DOUBLE-LAYER CAPACITANCE STUDY OF A NICKEL PHOSPHITE/PROPHRYIN-MODIFIED GRAPHITE ELECTRODE WITH WATER-SPLITTING CATALYTIC PROPERTIES

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Abstract

An electrode exhibiting water-splitting catalytic properties was manufactured by applying a combination between $Ni_{11}(HPO_3)_8(OH)_6$ and 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin on graphite substrate. The specimen was coded $G_{NiPh-TMeOPP}$ and its double-layer capacitance was investigated. The obtained value of 7.475 mF/cm^2 is higher than the ones determined for the unmodified graphite support and for the nickel phosphite-based graphite electrode. This result indicates that $G_{NiPh-TMeOPP}$ is the most likely to find application in the field of supercapacitors.

Introduction

The constant search for new catalysts possessing water splitting properties takes part within the broader context represented by the global energy crisis and climate change [1]. Nickel phosphite and porphyrins are among the materials identified so far as exhibiting electrocatalytic activity for the two half-cell reactions involved in the electrochemical decomposition of H_2O, namely the oxygen and the hydrogen evolution reactions [2-5]. Regarding $Ni_{11}(HPO_3)_8(OH)_6$, it is a member of the metal phosphites class and it has been reported as a highly active, very stable, robust and structurally versatile electrocatalyst for overall water splitting [3]. It was also investigated by Taranu *et al.* in water electrolysis studies [6-8]. As for porphyrins, there are many published articles in which these compounds have been revealed as catalytically active for the decomposition of water [9-12]. What makes them suitable for such an application are their specific structure and properties. Porphyrins are a class of aromatic organic pigments sharing the tetrapyrrole porphine macrocycle that can be substituted with a wide variety of functional groups and can bound in its centre almost any metal ion [13,14]. Whether free-base or metalated, porphyrin molecules can spontaneously associate to form stable and well-defined aggregates that have properties of their own, including water splitting electrocatalytic ones [4,15].

In a study published by Taranu *et al.* [8], the catalytic activity for the hydrogen evolution reaction (HER) of free-base porphyrin aggregates combined with nickel phosphite was investigated in alkaline medium. The experimental results have shown that the combination between the metal salt and the metal-free 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin was the most catalytically active for the specified reaction. The purpose of the current investigation is to further characterise the electrode manufactured using the specified mixture, but in terms of its electric double-layer capacitance (C_{dl}). This parameter, representing the capacitance from stored charge in the double-layer region at the electrode/electrolyte solution interface [16], is relevant when trying to determine whether an electrode material can be utilized in the field of supercapacitors. It should also be pointed out that $Ni_{11}(HPO_3)_8(OH)_6$ and members of the porphyrin class have been reported as suitable for the mentioned application [17-19].

Experimental

The nickel phosphite was obtained hydrothermally at high temperature and high pressure, in accordance with the literature [6,20]. 5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin (TMeOPP) was also synthesized following a previously published procedure [21], and its chemical structure can be seen in Scheme 1. Tetrahydrofuran (THF), purchased from Sigma-Aldrich, was employed to obtain the porphyrin solution that was used in the electrode manufacturing process. Other reagents involved in the study were potassium chloride (Merck), ethanol (Honeywell) and acetone (Chimreactiv). All aqueous solutions were prepared with laboratory produced double distilled water. A spectroscopic graphite rod (ø = 6 mm), type SW.114 ("Kablo Bratislava", National Corporation "Electrocarbon Topolcany" Factory, Bratislava, Slovakia), served as the substrate of the nickel phosphite/porphyrin modified electrode.
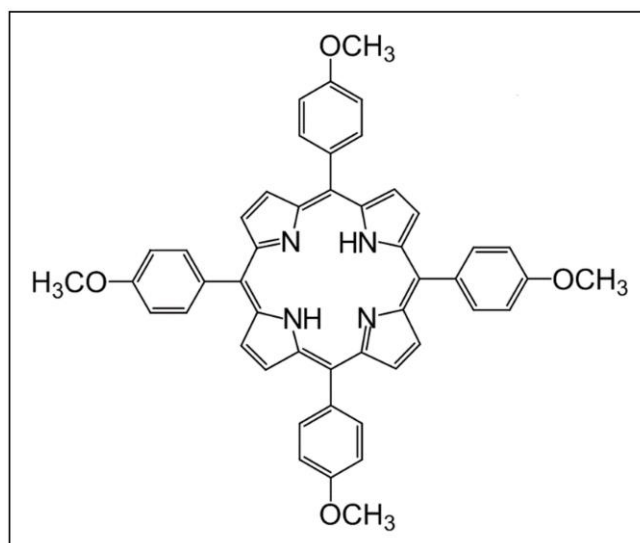
Scheme 1. The chemical structure of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin

The manufacturing process involved several steps: (1) The graphite rod was introduced inside a polyethylene tube; (2) A thermal treatment at 180 °C ensured the sealing between the rod and the tube; (3) The surface of one of the rod ends was polished with silicon carbide paper (grit sizes of 800 and 1200) and felt; (4) The polished surface was washed with double distilled water and dried at 23 ± 2 °C; (5) The nickel phosphite/TMeOPP composition was applied from a suspension on the dried graphite surface; (6) The modified surface was exposed to 40 °C for 4 h and 23 ± 2 °C for 20 h to ensure solvent evaporation.

As for the suspension containing the metal salt and TMeOPP, it was realized by first dissolving the porphyrin in 500 µL THF so as to obtain a 0.15 mM solution and by subsequently adding to it 1.5 mg nickel phosphite. After 40 minutes of ultrasonication, a volume of 10 µL was removed from the suspension and was drop-casted on the graphite substrate – see step (5) from the manufacturing process. The resulted modified electrode was coded $G_{NiPh-TMeOPP}$. Other specimens used in the study were the unmodified graphite support (G_0) and an electrode modified only with nickel phosphite (G_{NiPh}).

A Voltalab PGZ 402 potentiostat (Radiometer Analytical) connected to three electrodes inserted into a glass cell was employed throughout the electrochemical investigations. Each sample was utilized as working electrode (S_{geom} = 0.28 cm^2), the auxiliary electrode was a Pt plate (S_{geom} = 0.8 cm^2) and Ag/AgCl (sat. KCl) was the reference electrode. All the potentials are quoted versus the specified reference and all experiments were performed at 23 ± 2 °C in unstirred electrolyte solution.

In order to determine the C_{dl} value for every specimen a previously reported protocol was followed [22]. Basically, cyclic voltammograms were recorded in neutral medium (0.1 M KCl solution) at different scan rate (*v*) values and in a potential range where no faradic currents were present. The voltammetric data were subsequently used in Equation (1) to calculate the capacitive current density (i_{dl}). Lastly, the C_{dl} value was determined as the absolute value of the slope from the linear dependence between i_{dl} and the scan rate [23].

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

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 [24].

Results and discussion

The i_{dl}-*v* graphical representation for the studied specimens is shown in Figure 1, and Table 1 presents the obtained C_{dl} and R^2 values. The C_{dl} values are expressed both is mF/cm^2 (areal C_{dl}), as well as in mF (by considering the 0.28 cm^2 geometric surface of the electrodes). It can be seen that the highest value was found for $G_{NiPh-TMeOPP}$ and this result indicates that out of the investigated samples the electrode modified with the combination between nickel phosphite and TMeOPP is the most likely to find application as electrode material in supercapacitors.
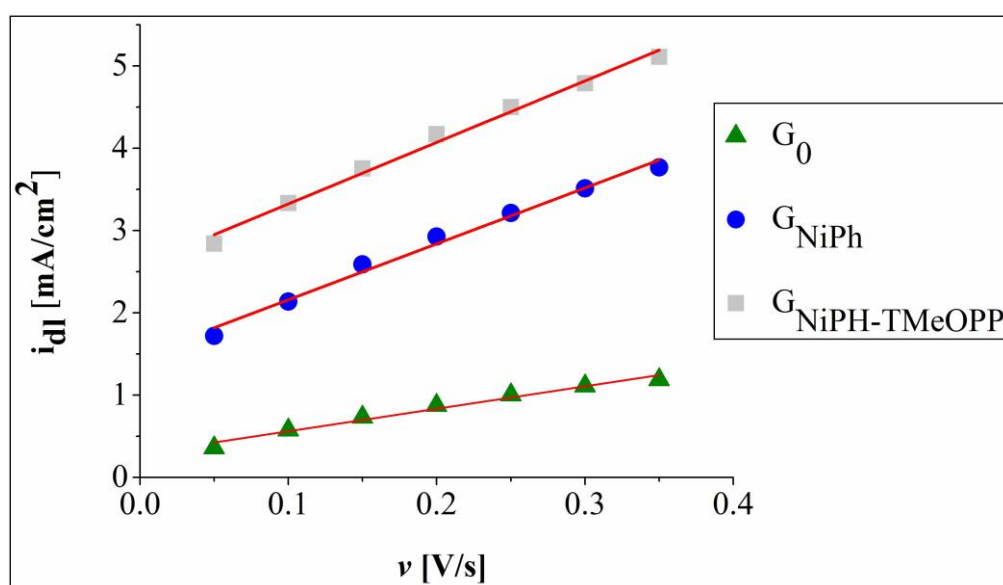

Figure 1. The i_{dl}-*v* plot for the G_0, G_{NiPh} and $G_{NiPh-TMeOPP}$ electrodes, obtained using the results from the cyclic voltammetry study of these specimens in 0.1 M KCl electrolyte solution, at *v* = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 V/s

The higher C_{dl} for $G_{NiPh-TMeOPP}$ can be explained in terms of the porphyrin species. As previously reported [8], compared with G_{NiPh}, $G_{NiPh-TMeOPP}$ benefits from the properties of both materials and it exhibits a larger electroactive surface area due to the intercalation between elongated nickel phosphite structures and self-assembled bundle-like TMeOPP aggregates.

Table 1. The C_{dl} and R^2 values obtained for the investigated electrodes

Electrode code	C_{dl}		R^2
	[mF/cm^2]	[mF]	
G$_0$	2.732	0.765	0.9734
G$_{NiPh}$	6.798	1.903	0.9869
G$_{NiPh-TMeOPP}$	7.475	2.093	0.9891

Conclusion

The double-layer capacitance of an electrode manufactured by drop-casting a combination between a transition metal phosphite – $Ni_{11}(HPO_3)_8(OH)_6$ – and a metal-free symmetrically substituted porphyrin on graphite support was successfully determined. The obtained value was higher than the ones found for the unmodified electrode and for the specimen manufactured by applying only the nickel phosphite on the graphite substrate, making the combination of the two materials more suitable to be used in the supercapacitors field.

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