

Gas-Generating Porous Electrodes: Effect of the Catalyst Activity on the Polarization Curves

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Received December 21, 2000; in final form, June 4, 2001

Abstract – Effect of activity of the catalyst in gas-generating porous electrodes (GPE) of the DSA type on the anodic branch of polarization curves is studied. The structure of the GPE porous space and the electrode kinetics are assumed to remain invariant. The quantities that are varied are the electrode thickness and the exchange current j_0 . Characteristics of GPE electrodes of high, medium, and low activity (j_0 of 1.2×10^{-2} , 1.2×10^{-4} , and 1.2×10^{-6} A cm⁻², respectively) are compared. The standard thickness, calculated for these electrodes, are 1, 5, and 20 μm. In GPE of high and medium activity, after the emergence of first gas pores, the gas generation region, which before this was localized in a narrow region near the front surface of GPE, can rapidly expand by tens of times, so can the overall current. With a further overvoltages increase, ohmic restrictions again press the gas generation region to the front surface of GPE. In the low-activity GPE, the expansion of the gas generation region and the increase in the overall current are insignificant. It is shown that the medium-activity GPE commonly used in the chlorine electrolysis may be viewed as optimal. However, this by no means implies that the DSA operation mechanism is ideal. Perfecting the porous-space structure of DSA even further gives one a chance to considerably enhance its electrochemical characteristics.

Keywords: Gas-Generating Porous Electrodes, Catalyst Activity, Polarization Curves, electrodes of the DSA type

INTRODUCTION

A gas-generating porous electrodes (GPE) may be viewed as exemplary if it satisfies the following requirements. First, the catalyst in it must be cheap (contain no platinum metals), corrosion resistant, and selective to the target product of the electrochemical reaction occurring in it. Second, the rate of the electrochemical conversions on a unit inner surface of GPE must be sufficiently high. For example, if the process is limited by a slow discharge, the exchange current must not be small. Third, the internal specific surface, on which the electrochemical process occurs, must be large. And fourth, the mechanism of removal of the formed product, gas, must be efficient.

The first three, especially the first two, conditions are virtually obvious. For a couple of tens years the electrochemists have been striving to find metal oxide electrocatalysts for porous anodes with sufficiently large specific surface area, which would ensure industrial production of oxygen, chlorine, and other gases, be corrosion resistant, and contain no expensive catalysts of the platinum group [1-8]. This field of electrochemical research is generally called “nonsacrificial” anodes (NSA). Such anodes are intended for use in electrolyzers of very different types [1-12], and the most lucky prototype of their design and production technique is the dimensionally stable anodes (DSA) used in the chlorine electrolysis.

The fourth requirement is new, has been realized only recently, and calls for explanation. The diffusion coefficient for and the solubility of a gas in an electrolytic solution are very small; that is why the removal of gas from pores of GPE may meet large inner-diffusion and outer-diffusion restrictions. And one can hope for obtaining significant overall currents in GPE only in the case where these restrictions are removed. How can one organize an effective removal of gas from GPE? All these become clear far from immediately. A massive experimental and theoretical effort was to be made

to give the required answers. And here, again, a prompt was supplied to the electrochemists and useful hints were dropped by DSA.

Offered at the beginning of the 1970s, DSA carried out a technological revolution in the chlorine electrolysis. These metal oxide anodes possess some remarkable properties, corrosion resistance and high selectivity being the most important. Another remarkable property of DSA is the possibility of obtaining large densities of the overall current in them. It was established experimentally that the DSA polarization curves (PC) may include the so-called low-polarizability portion (LPP, labeled so in [13]), which is a region of small overvoltage variations, where the overall current can increase by one to two orders of magnitude. Despite a large number of papers and reviews devoted to the chlorine generation in DSA, until recently, no one had even guessed at the crucial role the structure of the porous space in DSA plays in the ensuring of effective removal of gas formed in the electrode and, consequently, in the ensuring the possibility of reaching a high electrochemical activity of DSA. All theoretical problems concerning the mechanism of operation of GPE and DSA were formulated and solved theoretically in [14-22]. In this series of works, we established that it was not enough for NSA to have a high electrocatalytic activity of catalysts used in them, it was also necessary for NSA to have a certain structure of the porous space, which would permit removing a major part of restrictions on the gas removal. Only then NSA would acquire the ability to reach high values of overall currents.

DSA are manufactured by thermally treating a mixture of ruthenium and titanium chlorides deposited on a titanium support. The NSA electrodes are usually produced in the same fashion. Therefore, the structure of porous space NSA is likely to be similar to that in DSA. This encourages us to hope that the electrochemical activity of electrodes in NSA can also be made high. Only then the above four requirements to GPE happen to be met.

The question of optimal balance between electrocatalytic and structural requirements imposed on GPE must become the subject of special research into one or another type of samples of GPE of one or another type. The goal of this particular publication is much more modest: we aim at analyzing the way a change in the activity of electrocatalysts impacts the standard thickness, the polarization curve, the magnitude of the currents, the depth of penetration of the electrochemical process into the porous layer, and the other characteristics of GPE.

When performing calculations with formulas provided by the general theory of GPE we formulated in [14-22], we will presume that the structure of the porous space in GPE (the presence of regions of micropores and macropores, the character of distribution of pores by size in them) and the electrode kinetics (the limiting stage here will be assumed to be a slow discharge with true or apparent transfer coefficients for the anodic process) are invariant and coincide with what takes place in the DSA electrodes. We will also presuppose that the GPE activity is characterized by a single parameter, specifically, the exchange current j_0 . We will conditionally introduce a notion high-, medium-, and low-activity GPE (j_0 of 1.2×10^{-2} , 1.2×10^{-4} , and 1.2×10^{-6} A cm⁻², respectively; we adopted the value $j_0 = 1.2 \times 10^{-4}$ A cm⁻² in [22], when calculating DSA characteristics in the chlorine electrolysis). If we now start varying the overvoltage throughout the entire range of possible values for zero to η_{\max} , we will be able to distinguish four qualitatively different modes of gas generation: (i) region of small overvoltages, where $0 \leq \eta \leq \eta^*$ [14]; (ii) region of overvoltages $\eta^* \leq \eta \leq \eta^{**}$ [18, 19], where LPP starts to form; (iii) the LPP region proper, at $\eta^{**} \leq \eta \leq \eta^{***}$ [16]; and (iv) the region of ohmic restrictions, $\eta^{***} \leq \eta \leq \eta_{\max}$ [20, 21]. The notation we use when calculating GPE characteristics in this work is given at the end of the paper, together with the relevant constants and parameters. All the other details of calculations we repeatedly described elsewhere [14-22].

THE CALCULATIONS AND THE ANALYSIS OF RESULTS

Our nearest goal is to establish the standard thickness of GPE with high, medium, and low activities. When performing calculations we will presume that the structure of the porous space in GPE and the electrode kinetics are invariant and will vary the electrode thickness Δ . The results of performing such a calculation program appear in Fig. 1. With a gradual increase in Δ ,

PC takes a certain limiting shape. The value of Δ corresponding to this shape was taken to be the standard thickness of GPE. Specific features of the curves presented in Fig. 1 (critical overvoltages and corresponding currents, parameters of maximum convergence of real and ideal PCs) are shown in Tables 1–6.

GPE of Medium Activity

$j_0 = 1.2 \times 10^{-4} \text{ A/cm}^2$, $\varphi = 7.5$, $\eta_{\max} = 8.39$, $I_{\max} = 848 \text{ A/cm}^2$; $L_d^0 = 0.91 \text{ } \mu\text{m}$, $I_d = 30 \text{ mA/cm}^2$; $H_0 = 15 \text{ } \mu\text{m}$, $J_0 = 1.13 \times 10^{-10} \text{ A}$, $J_0 N_0 = 10^8 \text{ A/cm}^3$; $L_{\text{ohm}} = 5,45 \times 10^{-6} \text{ cm}$, $I_{\text{ohm}} = 551 \text{ A/cm}^2$, $\Delta^* = 5 \text{ } \mu\text{m}$.

Table 1. Critical overvoltages in GPE vs. electrode thickness

$\Delta, \mu\text{m}$	η^*	η^{**}	η^{***}
0.5	0.7	0.709	1.758
1	0.659	0.672	1.511
2	0.636	0.654	1.276
5	0.627	0.643	0.975
10	0.626	0.641	0.779

Table 2. Optimum currents in GPE vs. electrode thickness

$\Delta, \mu\text{m}$	$\dot{\eta}$	$\dot{I}, \text{ A/cm}^2$	$\dot{I}_{\max}, \text{ A/cm}^2$	\dot{I}/\dot{I}_{\max}
0.5	1.83	0.56	0.68	0.82
1	1.62	0.74	0.93	0.75
2	1.41	0.76	1.04	0.73
5	1.15	0.84	1.46	0.58
10	1.07	0.96	2.43	0.40

Note 1. Note large values of the characteristic current $J_0 N_0$ generated in a unit volume of GPE and characteristic ohmic current I_{ohm} and small value of the characteristic ohmic length L_{ohm} .

Note 2. The data in Table 1 speak of closeness of values of critical overvoltages η^* and η^{**} . This means that the event, which of crucial importance for GPE, i.e. the formation of a gas channel, occurs in a very narrow region of values of overvoltages. With increasing Δ , the instant of appearance of first gas pores (η^*) shifts towards small values. The same can be said of the point η^{***} , which signifies the beginning of the region of ohmic restrictions in PC.

Note 3. The second column in Table 2 contains values of overvoltages at which real and ideal PCs converge to a maximum degree. After the emergence of a gas channel (point of convergence of the region of small overvoltages 1 and LPP 2, Fig. 2), there begins a rapid convergence of real and ideal PCs. However, in the region of ohmic restrictions (portion 3 marked with a dashed line in Fig. 2), real and ideal PCs begin to rapidly diverge. The maximum convergence of real and ideal PCs occurs at overvoltage $\dot{\eta}$. At this point, real currents are marked by \dot{I} (third column in Table 2) and ideal currents are marked by \dot{I}_{\max} . Traditionally, the value $\Delta = 5 \text{ } \mu\text{m}$ was taken for the standard thickness of GPE. Table 2 testifies that this had been a right choice. Although the current at $\Delta = 10 \text{ } \mu\text{m}$ is higher than at $\Delta = 5 \text{ } \mu\text{m}$, the ratio \dot{I}/\dot{I}_{\max} perceptibly diminishes (0.4 against 0.58). And this means that the ohmic and diffusion restrictions for a DSA with $\Delta = 10 \text{ } \mu\text{m}$ increased as compared with DSA with $\Delta = 5 \text{ } \mu\text{m}$. Therefore, it is more reasonable to choose $\Delta^* = 5 \text{ } \mu\text{m}$ as the standard thickness (we discuss this at length in [22]).

GPE of High Activity

$j_0 = 1.2 \times 10^{-2} \text{ A/cm}^2$, $\varphi = 75$, $\eta_{\max} = 6.1$, $I_{\max} = 835 \text{ A/cm}^2$; $L_d^0 = 9.1 \times 10^{-6} \text{ cm}$, $I_d = 296 \text{ mA/cm}^2$; $H_0 = 1.5 \text{ } \mu\text{m}$, $J_0 = 1.13 \times 10^{-9} \text{ A}$, $J_0 N_0 = 10^9 \text{ A/cm}^3$; $L_{\text{OM}} = 1.72 \times 10^{-6} \text{ cm}$, $I_{\text{OM}} = 1742 \text{ A/cm}^2$, $\Delta^* = 1 \text{ } \mu\text{m}$.

Table 3. Critical overvoltages in GPE vs. electrode thickness

$\Delta, \mu\text{m}$	η^*	η^{**}	η^{***}
0.05	0.635	0.636	1.498

0.1	0.63	0.632	1.47
0.2	0.627	0.631	1.122
0.5	0.626	0.63	0.886
1	0.626	0.63	0.729

Table 4. Optimum currents in GPE vs. electrode thickness

$\Delta, \mu\text{m}$	$\dot{\eta}$	$\dot{I}, \text{A/cm}^2$	$\dot{I}_{\text{max}}, \text{A/cm}^2$	$\dot{I}/\dot{I}_{\text{max}}$
0.1	3.46	0.89	6.66	0.13
0.2	2.0	1.36	10.43	0.13
0.5	1.18	2.0	16.85	0.12
1	1.02	2.24	21.79	0.10

Note 4. Figure 1b and the data in Table 4 suggest that, for the standard thickness of a highly active GPE, we can take $\Delta^* = 1 \mu\text{m}$. A comparison of Tables 3 and 4 reveals that $\eta^{***} = 0.729 < \dot{\eta} = 1.020$ for such an electrode. Similar inequalities take place for both medium-activity GPE (Tables 1, 2) and low-activity GPE (Tables 5, 6). Taken in the aggregate, all this means (see also Fig. 2) that the maximum convergence of real and ideal PCs occurs in the region of ohmic restrictions. Hence, decreasing ohmic restrictions in GPE would have allowed one to raise the magnitude of the electrochemical activity of GPE.

GPE of Low Activity

$j_0 = 1.2 \times 10^{-6} \text{ A/cm}^2$, $\varphi = 0.75$, $\eta_{\text{max}} = 10.73$, $I_{\text{max}} = 774 \text{ A/cm}^2$; $L_d^0 = 9.11 \mu\text{m}$, $I_d = 2.96 \text{ mA/cm}^2$; $H_0 = 150 \mu\text{m}$, $J_0 = 1.13 \times 10^{-11} \text{ A}$, $J_0 N_0 = 10^7 \text{ A/cm}^3$; $L_{\text{om}} = 1.72 \times 10^{-5} \text{ cm}$, $I_{\text{om}} = 174.2 \text{ A/cm}^2$, $\Delta^* = 20 \mu\text{m}$.

Table 5. Critical overvoltages in GPE vs. electrode thickness

$\Delta, \mu\text{m}$	η^*	η^{**}	η^{***}
0.1	2.86	2.864	4.135
1	1.729	1.762	2.709
5	1.024	1.133	2.007
10	0.805	0.945	1.631
20	0.676	0.817	1.326
30	0.642	0.767	1.168

Table 6. Optimum currents in GPE vs. electrode thickness

$\Delta, \mu\text{m}$	$\dot{\eta}$	$\dot{I}, \text{A/cm}^2$	$\dot{I}_{\text{max}}, \text{A/cm}^2$
1	2.71	0.133	0.991
5	2.03	0.125	0.961
10	1.67	0.099	0.903
20	1.52	0.107	0.824
30	1.38	0.079	0.746

Note 5. An analysis of the behavior of the curves in Fig. 1c gives us a chance to choose $\Delta^* = 20 \mu\text{m}$ for the standard thickness of GPE of low activity. Regrettably, values in the third column in Table 6 display no definite tendency: values of currents “dance.” To our minds, this fact testifies that the method we put forth in [20] for determining critical overvoltage η^{***} (the beginning of the region of ohmic restrictions in PC) went “skidding” in the case of low-activity GPE, albeit the method was on its best behavior in the case of GPEs that have high and medium activities. In the case of the low-activity GPE, it is necessary to develop finer methods for estimating critical overvoltages.

GENERAL CONCLUSIONS

Figure 3 shows PCs for high-, medium-, and low-activity GPEs whose standard thicknesses are 1, 5, and 20 μm , respectively. As seen, with the activity of the catalytic layer in GPE decreasing, the LPP becomes shorter and shorter and practically disappears in the low-activity GPE (curve 3). The slope of LPP have frequently given rise to heated disputes. Figure 3 shows that the slope is defined by the catalyst activity: the lower the activity, the steeper LPP. Figure 4 shows how the reduced effective depth of penetration of the gas generation process into GPE depends on the overvoltage. We see that this quantity remains constant at low overvoltages: the gas forms here in a very narrow layer near the front surface of GPE. In LPP, δ begins to rapidly grow. The authors of [23] were the first to put forth the hypothesis concerning the possibility of existence of such a phenomenon. At high overvoltages, ohmic restrictions again press the gas generation zone to the front surface of GPE. The degree of localization of gas formation near the front surface of GPE and the expansion of this zone in LPP- all these processes are vividly demonstrated in Fig. 5. The maximum depth of penetration of the electrochemical process into GPE increases with decreasing catalyst activity. Figure 6 shows how the δ vs. η curve alters with a gradual decrease in the thickness of a medium-activity GPE ($\Delta^* = 5\mu\text{m}$). General results of our study appear in Tables 7–9.

Table 7. Critical overvoltage in GPE of standard thickness vs. exchange current

$j_0, \text{A/cm}^2$	η^*	η^{**}	η^{***}	$I^{***}, \text{A/cm}^2$	$\eta_{\text{пред}}$	$I_{\text{пред}}, \text{A/cm}^2$
$1.2 \cdot 10^{-2}$	0.626	0.630	0.729	0.877	6.10	835
$1.2 \cdot 10^{-4}$	0.627	0.643	0.975	0.538	8.39	848
$1.2 \cdot 10^{-6}$	0.676	0.817	1.326	0.069	10.73	848

Table 8. Optimum current in GPE of standard thickness vs. exchange current

$j_0, \text{A/cm}^2$	$\Delta^*, \mu\text{m}$	η	$\dot{I}, \text{A/cm}^2$	$\dot{I}_{\text{max}}, \text{A/cm}^2$	$\dot{I}/\dot{I}_{\text{max}}$
$1.2 \cdot 10^{-2}$	1	1.02	2.24	21.8	0.10
$1.2 \cdot 10^{-4}$	5	1.15	0.84	1.49	0.58
$1.2 \cdot 10^{-6}$	20	1.52	0.11	0.13	0.85

Table 9. Parameters of effective penetration depth of gas generation process in GPE of standard thickness vs. exchange current

$j_0, \text{A/cm}^2$	$\delta_0, \mu\text{m}$	δ_0/L_d^0	$\delta_{\text{max}}, \mu\text{m}$	$\delta_{\text{max}}/L_d^0$	$\delta_{\text{max}}/\delta_0$
$1.2 \cdot 10^{-2}$	$1.2 \cdot 10^{-3}$	0.01	0.1	1.13	87
$1.2 \cdot 10^{-4}$	0.11	0.12	2.9	3.17	27
$1.2 \cdot 10^{-6}$	5.13	0.56	16.5	1.81	3.2

The data we compiled in Table 8 (columns 4–6) are very revealing. By raising the exchange current (the electrochemical activity of layers in NSA), one can substantially raise the overall current. However, the diffusion and ohmic restrictions dramatically rise at the same time: GPE sustains only one tenth of the ideal current. The diffusion and ohmic restrictions become small in low-activity GPE, but then the overall current becomes small as well. Of considerable interest are also the data presented in Table 9 (columns 2, 4, 6). The gas generation process in highly-active GPE is squeezed onto the front surface ($\delta_0 = 1.2 \cdot 10^{-7}$ cm), and even in LPP, the electrode electrochemical process is capable of encompassing only a tenth of the overall electrode thickness ($\Delta^* = 1 \mu\text{m}$). As to GPE of medium activity, the gas generation region extends to 60% of its overall thickness. All these data give us grounds to draw the conclusion that the medium-activity GPEs, which have traditionally been used in the real chlorine electrolysis practice, are indeed optimum. But this conclusion by no means implies that the mechanism of operation of a medium-activity GPE is ideal and cannot be improved even further.

The structure of the porous space of DSA that are employed in the chlorine electrolysis, the existence of micropores and macropores in these electrodes have come to life spontaneously, this structure is a side effect of the state-of-the-art technology of DSA fabrication. No one has ever tried to control parameters of DSA. By doing this, one could hope to considerably improve electrochemical characteristics of DSA. Then one would have managed to reduce the working overvoltage and diminish ohmic restrictions, and these, according to calculations, are principal barriers that do not allow one to improve electrochemical characteristics of DSA and GPE, which are similar to DSA in the structure of the porous space.

Fig. 1. PC for GPE: (a) $j_0 = 1.2 \times 10^{-4}$ A/cm², Δ of (1) 0.5, (2) 1, (3) 2, (4) 5, and (5) 10 μm ; (b) $j_0 = 1.2 \times 10^{-2}$ A/cm², Δ of (1) 0.05, (2) 0.1, (3) 0.2, (4) 0.5, and (5) 1 μm ; and (c) $j_0 = 1.2 \times 10^{-6}$ A/cm², Δ of (1) 1, (2) 5, (3) 10, (4) 20, and (5) 30 μm .

Fig. 2. PC for GPE: (1–3) real curves, (1) portion of small overvoltages, (2) LPP, (3) portion of ohmic restrictions, and (4) ideal PC; (a) $j_0 = 1.2 \times 10^{-4}$ A/cm², $\Delta = 5$ μm (chlorine electrolysis in DSA); (b) $j_0 = 1.2 \times 10^{-2}$ A/cm², $\Delta = 1$ μm ; and (c) $j_0 = 1.2 \times 10^{-6}$ A/cm², $\Delta = 20$ μm .

Fig. 3. PC for GPE: (1) $j_0 = 1.2 \times 10^{-2}$ A/cm², $\Delta = 1$ μm ; (2) $j_0 = 1.2 \times 10^{-4}$ A/cm², $\Delta = 5$ μm (chlorine electrolysis in DSA); and (3) $j_0 = 1.2 \times 10^{-6}$ A/cm², $\Delta = 20$ μm .

Fig. 4. The δ / L_d^0 vs. η dependences for (a) $j_0 = 1.2 \times 10^{-4}$ A/cm², $\Delta = 5$ μm (chlorine electrolysis in DSA); (b) $j_0 = 1.2 \times 10^{-2}$ A/cm², $\Delta = 1$ μm ; and (c) $j_0 = 1.2 \times 10^{-6}$ A/cm², $\Delta = 20$ μm .

Fig. 5. The δ / Δ vs. η dependences for (1) $j_0 = 1.2 \times 10^{-2}$ A/cm², $\Delta = 1$ μm ; (2) $j_0 = 1.2 \times 10^{-4}$ A/cm², $\Delta = 5$ μm (chlorine electrolysis in DSA); and (3) $j_0 = 1.2 \times 10^{-6}$ A/cm², $\Delta = 20$ μm .

Fig. 6. The δ vs. η dependences for $j_0 = 1.2 \times 10^{-4}$ A/cm² and Δ of (1) 0.5, (2) 1, (3) 2, (4) 5 (chlorine electrolysis in DSA), and (5) 10 μm .

NOTATION

E , overvoltage

$\eta = FE/RT$, reduced overvoltage

η_{max} , maximum reduced overvoltage

η^* , reduced critical overvoltage at which first gas pores emerge near the rear surface of NSA

η^{**} , reduced critical overvoltage at which first gas pores emerge near the front surface of NSA

η^{***} , reduced critical overvoltage at which one must begin taking into account ohmic restrictions in NSA

η_1 , overvoltage corresponding to maximum convergence of real and ideal PCs

j , current density of electrochemical reaction

j_{max} , maximum possible current density of electrochemical reaction

j_0 , exchange current of electrochemical reaction

J_0 , characteristic current generated over half-length of an individual liquid pore in a lattice model

I , electrochemical activity of NSA

I_{max} , maximum electrochemical activity of NSA

\hat{I} , current corresponding to maximum convergence in real PC

\hat{I}_{max} , current corresponding to maximum convergence in an ideal PC

I_d , characteristic diffusion current of a porous electrode

I_g , characteristic current for electrolyte chamber

I_{ohm} , characteristic ohmic current

L_d^0 , characteristic diffusion length for a porous electrode

L_g , characteristic length for electrolyte chamber

L_{ohm} , characteristic ohmic length

H_0 , characteristic length of the current generation process at half-length of an individual liquid pore in a lattice model

Δ , thickness of active layer in NSA
 Δ^* , standard thickness of active layer in NSA
 α , apparent transfer coefficient for cathodic process
 β , apparent transfer coefficient for anodic process
 δ , effective penetration depth of the electrochemical gas generation process in NSA
 n , number of electrons taking part in an elementary electrochemical act
 F , Faraday's constant
 φ , parameter related to the depth of penetration of electrochemical process into a porous electrode
 D , diffusion coefficient for chlorine molecules in an electrolytic solution
 D_g , diffusion coefficient for chlorine molecules in a gas phase
 κ , ionic electroconductivity
 ψ , proportionality coefficient in expression for the overall flux of conversions of gas molecules into gas bubbles in a unit volume of electrolytic solution in electrolyte chamber per time unit
 r_0 , characteristic size of a gas nuclei
 r_{11} , minimum radius of micropores
 r_{12} , maximum radius of micropores
 r_{21} , minimum radius of macropores
 r_{22} , maximum radius of macropores
 g , porosity
 g_1 , porosity of micropores
 g_2 , porosity of macropores
 S , overall specific surface area of pores
 S_1 , specific surface area of micropores
 S_2 , specific surface area of macropores
 N_0 , characteristic number of intersections between liquid and gas pores in a unit volume of NSA in a lattice model

CONSTANTS AND PARAMETERS FOR ELECTRODES OF THE DSA TYPE

$RT/F = 30 \text{ mV}$
 $c_0 = 2.7 \times 10^{-6} \text{ mol cm}^{-3}$
 $n = 2$
 $F = 10^5 \text{ C mol}^{-1}$
 $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
 $D_r = 1 \text{ cm}^2 \text{ s}^{-1}$
 $\kappa = 0.1 \Omega^{-1} \text{ cm}^{-1}$
 $\alpha = 0$
 $\beta = 2$
 $\nu = 1$
 $r_0 = 1 \text{ } \mu\text{m}$
 $g = 0.5$
 $g_1 = g_2 = 0.25 (\epsilon = 2.29 \times 10^{-7}),$
 $r_{11} = 0.001 \text{ } \mu\text{m}$
 $r_{12} = 0.0025 \text{ } \mu\text{m}$
 $r_{21} = 0.05 \text{ } \mu\text{m}$
 $r_{22} = 0.4 \text{ } \mu\text{m}$
 $S_1 = 2.69 \times 10^6 \text{ cm}^{-1}$
 $S_2 = 1.85 \times 10^4 \text{ cm}^{-1}$
 $S = 2.71 \times 10^6 \text{ cm}^{-1}$
 $\psi = 1.45 \times 10^{-5} \text{ g.m. cm}^{-3} \text{ s}^{-1}$
 $L_r = 13.7 \text{ } \mu\text{m}$
 $I_r = 3.95 \text{ mA cm}^{-2}$
 $N_0 = 8.94 \times 10^{17} \text{ cm}^{-3}$

REFERENCES

1. Yakimenko, L.M., *Proizvodstvo khloro, kausticheskoi sody i neorganicheskikh khlorproduktov* (Production of Chlorine, Sodium Hydroxide, and Inorganic Chlorine Derivatives), Moscow: Khimiya, 1974.
2. Yakimenko, L.M. and Pasmanik, M.I., *Spravochnik po proizvodstvu khloro, kausticheskoi sody i osnovnykh khlorproduktov* (Handbook on the Production of Chlorine, Sodium Hydroxide, and Basic Chlorine Derivatives), Moscow: Khimiya, 1976.
3. Yakimenko, L.M., *Elektrodnye materialy v prikladnoi elektrokhemii* (Electrode Materials in Applied Electrochemistry), Moscow: Khimiya, 1977.
4. Abstracts of Papers, *IV Vsesoyuz. seminar "Maloiznashivaemye anody i ikh primeneniye v elektrokhimicheskikh protsessakh"* (IV All-Union Workshop on Nonsacrificial Anodes and Their Application in Electrochemical Processes), Moscow: NIITeKhim, 1979.
5. Yakimenko, L.M., *Poluchenie vodoroda, kisloroda, khloro i shchelochei* (Production of Hydrogen, Oxygen, Chlorine, and Alkalis), Moscow: Khimiya, 1981.
6. Fioшин, M.Ya. and Smirnova, M.G., *Tekhnika elektroliza* (The Electrolysis), Rostov-on-Don: Rostov. Univ., 1983.
7. Abstracts of Papers, *V Vsesoyuz. seminar "Maloiznashivaemye anody i ikh primeneniye v elektrokhimicheskikh protsessakh"* (V All-Union Workshop on Nonsacrificial Anodes and Their Application in Electrochemical Processes), Moscow, 1984.
8. Abstracts of Papers, *VI Vsesoyuz. seminar "Maloiznashivaemye anody i ikh primeneniye v elektrokhimicheskikh protsessakh"* (VI All-Union Workshop on Nonsacrificial Anodes and Their Application in Electrochemical Processes), Moscow, 1987.
9. Yakimenko, L.M., Modylevskaya, I.D., and Tkachek, Z.A., *Elektroliz vody* (Electrolysis of Water), Moscow: Khimiya, 1970.
10. Kryukov, Yu.I., Chernyshov, S.F., and Pshenichnikov, A.G., *Hydrogen Energy Progress*, VII, Veziroglu, T.N., et al., Eds., New York: Pergamon, 1988, vol. 1, p. 403.

11. Pshenichnikov, A.G., Kazarinov, V.E., and Naumov, I.P., *Elektrokhimiya*, 1991, vol. 27, p. 1555.
12. Chernyshev, S.F., Kryukov, Yu.I., and Pshenichnikov, A.G., *Elektrokhimiya*, 1992, vol. 28, p. 391.
13. Pecherskii, M.M., Gorodetskii, V.V., Evdokimov, S.V., and Losev, V.V., *Elektrokhimiya*, 1981, vol. 17, p. 1087.
14. Chirkov, Yu.G., *Elektrokhimiya*, 2000, vol. 36, p. 526.
15. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2000, vol. 36, p. 735.
16. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2001, vol. 37, p. 336.
17. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2001, vol. 37, p. 409.
18. Chirkov, Yu.G. and Chernenko, A.A., *Elektrokhimiya*, 2001, vol. 37, p. 546.
19. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2001, vol. 37, p. 557.
20. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2001, vol. 37, p. 987.
21. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2001, vol. 37, p. 1107.
22. Chirkov, Yu.G. and Rostokin, V.I., *Elektrokhimiya*, 2002, vol. 38, p. 316.
23. Erenburg, R.G. and Krishtalik, L.I., *Elektrokhimiya*, 1987, vol. 23, p. 8.



