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Gas-Generating Porous Electrodes: Why It Is that the “Standard” Thickness of DSA (Chlorine Generation) Equals Five Micrometers?

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Abstract – Overall polarization curves (PC) of gas-generation porous electrodes (GPE) that differ only in the active-layer thickness are calculated using constants close to those inherent in the chlorine generation in DSA. Calculations show that the optimum electrode thickness equals 5 μm and its further increase virtually fails to enhance electrochemical activity of DSA. Overall currents are evaluated at high overvoltages, where ohmic losses play a major role. The degree of maximum convergence of real (calculated) and ideal (in the absence of diffusion, ohmic, or any other restrictions of the gas generation) PC is also calculated.

THE PROBLEM FORMULATION

The chlorine electrolysis is the old electrochemical industry, begun as far as the 1880s. Today, it is the powerful source of chlorine and alkali: tens of millions of tons of these products are produced in the world every year (the largest-scale process in engineering electrochemistry). The chlorine electrolysis technology experienced revolutionary changes at the beginning of the 1970s, when a new type of anodes was proposed, namely, dimensionally stable anodes (DSA). These electrodes have two remarkable properties: corrosion resistance and selectivity – suppressed are side reactions of oxygen evolution.

Despite of large number of papers and reviews devoted to the chlorine generation in DSA [1-29], many important theoretical questions remained unsolved until recently. No one have made any attempt to raise the question of the mechanism of generation of gas pores in DSA, of how a powerful channel for the removal of gas generated in DSA (via string of gas pores) form in DSA. No one had even guessed at the crucial role of the structure of the porous space in DSA. The researchers' attention was largely focused on studying the nature of a special region in the anodic branch of polarization curve (PC) for DSA, namely, the low-polarization portion (LPP). This is a narrow overvoltage range where the electrode' electrochemical activity of DSA rapidly increases. This phenomenon had drawn attention of the reseachers. The point is it had seemed that the two remarkable properties of DSA could be complemented by a third one – large overall currents. The known attempts to explain the LPP phenomenon [9,20,29] had a common fallacy: no one attempted to take into account the effect the GPE structure has on the processes that lead

to the emergence of a gas phase in the electrode, thus affecting the shape of PC. That was why the true nature of LPP remained a mystery until recently. One more fallacy of previous works is that no one had ever estimated the effect of ohmic losses emerging in DSA. It had been assumed that these were insignificant. However, it is clear that the amount of electrolyte in the porous space of an electrode where gas pores emerged begins decreasing, giving rise to difficulties with the supply of electrolyte ions into the gas generation zone.

All the problems we enumerated in the foregoing were formulated and solved theoretically in [30-37], where a consummate theory of gas-generating porous electrodes (as opposed to gas-consuming porous electrodes used in fuel cell; the difference between these electrode types was expounded in [38-40]) was propounded. It was demonstrated how the structure of the porous space in GPE (the presence of micropores and macropores, the magnitude of their porosity, the pore distribution by size) render precise the behavior of all characteristics of GPE and, which is more, the shape of its PC.

The inflection in PC, which occurs after the Tafel portion and leads to a dramatic increase in the overall current, is due to the emergence of a network of electrolyte-free gas pores in GPE pores [30,35]. The channel for the gas removal is thus created in GPE and possesses an astounding capacity of removing the gas formed in GPE. In doing so, all inner-diffusion and outer-diffusion restrictions are removed, which exactly what leads to a considerable of the current.

And finally we have demonstrated in [36,37] how one should better perform calculations of GPE characteristics in the region of high overvoltages, where GPE pores are substantially depleted of electrolyte, which makes it necessary to take into account ohmic losses.

Here we are self-verifying this theory. Our desire is to set the prophecies of the theory against what is observed in real DSA operation. We strive to answer the question: why is it that the standard thickness of DSA used in the chlorine generation is taken to equal 5 μ m?

DSA PARAMETERS

The GPE theory to be much more complicated than the problems encountered by the electrochemists who studied mechanisms of operation of gas-consuming porous electrodes in fuel cells [41-44]. To comprehensively describe the GPE operation, it proved necessary to design methods for calculating GPE characteristics in four qualitatively different areas: (1) at small overvoltages, when all GPE pores are filled with electrolyte; (ii) where gas generation processes commence in GPE pores and LPP starts to form; (iii) in the LPP region of a rapid current growth; (iv) in an ohmic region depleted of electrolyte. It was impossible to report the entire theoretical material in one or two papers and that is why we issued a series of publications. However, any GPE theory, including that divulged in [30-37], would remain merely a dump of formulas if not compared with experiment. An attempt to do it for chlorine electrolysis in DSA is undertaken in this paper. Sadly enough, only the region of small overvoltages appeared to have thoroughly been investigated. Here, the presence of considerable complications connected with the gas removal in the electrolyte chamber was shown (large outer-diffusion restrictions).

The presence of an LPP portion was only declared, its nature stirred up a heated controversy, but virtually no one cared for studying it experimentally. As to the ohmic limitations (high overvoltages), it had been left outside experiment. All this makes it rather difficult to compare

the GPE theory developed in [30-37] with experiments involving chlorine evolution in DSA. That is why we offer the following, possibly the only really feasible technique for comparing theory and experiment. We will vary the DSA thickness and see how the principal indicator of the GPE operation, i.e. its PC, will change. We are going to prove that the empirical choice of 5 μm as the standard DSA thickness may be substantiated by theoretical calculations.

When calculating PC for DSA, we assume that the number n of electrons taking part in an elementary electrochemical act is equal to two, Faraday's constant $F = 10^5 \text{ C mol}^{-1}$, the diffusion coefficient for chlorine molecules in electrolyte $D = 10^{-5} \text{ cm}^2\text{s}^{-1}$, the gas solubility $c_0 = 2.7 \times 10^{-6} \text{ mol cm}^{-3}$ [45,46], the exchange current of the electrochemical reaction (electrochemical formation of gas molecules is presumably limited by slow discharge) $i_0 = 1.2 \times 10^{-4} \text{ A cm}^{-2}$, the characteristic radius of a gas nucleus $r_0 = 1 \mu\text{m}$, the coefficient in the expression for the effective diffusion coefficient $\nu = 1$, and the porosity $g = 0.5$. We have the following characteristic quantities and parameters, which, taken together, describe modes of the DSA functioning.

For a porous electrode: characteristic diffusion length $L_d^0 = 0.9 \mu\text{m}$; characteristic diffusion current $I_d = 29.6 \text{ mA cm}^{-2}$; minimum micropore radius $r_{11} = 0.001 \mu\text{m}$; maximum micropore radius $r_{12} = 0.0025 \mu\text{m}$; minimum macropore radius $r_{21} = 0.05 \mu\text{m}$; maximum macropore radius $r_{22} = 0.4 \mu\text{m}$ [28]; the porosity of micropore equals that of macropores, i.e. $g_1 = g_2 = 0.25$; specific surface area of micropores $S_1 = 2.69 \times 10^6 \text{ cm}^{-1}$; specific surface area of macropores $S_2 = 1.85 \times 10^4 \text{ cm}^{-1}$; and overall surface area of pores $S = 2.71 \times 10^6 \text{ cm}^{-1}$.

For the electrolyte chamber: at $\varphi = 7.5$ (parameter that determines the penetration length of electrochemical process into GPE) [34], characteristic length $L_r = 13.7 \mu\text{m}$; characteristic current $I_r = 3.95 \text{ mA cm}^{-2}$.

In the lattice model [47]: characteristic number of intersections between liquid and gas pores in a unit DSA volume $N_0 = 3 \times 10^{15} \text{ cm}^{-3}$, characteristic length of the current generation process at half length of an individual liquid pore $H_0 = 15 \mu\text{m}$, characteristic current generated at half length of an individual liquid pore $J_0 = 1.13 \times 10^{-10} \text{ A}$.

In an ohmic mode: characteristic ohmic length $L_{\text{ohm}} = 5.4 \times 10^{-6} \text{ cm}$, and characteristic ohmic current $I_{\text{ohm}} = 551 \text{ A cm}^{-2}$.

RESULTS AND DISCUSSION

Let us now turn our attention to results of numerical calculations. Figure 1 shows a series of PC calculated for several thicknesses Δ of the DSA active layer with formulas presented in [30-37]. As expected, for very thin electrodes (Fig.1a), calculated PC (curve 1) practically coincides with ideal PC (curve 2; complete removal of restrictions on the current generation) in a

Table 1. Critical overvoltages vs. The DSA active layer thickness

$\Delta, \mu\text{m}$	η^*	η^{**}	η^{***}
0,05	1,128	1,130	2,442
0,2	0,803	0,808	2,094
1	0,659	0,672	1,481
5	0,627	0,643	0,945

10 0,626 0,641 0,747

broad overvoltage range. For DSA, $L_d^0 = 0.9 \mu\text{m}$; therefore, ideal and calculated PCs diverge with increasing Δ (Figs. 1b-1e). In the absence of ohmic losses, ideal and calculated PCs would have coincided at high overvoltage (Figs. 1d, 1e; curves 3) [32]. The presence of ohmic losses makes the PCs diverge with increasing overvoltages (Figs. 1d, 1e; curves 1,2).

Table 2. Parameters of maximum convergence of real (calculated) and ideal PCs vs. Δ

$\Delta, \mu\text{m}$	η^*	I^*	I_{max}	I^*/I_{max}
0,05	2,011	0,075	0,089	0,84
0,2	2,006	0,296	0,353	0,84
1	1,567	0,558	0,714	0,78
5	1,150	0,814	1,460	0,56
10	1,059	0,877	2,377	0,37

All calculated PCs have each three critical points (Fig.1), which represent instants of reaching overvoltage η^* , η^{**} , and η^{***} . At η^* and η^{**} , first gas pores emerge near, respectively, rear and front side of DSA; and at η^{***} , one must begin accounting for ohmic restrictions. These quantities for DSA with various Δ appear in Table 1.

Table 3. The overall current in the region of ohmic limitations in DSA vs. overvoltage

η	1	1,4	1,8	2,2	2,6	3	
$\Delta = 5 \mu\text{m}$							
$I, \text{A cm}^{-2}$		0,56	1,31	2,32	3,64	5,45	8,20
$\Delta = 10 \mu\text{m}$							
$I, \text{A cm}^{-2}$		0,76	1,62	2,65	3,94	5,70	8,39

We see that the gas channel forms in DSA very fast, so the difference $\eta^{**} - \eta^*$ is very small. That is why we see only η^* in Fig. 1 (first inflection, where portion of small overvoltages converts into LPP). With increasing Δ , the region of ohmic limitations commences at ever decreasing η^{***} (Table 1).

Let us estimate how close the real (calculated) PCs are to ideal ones (curves 1 and 2 in Fig.1, respectively). In Table 2 we present overvoltages η^* , at which curves 1 are the closest to curves 2, and the corresponding real and ideal currents (I^* and I_{max} , respectively).

We see in Table 2 that the overall current in DSA increases with Δ and reaches its limit at $\Delta = 10 \mu\text{m}$. At the same time, the diffusion, ohmic, and other limitations that make it more difficult to reach I_{max} increases (last column in Table 2). For a final solution to the problem of the optimum thickness of the active layer of DSA, we combined all the curves of Fig. 1 in Fig. 2.

Figure 2 shows that the optimum thickness is 5 μm . This is exactly the standard thickness of DSA for the chlorine generation process. Table 3 shows how the overall current in the region of ohmic restrictions increases with η in DSA with Δ of 5 and 10 μm .

A marginal increase in the current with a twofold increase in the electrode thickness (Table 3) confirms the above conclusion that 5 μm is the optimum thickness of the DSA active layer.

Fig. 1. Calculated PCs for DSA (a) 0.05, (b) 0.2, (c) 1.0, (d) 5, and (e) 10 μm thick: (1) PC, (2) maximum currents in the absence of any limitations, and (3) PC at high overvoltages in the absence of ohmic limitations; see text for explanations.

Fig. 2. PCs calculated for DSA (1) 0.05, (2) 0.2, (3) 1.0, (4) 5, and (5) 10 μm thick.

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