5. S. K. Verma and H. Wilman, J. Phys. D. Brit. J. Appl. Phys., 4, No. 12, 2051 (1971).
6. J. L. Marti and G. P. Zanza, Plating, 56, 377 (1969).
7. J. L. Marti, Plating, 53, 1 (1966).
8. R. K. Asher and W. B. Harding, Plating, 49, 783 (1962).
9. J. W. Wolf, J. Appl. Phys., 33, 1152 (1962).
10. M. Grand and J. Royon, Trait. Surface, 12, No. 107, 37 (1970); 12, No. 108, 29 (1971).
11. Galvanisches Vernickeln in Sulfamatbädern [Galvanic Nickel Plating in Sulfamate Baths], International Nickel Co., London and Dusseldorf (1964), p. 53.
12. Yu. M. Polukarov and Z. V. Semenova, in: Electrochemical Processing in the Electrodeposition and Anodic Dissolution of Metals [in Russian], Nauka, Moscow (1969), p. 39.
13. Yu. M. Polukarov and Z. V. Semenova, Élektrokhimiya, 12, 1153 (1976).
14. Yu. M. Polukarov, Z. V. Semenova, and V. P. Moiseev, Élektrokhimiya, 12, 1157 (1976).
15. Yu. D. Gamburg, V. V. Orlenko, and Yu. M. Polukarov, Élektrokhimiya, 8, 468 (1972).
16. A. A. Sutyagina and K. M. Gorbunova, Zh. Fiz. Khim., 35, 2515 (1961).
17. A. F. Grane, Plating, 55, 594 (1968).
18. O. Gal'dikene and A. Bodnevas, in: Bright Electrolytic Coatings [in Russian], Yu. Matulis (editor), Mintis, Vilnius (1969), p. 175.
19. A. Knodler, Oberfläche. Surface, 10, 39 (1969).

DETERMINATION OF THE SPECIFIC SURFACE AREA OF OXIDE CATALYSTS BY THE VACUUM-ADSORPTION TECHNIQUE

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UDC 541.13

It is a difficult task in studies of catalytic and electrochemical processes to determine the true surface areas of support and catalyst separately. This same problem arises when the adsorption properties of oxide catalysts supported by highly disperse carbons are investigated.

It is the aim of the present work to determine the specific surface areas of carbon-supported oxide catalysts with spinel structure which are used for the activation of oxygen and air electrodes in electrochemical power sources [1-4].

The supports used in the present work were PM carbon black with a specific surface area of ~120-150 m^2/g, PM carbon black activated for 4 h at 900°C in CO_2 flow, with a surface area of 450 m^2/g, and also MD carbon with ~700 m^2/g.

The cobalt spinels Co_3O_4, $MgCo_2O_4$, and $MnCo_2O_4$ were prepared in the pure form and on supports (with spinel concentrations from 1 to 80%) by thermal decomposition of the twice recrystallized nitrates of Co, Mg, and Mn using ratios Me^{2+}: Me^{3+} = 1 : 2 [5]. The composition of the oxides was checked radiographically [2, 3]. The combined surface areas of the oxide–support systems were measured by the BET method.

The specific surface areas of the carbon-supported oxides were determined by chemisorption from the amount of oxygen adosrbed from the gas phase at room temperature and a pressure of 0.1 mm Hg [6-8].

The measurements were conducted with samples which in advance had been degassed for 2 h at a temperature of 300°C and a pressure of 10^{-6} mm Hg.

The combined specific surface areas (S_C) of the samples measured by BET (in m^2/g) can be written as

$$S_c = S_1\alpha + S_2(1-\alpha), \quad (1)$$

where S_1 is the surface area of the oxide on the support, α is the fraction of oxide in the catalyst, and S_2 is the surface area of the carbon support.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 13, No. 10, pp. 1550-1553, October, 1977. Original article submitted June 11, 1976.

 0038-5387/77/1310-1326 $07.50

TABLE 1. Catalyst Parameters

Catalyst	S_c, m^2/g	Oxygen adsorption from the gas phase at p = 0.1 mm Hg			S_{oxide}, m^2/g
		$\cdot 10^{-19}$, atoms/g of catalyst	$\cdot 10^{-19}$ atoms/g of oxide	$\cdot 10^{-13}$, atoms/cm^2	
Carbon black	13	–	0,9	6,95	–
Co_3O_4	120–150	0,018	–	0,012	–
Carbon black (120 m^2/g) + Co_3O_4 in percentages of:					
1	140	0,126	11,3	7,2	160
7	133	0,76	9,4	6,85	134
14	137	1,5	9,65	7,0	142
21	156	2,2	11,0	7,5	158
40	140	4,4	10,9	7,0	157
60	106	2,88	4,8	7,0	69
80	75	0,76	0,95	7,3	13
$MnCo_2O_4$	5	–	0,25	5	–
Carbon black + 14% $MgCo_2O_4$	157	1,16	8,2	–	164
$MgCo_2O_4$	27	–	1,24	4,6	–
Carbon black + 14% $MnCo_2O_4$	134	0,96	7	–	150
Carbon black (450 m^2/g) + Co_3O_4 in percentages of:					
14	450	4,32	30	6,0	420
21	276	3,2	15,5	7,0	220
40	154	1,05	2,6	3,5	40

The adsorption, Γ (in mole/g), of oxygen from the gas phase on oxide-promoted carbon supports is given by Eq. (2):

$$\Gamma = S_1 g_1 \alpha + S_2 g_2 (1-\alpha), \quad (2)$$

where g_1 and g_2 are the values of oxygen adsorption on the pure oxide and on the carbon support, respectively (in mole m^2).

The combination of Eqs. (1) and (2) leads to the expression

$$S_1 = \frac{\Gamma - S_c g_2}{\alpha (g_1 - g_2)}. \quad (3)$$

Putting experimental values into Eq. (3) one can calculate the surface area of the oxide in the catalyst.

The results of the adsorption measurements are presented in Fig. 1 and in Table 1.

It can be seen from these data that oxygen adsorption on the carbon black with surface area 120 m^2/g (curve 1 in Fig. 1) amounts to 10^{11} atoms/cm^2. If it is reckoned that there are 10^{15} atoms per cm^2 of the carbon black [9], then the surface coverage of the carbon black under the experimental conditions $\theta \sim 10^{-4}$. Under the same conditions, the adsorption of molecular oxygen on pure cobaltites is significantly higher than that on carbon black; for Co_3O_4 with a surface area of 13 m^2/g (curve 2), for example, it amounts to $7 \cdot 10^{13}$ atoms/cm^2, which corresponds to $\theta \sim 0.1$. It was assumed in estimating θ that in a monolayer, one oxygen atom is adsorbed on the surface area with the oxide's crystal lattice parameter of ~ 4 Å [9]. Oxygen adsorption increases relative to that on pure carbon black and pure oxide when the cobaltites of Co, Mg, and Mn are added to the carbon black (curves 3-5); this effect depends relatively little on the nature of the divalent cation.

Oxygen adsorption on cobaltite-promoted carbon black increases with the surface area of the carbon black (curve 6) and with the percentage of cobaltite in the catalyst. It can be seen from the data presented in Fig. 2 that oxygen adsorption increases linearly over the range of Co_3O_4 concentrations from 1 to 40%. The specific surface area of the carbon-black-supported cobaltites as calculated from Eq. (3) is substantially higher than that of the pure oxides obtained under analogous conditions. The increase in specific surface area of the oxides which is found when they are supported on carbon black is due to catalyst dispersion on the support. The extent of dispersion of the cobaltites found when they are deposited on the carbon supports depends on the composition of the mixture and on the specific surface area and nature of the support. The specific surface area of the cobaltites becomes equal to that of the carbon black when they are deposited on carbon black (~140 m^2/g) up to an oxide level of 40%. At higher cobaltite levels the adsorption of oxygen decreases (Fig. 2), and the specific surface area of the cobaltite decreases accordingly (Table 1). Thus, with 80% Co_3O_4 on carbon black (~140 m^2/g), the surface area of the cobaltite is about 13 m^2/g.

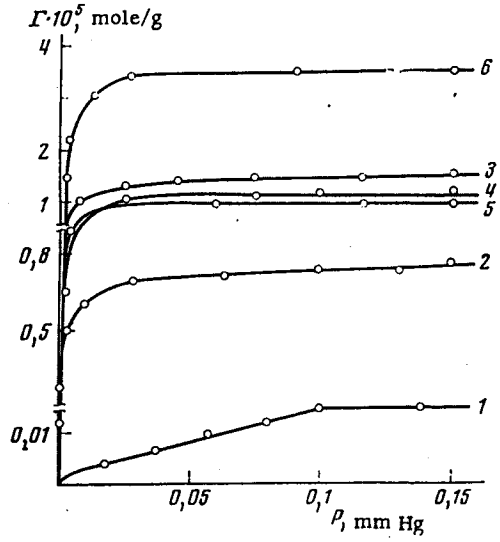

Fig. 1. Isotherms of oxygen adsorption from the gas phase on pure carbon black (S = 140 m^2/g) (1); on Co_3O_4 (2); on the above carbon black with 14% Co_3O_4 (3), with 14% $MgCo_2O_4$ (4), or 14% $MnCo_2O_4$ (5); and on carbon black (S = 450 m^2/g) with 14% Co_3O_4 (6).

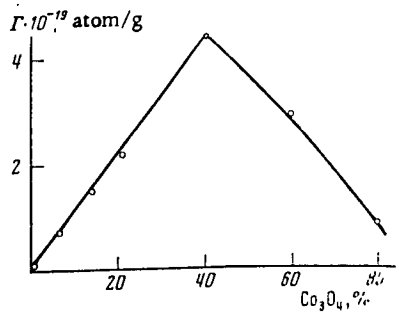

Fig. 2

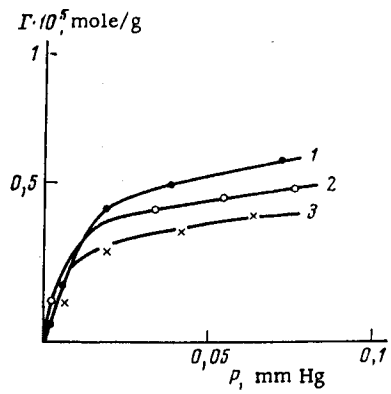

Fig. 3

Fig. 2. Oxygen adsorption as a function of the percentage of Co_3O_4 on carbon black with S = 140 m^2/g.

Fig. 3. Isotherms of oxygen adsorption from the gas phase on MD carbon (S = 670 m^2/g) (1) and on the same carbon with 1% Co_3O_4 (2) and 5% Co_3O_4 (3).

On carbon black with S = 450 m^2/g, the surface area increase of the cobaltite is found only up to an oxide level of 21% in the carbon black. The extent of dispersion of the cobaltites found when they are deposited obviously depends on the structure of the support particles. When the cobaltites are deposited onto active carbon having a high specific surface area and a developed system of micropores, oxygen adsorption not only fails to increase (Fig. 3) but it actually decreases somewhat (already in the range of oxide concentrations of 1 to 5%). This indicates that during the deposition of cobaltites on active carbon, the pores of the support become blocked with catalyst particles, which leads to a decrease in the surface area of the support and in its activity.

LITERATURE CITED

1. K. V. Kordesch, in: Handbook of Fuel Cell Technology, Prentice Hall (ed. by C. Berger), New Jersey (1968), p. 361.
2. R. Kh. Burshtein, M. R. Tarasevich, V. S. Silinskaya, F. Z. Sabirov, and A. M. Khutornoi, Élektrokhimiya, 9, 725 (1973).
3. R. Kh. Burshtein, M. R. Tarasevich, A. M. Khutornoi, V. S. Vilinskaya, F. Z. Sabirov, I. I. Astakhov, and G. L. Teplitskaya, Élektrokhimiya, 11, 1064 (1975).
4. M. R. Tarasevich, V. S. Vilinskaya, A. M. Khutornoi, R. Kh. Burshtein, F. V. Makordei, and Yu. A. Tkach, Élektrokhimiya, 12, 504 (1976).
5. T. V. Andrushkevich, L. M. Plyasova, A. A. Ostan'kovich, G. K. Boreskov, L. M. Nefeli, V. V. Popovskii, and G. D. Grazhdannikov, in: Methods of Investigating Catalysts and Catalytic Reactions, Vol. 3 [in Russian], Nauka, Novosibirsk (1965), p. 333.
6. R. Kh. Burshtein, N. A. Shumilova, and K. A. Gol'bert, Zh. Fiz. Khim., 20, 789 (1946).
7. R. Burshtein and N. Shurmovskaya, Surface Sci., 2, 210 (1964)
8. R. Kh. Burshtein, V. D. Kovalevskaya, and A. G. Pshenichnikov, Élektrokhimiya, 8, 1388 (1972).
9. J. d'Ans and E. Lax, Taschenbuch fur Chemiker und Physiker, Springer, Berlin (1943), p. 175.

POTENTIAL MEASUREMENT OF AN UNCHARGED BISMUTH SURFACE

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UDC 541.135

The reliability of uncharged surface potentials (usp) and null points is to a large degree dependent on the surface condition of the metal. Vagueness in describing surface preparation is probably the main reason for the scatter of data obtained by various authors. To decrease the scatter, measurements should be made on freshly formed faces and rapidly enough to exclude the possibility of surface contamination by impurities in the solution. Pachen [1] used this approach for measuring the usp of a mercury jet electrode. Metal-to-solution contact was made where the mercury stream broke into drops, thus minimizing the exposure time. The data were easily reproduced and quite reliable although no special care was used to purify the solutions.

These principles can be applied to solid metals if the usp is measured on cleavage faces of single crystals by an instantaneous contact or direct pulse method [2]. The single crystal must be split within the solution so that immediate contact is effected with the freshly formed surface. The solid metals capable of such measurements are Ge, As, Sb, Bi, and Mn.

We obtained usp values for freshly formed surfaces of Bi single crystals in 0.01 N HCl. The equipment is shown in Fig. 1. It consisted of a cell, a device for splitting the electrode, and a method for recording the signals produced.

In cell 1 was placed a conical glass core 2, filled with bismuth. The cleavage device consisted of a pin 3, a permanent manget 4, and a 30-cm-high guide tube 5. The recording apparatus consisted of an electrometer amplifier 6, a 1UT 971 integrated microcircuit (R_{max} = 680 mΩ) mounted on a base, a type S1-29 storage oscillograph 7, and a compensating voltage source 8. Sensitivity of the oscillograph was 0.100 V cm and the scanning rate was 2 to 5 m/sec. Measurements were made relative to a silver–silver chloride reference electrode 9. The cell was placed in an air thermostat, the grounded metal body of which served as an electrostatic shield.

One of the most important operations was to prepare the bismuth electrode. The process of filling the electrode with bismuth followed by a programmed cooling procedure to produce a single crystal was accomplished with especially constructed equipment consisting of a small electric furnace, a power pack, and a cooling controller with a clock drive. The electric furnace was essentially a Teflon-encased steel cylinder with a brass heat dissipator. The center of the steel cylinder contained a conical opening for the glass core and the upper cylinder section was grooved to accomodate a heating coil. The latter was actuated by a stable,

Kiev Polytechnic Institute. Translated from Élektrokhimiya, Vol. 13, No. 10, pp. 1553-1555, October, 1977. Original article submitted July 5, 1976.

0038-5387/77/1310-1329 $07.50