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Conference Paper

Hydrogen Evolution on Pyrolytic Graphite*

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The hydrogen evolution reaction from acid solutions was studied on highly oriented pyrolytic graphite at different surfaces obtained by cutting graphite under the various angles in respect to the basal plane. The experiments were done galvanostatically on the polished samples of desired orientation, in a cell which enabled the pretreatment of graphite at 1000° C in argon and use of prepurified $Na_2SO_4 + H_2SO_4$ solutions.

Tafel lines with 2 RT/F slopes were obtained in all the experiments with i_0 varying from ca 10^{-9}A/cm^2 for cleavage plane to ca 10^{-8}A/cm^2 for edge plane. The transients show the considerable pseudo-capacitances of 250—500 μF/cm^2 being larger at more negative potentials and edge surfaces.

The experimental data are consistent with the slow discharge — electrochemical desorption mechanism with the limited number of sites of H adsorption but also with the coupled discharge — recombination reaction for hydrogen evolution.

INTRODUCTION

Little work has been done so far on the kinetics and mechanism of hydrogen evolution on pure carbon materials. Early work of Erdey-Gruz and Wick[1] served Vetter[2] as the source of some indication about the behaviour of carbon as hydrogen electrode. More recently Drossbach and Schulz[3] published results of a more comprehensive investigation of hydrogen evolution and dissolution on different sorts of graphite. Basic shortcoming of this study is in that the manner of electrode preparation could not provide a well defined and highly pure surface. Hence, some doubts could be placed on the validity of the figures for electrodic parameters of the reaction.

The use of carbon as electrode material is anything but loosing ground in modern electrochemical practice. Hence, it was considered to be of interest to find out in more detail its behaviour as hydrogen electrode. The first difficulty encountered in such an attempt is that of obtaining well defined material giving reproducible results and thus rendering itself to a systematic study. It was felt that this could be overcome if highly oriented pyrolytic graphite, now available, is used to perform experiments under conditions of extreme purity considered as essential in electrode kinetics measurements.

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With such a material the electrochemical behaviour could be studied also as a function of orientation of unit cells of the graphite crystals. The results of such a study are reported below.

EXPERIMENTAL

Three samples of pyrolytic graphite were used in these experiments: *(a)* pyrographite of the General Electric Co (USA) with $\Delta\Theta$ (width of the orientation diagram at the half height of the maximum[4]) of 21^0; *(b)* pyrographite of the Union Carbide Co (USA), with $\Delta\Theta = 23.5^0$ and *(c)* pyrographite of the Société Carbone-Lorraine (France) with $\Delta\Theta = 6.5^0$.

Electrodes were made by cutting out cylindrical pieces with an axis at a desired angle (α) with respect to the basal plane of the crystallites, polishing cylinder bases with a series of emery papers ending with 0000 and heating them in an oven at 1000^0 C for $^1/_2$ hour in an atmosphere of highly purified argon.

The electrodes were transferred to the bottom of the electrolytic cell shown in Fig. 1 without any contact with the open atmosphere. The cell was filled with an electrolyte containing Na_2SO_4 and H_2SO_4 to the total ionic strength of 2, in a ratio necessary to provide a desired *p*H value, prepurified in a purification train by standard electrodic procedures. Hydrogen of high purity was bubbled through the cell for 2 hours prior to measurements.

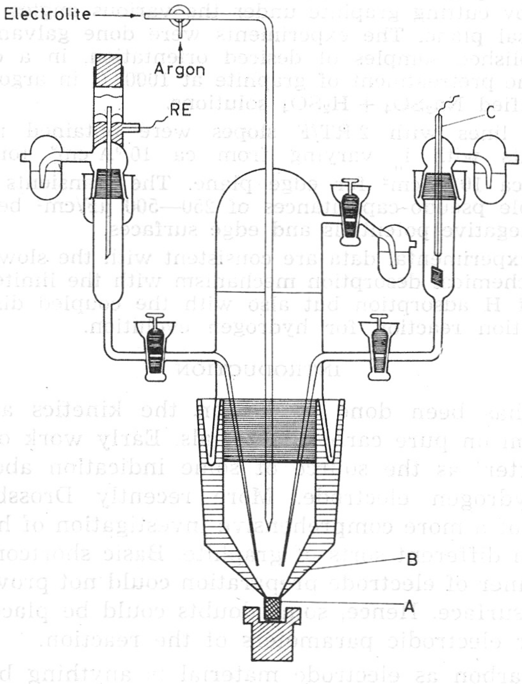

Fig. 1. Electrolytic cell. ***A*** **— graphite sample;** ***B*** **— teflon cell;** ***C*** **— counter electrode;** ***RE*** **— reference electrode.**

Measurements were made by standard galvanostatic technique. The purity of the system was checked by replacing the graphite with mercury and with amalgamated gold electrodes. Tafel lines obtained from plateaus of galvanostatic transient in both cases agree with those found in the literature[2].

RESULTS

State of the Samples

Graphite samples of different make behaved in about the same manner. No equilibrium potential could ever be established by bubbling hydrogen (remaining trace impurities produced a drag to more positive values). Hence, all electrodes were maintained under the small constant cathodic current (0.16 mA cm^{-2}) before and inbetween the measurements (prepolarisation). After this current was put through a freshly prepared system, the cathode potential was found to go negative during 0.5 to 1 hour, reach a maximum negative potential and then undergo a slow shift in the positive direction for about 100 mV to reach a final steady-state value. The latter was found to vary from sample to sample within about 200 mV (— 405 to — 650 mV *vs.* NHE).

It appears that prolonged cathodic polarisation leads to a continuously increasing i_0 value. Fig. 2 shows the change in potential with time at a relatively high constant current density of 1.1 mA cm^{-2}. It is seen to exhibit an asymptotic tendency but with a charge still persisting even after 30 hrs.

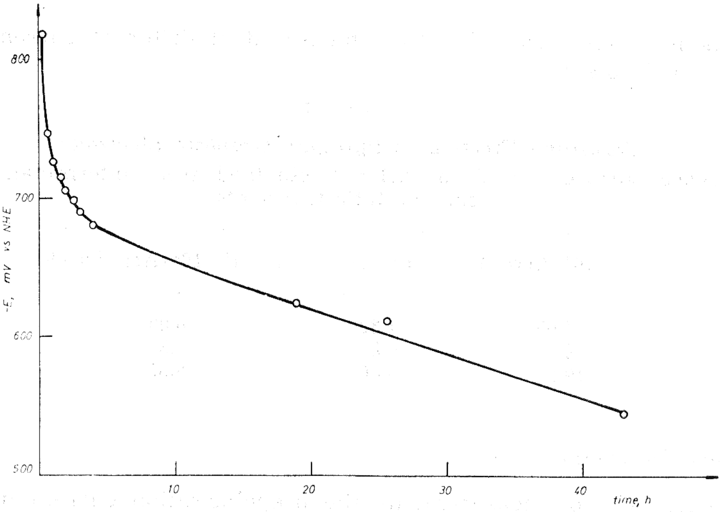

Fig. 2. Change of the graphite electrode potential with time at constant current density of 1.1 $mAcm^{-2}$.

Transient Behaviour and Transition Time

Galvanostatic transients were typical of combined activation control and subsequent concentration polarisation in respect to some intermediate species (pseudo-capacitance effect, double slope rise shown in Fig. 3 in microseconds) and a flat plateau in 10—100 millisecond range of the time scale up to relatively high current densities. The pseudo-capacitance effect was obtained earlier[5] by A. C. measurements also.

With increasing *p*H, further concentration polarisation arose with transition times, τ, observed in the time scale of seconds, leading to a second

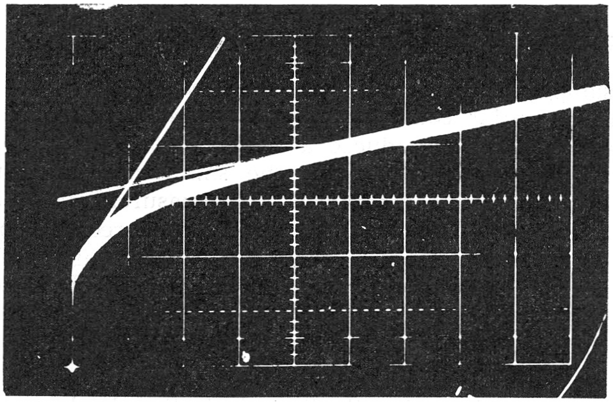

Fig. 3. Initial part of a galvanostatic transient with two slopes. Scale: 0.1 mscm^{-1}, 10 mVcm^{-1}, i = 7.15 mAcm^{-2}.

plateau. Some values transition time measured at different current densities are shown in Table I.

TABLE I

Transition Times at a Pyrolytic Graphite Electrode
(cleavage surface, $\alpha = 0^0$) at pH = 2, obtained from interpretation of galvanostatic transients

i × 10^3 (Acm^{-2})	τ (sec)	i × $\tau^{1/2}$ 10^3 (Acm^{-2} sec$^{1/2}$
4.65	1.32	8.05
9.75	0.87	7.3
19.2	0.66	8.35

Capacitance Determinations

In special sets of measurements the prepolarisation current density was changed and a galvanostatic transient at a superimposed constant current pulse was recorded at each new current density value. Two sets of capacitance values were extracted from the initial and the second slope of the charging curves. Average values of the capacitance calculated from the first slope, corresponding to the double layer capacitance was about 70 μF cm^{-2}. The capacitance values corresponding to the pseudo-capacitance were calculated from the second slope for the two cutting angles of graphite samples.

The pseudo-capacitances obtained in such a way were related to corresponding steady-state potential values and Fig. 4 was obtained. Although considerable dispersion of values with different samples and pulse current densities is evident, two conclusions are indicated beyond doubt: *(a)* Capacitance values at the cutting angle of 0° (cleavage surface), at one and the same potential value, are lower than those at the cutting angle of 90° (edge surface) by about 180 μF cm^{-2} at — 500 mV; *(b)* at both cutting angles the capacitance increases with increasing negative potential.

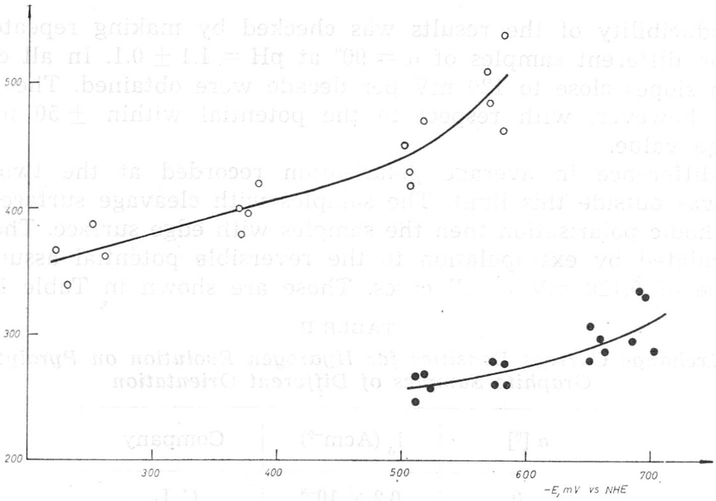

Fig. 4. Plot of pseudo-capacitance *versus* electrode potential for $\alpha = 90^0$ (upper curve) and $\alpha = 0^0$ (lower curve).

Steady-state Polarisations

Since cathodic pulses were of relatively short duration, the plateaus recorded on the transients could be considered to represent the »steady-state« values of potential for the given current density and for the state of the surface formed by the steady prepolarisation current.

These sets of potential values, as obtained from the first and the second plateau, of the galvanostatic transients were plotted *vs.* log current density. Reasonable Tafel lines resulted as typified by Fig. 5.

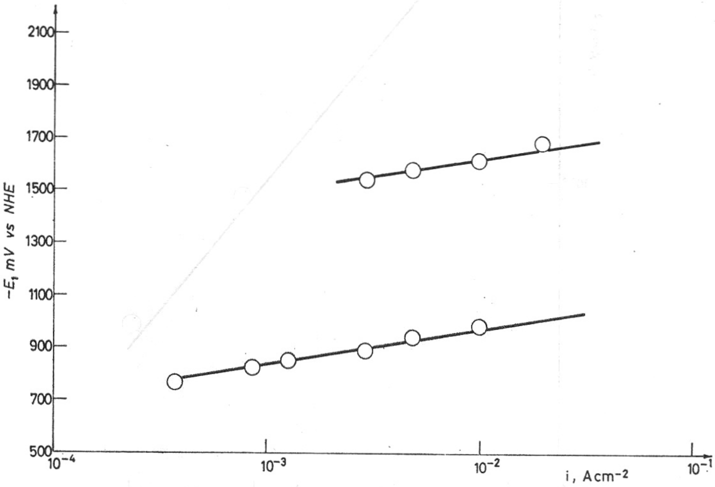

Fig. 5. Typical Tafel plots obtained from the first and the second plateau of the galvanostatic transients (pH = 2) at pyrolytic graphite electrode ($\alpha = 90^0$).

Reproducibility of the results was checked by making repeated measurements on different samples of $\alpha = 90°$ at $pH = 1.1 \pm 0.1$. In all cases Tafel lines with slopes close to 120 mV per decade were obtained. The lines were dispersed, however, with respect to the potential within ± 50 mV around an average value.

The difference in average polarisation recorded at the two different surfaces was outside this limit. The samples with cleavage surface exhibited larger cathodic polarisation then the samples with edge surface. The i_0 values were calculated by extrapolation to the reversible potential assumming the Tafel slope of 0.120 mV in all cases. Those are shown in Table II.

TABLE II

Exchange Current Densities for Hydrogen Evolution on Pyrolytic Graphite Samples of Different Orientation

α [°]	i_0 (Acm^{-2})	Company
0	0.2×10^{-8}	C. L.
15	0.6×10^{-8}	U. C.
90	2.0×10^{-8}	C. L.
90	2.1×10^{-8}	U. C.
90	2.5×10^{-8}	U. C.

The plot of log i *vs.* *p*H at an arbitrarily chosen potential of — 800 mV *vs.* NHE, is shown in Fig. 6. It indicates a slope $(\partial \log i/\partial pH) = 1$ *i. e.* the reaction order of 1 for H^+ ions.

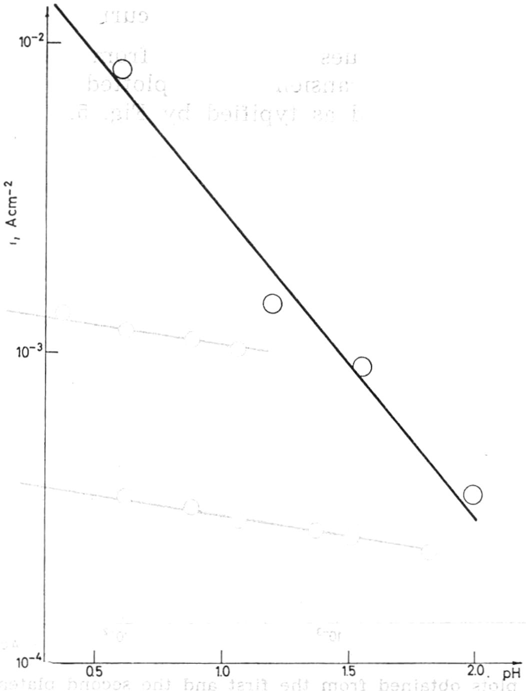

Fig. 6. Plot of log i at — 800 mV (NHE) *vs.* *p*H for a pyrolytic graphite sample ($\alpha = 90°$).

DISCUSSION

Obtained transition times leave little doubt that the first and the second galvanostatic plateau pertain to hydrogen evolution from hydrogen ions and water respectively. The value of the product $i \cdot \tau^{1/2}$ calculated for H^+ ions at $pH = 2$ using Sand's equation is 7×10^{-3} A cm^{-2} sec$^{1/2}$. The agreement with the experimental values given in Table I is satisfactory. This is confirmed also by the fact that the Tafel lines from the first plateau are *p*H dependent with the reaction order of 1, while those from the second are not.

A speculation regarding the reaction mechanism operative at this surface could be made from the consideration of two experimental facts: *(a)* the Tafel slope of 2 RT/F and *(b)* the finding that the pseudo-capacitance increases with cathodic overpotential.

It can be shown that if the surface is taken to be homogeneous, no mechanism designed so far could render such behaviour, if assummed that one of the two steps is so much faster than the other that it could be considered to be at equilibrium with the first step as the rate determining step (r. d. s.). Thus, the slow discharge-recombination reaction mechanism would allow for the 120 mV slope, but the pseudo-capacitance should be independent of potential as indicated in Table III. If the second step was

TABLE III

Tafel Slopes and Changes of Pseudocapacitances with Overpotential for Various Mechanisms of Hydrogen Evolution ($\beta = 0.5$)

Mechanism	Condition $\Theta \to 0$		Condition $\Theta \to 1$	
	$\frac{\partial \eta_{cath}}{\partial \ln i}$	$\frac{\partial C_{ps}}{\partial \eta_{cath}}$	$\frac{\partial \eta_{cath}}{\partial \ln i}$	$\frac{\partial C_{ps}}{\partial \eta_{cath}}$
Slow discharge — fast recombination	$-\frac{RT}{\beta F}$	0	$-\frac{RT}{\beta F}$	0
Fast discharge — slow recombination	$-\frac{RT}{2F}$	>0	∞	<0
Slow discharge — fast electrochemical desorption	$-\frac{RT}{\beta F}$	<0	$-\frac{RT}{(1+\beta) F}$	>0
Fast discharge — slow electrochemical desorption	$-\frac{RT}{(1+\beta) F}$	>0	$-\frac{RT}{\beta F}$	<0
Coupled discharge — recombination	$-\frac{RT}{\beta F}$	>0	—	—
Coupled discharge — electrochemical desorption	$-\frac{RT}{\beta F}$	0	$-\frac{RT}{\beta F}$	0

the rate-determining one the C_{ps} should increase with overpotential but the slope should be 30 mV per decade. For the discharge-electrochemical desorption reaction path one could deduce that in the region of low surface coverage the slow first step would again render the 120 mV slope but the C_{ps} should be decreasing with an increasing overpotential, while in the region of high coverages ($\Theta \rightarrow 1$), the C_{ps} should increase with overpotential but the slope should be 40 mV per decade. An inverse situation should be found if the desorption step was the rate-determining.

A situation, like the one founds experimentally, of 120 mV slope and increasing C_{ps} with overpotential, could be obtained if the surface possessed a limited concentration of active sites for adsorption of atomic hydrogen and the dicharge-desorption mechanism was operative with the discharge step as the r. d. s. with a high degree of occupation of the active sites. In that case the discharge reaction could proceed at the bare portions of the surface with $(1 - \Theta_H)$ factor negligible (hence, the 120 mV slope) and yet the C_{ps} could increase with increasing Θ_H, which for this case is obtained only if $\Theta_H > 0.5$, *i. e.* if the maximum in the C_{ps} *vs.* Θ_H curve is passed.

However, beside those possibilities, one should consider also the same set of mechanisms but under circumstances when no step can be considered at equilibrium. This can arise if overpotential is so highly negative that all anodic partial currents are negligible (coupled reactions, cf. *e. g.* Ref. 6).

In such a case it can be shown that the discharge-desorption mechanism should render Θ_H and hence the C_{ps} independent of overpotential, which is contrary to experimental findings.

The discharge-recombination mechanism on the other side, could give both the 120 mV slope and the increasing overpotential while the recombination has also to be accelerate but with an increasing concentration of atomic hydrogen at the surface.

Whatever the case, the results indicate that at pyrolytic graphite the discharge reaction is slow and it makes the Tafel dependence run with a 2 RT/F slope. The second step may be either the desorption reaction at high degree of occupation of active sites for hydrogen adsorption or the discharge reaction at low degree of surface coverage. The two diagnostic criteria do not allow a conclusive view.

One could maintain that another fact points out to the second case as more probably the pertinent one, namely that of a very high polarizability of the surface, *i. e.* the very small concentration of impurities producing the drag to positive potential values. This could be so only if atomic hydrogen was at such a low concentration that the small impurity flux could change it by chemical reaction to a considerable extent. This could hardly occur if considerable amounts of atomic hydrogen were present at the surface.

Whatever the case, the i_0 values of the order of 10^{-8} A cm^{-2}, place pyrolytic graphite in the group of electrode materials with intermediate catalytic activity for the hydrogen evolution reaction. They are seen to be somewhat dependent on the crystal plane. The values on the edge surface appear to be higher than those at the cleavage surface by about an order of magnitude. However, there are reasons to believe that surface roughness is somewhat higher at the former than at the latter, so that the conclusion should be taken as qualitative.

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IZVOD

Izdvajanje vodonika na pirolitičkom grafitu

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Proučavana je reakcija izdvajanja vodonika iz kiselih rastvora na visoko-orijentisanom pirolitičkom grafitu. Ispitivanja su vršena na površinama dobijenim sečenjem grafita pod različitim uglovima u odnosu na osnovnu ravan. Galvanostatska merenja su vršena na poliranim uzorcima željene orijentacije, u ćeliji koja je omogućavala prethodno tretiranje grafita na 1000^0 u argonu i korišćenje prethodno prečišćenih rastvora Na_2SO_4 i H_2SO_4.

U svim eksperimentima dobijene su Tafelove prave sa nagibima 2 RT/F, gde je i_0 varirala od cca 10^{-9} A/cm^2 za poluprovodničku ravan do cca 10^{-8} A/cm^2 za elektronsku ravan. Krive prelaznog stanja pokazuju značajne pseudokapacitete od 250—500 μF/cm^2 koji rastu sa negativiranjem potencijala. Isto tako, oni su veći za elektronsku ravan.

Eksperimentalni rezultati su u saglasnosti sa mehanizmom elektrohemijske desorpcije sa sporim razelektrisanjem, pri ograničenom broju mesta za adsorpciju vodonika, ali i sa kuplovanom reakcijom razelektrisanja i rekombinacije.

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