



# Incorporation of Pt, Ru and Pt-Ru nanoparticles into ordered mesoporous carbons for efficient oxygen reduction reaction in alkaline media



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## ABSTRACT

Ordered mesoporous carbon, volume-doped up to 3 w.% with Pt, Ru and Pt-Ru nanoparticles was synthesized by evaporation-induced self-assembly method, under acidic conditions. The content of incorporated metal was determined by EDX analysis. The X-ray diffractometry confirmed the existence of highly dispersed metallic phases in doped samples. Specific surface area was determined by N<sub>2</sub>-physisorption measurements to range between 452 and 545 m<sup>2</sup> g<sup>-1</sup>. Raman spectroscopy of investigated materials indicated highly disordered carbon structure with crystallite sizes around 1.4 nm. In a form of thin-layer electrode on glassy carbon support, in 0.1 M KOH solution, the prepared materials displayed high activity toward oxygen reduction reaction (ORR) in alkaline media, with onset potentials more positive than -0.10 V vs. SCE. The kinetics of O<sub>2</sub> reduction was found to be affected by both the specific surface area and the concentration of metal dopants. The ethanol tolerance of (Pt, Ru)-doped OMCs was found to be higher than that of common Pt/C ORR catalysts. Presented study provides a new route for the synthesis of active and selective ORR catalysts in alkaline media, being competitive with, or superior to, the existing ones in terms of performance and price.

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## 1. Introduction

Ever growing demand for portable/stationary devices that deliver electrical energy on demand presents a driving force for industrial advancement. Among various device types fuel cells present a clean way of producing electric energy through redox reactions using hydrogen and lower alcohols as fuel. A major drawback for their commercialization is the use of Pt-group metals, being the most active electrocatalysts for low temperature fuel cells, which significantly increases the cost of these devices. Hence the development of new electrocatalytic materials with high catalytic activity towards oxygen reduction reaction (ORR) is of significant interest. Alloying Pt with other metals in a form of

either bulk alloys [1–3] or Pt-monolayer over less precious metal nanoparticles [4,5] has resulted in superior ORR catalysts being developed. Alternative direction for the advancement is found through the use of carbon-based ORR catalysts which display high intrinsic ORR activity in alkaline media [5,6], being attractive in the field of alkaline fuel cells (AFC) and metal-air batteries. In addition, doping with different heteroatoms (nitrogen, boron, sulfur, etc.) their activity can be altered to reach Pt-based catalysts in terms of ORR activity [8–10]. However, these metal-free carbonaceous catalysts require appropriate pore structure for high ORR activity to arise, providing the access for O<sub>2</sub> to large fraction surface area where it is reduced to HO<sub>2</sub><sup>-</sup> or OH<sup>-</sup>, depending on the applied electrode potential and the state of materials surface [11].

Ordered mesoporous carbons (OMCs) have drawn great attention in recent years owing to their high surface area, large pore volume, chemical inertness, good thermal and mechanical stability, easy handling and low cost of manufacture [12]. Structure alterations, morphology and composition result many different

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applications particularly in catalysis as catalysts and catalyst supports [13,14], for the separation [15], as adsorbents [16], for the energy storage [17]. Related to electrochemical power source applications, OMC has been proven as a versatile material where single one material can be used in different fields without compromising the performances [18].

Attractive properties of OMCs define this class of materials as a basis for further modification and optimization for specific applications. As overviewed by Muylaert et al. [19] and Ma et al. [20], incorporation of metals in OMC can be done either after carbonization of polymeric resin (post-synthetic modification) or by addition of metal source into the resin before carbonization (*in situ*). Post synthetic modification of OMC with Pd [21] and Pt [22,23] was reported, while in the case of Ru both post-synthetic [24] and *in situ* approach were used [25,26]. According to Muylaert et al. [19], metal-modified OMCs were usually used in the field of heterogeneous catalysis, but also in some cases its capacitive properties were addressed [27]. Regarding the use of metal-modified OMC in ORR electrocatalysis, there are several examples found in the literature [22,28,29]. Typically, this functionalization used *in situ* Pt reduction with hard templates employed to synthesize OMC and rather high Pt loadings on OMC support, reaching up to 30% [29]. The necessity to remove the template after the synthesis complicates the route to obtaining the catalyst, while high Pt loading affects the price of such material.

In this contribution we present the synthesis of ordered mesoporous carbons doped with Pt, Ru, and their mixture with the aim to demonstrate catalytic activity and selectivity of such doped carbonaceous material towards ORR in alkaline media. The proposed synthesis of OMC doped with Pt and Ru for highly efficient ORR catalysis has several advantages over previously reported ones: (i) due to the use of the evaporation-induced self-assembly (EISA) method there is no need for hard template during the preparation of polymeric precursor and its removal upon carbonization, (ii) modification of OMC by Pt and Ru is achieved *in situ* which reduces the number of step during the production of such ORR catalysts and (iii) the loading of the precious metals is much lower than typically reported. Materials were characterized by energy dispersive X-ray spectroscopy (EDX),  $N_2$ -physisorption, X-ray powder diffraction and Raman spectroscopy. Assembled data on physico-chemical properties of prepared materials were used to rationalize high ORR activity displayed by these materials, which was investigated in alkaline media.

## 2. Experimental

### 2.1. Synthesis

(Pt,Ru)-doped OMC materials were prepared using EISA method. Initially, 4.52 g of Pluronic F127 ( $EO_{106}PO_{70}EO_{106}$ ) (Sigma-Aldrich) was dissolved in the mixture of 18 cm<sup>3</sup> of deionized water and 18 cm<sup>3</sup> of ethanol (95 wt.%) and vigorously stirred for 15 min at room temperature. Then, 3 g of resorcinol was added and stirred for the next 30 min when the mixture was acidified with 0.35 cm<sup>3</sup> of HCl (37 wt. %). In this step,  $H_2PtCl_6 \cdot 4H_2O$  (Sigma-Aldrich) and  $RuCl_3 \cdot H_2O$  (Sigma-Aldrich) were introduced along with 0.1 g of  $NaBH_4$  (JT Baker) as reducing agent. Different amounts of dopants were used in order to obtain various Pt-to-Ru mass ratios in the final material. After 2 h, 4.5 cm<sup>3</sup> of formaldehyde (37 wt. %) was slowly added dropwise, stirred for another hour, aged covered at room temperature for 3 days and dried at 85 °C for two days. Obtained polymeric cakes were carbonized under nitrogen at 800 °C for 3 h at a ramping rate of 5 °C/min, cooled down in the same atmosphere and used for further examination.

### 2.2. Characterization

The morphology of investigated materials was investigated using scanning electron microscope (SEM) JEOL JSM-5800. The chemical composition of the samples was analyzed using an Energy Dispersive Spectrometer (EDS) Isis 3.2, with a SiLi X-ray detector (Oxford Instruments, UK) connected to the scanning electron microscope (SEM) JEOL JSM-5800 at 20 kV and a computer multi-channel analyzer.

Porous structures of the samples were characterized by  $N_2$  adsorption/desorption using the gravimetric McBain method. From the obtained isotherms, the specific surface area ( $S_{BET}$ ), pore size distribution, mesopore including external surface area ( $S_{meso}$ ) and micropore volume ( $V_{mic}$ ) of the samples were calculated. Pore size distribution was estimated by applying BJH method [25] to the desorption branch of the isotherms. Mesopore surface and micropore volume were estimated using the high-resolution  $\alpha_s$ -plot method [30–33]. Micropore surface ( $S_{mic}$ ) was calculated by subtracting  $S_{meso}$  from  $S_{BET}$ .

All powders of OMC-Pt-Ru were characterized at room temperature by XRPD using Ultima IV Rigaku diffractometer, equipped with  $Cu K\alpha 1,2$  radiation source, using a generator voltage of 40.0 kV and a generator current of 40.0 mA. The range of 10 – 90 °2 $\theta$  was used for all powders in a continuous scan mode with a scanning step size of 0.02 ° and at a scan rate of 2 ° min<sup>-1</sup>.

Raman spectra excited with a diode pumped solid state high-brightness laser (532 nm) were collected on a DXR Raman microscope (Thermo Scientific, USA) equipped with an Olympus optical microscope and a CCD detector. The powdered sample was placed on X–Y motorized sample stage. The laser beam was focused on the sample using an objective magnification 10X. The scattered light was analyzed by the spectrograph with a grating 900 lines mm<sup>-1</sup>. Laser power was kept at 2 mW.

### 2.3. Electrode preparation and electrochemical measurements

Electrode material suspension was prepared by dispersing 5 mg of metal-doped OMC sample in 1 cm<sup>3</sup> of ethanol/water mixture (40 v/v %), followed by 30 min homogenization in an ultrasonic bath. Glassy carbon (GC) disk electrode (geometrical cross section 0.196 cm<sup>2</sup>) was subsequently covered with a 10  $\mu$ L drop of the prepared suspension and dried under  $N_2$  stream. Drying was followed by the addition of 10  $\mu$ L of 0.05 wt.% Nafion in ethanol to insure the stability of the thin carbon layer. The solvent was removed by evaporation. Electrodes prepared in the described manner were further tested by cyclic voltammetry (CV) to investigate the capacitive and electrocatalytic properties of the samples in alkaline media. Conventional one-compartment three-electrode electrochemical cell with wide Pt foil as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode was used to conduct the CV measurements. Electrocatalytic activity towards ORR was investigated in  $O_2$ -saturated 0.1 mol dm<sup>-3</sup> KOH aqueous solution using rotating disk electrode (RDE) voltammetry. High (5N) purity  $N_2$  and  $O_2$  were used for these experiments. Measurements were done using Gamry PCI-4/750 potentiostat/galvanostat.

## 3. Results and Discussion

### 3.1. Morphology of (Pt-Ru)-OMC samples

SEM analysis of prepared samples (Fig. 1) shows that metal doping of polymeric precursor does not affect the morphology of the final carbonaceous materials. Irregular morphology with no characteristic features has been observed while (Pt,Ru)-doped OMC particles have different sizes, ranging from nano to

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