



Electrocatalysis of oxygen reduction reaction on polyaniline-derived nitrogen-doped carbon nanoparticle surfaces in alkaline media

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HIGHLIGHTS

- ▶ Nitrogen-doped carbon nanomaterials were synthesized from polyaniline salts.
- ▶ Electrocatalytic activity toward ORR in alkaline solution was examined.
- ▶ Electrochemical data were correlated to the structural and textural data.
- ▶ Excellent electrocatalytic activity was found for carbonized PANI 5-sulfosalicylate.
- ▶ Electrocatalytic activity was correlated to electrical double layer capacity.

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ABSTRACT

Nitrogen-doped carbon nanomaterials were synthesized by the carbonization of three different nanostructured polyaniline (PANI) salt precursors: PANI 3,5-dinitrosalicylate nanorods, PANI 5-sulfosalicylate nanorods/nanotubes, and PANI hydrogen sulfate nanorods/nanotubes/nanosheets. A comparative study of the electrocatalytic activity of these materials for oxygen reduction reaction (ORR) in alkaline solution was performed by using rotating disk electrode voltammetry. The electrochemical data were correlated to the structural and textural data obtained by Raman spectroscopy, X-ray diffractometry, X-ray photoelectron spectroscopy, elemental analysis and nitrogen sorption analysis. A fine interplay of textural characteristics, overall content of surface nitrogen and content of specific surface nitrogen functional groups were found to be responsible for a considerable variations in electrocatalytic properties toward ORR, involving variations in apparent number of electrons exchanged per O₂ molecule (from 2 to nearly 4) and variations in onset potential. The catalyst loading was found to influence remarkably the ORR kinetics. The excellent electrocatalytic activity was found for carbonized PANI 5-sulfosalicylate. Namely, it exhibited the most positive onset potential amounting to -0.05 V vs. SCE at a catalyst loading of $500 \mu\text{g cm}^{-2}$. The interrelation between the electrocatalytic activity and the electrical double layer charging/discharging characteristics of the investigated N-doped nanocarbon materials was revealed.

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1. Introduction

High efficiency and environmental friendliness of low-temperature fuel cells as a promising power source for various applications have stimulated extensive research in recent years

[1,2]. High cost and scarcity of platinum, used in both cathode and anode catalyst layer, and limited durability of electrode materials limit a commercial application of fuel cells. Therefore, research was recently focused on the reduction of the use of platinum, up to its full substitution by nonprecious catalysts. Among various electrocatalysts, either metal-doped or pure nitrogen-containing carbon nanostructures (NCNS), were investigated as a suitable alternative [3,4]. Numerous research groups reported recently a high electroactivity of N-containing carbon-based catalysts toward oxygen

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reduction reaction (ORR) [4–11]. Some of the authors stressed that the presence of metals during the preparation of the catalysts plays an important role in the electrocatalytic activity [5,6]. Other studies suggested that pyridinic nitrogen acts as the major active site for ORR [7–9]. Nonetheless, the nature of the active sites for oxygen reduction in catalysts based on N-containing carbon materials remained still disputable [12–21]. Besides fuel cell application, the use of N-containing carbon materials as cathode materials in metal-air batteries presents nowadays an attractive field of research [22–24].

Commonly reported procedures for NCNS synthesis, such as post synthesis modification of carbon nanostructures with nitrogen-containing organic molecules [25–27] or laser ablation [28,29] and arc discharge [30,31] of graphite in the presence of a nitrogen source, usually require sophisticated equipment which is not suitable for large-scale production. On the other hand, NCNS can be easily prepared by a pyrolysis of N-containing organometallic macromolecules [6,9,32–36] or nitrogen-containing organic molecules [22,34,37–40]. Carbonization of nitrogen-containing aromatic polymer nanomaterials such as PANI nanostructures (which may simply be prepared under moderate and well controlled conditions by using both template-based and template-free methods [41]), was reported to be a proper way to prepare NCNS retaining the morphology of the nanostructured precursor [10,42–45]. It has recently been suggested [46] that the type of nanostructured PANI salt precursors used for preparation of NCNS determines special chemical, physical and textural properties of the obtained nanomaterials and, consequently, their performance in various applications, such as charge storage and electrocatalysis. It was also proposed that highly active catalysts could be obtained from structurally/morphologically optimized polymer precursors [46]. However, any systematic study in that sense did not appear in the literature until now.

The purpose of the present study was to compare the electrocatalytic activities of different carbonized PANI nanostructures toward ORR in alkaline media. Carbonized PANI hydrogen sulfate (C-PANI) nanorods/nanotubes/nanosheets [42,44], carbonized PANI 5-sulfosalicylate (C-PANI.SSA) nanorods/nanotubes [10], and carbonized PANI 3,5-dinitrosalicylate (C-PANI.DNSA) nanorods [45] were selected because they are expected to provide similar molecular structure and morphology, and, at the same time, crucial differences in textural properties, surface nitrogen and carbon concentration. The question of how diverse pore structures and nitrogen surface functional groups of similar N-containing carbon nanomaterials influence their different activity toward ORR is addressed for the first time in detail.

2. Experimental

2.1. Materials

Aniline (p.a., Centrohem, Serbia) was distilled under reduced pressure and stored under argon prior to use, in order to remove the impurities (e.g. aniline dimers, formed by aerial oxidation during prolonged storage of commercially available aniline) which may significantly influence the course of aniline oxidative polymerization [41].

Ammonium peroxydisulfate (APS), 5-sulfosalicylic acid (SSA) dihydrate and 3,5-dinitrosalicylic acid (DNSA) of analytical grade were used as received from Centrohem (Serbia).

N-containing nanostructured carbon materials, C-PANI, C-PANI.SSA and C-PANI.DNSA, were prepared *via* the gram-scale syntheses of PANI precursors and subsequent carbonization [10,42,45]. Nanostructured PANI precursors were synthesized by the template-free oxidative polymerization of aniline with ammonium

peroxydisulfate (APS) as an oxidant in three different media: 1. in water, without added acid (nanoPANI), 2. in the aqueous solution of SSA (nanoPANI.SSA), and 3. in the aqueous solution of DNSA (nanoPANI.DNSA). The nanoPANI precursor, containing hydrogen sulfate anions as prevalent counter-ions, was prepared according to the recently reported procedure [11,42]: the aqueous solutions of aniline (18.6 g, 500 ml) and oxidant APS (57.05 g, 500 ml) were mixed to start the oxidation, and the reaction mixture was stirred for 2 h. The precipitated nanoPANI was collected on a filter, rinsed with 5×10^{-3} M sulfuric acid and dried in vacuum. The nanoPANI.SSA precursor was prepared by the modified procedure [10] of Janošević et al. [47]: 12.26 g of aniline was dissolved in 1140 ml of aqueous solution containing 8.39 g SSA and the solution was heated to boiling, cooled to room temperature, then the aqueous solutions of monomer and oxidant APS (30.12 g, 600 ml) were mixed to start the oxidation, and the reaction mixture was stirred for 24 h. The precipitated nanoPANI.SSA was collected on a filter, rinsed with 5×10^{-3} M SSA and dried in vacuum. The modification enabled a rapid synthesis of larger quantities of the sample needed for its detailed characterization performed in this study. The modified procedure [45] of Janošević et al. [48] was applied for the synthesis of nanoPANI.DNSA precursor: 2.45 g of aniline was dissolved in 1140 ml of aqueous solution containing 3.01 g of DNSA and the solution was heated to boiling, cooled to room temperature, and then the aqueous solutions of monomer and oxidant APS (7.53 g, 60 ml) were mixed to start the oxidation, and the reaction mixture was stirred for 24 h. The precipitated nanoPANI.DNSA was collected on a filter, rinsed with 1.6×10^{-2} M DNSA and dried in vacuum. All syntheses of PANIs were performed at room temperature. The precursors nanoPANI, nanoPANI.SSA and nanoPANI.DNSA were then carbonized by means of gradual heating in a nitrogen atmosphere up to 800 °C at a heating rate of 10 °C min⁻¹ to obtain C-PANI, C-PANI.SSA and C-PANI.DNSA, respectively. A Carbolite CTF 12/75/700 tube furnace with temperature regulation by Eurotherm 815P Prog/Controller was used for the carbonization.

2.2. Characterization: morphology, elemental composition, structure and conductivity

A scanning electron microscope (SEM) JEOL JSM 6610 LV was used to characterize the morphology of the samples. Powdered materials were deposited on adhesive tape fixed to specimen tabs and then ion-sputter-coated with gold using a BAL-TEC SCD 005 Sputter Coater prior to SEM measurements.

Elemental analysis (C, H, N, and S) was carried out by the Elemental Analyzer Vario EL III (Elementar). The content of oxygen was determined by difference.

XPS spectra were recorded on a Kratos Axis Ultra DLD (Kratos Analytical, Manchester U.K.), using monochromatic Al K α X-rays (1486.69 eV) with X-ray power of 150 W. Survey spectra were collected with 160 eV pass energy, whilst core-level scans were collected with pass energy of 20 eV. The base pressure in the system was 2×10^{-9} Torr. The analysis area for the data collection using the hybrid electrostatic and magnetic lens system and the slot aperture is approximately 300 × 700 mm. Data analysis was performed using CasaXPS using Kratos' relative sensitivity factors. Core-level scans were calibrated based on a peak fit to the C1s scan, with the component due to aromatic carbon set to 284.7 eV. Shirley backgrounds were used throughout. Gaussian–Lorentzian product lineshapes were used with 30% Lorentzian weighting.

Raman spectra were collected on a Thermo Scientific DXR Raman microscope, equipped with an Olympus optical microscope and a CCD detector. A diode-pumped solid-state laser with excitation wavelength of 532 nm was used. Raman spectra were fitted within 900 and 1840 cm⁻¹ using two Gaussian components for G

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