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The Influence of Carbon and Graphite Substrates on Electrochemical Properties of Epoxy-resin-impregnated Electrodes in Voltammetric Measurements. Part II. Measurements in Positive Range of Potentials

Wpływ rodzaju tworzywa węglowego i grafitowego na elektrochemiczne właściwości impregnowanych żywicą epoksydową elektrod do pomiarów woltamperometrycznych. Część II. Badania w dodatnim zakresie potencjałów

Влияние вида угольного и графитного материала на электрохимические свойства импрегнированных эпоксидной смолой электродов для вольтамперметрических измерений. Часть II. Исследования в положительном диапазоне потенциалов

INTRODUCTION

It has been estimated that various types of graphite and carbon electrodes constitute 80 % of all electrodes used as working electrode in voltammetric (VA) and anodic stripping voltammetry (ASV) measurements [1]. B r a y n i n a and N e i m a n [1] as well as C l e m [2, 3] think that graphite impregnated electrode, most frequently used in VA measurements are at least as good as GC electrodes and recommended them becouse they are easily produced and prepared for measurements as well as commercially available.

On the other hand it has been stated [1] that impregnated electrode (IE) quality and forms of deposited metals including mercury film depend on the kind of substrate used. But the problem of the

influence of electrode rode type on IE quality has not been fully studied [4, 5]. D i e k e r et al. [6] have used in their studies of residual current by DC voltammetry, normal and differential puls VA different types of GC, paraffin impregnated graphite electrodes, carbon paste electrodes, Pt and Au electrodes. E i s n e r and M a r k [7] came to the conclusion that much more heterogeneous silver deposit is obtained on pirolytic graphite in comparison with that obtained on the impregnated graphite electrode which being poly-microcrystalline in nature has more active sites. .

Spectral graphite rods and graphite electrodes are assumed to be used in spectrographic measurements and in industry e.g. in Cl_2 production. The influence of such factors as: kind of component used, their proportions and technology on the final product quality is the subject of investigations carried out by investigation centres within industry plants. However, these investigations refer only to the basic application of graphite rods [8, 9, 10].

The influence of the above mentioned factors on electrochemical characteristics of IE (made of spectrographic rods) used in VA measurements has not been fully studied. The previous part [11] included the description of the method used in preparation of carbon and graphite materials possessing defined composition and technology. The aim of this paper is to study (part I) IE applicability in electro-chemical measurements carried out in positive range of potentials. An attempt has been made to fined qualitative dependences between material composition as well as technology and electrochemical charac-teristics of impregnated electrodes. Similar investigations were carried out on electrodes made of glassy carbon (Atomergie Chemetals Co. N.Y. USA).

EXPERIMENTAL

Reagents and solutions

The solutions were prepared with reagent grade or Suprapur chemicals and twice-distilled water. Standard solutions with the known Br^-, $[Fe/CN/_6]^{3-}$, $[Fe/CN/_6]^{4-}$, Ce^{3+} contents were prepared by diluting 0.1 M solutions with redistilled water and stored in polyethylene bottles rinsed with acid. Redistilled water was used throughout. The

solutions were stirred during the plating period by a metered high-
-purity nitrogen stream, which was also used to deoxygenate the so-
lutions. All the experiments were performed at ambient room tempera-
ture.

INSTRUMENTS

All voltammetric curves were recorded using a threeelectrode
arrangement with an instrumentation consisting of multiple voltammetric
analyser with programming of measurements, which was built in our
laboratory, equipped with an N306 X-Yrecorder (USSR). As a refe-
rence electrode the saturated calomel electrode was used.

Useful potential range and residual current

Cyclic voltammetric curves for all electrodes were recorded in
0,1 M solutions of $HClO_4$, $NaClO_4$ and KOH. 10 ml of solution were
poured into a measurement cell. The investigated electrode, SCE and
Pt electrodes were placed in a holder. The solution was deoxidized
for 10 min, whereby capillary outlet bringing nitrogen into the solution
was directed straight to IE electrochemical active surface [12].
Then nitrogen stream was passed over the solution. After 30s when
the solution was "calm" there were recorded VA cyclic curves from
the potential of 0,00V to the negative values. The potential scan rate
was 0,5 V min^{-1}. When the measurement was over the investigated
electrode was replaced by another one and nitrogen was passed
through the solution for another 5 min. Then VA cyclic curves were
recorded as previously. Using this method all electrodes were examin-
ed in the above mentioned electrolytes, whereby each series of
measurements was carried out without solution exchange. In the final
stage of each experimental series solution purity and measurement
reproducibility were examined recording the same cyclic curves for
the first two or three electrodes. The obtained dependences are
presented in Fig. 1-3. They result from the measurements repeated
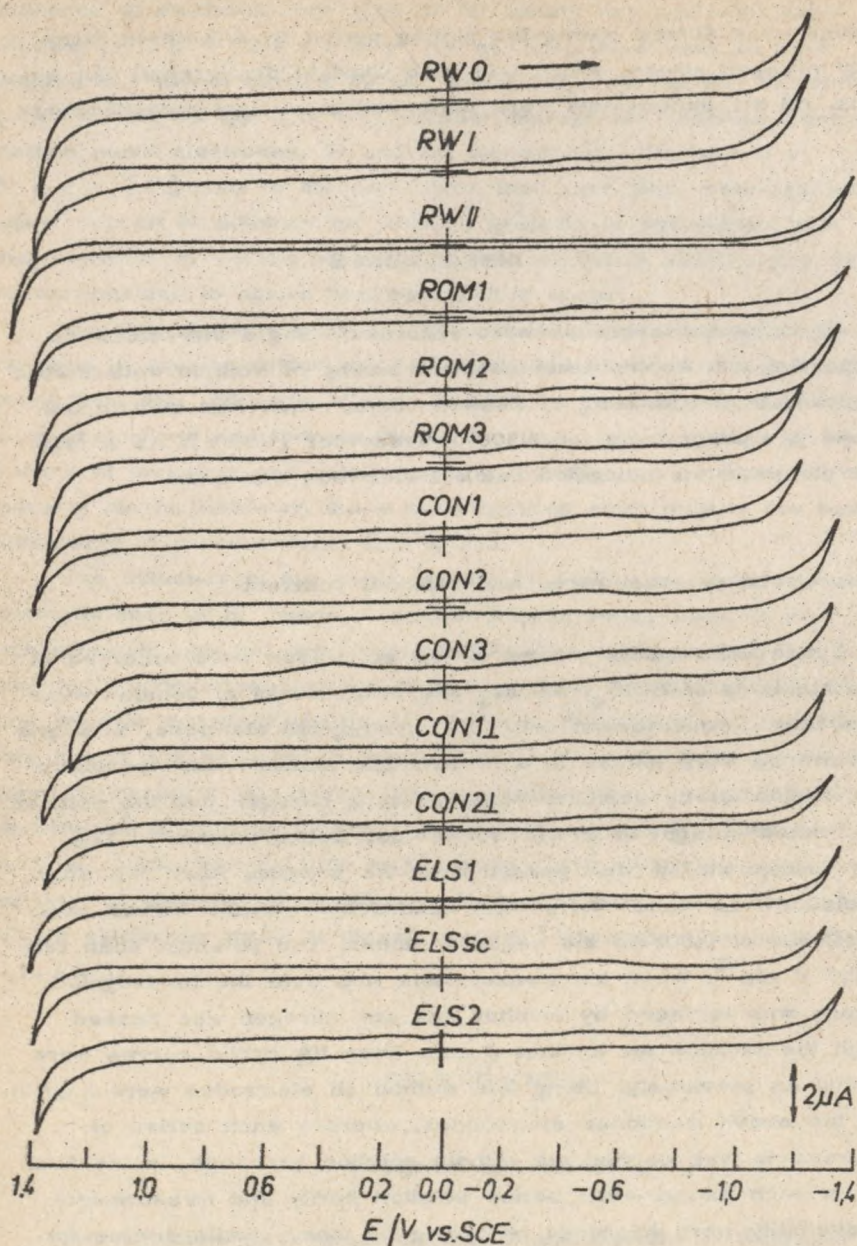several times for two series of examined electrodes.

Fig. 1. Useful potential range and residual current in 0,1 M HClO₄.
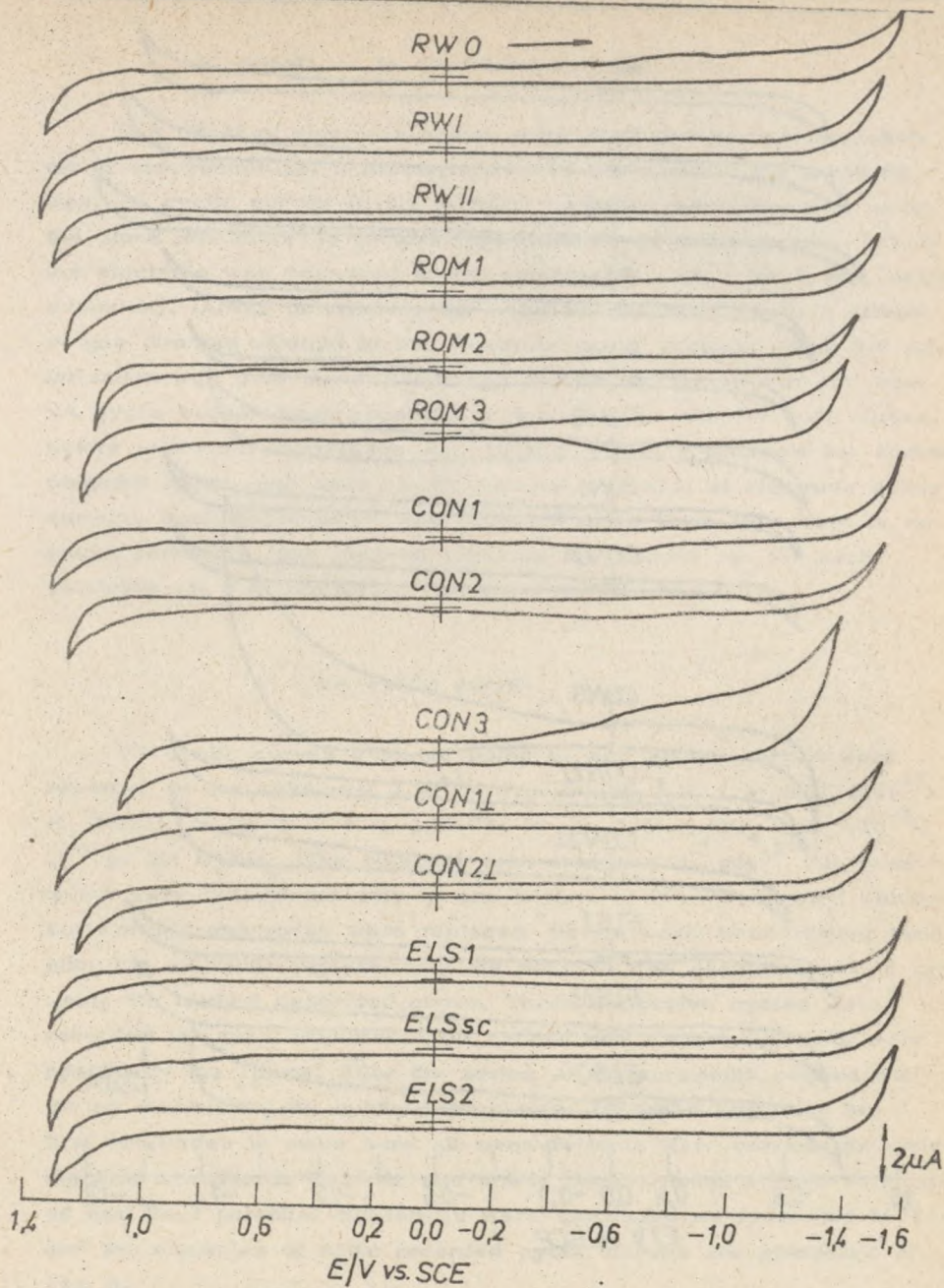Voltage scan rate 0,5 V min⁻¹

Fig. 2. Useful potential range and residual current in 0,1 M NaClO₄. Voltage scan rate 0,5 V min⁻¹
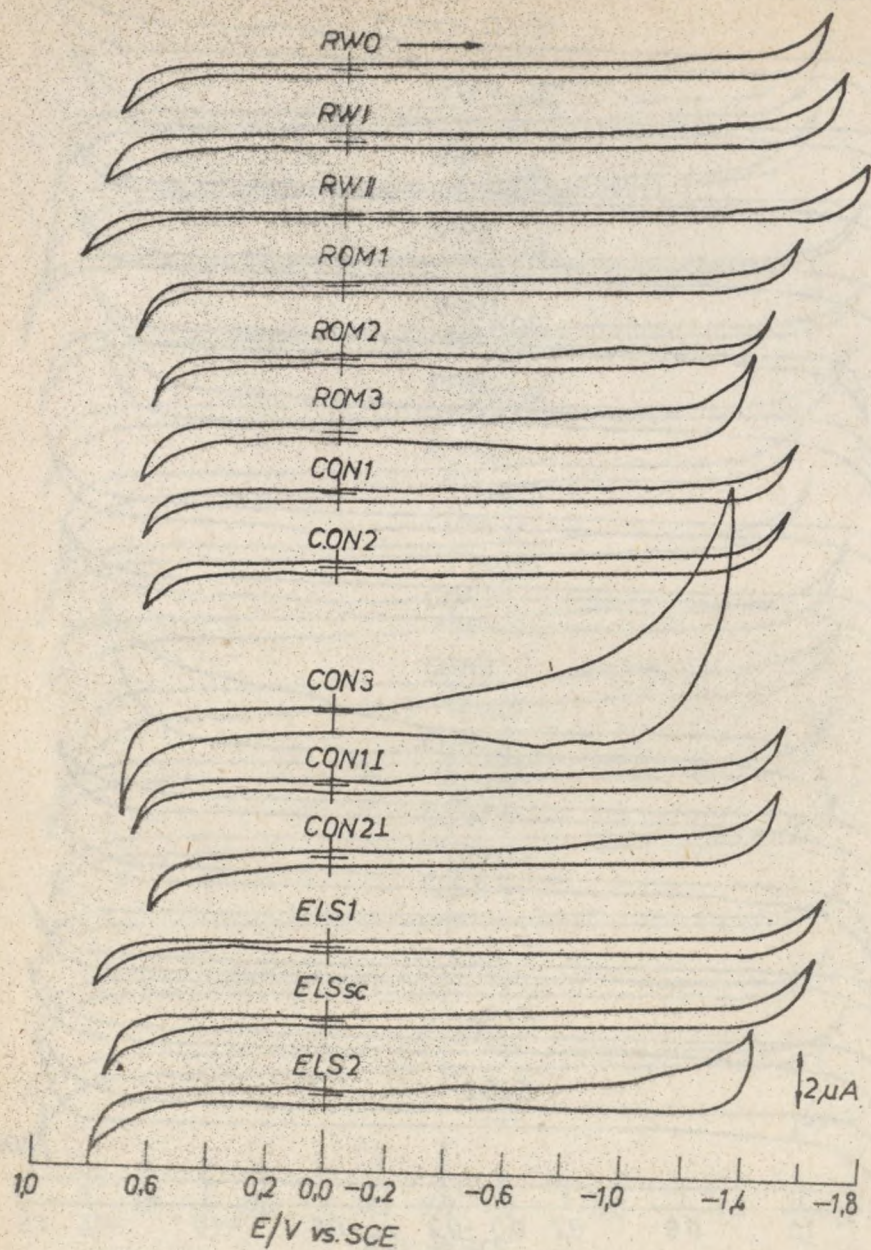
Fig. 3. Useful potential range and residual current in 0,1 M KOH. Voltage scan rate 0,5 V min^{-1}

IE resistance to electrochemical oxidation

The effect of electrode active surface electrochemical oxidation on IE electrochemical characteristics was examined in the following way. VA cyclic curves in $0,1$ M $HClO_4$ solution were recorded using the same procedure as in useful potential range determination. Then the electrode was polarized at the potential of $+1,5$ V for 3 min (oxigen evolution). During polarization the solution was stirred with a stream of gas directed straight to the electrode active surface. When the polarization was over the solution was doexidized for 10 min and next VA cyclic curves were recorded. Potential scan rate for both curves, before and after polarization was 1V min^{-1}. Fig. 4 presents the curves obtained before and after electrochemical oxidation of electrode active surface. Each dependence was recorded three times from zero to negative potentials. The diagram presents the second run for each electrode as it is practically the same as the next ones.

VA cyclic curves

VA cyclic curves obtained using IE and glassy carbon were recorded in the solutions: 2.10^{-3}M $K_3[Fe/CN/_6]$ in 1 M KCl, 2.10^{-3}M $K_4[Fe/CN/_6]$ in 1 M KCl, 1.10^{-3}M Br^- in 1 M H_2SO_4 and 5.10^{-3}M C^{+3} in 1M H_2SO_4. The potential scan rate was 1V min^{-1}. All measurements were carried out only in one portion of the investigated solution but working electrodes were replaced. Before each measurement (and after the electrode replacement) the solution was deoxidized for 5 min using the method described above. Three succesive cycles were recorded for each electrode. The second and successive runs were practically the same. After the series of measurements carried out for all electrodes, VA cyclic curves were recorded again for two first electrodes to make sure all measurements were carried out under identical conditions. Cathode and anode peak potentials were determined and their potential differences were calculated as presented in Tab.1. and the examples of some recorded cyclic curves are presented in Fig. 5.
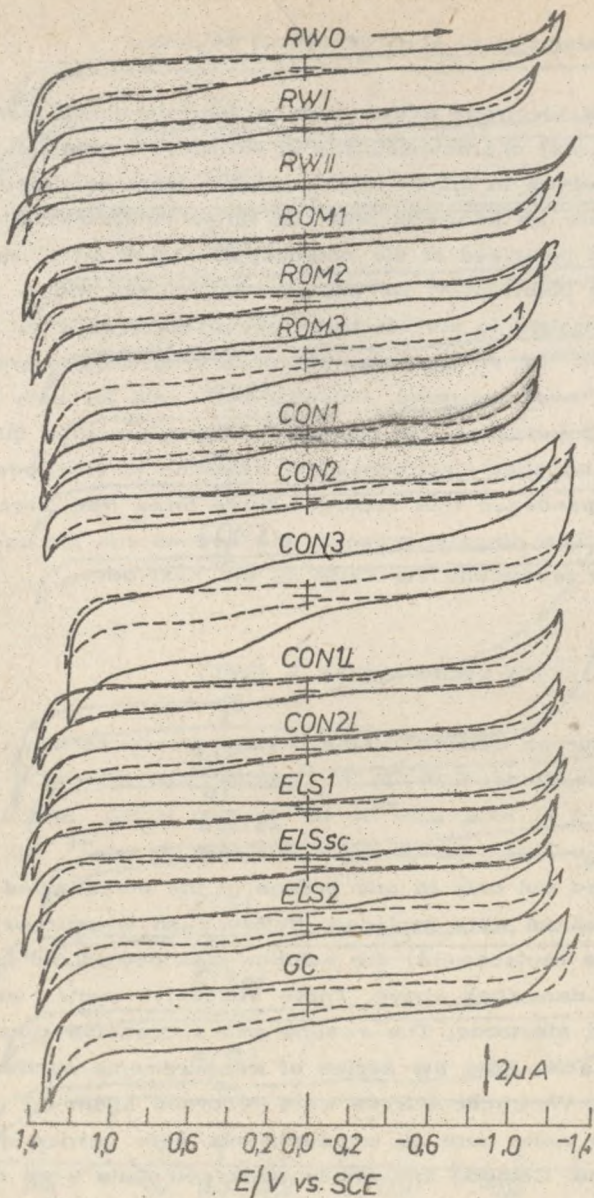
Fig. 4. IE and GC resistance to electrochemical oxidation in 0,1 M HClO$_4$. Voltage scan rate 1 V min^{-1}, (– – – –) before polarization, (———) after polarization at +1,5 V for 3 min.
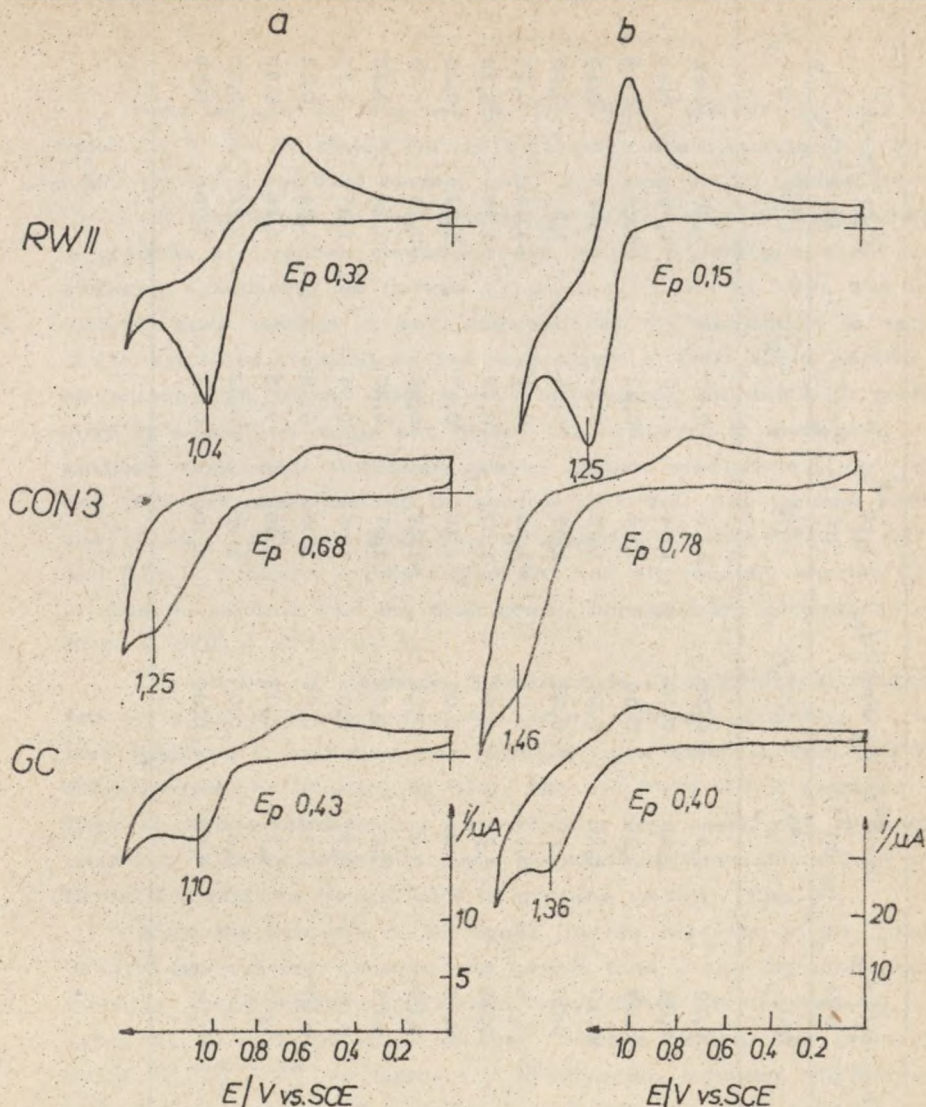
Fig. 5. Examples of the cyclic curves obtained for solution: (a) 1.10^{-3} M Br$^-$ in 1 M H_2SO_4; (b) 5.10^{-3} M Ce^{3+} in 1M H_2SO_4. Voltage scan rate 1V min^{-1}

Table 1. Voltammetric behaviour of tested electrodes in various examined solutions. Voltage scan rate 1V min^{-1}

Type of electrode	2.10^{-3} $K_3[Fe/CN/_6]$ in 1M KCl		2.10^{-3} M[K_4 Fe/CN/$_6$] in 1M KCl		1.10^{-3} M Br$^-$ in 1M H_2SO_4		5.10^{-3} M Ce^{3+} in 1M H_2SO_4	
	E_p^a/V	ΔE_p/V	E_p^a/V	ΔE_p/V	E_p^a/V	ΔE_p/V	E_p^a/V	ΔE_p/V
RW O	0,28	0,12	0,41	0,25	1,08	0,45	1,26	0,16
RW I	0,28	0,08	0,28	0,10	1,04	0,29	1,26	0,13
RW II	0,28	0,09	0,29	0,09	1,04	0,32	1,25	0,15
ROM 1	0,28	0,10	0,29	0,09	1,05	0,37	1,26	0,16
ROM 2	0,28	0,08	0,27	0,06	1,07	0,36	1,25	0,16
ROM 3	0,27	0,08	0,28	0,07	~1,15	0,53	~1,45	0,73
CON 1	0,27	0,06	0,27	0,05	1,07	0,40	1,28	0,18
CON 2	0,27	0,06	0,26	0,05	1,10	0,47	1,32	0,25
CON 3	0,28	0,07	0,27	0,06	~1,25	0,68	~1,46	0,78
CON 1⊥	0,27	0,06	0,27	0,06	1,05	0,32	1,28	0,18
CON 2⊥	0,26	0,06	0,27	0,05	1,06	0,34	1,27	0,17
ELS 1	0,28	0,07	0,28	0,07	1,04	0,28	1,24	0,13
ELS 2	0,28	0,05	0,27	0,05	1,06	0,35	1,28	0,18
ELS sc	0,27	0,06	0,27	0,06	1,05	0,32	1,24	0,15
GC	0,27	0,06	0,28	0,06	1,10	0,43	1,36	0,40

Discussion and results

From i-E curves recorded in $0.1M$ $HClO_4$ and $NaClO_4$ and KOH solutions it can be stated that all electrodes are characterized by relatively small residual current (RC) and long useful potential range (UPR). It constitutes an experimental evidence of good impregnation of graphite and carbon electrodes and proper polishing of their active surfaces. Comparing i-E curves (Figs. 1-3) it can be seen that a strongly basic medium is most differentiating for electrodes. In each of the examined electrolytes but particularly in $0.1M$ KOH, carbon electrodes ROM 3 and CON 3 have significantly shorter UPR particularly in a positive range and higher RC compared to analogous graphite electrodes. Moreover, coarse grained electrodes (CGE) ROM and CON are characterized by shorter UPR than fine grained electrodes (FGE) RW II and ELS. The saturated electrodes ROM 2, CON 2 and ELS 2 possess a little higher RC and significantly shorter UPR in alkaline medium than the analogous nonsaturated graphite electrodes ROM 1, CON 1 and ELS 1.

The studies of electrode resistance to electrochemical oxidation proved to be very interesting. All carbon materials including GC are less resistant to oxidation than graphite ones which is indicated by RC increase and shorting of UPR. The electrode RW II made on the base of carbon black shows exceptionally high resistance to electrochemical oxidation. Moreover, this electrode is characterised by the lowest RC and the widest UPR in alkaline medium (Fig. 3).

From the analysis of VA cyclic curves recorded in the solutions of ferro-ferricyanide, bromide and cerium ions it can be concluded that there are no significant differences in electrode electrochemical behaviour in potential range of small positive values. The greatest value of $(E_p^a - E_p^k)$ in ferro- and ferricyanide solutions are achieved with RW O electrode. It probably results from its softness (the highest graphitization temperature) which causes improper polishing of its active surface.

The greatest differences in electrochemical behaviour of electrodes occur when measurements are carried out in the range of large positive potentials - oxidation of bromide ions to free bromine and cerous ions to cerium ions. Two effects influence oxidation curves of bromide ions

e.g. oxidizing effect of the evolved bromine and work at the potentials higher than + 1V (evolution of oxygen).

The greatest shift of peaks is achieved with carbon electrodes ROM 3 and CON 3 as well as with GC. It clearly follows from Tab. 1 that these materials are unsuitable to carry out measurements in this range of potentials. The electrode RW II is an exception as it is made of quite different material namely of carbon black. As for other electrodes one can see that much greater shift of peaks is achieved in the case of Br⁻ than cerous ions oxidation, though in the latter case it takes place at more positive potentials. It results from the oxidizing properties of the generated free bromine.

RW O electrode, not taking carbon ones into account, gives greater shift of peaks compared to others. It is probably due to change of graphite material resistance to oxidation in relation to graphitization temperature [13]. RW O electrode being strongly graphitized is less resistant to free bromine than other electrodes but in the case of cerous ion oxidation it gives close to other electrodes (excluding carbon electrode) dependences. It allows to carry out quantitative determination of Ce^{3+} in 1 M H_2SO_4 solution even using RW O electrode Fig. 6.

From VA cyclic curves of bromide ion oxidation Tab. 1 it follows that coarse grained electrodes ROM and CON have slightly greater peak shifts than fine grained ones. CGE ROM and CON are made of high orderly structure cokes – fibrous and needle structures – which are probably less resistant to oxidizing agents. It results from the fact that high orderly structures possess diversified active centres. The most active centres situated along plane edges of each coke layer can be easier poisoned (destructed) by an oxidizing agent. Cyclic curves obtained with FGE ELS, also made of fibrous cokes, confirm this supposition. The peak shifts in this case are slightly smaller than those obtained with CGE ROM. Becouse of smaller coke grains, the active electrode surface is less orderly. Then the contribution of grain edges of cokes and saturants is significantly greater than that of coke plane edges. Moreover, coke grains are spatially ordered to a less degree while forming rods than in the case of CGE.

The analysis of cyclic curves of cerous ion and particularly bromide ion oxidation gives information about saturant effect on electrode resistance to electrochemical oxidation. Chemical oxidation
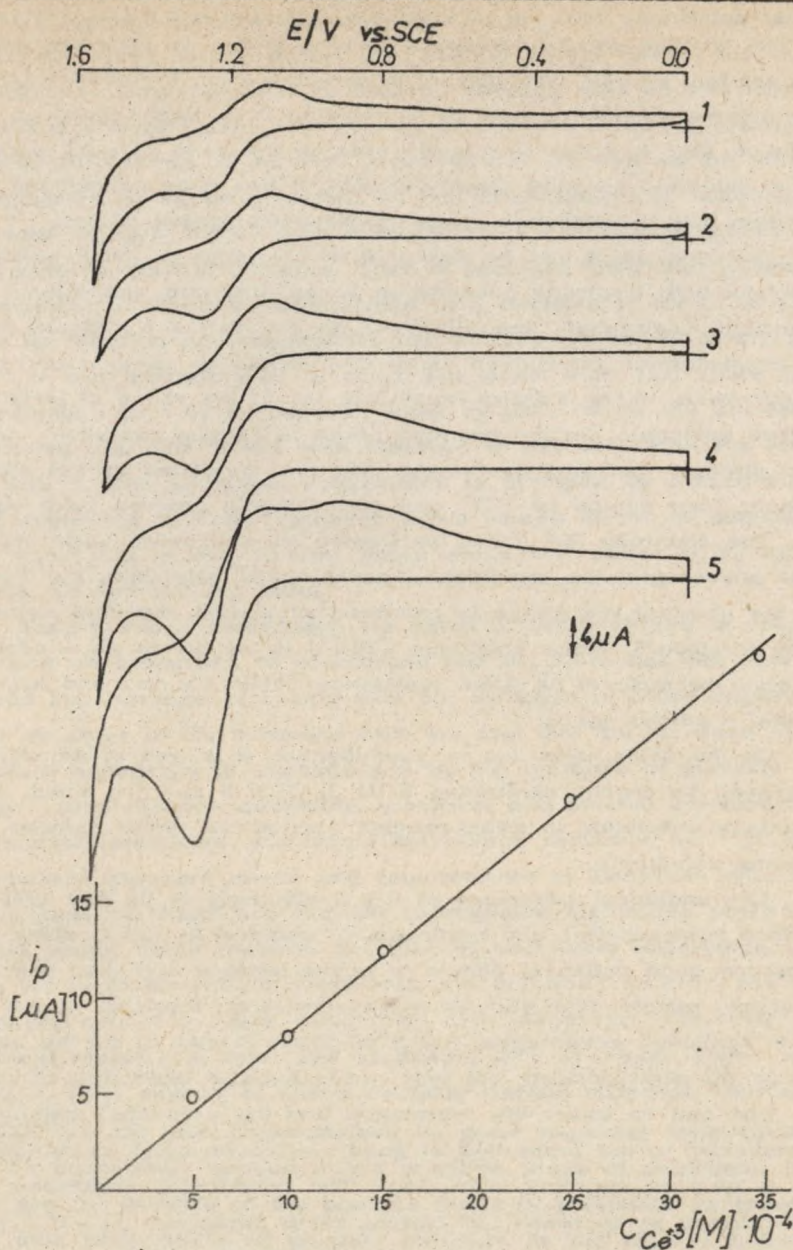
Fig. 6. Cyclic curves of stepwise standard addition of Ce to 1M H_2SO_4 and calibration curve for Ce^{+3}. Voltage scan rate 1V min^{-1}. (1) 5.10^{-4}M; (2) 1.10^{-3}M; (3) $1,5.10^{-3}$M; (4) $2,5.10^{-3}$M; (5) $3,5.10^{-3}$M. RW O as a working electrode

by free bromine can be observed as well. It can be generally stated
that saturant causes decrease of IE resistance to oxidation which
also follows from the curves of IE resistance to electrochemical
oxidation Fig. 4. It can be clearly seen in the case of FGE ELS
where saturated graphite electrodes ELS 2 are more susceptible to
oxidation than corresponding non-saturated electrodes ELS 1.

    Summing up, it can be said that in the range of small positive
potentials both electrode composition (coke structure, graininess) and
technology (saturation, graphitization) do not play a significant role.
But non-saturated graphitized electrodes should be used to carry out
measurements under extreme conditions i.e. in the range of large
positive potentials (in the potential range of oxygen evolution) and
when strongly oxidizing agents e.g. Br_2 are generated on the electrode
surface. They should be FGE and of not highly ordered coke structure.

    The electrode RW II can be treated as a peculiar case because
of its advantages; the broadest range of useful potentials, the lowest
RC, the greatest resistance to electrochemical and chemical oxidation.
In the Ringsdorff Werke catalogue [12] it is mentioned as a carbon
electrode because of its great resistance (6000 $\mu\Omega$ cm) and initial
material - carbon black.

    On the other hand due to graphitization it is free of defects
possessed by carbon electrodes ROM 3, CON 3 and GC which are
practically unsuitable in measurements carried out under extreme,
oxidizing conditions.

    The additional advantage of RW II electrode is its fine graininess
(surface homogeneity) and hardness. In contrast to RW O electrode
it ensures good polishing effects of active surface and also refreshing
(cleaning) effects after succesive measurements. Because of the
above mentioned advantages, RW II electrode seems to be the most
suitable for measurements not only under extreme, oxidizing conditions.

    One can be under the impression that the presented results are
contradictory to the properties of good electrodes used in industry.
This is only an apparent impression. The commercial electrodes are
characterized by increase of resistance to oxidation [13-15] in
the case of increase: i - petroleum coke structure order, ii - satura-
tion, iii - temperature of electrode rod treatment. It should be kept
in mind that the electrodes used in industry are porous in contrast
to IE used in VA measurements what results in different behaviour
of commercial and IE electrodes. As follows from the investigations

[16-20], thermal and chemical oxidation of graphite electrodes used
in industry takes places mainly in electrode pores. Hence, electrode
saturation causing decrease of material porosity also causes increase
of thermal and electrical conductivity, electrode mechanice resistance
(significant features in industry requirements) as well as the increase
of resistance to agresive media. On the other hand it is believed [14]
that coke bridges formed from a saturant are oxidized as the first in
the saturated graphite material. Then it becomes clear that saturant
participation in electrode composition is a decisive factor in IE resis-
tance to chemical and electrochemical oxidation. It refers to the pro-
duced in our laboratory IE of pores not larger than 75Å (pore size
determination limit by porosimeter used by us). Hence the saturated
electrodes e.g. ELS 2 are less resistant to oxidation than the electro-
des ELS 1. The additional confirmation is provided by Pötsch theory
[21] according to which oxidation takes places mainly in sufficiently
wide pores but in very narrow pores which may occur in IE, oxidation
velocity is approaching zero.

Taking into consideration the effect of order degree in coke
structure on properties of commercial and IE, there has not been
noticed the increase of quality with the increase of order degree of
coke structure in IE. It results from the fact that the increase of coke
structure anisotropy is accompanied by the increase of porosity aniso-
tropy, graphitization capability, electrical and thermal conductivity,
mechanical resistance, significant microcrack reduction etc. These are
particularly important needs and requirements of electrode industry.
In the case of "fully" and durably impregnated electrodes presented
in this paper, these features becomes of secondary importance. To
meet VA measurements, requirements, the electrode material should
be characterized besides sufficiently high electrical conductivity by:
chemical resistance, electrode hardness, lack of closed pores and
probably high number of active centres. Carbon materials (burnt off
to 1200°C) are also characterized by good electrical conductivity and
can be succesfully applied in the negative range of potentials. But
they are not suitable in the positive range of potentials as resulting
from little participation of graphite structure in this type of material

which is in agreement with the results of commercial electrode
investigations [13-15].

On the basis of our investigations it can be stated that the best
suited for work under extreme conditions are fine grained substrates
ELS (fibrous structure coke) and even very fine grained - crystallites
of a few nm size - RW II, graphitized electrode made on the base of
carbon black, then having the lowest anisotropy. It may be a result
of a great number of active centres of various energy in contrast to
CGE made of needle structure cokes possessing great degree of
anisotropy.

The presented results of the investigations on the factors influenc-
ing IE electrochemical properties in the positive range of potentials
made it possible to determine the effects of electrode material compo-
sition and technology on IE properties. At present our laboratory in
cooperation with GEF Racibórz is curring out investigations which
will provide more detailed and quantitative interpretation of the effect
of basic factors on IE electrochemical properties. We hope that they
will enable to work out and produce electrode rods of optimal para-
meters from the point of view of VA measurements requirements.

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STRESZCZENIE

Do badań użyto impregnowanych elektrod, których opis wykonania przedstawiono w części I, oraz elektrodę z węgla szklistego. Przedstawiono badania: 1) użytecznego do pracy zakresu potencjałów oraz wielkości prądu szczątkowego, 2) odporności elektrod na elektrochemiczne utlenianie, 3) pomiarów woltamperometrycznych w wybranych elektrolitach.

Na podstawie wyników badań stwierdzono, że elektrody węglowe nie nadają się do prowadzenia pomiarów w dodatnim zakresie potencjałów. Najbardziej różnicującym środowiskiem okazał się roztwór silnie alkaliczny. Stwierdzono nieco większą odporność na elektrochemiczne utlenianie tworzyw drobnoziarnistych, nienasyconych i o średniej temperaturze grafityzacji w stosunku do tworzyw gruboziarnistych,

nasyconych i o wysokiej temperaturze grafityzacji. Wyjątkowo odporną elektrodą na utlenianie w szerokim zakresie potencjałów i niskim prądzie tła okazała się elektroda wykonana z sadzy węglowej.

РЕЗЮМЕ

Для исследований использовали импрегнированные электроды, описание изготовления которых представили в ч. I , а также электрод из стекловидного угля. Представили исследования: 1/диапазона потенциалов, полезного для работы, а также величины остаточного тока, 2/ устойчивости электродов к электрохимическому окислению, 3/ вольтамперметрические измерения в избранных электролитах. На основе результатов исследований отметили, что угольные электроды не пригодны к проведению измерений в положительном диапазоне потенциалов. Наиболее дифференцирующей средой оказался сильно щелочный раствор. Отметили несколько большую устойчивость к электрохимическому окислению мелкозернистых, ненасыщенных и со средней температурой графитизации материалов относительно крупнозернистых, насыщенных и с высокой температурой графитизации. Исключительно устойчивым электродом к окислению в широком диапазоне потенциалов и низком токе фона оказался электрод из угольной сажи.