

Electrochemical Reduction of Oxygen to Hydrogen Peroxide in a Gas-Diffusion Electrode Based on Mesoporous Carbon

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Abstract—Mesoporous carbon prepared by template synthesis using SBA-15 mesostructured silicate material was tested as an electrocatalyst for electrochemical synthesis of H_2O_2 from O_2 in a two-layer gas-diffusion electrode. Preparative syntheses of H_2O_2 in 0.06 to 2.0 M aqueous solutions of various electrolytes (pH 2–8) were performed at current densities in the interval 0.05–0.19 A cm^{-2} . Solutions with an H_2O_2 concentration of 1–2.8 M were prepared with 46–70% current efficiency. Thus, the material tested shows promise as an electrocatalyst of two-electron reduction of oxygen to H_2O_2 .

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Much attention is paid in the literature to electrochemical advanced oxidation processes (EAOPs) [1–3], in particular, to the electro-Fenton process and various hybrid technologies involving it, i.e., to processes of indirect oxidation of organic and inorganic substances with hydrogen peroxide electrochemically generated in situ from oxygen in acid solutions [2–4], with the aim of decompose these substances in wastewaters. The process involves continuous electrochemical generation of H_2O_2 in a carbon-containing gas-diffusion electrode from pure oxygen or air fed into the vessel, reaction of H_2O_2 with Fe^{2+} catalyst in the solution to form a strong oxidant, hydroxyl radical OH^\bullet , and its subsequent reactions with contaminants, with the reduction of Fe^{3+} to Fe^{2+} on the cathode or by another procedure.

In contrast to direct electrolytic oxidation of organic substances, usually occurring at high anode potentials, where almost always there are problems with the corrosion resistance of electrode materials, thermodynamic stability of aqueous electrolyte solutions, and tarring of products on the electrode surface, in indirect oxidation such problems do not arise, because the cathodic generation of H_2O_2 occurs at relatively low electrode potentials and the chemical reaction occurs

in a homogeneous medium. The use of the electro-Fenton reaction allows complete mineralization of organic substances to oxides of the constituent elements (H_2O , CO_2 , etc.) or their decomposition to substances allowing the use of other decontamination methods, e.g., microbiological [4].

Electrochemical synthesis of H_2O_2 is also promising for preparing solutions of salts forming molecular adducts with H_2O_2 , peroxy solvates [5]. These solutions can be concentrated, and solids containing up to 50 wt % H_2O_2 can be obtained. These compounds are highly stable in the solid state, can be stored for a long time, and can be used when necessary in food industry and medicine, for disinfection and detoxification of soil [6], as oxidants in organic synthesis, etc. H_2O_2 solutions with an electrolyte can be used in current sources for accumulation of the electricity obtained from renewable power sources [7]. It should be noted that H_2O_2 can be obtained on the site of its consumption; its isolation in the pure form, transportation, and storage are not required, and the procedure is waste-free.

The electrochemical synthesis of H_2O_2 from O_2 is mainly performed using various graphitic carbon materials as constituents of gas-diffusion electrodes

(GDEs) [2, 3, 5, 8–10]. The electrochemical synthesis efficiency depends on the physicochemical and structural properties of carbon materials. Therefore, active studies are being performed in the world with the aim of developing new promising carbon materials for use in electrochemical units, in particular, for two-electron oxygen reduction.

Mesoporous carbon materials (MCMs) are a new class of materials promising for various electrochemical applications [11, 12]. MCMs prepared by template synthesis have large specific surface area, ordered mesoporous structure, high mechanical strength, and high electrical conductivity. The possibility of using mesoporous carbon for electrochemical synthesis of hydrogen peroxide from oxygen on a rotating disk electrode was demonstrated by Perazzolo et al. [13, 14]. The structure of such material favors more rapid removal of the synthesized H_2O_2 from the reaction zone, which prevents its chemical decomposition or further electrochemical reduction to water. Perazzolo et al. [14] demonstrated the possibility of using mesostructured carbon for mineralization of Methyl Orange by its indirect oxidation with electrochemically synthesized H_2O_2 .

This study was aimed at evaluating the efficiency of the electrochemical synthesis of H_2O_2 in various aqueous electrolyte solutions in GDE with MCM.

EXPERIMENTAL

The MCM was prepared using the procedure described in [12]. SBA-15 mesostructured silicate material was used as a template. The experiment conditions, design of the electrolyzer, and electrode fabrication procedure were similar to those described in [3, 5, 10].

The electrode mass was prepared by joint coagulation of an aqueous suspension of polytetrafluoroethylene (PTFE) and a suspension of the carbon material. After coagulation, the mass was filtered off, washed with water, dried in an oven at 120°C to constant weight, milled in a knife mill, and sieved through a sieve with the opening size of 0.25 mm. Then, the mass was heated at 300°C for 1 h. The Teflon concentration in the gas-feeding layer with A437E acetylene black was 50 wt %, and in the working layer with MCM it was 60 and 70 wt %. Electrodes with 60 vol % porosity were formed in a mold with restricted punch stroke in the form of flat 0.9-mm-thick disks with a 0.1-mm-thick nickel grid

as a current lead in the middle of the gas-feeding layer. The weight ratio of the working and gas-feeding layers was approximately 1 : 1. The weight of the working layer per unit geometric surface area of the electrode was 32 mg cm^{-2} . The electrodes were sintered in a heated mold at 360°C for 10 min. Prior to experiments, the electrodes were impregnated with an electrolyte at a current of 0.1 A for 1 h, and the electrolyte porosity was determined by hydrostatic weighing in water. The electrolyte porosity of the electrodes with 60 and 70 wt % PTFE was 17 and 12 vol %, respectively.

Experiments were performed in a three-chamber glass cell of the electrolyzer [10]. GDE (cathode) was arranged between the cathode and gas chambers. The catholyte and anolyte (1–2 M H_2SO_4) were separated by MF-4SK-100 cation-exchange membrane. A platinum plate served as an anode. Aqueous solutions of potassium salts with different pH values were used as electrolytes. The polarization curves were recorded at a potential sweep rate of 1 mV s^{-1} . The current density was calculated per unit of the visible frontal surface area of the electrode (5 cm^2). The electrode potential was measured vs. saturated silver chloride reference electrode (EVL-1M1). Preparative electrochemical synthesis of H_2O_2 was performed at $20\text{--}25^\circ\text{C}$ in the constant-current mode. Oxygen was fed to the electrode continuously from its rear side through a gas chamber at atmospheric pressure with a small excess, which was discharged into the atmosphere.

In the course of preparative synthesis of H_2O_2 , we determined the fraction of current, γ , spent for the synthesis of hydrogen peroxide [10] in GDE, because H_2O_2 can be reduced to H_2O . To this end, we determined by a gasometric method at a constant current the time required for the uptake of a definite amount of oxygen. The quantity γ characterizes the processes occurring in the electrode, and the current efficiency characterizes the efficiency of the overall electrochemical synthesis process, as it takes into account also the H_2O_2 decomposition in the cathode chamber. Naturally, the rate of the H_2O_2 reduction and decomposition to water increases as the H_2O_2 concentration in the electrolyte is increased.

Stirring of the electrolyte plays a significant role in the mass exchange, influencing the rate of the H_2O_2 removal from the frontal electrode surface and of the supply of hydrogen cations participating in the H_2O_2 formation in acid solutions [3] to the electrode, which, in

turn, influences the value of γ and the current efficiency. In our case, stirring was performed by air bubbling through the electrolyte at different rates determined in preliminary experiments.

The H_2O_2 concentration was determined by titration with potassium permanganate. Prior to sampling, the electrolyte was stirred in the case if it had not been continuously stirred in the course of the experiment.

RESULTS AND DISCUSSION

Preliminary experiments have shown that MCM is wetted with aqueous electrolyte solutions very well, e.g., as compared to acetylene black electrodes with 60 wt % PTFE, whose electrolyte porosity is as low as 3.6 vol % [15]. Therefore, to create between the electrolyte, catalyst, and hydrophobizing agent the most developed three-phase interface on which the oxygen reduction occurs, we used high PTFE concentrations when preparing the working mass of the electrodes.

Figure 1 shows three typical polarization curves of oxygen reduction in two solutions, obtained with our electrodes. The other curves are similar to curve 1 and are not given.

As seen from Fig. 1, the electrode activity considerably increases when a working MCM layer is applied onto the gas-feeding acetylene black layer. The activity of the gas-feeding layer taken along is appreciably lower than that in a solution with low electrical conductivity. When using the electrolyte of a lower concentration, the electrode polarization increases, which is due to a decrease in the electrical conductivity of the solution and to a significant increase in the ohmic constituent of the polarization. However, the use of solutions with low electrolyte concentration is necessary in some cases, e.g., for disinfection and detoxification of soil [6].

The results of preparative electrolyses in different electrolytes are given in Fig. 2 and in the table. The curve obtained in KF is not given, because it coincides with curve 1. It should be noted that the catholyte volume increases in the course of the synthesis owing to the production of H_2O_2 and H_2O , and also to the transfer of water with a proton from the anode chamber through the cation-exchange membrane, which decreases the electrical conductivity of the electrolyte and increases the electrode polarization. The rate at which the electrolyte volume increases depends on the current density, on the H_2O_2 current efficiency, on the electrolyte composition,

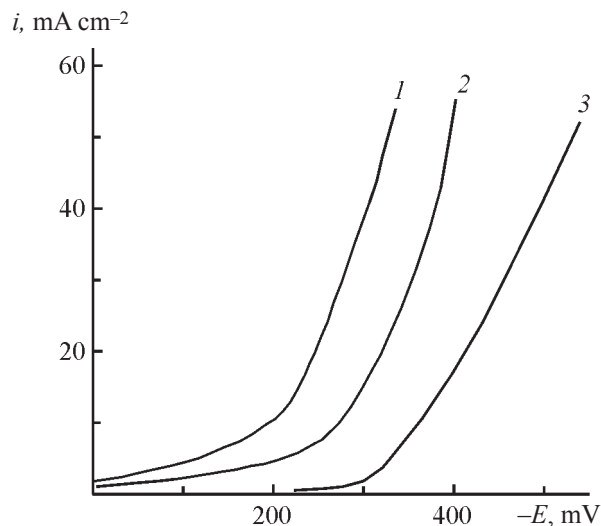


Fig. 1. Polarization curves of O_2 reduction in GDE (1, 2) with MCM, 70 wt % PTFE in the working layer, and (3) without MCM, A437E carbon black, 50 wt % PTFE. Solution: (1, 3) 0.6 M K_2SO_4 + 0.15 M H_2SO_4 and (2) 0.05 M K_2SO_4 + 0.01 M H_2SO_4 . (*i*) Current density and (*E*) potential.

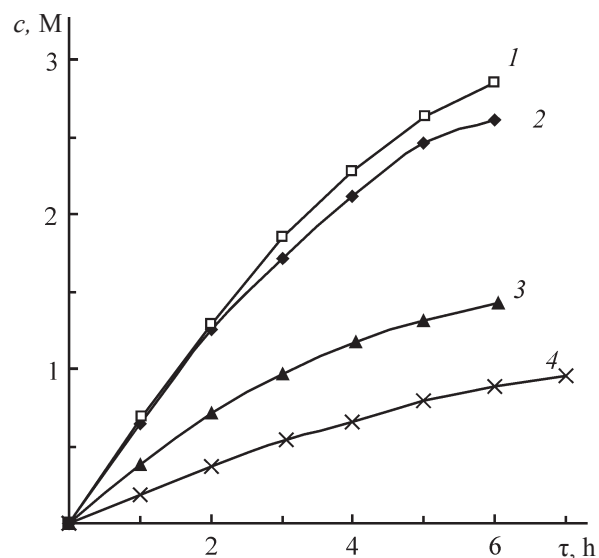


Fig. 2. H_2O_2 accumulation curves obtained on electrodes with MCM, containing (1, 3, 4) 70 and (2) 60 wt % PTFE, at current densities of (1, 2) 0.19, (3) 0.1, and (4) 0.05 A cm^{-2} . Electrolyte composition: (1, 2) 0.6 M K_2SO_4 + 0.15 M H_2SO_4 and (3, 4) 0.05 M K_2SO_4 + 0.01 M H_2SO_4 . (*c*) H_2O_2 concentration and (τ) time.

concentration, and pH, and on the membrane type. In our case, the rate at which the catholyte volume increased varied from 0.14 mL h^{-1} in 0.05 M K_2SO_4 + 0.01 M H_2SO_4 at 0.05 A cm^{-2} to 1.1 mL h^{-1} in 0.6 M K_2SO_4 + 0.15 M H_2SO_4 at 0.19 A cm^{-2} . The curves in Fig. 2 do

Results of electrochemical synthesis of H₂O₂ in electrodes with mesoporous carbon in different electrolytes (electrolysis time 6 h)

Electrolyte, M	Electrolyte stirring rate, mL min ⁻¹	Current density per geometric surface area, A cm ⁻²	Negative potential, ^a V	H ₂ O ₂ concentration, M	Current efficiency, %	γ, fractions of unity, at indicated C _{H₂O₂} , M		
						0	1	2.6
Electrode with 70 wt % PTFE								
2KF (pH 7–8)	45	0.19	0.52–0.63	2.8	70	0.95	0.95	0.95
0.6K ₂ SO ₄ + 0.15H ₂ SO ₄ (pH ≈ 2)	18	0.19	0.51–0.67	2.8	70	0.92	0.92	0.73
0.05K ₂ SO ₄ + 0.01H ₂ SO ₄ (pH ≈ 2.5)	0	0.05	0.38–0.42	1.0	61	0.98	0.45	–
		0.1	0.43–0.6	1.4	46	0.98	0.4	–
Electrode with 60 wt % PTFE								
0.6K ₂ SO ₄ + 0.15H ₂ SO ₄ (pH ≈ 2)	18	0.19	0.45–0.5	2.6	66	0.92	0.89	0.7

^a The potential at the beginning and end of electrolysis.

not differ in shape from those obtained on other GDEs [5, 8–10]. This fact indicates that the relationships of the H₂O₂ accumulation are similar to those observed on all the other electrodes. The curves will flatten out with increasing electrolysis time, when the H₂O₂ synthesis rate will become equal to the rate of the H₂O₂ decomposition and further reduction to water.

As can be seen, in different electrolytes on MCM electrodes it is possible to obtain H₂O₂ solutions of relatively high concentration at high current densities and with relatively low electrode polarization. For comparison, e.g., on acetylene black electrodes in 2 M KF at a current density of 0.1 A cm⁻², which is almost 2 times lower than in our case, and equal H₂O₂ concentration, the polarization was 0.53–0.64 V [3] (vs. Ag/AgCl electrode). On GDE with Printex 6L carbon black at a current density of ≈0.2 A cm⁻² in 1 M KOH, the electrode potential was 0.9 V (reference electrode Ag/AgCl) [8].

Lower polarization can be caused by several factors. The specific surface area of MCM, about 900 m² g⁻¹ [12], is considerably higher than that of acetylene black (110 m² g⁻¹ [10]) or of Printex 6L (260 m² g⁻¹ [8]), which can increase the area of the catalyst–oxygen–electrolyte three-phase contact, leading to a decrease in the true current density and hence in the electrode polarization.

The presence of a large amount of mesopores in the MCM structure favors, as noted in [13, 14], better removal of H₂O₂ from the electrode, which decreases the concentration and ohmic constituents of the polarization. A decrease in the polarization may also be due to higher catalytic activity of MCM.

On electrodes with 60 wt % PTFE, the polarization is lower. This is due to higher electrolytic porosity and hence to lower ohmic loss, but the conditions for the electrochemical synthesis in this case become less favorable.

The electrolyte concentration or, more precisely, the concentration of alkali metal cations significantly influences the H₂O₂ synthesis efficiency. As the concentration of potassium cations is decreased, γ decreases, and to preserve the acceptable current efficiency it becomes necessary to decrease the current density. Similar influence of the electrolyte concentration is observed with different GDEs, e.g., in [9]. This is associated with a decrease in the size of the reaction zone across the electrode thickness due to a decrease in the electrolyte conductivity, with an increase in the true current density, and with an increase in the limiting diffusion currents and migration of hydrogen cations in acid solutions [16], leading to acceleration of the further reduction of H₂O₂ to water.

CONCLUSIONS

Our studies of porous gas-diffusion electrodes with a mesoporous carbon material demonstrated the possibility of preparing H₂O₂ solutions of high concentration at high current densities and relatively low electrode polarization in solutions of different electrolytes with widely varied concentrations and pH values.

It is undoubtedly promising to use mesoporous carbon prepared by template synthesis on the basis of SBA-15 mesostructured silicate material for electrochemical synthesis of H₂O₂ from O₂ in gas-diffusion electrodes.

REFERENCES

1. Moreira, F.C., Boaventura, R.A.R., Brillas, E., and Vilar, V.J.P., *Appl. Catal. B: Environmental*, 2017, vol. 202, pp. 217–261.
2. Pliego, G., Zazo, J.A., Garcia-Munoz, P., et al., *Crit. Rev. Environ. Sci. Technol.*, 2015, vol. 45, no. 24, pp. 2611–2692.
3. Kornienko, V.L., Kolyagin, G.A., Kornienko, G.V., et al., *Russ. J. Appl. Chem.*, 2014, vol. 87, no. 1, pp. 1–15.
4. Riccobono, G., Pastorella, G., Vicari F., et al., *J. Electroanal. Chem.*, 2017, vol. 799, pp. 293–298.
5. Kolyagin, G.A. and Kornienko, V.L., *Russ. J. Electrochem.*, 2015, vol. 51, no. 2, pp. 185–189.
6. Viisimaa, M. and Goi, A., *J. Environ. Eng. Landscape Manag.*, 2014, vol. 22, no. 1, pp. 30–39.
7. Fukuzumi, S. and Yamada, Y., *ChemElectroChem*, 2016, vol. 3, no. 12, pp. 1978–1989.
8. Barros, W.R.P., Ereno, T., Tavares, A.C., and Lanza, M.R.V., *ChemElectroChem*, 2015, vol. 2, no. 5, pp. 714–719.
9. Soltani, R.D.C., Rezaee, A., Khataee, A.R., and Godini, H., *Res. Chem. Intermed.*, 2013, vol. 39, no. 9, pp. 4277–4286.
10. Kornienko, V.L., Kolyagin, G.A., and Saltykov, Yu.V., *Elektrosintez v gidrofobizirovannykh elektrodakh* (Electrosynthesis in Hydrophobized Electrodes), Tomilov, A.P., Ed., Novosibirsk: Sib. Otdel. Ross. Akad. Nauk, 2011.
11. Inagaki, M., Toyoda, M., Soneda, Y., et al., *Carbon*, 2016, vol. 107, pp. 448–473.
12. Solyanikova, A.S., Chayka, M.Yu., Boryak, A.V., et al., *Russ. J. Electrochem.*, 2014, vol. 50, no. 5, pp. 419–428.
13. Perazzolo, V., Durante, C., Pilot, R., et al., *Carbon*, 2015, vol. 107, pp. 448–473.
14. Perazzolo, V., Durante, C., and Gennaro, A., *J. Electroanal. Chem.*, 2016, vol. 782, pp. 264–269.
15. Kolyagin, G.A. and Kornienko, V.L., *Russ. J. Appl. Chem.*, 2017, vol. 90, no. 4, pp. 553–557.
16. Pirogov, B.Ya. and Zelinskii, A.G., *Russ. J. Electrochem.*, 2009, vol. 45, no. 3, pp. 336–344.