Platinum-free catalysts for low temperature fuel cells

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Abstract. In this work, we have successfully prepared Zn/Co-N/C and Zn/Co-Fe/N/C composites, both derived from single zeolitic imidazolate framework (ZIF) precursor Zn/Co-ZIF containing equivalent quantities of Zn and Co metal sites. The composites were formed by pyrolysis of the precursor at 700 °C in inert gas atmosphere as such and after mixing it with Fe(II) salt and 1,10-phenontraline in ethanol. Catalytic tests for oxygen reduction reaction (ORR) in electrochemical cell demonstrated promising results allowing us to consider these composites as potential Pt-free catalysts for low temperature fuel cells.

1. Introduction

Due to the limitedness of natural resources like gas and oil there is a tendency in modern world to replace the conventional energy sources with the alternative ones. Huge markets like car-building industry demand the new feasible technological solutions based on power production without burning hydrocarbons. One of the emerging technologies is based on production of electricity on board of a vehicle by electrochemical fuel cells. These low-temperature fuel cells offer a direct conversion between chemical and electrical energy, so energy losses are minimized [1].

Nowadays, the air-hydrogen fuel cells are in focus of research efforts around the globe, because they produce water as the main product of the reaction with a few byproducts. The efficiency is limited by the rate of the ORR [2]. In such cells the commercially available cathodic catalysts usually contain platinum and its alloys (e.g. Pt/C, Pt_3Co/C). Unfortunately, they are too expensive for common use, furthermore, they can degrade over time. The challenging solution for this problem is the development of efficient platinum-free electrocatalysts [3].

Different compounds have been employed as alternative catalysts for the ORR. Recently, metal-organic frameworks (MOFs) and their derivatives are emerged among the most promising ones. The advantages of MOFs include good thermal stability and endless variety of topologies. However, for certain cases it is hard to obtain chemically stable MOFs [4]. The MOFs are also known to exhibit catalytic activity in the ORR [5], but more importantly, they can serve as precursors for fuel cell catalysts. For instance, MOF HKUST-1 shows electrocatalytic activity in neutral media [6] and it was used as a precursor to produce Cu@N/C catalyst [7]. More generally, such catalytic system can be marked as M-N/C, where M is an atom of transition metal (Cu, Fe, Co) and N/C stands for nitrogen-doped porous carbon. Some of M-N/C catalysts reportedly demonstrate characteristics approaching the Pt-based catalyst performance [8]. The chemical stability of such materials remains the question of high importance. For example, Fe-N/C type catalyst showed high electrochemical activity and stability in alkaline, acidic [9] and neutral media [10].

Currently, the production of the M-N/C materials is based on the mixing of carbon sources (MOFs), metal-containing (often Fe(II)) compounds and nitrogen sources followed by pyrolysis of the mixture. Further enrichment can be done if chosen MOF already contains more than one metal. ZIF family of MOFs includes ZIF-8 containing Zn, and ZIF-67 containing Co. Considering imidazolic linker as a source of both nitrogen and carbon we may count on this MOF as an ideal pyrolysis precursor. Although, a lot of work has been done on designation the structure of the catalytic sites of the Pt-free electrocatalysts [12-13], but the complexity of the matter keeps question open.

It should be also mentioned, that pyrolysis temperature influences the state of final product. According to reported in the literature, the most effective one for Fe-N-C materials is 700 ºC [8]. Another crucial characteristic is the porosity of the product. The samples with the higher porosity tend to demonstrate higher electrochemical activity [13-14]. Assuming that active site is a five-coordinated iron atom, micropores are the only place, where they can be located [15].

In this communication we describe some results on preparation and electrocatalytic activity tests of the composites containing transition metals embedded into N-doped porous carbon support.

2.1 Synthesis of the samples
2.1.1 Preparation of MOF
At the first stage MOF with both Co, Zn atoms and 2-methylimidazole (mIm) as linker was synthesized. For this purpose solution (total volume 18 ml) of dimethylformamide (DMF) containing 0.273 g of $Co(NO_3)_2 \cdot 6H_2O$, 0.308 g of mIm, 0,279 g of $Zn(NO_3)_2 \cdot 6H_2O$ was prepared. Then the resulting solution was heated in microwave oven (MARS 6, CEM, USA) for 120 min at 140 °C. Obtained powder was collected by centrifugation, washed several times with methanol, kept in methanol for 48 h and dried at 60 °C.
2.1.2 Carbonization of MOF
At the second stage prepared MOF was mixed with 0.0207 g of 1,10-phenontraline, 0.0012 g of Fe(II) acetate and ethanol. After sonication powder was filtered, washed, dried and annealed under Ar flow for 3 h at 700 °C with the heating rate of 10° C per minute.
As-prepared MOF without addition of iron salt and 1,10-phenontraline was also annealed at the same conditions.
Pure MOF will be further referred as Zn/Co-ZIF, MOF after heat treatment as Zn/Co-N/C and those obtained after heat treatment with addition of iron salt and 1,10-phenontraline as Zn/Co-Fe/N/C.
2.2 Characterization
X-ray diffraction (XRD) of the MOF was detected using Bruker D2 Phaser diffractometer (Cu k_α, λ= 0,15406nm).The Brunauer-Emmett-Teller (BET) specific surface area was determined by nitrogen adsorption-desorption at 77 K on an ASAP 2020 analyzer. Prior to the measurements, the samples were degassed at 140 °C for 12 h. Transmission electron microscopy (TEM) images were acquired on a Tecnai G2 Spirit BioTWIN microscope operated at an accelerating voltage of 120 kV.
The electrochemical measurements were performed in a typical three-electrode cell in 0.1 M KOH or 0.1 M H_2SO_4 solution with a Pt electrode and Ag/AgCl (sat.KCl solution) as the counter electrode and reference electrode, respectively. The electrochemical properties of all materials were investigated by cyclic voltammetry (CV) and liner sweep voltammetry (LSV). A rotating disk electrode was used as the substrate for the working electrode. For the preparation porous carbons-based catalytic inks 7 mg of the sample was dispersed in the solution containing 900 μl of isopropanol and 100 μl of 0.5 % Nafion solution. After sonication and stirring 28 μl of the catalyst ink was dripped onto the glassy carbon surface. In the case of pure MOF testing 3 mg of the sample was mixed 3 mg of carbon (Vulcan XC-72). The next procedure for catalytic inks preparation is the same.
Before investigation of the samples catalytic activity in ORR all materials were cycled in Ar-saturated electrolytes without rotation with a sweep rate of 50 mV s⁻1. LSV curves were recorded at different speed rates (400, 625, 900, 1000, 1225, 1600, 1935 rpm). All the potentials reported in this work are vs. the standard hydrogen electrode (SHE).

3. Results

The XRD spectrum (Figure 1) of pure dual metal (Zn and Co) ZIF-type material (Zn/Co-ZIF) exhibits sharp peaks and are in good agreement with the literature data [16]. The diffraction peaks at $2\theta = 7.4\,°$, $10.4\,°$, $12.8\,°$, $14.8\,°$, $16.5\,°$, $18.1\,°$, $22.2\,°$, $24.6\,°$, $25.7\,°$, $26.8\,°$, $29.8\,°$ can be indexed to the (011), (002), (112), (022), (013), (222), (114), (233), (224), (134) and (044), planes of Zn/Co-ZIF material.
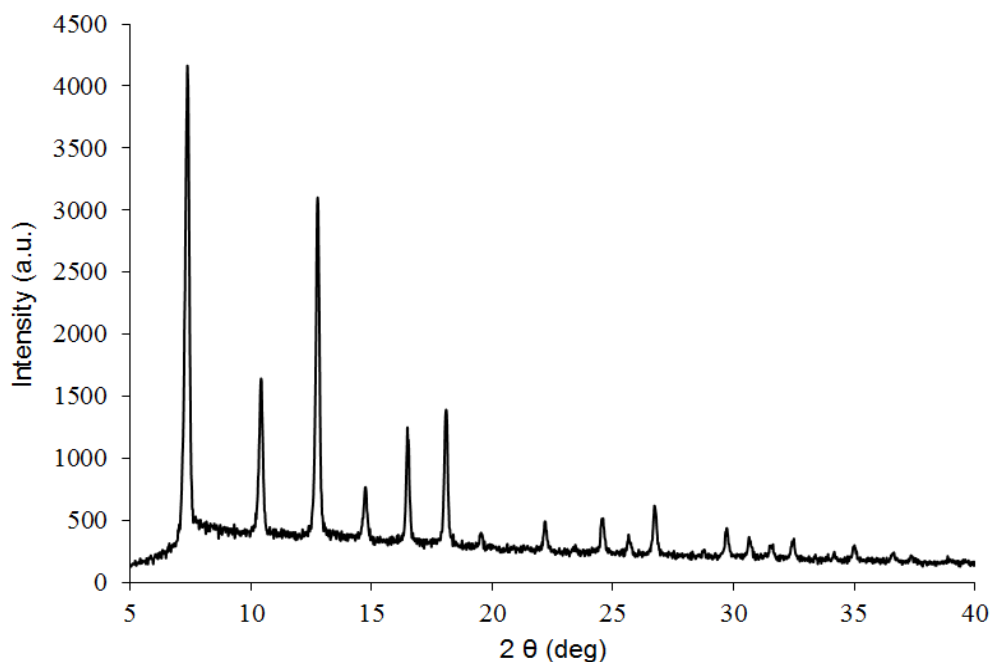

Figure 1. XRD spectrum of Zn/Co-ZIF

The surface area values for the catalyst before and after annealing were found from nitrogen physisorption at 77 K isotherms (composed of adsorption and desorption branches), presented in Figure 2. Both isotherms exhibit profiles attributed to Type I (microporous solids) according to IUPAC classification. Slight hysteresis of H4 type (IUPAC) is also observed, which in combination with given type of isotherm is known to be indicative for microporosity. A tremendous difference in gas uptake is clearly seen from the significant separation of two isotherms ($\sim 250\ cm^2/g$). The calculated values of surface areas are 1168 m^2/g (BET model) and 1406 m^2/g (Langmuir model) Zn/Co-ZIF sample, and 233 m^2/g (BET) and 284 m^2/g (Langmuir) for Zn/Co-Fe/N/C one. The reduction of the surface area due to annealing of a starting sample (which is a MOF, who typically possesses high surface area) is reasonable expected, and a decrement factor in this case is 5 times.
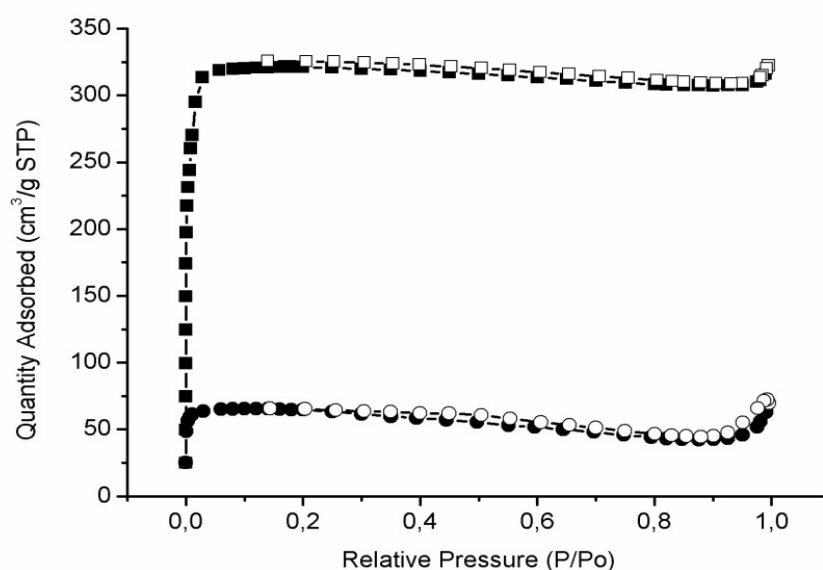
Figure 2. N_2 physisorption isotherms for Zn/Co-N/C (squares) and Zn/Co-Fe/N/C (circles) samples. The adsorption branch is shown with filled symbols, while the desorption one   with open symbols.

The morphology of Zn/Co-ZIF and Zn/Co-Fe/N/C samples was characterized by TEM (Figure 3). It can be seen that as-prepared MOF (Figure 3A) material consisted of crystals of rhombic dodecahedral shape. In the case of Zn/Co-Fe/N/C sample, it was clearly shown that well-separated metals nanoparticles of around 7.5 nm in size are well dispersed on the carbon carrier (Figure 3B).
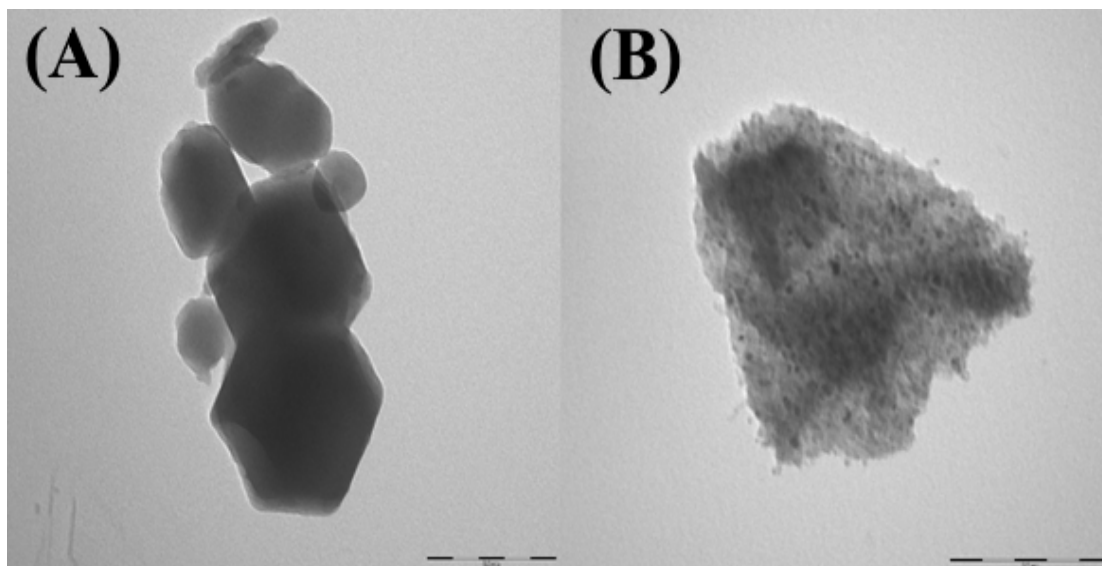
Figure 3. TEM images of Zn/Co-ZIF (A) and Zn/Co-Fe/N/C materials.The scale bar corresponds to 200 nm.

The CV curves for all materials are presented at Figure 4. It shows that electrocatalytic activity of Zn/Co-N/C material is much poorer than those of the Zn/Co-Fe/N/C catalyst in both electrolytes, especially in 0.1 M H_2SO_4 solution.Voltammetry measurements indicate that the catalytic activity of

the porous carbons mainly stems from the Fe-doping. In the case of Zn/Co-Fe/N/C sample a big peak in cathodic area appears at ~0.5 V is assosiated with Fe presence on the surface of material. Also it can evidence that Fe doping can act as a mediator in the electron-transfer process for ORR [17].
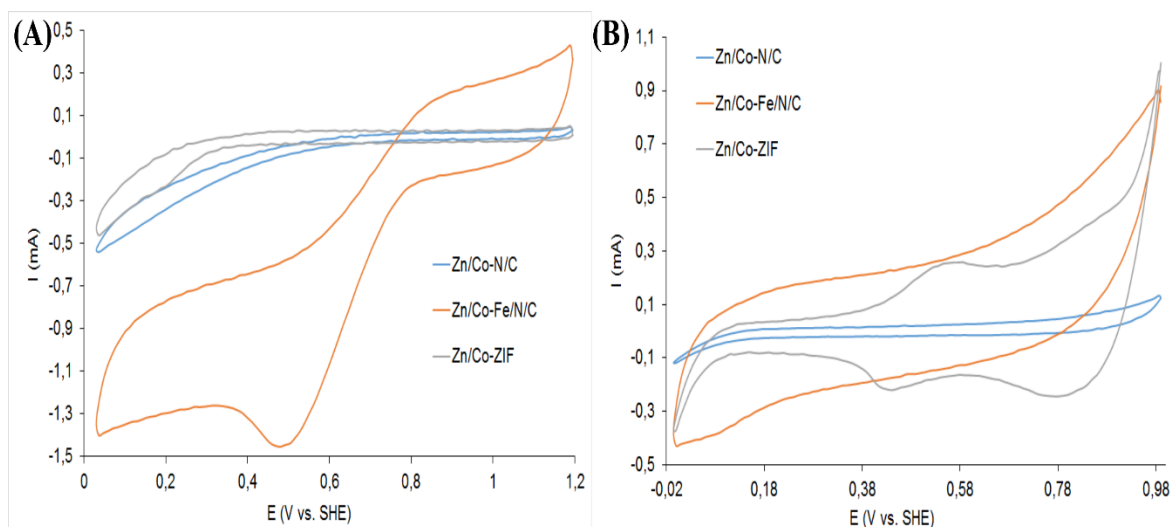
Figure 4. CVs of different samples in O_2-saturated 0.1 M H_2SO_4 (A) and 0.1 M KOH solutions at 1600 rpm at room temperature. Scan rate - 50 mV s^{-1}.

Conclusions

In summary, we report a step-by-step preparation of the electrocatalytic active Fe/N- and N-doped porous carbons. The catalytic activity of such materials is significant higher at acidic conditions. Cyclic voltammetry for ORR in three-electrode cell demonstrated promising results allowing us to consider these composites as potential Pt-free catalysts for low temperature fuel cells.

Acknowledgments

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