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The Influence of Carbon and Graphite Substrates on Electrochemical Properties of Epoxy-resin-impregnated Electrodes in Voltammetric Measurements. Part I. Preparation of Impregnated Electrodes from Electrode Rods Possessing Defined Properties

Wpływ rodzaju tworzywa węglowego i grafitowego na elektrochemiczne właściwości impregnowanych żywicą epoksydową elektrod do pomiarów woltamperometrycznych. Część I. Wykonanie impregnowanych elektrod z prętów o zdefiniowanych właściwościach

Влияние вида угольного и графитного материала на электрохимические свойства импрегнированных эпоксидной смолой электродов для вольтамперметрических измерений. Часть I. Изготовление импрегнированных электродов из стержней определенных свойств

INTRODUCTION

It has been generally known that electrochemical characteristics improvement of the electrode used in voltammetric measurements [1,2] is achieved by impregnation process. Though investigators devoted a lot of effort to impregnation techniques and construction of various types of electrodes [3,4], the information concerning the characteristics of materials used is rather scanty. Generally only symbols and produces of spectrographic rods can be found in literature [5-15] but even not all papers include this information [16-18].

Copeland et al. [2] made some efforts to study the influence of graphite density on wax impregnated electrode appli-

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cability in DPASV measurements. According to them the highest peaks in DPASV measurements, good reproducibility and sufficiently good mercury film covering can be achieved with the hardest and least porous graphite rods. In the case of very dense graphites, wax impregnation proved useless because the height of lead peaks (4μg/l) was the same on impregnated and unimpregnated electrodes. However, in their further studies, glassy carbon electrodes (GC) were used giving better results than those impregnated.

McLaren and Batley [19] studied the influence of graphite type and impregnators on impregnated electrode (IE) analytical applicability in DPASV measurements. According to them badly impregnated electrodes are characterized by high background current and so low hydrogen evolution overpotential that it disturbed Zn and Cd peaks. Moreover, the soft electrode of high porosity was less sensitive to Zn than that made of small porosity hard rod. Both electrodes were characterized by much shorter useful potential range even at pH=4,6 than that made of glassy carbon. As follows from the above mentioned examples, the influence of graphite type on IE electrochemical properties has been neglected and an electrode rod was treated somehow as one component homogeneous material without an internal structure.

The aim of this paper is to investigate the influence of material type i.e. initial material composition and technology used in electrode rod production on impregnated electrode properties.

RESULTS

Electrode rod production

Electrode rods were produced by Graphite Electrode Factory Racibórz, Poland using the scheme presented in Fig. 1. Rumanian calcinated petroleum coke and that produced by Conoco (USA) were used as solid materials. The mixture of tar and coal pitch was used as liquid materials (binder) and a saturant. After raw rod burn-off within 21 days to 1100°C, electrode rods further called carbon rods (resistance about 40 μΩM) according to the adopted nomenclature [23] were obtained.

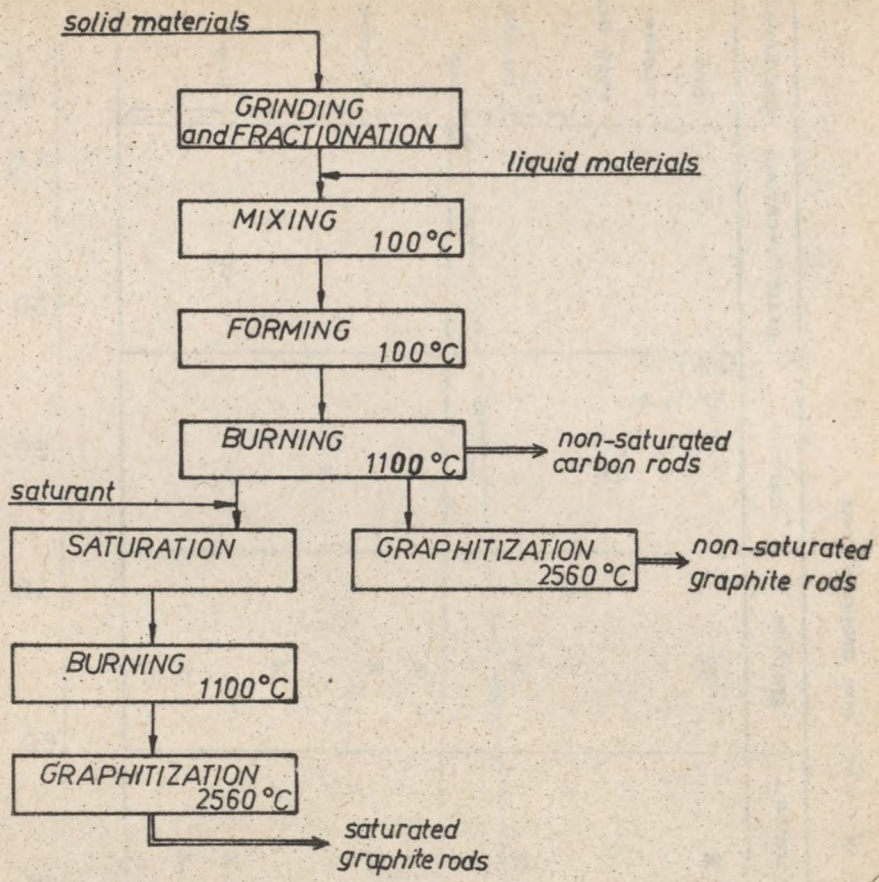


Fig. 1. The production scheme of electrode rods

Some of those rods were saturated. Then saturated and nonsaturated carbon rods being subjected to heat treatment to 2560°C for several hours resulted in saturated and nonsaturated graphite rods of the resistance of a few $\mu\Omega$m [20].

All rods of Rumanian coke were designated ROM and those of Conoco coke CON.

IE were also made of spectrographic graphite and carbon rods produced by Ringsdorff Werke (GFR) designated RW O, RW I, RW II (these symbols are also used in this paper) and of ELS 395 spectrographic rods (ELS 1 in this paper) produced by GEF

Tab. 1. Characteristics and designation of carbon and graphite rods

Rods	non-saturated	saturated	graphite	carbon	graphite-carbon	graininess
RW O		X	X			fine
RW I	X		X			coarse
RW II	X			X		very fine
ROM 1	X		X			coarse
ROM 2		X	X			
ROM 3	X			X		
CON 1	X		X			coarse
CON 2		X	X			
CON 3	X			X		
ELS 1	X		X			fine
ELS sc		X			X	
ELS 2		X	X			

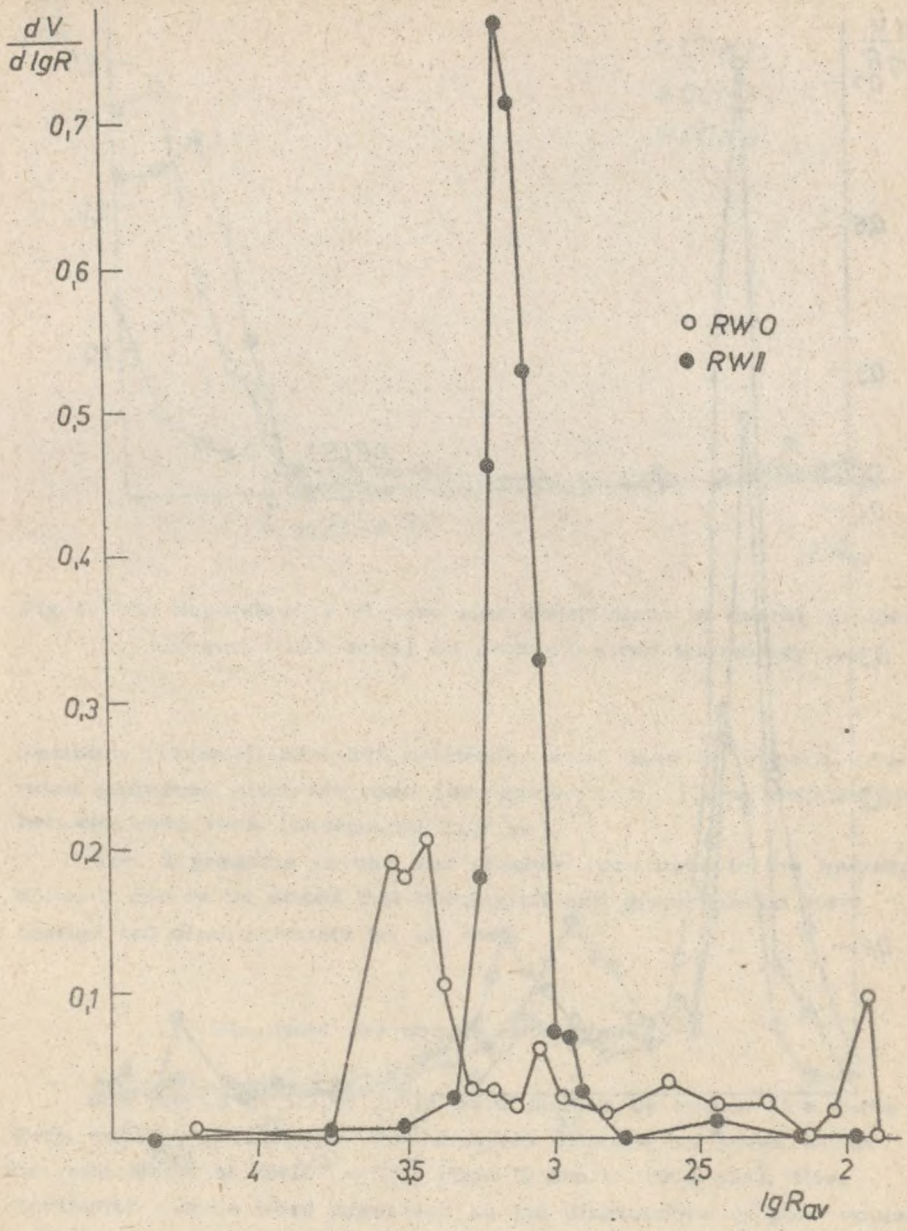
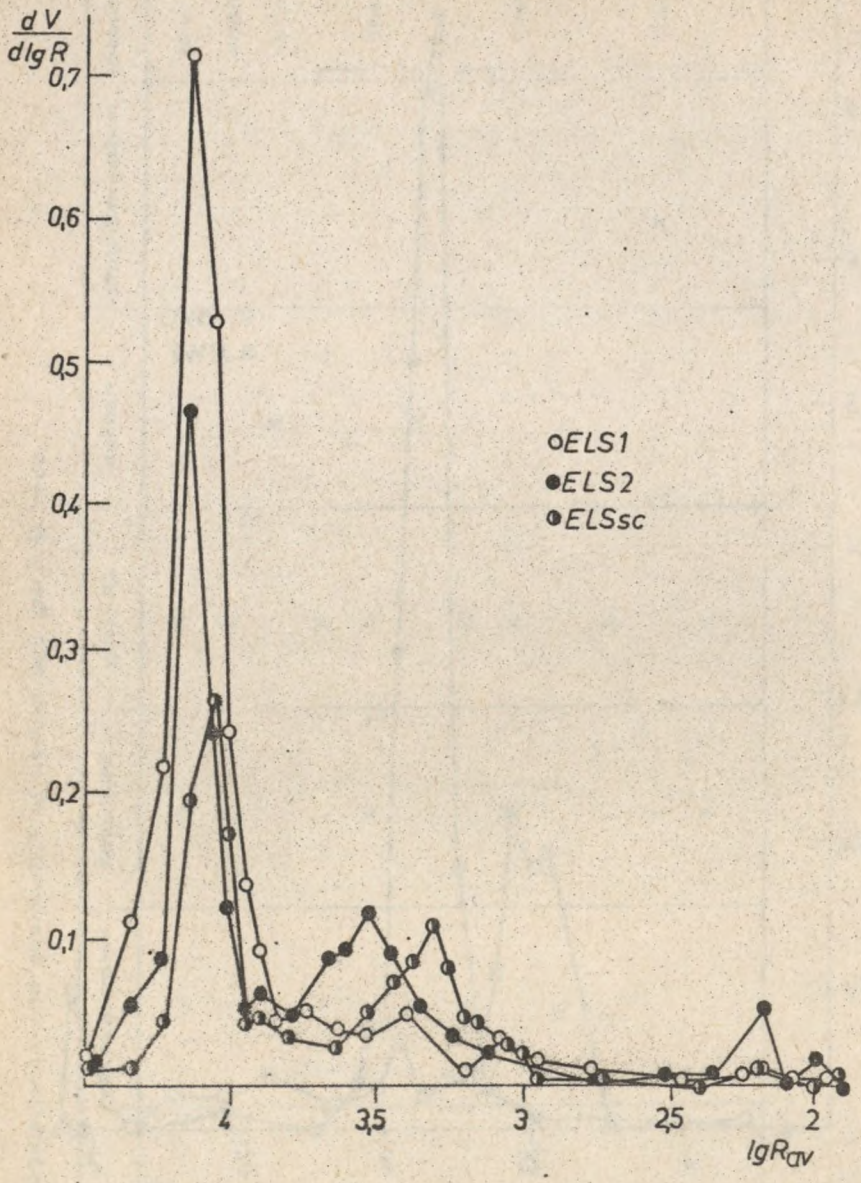
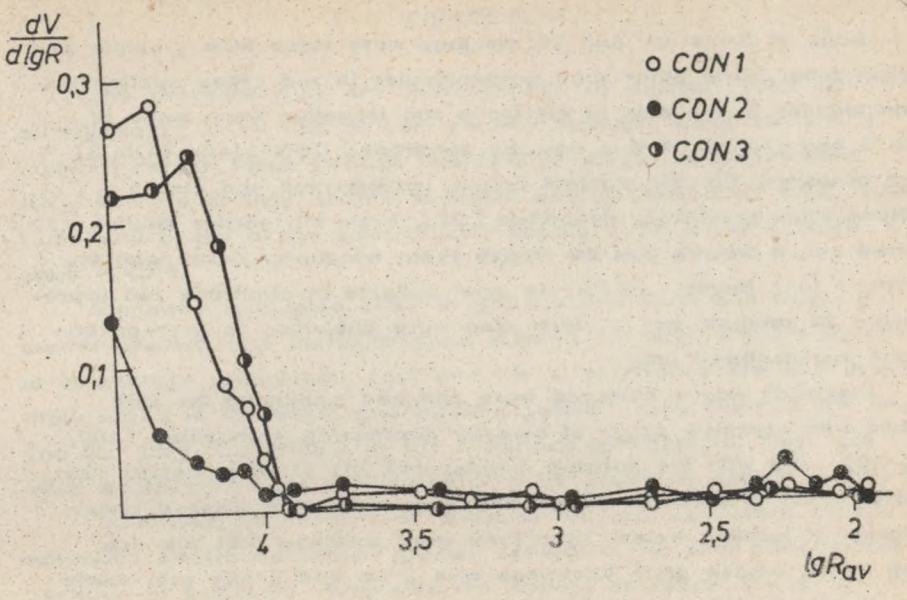


Fig. 2. The dependences of pore size distributions in RW O and RW II electrode rods



Rig. 3. The dependences of pore size distributions in fine grained material (ELS rods) on production rod technology



Rig 4. The dependences of pore size distributions in coarse grained material (CON rods) on production rod technology

Racibórz (Poland). ELS 395 electrodes were used to prepare saturated graphized electrode rods (designated ELS 2) and graphite-carbon electrode rods (designated ELS sc).

Tab. 1 presents carbon and graphite rods used in the investigations. It should be added that burning-off and graphitization were carried out simultaneously for all rods.

Electrode rod porosimetric studies

Rod pieces of 1,2 to 1,5 g were studied by means of a Carlo Erba mercury porosimeter. The analysis covered the pores within the radii range of $75 \cdot 10^3$ - 75Å (from 1 atm to 1000 atm). Pore distribution curves were presented as the distributions of pore volume dV/dlgR as a function of pore radius lgR average - fig. 2, 3, 4.

Impregnated electrode preparation

Rolls of ϕ = 4 mm and 20 mm long were made from graphite and carbon rods. Some other rolls perpendicular to rod cross section i.e. perpendicular to the axis of electrode rod formation were made of CON 1 and CON 2. In this way the electrodes CON 1⊥ and CON 2⊥ were prepared. Electric contact output, impregnation and curing methods were previously described [21]. From the earlier studies [22] carried out, it follows that the epoxy resin lekutherm X-100 with the hardener (M.) Bayer, (GFR) is most suitable in electrode rod impregnation. 28 profiles, two of each kind were subjected to impregnation in one manufactured unit.

Electrode active surfaces were polished employing the wet method with abrasive paper of steadily decreasing granulation (400, 600, 800) and with the polisher Montasupal 201 (GDR). Before using another sheet of abrasive paper, the electrodes were washed under a stream of running water. Then they were polished first with felc using Cr_2O_3 whose grain thickness was 1 um and finally with newly precipitated aluminium hydroxide. After thorough washing, the electrodes were drenched in diluted hydrochloric acid for 10 min. After rinsing with redistilled water, the electrodes were dried and kept in glass testtubes.

IE active surface microscopic studies

Electrode surface microscopic photographs were obtained using the metalographic microscope Neophot 2 (GDR) with two magnifications 80x and 400x - Fig. 5. It was possible to appreciate structural, granulation and density differences of materials from the photographs. Moreover, quality of impregnation process electrode surface conditions and polishing effect could be evaluated.

DISCUSSION

The prepared rods are characterized by different coke structure arrangement [23] - Fig. 5; from entirely isotropic electrode RW II made of carbon black through intermediate stages of leaflet whirl RW I to more orderly fibrous structure of Rumanian coke (ROM and ELS) and finally to the most orderly needle structure of Conoco coke (CON).

Electrode rods also differ in grain sizes. ROM and CON are coarse-grained (the maximum grain size is 0,2 mm), RW I electrode is of average granulation, ELS and RW O electrodes are fine grained while RW II is the finest grained of crystallite size being a few nm. (on the grey background in RW II surface photographs there are white spots which are admixtures of coke grains to carbon black).

Moreover, electrode rods possess different appearent density - saturated electrodes are of greater density - and also composition, because in saturated electrodes the amount encrease of the cokes formed after burning-off and graphitization of a saturant is observed.

To study rod thermal treatment effect i.e. the influence of rod graphitization degree on IE electrochemical properties, the rods of the same initial material composition but of different final heating temperature were made. The carbon electrodes (CON 3 and ROM 3) and graphite electrodes (CON 1 and ROM 1) were obtained. The average graphitization temperature was chosen to be 2560 ^{o}C.

Different rods, fine and coarse grained, isotropic and of great anisotropy, saturated and non-saturated, carbon and graphite as well as of mixed character (ELS sc) were prepared for investigations.

The dependences of pore size distributions in electrode rod technological process and kind of material used are presented in Fig. 2, 3, 4. It can be clearly seen that the fine grained and saturated rods (RWO) possess pores from medium to very small radii sizes - Fig. 2. Moreover, they are highly graphitized rods that points to high graphitization temperature used in the technological process. Hence, there is a relatively great amount of pores of small $R_{average}$ about 75Å. RW O rods are soft and difficult to be polished as Fig. 5 shows.

In the case of fine grained ELS electrodes, pores are of a few sizes but most of them are medium. The dependence of pore size distribution in fine grained material on production rod technology is shown

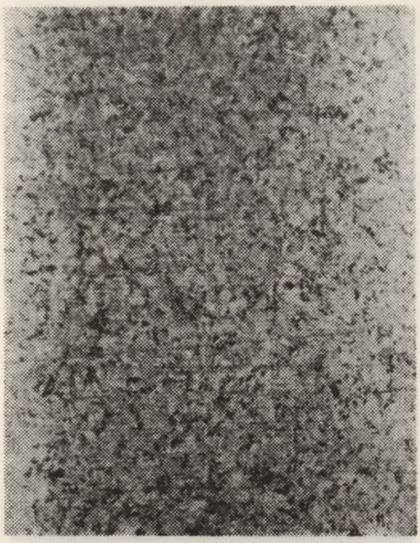
in Fig. 3. The greatest number and largest pores can be found in graphite ELS 1 but pores within the radii range of several hundreds to 75Å can scarcely be found. After saturation and heating of ELS 1 rods to 1100°C i.e. in ELS sc, considerable decrease of general pore amount and displacement distribution towards slightly smaller value pores are observed. Very small pores are also not observed. After graphitization of ELS sc. rods, then in ELS 2 rods obtained, general amount of pores increase as well as distribution change are observed in comparison with ELS sc. However, pore valume in ELS 2 is considerably smaller than in ELS 1 but new pores of 250-75Å appear. They are undoubtedly formed in a graphitized saturant. Then saturation decreases porosity but in the same way very small pores are formed and their impregnation in some cases may be difficult.

Pore size distribution in coarse grained material CON and its change during production process of carbon and graphite rods are presented in Fig. 4. Large pores dominate in this case. Carbon material CON 3 does not possess smaller pores than 4000Å. After CON 3 graphitization i.e. in the rods CON 1 contribution of very large pores slightly increases but medium size pores within the radii range of 4000-1000 Å appear. Very small pores are still absent. In the saturated graphite rod CON 2 the total porosity decreases significantly while medium size pores contribution increases which is accompanied by very small pores appearance. It has been confirmed once more that very small pores come mainly from graphitizated saturant.

Porosimetric measurement results of RW I and ROM rods were not given because they have similar pore size distributions to those of CON rods.

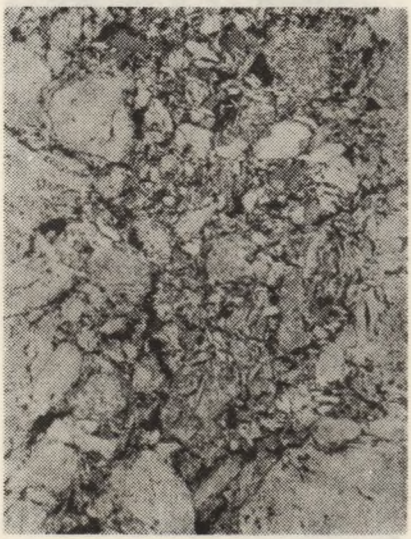
RW II rods proved to be quite interesting as material possessing one relatively narrow range of pores within the radii range of 1000-2000Å.

Studying the results for their applicability in impregnation particularly be relatively high viscosity and density agents, non-saturated electrode rods are preferable because very small pores contribution is the lowest. Then it becomes quite clear that C o p e l a n d et al. [2] have not observed property differences between unimpregnated and wax impregnated very dense rods, because wax did not impregnate very small pores. It resulted in much worse properties of these electrodes in comparison with glassy carbon ones.



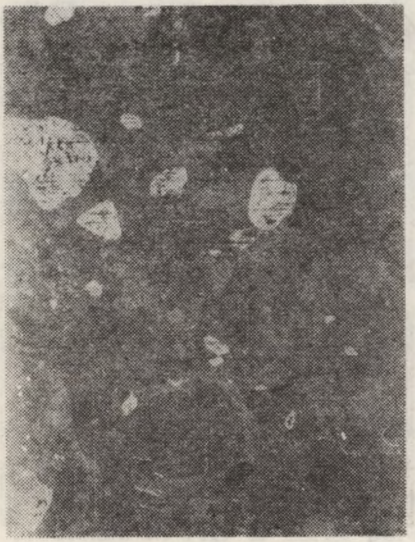
RW 0a

RW 0b

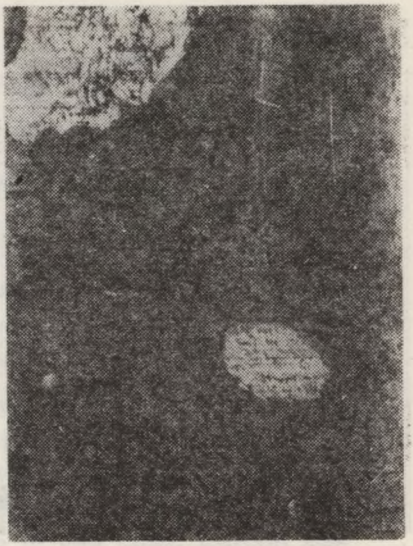


RW Ia

RW Ib



RW IIa

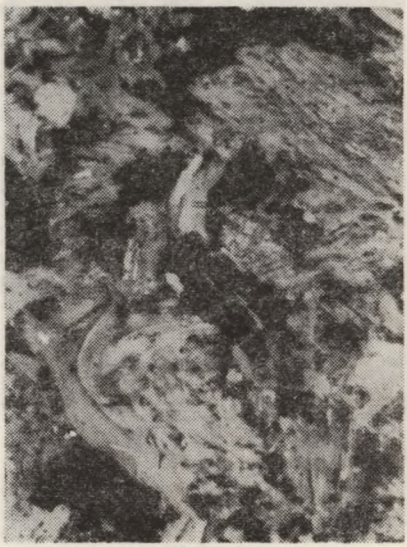


RW IIb

ROM 1a

ROM 1b

ROM 3a



ROM 3b

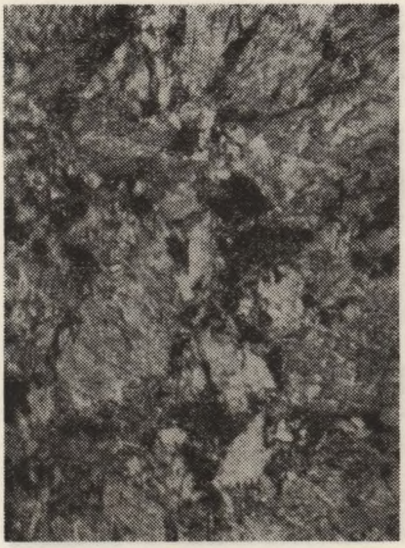
CON 1a

CON 1b

CON 1 ⊥ a

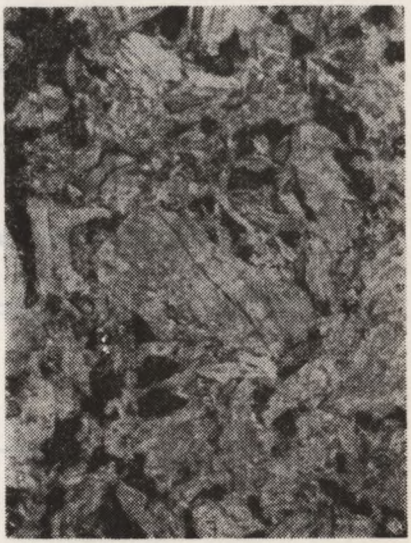
CON 1 ⊥ b

ELS 2a



ELS 2b

ELS_{SC} a



ELS_{SC} b

Fig. 5. The microscopic photographs of the electrode electroactive surfaces. Magnifications: a — 80×; b — 400×

Fig. 7. The microscopic photograph of impregnated electrode suspending in a cured resin phase

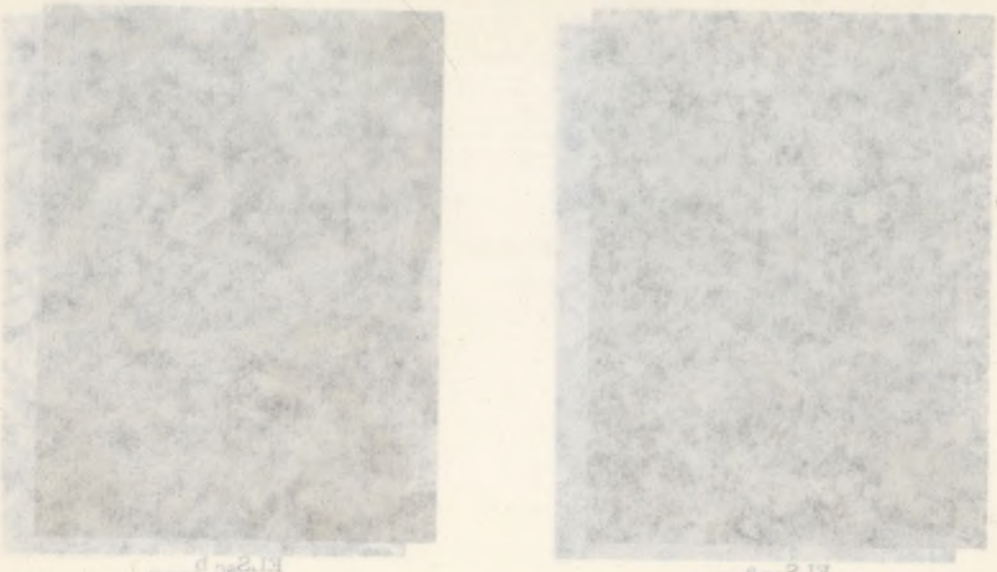
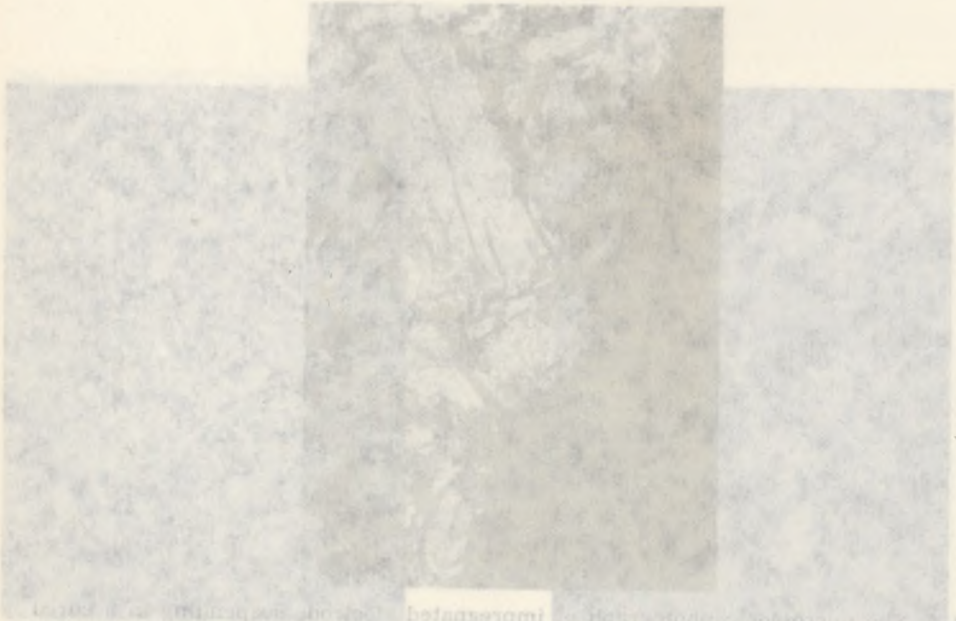


Fig. 5. The microscopic photographs of the electrode electroactive surfaces. Magnifications: a — 80×; b — 400×



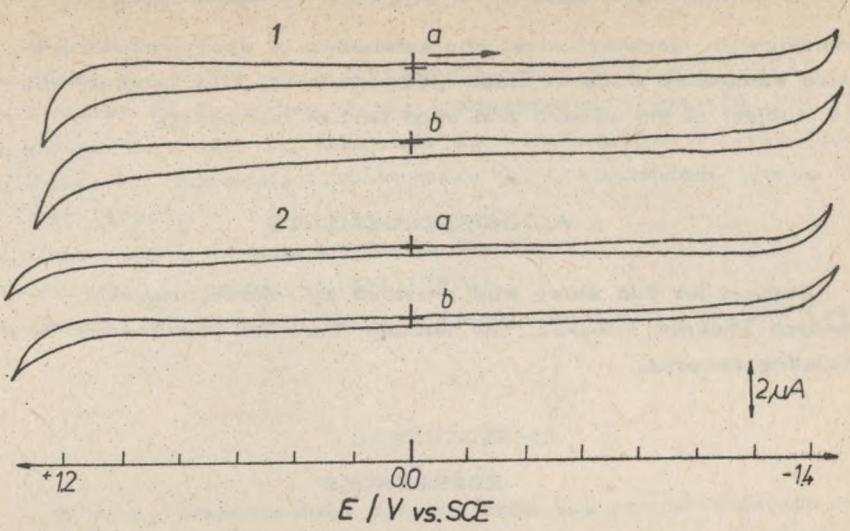


Fig. 6. The stability of IE electrochemical characteristics in time. 0,1 M $NaClO_4$; voltage scan rate 0,5 $Vmin^{-1}$; 1 - RW O, 2 - ELS 1, a - 1980 year, b - 1983 year

Porosimetric studies of epoxy-resin-impregnated electrodes did not detect pores in the measurement range of $75 \cdot 10^3$ - 75 Å.

Both IE active surface microscopic photographs and porosimetric studies proved that both impregnating agent and impregnation method were correct. The way of electrode preparation i.e. simultaneous impregnation of several scores of electrode rods and curing carried out under the same conditions allowed to obtain IE whose electrochemical properties depend largely on the properties of electrode rods. Thus the basic condition to achieve the aim of the investigations has been satisfied. Another condition - stability of IE electrochemical characteristics in time - has also been satisfied as it follows from IE curves obtained with the same two electrodes after 3 years - Fig. 6. Besides the way of electrode preparation [21] by suspending the impregnated electrode rod in a cured resin phase (Fig. 7) eliminates negative effect caused by impregnated rod insertion or pressing into a tube [24].

Satisfying these conditions made it possible to investigate the influence of material composition and electrode rod production

technology on electrochemical characteristics of epoxy-resin-impregnated electrodes made of these electrode rods. This problem will be a subject of the second and third part of our paper.

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STRESZCZENIE

W pracy przedstawiono schemat produkcji prętów elektrodowych węglowych i grafitowych o zdefiniowanych właściwościach. Do badań użyto różnego rodzaju pręty, tj. grubo- i drobnoziarniste, węglowe i grafitowe, izotropowe i o dużym stopniu anizotropii, nasycone i nienasycone. Przedstawiono wpływ rodzaju materiału i technologii produkcji na rozkład porów w prętach elektrodowych. Wykazano, że bardzo drobne pory pochodzą głównie ze zgrafitowanego syciwa. Przedstawiona metoda wykonania impregnowanych elektrod pozwala uzyskać elektrody, których elektrochemiczne właściwości są niezmienne w czasie, a zależą od rodzaju użytego prętą elektrodowego.

W pracy przedstawiono zdjęcia czynnych powierzchni impregnowanych elektrod.

РЕЗЮМЕ

В работе представили схему продукции электродных угольных и графитных стержней определенных свойств. Для исследований использовали разного вида стержни, т.е. крупно- и мелкозернистые угольные и графитные, изотропные и с большой степенью анизотропии, насыщенные и ненасыщенные. Показали влияние вида материала и производственной технологии на распределение пор в электродных стержнях. Доказали, что очень мелкие поры происходят главным образом из графитированной пропитки. Представленный метод изготовления импрегнированных электродов позволяет

получить электроды, электрохимические свойства которых неизменимы во времени, но зависят от вида примененного электродного стержня. В работе показали снимки активных поверхностей импрегнированных электродов.

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