Determination of the Relative Effective Area of Electrodes by Polarization Measurements

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It is of great importance in many cases to have a measure of the true surface area of solid materials. Porous metal and graphite bodies may serve as examples. Their true surface area can be obtained by the wellknown BET method. When such bodies are used as electrodes there is reason to believe, however, that their electrochemically effective area is smaller than their total or BET area. Hydrated ions will not penetrate into the finest pores and the penetration of the current is limited by its throwing power. The ratio of the electrochemically effective areas of two electrodes is therefore probably different from their BET area ratio. An electrochemical method for the determination of relative surface areas would therefore seem desirable in this case.

Such a method is the capacitance method, in which the double layer capacity of the electrode/electrolyte interface is measured by an a.c. bridge or by an oscillographic analysis of square waves passed through the interface. This method is very sound in principle but the results depend on the frequency used and may thus be difficult to interpret.¹⁻⁵

Another electrochemical method which is close at hand but of which, remarkably enough, there seems to be no published account, is the polarization method. It is based on the principle that the polarization is a definite function of current density and hence of surface area. Two cases should be distinguished

I. At small values of the current density i , i.e. high values of surface area A , we have

$$\eta = c \cdot i = c \cdot I/A$$

where η = activation polarization, c = a constant and I = current. If η is recorded as a function of I for several electrodes of the same material but differing in area, we obviously obtain converging straight lines, the slopes S of which are inversely proportional to the surface area. For two electro-

des we thus find $A_2/A_1 = S_1/S_2$ giving the ratio between the effective surface areas.

II. At higher values of the c.d. i , i.e. smaller surface area A , we have the well-known Tafel equation

$$\begin{aligned}\eta &= a + b \log i = a + b \cdot \log I/A \\ &= a + b \cdot \log I - b \cdot \log A\end{aligned}$$

where a and b are constants. If η is again recorded as a function of I for two electrodes of the same nature but of different area, we will expect parallel straight lines whose difference in η determines the ratio of the respective surfaces by the relation $\log (A_2/A_1) = (\eta_1 - \eta_2)/b$.

In both the cases referred to, the conditions of electrolysis should be such that the current is uniformly distributed over the effective cathode surface. This means that the electrolytic throwing power T , defined by the expression $T = (\kappa/d)(d\eta/di)$, where κ = conductivity of electrolyte, $d\eta/di$ = slope of η/i -relation and d = electrode distance, should be as high as possible. An electrolyte of high conductivity can usually be found, although one requirement is that it must not corrode the electrode. The electrode process used should preferably have a high activation polarization. The choice is very limited, however. Hydrogen evolution, oxygen reduction and oxidation-reduction systems not corroding the metal may be considered. It is evidently more advantageous from this point of view to

Fig. 1. Tafel lines for hydrogen evolution on nickel wire net cathodes.

Table 1. Polarization curves for hydrogen evolution on nickel wire net cathodes.

i mA	$\log i$	Potential vs SCE mV	Slope, b mV	$\eta_1 - \eta_2$ mV
Single net. Area = A_1				
0.3	-0.5229	-1 277.3		-52.5
0.5	-0.3010	-1 293.8	-74.4	-52.2
0.7	-0.1549	-1 304.1	-70.4	-52.3
1.0	0.0000	-1 315.1	-71.0	-52.2
1.5	0.1761	-1 328.3	-74.9	
2.0	0.3010	-1 338.0		
			$M = -72.1$	$M = -52.4$
Five nets. Area = A_2				
1	0.000	-1 263.0		
2	0.3010	-1 284.7	-72.1	-52.3
5	0.6990	-1 313.5	-72.4	-53.0
10	1.0000	-1 335.6	-73.4	-52.2
15	1.1761	-1 350.5		
			$M = -72.6$	$M = -52.5$

$$\log \frac{A_2}{A_1} = \frac{-52.4}{-72.7} = 0.720; \frac{A_2}{A_1} = 5.25$$

work at a low c.d., since $d\eta/di$ is then higher due to the logarithmic nature of the η/i relation. In applying hydrogen evolution for the purpose the method should, for the same reason, have the best prospects with metals of high hydrogen overvoltage.

In exploring the possibilities of the method, some electrolysis experiments were made with hydrogen evolution on nickel, although this is not a particularly favorable case, since nickel has a low hydrogen overvoltage. Two wire net electrodes of surface ratio 5 were used, one being a single 3×3 cm net with a wire diameter of 0.2 mm and having 8 meshes per cm, the other consisting of five such nets. The areas were estimated to be 9 and 45 cm² respectively. With the instruments available, the experiments had to be carried out in the logarithmic range, which is also not very favorable. The electrolyte was 27 % KOH solution, having a very good conductivity and being only slightly corroding to solid nickel. In an electrolysis cell, the cathode was placed in a horizontal position in the cathode compartment, separated by a long electrolyte path from the anode compart-

ment. In the latter a platinum anode was placed close to the electrolyte surface. Through both the anolyte and the catholyte pure hydrogen, freed from oxygen by passing through vanadium(II)sulphate solution, was bubbled vigorously in order to prevent oxygen from entering the cathode compartment. The electrodes were pre-electrolyzed at the lowest currents used (0.3 and 1 mA, respectively) for 100 min. Cathode potentials were determined by the direct method using a saturated calomel electrode as reference. Readings were taken at 2 min intervals. The results are recorded in Table 1. The two Tafel lines obtained are shown in Fig. 1 with different $\log I$ axes. As shown in Table 1, the area ratio experimentally found is 5.25 in good accordance with the real value. The method can obviously be used for the determination of the area of irregular surfaces, a problem encountered for instance in dentistry.

Measurements on nickel powders and sintered nickel plates in the same cell and with currents of the same magnitude give good linear relations if diluted KOH solutions are used. The throwing power is, however, too low. In concentrated KOH solutions, on the other hand, the active porous nickel electrodes are corroded, in accordance with the potential-pH-diagram for nickel. This diagram suggests a less corroding electrolyte, viz. 1 M K₂CO₃, 1 M KHCO₃ with a resulting pH of 10.25. Measurements on two nickel wire nets of the kind described above and with the weight ratio 5:1 gave the surface area ratio 4.94:1. This electrolyte appears promising for porous nickel electrodes.

For porous silver electrodes, also of great potential interest, the prospects with concentrated KOH solution seem good since silver is not corroded and has, furthermore, a high hydrogen overvoltage. The investigations are being continued.

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