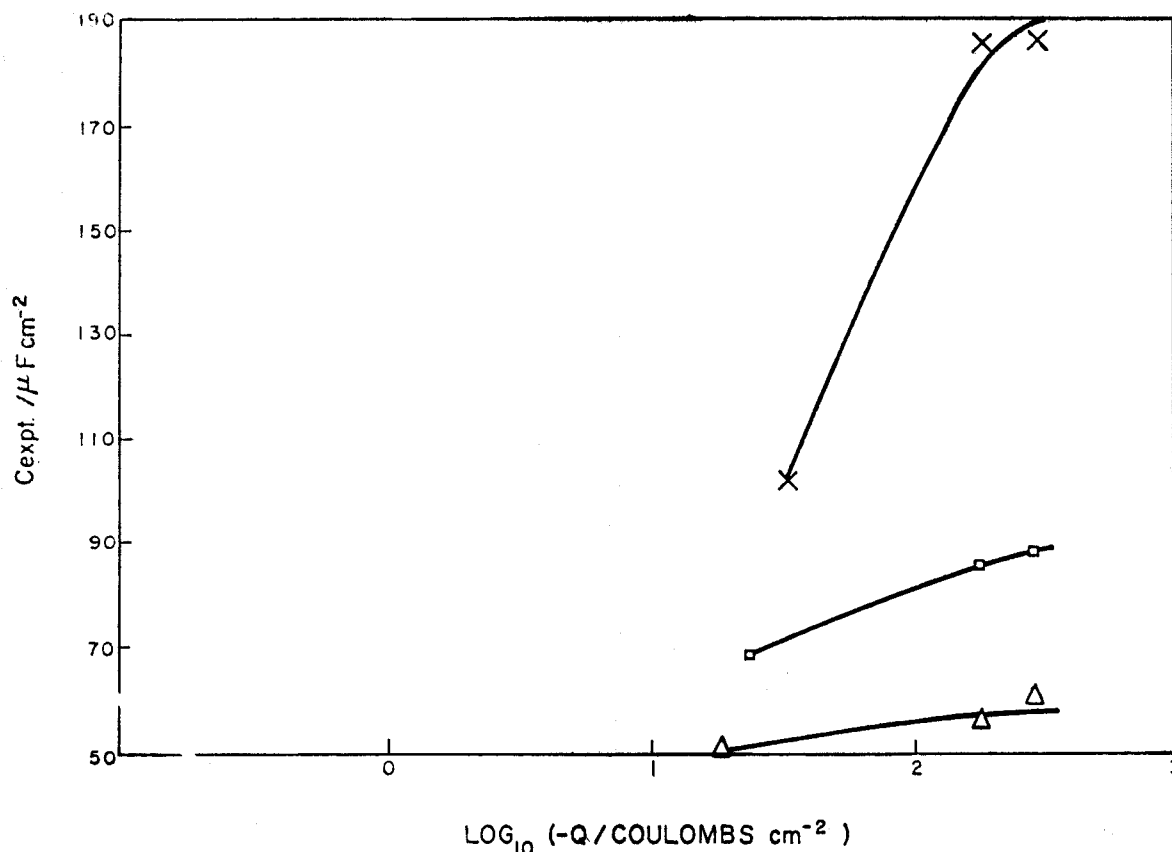


Fig.6 Relationship between electrode capacitance at constant  $-\eta$ 's ( $\Delta$ , 280 mV.;  $\square$  325 mV.;  $\times$ , 366 mV.) and  $\log_{10}(-Q)$  for electrode B2.

phenomenon which causes the increase of  $-\eta$  with  $-Q$  occurred on all electrodes. The changes in slope indicate that the charging of the double layer is not the only process occurring during this increase of overvoltage.

In general, the trend of overvoltage increasing during long periods of cathodic polarisation was common for all silver electrodes. The increase of overvoltage with  $-Q$  may be attributed to the adsorption or absorption of hydrogen atoms on or in silver electrodes during cathodic hydrogen evolution reaction in much the same way as Ives and Smith [24a] suggested for the decrease of overvoltage of lead.

### (b). Capacitance Measurements of Silver Cathodes

The measured electrode capacitances and overvoltages for different experiments at various current densities after different periods of constant current cathodisation show that the increase of  $C_{\text{expt.}}$  was generally accompanied by an increase of  $-\eta$ . Tables 1 and 2 detail the measured electrode capacitances and overvoltages for experiments B1 and B2 at various

c.d.'s after different periods of constant current cathodisation. These data show that the increase of  $C_{\text{expt.}}$  was generally accompanied by an increase of  $-\eta$ , e.g. in B1 at  $i = -1.16 \text{ mA cm}^{-2}$ ,  $C_{\text{expt.}}$  increased from 54.3 to  $68.4 \mu\text{F cm}^{-2}$ , while  $-\eta$  increased from 250 to 277 mV during passage of an additional  $190^\circ \text{C cm}^{-2}$  at  $-0.231 \text{ mA cm}^{-2}$  (see Table 1) and in B2 at  $i = -1.16 \text{ mA cm}^{-2}$ ,  $C_{\text{expt.}}$  rose from 37 to  $57.7 \mu\text{F cm}^{-2}$  while  $-\eta$  increased from 233 to 264 mV during passage of an additional cathodic charge of  $274^\circ \text{C cm}^{-2}$  at  $i = -1.16 \text{ mA cm}^{-2}$ .

Figures 3 and 4 show the essential features of experiments B1 and B2, i.e. the relationship between  $C_{\text{expt.}}$  and  $-\eta$  at particular values of  $-Q$ . In all cases, the electrode capacitance increased monotonically with  $-Q$ , in some cases by large amounts, e.g. in  $0.1 \text{ mol l}^{-1} \text{ HClO}_4$  the increase of  $C_{\text{expt.}}$  at high c.d.'s was greater than in more concentrated acid.

It is evident from Tables 1 and 2 that the variation of overvoltage is small whereas that of the capacitance is large at high c.d.'s. The trend is reversed at the lower c.d.'s, at which the capacitance was measurable. In most cases a large change of overvoltage and capaci-

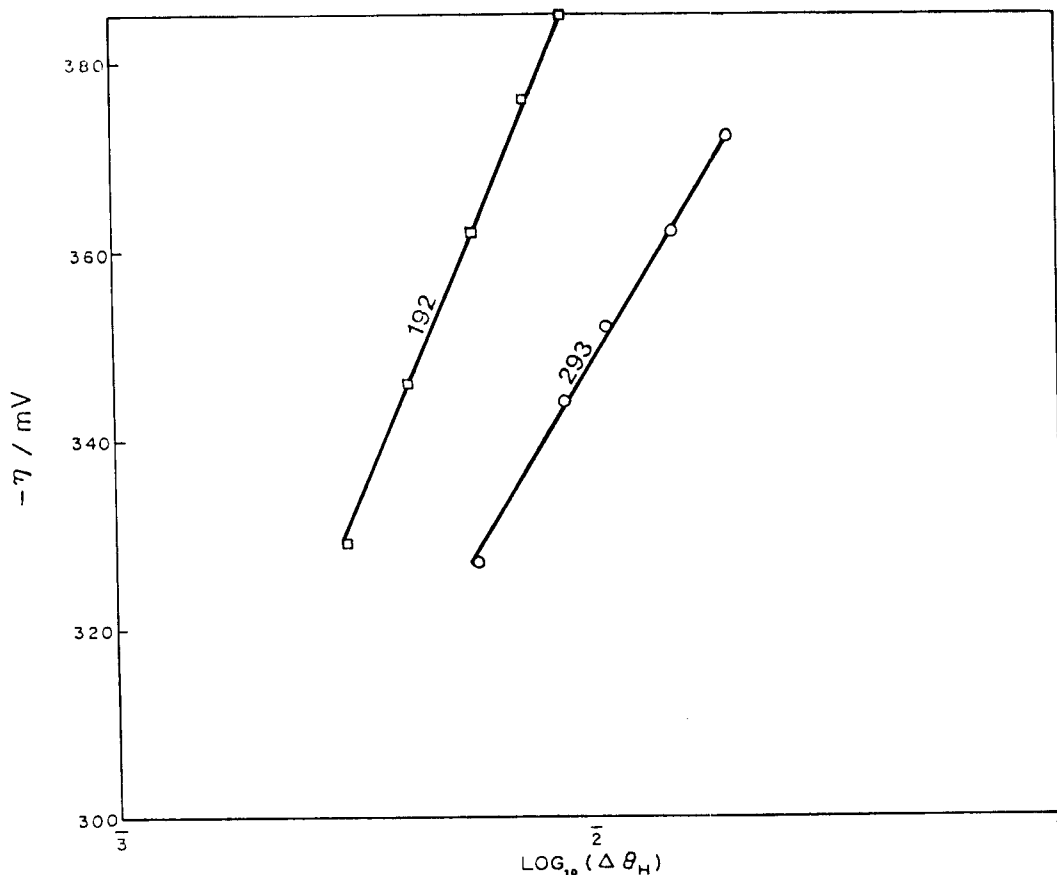


Fig.7 Linear relationship between overvoltage and logarithm of increase in hydrogen coverage in experiments, B1,  $\square$ ; ( $1 \text{ mol l}^{-1} \text{ HClO}_4$ ); B2,  $\circ$ ; ( $0.1 \text{ mol l}^{-1} \text{ HClO}_4$ ) numbers on each curve is total charge passed in  $\text{C cm}^{-2}$ .

tance was observed between the first two consecutive capacitance measurements after which the increase both of  $-\eta$  and of  $C_{\text{expt.}}$  was much slower. The increase of  $C_{\text{expt.}}$  in experiment B2 with  $0.1 \text{ mol l}^{-1} \text{ HClO}_4$  at a particular c.d. and charge, was larger than in experiment B1 using the more concentrated  $1 \text{ mol l}^{-1} \text{ HClO}_4$ .

Taking values of  $C_{\text{expt.}}$  at various values of  $-Q$  on a given electrode at constant  $-\eta$ , it was possible to demonstrate that  $C_{\text{expt.}}$  increases with  $\log_{10}(-Q)$  at least for not too large values of  $-Q$ . A number of plots of  $C_{\text{expt.}}$  versus  $\log_{10}(-Q)$  at three different overvoltages are given in figures 5 and 6. It is apparent from these figures that at a particular overvoltage on a given electrode,  $C_{\text{expt.}}$  does indeed increase with  $\log_{10}(-Q)$  up to ca.  $60 \text{ C cm}^{-2}$ . These increases are probably indicative of a pseudocapacitance caused by hydrogen adsorbed on the silver electrodes. At higher charges ( $>60 \text{ C cm}^{-2}$ ) this increase is followed by a plateau region of essentially constant  $C_{\text{expt.}}$ . A similar trend was also observed in the relationship between  $-\eta$  and  $\log_{10}(-Q)$  as presented in figure 2.

### (c). Calculation of Hydrogen Coverage

This increase of electrode capacitance,  $C_{\text{expt.}}$ , with  $-Q$  is presumed to have been caused by a continuous increase in surface coverage with adsorbed hydrogen,  $\theta_{\text{H}}$ . By observing the increase of  $C_{\text{expt.}}$  at a given overvoltage, from the initial low value of  $-Q$  to the value at various higher quantities of  $-Q$  (increase of cathodic charge  $-\Delta Q$ ) and deducting the former  $C_{\text{expt.}}$  from the latter, the increase in pseudocapacitance,  $\Delta C_{\text{ps}}$ , has been estimated. The increase in pseudocapacitance has been calculated in this way as a function of overvoltage at higher values of  $-Q$  (towards the end of capacitance measurements in a given experiment) and the results presented in Tables 3 and 4. These results have been used to estimate hydrogen coverages or rather, the increase in hydrogen coverage,  $\Delta\theta_{\text{H}}$ , from the lowest overvoltage at which measurements were made. Data of Tables 3 and 4 are plotted in Figure 7 which shows that  $-\eta$  increases linearly with  $\log_{10}(\Delta\theta_{\text{H}})$ .

An intermediate step is the calculation of the charge equivalent to the adsorbed hydrogen, or rather,

its increase  $\Delta q_H$ , relative to the value of  $q_H$  at the lowest  $-\eta$  of the measurements. The equations defining  $\Delta q_H$  and  $\Delta \theta_H$  are:

$$\Delta q_H = K \Delta \theta_H \quad \text{where} \quad K' = \frac{nF}{N} \quad (5)$$

$$\Delta q_H = - \int_{(-\eta)_{\min}}^{-\eta} \Delta C_{ps} d\eta \quad (6)$$

$$\Delta \theta_H = \int_{\theta_{\min}}^{\theta} = \frac{1}{K'} \int_{\eta_{\min}}^{\eta} \Delta C_{ps} d\eta$$

$$= \frac{N}{nF} \int_{(-\eta)_{\min}}^{-\eta} \Delta c_{ps} d\eta \quad (7)$$

Where  $K$  is the value of  $q_H$  at  $\theta_H = 1$ , or the total charge required to form a monolayer of adsorbed hydrogen atoms,  $N$  is Avogadro's number,  $n$  is the number of adsorption sites  $\text{cm}^{-2}$  and  $F$  is the faraday.

Although polycrystalline silver samples were used, in order to estimate the reasonable assumption was made that the low index planes (100 to 110) of silver are, on the average, equally exposed at the surface. This assumption was also made by Spenadel and Boudart [25] for platinum and by Anderson and Baker [26] for tungsten for determination of the surface areas of platinum and tungsten, respectively. The site densities (number of silver atoms per  $\text{cm}^2$ ) of (100) and (110) faces of face-centred cubic silver crystals are  $1.20 \times 10^{15}$  and  $8.47 \times 10^{14}$ , respectively, giving an average of  $1.02 \times 10^{15}$  sites  $\text{cm}^{-2}$ . From the average number of sites  $\text{cm}^{-2}$  with the assumption of one hydrogen atom per silver atom,  $k^1 = 163 \mu\text{C cm}^{-2}$  was calculated.

Increases of hydrogen coverage up to 2% in 0.1 mol  $\text{l}^{-1}$   $\text{HClO}_4$  are indicated by these calculations. The values of 2% and 0.89% were calculated for silver electrodes in experiment B2 (see Table 4) and B1, respectively, (see Table 3) after passage of some 293 and 192  $^\circ\text{C cm}^2$ . Interpretations arise from these calculations and in others, suggest that  $\Delta C_{ps}$  or  $\Delta \theta_H$  increased with the increase of hydrogen overvoltage on silver. Calculation of increase in fractional surface coverage with adsorbed hydrogen atoms of silver,  $\Delta \theta_H$  suggests that the values in 0.1 mol  $\text{l}^{-1}$   $\text{HClO}_4$  are higher than in 1 mol  $\text{l}^{-1}$   $\text{HClO}_4$ . This estimate of  $\Delta \theta_H$  for silver may be low because the integration was carried out over the very narrow range

**Table 3.** Calculation of increase of hydrogen coverage for silver electrode B1 cathodised in 1 mol  $\text{l}^{-1}$   $\text{HClO}_4$  at a current density 0.231 mA  $\text{cm}^{-2}$  after the passage of additional cathodic charge  $-\Delta Q = 190^\circ\text{C cm}^{-2}$ . Total cathodic charge  $-Q = 192^\circ\text{C cm}^{-2}$ .

$-\eta/\text{mV}$	$\Delta C_{ps}/\mu\text{F cm}^{-2}$	$\Delta q_H/\mu\text{C cm}^{-2}$	$\Delta \theta_H$
277	9.5	—	—
329	10	0.51	0.0031
346	11.5	0.69	0.0042
362	18	0.93	0.0057
376	22.5	1.21	0.0074
386	26*	1.45	0.0089

\*Obtained by extrapolation.

of  $-\eta$  which has been studied on the silver electrode and in particular because of the lack of  $C_{\text{expt}}$  data extending to  $\eta = 0$ .

### Discussion

The most important phenomena observed in this work are the simultaneous rise of overvoltage and increase in capacitance with the logarithm of the total charge passed up to about  $60^\circ\text{C cm}^{-2}$ . The possibility that these phenomena are due to oxygen evolution at the anode, impurities, Pt dissolution from the anode and plating out on the cathode, changes in condition of the electrode, e.g. area increase or decrease, or anion adsorption can be discounted for the following reasons:

(I) The presence of  $\text{O}_2$  in the electrolyte solution would cause a complete reversal of the increase of  $-\eta$  with  $-Q$ . This has in fact been observed in the initial overvoltage measurements in experiments A1 to A3; The decrease of overvoltage for about 30 minutes from the beginning of the experiment could be attributed to the removal of  $\text{O}_2$  from the electrolyte solution.

It has been found that  $\text{O}_2$  is chemisorbed on silver

**Table 4.** Calculation of increase of hydrogen coverage for silver electrode B2 cathodised in 0.1 mol  $\text{l}^{-1}$   $\text{HClO}_4$  at current densities 0.116 and 1.16 mA  $\text{cm}^{-2}$  after the passage of additional cathodic charge  $-\Delta Q = 272^\circ\text{C cm}^{-2}$ . Total cathodic charge  $-Q = 293^\circ\text{C cm}^{-2}$ .

$-\eta/\text{mV}$	$\Delta C_{ps}/\mu\text{F cm}^{-2}$	$\Delta q_H/\mu\text{C cm}^{-2}$	$\Delta \theta_H$
264	10.0	—	—
327	20.0	0.95	0.0058
344	41.3	1.45	0.0089
352	52.5	1.84	0.0110
362	66.3	2.44	0.0150
372	92.5	3.23	0.0200

in both the atomic and molecular forms [27]. The predominance of one or other form depends on the coverage of the surface by O<sub>2</sub> and the time of contact of O<sub>2</sub> with the metallic surface.

In the present investigation hydrogen-saturated acid solutions were used so that even if oxygen is evolved at the anode it would not be likely to interfere, because oxygen evolved in the anode compartment should have been removed by the stream of purified hydrogen passing through that compartment. The large anode used in this work minimized the anodic processes (such as O<sub>2</sub> evolution and Pt dissolution) by increasing the surface available for the oxidation of H<sub>2</sub>, i.e. decreasing the current density at the counter electrode.

(II) Hydrogen overvoltage measurement on silver in solutions containing Ag<sup>+</sup> ions are associated with a decrease of  $-\eta$  during cathodisation [28]. The increase of  $-\eta$  and C<sub>expt.</sub> with  $-Q$  is unlikely to be due to the presence of impurities such as surface-active compounds and foreign metal cations because this increase was observed both in pre-electrolysed solutions and those also purified by passage over activated charcoal.

The above arguments strongly suggest that both the increase in  $-\eta$  and rise in electrode capacitance with  $-Q$  are not associated with the presence of impurities in solution.

(III) A decrease or increase in surface area of silver electrode with cathodisation was also considered as a possible explanation for the increase of  $-\eta$  and rise in C<sub>expt.</sub> with  $-Q$ . A decrease in surface area would cause an increase in current density, increasing  $-\eta$  and decreasing the electrode capacitance. However, in the present work it was observed that both  $-\eta$  and C<sub>expt.</sub> increased with  $-Q$  in charcoal cleaned pre-electrolysed solutions, so this hypothesis will not explain the observations.

(IV) The present phenomena are not caused by anion adsorption because the measurements were carried out in aqueous HClO<sub>4</sub> and according to Noninski and Lazarova [29], there is insignificant specific adsorption of ClO<sub>4</sub><sup>-</sup> on a polycrystalline silver electrode.

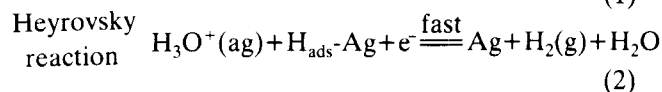
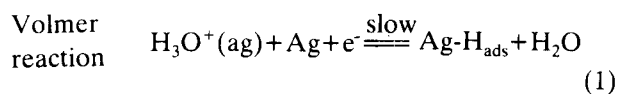
Thus, with the above arguments it is obvious that the silver + hydrogen + hydronium ion system is not well suited to critical examination of the hydrogen evolution reaction unless a high degree of purity and deoxygenation have been approached in this work, which involved electropolished-silver in HClO<sub>4</sub>, pre-electrolysis of the solution for sufficient time and the use of activated-charcoal. In the satisfactory experi-

ments the overvoltage increased with periods of cathodisation and also capacitances have been found to increase with the cathodic charge when compared at constant  $-\eta$  (see Figures 5 and 6).

The variation of  $-\eta$  with time of electrolysis during the h.e.r. has been observed for many metals, such as Fe [30], Pd [31], Ta, Tl and Mo [32]. Increase in  $-\eta$  with time on these metals have been interpreted in terms of adsorption of hydrogen on the surface of Ta, Tl and Mo and a change in the properties of Fe and Pd due to hydrogen absorption.

It was concluded from the results of increase in  $-\eta$  with  $-Q$  that the hydrogen surface coverage of a silver electrode might increase in the course of cathodisation. The growth of hydrogen coverage (see Tables 3 and 4) which appears to be the only reasonable explanation of the pseudocapacitance data obtained in the present work, the fact is that both  $-\eta$  and C<sub>expt.</sub> increased, linearly with log<sub>10</sub> ( $-Q$ ) and finally reached a plateau. The measured capacitances increased with the time of cathodisation by quite large amounts and it is difficult to conceive of any other explanation (refer to the alternative possibilities discussed above) consistent with all of the facts and that of a growing hydrogen adsorption pseudocapacitance.

The hydrogen surface coverage deduced ranged up to about 2% of a monolayer, i.e.  $\Delta\theta_H = 0.02$  for 0.1 mol l<sup>-1</sup> HClO<sub>4</sub>, produced after the passage of an additional 274 C cm<sup>-2</sup>. The coverage was smaller,  $\Delta\theta_H = 0.009$  in the case of the more concentrated 1 mol l<sup>-1</sup> HClO<sub>4</sub> after passage of an additional amount of charge of 190 C cm<sup>-2</sup>. The degree of hydrogen coverage observed by others for silver in alkaline solutions [11,18] is much higher than the values deduced for acid solutions. These higher values of  $\theta_H$ , i.e. 10% of a monolayer in 0.1 mol l<sup>-1</sup> NaOH support the view that  $\theta_H$  increases with increasing pH as found for the acid solutions in this investigation. A possible reason for the difference in hydrogen coverage using 0.1 and 1 mol l<sup>-1</sup> HClO<sub>4</sub> might be due to an increase in the rate of the Heyrovsky reaction in more concentrated acid solution because the (H<sub>3</sub>O<sup>+</sup>) plays an important role in the electrochemical desorption step. Therefore, the mechanism of the h.e.r. at silver cathodes might be a slow discharge followed by rapid electrochemical desorption.



Further work is needed to determine diffusivity and solubility of electrolytically generated hydrogen in silver electrode.

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