Wood-based nitrogen doped activated carbon for fuel cells

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Abstract. The current study is devoted to the nitrogen doped carbons for application as fuel cell oxygen reduction catalysts, where wood char and highly porous activated carbons were used as precursors. Conditions of nitrogen introduction and its content in the carbonaceous material, as well as porous structure characteristics, such as specific surface and pore size distribution, were studied. It was found that the efficiency of doping reaction depends on the elemental oxygen content in the activated carbon. Relationships between nitrogen content, porous structure characteristics and electrodes electrochemical properties are demonstrated.

1. Introduction

Nowadays energy consumption constantly increases and the development of effective and cheap electrochemical sources of power, such as fuel cells and electrochemical capacitors, is highly relevant.

Power specifications and minimal price of H\textsubscript{2}-O\textsubscript{2} fuel cells are limited by the expensive platinum-based catalysts, therefore prices of platinum increase while their reserves dwindle. Thus, the development of catalysts aimed to replace platinum-group metals is the most important for fuel cell design [1].

The main direction in the development of non-platinum catalysts for oxygen reduction is the study of cheap porous carbonaceous materials, which can be obtained by the pyrolysis of polymers including renewable biomass. It is well known that nitrogen atoms in carbon materials determine the properties of the doped activated carbons, such as high electrochemical stability, hardness, electric resistance, etc., as well as their catalytic properties [1,2] - doped materials have better electrical conductivity compared to precursors, which leads to high electrocatalytic activity [3].

There are several ways for a synthesis of porous carbon materials with N-containing heteroatoms using various nitrogen-rich compounds, such as ammonia, carbamide, melamine, etc. [4]. Traditionally N-doped carbons are synthesized using ammonia at high temperatures, by pyrolysis of nitrogen-containing carbon precursors [5], or doping with nitrogen-containing doping agents [6].

The lack of sufficient knowledge on the doping of the carbon materials calls for the ongoing researches of properties and structure of modified carbon matrix.

2. Experimental
Activated carbons based on alder wood char (SIA “Fille”, Latvia) were obtained using chemical activation method with NaOH, activator ratios to precursor $K = 2$ and $3$ and activation temperatures $600 ^\circ C$, $650 ^\circ C$ and $700 ^\circ C$ in the stream of argon, washed with deionised water, HCl, and water again up to neutral pH, and then dried overnight at $105 ^\circ C$. The main variables in the experiment were activation temperature and activator/charcoal ratio (further denoted as $K$).

Nitrogen was introduced into samples using dicyandiamide (DCDA) solutions with mass ratio carbon material/DCDA $1:20$ and $1:10$ and consequent treatment at $800 ^\circ C$. Two DCDA solvents were compared – ethanol (Et) and dimethylformamide (DFA) (the rest of the samples).

Specific surface area ($\text{m}^2/\text{g}$), micropore and total pore volumes ($\text{m}^3/\text{g}$), and pore width (nm) were determined from nitrogen adsorption isotherms using the Quantachrome Nova 4200c instrument.

The electrochemical measurements were performed with a standard three-electrode system using the rotating disk electrode (RDE) method. The undoped, doped and reference materials (nanotubes and Pt-C) suspensions in ethanol (1 mg/ml) containing 0.0625% of Tokuyama OH- ionomer AS-4 were pipetted onto the GC disk electrodes. The catalyst loading for all materials was thus 0.1 mg/cm$^2$. Saturated calomel electrode was used as a reference electrode and Pt foil was used as a counter electrode. The software used for controlling the experiments was Nova 2.1.2 and the potential was applied with a potentiostat/galvanostat Autolab PGSTAT 128N (Metrohm Autolab P.V). Measurements were performed in 0.1 M KOH solution at room temperature ($23 \pm 1 ^\circ C$) at rotation rate 1900 rpm. For the substrate material, GC disks (GC-20SS, Tokai Carbon) with a geometric area ($A$) of 0.2 cm$^2$ were pressed into a Teflon holder and the electrodes were polished and cleaned.

3. Results and discussion

To investigate the obtained samples pre-and post-doping analysis of the porous structure of materials was carried out. Table 1 shows that wood charcoal has low porosity. In the case of nitrogen doped non-activated wood charcoal (samples with index N) specific surface, total pore volume and micropore volume decreased almost twofold after the doping process. As a result of the destruction of the micropores walls and the formation of larger pores at $800 ^\circ C$ (doping temperatures), the average pore volume increases.

Choice of solvent and ratio of DCDA addition (10 or 20) did not influence porous structure significantly. Results are similar for Et and DMF, thus the solvent with better ability to dissolve DCDA, namely DFA, was chosen for the further experiments.

Table 1. Comparison of the porous structure of wood char (WC) depending on solvent and doping temperature.

| Sample       | Specific surface, $\text{m}^2/\text{g}$ | Total pore volume, $\text{mm}^3/\text{g}$ | Micropore volume, $\text{mm}^3/\text{g}$ | Pore width, nm |
|--------------|----------------------------------------|------------------------------------------|------------------------------------------|----------------|
| WC           | 279                                    | 226                                      | 105                                      | 1.40           |
| WC- DFA, 10N | 145                                    | 229                                      | 40                                       | 1.96           |
| WC- DFA, 20N | 101                                    | 113.8                                    | 42                                       | 1.75           |
| WC- Et, 20N  | 111                                    | 109                                      | 48                                       | 1.91           |

Liquid nitrogen sorption experiments revealed that wood charcoal has low porosity, and all of the activated samples have highly developed specific surface, however, their structure and pore size distribution are related to activation rate and temperature. The volume of adsorbed gas and the slope of isotherms for activated carbons (AWC) obtained at lower temperatures and especially using activator ratio $K = 2$ is characteristic for microporous sorbents (Figure 1). From the shape of the isotherm (Figure1) it can be observed that the adsorption mechanism of AWC obtained in $700 ^\circ C$ and activator ratio $K = 3$ is different, which indicates that both micro- and mesopores are present [7].
Figure 1. Nitrogen adsorption-desorption isotherms of wood char (WC), activated wood char (AWC) (activation temperature 600°C, 650°C and 700°C and activator ratio K = 2 and 3).

Figure 2. Comparison of the specific surface, total pore volume, and micropore volume of AWC depending on chemical activation conditions.

Elemental analysis results are presented in Table 2 – it illustrates that nitrogen content is significantly influenced by aromatic structure defects and oxygen content of precursor. Non-activated wood char has the highest nitrogen content after doping – 20.67%. For all AWC samples, the nitrogen content is 5-6%. Choice of DCDA solvent had a small influence on the nitrogen contents of doped wood char and AWC – the results are similar for ethanol and DFA.

Table 2. Elemental composition pre-and post-doping of wood char (WC) and activated wood char (AWC) (activation temperature 700°C, doping temperature 800°C)

| Raw material | K | Solvent | Mass ratio carbon material/DCDA | N, % | C, % | H, % | S, % | O, % |
|--------------|---|---------|---------------------------------|------|------|------|------|------|
| WC           |   | -       | -                              | 1.00 | 91.54| 0.13 | 0.12 | 7.21 |
|              |   | DFA     | 10                             | 19.13| 75.13| 0.18 | 0.15 | 4.41 |
|              |   | DFA     | 20                             | 20.67| 73.84| 1.00 | 0.08 | 4.41 |
|              |   | Et      | 20                             | 20.25| 73.29| 0.22 | 0.23 | 6.01 |
| AWC          | 3 | -       | -                              | 0.70 | 93.8 | 0.62 | 0.13 | 4.75 |
|              | 3 | DFA     | 20                             | 5.55 | 90.97| 0.89 | 0.12 | 2.48 |
|              | 3 | Et      | 20                             | 6.17 | 89.60| 0.14 | 0.09 | 4.00 |

For the tests of electrochemical properties sample of AWC, activated at 700°C, K=3 and subsequently doped at 800°C with DCMA, was refined and additionally treated at 800°C. Figure 3 illustrates catalyst polarization curves of the electrode made from this doped wood char (WC-N), activated wood char (AWC) and doped activated wood char (AWC-N) compared to commercial 20% Pt/C catalyst and carbon nanotubes (MWCNT) electrode. The shape of the polarization curves and diffusion current limits of WC-N, MWCNT demonstrate that they have low activity. The onset potential and half-wave potential for
AWC-N are much more positive compared to WC-N and MWCNT. The negligible negative shift of the onset potential is observable in comparison with 20% Pt/C, but at the same time diffusion limited current density is reaching much higher value in comparison to the commercial platinum catalyst. The overall electrocatalytic activity of doped AWC sample in KOH electrolyte was higher than that of commercial 20% Pt/C catalyst. The described electrocatalytic properties of the synthesized N-doped wood-derived carbon catalysts may be associated with the extremely high surface area and highly developed micro- and mesoporosity of the catalyst, as well as structural qualities of the biomass based carbon materials, e.g. presence of structural defects providing activity. It could also be associated with the high percentage of pyridinic nitrogen in the N-doped material and lack of stacking defects of graphene layers.

4. Conclusions
The studied samples of wood char were modified by introduction of nitrogen into their structure pre- and post- activation with the aim to apply them as catalysts for oxygen reduction in fuel cells. The most favourable doping reaction conditions, namely, doping agent dicyandiamide, DMF solvent and treatment temperature of 800 °C, were determined. It was found that the highest amount of nitrogen (more than 20%) can be introduced into wood char. The results show that nitrogen doped activated wood char (with 5-6% content of nitrogen) is a promising material for application in fuel cells for oxygen reduction.

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