

Fig. 3. Change in the total pressure of the layer on the barrier in time (1 - experiment; 2 - calculation using (10): a) ash ($H_b = 0.165$ m; $V_0 = 0.767$ m/sec; $d_p = 23$ μ m); b) cinders of mercury-antimony concentrate ($H_b = 0.92$ m; $V_0 = 0.313$ m/sec; $d_p = 10$ μ m).

LITERATURE CITED

1. A. F. Ryzhkov and E. M. Tolmachev, *Teor. Osn. Khim. Tekhnol.*, **17**, No. 2, 206-213 (1983).
2. G. K. Klein, *Structural Mechanics of Loose Bodies* [in Russian], Moscow (1977).
3. G. M. Ostrovskii, *Pneumatic Transport of Loose Materials in the Chemical Industry* [in Russian], Leningrad (1984).
4. V. G. Bulychev, *Mechanics of Dispersed Soils* [in Russian], Moscow (1974).
5. I. I. Biekhman and G. Yu. Dzhanelidze, *Vibrational Displacement* [in Russian], Moscow (1964).
6. D. D. Barkan, *Vibration Method in Construction* [in Russian], Moscow (1959).
7. G. A. Geniev and M. I. Estrin, *Dynamics of Plastic and Loose Media* [in Russian], Moscow (1972).
8. I. F. Goncharevich and K. V. Frolov, *Theory of Vibrational Technique and Technology* [in Russian], Moscow (1981).
9. A. S. Kolpakov, "Intensification of heat and mass transfer in a bed of finely dispersed particles by vibrational fluidization in resonance regimes," Candidate's Dissertation, Technical Sciences, Sverdlovsk (1983).
10. M. V. Aleksandrov, V. V. Malyvshin, V. G. Bakalov, et al., *Inzh.-Fiz. Zh.*, **38**, No. 1, 23-28 (1980).
11. Yu. A. Buevich and G. A. Minaev, *Inzh.-Fiz. Zh.*, **28**, No. 6, 773-780 (1975).

ELECTROCHEMICAL PROPERTIES OF COMPOSITE MATERIALS BASED ON GRAPHITE AND VANADIUM DISILICIDE

N. P. Matveiko, P. G. Kramtsov,
and G. E. Slepnev

UDC 541.13

Electrodes with different composition were prepared by the method of pressing followed by sintering of the graphite and vanadium disilicide powders, and their electrochemical and corrosion properties in water solutions of electrolytes were studied.

Vanadium disilicide, as demonstrated in [1, 2], exhibits high corrosion resistance in water solutions of mineral acids owing to the formation of silicon oxide (SiO_2), which is insoluble in these electrolytes on its surface.

The high corrosion resistance of VSi_2 and its high electrical conductivity [3] suggest that this compound can be employed as an electrode material in carrying out cathodic and anodic electrochemical processes in water solutions of electrolytes.

It should be noted, however, that according to [4] a passive oxide film, exhibiting semiconductor properties with a large gap width, is formed on silicon with anodic polarization in water solutions of electrolytes. Because of the low conductivity of this film

Belorussian Polytechnic Institute. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 52, No. 5, pp. 802-707, May, 1987. Original article submitted February 20, 1986.

a large part of the jump in the potential is localized in the film and any anodic electrochemical processes are inhibited. As a result, vanadium disilicide can be used to carry out anodic electrochemical processes only in the case if the oxide film forming exhibits electronic conductivity. This is achieved, as a rule, by introducing different types of dopants, which either impart to the film extrinsic conductivity or serve as electrically conducting bridges in the oxide film formed [5].

It is of interest to study the effect of graphite dopants on the electrochemical behavior of vanadium disilicide in cathodic and anodic processes in water solutions of electrolytes.

The process of liberation of hydrogen at the cathode from solutions of sulfuric acid and also the processes of production of chlorine at the anode from NaCl solutions and potassium iodate from alkali solutions of KI were studied on electrodes prepared from a mixture of vanadium disilicide and graphite powders with different composition, employing the method of pressing under a pressure of 500 mPa followed by sintering in a hydrogen atmosphere at 1300-1400°K for 4 h.

It may be conjectured that in so doing the vanadium disilicide is preserved, while the graphite is in the free state, since the affinity of silicon and the metal is higher than that of graphite [3].

The samples prepared consisted of disks 12 mm in diameter and 3-4 mm thick. The volume porosity of the samples determined by the procedure of [6] equaled 10-16% with a graphite content of less than 80 mass % and 25% for a sample consisting of 80 mass % graphite. The resistivity, measured with the help of an MO-61 dc bridge, was virtually independent of the composition of the sample and equaled $1.75 \cdot 10^{-4}$ - $2.97 \cdot 10^{-4}$ $\Omega \cdot m$.

The polarization curves were measured with the help of a P-5848 potentiostat with a rate of change of the potential of 0.8 mV/sec in solutions of electrolytes prepared from chemically pure reagents in distilled water. The temperature of the solution was maintained constant with the help of a UT-15 ultrathermostat. In all cases the solution was mixed intensively with a magnetic mixer. The comparison electrode consisted of a chlorine-silver half-cell. The data presented below are the average values for four measurements.

As one can see from Fig. 1a the rate of the process is higher on electrodes containing 5 and 10 mass % graphite than on pure VSi_2 and electrodes containing 20 mass % graphite and higher, and at the same time as the graphite content increases the activity of the electrodes decreases gradually and approaches the activity of pure graphite. We observed this dependence of the activity of electrodes consisting of a metal disilicide and graphite on their composition previously, for example, for $MoSi_2$, WSi_2 , and $TaSi_2$. It is linked with the fact that small quantities of graphite, by increasing the conductivity of the oxide film, make the electrode more active than pure disilicide, but with a high content of graphite the activity drops, since the process begins to occur on sections of pure graphite also.

Chlorine is not liberated at the anode on an electrode consisting of pure VSi_2 (Fig. 1b). The significant current observed in this case, which is virtually independent of the potential, could be linked with the oxidation of the electrode material, and at the same time a mixed film of vanadium and silicon oxides apparently forms and vanadium is partially dissolved because of defects in this film and because of its low conductivity. It should be noted that for vanadium repassivation occurs with anodic polarization under such conditions already when $\varphi \geq 0.6$ V [7].

As graphite is added to the electrode the activity of the electrode during liberation of chlorine at the anode increases and approaches the activity of pure graphite (see Fig. 1b; curves 5-7). It should be noted, however, that the electrode and primarily the graphite inclusions dissolve at the same time. This can be observed visually in the change of the state of the surface. Corrosion tests have shown that for $i = 100$ mA/cm² and at a temperature of 20°C the consumption of the anode ranges from 0.9 g/1000 A·h for electrodes containing a large quantity of VSi_2 up to 3.7 g/1000 A·h for electrodes which are rich in graphite, and at the same time ~10% of the decrease in the weight is associated with the dissolution of vanadium.*

*Determined from the vanadium content in the electrolyte solution using the procedure described in [8].

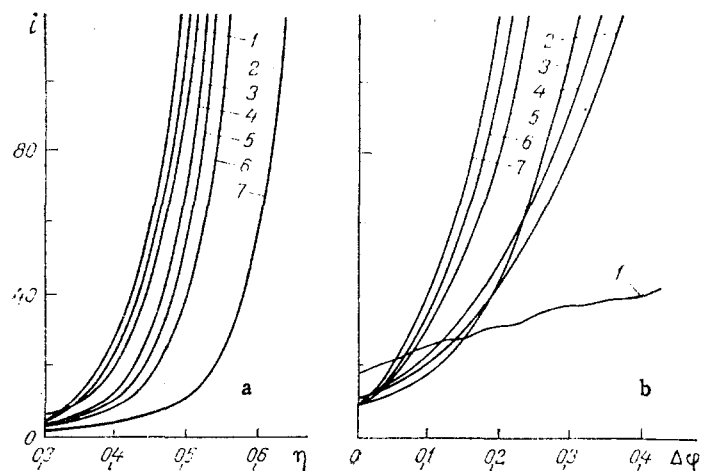


Fig. 1. Polarization curves of the process: a) hydrogen liberation from a 1.6 N solution of H_2SO_4 at the cathode and b) chlorine liberation from a 4 N solution of NaCl at the anode on electrodes prepared from a mixture of VSi_2 and graphite (mass %): 1) 100-0; 2) 95-5; 3) 90-10; 4) 80-20; 5) 50-50; 6) 40-60; 7) 20-80. The temperature of the solution equals 20°C . i , mA/cm^2 ; η and $\Delta\phi$, V.

Anodic oxidation of alkali water solutions of potassium iodide for all practical purposes does not occur on a VSi_2 electrode. This is attributable to the formation of a passive, electronically nonconducting film on the surface. The addition of graphite increases the electronic conductivity of this film and makes possible the oxidation of iodide to iodate. It should be noted that the activity of electrodes in this process (though it is not very appreciable) increases as the graphite content in the electrode increases, and approaches the activity of pure graphite. Thus for an electrode with 80 mass % graphite the polarization for $i = 120 \text{ mA}/\text{cm}^2$ is 50 mV lower than for an electrode with 5 mass % graphite.

The polarization curves for liberation of hydrogen at the cathode for all samples studied obey Tafel's equation in the current density range $10\text{--}120 \text{ mA}/\text{cm}^2$. The polarization curves for anodic oxidation of NaCl and KI for samples with 50 mass % graphite and higher obey Tafel's equation in the same current density range. In the case of samples with 5, 10, and 20 mass % graphite the Tafel dependence for anodic processes is preserved up to a current density of $80 \text{ mA}/\text{cm}^2$.

The coefficients a and b and the exchange current density were calculated from the rectilinear sections of the polarization curves in the Tafel coordinates [9]. The results are presented in Table 1. As one can see from the table, the coefficient b for liberation of hydrogen at the cathode gradually increases as the graphite content in the electrode decreases, which is probably attributable to the presence of an oxide film on the surface of electrodes which are rich in VSi_2 [4]. At the same time the true value of b is close in all cases to 0.118, and indicates that the reaction is limited by the electrochemical stage with the participation of one electron [9].

The distortion of the polarization curves associated with the presence of an oxide film on the surface of the electrodes and also with the fact that the electrode is dissolved as the main process proceeds leads to the fact that the coefficient b for liberation of chlorine at the anode is two and more times greater than the value characteristic for reactions with a slower single-electron transfer stage. At the same time, as one can see from Table 1, the value of the coefficient b increases as the graphite content in the electrode decreases. Of course, the porosity of the electrode also makes a significant contribution to our value of the coefficient b [10].

The coefficient b for anodic oxidation of iodide ions is virtually independent of the composition of the electrode and is close to 0.1. It is possible that even in this case the presence of an oxide film on the surface leads to some increase in the values of the coefficient b , which for pure graphite and glassy carbon equals 0.04-0.06 [11].

TABLE 1. Main Parameters of Electrochemical Processes on Electrodes Consisting of a Mixture of Graphite and Vanadium Disilicide at 20°C

Comp. of electrode (mass %)		Cathodic liberation of hydrogen (1.6 N H ₂ SO ₄)			Anodic liberation of chlorine (1 N NaCl)			Anodic oxidation of KI (1.2 N KI, 2g/1 of K ₂ Cr ₂ O ₇ , pH = 13.2)		
graphite	VSi ₂	a	b	$i_0 \cdot 10^7$ A/cm ²	a	b	$i_0 \cdot 10^5$ A/cm ²	a	b	$i_0 \cdot 10^5$ A/cm ²
80	20	0,76	0,12	4,67	0,96	0,21	2,69	0,31	0,10	3,71
60	40	0,68	0,13	21,8	0,92	0,21	4,17	0,32	0,10	2,69
50	50	0,66	0,13	31,6	0,81	0,24	13,8	0,33	0,10	1,94
20	80	0,65	0,13	38,0	0,78	0,22	19,5	0,33	0,09	1,94
10	90	0,63	0,13	56,2	0,74	0,30	30,2	0,33	0,08	1,94
5	95	0,62	0,14	67,6	0,79	0,32	17,4	0,34	0,07	1,38
0	100	0,65	0,15	38,0	—	—	—	—	—	—

Note. In calculating the exchange current density for each process we employed the lowest value of the coefficient b.

TABLE 2. Orders of Reactions and Values of the Effective Activation Energy ($A_{\Delta\varphi}$, kJ/mole) for Electrochemical Processes on Electrodes Consisting of a Mixture of VSi₂ and Graphite

Electrode comp. (mass %)		Liberation of hydrogen at the cathode			Chlorine liberation at the anode			Anodic oxidation of potassium iodide
VSi ₂	graphite	reaction order based on H ⁺ ions ($\Delta\varphi = 0,5$ V)	$A_{\Delta\varphi}$ in 1.6 N H ₂ SO ₄		reaction order accord. to Cl ion ($\Delta\varphi = 0,55$ V)	$A_{\Delta\varphi}$ in 4 N NaCl		order of reaction according to I ⁻ ions with $\Delta\varphi = 0,3$ V
			$\Delta\varphi = 0,4$ V	$\Delta\varphi = 0$		$\Delta\varphi = 0,5$ V	$\Delta\varphi = 0$	
100	0	0,86	32,93	61,70	—	—	—	—
95	5	0,88	21,39	53,17	0,50	30,18	63,82	1,33
90	10	0,93	35,46	67,80	0,76	33,94	61,75	1,26
80	20	0,90	34,89	61,65	0,83	32,89	61,60	1,22
50	50	0,88	36,72	67,93	0,73	30,05	60,53	1,20
40	60	0,78	31,46	60,55	0,61	22,30	59,40	1,17
20	80	0,92	30,89	59,87	0,85	28,60	61,70	1,06

Investigation of the effect of the pH and the temperature of the solution on hydrogen liberation at the cathode confirms the fact that this process is limited on all electrodes by the stage with the participation of one electron (see Table 2): the order of the reactions is close to unity, the value of the effective activation energy decreases with the overvoltage, and for $\Delta\varphi = 0$ corresponds to a value which is more characteristic for chemical than for diffusion processes.

The order of the reaction for anodic oxidation of chloride ions approaches unity, i.e., the value characteristic for this process, only on an electrode with 80 mass % graphite [12]. On all other electrodes the order of the reaction is less than unity, which is attributable to the oxidation state of the surface. The dependence of the effective activation energy on the polarization and its value for $\Delta\varphi = 0$ (see Table 2) indicate the slowness of charge transfer [13].

In the case of anodic oxidation of iodide ions the order of the reaction for all electrodes is greater than unity and at the same time increases as the graphite content in the electrode decreases.

Interesting results were obtained in the study of the effect of the temperature on the process of anodic oxidation of the iodide ions. Examination of the polarization curves for all electrodes studied reveals two features: 1) for weak polarization the currents increase as the temperature increase and 2) the rate of anodic oxidation of KI is independent of the temperature and it sometimes decreases as the temperature increases. It may be conjectured that in alkali water solutions (vanadium and silicon dissolve under these conditions [7, 4]) the rate of growth of the oxide film on the VSi₂ surface increases as the temperature increases, in spite of the fact that it is chemically stable in alkalis [3]. Chemical

TABLE 3. Anode Consumption in Preparation of a Potassium Iodate and Chlorine from the Following Solutions: 1.2 N KI, pH = 13.3 and 4 N NaCl, pH = 6.4. Temperature 20°C, Current Density 100 mA/cm²

Electrode comp. (mass %)		Potassium iodate production at the anode		Liberation of chlorine at anode	
VSi ₂	graphite	weighing method, g/1000 A·h	from analysis of solution for vanadium	weighing method, g/1000 A·h	from analysis of solution for vanadium center, g/1000 A·h
95	5	0.4	0.36	0.9	0.11
80	20	0.6	0.52	1.8	0.18
40	60	1.5	0.31	2.4	0.25
20	80	1.9	0.24	3.7	0.36

dissolution of the film, which also increases as the temperature increases, occurs at the same time.

The oxidation of iodide ions occurs on the surface of electrodes with an oxide film, which becomes thicker as the temperature of the solution increases. As a result of this as the temperature increases the potential drop in the film, which overlaps the drop in the polarization owing to the acceleration of the anodic oxidation of iodide ions, increases as the temperature increases, which leads to superposition of polarization curves at all temperatures studied, especially since the temperature coefficient of the rate of anodic oxidation of iodide ions, as established for graphite and glassy carbon [11], is small and equals about 1 mV/deg.

It should be noted that these effects are substantially reduced on electrodes with a high graphite content.

Corrosion tests of electrodes when obtaining calcium iodate, performed by the weighing method and from an analysis of the solution for the vanadium content [8], showed that for a current density of 100 mA/cm² and at a temperature of 20°C the consumption ranges from 0.4 g/1000 A·h for an electrode with 95 mass % VSi₂ up to 1.9 g/1000 A·h for an electrode with 20 mass % VSi₂, and at the same time in the first case the reduction in the mass of the electrode is associated primarily (90%) with the dissolution of VSi₂, while in the second case it is associated with the destruction of the graphite (Table 3).

LITERATURE CITED

1. G. Jangg, R. Kieffer, E. Prem, and E. Heidler, *Werks. Korros.*, **20**, 98-102 (1969).
2. G. Jangg, R. Kieffer, and H. Kogler, *Werkst. Korros.*, **21**, 699-703 (1970).
3. R. Kiffer and F. Benezovskii, *Solid Materials* [in Russian], Moscow (1968).
4. E. A. Efimov and I. G. Erusalimchik, *Electrochemistry of Germanium and Silicon* [in Russian], Moscow (1963).
5. N. D. Tomashov, T. V. Chukalovskaya, and G. P. Chernova, *Zashch. Met.*, No. 5, 547-552 (1972).
6. A. P. Baranov, G. V. Shteinberg, and V. S. Bagotskii, *Elektrokhimiya*, **7**, No. 3, 387-390 (1971).
7. A. Ya. Shatalov, T. P. Bondareva, and L. E. Tsygankova, *Zh. Prikl. Khim.*, **36**, No. 3, 588-594 (1963).
8. Z. Marchenko, *Photometric Determination of Elements* [in Russian], Moscow (1971).
9. L. I. Antropov, *Theoretical Electrochemistry* [in Russian], Moscow (1965).
10. R. G. Erenburg and L. I. Krishtalik, *Elektrokhimiya*, **4**, No. 8, 923-929 (1968).
11. N. P. Matveiko, G. E. Slepnev, and N. N. Pisarchik, "Electrochemical oxidation of potassium iodide in alkaline water solutions," Moscow (1984), Deposited in NIITEKhim, March 30, 1984, No. 276.
12. T. Yokoyama and M. Enyo, *Electrochim. Acta*, **15**, No. 12, 1921-1943 (1970).
13. S. F. Belevskii and S. V. Gorbachev, *Zh. Fiz. Khim.*, **36**, 742-746 (1962).