Oxygen Electroreduction on Platinum Nanoparticles Deposited onto D-Glucose Derived Carbon

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Microporous-mesoporous carbon material synthesized from D-(-)-glucose using hydrothermal carbonization method was used as a porous support for platinum nanoparticles catalyst for oxygen electroreduction reaction (OER). The platinum nanoparticles were deposited on the support using sodium borohydride reduction method. The XRD, HRTEM, HRSEM, EDX, Raman spectroscopy and low-temperature N₂ adsorption/desorption techniques were used to characterize the structures of unmodified and Pt-nanoclusters modified materials. The carbon support with high specific surface area (1190 m² g⁻¹) composes of almost ideally spherical amorphous microporous particles. The platinum nanoparticles are well dispersed on the surface of carbon particles. Cyclic voltammetry, rotating disc electrode and electrochemical impedance spectroscopy were applied to investigate the electrochemical behavior and OER kinetics at the materials in 0.5 M H₂SO₄ aqueous solution. The Pt-nanocluster modified material has good OER activity but on the non-modified carbon support the OER is sluggish. Cyclic voltammetry and impedance data showed that unmodified and Pt-nanoclusters modified materials have noticeable double layer (∼ 200 F g⁻¹) and faradaic capacitances (up to 250 F g⁻¹).

Over the few last decades, intensive studies have been done on oxygen reduction reaction (ORR) on the Pt catalysts because the main obstacle on the development of the polymer electrolyte membrane fuel cell (PEMFC) is the slow cathodic oxygen electroreduction.

Numerous carbon materials have been tested to establish the better performance, but there are only few papers analyzing the impact of the highly microporous-mesoporous carbon materials on ORR. Applying the different preparation methods of the carbon material, carbons with variable physical and chemical properties could be prepared. Specific surface area, pore size distribution and graphitization level are the most important characteristics of carbon support because of the impact they have on the interaction of catalyst support and platinum determining the rate of electrochemical processes.

Very interesting group of carbons produced using hydrothermal carbonization (HTC) processes has been reviewed by B. Hu et al. Carbons synthesized via low-temperature HTC process have various surface functional groups, well-developed microporosity/mesoporosity and high ORR activity. These carbonaceous materials can be used to form nanocomposites with other materials. They are used in many fields including electrocatalysis, fuel cell technology and energy storage. Pt and Pd activated carbon microspheres obtained by HTC process have been tested as possible catalysts for methanol oxidation in direct methanol fuel cells (DMFC). The mesoporous carbon with highly distributed core-shell Pt-C nanoparticles in the nanochannels has been used as a methanol-tolerant cathode catalyst in DMFC. Pt deposited onto the surface of hollow carbonaceous composite (noted as Pt/CMSs), prepared using HTC process, has shown higher catalytic activity and better stability for methanol oxidation.

The main aim of this work was to synthesize a new microporous-mesoporous catalyst support and thereafter to activate it by deposition of platinum on/in it. The catalyst support was D-glucose derived carbon material, prepared using low-temperature HTC process, and additionally activated thereafter with CO₂. The influence of porosity, pore size distribution and crystallinity of carbon support and Pt-nanoparticle catalyst on the ORR kinetics, including the capacitive behavior of materials, were studied in 0.5 M H₂SO₄ aqueous solution at 22 ± 1°C.

Experimental

Preparation of the catalyst support.— The microporous-mesoporous carbon support was prepared from D-glucose (≥ 99.5% purity, Sigma). The hydrothermal carbonization of a D-(-)-glucose solution was carried out in an autoclave, which was placed into a tube furnace (260°C for 24 hours). The resulting dry carbonaceous material was dried in a vacuum oven under Ar (purity 99.999% AGA, 80°C, 100 mbar) and then pyrolysed in a tube furnace (Ar flow rate 500 dm³ min⁻¹ at 800°C for 2 hours). After carbonization, the row carbon powder was activated with CO₂ (purity 99.999% AGA, CO₂ flow rate: 50 cm³ min⁻¹) using the chemical reaction CO₂ + C → 2CO at 900°C and the carbon prepared has been noted as C(HTC).

The activation process enhances the porosity within the porous carbon. The obtained material was treated with H₂ (purity 99.999%) at 800°C for 2 hours to remove reaction intermediates from the surface of the porous material as well as to minimize the amount of oxygen-containing functional groups at the C(HTC) surface. However, the cyclic voltammetry (CV) data measured indicate that there are some oxygen containing groups (mainly quinone/hydroquinone) at the C(HTC) surface. The CV, rotating disc electrode (RDE) and electrochemical impedance spectroscopy (EIS) methods were used to study the electrochemical characteristics of the support prepared. The recorded data were used as the reference data for further comparison with Pt-nanoclusters activated catalyst received after precipitating the Pt nanoparticles onto a C(HTC) support.

Preparation of Pt catalyst.— The platinum catalyst was prepared by deposition the Pt nanoparticles onto a microporous-mesoporous carbon material using sodium borohydride reduction method. Required amount of H₂PtCl₆·6H₂O (99.9%, Alfa Aesar) was measured and dissolved in Milli-Q water (18.2 MΩ cm). The mixture was diluted to reach the presumed concentration of Pt in the mixture (~0.9 mM). After stirring of the solution for 1 hour, the pH of the solution was adjusted to ~8 by dropwise addition of 20 wt% (weight percent) NaOH (99.9%, Sigma-Aldrich) solution. Uniform slurry was prepared from microporous-mesoporous carbon and Milli-Q water and added to the aqueous solution of H₂PtCl₆. Thereafter, the NaBH₄ solution, prepared from NaBH₄ (~ 98.0%, Aldrich) and Milli-Q water, was added into the carbon suspension. This mixture was stirred for 2 hours and was left to settle overnight. Thereafter, the prepared catalyst was filtered and rinsed with Milli-Q water and dried in vacuum oven (50 mBar, 80°C). According to the calculations, the catalyst powder contained 74 wt% of Pt and it is denoted as Pt-C(HTC).

Preparation of catalyst ink and electrodes.— A 5 mm diameter glassy carbon disc electrode (GCD) with cross-sectional area of 0.196 cm², pressed into a Teflon holder was used as a catalyst support. The GCDE was polished with 0.05 μm alumina slurry (Buehler), washed with Milli-Q water and sonicated in Milli-Q water for a few minutes to give a clean surface. To prepare the catalyst ink, the required amount of the catalyst was dispersed in Milli-Q water.

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water and stirred by an ultrasonic bath for 30 min. Nafion dispersion solution (Aldrich) was added into the mixture to give a 5 wt% of Nafion ionomer in dry catalyst layer. After 1 hour sonication at room temperature, the ink was deposited onto the GCDE surface and left to dry at room temperature.

According to the calculations, the loading of the Pt-C-HTC catalyst on GCDE was nearly 1 mg cm$^{-2}$. The Milli-Q$^+$ water was used to impregnate the catalyst layer before performing electrochemical experiments.

**Table I. Results of $N_2$ sorption measurements.**

<table>
<thead>
<tr>
<th>Material / Parameter</th>
<th>$S_{BET}$ / m$^2$ g$^{-1}$</th>
<th>$S_{mic}$ / m$^2$ g$^{-1}$</th>
<th>$V_{pt}$ / cm$^3$ g$^{-1}$</th>
<th>$V_{mic}$ / cm$^3$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-HTC</td>
<td>1190</td>
<td>1140</td>
<td>0.75</td>
<td>0.62</td>
</tr>
<tr>
<td>Pt-C-HTC</td>
<td>250</td>
<td>200</td>
<td>0.28</td>
<td>0.09</td>
</tr>
</tbody>
</table>

$S_{BET}$, multi point BET surface area; $S_{mic}$, micropore area calculated using t-pot method; $V_{pt}$, total pore volume; and $V_{mic}$, micropore volume.

**Results and Discussion**

Analysis of physical characteristics.— Catalyst support was investigated by the HRTEM technique before and after Pt nanoparticles precipitation to determine the morphology of the samples. Amorphous structure of the synthesized carbon support was established (Fig. 1a) in agreement with previous studies of the D-glucose derived carbon material. The HRTEM data for a Pt-nanoclusters modified sample approved the presence of Pt nanoparticles on the carbon support (Fig. 1b). Based on the statistical analysis, Pt nanoparticles have a good dispersion on the support and there are only some bigger agglomerates at the carbon surface. The number averaged size of Pt nanoparticles calculated was 3.8 nm (with standard deviation of $\sigma = 0.4 \text{ nm}$) (Fig. 1c) and only the non-agglomerated particles were used for calculations. Based on the data presented in Fig. 1b, the Pt particle size distribution is narrow and follows the normal distribution. The Pt nanoparticles were bounded to the carbon and the structure of carbon did not change during the deposition process of the Pt nanoparticles. The distance between Pt atomic rows (inset in Fig. 1b) is 0.23 nm, being in an agreement with the face centered cubic structure (fcc) of Pt.

HRSEM data for a carbon support are given in Fig. 2a. Almost ideally spherical micrometer size particles were formed. The number averaged particle size equal to 1.08 $\mu$m ($\sigma = 0.06 \mu$m) and particle size distribution is very narrow (Fig. 2b). However, some particles have the defected areas. Comparison of the data presented in Figs. 1 and 2 indicates that the precipitating of the Pt particles onto the support did not change noticeably the structure of the carbon support material.

The spherical shape and presence of the Pt nanoparticles on the surface of the carbon particles has been approved also by HRTEM experiment (Fig. 3a). Dispersion of the Pt nanoparticles on the support was verified using HRSEM image, however, some agglomerates were observed. The particle size distribution was determined from the histogram (Fig. 3b) obtained by measuring the size of 200 individual particles. The number averaged size of the Pt nanoparticles estimated was 9.1 nm ($\sigma = 1.7 \text{ nm}$). This value is about two times higher than that estimated using the HRTEM measurements data. The shape of the particle size distribution function obtained from HRSEM images deviates from normal distribution within the region of small particles ($< 8 \text{ nm}$). Thus, probably the fractions of smaller particles are somewhat underestimated. The SEM-EDX data (Fig. 3c) confirm the presence of platinum particles on the Pt-C-HTC catalyst and the sulfur, oxygen and fluorine detected are forming the Nafion binder. No other elements have been detected.

XRD data collected for unmodified and modified carbon materials are shown in Fig. 4. The XRD pattern for carbon catalyst has two peaks: at $\sim 43^\circ$ and $\sim 80^\circ$, respectively, being characteristic of the C(100)/C(101) and C(110)/C(112) planes. Surprisingly, the peaks C(002) at 2θ = 26.43° and the peaks C(100), C(101), C(110) and C(112) are very broad, and hence, the C-HTC material is mainly amorphous. The X-ray diffraction data for Pt-C-HTC (Fig. 4) confirmed the deposition of the nanoparticles with a well crystallized
structure onto the C(HTC) support. The XRD patterns indicate the presence of the Pt(111), Pt(200), Pt(220), Pt(311) and Pt(222) orientations, characteristic of the fcc crystal structure, being in a good agreement with results discussed in the literature. The lattice parameter calculated for Pt is 0.3917 nm and is in an agreement with the results of similar studies. The average crystallite size of the Pt crystallites has been estimated by using the Scherrer's equation:

$$d = \frac{k \cdot \lambda}{B \cdot \cos \theta}$$

where $d$ is the average size of the crystallites (nm), $k$ is the coefficient (taken equal to 0.9 in this study), $\lambda$ is the X-ray wavelength; $B$ is...
the width of the diffraction peak at half height (rad), and \( \theta \) is the half of the angle for selected peak maximum. To calculate \( B \), the Pt(220) reflection has been selected (around \( 2\theta = 68^\circ \) (Fig. 4)). The mean crystallite size obtained is nearly 5.6 nm, being slightly higher compared to that calculated for the Pt/CMs catalyst (\( d_{\text{Pt}} = 5.0 \) nm, 17 wt% Pt) prepared without CO\(_2\) posttreatment of HTC carbon support.\(^{14}\)

According to the data in Table I, the carbon support synthesized from D-glucose has a comparatively high surface area and is mainly microporous. The specific surface area of synthesized carbon is much higher (\( S_{\text{BET}} = 1190 \) m\(^2\) g\(^{-1}\)) compared to the carbon without CO\(_2\)-posttreatment (\( S_{\text{BET}} = 256 \) m\(^2\) g\(^{-1}\)).\(^{14}\) It is suggested that higher surface area provides more centres for Pt nanoparticle formation and therefore the electrochemical surface area would be higher.\(^{14}\) After modification of the carbon support with the Pt-nanoclusters, the surface area decreases five times but the total pore volume decreases only three times which is mainly caused by the additional structural changes of the catalyst. It should be noted that three times lower amount of carbon in the catalyst powder of Pt-C(HTC) has been involved (~30 wt% of C in modified catalyst compared with unmodified carbon material). However, surprisingly, the Pt-C(HTC) catalyst has higher relative content of mesopores compared with unmodified carbon support.

Fig. 5b presents the dependency of differential pore volume on the pore width in C(HTC) before and after Pt nanoparticles deposition. The distribution of micropores in the material has not changed much after modification, however, Pt-C(HTC) modified electrode material is much more mesoporous and differential pore volume has changed noticeably in the region of pores with median width higher than 10 nm. The HRTEM and HRSEM data for modified carbon material showed

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**Figure 3.** a) High resolution SEM image of Pt-C(HTC), b) Pt particle size distribution obtained from HRSEM image (\( N_{\text{particles}} = 200 \) from 1 image) and c) EDX spectrogram for Pt-C(HTC) (with 5 wt% Nafion) material.

**Figure 4.** X-ray diffraction data for C(HTC) and Pt-C(HTC) materials.

The porosity of the catalyst support and Pt-nanoclusters activated catalyst powders has been characterized using nitrogen sorption method. I type of isotherm with H\(_1\) type hysteresis for unmodified material and IV type of isotherm with H\(_1\) type hysteresis for Pt-C(HTC) material (IUPAC classifications) has been observed\(^{26}\) explained by the capillary condensation of nitrogen in the mesopores of the catalysts (Fig. 5a).

**Figure 5a.** X-ray diffraction data for C(HTC) and Pt-C(HTC) materials.
existence of wider mesopores compared to the unmodified with CO2 carbon, which confirmed the presence of the Pt nanoparticles on the surface and most probably inside of the amorphous structure (Figs. 1b and 3a).

Raman spectrum for the carbon support is given in Fig. 6. For perfect ordered monocrystalline graphite only one peak can be observed at ∼1577 cm⁻¹, whereas generally two peaks can be detected for the disordered amorphous carbon. Results of this experiment confirmed the presence of a disordered amorphous carbon that demonstrates two peaks (Fig. 6), the graphite (G) peak observed at ∼1587 cm⁻¹, and disorder-induced (D) peak at ∼1345 cm⁻¹. Raman spectra also presented a second order 2D peak at ∼2700 cm⁻¹ explained by the crystallographic ordering of the graphitic planes/areas at/inside of C(HTC).

Electrochemical characterization—Cyclic voltammetry.— In this study, the values of capacitance ($C_{CV}$) have been calculated from current densities ($j$) using the equation $C_{CV} = j/v$. Collected CV data show high double layer capacitance for unmodified C(HTC) and faradaic capacitive behavior for Pt nanoparticles modified electrodes in 0.5 M H₂SO₄ solution saturated with Ar (Fig. 7). The so-called double layer capacitance is very high for C(HTC) | 0.5 M H₂SO₄ interface, reaching up to 200 F g⁻¹.

According to the data in Fig. 7, the increase of the capacitance for Pt-C(HTC) in the region of so-called electrical double layer region for Pt (potential region from 0.3 to 0.6 V) is mainly caused by the support material. The capacitance of Pt-C(HTC) is only about 30% of capacitance of carbon at potentials from 0.3 V to 0.6 V. This result is in agreement with sorption data (Fig. 5 and Table I) since the porosity had decreased dramatically due to the lower amount of porous carbon in the catalyst material.

Results for unmodified and modified materials indicate also the faradaic capacitive behavior. This effect occurs when the application of the potential induces faradaic current caused by electroreduction of H₂O⁺-ions and ionization of H₂ or reduction of the surface of a catalyst. However, more detailed analysis shows, that there is also a faradaic capacitive peak at 0.5 V for pure carbon. The positions of peaks (Fig. 7) do not depend on the potential sweep rate and the peak current depends linearly on the sweep rate. Therefore this peak is mainly caused by the reversible faradaic quinone/hydroquinone transformation on the carbon surface:

$$> C_x O + H^+ + e^{-} \rightleftharpoons > C_x OH$$

[2]

The decomposition of water starts at potentials more negative than −0.2 V. Faradic oxidation of the carbon surface is probable at more positive potentials than 1.0 V.

After the modification of the C(HTC) with Pt nanoparticles there appear two distinctive regions associated with the two faradaic

![Figure 5](image1.png)  
**Figure 5.** a) Low-temperature nitrogen adsorption/desorption isotherms and b) differential pore volume distribution vs. pore width plots for C(HTC) and Pt-C(HTC) powders.

![Figure 6](image2.png)  
**Figure 6.** Micro-Raman spectrum for C(HTC) powder.

![Figure 7](image3.png)  
**Figure 7.** Capacitance vs. potential dependencies for Pt-C(HTC) and C(HTC) electrodes in 0.5 M H₂SO₄ solution at different potential scan rates $v$ (noted in figure), saturated with Ar.
processes within the potential region of formation and oxidation of hydrogen adatoms (0 to 0.3 V) and oxygen adsorption/desorption (or reduction/oxidation of oxygen containing surface functional groups) within \( E \) from 0.6 to 1.0 V.

To estimate the catalytically active surface area of the Pt-C(HTC), the \( C_{CV} \) values were integrated within the potential region of \( H_{ads} \) formation and oxidation.\(^{32,33} \) The Pt nanoparticle dispersion has been calculated:

\[
\text{Dispersion} \% = \frac{n_1}{n_2}
\]

being 10%. In equation 3 \( n_1 \) is the number of Pt moles on the surface of the electrode which has been estimated from the value of coulombic charge for \( H_2O \)\(^+ \) eleetroreduction/H adatoms ionization region\(^{32,33} \) and \( n_2 \) is the total number of the Pt moles in the catalyst calculated from the data of the synthesis procedure. The corresponding charge values have been calculated applying the following equation:

\[
Q_H = Q_{total} - Q_{DL}
\]

where \( Q_{total} \) is the charge transferred within the proton reduction/hydrogen adsorption/desorption/oxidation potential region and \( Q_{DL} \) is the charge calculated for double layer formation. The \( Q_{DL} \) has been calculated using the data for unmodified C(HTC) electrode measured at the same experimental conditions and at the same potential scan rates. Thus, the average \( Q_H \) calculated was 47 C g\(^-1 \). Thereafter, the electrochemical surface area \( (A_{EL} \text{ in m}^2 \text{ g}^{-1}) \) of platinum was calculated with respect to the mass of platinum (mg) from the following formula:

\[
A_{EL} = \frac{Q_H}{m_P \cdot \sigma}
\]

where \( m_P \) is the mass of Pt in the electrode (mg) and \( Q_{ocel} \) is the charge required to oxidize/reduce a monolayer of hydrogen adatoms on polycrystalline metallic (compact) Pt (assumed as 0.21 mC cm\(^{-2}\))\(^{25,33} \). The average diameter of the spherical Pt nanoparticles was obtained from CV data using equation:

\[
d_{v/2} = \frac{6}{\rho A_{EL} \cdot \sigma}
\]

where \( \rho \) is the density of platinum (\( \rho = 21.4 \text{ g cm}^{-3} \)).\(^{33} \) The average diameter calculated was equal to 12 nm (\( \sigma = 0.5 \text{ nm} \)) for the electrochemically active Pt nanoparticles.

The calculated values of \( A_{EL} \) and \( d \) are presented in Table II. It was found that the results obtained from XRD and HRTEM measurements are comparable suggesting that the average crystallite size varies from 4 to 6 nm. However, surprisingly the CV and HRSEM give nearly two times higher values. There could be several explanations for this disagreement. First of all the XRD gives estimation of crystallite size, however, the particles could be composed of several smaller crystallites. HRSEM is able to detect particles deposited only onto the surface of the C(HTC) but not into the pores, but HRTEM can also visualize the particles inside of the pores. CV and HRSEM results might be comparable because particles on the surface could mainly participate in the charge transfer process and platinum nanoparticles deposited inside of the micropores are not entirely accessible.

According to the analysis made, \( A_{EL} \) of Pt-C(HTC) is much lower compared to the specific surface area of C(HTC). The \( A_{EL} \) of Pt-C(HTC) is comparable to the Pt catalyst \( (A_{EL} = 29 \text{ m}^2 \text{ g}^{-1}) \) which was encapsulated into microporous-mesoporous carbon prepared using HTSC process without CO\(_2\)-posttreatment, but the calculated wt% of Pt was only 20.\(^{14} \) Considering the general trend established between \( A_{EL} \) and wt% of Pt in catalyst, given in overview,\(^{25} \) the value of \( A_{EL} \) for material synthesized is reasonable being higher than 20 m\(^2\) g\(^-1\). ORR has been investigated on C(HTC) and Pt-C(HTC) materials by CV method. The current densities, \( j_c \), corrected for charging currents in Ar saturated solution, are presented in Fig. 8. At various potential scan rates, two peaks have been observed for non-modified carbon. Taylor et al. also observed two reduction peaks for ORR on the glassy carbon electrode\(^{6,37} \) and the appearance of these peaks was attributed to ORR with peroxide formation on different sites.\(^{36} \) Reduction process characterized with the peak 1 has also a corresponding oxidation process peak (peak 1'). This first peak could be considered as reversible reduction (1) and oxidation (1') of the species adsorbed on the surface of C(HTC), i.e. inside the microporous matrix or of the surface functional groups because 1) the peak potential does not depend on the sweep rate, 2) \( j_p \) versus \( v \) dependencies are linear for the reduction as well as oxidation processes (inset B in Fig. 8a), and

\[
\text{Table II. Summary of Pt particle size calculation using different methods.}
\]

<table>
<thead>
<tr>
<th>Method / Parameter</th>
<th>( d_i ) / nm(^* )</th>
<th>( d_{v/2} ) / nm(^* )</th>
<th>( d_v ) / nm(^* )</th>
<th>( A_{EL} ) / m(^2) g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRSEM</td>
<td>9.1</td>
<td>9.7</td>
<td>10</td>
<td>28</td>
</tr>
<tr>
<td>HRTEM</td>
<td>3.8</td>
<td>4.1</td>
<td>4.3</td>
<td>68</td>
</tr>
<tr>
<td>XRD</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CV</td>
<td>—</td>
<td>12</td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) Electrochemical surface area was calculated based on volume averaged diameter \( (d_v) \) obtained from XRD data.\(^{33,35} \)

![Figure 8](https://example.com/figure8.png)
3) the charge of the cathodic peak is very close to the charge of the anodic peak. At potentials less positive than 0.3 V the reduction of oxygen takes place at the whole carbon surface. The insets in Fig. 8a (A) and 8b confirm the linear dependence of the peak current on $v^{1/2}$ for both Pt-C(HTC) modified and unmodified C(HTC) (in the region of peak 2) samples, indicating that the ORR is limited mainly by slow diffusion and charge transfer steps in the potential region of these peaks.

**Rotating disc electrode data.—**The ORR currents collected from the RDE measurements are presented in Fig. 9. The current density values were corrected for the background current densities established for Ar saturated 0.5 M H$_2$SO$_4$ solution.

Calculations revealed much lower overvoltage for ORR ($\Delta E \sim 0.6$ V) at Pt-C(HTC) compared with that for unmodified HTC material (Figs. 8 and 9). The half-wave potential for ORR (at 1600 rpm) measured for our Pt-C(HTC) is about 150 mV more positive compared that for the Pt catalyst, which was encapsulated into meso- and macroporous carbon, prepared using HTC process with CO$_2$ posttreatment. The size of Pt-nanoparticles in Ref. 13 was calculated to be within the catalyst structure in comparison with the catalyst used in Ref. 13. The increase in porosity for Pt-C(HTC) is caused by the CO$_2$-posttreatment.

Within the region of diffusion limited process the Levich plots for C(HTC) (−0.2 V < $E$ < 0 V) and Pt-C(HTC) (0 V < $E$ < 0.6 V) (Fig. 10a) are linear and the slope values of these plots are independent of the potential applied. The slope of the Levich plot for Pt-C(HTC) is about two times higher compared that for C(HTC), hence, the number of electrons transferred per one O$_2$ molecule reduction differs nearly two times. For the C(HTC) support within the region of potentials from 0.4 V to 0.6 V the process is not limited by diffusion in the solution phase and probably the oxidation and reduction currents are caused by the reversible reduction and oxidation of surface species or surface functional groups inside the porous catalyst layer. The nature of these surface species or surface functional groups might be confirmed by performing the in situ FTIR measurements.

The measured RDE current density consists of three different contributions:

$$\frac{1}{j_c} = \frac{1}{k} + \frac{1}{j_b} + \frac{1}{j_i}$$  \[7\]

where $j_c$ is the current density corrected for the currents measured in Ar saturated electrolyte, $j_b$ is the kinetic current density, $j_b$ is the diffusion step limited charge transfer current density and $j_i$ is the current density in the Nafion film with thickness $L$. According to Behm et al.,$^{38}$ for thin-film electrodes the Nafion layer effect is negligible if the thickness of an active catalyst layer is very small. In this study, assuming a film density of 2.0 g cm$^{-3}$,$^{38}$ the thickness of Nafion layer calculated is only 0.25 μm. Therefore, to the first approximation the classical Koutecky-Levich (K-L) equation can be used for the analysis of RDE data:

$$\frac{1}{j} = \frac{1}{k} + \frac{1}{j_b} = -\frac{1}{nFk_bC_{O_2}^b} + \frac{1}{0.62nFC_{O_2}bD_{O_2}^{1/2}v^{-1/2}ω^{1/2}}$$  \[8\]

In equation 8, $n$ is the number of electrons transferred per one oxygen molecule electrode reaction, $F$ is the Faraday constant (96485 C mol$^{-1}$), $k_b$ is the electrochemical rate constant for ORR, $C_{O_2}^b$ is the concentration of O$_2$ in the electrolyte ($1.3 \times 10^{-6}$ mol cm$^{-3}$), $D_{O_2}$ is the diffusion coefficient for oxygen in the electrolyte ($1.8 \times 10^{-5}$ cm$^{2}$ s$^{-1}$), $v$ is the kinematic viscosity of the solution (0.01 cm$^2$ s$^{-1}$) and $ω$ is the angular frequency (rad s$^{-1}$).$^{22,38}$

Calculated K-L plots for both non-modified C(HTC) and Pt-C(HTC) nanoparticle activated Pt-C(HTC) electrodes (Fig. 10b) are linear and the intercept values of the extrapolated K-L plots depend on the potential applied. The slope of the K-L plots for modified and unmodified carbon is different as it was already expected based on the Levich analysis data (Fig. 10a). The reaction order nearly equal to

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**Figure 9.** The ORR data in O$_2$ saturated solution for C(HTC) and Pt-C(HTC) electrodes corrected for current densities measured in 0.5 M H$_2$SO$_4$ solution saturated with Ar, at potential scan rate $v = 10$ mV s$^{-1}$ and at different electrode rotation rates, noted in figure.

**Figure 10.** a) Levich plots and b) Koutecky-Levich plots for C(HTC) and Pt-C(HTC) electrodes in 0.5 M H$_2$SO$_4$ solution saturated with O$_2$ at different $E$, noted in figure (corrected for Ar saturated solution data).
one for oxygen electroreduction is similar like established by Behm et al.\textsuperscript{38}

The number of electrons transferred during the oxygen molecule electroreduction has been calculated (inset in Fig. 11) for C(HTC), and it is approximately 2. This is in agreement with the results established for ORR on pyrographite,\textsuperscript{39,40} for edge and basal planes of the pyrolytic graphite,\textsuperscript{41} glassy carbon\textsuperscript{37} and Vulcan XC72R\textsuperscript{42} in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. Thus, the only product generated was hydrogen peroxide which did not react further. However, ORR on Pt-C(HTC) is nearly a four-electron process generating water as a final product.\textsuperscript{22,35,38} The kinetic current densities have been calculated using linear extrapolation process of the K-L plots to \(\omega^{-1/2} \rightarrow 0\). The kinetic current densities are presented in Fig. 11 and the slope of Tafel-like plot for Pt-C(HTC) is 102 mV within the region of low current densities. However, the value of Tafel-like plot slope starts to increase at higher current densities. The similar behavior was observed in other investigations\textsuperscript{43} and has been explained by the change of adsorption isotherm from single Langmuir type toward more complicated adsorption isotherm determining the ORR mechanism within high current density region.\textsuperscript{2,3,42}

Surprisingly, for C(HTC) support there are three regions in the Tafel-like plot for the cathodic and anodic scans. Within the medium overvoltages region, the Tafel-like plot slope is 199 mV and it increases as the potential becomes more negative. The cathodic and anodic scans overlap at potentials more negative than 0.35 V. The Tafel-like plot slope for the anodic scan is 201 mV. Comparable slope values were observed also by Taylor et al.\textsuperscript{45} for glassy carbon disc electrode in the acidic solutions, by Tarasevich et al.\textsuperscript{44,45} for pyrographite (170 mV) and Zhutaeva et al.\textsuperscript{42} for Vulcan XC72R (120–130 mV) in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution and explained by the slow transfer of the first electron for O\textsubscript{2} molecule: O\textsubscript{2} + e\textsuperscript{−} \(\rightarrow\) O\textsubscript{2}\textsuperscript{−} followed by the protonation of O\textsubscript{2}\textsuperscript{−} in the solution.

The overvoltage for ORR on C(HTC) support is lower compared to that established for Vulcan XC72R\textsuperscript{43} and much lower compared to the edge plane of pyrolytic graphite.\textsuperscript{41} It could be explained by higher specific surface area and larger number of edge plane sites at the C(HTC) samples compared to carbon Vulcan XC72R (\(S_{BET} = 240 \text{ m}^2 \text{ g}^{-1}\)) as well as to other flat carbons. However, at the same time, the activity of C(HTC) is lower compared to molybdenum carbide derived carbons synthesized at chlorination temperatures lower than 900 °C and having noticeably more amorphous structure, higher specific surface area and the higher amount of mesopores.\textsuperscript{43}

**Electrochemical impedance spectroscopy.**—Electrochemical impedance data (Figs. 12 and 13) characterize the electroreduction of oxygen at low ac frequencies (\(f < 1 \text{ Hz}\)) being mainly controlled by the rate of adsorption/desorption limiting step in the porous structure of the materials analyzed.

The Bode phase angle, \(\theta\), vs. \(\log f\), and \(\log |Z|, \log f\)-plots, presented in Fig. 13, show weak dependence on potential applied, where \(|Z|\) is the impedance modulus. At ac frequencies \(f > 100 \text{ Hz}\), pure resistive behavior has been observed for electrodes prepared from Pt-C(HTC) and C(HTC) materials. In this region, the phase angle values are nearly 0° and the shape of the Nyquist plots is independent of potential and the oxygen concentration in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. The high-frequency series resistance \(R_S\) = \(|Z| (f \rightarrow \infty)\) values (insets in Figs. 12a and 12b) are independent of potential and material under study. Hence, \(R_S\) is resulted from the uncompensated resistance of solution between the electrode surface and the Luggin capillary.

At lower ac frequencies (\(f < 1 \text{ Hz}\)), \(|Z|\) and \(Z\) values (\(Z\) is the resistive component of impedance) decrease with the rise of the ORR overpotential resulting in the increase in ORR kinetic current (Figs. 8, 9 and 13).

According to the data given as Bode plots (Fig. 13), the phase angle value approaches very negative values (from −85° to −88°) at low ac frequencies (\(f \leq 0.1 \text{ Hz}\)) in case of both C(HTC) and Pt-C(HTC) materials and, thus, nearly ideal capacitive behavior (with slope values less than −0.94, obtained from log \(|Z|\), log \(f\)-plots (Table III)), has been established (\(Z\) is the imaginary part of impedance). Thus, the adsorption step limited capacitive processes at (HTC) and Pt-C(HTC) in 0.5 H\textsubscript{2}SO\textsubscript{4} solution has been investigated. Comparing the slope values for samples under study, only weak deviation from ideal capacitive behavior has been observed for C(HTC) and Pt-C(HTC) (Figs. 12 and 13 and Table III).

Based on the analysis of the electrochemical impedance data, including Nyquist plots, the series capacitance, \(C_s\), and parallel capacitance, \(C_P\), were calculated (Fig. 14) using the mathematical relationships discussed in Ref. 6. Surprisingly at \(f \rightarrow 0\), \(C_s\), log \(f\)- and \(C_P\), log \(f\)-dependencies overlap, demonstrating that almost the blocking.

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**Figure 11.** Tafel-like plots for C(HTC) and Pt-C(HTC) electrodes (noted in figure) in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution saturated with O\textsubscript{2}. Inset: number of electrons transferred per O\textsubscript{2} molecule during the ORR, the electrode materials are noted in inset.

**Figure 12.** Nyquist plots for a) C(HTC) and b) Pt-C(HTC) electrodes in O\textsubscript{2} saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} solution at different potentials, noted in figure.
Figure 13. Bode phase angle $\theta$, $\log f$ and $\log |Z|$, $\log f$-plots for a) C(HTC) and b) Pt-C(HTC) electrodes in O$_2$ saturated 0.5 M H$_2$SO$_4$ solution at different potentials, noted in figure.

Table III. The slope values obtained from $\log |Z''|$ vs. $\log f$-dependencies for C(HTC) and Pt-C(HTC) in O$_2$ saturated 0.5 M H$_2$SO$_4$ solution (frequency region is between 0.01 and 1 Hz for both samples). For purely capacitive material, the slope value should be equal to $-1$.

<table>
<thead>
<tr>
<th>$E$ vs. SHE / V</th>
<th>$C$ (HTC)</th>
<th>$C$ (Pt-C(HTC))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>-0.93</td>
<td>-0.95</td>
</tr>
<tr>
<td>0.75</td>
<td>-0.94</td>
<td>-0.94</td>
</tr>
<tr>
<td>0.35</td>
<td>-0.96</td>
<td>-0.99</td>
</tr>
<tr>
<td>0.15</td>
<td>-0.96</td>
<td>-0.99</td>
</tr>
</tbody>
</table>

Figures 14. Dependencies of $C_s$ and $C_p$ on $\log f$ for a) C(HTC) and b) Pt-C(HTC) in O$_2$ saturated 0.5 M H$_2$SO$_4$ solution at different potentials, noted in figure.

This is in agreement with the physical characterization data (Fig. 5b and Table I) and CV data (Fig. 7). Inaccessibility of the micropores could limit the adsorption of reaction intermediates within the potential region of the oxygen electroreduction reaction by adsorption of H$_2$ molecules (being the final product for H$_3$O$^+$ coelecctroreduction) inside the microporous-mesoporous structure. However, differently from unmodified C(HTC) material, the maximum capacitance values for Pt-C(HTC) have been established at $E = 0.15$ V, i.e. within the region of H$_2$O$^+$ electroreduction/ionization reaction.

The high capacitive electrical double layer charging/discharging currents are in favor for the PEMFC systems applicable for electrical cars due to their ability for quick and short-time high power delivery which improves the speed uptake of the cars, and others PEMFC based transportation systems under development.

Conclusions

The microporous-mesoporous carbon powder was prepared from D-glucose by the hydrothermal carbonization method (noted as C(HTC)) applying the subsequent pyrolysis and thereafter additionally activated using the carbon dioxide activation method. Corresponding powders prepared have been studied by the various physical characterization methods like XRD, Raman spectroscopy, N$_2$ adsorption/desorption, HRSEM and HRTEM. The calculated specific surface area using N$_2$ adsorption/desorption method was 7 times higher compared with that for the commercial carbon Vulcan XC72R.
The Pt-nanoclusters were deposited onto the C-HTC support by borohydride reduction method (The prepared catalyst has been noted as Pt-C-HTC). According to the results obtained from electrochemical experiments, the medium Pt particle size calculated was 12 nm. The Pt-C-HTC catalyst has been studied also by physical characterization methods. Nitrogen adsorption/desorption data demonstrated lower specific surface area values for Pt-C-HTC catalyst compared to pure C-HTC powder explained by the lower amount of C-HTC particles (surface area) free from Pt nanoparticle deposits in the structure of Pt-C-HTC.

Both modified and unmodified materials have been investigated by electrochemical characterization techniques (cyclic voltammetry, rotating disc electrode and impedance spectroscopy methods). According to the data obtained, nearly double layer capacitive behavior has been observed for C-HTC and Pt-C-HTC materials in 0.5 M H2SO4 solution due to the more amorphous microporous-mesoporous structure and higher electrochemically active surface area compared to commonly used catalysts. The ORR activity of Pt-C-HTC was noticeably higher than that for unmodified C-HTC electrode material. The CO2 posttreatment increased the porosity of (C-HTC) and substantially reduced the oxygen electroreduction overpotential for Pt-C-HTC compared to Pt-nanoclusters activated electrode deposited onto C-HTC carbon without CO2 posttreatment.

The number of electrons transferred per electroreduction of one O2 molecule has been estimated for both electrode materials using Koutecky-Levich method. The four-electron process has been detected for Pt-C-HTC. For unmodified C-HTC electrode, the number of electrons transferred varies from 1.8 to 2.1, hence, only H2O2 formation occurs.

Analysis of the impedence data indicated moderate series and parallel capacitance values for both Pt-C-HTC and unmodified C-HTC based electrodes. These results have been confirmed by the CV data demonstrating the capacitance values up to 200 F g⁻¹ (C-HTC) and 250 F g⁻¹ (Pt-C-HTC) within the hydrogen adatom formation/oxidation potential region.

Acknowledgments

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