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CATHODIC SATURATION CURRENT OF THE HYDROGEN ELECTRODE REACTION ON COPPER AND ITS ABSENCE ON MERCURY: PART I. COPPER

By

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Abstract

The present paper is concerned with an experimental investigation of the cathodic saturation current expected from the catalytic mechanism of the hydrogen electrode reaction on copper.

Measurements were carried out by the constant current pulse technique, mostly on an electrodeposited copper electrode in sulfuric acid and in sodium perchlorate solutions of various concentration at room temperature.

The results are as follows. (i) Straight TAFEL lines are observed over the range of current densities, i, from 10^{-4} to 1 A cm^{-2}. The TAFEL slopes were 131 ± 10 mV and the logarithms of the exchange current density were -5.9 ± 0.5 uniformly in all solutions investigated. (ii) At $i > 1$ A cm^{-2}, a large positive deviation of the overvoltage from the TAFEL line is observed, indicating the existence of a cathodic saturation current.

These results verify the catalytic mechanism on the copper electrode.

The positive value of the rest potential is discussed with reference to copper dissolution and reduction of residual oxygen in solution. A cathodic build-up curve associated with a weak plateau was observed.

Introduction

The hydrogen electrode reaction has been studied since TAFEL in 1905[1] as a typical example of electrode reactions and also as the prototype of a catalysed reaction. Several mechanisms have been proposed; among them, the following are most commonly discussed.

i) the "slow discharge mechanism"

$$H^+ + e^- \rightarrow H(a), \begin{cases} 2H(a) \longrightarrow H_2 \\ \text{or} \\ H(a) + H^+ + e^- \longrightarrow H_2, \end{cases}$$

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ii) the "catalytic mechanism"

$$H^+ + e^- \longrightarrow H(a), \quad 2H(a) \not\rightarrow H_2, \qquad (1a), (1b)$$

and iii) the "electrochemical mechanism"

$$2H^+ + e^- \longrightarrow H_2^+(a), \quad H_2^+(a) + e^- \not\rightarrow H_2,$$

where $\not\rightarrow$ denotes the rate-determining step, (a) the adsorbed state, and H^+ the proton attached to BRÖNSTED base, respectively. The slow discharge mechanism has been supported by many workers on the grounds of the observed TAFEL slope, 2RT/F, *i.e.* the TAFEL constant of 0.5. HORIUTI *et al.*[2] have shown that the slow discharge mechanism is inadequate to account for observed values of electrolytic separation factors of the hydrogen isotopes, and that the TAFEL slope is reasonably deduced from (ii) and (iii) by taking into account mutual interactions of intermediates adsorbed on the electrode surface. They thus concluded[3] that the so called *dual mechanim* is operative, which consists in the alternative applicability of the mechanisms (ii) and (iii), depending on experimental conditions.

The hydrogen electrode reaction on copper has been studied by many authors. HICKLING and SALT[4] experimented with various electrodes and assigned the hydrogen electrode reaction on copper to the group in which the overvoltage approached a constant value with increase of current density to about $0.1 \sim 1$ A cm^{-2}. However, their finding was not reproduced in later work which was conducted with an improved technique.

BOCKRIS *et al.*[5] removed the depolarizing effect of oxygen in solution to a great extent by means of pre-electrolysis. They thus observed[6] the hydrogen electrode reaction on copper and concluded that the slow discharge mechanism applies. Their results, confirmed later by the same authors[7], do not necessarily lead to the slow discharge mechanism but can be equally well accounted for by the catalytic mechanism, as shown previously with special reference to the nickel hydrogen electrode[2b,8].

The catalytic mechanism of the hydrogen electrode reaction on copper was verified by HORIUTI *et al.*[3] on the basis of the theoretical value[9] of the separation factor of deuterium in accord with observation, and this has been recently supported by KITA[10] by an analysis of the periodic variation of the exchange current density with the atomic number of the electrode metals. It was found that the logarithm of the exchange current density decreases linearly with the heat of adsorption of hydrogen and increases linearly with work function in the case of d-metals (transition metals including Cu, Ag and Au), but remains unchanged for sp-metals (the metals following the former in the Periodic Table). These relations were qualitatively interpreted as consequences

of the catalytic mechanism for the d-metals and the electrochemical mechanism for the sp-metals respectively.

A decisive piece of evidence for the catalytic mechanism is the appearance of a *cathodic saturation current*, such as in the cases of the Ni[11] and Ag[12] hydrogen electrodes. This is based on the following. When the overvoltage*) is increased, step (1 a) of the catalytic mechanism remains in equilibrium but the equilibrium is shifted toward the right-hand side. At sufficiently high a value of overvoltage, the electrode surface will be practically completely covered with H(a), and the rate of the rate-determining step (1 b) becomes almost constant independent of overvoltage, since its rate depends on the population of H(a) on the electrode surface[2b,11]. This limiting value of the rate is called the cathodic saturation current.

The aim of the present work is to test experimentally the above prediction from the catalytic mechanism by following the current density of the hydrogen electrode on copper to its highest possible value.

Experimental

The experimental methods were essentially the same as those described elsewhere[11]. The constant current pulse technique was used in order to avoid any possible local heating of the electrode and local change in the concentration of reactants and products near the electrode at high current densities.

Apparatus

The apparatus consisted of a purification train of hydrogen, the cell, a pulse generator, and a recorder for the potential of electrodes. The cell was an all-glass vesseles used in previous work[11], and consisted of three compartments. The main compartment contained serveral of test electrode, a counter electrode, and a cathode for pre-electrolysis, all sealed into sliding ground glass tubes fitted to the cell cap by means of sleave joints. An anode for pre-electrolysis was contained in a compartment separated from the main compartment by a sintered glass disk and a closed tap. Another compartment, for a hydrogen reference electrode, was connected to the main compartment through a LUGGIN capillary. The pulse generator could supply a constant current of 10^{-5} to 1 A for time intervals longer than 10^{-5} sec. The rise time of the individual pulse was *ca.* 1 μsec. On some occasions, the pulse generator PG2 of IWASAKI Communication Apparatus Ltd, Tokyo, was used which has a very short rise time, less than 20 nsec. A cathode ray oscilloscope (SS 5302, IWASAKI Com-

*) The value of the potential of the test electrode, referred to a reversible hydrogen electrode under the same conditions, and taken with negative sign.

munication Apparatus Ltd, Tokyo) and an electronic recorder (EPR-2T, TOA Electronics Co. Ltd, Tokyo) were used for recording the potential.

Materials

Hydrogen from cylinders was purified by passage through columns of silica-gel, soda lime, platinum asbestos kept at 350°C, silica-gel, and three consecutive traps cooled by liquid N_2, the first two of them containing either tablets of active charcoal or molecular sieves 5 A. Analysis by a mass spectrometer (RMU-6, HITACHI Ltd, Tokyo) showed that 0.2 volume % oxygen contained in the cylinder hydrogen, was removed by the purification to a level undetectable by the instrument (less than 10^{-6} volume %).

An aqueous solution of sulfuric acid was used in most cases, and occasionally sodium perchlorate solution or sodium sulfate solution acidified by sulfuric acid were used. All chemical reagents used here were of special grade supplied by WAKO Pure Chemical Industries Ltd, Osaka. Solutions were purified by pre-electrolysis with currents of *ca.* 20 mA cm^{-2} for 2 to 3 days under bubbling of the purified hydrogen. The pre-electrolysis was terminated by pulling the electrode up from the solution.

Electrode

At an early stage of the present work, the test electrodes were prepared from wire (0.1 mm diameter, *ca.* 2 mm length, and 99.99% purity, from FURUKAWA Denko Co., Tokyo, and JOHNSON-MATHEY and Co., London). The wire, after degreasing with benzene and washing with ethyl alkohol and conductivity water, was rinsed gently in 6N H_2SO_4 solution for a few minutes (electrode (a)) or chemically polished for 1 minute in a mixture of 20 cc of conc. HNO_3, 55 cc of conc. H_3PO_4, and 25 cc of glacial acetic acid at 60～70°C (electrode (b)). At the later stage, the test electrodes were prepared by electrodeposition of copper from acidic sulfate solution (10.5 g $CuSO_4$ in 100 cc aqueous solution) on platinum wire (0.05 mm diameter) which was sealed into glass tubes (electrode (c)) and sometimes given further treatment by cathodic pre-polarization with currents of 10 to 60 mA cm^{-2} for 1 to 2 days in a purified hydrogen atmosphere and the electrolyte solution under investigation (electrode (d)).

The surface area of the electrodeposited electrode was determined from the value of the differential capacity referring to the value of 18 μF cm^{-2} for the mercury electrode[13]. The counter electrode was a cylindrical platinized platinum gauze (2 cm diameter and 2 cm length); other electrodes for pre-electrolysis and reference, were all platinized platinum foil.

Experimental Procedure

The cell was cleaned with a mixture of concentrated nitric and sulfuric acid overnight before each measurement. After rinsing it thoroughly with conductivity water the electrodes were mounted in the cell. The electrolyte solution was introduced by applying pressure of purified hydrogen. Pre-electrolysis was then conducted as described above.

Measurements were carried out as follows. Single pulses of a constant current of magnitudes ranging from 10^{-3} to 10^{2} A cm^{-2} were applied between the test and the cylindrical counter electrodes, the former being situated just in front of the LUGGIN capillary tip located at the center of counter electrode. Potential changes of the test electrode with time were displayed on an oscilloscope and photographed. The overvoltage at a given current density was estimated by subtracting the *IR* drop due to solution resistance, identified with the initial jump of the potential in the build-up or decay curve. After the measurements, the pH of the acidic solution was determined by titration. All measurements were carried out at room temperature.

Results and Discussion

Rest Potential

The open circuit potential of the test electrode is an important quantity, indicating the extent to which the electrode reaction predominates in the reaction observed ; any deviations of the rest potential from that of the reversible hydrogen electrode indicate an occurrence of some side reaction.

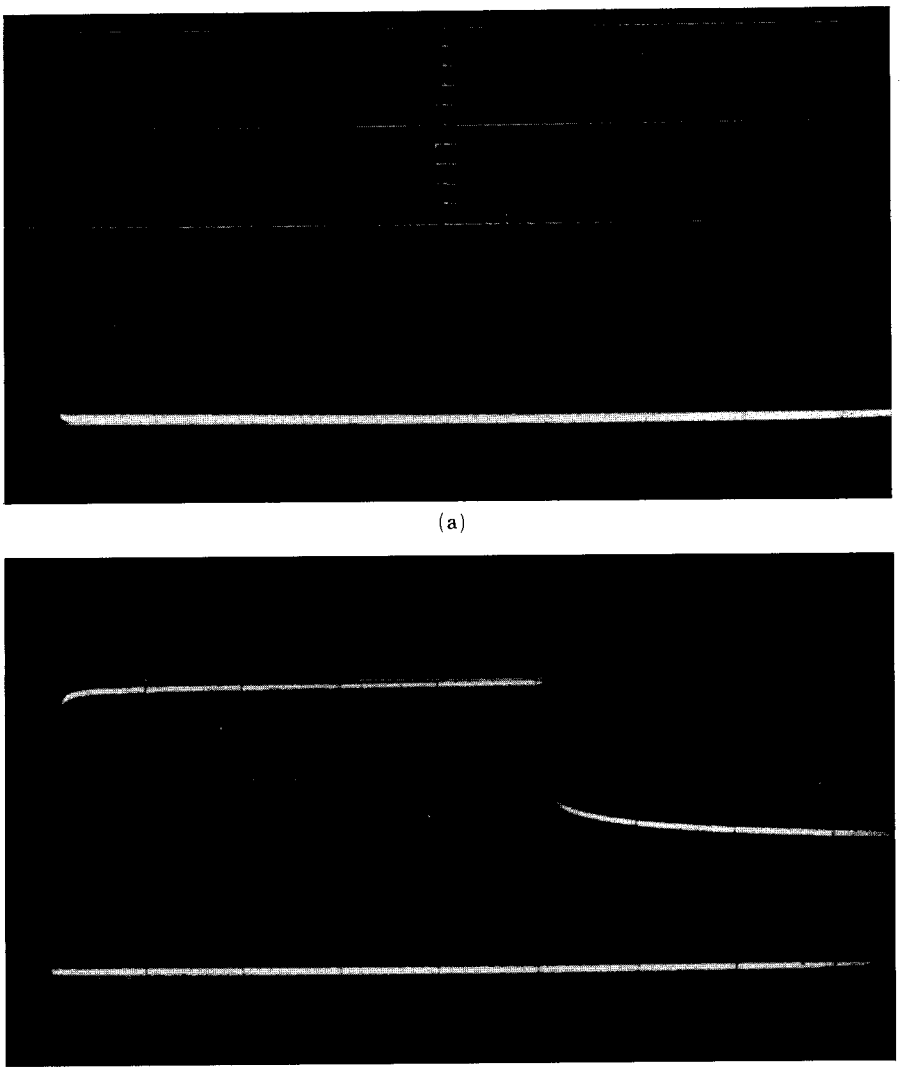
Copper wire, without any treatment or electropolished one (No. 1 in Table 1) showed a rest potential of *ca.* + 200 mV (reversible hydrogen scale) in 5N H_2SO_4, 0.5N KCl, and 5N $NaClO_4$ solutions. Such a deviation of the rest potential from zero is understood to be due to surface oxides on the wire, which are expected to be present from its darkish color. Much smaller values than those were observed on the electrodes (a) and (b) as listed in Table 1, where the surface is treated in a gentle manner only by rinsing in 6N H_2SO_4 solution or by chemical polishing for a short time as described above. These electrodes exhibit the bright metallic color of copper, hence surface oxides, if any, must be remarkably reduced. The electrode of No. 9 in Table 1 which shows a higher rest potential was prepared by mounting the wire in a Teflon holder by means of melted Neoflon (Tetrafluoroethylene-hexafluoropropylene copolymer), where sealing was found not perfect, hence surface oxides probably formed in course of mounting. The electrodeposited electrodes (c) developed a rest potential similar in magnitude to those of (a) and (b). Cathodic pre-polarization which was conducted in order to remove any traces of surface oxides, appeared not to improve the rest potential as seen from the results on the electrode (d) in

TABLE 1

No.	Solution	Electrode	Rest potential (mV)	Slope (mV)	log i_0 (A cm^{-2})	η (V) at $i=0.1$ A cm^{-2}	Logarithm of saturation current (A cm^{-2})
1	5N $NaClO_4$	Electro-polished	220	148	− 5.23	0.63	—
2	7.5N $NaClO_4$	a	6.9	146	− 5.68	0.69	—
3	"	a	11.8	138	− 6.46	0.76	—
4	4.9N H_2SO_4	b	0.6	138	− 5.11	05.7	—
5	"	"	5.8	124	− 6.20	0.64	—
6	"	"	44.6	142	− 5.67	0.66	—
7	"	"	151	133	− 6.15	0.74	—
8	"	"	127	124	− 6.84	0.72	—
9	1.0N H_2SO_4	"	227	120	− 6.78	0.67	—
10	"	c	17.5	121	− 6.56	6.68	—
11	"	"	6.7	105	− 6.12	0.54	0.4
12	"	d	162	142	− 6.02	0.71	1
13	"	"	28	124	− 6.61	0.69	1
14	"	"	63	124	− 6.37	0.67	1
15	"	"	68	152	− 5.46	0.68	1
16	"	"	17.2	125	− 6.32	0.67	1.5
17	"	"	3.7	123	− 5.68	0.58	1.5
18	"	"	42	133	− 5.64	0.62	—
19	"	"	37	147	− 5.78	0.70	—
20	"	"	6.1	137	− 5.68	0.64	—
21	0.11N H_2SO_4	"	45	140	− 5.85	0.68	1
22	"	"	0.7	121	− 5.86	0.58	—
23	0.11N H_2SO_4+ 1N Na_2SO_4	"	5.8	121	− 5.70	0.57	1
24	3.1N H_2SO_4	"	not measured	130	− 4.90	0.52	1.5
25	"	"		131	− 5.26	0.57	1.5
			Mean	131 ± 11	− 5.0 ± 0.5		

Table 1. Thus, the deviation of the rest potential on electrodes (a) to (d) can not be due to surface oxide but ought to be due to some impurity in solution.

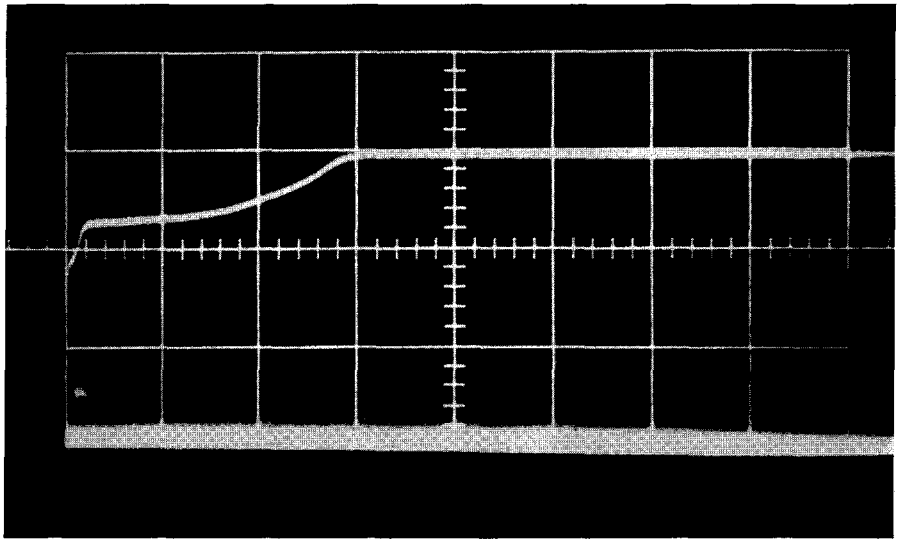
Dissolution of the copper electrode was confirmed to be one of the possible electrode reactions. The weight of copper wire (0.1 mm diameter, 99.99 % purity) of 156.9 mg was reduced by 1.7 mg when keeping the wire in 1N H_2SO_4 solution under bubbling of purified hydrogen for 125 hrs, while the rest potential



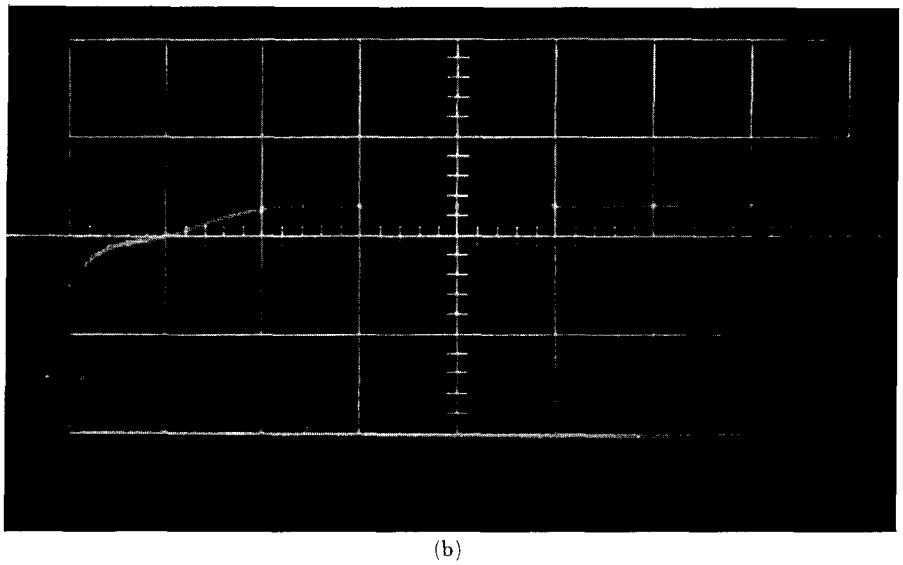
(a)

(b)

Plate 1. Galvanostatic cathodic build-up curve on copper in 4.9N H_2SO_4 solution ($i = 3.81$ A cm^{-2}).
(a) Ordinate; 0.5 V/div., Abscissa; 2 μsec/div.
(b) Ordinate; 0.5 V/div., Abscissa; 50 μsec/div.
Horizontal trace indicates the potential of the reversible hydrogen electrode at the same conditions.



(a)



(b)

Plate 2. Galvanostatic cathodic build-up curve on copper in 0.11 N H_2SO_4 +1 N Na_2SO_4 solution ($i = 3.33$ A cm^{-2}).
(a) Ordinate; 1 V/div., Abscissa; 0.2 m sec/div.
(b) Ordinate; 1 V/div., Abscissa; 20 μ sec/div.
Horizontal trace indicates the potential of the reversible hydrogen electrode at the same conditions.

of the wire stayed constant at around +200 mV as measured periodically. After removing the test electrode, the solution was electrolysed and deposition of copper from the solution was detected. A second electrode reaction that steadily consumes the electrons left on the electrode by dissolution of copper is necessary. The positive values of the rest potential as referred to the reversible hydrogen electrode (Table 1), however, exclude the possibility of having hydrogen evolution as such an electrode reaction. It is probable that reduction of traces of oxygen takes place instead. A vacuum technique would have to be applied in order to remove this disturbance.

Transients

Plates 1 (a) and 1 (b) show the cathodic build-up curve at constant current in sulfuric acid solution. A rapid sweep as in Plate 1 (a) revealed a slight plateau which disappeared when a much lower sweep rate was used to determine the steady value of potential, as in Plate 1 (b). This slight plateau was observed on all the electrodes dealt with in the present work but was always absent in the second sweep applied immediately after the first one under the same conditions. It is interesting to note that the addition of sodium ion (No. 23 in Table 1) creates another quite conspicuous plateau as shown in Plate 2 (a), while in Plate 2 (b), taken with a much faster sweep than Plate 2 (a), one recognizes a slight plateau similar to that seen on Plate 1 (a). The conspicuous plateau may be understood in connection with the formation of sodium intermetallic compound on the electrode surface as reported by KABANOV *et al.*[14] for Ag, Cd, Pb and Zn and supported by MATSUDA *et al.*[15] for the case of Pt.

TAFEL plots*)

Fig. 1 shows a typical TAFEL plot obtained (No. 14 in Table 1). The TAFEL line extends up to several tenths A cm^{-2} current density. Table 1 shows the appropriate values of slope, logarithm of exchange current density, log i_0, and overvoltage at 0.1 A cm^{-2}. These values fluctuate considerably but reveal no correlation with the concentration of sulfuric acid or with the species of electrolyte. TAFEL paramters are not affected by addition of sodium ion (No. 23 in Table 1) which gives rise to the conspicuous plateau in the build-up curve. The mean value of the slope is 131 ± 11 mV, that of log i_0 is -5.9 ± 0.5, respectively.

The overvoltage deviates, however, at high cathodic current densities from the TAFEL line, *viz.* it rises too fast, as seen from Fig. 1. This signals

*) The relation between η and log i is called "TAFEL plot" here irrespective of its being linear or not, while "TAFEL line" signifies the linear relation between η and log i.

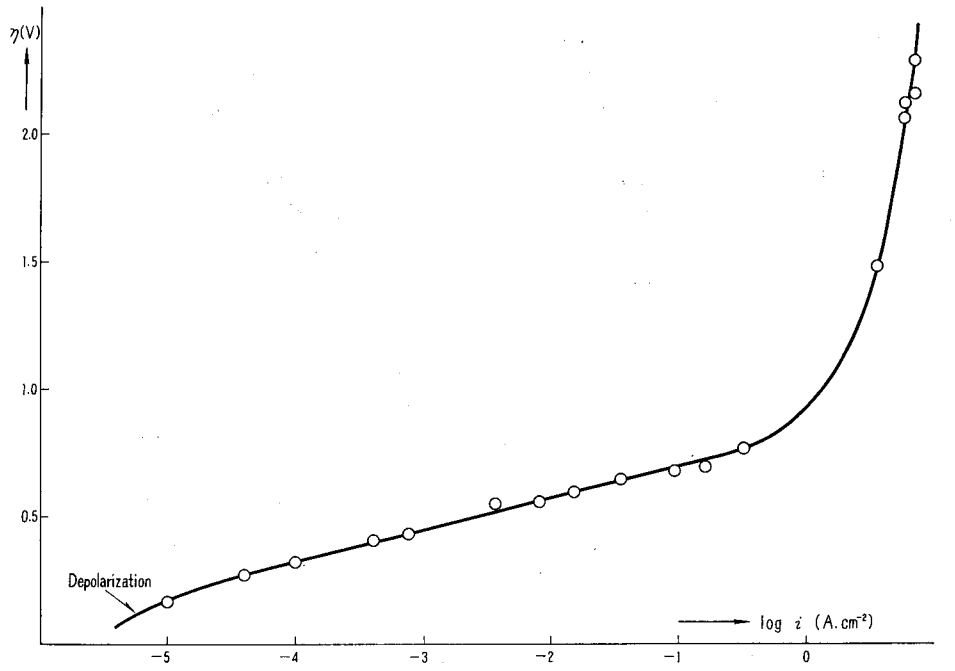


Fig. 1. η *vs* $\log i$ curve on copper in 1.0 N H_2SO_4 solution. Preelectrolysis; 20 mA, 3 days, Pre-cathodic polarization; 40 mA, a day, Rest potential; +63 mV.

existence of a cathodic saturation current as expected for the catalytic mechanism. From the experimental results, the value of the saturation current is roughly estimated at 10 to 30 A cm^{-2}, which is somewhat smaller than the value of *ca.* 100 A cm^{-2} observed on Ni[11]. The *IR* drop becomes predominant at high current densities, especially at $i>1$ A cm^{-2}, which obscures the reaction overvoltage. The resistance of the solution is calculated to be 8 ohm by the equation, $R=(1/2\pi\kappa l)\ \ln a/b$, where κ is the conductivity of the electrolyte solution, l the length of wire, a and b the radius of the cylindrical counter electrode and the test electrode respectively. The *IR* drop amounts to 8 V at $I=1$ A where the steady potential is around 9.5 to 10 V, hence the overvoltage amounts only to 15 to 20% of the steady potential. It is thus required to determine the *IR* drop very precisely at high current densities. In the present work, the *IR* drop was estimated by extrapolating the initial part of build-up curve (Plate 1 (a)) at $t=0$. The accuracy of the extrapolation depends critically on the rise time of the constant current pulse used. A rise time of *ca.* 1 μ sec as used in the present work was affirmed to be short enough to

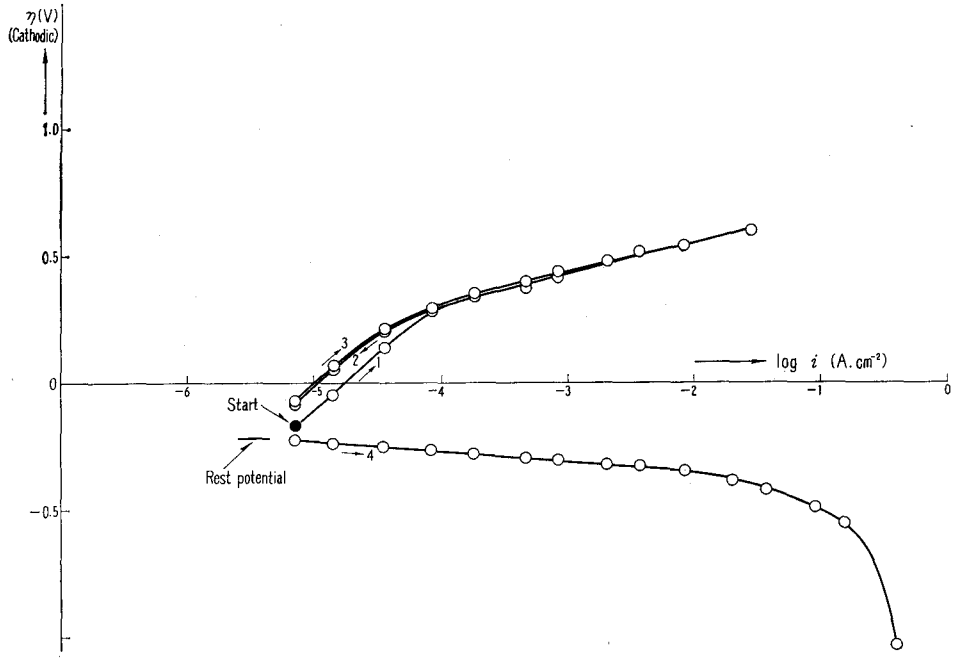


Fig. 2. η *vs* log i curve on copper in 1.0N H_2SO_4 solution. Pre-electrolysis; 10 mA, 46 hrs, Chemical polishing; 1 min, Rest potential; +227 mV.

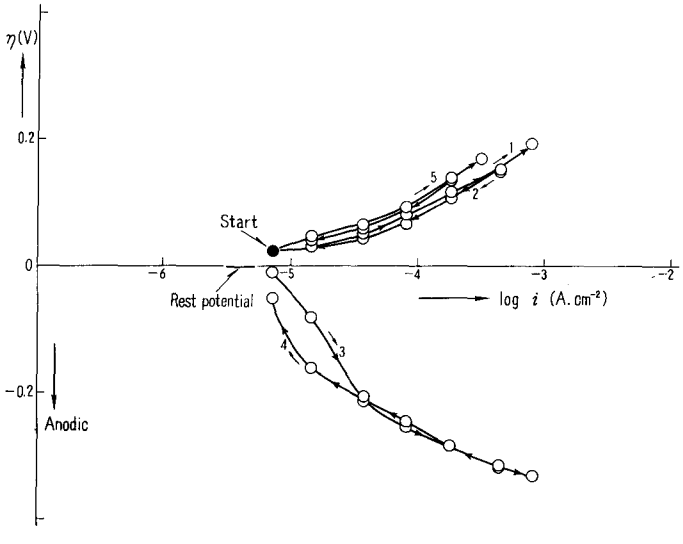


Fig. 3. η *vs* log i curve at low current densities on copper in 1.0N H_2SO_4 solution.

give an accurate extrapolation, by the fact that the value of the *IR* drop thus obtained was exactly reproduced when a pulse generator, PG2, was used which has the much shorter rise time of 20 nsec. In the last column of Table 1, — signifies cases where the relation between η and $\log i$ was not followed up to high current densities or, where it was followed, the results were not reliable because of lack of proportionality between *IR* and *I*; the *IR* drop grew less than proportional to *I* with increase of current density, which gave more enhanced positive deviation of η from the TAFEL line.

At current densities lower than 10^{-4} A cm^{-2}, there was observed a tendency of depolarization or depression of the TAFEL plot from the extrapolated TAFEL line as seen in Fig. 1, which is the more pronounced, the more positive the rest potential. Figs 2 and 3 show the TAFEL plot at low current densities in the respective cases where the rest potential is either far from or close to the reversible hydrogen electrode. Numbers and arrows in the figures indicate

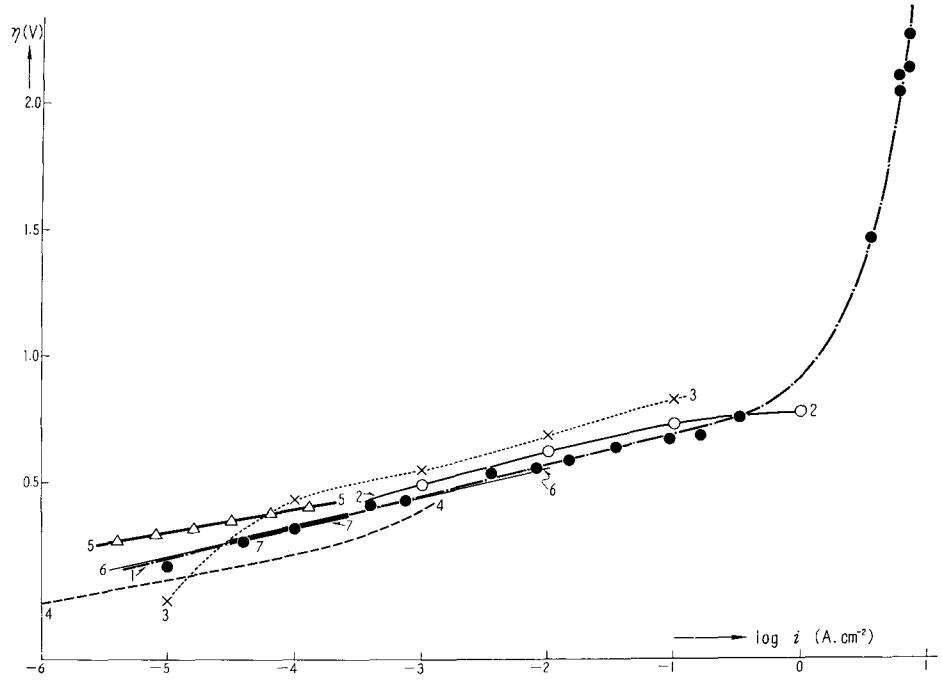


Fig. 4. Comparison of the present result with others.
1; Present result (1N H_2SO_4), 2; HICKLING and SALT[4] (1N HCl, 16±1°C) 3; AZZAM, BOCKRIS, CONWAY and ROSENBERG[5] (HCl solution), 4; BOCKRIS and PENTLAND[6] (0.02N NaOH, 17°C), 5; SENETT and HISKEY[16] (1N HCl, time of aging, 2 hrs), 6; CONWAY[17] (0.2N HCl, 26±1°C), 7; BOCKRIS, PENTLAND and SHELDON[18] (0.1N HCl).

the sequence of measurements.

One of the present results is compared with those of other authors[4~5,16~18] both in alkaline and acidic solutions in Fig. 4.

The present results are in agreement with all others over the range of current densities below 10^{-1} A cm^{-2}, but only the present work reveals saturation currents in the region of higher current densities, and this contradicts the only work in this region by HICKLING and SALT[4].

Conclusive Remarks

The hydrogen evolution reaction on the copper electrode was observed over the range of current densities from 10^{-5} to 10~30 A cm^{-2}. It was found that there exists a cathodic saturation current at around 10 to 30 A cm^{-2}, whereas at lower current densities, the TAFEL line hold with parameters not depending on the concentration of sulfuric acid and the kind of other electrolytes studied. The catalytic mechanism of the hydrogen electrode reaction is thus verified with the hydrogen electrode of copper.

Acknowledgments

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