

Phosphorus and nitrogen-containing carbons obtained by the carbonization of conducting polyaniline complex with phosphites



Patrycja Bober^{a,*}, Miroslava Trchová^a, Zuzana Morávková^a, Jana Kovářová^a, Iva Vulić^b, Nemanja Gavrilov^b, Igor A. Pašti^b, Jaroslav Stejskal^a

^a Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

^b University of Belgrade, Faculty of Physical Chemistry, Belgrade 11158, Serbia

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ABSTRACT

Non-conducting polyaniline base interacts with organic phosphites to a conducting product resembling classical polyaniline salts. Polyaniline–phosphite complexes were carbonized in inert atmosphere at 650 °C to phosphorus- and nitrogen-containing carbons. The resulting materials were tested with respect to their electrochemical performance by considering their capacitive properties and electrocatalytic activity towards oxygen reduction reaction (ORR). Carbonized polyaniline–diphenyl phosphite displayed the highest capacitance among all investigated carbons, reaching the values above 100 F g^{−1} at 5 mV s^{−1} in concentrated potassium hydroxide solution, while the same material also displayed the highest ORR activity in alkaline media. Considering small specific surface area of obtained carbon materials, the synthetic procedures lead to the surface structures which are exceptionally active for charge storage and in electrocatalysis of ORR. It is proposed that further improvement of electrochemical properties can be obtained by preserving the type of the present surface functional groups with simultaneous increase of their number by the increase of the specific surface.

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1. Introduction

Platinum is the best electrocatalyst among all materials used in the fuel cells in hydrogen evolution and oxygen reduction reactions (ORR) [1]. The price and limited availability of platinum prevent the extensive use in the energy-conversion devices. The search for platinum-free catalysts has recently come to the forefront. The application of various platinum-free electrocatalysts has recently been reviewed [1]. For example, the materials combining conducting polymers, such as polyaniline or polypyrrole, and compounds of non-platinum metals have been found to display both electrocatalytic [2–4] or photocatalytic [5,6] activity. Conducting polymers alone have proved to be efficient heterogeneous catalysts in organic synthesis [7]. Considering their intrinsic conductivity, the potential application as electrocatalysts seems to be promising, and has indeed been demonstrated [8–10].

Carbonized conducting polymers become of increasing interest because of the ease of their preparation [11,12]. It is expected that

the incorporation of nitrogen atoms to carbon structure during carbonization may affect the adsorption of reactants and thus also the catalyst efficiency. Catalysts for heterogeneous reaction require neither too strong nor too weak adsorption of reactants or reaction intermediates to the catalyst active sites [1]. Both carbonized polyaniline [13] and carbonized polypyrrole [14,15] had high activity towards ORR.

During the carbonization of conducting polymers, the features of their morphology are preserved [11,15–17]. This opens the possibility to control not only the morphology and nanostructure of resulting materials but also the specific surface area by tuning the reaction conditions during the synthesis of conducting polymers. The preparation of nanotubes and their conversion to nitrogen-enriched carbon nanotubes serves as an example [15–17].

In addition to nitrogen, also other atoms may be introduced to the structure of carbon and further affect the catalytic properties. There have been frequent approaches to incorporate boron [18,19], cobalt [20], fluorine [21], iron [22], oxygen [23–25], sulfur [26] or vanadium [27] atoms into carbon structure along with nitrogen [23]. Such materials have been exploited especially in supercapacitor electrodes [23–25] or as electrocatalysts in ORR [18–20,22].

* Corresponding author.

E-mail address: bober@imc.cas.cz (P. Bober).

It has recently been observed that organic H-phosphonates (or their tautomeric form, phosphites), interact with a non-conducting polyaniline base to a conducting product [32]. This reaction resembles the classical base-salt transition based on the protonation of polyaniline base. No protons, however, are available in H-phosphonates. As this new organic material contains both nitrogen and phosphorus atoms, it is reasonable to assume that in its carbonized analogue these atoms will also be present. This hypothesis is tested in the present paper. Furthermore, we have investigated electrochemical properties of produced carbon materials as electrode materials for supercapacitors and as electrocatalysts for oxygen reduction reaction. As already mentioned, carbon materials with heteroatoms incorporated in carbon matrix are particularly interesting in these fields, and the understanding of their electrochemical behavior can lead to the development of novel classes of electrodes for supercapacitors and noble metal-free catalysts for ORR.

2.1. Preparation

Polyaniline–phosphite complexes were placed into an electric oven and heated in a stream of nitrogen up to 650 °C. The power was then switched off and the sample was left to cool still in inert atmosphere. The codes of carbonized samples include terminal C, e.g., PANI-DMPH-C.

Surface areas of the samples dried at 120 °C for two hours were determined from argon adsorption curves at 77 K by the BET method on a home-made glass volumetric apparatus. The morphologies of prepared materials were characterized with the scanning electron microscopy using a JEOL 6400 microscope. An energy dispersive X-ray analysis (EDAX) spectrum was recorded with a FEI Quanta F200, USA, for elemental surface analysis. Thermogravimetric analysis (TGA) in nitrogen atmosphere has been used for the analytical carbonization of polyaniline. It was carried out at 50 cm³ min⁻¹ gas flow, at the heating rate of 10 °C min⁻¹ to selected temperature with a Pyris 1 Thermogravimetric Analyzer (Perkin-Elmer, USA).

Raman spectra were recorded with a Renishaw InVia Reflex Raman microspectrometer. The spectra were excited with Ar-ion 514 nm and diode 785 nm lasers. The scattered light was registered with a Peltier-cooled CCD detector (576×384 pixels) and analyzed with the spectrograph with holographic grating 2400 and 1200 lines mm^{-1} , respectively.

Electrochemical measurements were performed in a conventional one-compartment three-electrode electrochemical cell with wide platinum foil as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. Capacitive response of investigated carbons was evaluated using cyclic voltammetry in concentrated solutions of alkali-metal hydroxides. Electrocatalytic activity towards ORR was investigated in oxygen-saturated 0.1 M aqueous solution of potassium hydroxide using rotating disk electrode (RDE) voltammetry. Measurements were done with a Gamry PCI4/750 Potentiostat/Galvanostat equipped with a Pine rotator. Before and during the measurements, a gentle gas flow of nitrogen or oxygen was introduced just beneath the electrolyte surface. All the measurements were carried out at room temperature, 25.0 ± 0.5 °C.

3.1. Synthesis

Spectroscopic studies have proved and quantum-chemical calculations confirmed that polyaniline base interacts with

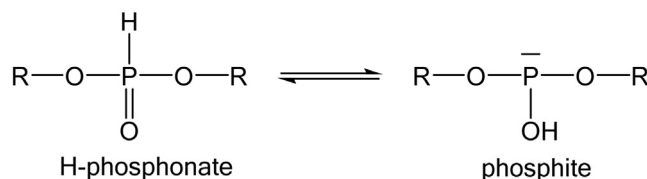


Fig. 1. The tautomers, H-phosphonate and phosphite, are organic esters derived from phosphonic and phosphorous acids, respectively. R stands for alkyl or aryl substituent.

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