THE WORKING MECHANISM OF DIFFUSION ELECTRODES

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The double-layer nickel metalloceramic electrode of Bacon [1,2] represents a considerable advance in means of producing effective diffusion electrodes.

In order to understand the working mechanism of double-layer electodes, it was of interest to elucidate the roles of the fine porosity and coarse porosity layers in the kinetics of the electrochemical process at hydrogen and oxygen electrodes and to investigate the relation between electrochemical characteristics, electrode structure, and drop in pressure. Electrodes 3 mm thick were prepared from nickel powder obtained from nickel carbonyl. Changes in electrode structure were produced by adding to the main part (layer I) of the electrode various percentages of ammonium bicarbonate of different particle size. The finely porous layer (layer II), of thickness 0.3 mm, was made from nickel powder without NH_4HCO_3. The electrode structure was investigated by the Ritter and Drake method of forcing in mercury [3]. With our apparatus it was possible to measure pore distribution over the radius range 50 μ to 100 A [4].

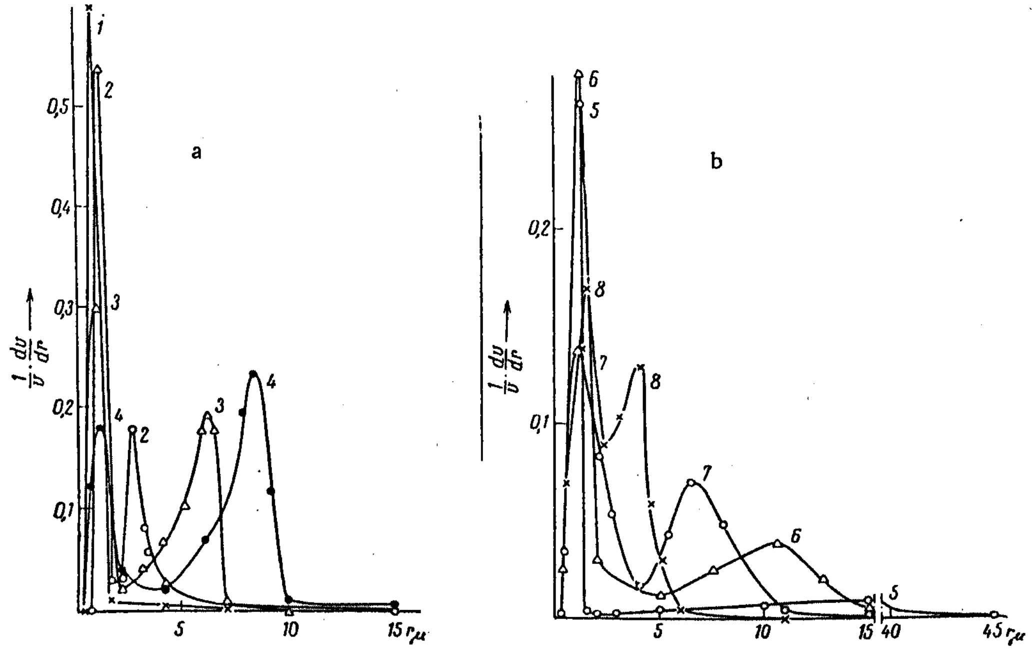

Fig. 1. The pore radius distribution function for electrodes of different structures. The curve numbers correspond to the structure numbers in Table 1.

The electrochemical measurements were carried out with 7 N KOH in a glass cell at 95°C, with atmospheric pressure on the electrolyte and with various pressure differences between gas and electrolyte (Δ p). Fig. 1 shows the results obtained as a function of pore radius. It is clear that there were two maxima for all the curves except 1, where the wide pore volume was extremely small. The second maximum corresponded to the widest pores formed by volatilization of ammonium bicarbonate. If the porosity of the second layer is subtracted from the porosity corresponding to the first maximum, then it is possible to determine the porosity of the narrow pores in the first layer (η_2).

TABLE 1

Structure No.	NH_4HCO_3, %	NH_4HCO_3 grain size, μ	η_0, cm^3/cm^3	η_1, cm^3/cm^3	η_2, cm^3/cm^3	S, cm^2/cm^3	r	i
	0		0,50					
1	5	44—61	0,49	0,008	0,48	70		30
2	10	44—61	0,62	0,12	0,50	750	2,5	82
3	20	44—61	0,74	0,46	0,28	1800	6,0	105
4	40	44—61	0,89	0,73	0,16	2000	8,7	48
5	20	270—580	0,57	0,32	0,26	360	20	18
6	20	104—140	0,63	0,42	0,21	860	9,5	35
7	20	44—61	0,62	0,39	0,23	1300	7,5	46
8	20	<44	0,60	0,36	0,24	1650	4,0	71

Note: η_0 is the total porosity, η_1 is the volume of the wide pores, η_2 is the volume of the narrow pores, S is the surface of the wide pores, r is the pore radius at the second maximum, i is the current density at ϕ = 180 mv and Δp = 100 for H_2 electrode.

It follows from these results that, for structures 5, 6, 7, and 8, the pore radius corresponding to the second maximum decreased considerably with decreasing size of the NH_4HCO_3 particles, and that the surface of the wide pores (S) increased. However, the total porosity of the electrode (η_0) and also the porosities corresponding to the wide and the narrow pores remained approximately constant. From the results obtained for structures 1, 2, 3, and 4, where the structural changes were produced by adding different amounts of NH_4HCO_3 to the electrode, it follows that increasing the amount of NH_4HCO_3 led to an increase in pore radius, while the surfaces of the wide pores of structures 2, 3, and 4 did not decrease as the result of the change in total porosity, but even increased slightly. Structures 1, 2, 3, and 4 were characterized by an abrupt change in the porosities of the wide and narrow pores.

The electrode structures 1, 2, 3 and 4 were baked at lower temperatures than were 5, 6, 7, and 8, so that structures 3 and 7 differed somewhat.

In order to elucidate the roles of coarsely porous and finely porous layers in the electrochemical process at a gas electrode, we carried out experiments in which the finely porous sealing-off layer was in one case made of nickel and in the other case of glass of the same grain size. These experiments showed that electrodes with both compositions of second layer had the same electrochemical activity. This established that the electrochemical process took place mainly on the walls of the wide pores.

An important characteristic, showing the effect of the structure of the two-layer electrode on the electrochemical activity, was the dependence of the latter on the pressure drop between gas and electrode. We investigated this relationship for both hydrogen and oxygen electrodes.. At a hydrogen electrode in alkaline solution, where hydrogen ionizes to form water: $2H_{ads} + 2OH^- = 2H_2O + 2e$, the relation between electrode potential (φ) and current density (i) was approximately linear owing to differences in accessibility of different parts of the surface for the occurrence of the electrochemical process. Fig. 2 and Table 1 show the relation between i and Δ_p, for φ = 180 mv, for hydrogen electrodes in the same solution. These electrodes had structures corresponding to those of Fig. 1. It follows from Fig. 2b that, with a low pressure drop, the electrochemical activity decreased with increasing pore radius of the coarsely disperse layer. It is evident from the S values for structures 5, 6,7, and 8, shown in Table 1, that the reason for this was that, with increasing pore radius corresponding to the second maximum, the total surface of these pores decreased. However, comparison of the S values for structures 1,2,3, and 4 with the data of Fig. 2a shows that, at low pressure drop, the change in electrochemical activity could not be explained only by the change in the value of the surface and the corresponding change in pore radius. This is discussed further below.

It is well-known that the reaction at the oxygen electrode is: $O_2 + 4e + 2H_2O = 4OH^-$. The potential of the nickel oxygen electrode is 300 mv more negative than that of a reversible oxygen electrode. As in the case of a hydrogen electrode, the relation between potential and current density was almost linear.

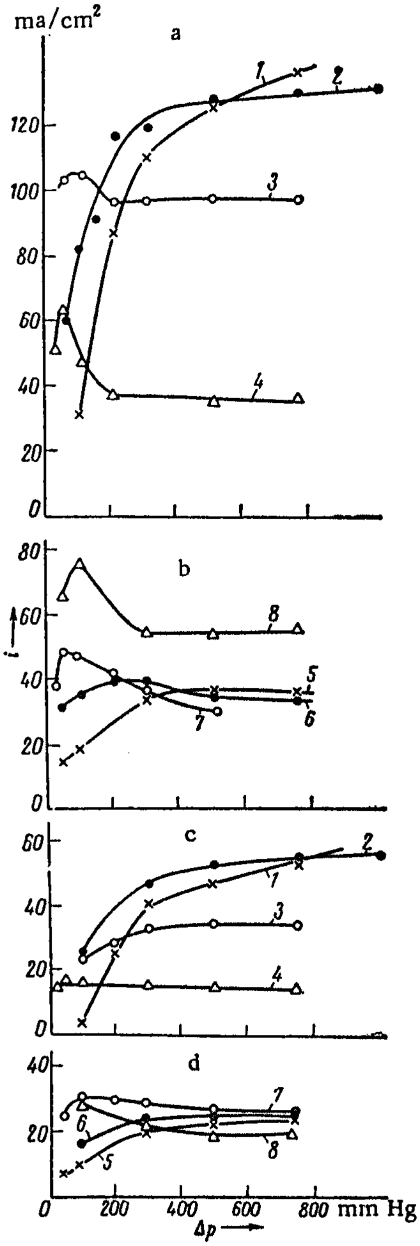

Fig. 2. Relation between the electrochemical activity and pressure drop for porous electrodes of different structures. The curve numbers correspond to the structure numbers in Table 1 : a), b) electrooxidation of hydrogen; c),d) electroreduction of oxygen ; t = 95°C.

Figures 2c and 2d show the results obtained in a study of the effects of pressure drop and electrode structure on the electrochemical activity of an oxygen electrode at φ = 730 mv with respect to a hydrogen electrode in the same solution. It is clear that there were some differences between the curves for hydrogen and oxygen electrodes. In particular, the i - Δp curves 3, 4, 6, 7, 8 for hydrogen electrodes had well-defined maxima, while only curves 7 and 8 showed maxima for oxygen electrodes. Differences in electrode wettability, resulting from potential changes, may have had some effect on the relation between electrode activity and pressure drop. When comparing the results of electrochemical changes as a function of pressure with data obtained from investigations of electrode structure, it must be noted that it was difficult to establish a linear relation between Δp and $\underline{r}$, particularly as there was very little data available on the angle of contact in wetting, etc, under the conditions used in our experiments. In the consideration of structural and electrochemical measurements we obtained more detailed results for the hydrogen electrode. It is clear from Fig. 2a and 2b that structures 3, 7, and 8 had their maxima on the i- Δp curves at a pressure drop of approximately 100 mm. If it is accepted that these maxima corresponded to the pressure at which the wide pores became emptied of electrolyte and filled with gas, then, in the case of structures 4, 5, and 6 which had the largest pore radius, the electrolyte should certainly have been displaced from the wide pores. The absence of a maximum on some of the i-Δp curves can be explained by postulating either that the wide pores differed little in radius from the narrow pores, or that the surface S was small (structures 1, 2, and 5).

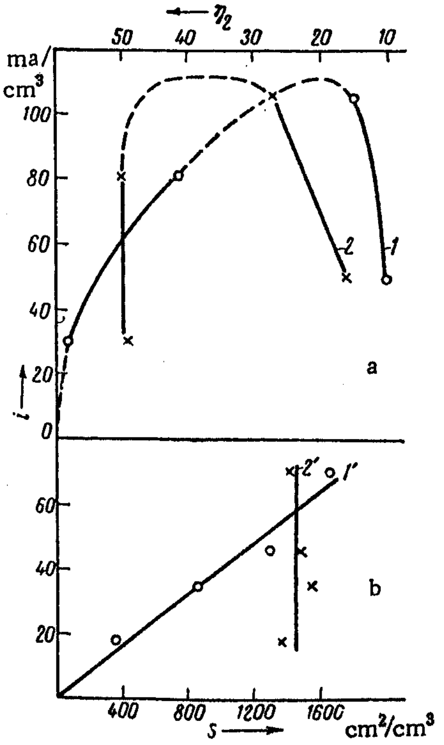

Fig. 3. The dependence of electrochemical activity on S (1, 1') and on η_2 (2,2'). a) Structures 1,2,3,4 ; b) structures 5,6,7,8.

Figure 3 shows the electrochemical activity (i at Δ_p = 100 mm H_g) as a function of S and of η_2. If η_2 did not alter much, the electrochemical activity was proportional to the surface (Fig. 3b). When η_2 decreased markedly, i decreased abruptly in spite of an increase in surface (Fig. 3a).

It follows from the above data that the electrochemical activity of the electrode did not only depend on the value of the surface where the electrochemical process occurred, but also on η_2, which was a measure of the total cross-sectional area of the narrow pores (assuming them to be of uniform length) conveying the electrolyte to the wide pores. The characteristics obtained for hydrogen electrodes, whose activity depended little on the pressure drop, clearly indicated that the structures had such a pore size distribution that the relation between cross-section of pores filled with electrolyte and surface of pores emptied of electrolyte varied little with pressure.

The results of this investigation enable us to present the following scheme for the operation of a porous gas electrode. The narrow pores, which are not emptied of electrolyte, serve to feed electrolyte to the wide pores. The electrochemically active gas enters the wide pores, which are emptied of electrolyte, and is adsorbed on the pore surface, and the reduction or oxidation reactions occur in the vicinity of the narrow pores. The optimum electrochemical activity is achieved when there is a definite relationship between the total cross-section of the narrow pores and the surface of the wide pores.

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