DOUBLE-LAYER CAPACITANCE CHARACTERIZATION OF PORPHYRIN-MODIFIED GRAPHITE ELECTRODES

Bogdan-Ovidiu Taranu[1], Eugenia Fagadar-Cosma[2]

[1]*National Institute for Research and Development in Electrochemistry and Condensed Matter, Dr. A.P. Podeanu street, No. 144, 300569, Timisoara, Romania*
[2] *Institute of Chemistry "Coriolan Dragulescu", Mihai Viteazu Ave. 24, 300223 Timisoara, Romania*
e-mail: b.taranu84@gmail.com

Abstract
Porphyrin-modified graphite electrodes were manufactured and evaluated in terms of their double-layer capacitance. The highest value, of 14.017 mF/cm^2, was obtained for the electrode resulted by drop-casting a layer of 5,10,15,20-tetrakis(4-methoxy-phenyl)-porphyrin from benzonitrile on graphite support. Since a high double-layer capacitance value is characteristic of supercapacitors, out of the investigated samples, this electrode is the most likely to find application in their field.

Introduction
Porphyrins are a class of aromatic compounds that share the basic porphine structure, which is comprised of C, N and H atoms organized as a tetrapyrrolic ring, and is referred to as the porphyrin macrocycle. The structure can be peripherally substituted with different functional moieties and, additionally, almost any metal cation can be bound in its inner core. Changes to the macrocycle lead to porphyrin derivatives that possess various properties, which make them suitable for different applications [1]. For example, in a study reported by Taranu and Fagadar [2], the water splitting electrocatalytic properties of four free-base porphyrin structures were evaluated in alkaline medium after being used to manufacture a series of electrodes *via* their drop-casting on graphite substrates from different organic solvents, in one to three layers. The experimental results allowed the identification of the most electrocatalytically active porphyrin-modified graphite electrodes for the oxygen and hydrogen evolution reactions.

The present work is a continuation of the aforementioned study and focuses on the further electrochemical characterization of these electrodes, in terms of their electric double-layer capacitance - a parameter of importance in the field of supercapacitors. Organic electrode materials, such as porphyrins, are suitable for supercapacitor applications, because their morphology can be tailored and controlled, and they have very fast redox kinetics due to the small HOMO–LUMO gaps, which is consistent with the enhanced electrical conductivity of the material [3].

Experimental
The porphyrins employed in the study are 5-(4-pyridyl)-10,15,20-tris(4-phenoxy-phenyl)-porphyrin (P1), 5,10,15,20-tetrakis(4-methoxy-phenyl)-porphyrin (P2), 5,10,15,20-tetrakis(4-allyloxy-phenyl)-porphyrin (P3) and 5,10,15,20-tetrakis(*p*-tolyl)-porphyrin (P4), and their synthesis was performed using previously published procedures [4-7]. The organic solvents utilized to obtain the porphyrin solutions are N,N-dimethylformamide (DMF), dichloromethane (DCM) and benzonitrile (BN), purchased from Sigma Aldrich and Merck. Potassium chloride from Merck, ethanol from Honeywell and acetone from Chimreactiv (Bucharest) were also used during the study. Aqueous solutions were obtained with double

distilled water. The graphite substrates for electrode manufacturing were rods of spectroscopic graphite, type SW.114 from "Kablo Bratislava", National Corporation "Electrocarbon Topolcany" Factory (Slovakia).

The rods were wrapped in PE tubes, tightly attached to them *via* thermal treatment at 180 °C. The two rod ends were used as follows: one of them was connected to the potentiostat during the experiments, while the surface of the other was modified with the porphyrins by drop-casting them from different solvents and, while the voltammograms were recorded, was immersed into the electrolyte solution. The modification procedure involved: a) the polishing of the substrate surface using silicon carbide paper (800 and 1200 grit sizes) and felt; b) the subsequent washing with double-distilled water, ethanol and acetone; c) the drying at room temperature; d) the application of the porphyrin solution having 0.15 mM concentration on the polished surface (a volume of 10 µL was used to obtain each porphyrin layer) and e) the solvent evaporation stage. Table 1 presents the tags of the manufactured electrodes.

Table 1. The tags given to the porphyrin-modified graphite electrodes

Electrode tag	Porphyrin	Solvent	No. of porphyrin layers
$G_{P1-DCM-1}$	P1	DCM	1
$G_{P1-DMF-3}$	P1	DMF	3
$G_{P2-BN-1}$	P2	BN	1
$G_{P3-DCM-1}$	P3	DCM	1
$G_{P3-BN-1}$	P3	BN	1
$G_{P4-BN-1}$	P4	BN	1

The use of different solvents is justified in light of the ability of porphyrin molecules to self-assemble, resulting in aggregates bearing particular morphologies and properties. One way in which such structures are formed is by drop-casting the porphyrins on solid substrates from solvents having different polarity [8], thus influencing the aggregation mechanism.

The electrochemical setup consisted in a glass cell with three electrodes connected to a potentiostat (Voltalab PGZ 402 from Radiometer Analytical). A Pt plate ($S_{geom} = 0.8$ cm^2) served as auxiliary electrode, the Ag/AgCl (sat. KCl) electrode was employed as reference and the samples presented in Table 1 were utilized as working electrodes. The electrolyte was 0.1 M KCl aqueous solution. The experiments consisted in the recording of cyclic voltammograms at different scan rate (*v*) values. The cyclic voltammetry method can be used to determine the electric double-layer capacitance (C_{dl}), namely the capacitance from stored charge in the double-layer region at the interface between the electrode and the electrolyte [9]. First, voltammetry cycles were recorded in a potential range where no faradic currents were present. Second, the capacitive current density (i_{dl}) was calculated using equation (1) and third, the C_{dl} value was obtained as the absolute value of the slope from the i_{dl}-*v* linear dependence [6, 10].

$$i_{dl} = (i_a + i_c)/2 \qquad\qquad\qquad (1)$$

Where: i_{dl} [A/cm^2] is the capacitive current density; i_a and i_c [A/cm^2] are the absolute values of the anodic and cathodic current densities at a potential value where only double-layer adsorption and desorption features are present [11].

All potentials are expressed *vs.* the Ag/AgCl (sat. KCl) electrode and all experiments were performed at 23±2 °C.

Results and discussion

Figure 1 presents the plot of the dependence between the capacitive current density and the scan rate for the porphyrin-based graphite electrodes, while Table 2 shows the double-layer capacitance and R^2 values obtained for the same samples.
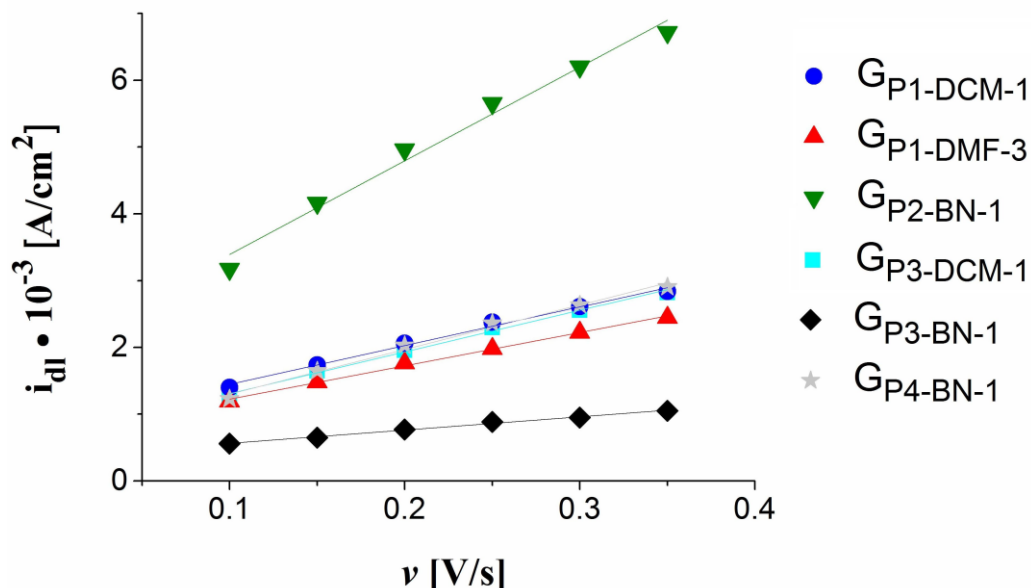

Figure 1. The graphical representation of the dependence between i_{dl} and v for the porphyrin-modified electrodes specified in Table 1, based on data from cyclic voltammograms recorded in 0.1 M KCl electrolyte solution, at v = 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 V/s.

Table 2. The C_{dl} and R^2 values obtained for the porphyrin-modified electrodes

Electrode tag	C_{dl} [mF/cm^2]	R^2
$G_{P1-DCM-1}$	5.798	0.9915
$G_{P1-DMF-3}$	4.982	0.9961
$G_{P2-BN-1}$	14.017	0.9803
$G_{P3-DCM-1}$	6.239	0.9934
$G_{P3-BN-1}$	1.983	0.9933
$G_{P4-BN-1}$	6.251	0.9927

As can be seen, the highest C_{dl} value, of 14.017 mF/cm^2, was obtained for $G_{P2-BN-1}$. The C_{dl} was also expressed in mF by taking into consideration the geometrical surface of the respective electrode (S_{geom} = 0.28 cm^2), and it became ~3.925 mF. Since a high value of this parameter is characteristic of supercapacitors, out of the investigated electrodes the one modified with the P2 porphyrin is the most likely to find application in their domain. It can also be observed that the C_{dl} values for $G_{P3-DCM-1}$ and $G_{P3-BN-1}$ are quite different, even though only the solvent was changed during their manufacturing. Considering the ability of porphyrin molecules to self-organize into aggregates, this result shows that applying the same porphyrin on graphite substrate from solvents having different polarity can lead to the formation of assemblies with distinct properties.

Conclusion

The porphyrin-modified electrodes that were found in a previous study to possess the best water splitting electrocatalytic properties from a series of such samples have been characterized in the present work in terms of their double-layer capacitance. The highest value was obtained for the $G_{P2-BN-1}$ electrode, manufactured by drop-casting one layer of 5,10,15,20-tetrakis(4-methoxy-phenyl)-porphyrin from benzonitrile on graphite substrate.

As a new approach perspective, porphyrins might serve as bipolar organic electrodes by exploiting their capacity of donating or accepting electrons at their inner core. Based on the fact that porphyrins have small HOMO–LUMO gaps, enabling the facile uptake and release of electrons, and thus leading to fast redox reactions, they are suitable for porphyrin-based flexible supercapacitor electrode materials [12].

References

[1] E. Fagadar-Cosma, D. Vlascici, G. Fagadar-Cosma, Porfirinele de la sinteză la aplicații, Eurostampa, Timisoara, Romania, 2008, pp. 10.

[2] B.-O. Taranu, E. Fagadar-Cosma, Processes 10 (2022) 611.

[3] H. Yang, S. Zhang, L. Han, Z. Zhang, Z. Xue, J. Gao, Y. Li, C. Huang, Y. Yi, H. Liu, Y. Li, ACS Appl. Mater. Interfaces 8 (2016) 5366.

[4] E. Fagadar-Cosma, G. Fagadar-Cosma, M. Vasile, C. Enache, Curr. Org. Chem. 16 (2012) 931.

[5] E. Fagadar-Cosma, C. Enache, R. Tudose, I. Armeanu, E. Mosoarca, D. Vlascici, O. Costisor, Rev. Chim. 58 (2007) 451.

[6] B.O. Taranu, E. Fagadar-Cosma, I. Popa, N. Plesu, I. Taranu, Dig. J. Nanomater. Bios. 9 (2014) 667.

[7] E. Fagadar-Cosma, C. Enache, I. Armeanu, D. Dascalu, G. Fagadar-Cosma, M. Vasile, I. Grozescu, Mater. Res. Bull. 44 (2009) 426.

[8] M. Birdeanu, E. Fagadar-Cosma, in: M.V. Putz (Ed.), Quantum Nanosystems: Structure, Properties, and Interactions, Apple Academic Press: Toronto, Canada, 2015, pp. 173.

[9] N.I. Ramli, N.A.B Ismail, F. Abd-Wahab, W.W.A.W. Salim, in: K. Pal (Ed.), Transparent Conducting Films, IntechOpen, London, UK, 2018, pp. 75.

[10] Z. Zhou, W.Q. Zaman, W. Sun, L. Cao, M. Tariq, J. Yang, Chem. Commun. 54 (2018) 4959.

[11] A. Kellenberger, D. Ambros, N. Plesu, Int. J. Electrochem. Sci. 9 (2014) 6821.

[12] J. N'Diaye, M. Elshazly, K. Lian, ACS Appl. Mater. Interfaces, 14 (2022) 28359.