

# ELECTROCHEMICAL PROPERTIES OF VITREOUS CARBON SAMPLES OBTAINED AT DIFFERENT TEMPERATURES

Yu. B. Vasil'ev, L. S. Kanevskii,  
V. I. Lushnikov, and A. M. Skundin

UDC 541.138

A special place among the graphitic carbon materials belongs to vitreous carbon, which has high mechanical strength, stability in aggressive media, impermeability to gases, and isotropy of the mechanical, thermal, and electrical properties [1-3]. Papers concerned with the electrochemical properties of vitreous carbon have appeared recently in the literature [4-9]. But practically nowhere in this work has any attention been paid to the form of vitreous carbon used, or in particular to the temperatures at which it was produced, while it is known that a number of important physicochemical properties of this material, i.e., its structure, electrical conductivity, oxygen content, and other characteristics, strongly depend on the temperature at which the heat treatment was conducted during manufacture [1, 3].

In the present work we have compared some electrochemical and adsorption properties of various domestic brands of vitreous carbon which differed in the temperature of heat treatment: SU-9, SU-12, SU-20, and SU-30 where the temperature of the heat treatment is 900, 1200, 2000, and 3000°C, respectively. The SU-9 material is distinguished by insufficiently complete carbonization. It contains only about 91% carbon and more than 4% oxygen [3]. The remaining samples are almost completely carbonized, and SU-30 vitreous carbon already has the properties of partially graphitized material.

All investigations were performed at a temperature of 20°C in 1 N H<sub>2</sub>SO<sub>4</sub> ("os.ch." ["especially pure"] grade) in a cell with an auxiliary electrode of vitreous carbon and a reversible hydrogen reference electrode. A Tacussel PRT-20-10x potentiostat was used in the measurements. In order to examine the adsorption properties we recorded potentiodynamic  $i-\varphi$  curves using triangular potential sweeps with a rate of potential scan of 20 mV/sec. Stationary polarization curves were recorded when examining the kinetics of hydrogen and oxygen evolution. The techniques used in fabricating and preparing the electrodes of vitreous carbon are described in detail in [10]. The electrodes underwent cathodic and anodic activation over the potential range between 2.0 and -2.0 V before each  $i-\varphi$  curve was recorded.

Typical  $i-\varphi$  curves recorded on SU-9, SU-12, SU-20, and SU-30 vitreous carbon are reported in Fig. 1. It can be seen that there are two maxima on the anodic branches of all  $i-\varphi$  curves. It has been suggested in [6, 7] that these maxima are due to oxygen chemisorption, possibly in two different forms. It can be seen that the oxidation becomes somewhat easier as the temperature of the heat treatment of vitreous carbon is increased from 900 to 2000°C; the potentials of the first half-wave for samples SU-9, SU-12, and SU-20 are 0.75, 0.50, and 0.30 V, respectively. The potentials of the first maximum are 0.86, 0.62, and 0.52 V, respectively. The second anodic maximum is found at potentials of 1.6 to 1.7 V for all vitreous carbon brands examined.

On the cathodic branches of the  $i-\varphi$  curves recorded below the onset of oxygen evolution there are clearly pronounced maxima: one for samples SU-9 and SU-30, and two for samples SU-12 and SU-20. The potential of the first of these maxima, which probably is due to the reduction of chemisorbed oxygen [6, 7], is more positive the higher the temperature of heat treatment of the vitreous carbon. Thus, the adsorption and desorption of oxygen on vitreous carbon obtained at higher temperature proceeds less irreversibly. The potential differences between the first anodic and first cathodic maxima are 1.1, 0.6, and 0.4 V for the samples SU-9, SU-12, and SU-20, respectively (in [7] this difference was 0.4 V).

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from *Élektrokhiimiya*, Vol. 13, No. 3, pp. 440-443, March, 1977. Original article submitted May 10, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

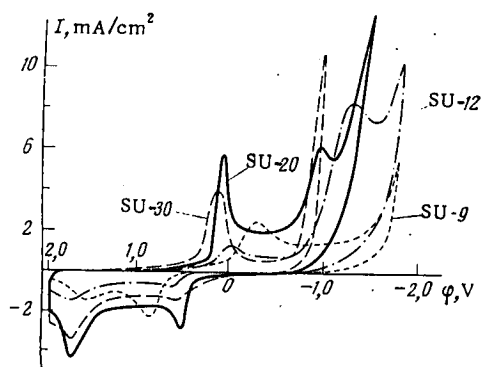


Fig. 1

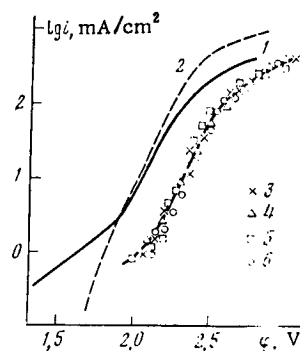


Fig. 2

Fig. 1. Potentiodynamic curves in 1 N  $\text{H}_2\text{SO}_4$  for different brands of vitreous carbon. Rate of potential scan 20 mV/sec.

Fig. 2. Polarization curves of oxygen evolution at pyrographite (1) and platinum (2), on different brands of vitreous carbon: SU-9 (3), SU-12 (4), SU-20 (5), and SU-30 (6).

The potential of the second cathodic maximum is  $-1.3$  V for sample SU-12 and  $-1.0$  V for sample SU-20. This maximum is not developed on sample SU-30, probably because of the lower hydrogen overvoltage; hydrogen evolution occurs at a perceptible rate already at potentials around  $-0.8$  V.

By integrating the anodic part of the  $i-\phi$  curves we calculated the corresponding amounts of charge passed between 0.0 and 2.0 V. It was found that these amounts for all the samples examined by far exceed the amount of charge required for monolayer coverage of the surface with oxygen. Thus, for the SU-12 sample we found about  $90 \text{ mC/cm}^2$  of apparent surface area. Only about  $0.5 \text{ mC/cm}^2$  is necessary for monoatomic coverage of the vitreous-carbon surface with oxygen (under the assumption that each adsorbed oxygen atom corresponds to one carbon surface atom). Such a large difference cannot be explained by a high roughness factor (of about 200). Experiments on low-temperature krypton adsorption have shown\* that the surface roughness factor of the vitreous carbon used in the present work is less than 10 (limit of detection). It may be that during the anodic polarization of vitreous carbon some bulk oxidation takes place, which is equivalent to an absorption of oxygen. It had been shown in [11] that on the surface of pyrocarbon there are hydroquinone groups which can be oxidized to quinone groups. It is possible that the structure of vitreous carbon (even at a production temperature of  $2000^\circ\text{C}$  it contains up to 1.5% hydrogen) also can take up some quantity of oxygen.

It can be seen that the hydrogen evolution overvoltage is not the same on the various samples, so that any comparison between the amounts of charge used up in the anodic and cathodic sweep is arbitrary. It must be noted, however, that (cf. Fig. 1) the amount of charge in the cathodic sweep,  $Q_c$ , which was obtained by integration in the limits from 1.0 V to the potential of hydrogen evolution is significantly higher than the quantity  $Q_a$  of oxygen from the bulk of the vitreous carbon. One can suggest that the higher  $Q_c$  values are due to some desorption obtained at temperatures above  $1000^\circ\text{C}$  is low (the SU-12 samples contained about 0.1 wt. % of oxygen), but it is still enough to explain the difference between  $Q_a$  and  $Q_c$ . Prolonged cycling over the potential range between 2.0 V and hydrogen evolution led to a gradual decrease of the  $Q_c$  value. It is characteristic that  $Q_c$  increases in the series SU-30, SU-20, SU-12, but decreases again as one goes to SU-9. This decrease undoubtedly is due to appreciable irreversibility of oxygen removal from this material.

The stationary polarization curves for the anodic process on vitreous carbon are reported in Fig. 2. This process consists of the evolution of oxygen as well as carbon monoxide and dioxide [6]. It can be seen that these curves practically coincide for all brands of vitreous carbon used here. The polarization curves are described by the Tafel equation with constants  $a = 1.5$  V and  $b = 0.24$  V. It can be seen that the slope of the polarization curves for the anodic process at vitreous carbon is the same as that at pyrographite and platinum, but the overvoltage at vitreous carbon is approximately 0.25 V higher than that at platinum.

\* These measurements were made in the Institute of Organic Catalysis and Electrochemistry, Academy of Sciences of the KazSSR, by V. Sh. Palanker to whom the authors express their profound gratitude.

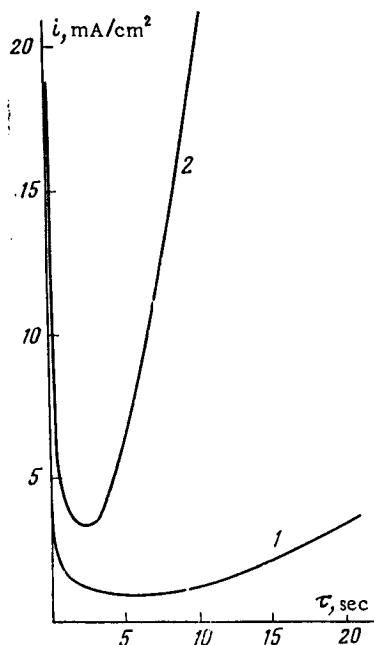


Fig. 3

Fig. 3. Potentiostatic curves of hydrogen evolution at SU-12 at -1.1 (1) and -1.4 V (2).

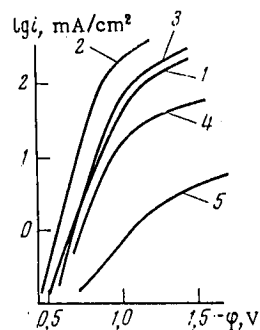


Fig. 4

Fig. 4. Polarization curves for hydrogen evolution at pyrographite (1) and at the reduced surfaces of different brands of vitreous carbon: SU-30 (2), SU-20 (3), SU-12 (4), and SU-9 (5).

The rate of hydrogen evolution at vitreous carbon depended strongly on its degree of oxidation; surface reduction led to noticeable activation. This result contradicts the data of [5, 9] where it was found that hydrogen evolution from alkaline solutions is accelerated when the vitreous carbon surface is strongly oxidized by chromic acid or by anodic treatment. Potentiostatic curves obtained at an SU-12 vitreous carbon sample when switching the potential from -0.5 V to values of -1.1 and -1.4 V are reported in Fig. 3. Right after the switching when the electrode surface is not sufficiently reduced, the current of hydrogen evolution is low but there is a significant nonstationary current due to reduction of the vitreous carbon. This nonstationary current falls off with time, but the stationary current of hydrogen evolution becomes higher with the progress in surface reduction.

Stationary polarization curves for hydrogen evolution at the reduced surfaces of different brands of vitreous carbon and at pyrographite are reported in Fig. 4. To become reduced the electrodes were held for 15 min at a potential of -2.0 V, and then for 1 min at 0.0 V, before the polarization curves were recorded. It can be seen that the polarization curves for hydrogen evolution at the different brands of vitreous carbon are markedly different. Hydrogen is evolved with the lowest overvoltage at SU-30 vitreous carbon, which is that produced at the highest temperature. The overvoltage increases as the temperature where the vitreous carbon is produced becomes lower, and the Tafel slope becomes higher: It is 130, 140, 280, and 390 mV for SU-30, SU-20, SU-12, and SU-9, respectively. The slopes for SU-30 and SU-20 are close to the values characterizing the other graphitic carbon materials [12].

Thus, with respect to the size of hydrogen overvoltage the different brands of vitreous carbon (which were obtained at different temperatures) are forming the same sequence as previously found for methanol oxidation [10].

#### LITERATURE CITED

1. B. Findeisen, *Technik*, **23**, 392 (1968).
2. V. D. Chekanova, in: *New Developments in Electrocarbon Manufacture* [in Russian], No. 3, Informstandart-élektro, Moscow (1969), p. 81.
3. V. D. Chekanova and A. S. Fialkov, *Usp. Khim.*, **40**, 777 (1971).

4. L. Dunsch, *Z. Chemie*, **14**, 463 (1974).
5. M. P. Brennan and O. R. Brown, *J. Appl. Electrochem.*, **2**, 43 (1972).
6. F. Hine, M. Yasuda, and M. Iwata, *J. Electrochem. Soc.*, **121**, 749 (1974).
7. D. Laser and M. Ariel, *J. Electroanal. Chem.*, **52**, 291 (1974).
8. H. E. Zittel and F. J. Miller, *J. Electroanal. Chem.*, **13**, 193 (1967).
9. R. J. Taylor and A. A. Humffray, *J. Electroanal. Chem.*, **42**, 347 (1973).
10. Z. F. Bezrukova, Yu. B. Vasil'ev, L. S. Kanevskii, E. P. Kovsryan, V. I. Lushnikov, N. T. Presnova, R. G. Pryadkina, G. A. Tarkhanov, and V. D. Chekanova, *Élektrokhimiya*, **12**, 783 (1976).
11. B. D. Epstein, E. Dolle-Malle, and J. S. Mattson, *Carbon*, **9**, 609 (1971).
12. T. Erdey-Gruz and H. Wick, *Z. Phys. Chem., Abt. A*, **162**, 53 (1932).

# KINETICS AND MECHANISM OF ELECTRODEPOSITION OF HEXAGONAL SELENIUM FROM STRONGLY ACIDIC ELECTROLYTES

V. M. Bigelis, A. Rakhmanov,  
and O. A. Abrarov

UDC 541.132+546.23

Hexagonal selenium ( $\gamma$ -Se) of the p-type can be deposited with relatively low overvoltage from strongly acidic electrolytes (840 g  $\text{SeO}_2$  per liter of 9 M  $\text{H}_2\text{SO}_4$  or  $\text{H}_2\text{SeO}_4$ ), and crystallizes at the highest rate at temperatures of 90–100°C [1]. Unlike the weakly acidic electrolytes where cathodic polarization is determined chiefly by the low concentration of minority carriers [2], in strongly acidic solutions the selenium electrode behaves like a reversible metal electrode, the only difference being that at high current densities the ohmic resistance of the electrode itself is felt [3]. It is possible, therefore, to examine in more detail the kinetic parameters and the mechanism, not only of the anodic but also of the cathodic process, which is not complicated by the electrode's semiconductor properties. This was the chief aim of the present work.

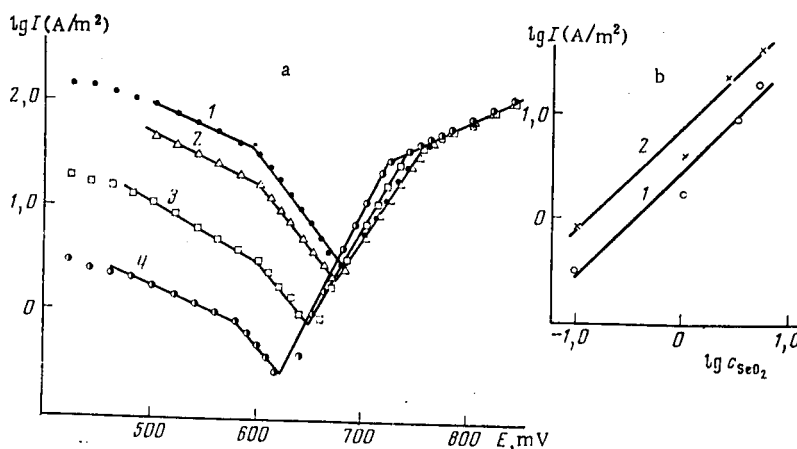


Fig. 1. Polarization curves of the selenium electrode in 9 M  $\text{H}_2\text{SO}_4$  solution as a function of selenium dioxide concentration (a), and the determination of reaction order with respect to selenium at potentials of 620 (1) and 580 (2) mV (b). Selenium concentrations in part a: 1) 5 M; 2) 3 M; 3) 1 M; 4) 0.1 M.

Institute of Nuclear Physics, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Élektrokhimiya*, Vol. 13, No. 3, pp. 443–447, March, 1977. Original article submitted May 17, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.