Electrochemical impedance characteristics and electroreduction of oxygen at tungsten carbide derived micromesoporous carbon electrodes

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Abstract

The electrical double layer characteristics and oxygen electroreduction kinetics in 0.5 M H2SO4 aqueous solution has been studied at micromesoporous tungsten carbide derived carbon C(WC) electrodes. Carbon powders with various specific surface areas (1280–2116 m2 g−1) have been prepared from WC at chlorination temperatures 900 °C, 1000 °C and 1100 °C. The porous structure of carbon substrate was characterized using nitrogen sorption, X-ray diffraction, high resolution TEM, electron energy loss spectroscopy, selected area electron diffraction and scanning electron microscopy with energy-dispersive X-ray spectroscopy methods. Cyclic voltammograms at various potential scan rates from 2 to 70 mV s−1, and rotating disc electrode data at rotation velocities from 0 to 3000 rev min−1, were measured within the region of potentials from +0.4 V to −0.6 V vs. HgHg2SO4sat.K2SO4 in H2O (MSE). At E > −0.2 V, the electroreduction of oxygen is mainly limited by the charge transfer step, and at −0.6 V < E < −0.2 V, by the mixed kinetics. The oxygen electroreduction mainly proceeds through the peroxide formation intermediate step on all electrodes studied. Despite of the fact that the electrodes tested were very stable during the electrochemical experiment, indicating that the C(WC) is a suitable catalyst support material for polymer electrolyte membrane fuel cell. The electroreduction rate of oxygen depends strongly on the structure (graphitisation level) of carbide derived carbon used for preparation of an electrode and the oxygen reduction overvoltage decreases in the order C(WC) 1100 °C > C(WC) 1000 °C > C(WC) 900 °C. Very high low-frequency capacitance values, independent of alternative current (ac) frequency at f < 0.1 Hz, have been established for C(WC) 1100 °C, demonstrating that at ac f → 0, mainly pseudocapacitive behaviour with adsorption limited step of reaction intermediates has been observed.

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1. Introduction

Polymer electrolyte membrane fuel cells are promising energy sources for mobile and portable applications. Over the last several decades, an intensive research has focused on the development of electrocatalyst for the oxygen electroreduction reaction (ORR) because in a polymer electrolyte membrane fuel cell (PEMFC), the major limit on performance is the slow kinetics of the cathodic electroreduction of oxygen [1–11]. During long lasting catalyst optimization studies, various carbon supports have been used [1,4,8,10,11], but influence of the structure of micromesoporous materials on the oxygen electroreduction kinetics has not fully understood. It has been recognized that, depending on the heat-treatment temperatures, different carbon materials exhibit different physical properties, such as specific surface area, porosity, pore size distribution, electrical conductivity [12–16] and oxygen electroreduction activity [4,8,17].

ORR has also been studied on materials composed of WC [18] and W2C [19], prepared from Vulcan X-72 carbon and tungsten powder, using intermittent microwave heating. Pure WC and W2C were inactive within the potential region studied (E from 0.04 V to 0.49 V vs. MSE, and E from −0.01 V to 0.49 V vs. MSE, respectively) comparable with the potentials applied in this work [18,19]. However, if these materials were combined with platinum nanoparticles, they demonstrated higher activity towards ORR in 0.5 M H2SO4 solution compared with platinum based materials.

Recent studies have revealed that the specific surface area, pore size distribution and crystallinity (i.e. graphitisation level and linear dimensions of graphitic areas) of various carbon supports have an important impact on the rate of electrochemical processes, influencing even fuel oxidation reaction mechanism and balance between rate limiting kinetics steps. Thus, the rate of charge transfer, adsorption or mass transfer steps depends on the carbon material support used [1–9,20]. For better performance of PEMFC catalysts the carbon supports with optimized micromesoporosity, pore size distribution and good electrical conductivity as well as optimal specific surface area would be designed. Our systematic
studies in the field of electrical double layer capacitors [12–16] show that binary metal carbide derived carbon (CDC) materials have been characterised with very high specific surface area, low carbon degradation rate and chemical stability at extreme potentials applied (very low so-called “carbon corrosion rate”), as well as increased electrical conductivity. It was demonstrated that carbon powders with well determined micromesoporosity and pore size distribution, ratio of micro- and mesopore areas and volumes, can be synthesised using selective chemical reaction of molecular chlorine with various binary carbides [12–16]. Based on mentioned synthesis method, microporous C(TiC) and C(α-SiC), as well as partially mesoporous carbons C(VC) and C(WC), and mainly mesoporous C(Mo2C) have been synthesised using TiC, α-SiC, VC, WC and Mo2C as raw materials, respectively [12–16].

The main aim of this work was to study and compare the electrochemical properties of various micromesoporous C(WC) electrodes, prepared from WC powder at following synthesis temperatures Tsyn: 900 °C, 1000 °C and 1100 °C (referred to as C(WC) 900, C(WC) 1000 and C(WC) 1100, respectively [15]) and analyse an influence of materials porosity on the ORR in 0.5 M H2SO4 aqueous solution. Influence of the graphitisation level of C(WC) (i.e. ratio of the amorphous and graphitic areas), prepared at different Tsyn, on the rate of electrochemical processes has been demonstrated. In addition, the electrical double layer characterisations for systems under study have been calculated using impedance spectroscopy and cyclic voltammetry (CV) methods. Main information of this work will be used for the development of improved carbon supported Pt and Pt–Ru catalysts for oxygen reduction and methanol oxidation processes in PEMFC, respectively.

2. Experimental

2.1. Electrode preparation

Glassy carbon disk electrode (GCDE), (5 mm diameter, 0.196 cm2) (Pine Instrument Company), pressed into a Teflon holder, served as the substrate for the catalyst, was polished to a mirror finish (0.05 μm alumina slurry, Buehler). After polishing GCDE was washed with Milli-Q water and sonicated in Milli-Q water for a few minutes. Thereafter GCDE was covered with a C(WC) 900 °C, C(WC) 1000 °C or C(WC) 1100 °C catalyst ink [4,11,21], prepared by suspending the C(WC) powder in Milli-Q water and agitated in an ultrasonic bath for 15 min for thorough wetting as well as to disperse the carbon powder homogeneously. Thereafter Nafion® dispersion solution (Aldrich) was added to the catalyst mixture (to give a dry ink with fixed composition of 1 wt% of Nafion® ionomer in the CDC electrode) and sonicated for next 30 min at room temperature to prepare uniformly dispersed ink. The catalyst ink was pipetted onto the GCDE surface and dried at room temperature. The mass of WC-CDC loading was applied. The data obtained (Fig. 2) show that electrodes prepared have hierarchical structure and open micromesoporosity. EDX data (Table in Fig. 3) show that there is no chemical contamination of C(WC) electrode with residual chlorine, WCl3, or raw WC. In some areas the binding material Nafion® filaments (as element F in surface chemical analyses Table) and small oxygen concentration (probably existing as functional groups at the surface) have been observed.

For morphological studies, C(WC) was examined using high resolution transmission electron microscopy (HRTEM, Tecnai 12 instrument operating at the 120 kV accelerating voltage), and complementary techniques, such as electron energy loss spectroscopy (EELS) and selected area electron diffraction (SAED) methods (Fig. 3) [15]. Similarly to the results given in [15], the HRTEM, EELS and SAED data show that C(WC) 900 °C has mainly amorphous structure (not shown for shortness), but in some areas of C(WC) 1100 °C, the existence of a somewhat ordered graphitic particles in the sample surface layer (Fig. 3) has been observed [15], increasing noticeably the electronic conductivity of C(WC) 1100 °C in comparison with C(WC) 900 °C (demonstrated later by impedance data). The SAED pattern displays hk0-type diffraction rings of graphite (Fig. 3b), which are consistent with a nanostructure consisting of poorly-stacked graphene layers. EELS data i.e. more well developed and narrow π*- and δ-peaks for C(WC) 1100 °C compared with C(WC) 900 °C, (not shown for shortness) show that the carbon-K ionization edge gives important information about the bonding nature and the crystallinity of the material. Most importantly, in agreement with EDX data, the TEM-EELS data show that there is no WC, WCl3 or chlorine residuals in the electrode materials under study. The first-order and second order Raman spectra are in a good agreement with EELS and SAED data, indicating the partial graphitisation of C(WC) 1100 °C material, similarly to our previous data [15].

2.3. Electrochemical measurements

The electrochemical measurements were carried out in a three-electrode electrochemical cell using a rotating disk electrode (RDE) system [21–25]. For ac impedance measurements [26], the electrode potential E was applied with a potentiostat/galvanostat (AutoLab PGSTAT 100 with FRA, Eco Chemie B.V.), and the experiments were controlled with General Purpose Electrochemical System and Frequency Response Analyser software. Working electrode potentials were determined using a Hg|Hg2SO4, saturated K2SO4 reference electrode (MSE), separated from the cell by a Lug-

<table>
<thead>
<tr>
<th>Parameter/material chlorine temperature (°C)</th>
<th>S_BET (m² g⁻¹)</th>
<th>S_micro(m² g⁻¹)</th>
<th>V_micro (cm³ g⁻¹)</th>
<th>V_tot (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(WC) 900</td>
<td>1290</td>
<td>1280</td>
<td>0.60</td>
<td>0.64</td>
</tr>
<tr>
<td>C(WC) 1000</td>
<td>1280</td>
<td>1260</td>
<td>0.61</td>
<td>0.66</td>
</tr>
<tr>
<td>C(WC) 1100</td>
<td>2116</td>
<td>1980</td>
<td>1.26</td>
<td>1.53</td>
</tr>
</tbody>
</table>

gin capillary in order to avoid contamination and the distance between Luggin tip and working electrode surface was more than 1 cm (to avoid distortion effect for rotating disk electrode data). The counter electrode was a very large Pt wire mesh, separated from the main solution by a fritted glass membrane.

The cyclic voltammetry (CV) curves were obtained on standing electrode at potential scan rates from 2 to 70 mV s$^{-1}$ and RDE data were measured at rotation velocities from 0 to 3000 rev min$^{-1}$ ($v = 10 \text{ mV s}^{-1}$) and in the region of potentials from +0.4 V to −0.6 V vs. MSE. CV curves were corrected for IR-drop, where solution resistance $R_s$ was obtained from impedance data at a frequency $f \geq 1 \times 10^4 \text{Hz}$, discussed later. First group of CV measurements was conducted in 0.5 M H$_2$SO$_4$ (Fluka, TraceSelect Ultra) electrolyte solution saturated with Ar (99.9999%, AGA) to measure the so-called reference $j$, $E$-curve, where $j$ is the current density, and the second group of $j$, $E$-curves was obtained...
in the same solution, but saturated with the molecular oxygen (99.999%, AGA) for 30 min before the measurements to study the ORR kinetics (Figs. 4–7). The standby potential was fixed at +0.40 V vs. MSE. Electrochemical impedance data were obtained at fixed ac frequencies \(f\) from 0.01 to \(10^5\) Hz (5 mV modulation) at fixed \(E_{\text{f}}\): −0.5, −0.35, 0, +0.15, +0.25 and +0.4 vs. MSE. All measurements were carried out at temperature 22 ± 1 °C.

3. Results and discussion

3.1. Rotating disc electrode data

The RDE data [21–25], given in Fig. 4 (current densities measured in Ar-saturated, i.e. deaerated 0.5 M H\(_2\)SO\(_4\) supporting electrolyte solution, given as solid line in Fig. 4a) show that high current density values (\(|j| > 25 \text{ A m}^{-2}\)) have been achieved for the electrode, prepared from C(WC) 900 °C in 0.5 M H\(_2\)SO\(_4\) solution saturated with O\(_2\). The current densities for ORR (Fig. 4) were minimal at the standby potential (+0.40 V) selected. After correction for the supporting electrolyte current densities in Ar saturated conditions, the RDE curves with shape (within the potential range from −0.59 V to −0.31 V vs. MSE) (Fig. 4b) characteristic for the mixed kinetics processes, have been observed. The RDE data (Fig. 4b) show that current densities noticeably depend on the C(WC) synthesis temperature \(T_{\text{syn}}\), increasing with the decrease of \(T_{\text{syn}}\). Thus, the mixed kinetic current densities depend strongly on the amorphous structure and on the graphitisation level of the carbon powder used for preparation of electrodes.

The half-wave potential shifts toward more negative potentials, i.e. the electroreduction activity of O\(_2\) decreases with the increase of synthesis temperature of carbon powder. For the electrode, deposited using C(WC) 900 °C powder based ink, the comparatively high current densities were measured within the mixed kinetics region. The higher current densities of more amorphous C(WC) 900 °C powder based electrode can be explained by the higher concentration of surface defects expressed at amorphous C(WC) 900 °C, (probably by the existence of edge planes), compared with that for partially graphitized C(WC) 1100 °C. CV and RDE data show that the current densities (within potential range from −0.6 V to 0 V vs. MSE) noticeably decrease with the increase of BET surface area \(S_{\text{BET}}\) and total pore volume \(V_{\text{tot}}\) values (Table 1).

To analyse the RDE data, the measured current density, \(j\), was described by the following relation [22]

\[
\begin{align*}
\frac{1}{j} = & \frac{1}{j_k} + \frac{1}{j_0} + \frac{1}{j_f} + \frac{1}{j_k} + \frac{1}{j_k} + \frac{1}{nFj_DG} + \frac{1}{nFD_Gc} \frac{L}{j_f}
\end{align*}
\]
where \( j_k \) and \( j_D \) are the kinetic and diffusion limited current densities, respectively and the Nafion\(^*\) film diffusion limited current density, \( j_f \). The other parameters are the Levich constant \( B \), the reactant concentration in the solution \( c_0 \), the film thickness \( L \), the reactant concentration in the Nafion\(^*\) film \( c_f \) and the diffusion constant in the Nafion\(^*\) film \( D_f \), the number of electrons transferred per one reduced \( \text{O}_2 \) molecule \( n \), and the Faraday constant \( F \) (96485 C mol\(^{-1}\)).

For smooth electrodes, the \( j_f \) term does not exist in Eq. (1) and \( j \) depends only on \( j_k \) and \( j_D \), as shown in Eq. (2). Analysis of data presented in [22] demonstrates that for thin film electrode, i.e. at low catalyst loading, the role of \( j_f \) is unimportant as the \( j_f \) values are noticeably higher than \( j_k \) and \( j_D \) values, and to the first approximation the simplified Eq. (2), known as Koutecky–Levich (K–L) equation, can be used for calculation of kinetic current densities. 

Taking into account the small thickness of catalyst layer and the low catalyst loading, as well as the fact, that the active catalyst layer thickness has been kept constant for all C(WC) electrodes prepared in this work, the kinetic current densities were calculated from the

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**Fig. 6.** log \( j_k \) vs. E-curves for various C(WC) powder based electrodes (noted in figure), calculated from RDE data for C(WC)|GCDE in 0.5 M H\(_2\)SO\(_4\) solution, saturated with \( \text{O}_2 \) (inset – the number of electrons transferred per \( \text{O}_2 \) molecule calculated for C(WC) 900 °C|GCDE).

**Fig. 7.** C\(_{CV}\) vs. E-plots for C(WC) 1100 °C|GCDE in 0.5 M H\(_2\)SO\(_4\) solution saturated with Ar (a) and \( \text{O}_2 \) (b) at different \( v \) (mV s\(^{-1}\), noted in figure) and time stability of cyclic voltammograms (inset in Fig. b) in the case of the 0.5 M H\(_2\)SO\(_4\) solution saturated with oxygen (\( v = 10 \) mV sec\(^{-1}\)).
practically linear $j^{-1}, \omega^{-1/2}$ plots (at $E \leq -0.31$ V) and were analysed using the K–L equation [1,4–6,23–25]

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_D} = \frac{1}{nFk_{\text{cat}}C_D} - \frac{1}{0.62nFD_{O_2}^{-1/6}C^{3/2}_O},$$

where $c_{D}^{3/2}$ is the concentration of $O_2$ in the bulk (1.3 × 10^{-6} mol cm^{-3} in 0.5 M H_2SO_4 at $T = 298$ K [5]), $k_{\text{cat}}$ is the electrochemical rate constant for $O_2$ reduction, $D_O$ is the diffusion coefficient of oxygen (2.2 × 10^{-5} ± 0.2 cm^2 s^{-1}) [4,23–25], $\nu$ is the kinematic viscosity of the solution (0.01 cm^2 s^{-1}) [23–25] and $\omega$ is the rotation velocity of the electrode. The K–L plots were linear (correlation coefficient $R^2 > 0.846$) within the region of electrode potentials from $-0.31$ V to $-0.59$ V vs. MFE (Fig. 5) and the intercept of the extrapolated K–L plot (giving the kinetic current density $j_k$ value) depends on the potential applied. However, the slope for $j^{-1}, \omega^{-1/2}$ plots for electrode potentials from $E = -0.31$ V to $-0.43$ V is close to zero, demonstrating that the electrochemical reaction rate is controlled by processes independent of the electrode rotation rate, i.e. controlled by the faradaic charge transfer step and/or mass transfer process through the thin surface layer of catalyst that rotates together with the electrode.

Fig. 6 demonstrates that the $j_k$ values noticeably depend on C(WC) material studied, being highest for material with lowest with C(WC) electrode potentials, if $E \geq -0.5$ V. Thus, at less negative C(WC) electrode potentials, the crystallinity of C(WC) electrodes and graphitisation level has noticeable influence on the electrocatalytic activity of electrodes for oxygen electroreduction process under study. As summarised by Compton and Gara [27], the oxygen reduction on carbon electrode in acidic solutions usually proceeds through the more common two electron transfer mechanism, i.e. through the peroxide formation pathway. However, the number of electrons transferred during electroreduction process to $O_2$ molecule, somewhat higher than 2, established in this work (inset in Fig. 6), is in a good agreement with literature data [1–3,5], and indicate that the peroxide formed partially reduces further at $E < -0.3$ V [27]. The number of electrons transferred depends somewhat on $T_{\text{ox}}$ being higher for C(WC) 900 °C.

More detailed analysis of CV data, given in Fig. 7, shows that nearly pseudocapacitive behaviour for Ar saturated (Fig. 7a), as well for $O_2$ saturated C(WC)|GCDE systems, has been established (Fig. 7b). The values of capacitance, $C_{\text{CV}}$, have been calculated using the relation $C_{\text{CV}} = j/\nu$. $C_{\text{CV}}$ values, calculated for Ar and $O_2$ saturated systems (Fig. 7a and b), only weakly depend on $\nu$ applied, similarly to the micromesoporous carbon electrodes, tested by us before [13,14]. Very weak dependence of capacitance on $\nu$ indicates the dominating pseudocapacitive behaviour of studied systems [26,28–31]. Comparison of data for Ar and $O_2$ saturated solutions (Fig. 7a and b) show, that for $O_2$ saturated system only weakly higher $j$ and $C_{\text{CV}}$ values (Fig. 7b) have been obtained within the potential region from $-0.2$ V to $-0.6$ V vs. MFE, where ORR has been established using RDE data, indicating the slow mass transfer processes of $O_2$ molecules inside micromesoporous carbon electrodes at normal pressure conditions applied in our CV experiments. In addition, the wide oxidation (with peak potential $E_{\text{ox}}$) and reduction (with $E_{\text{red}}$) maxima in Fig. 7a and b, practically independent of $O_2$ concentration in solution, have been established. Difference between $E_{\text{ox}}$ and $E_{\text{red}}$ ($\Delta E$) is lower than 50 mV and $\Delta E$ is nearly independent of the molecular oxygen concentration in solution indicating that the population density of the oxygen containing surface active groups is practically independent of $O_2$ concentration in solution. Thus, at $O_2$ diffusion limited conditions, the micromesoporous area is not active at atmospheric (normal) pressure conditions due to the absence of quick oxygen transfer into/inside of the microporous C(WC) structure.

Based on the CV data (inset in Fig. 7b), the time stability of cyclic voltammograms in the case of 0.5 M H_2SO_4 solution, saturated with oxygen is good, despite of the fact that the oxygen reduction on these carbon materials proceeds mainly by the two electron mechanism, i.e. through the peroxide formation pathway. The stability of electrodes has been tested additionally using repetitive cyclation of electrode potential within the region from $-0.6$ V to $0.4$ V vs. MFE. The data presented in Fig. 7b inset indicate, that the current densities are the same at the beginning and at the end of experiment thus after more than 100 potential cycles, within the E region mentioned, has been made.

### 3.2. Electrochemical impedance results

Electrochemical impedance (EIS) data given as Nyquist (−$Z'\omega$, $Z'$), phase angle $\phi$ vs. log $f$ and log ($−Z'$) vs. log $f$ plots [23,28–31], given in Figs. 8–10, show that in the region of low ac frequency ($f < 10$ Hz) the electroreduction of oxygen is mainly limited by the adsorption step limited process at the porous surface areas of
the C(WC) electrode. At \( f > 10^2 \) Hz, the phase angle values (Fig. 9) are close to zero and in this frequency area [26] the impedance spectra are practically independent of oxygen concentration in 0.5 M \( \text{H}_2\text{SO}_4 \) solution. Only at \( f > 10^3 \) Hz, some differences in Nyquist plots have been established for \( \text{O}_2 \) and \( \text{Ar} \) saturated solutions. Thus, the oxygen electroreduction reaction at open surface areas of C(WC) seems to be very quick (Figs. 8–10) and the kinetics of charge transfer step at open surface areas cannot be analysed using impedance method [26,30]. At lower ac frequency, \( f < 10 \) Hz, the “knees” in \(-Z^*\) plots can be seen, indicating that the so called nearly “blocking adsorption” pseudocapacitive behaviour has been established, similarly to Pt–Ru–C(Mo2C) electrodes [21] and Ru|RuO2–C electrodes [30–36] as well as for C(WC) in acetonitrile or in aqueous \( \text{Na}_2\text{SO}_4 \) surface inactive electrolyte solutions [37,38]. Fig. 10b shows that the high frequency series resistance \( (Z^* (f \to \infty) = R_s) \) is independent of potential applied and thus, the electrolyte series resistance \( R_e \) can be calculated at \( f \approx 10 \) kHz. These \( R_s \) values have been used for IR-compensation of \( j, E \)-curves, given in Figs. 4–6 [4–7]. Weak decrease of \( Z^* \) or \( Z \), in comparison with C(WC) 900°C and C(WC) 1000°C, can be seen only for the

Fig. 9. Phase angle \(-\theta\) vs. log\( f\) plots for various C(WC)|GCDE electrodes in 0.5 M \( \text{H}_2\text{SO}_4 \) solution, saturated with \( \text{O}_2 \) (at different \( E \), noted in figure).

Fig. 10. Dependencies of log \((-Z^*)\) (a) and log \( Z \) vs. log\( f\) plots (b) for various C(WC)|GCDE systems (noted in figure) in 0.5 M \( \text{H}_2\text{SO}_4 \) solution, saturated with \( \text{O}_2 \) (at different \( E \), noted in figure).
partially graphitized C(WC) 1100 °C electrode due to better solid phase conductivity. At f < 1 Hz, \( \log Z \) (Fig. 10b) and \( \log Z \) values increase with the decrease of negative electrode potential indicating the deviation of the system from the mixed kinetic mechanism at \( E > 0 \) V toward the adsorption limited mechanism at \( E \leq -0.35 \) V. The phase angle values \( \theta \sim -87^\circ \) at f < 1 Hz, can be explained by the adsorption step limited processes at micromesoporous C(WC) electrodes in H\(_2\)SO\(_4\) aqueous solution [17,24–26,30–35,37–41]. As it was demonstrated by Orazem et al. [28,39–41], the absolute value of the slope of the log (\( -Z^\prime \)) vs. log f plot is equal to the constant phase element (CPE) fractional exponent, where CPE impedance is given as \( Z_{\text{CPE}} = Q(j\omega)^{-\alpha_{\text{CPE}}} \) (\( \alpha_{\text{CPE}} \) is CPE fractional exponent and Q is the constant phase element coefficient, \( j = \sqrt{-1} \) and \( \omega = 2\pi f \)). Fig 10a shows that a plot of the log (\( -Z^\prime \)), log f yields a straight line with a slope of \(-0.98\) at frequencies lower than \( 10 \) Hz, which indicates CPE behaviour with a CPE exponent of 0.98. For more microporous C(WC) 900–1100 °C|H\(_2\)SO\(_4\) solution, saturated with O\(_2\) interface, the \( \alpha_{\text{CPE}} \) values are somewhat lower than 0.96, demonstrating the more pronounced influence of mass transfer step on the mainly adsorption step limited processes.

To the first approximation the impedance response for micromesoporous C(WC) based electrochemical systems reflects a distribution of reactivity that could represented with an equivalent electrical circuit as a CPE in parallel with charge transfer resistance. Huang et al. [29] have shown that current and potential distributions induce a high frequency pseudo constant phase element behaviour in the global impedance response of an ideally polarized electrode due to better solid phase conductivity. At micromesoporous C(WC) material.

4. Conclusions

Micromesoporous carbon electrodes from C(WC) powders (with various specific surface areas from 1280 to 2116 m\(^2\) g\(^{-1}\)) were synthesized from WC at different fixed temperatures from 900 °C to 1100 °C, using chlorination method [15]. Analysis of XRD, SEMEDX, Raman, HRTEM, EELS, SAED, CV, RDE and EIS data show that highly porous electrodes have been prepared for which the moderate cathodic O\(_2\) electrode reduction current densities (\( \sim 25 \) A m\(^{-2}\)) were obtained. Hence, the C(WC) can be used as supports for various catalysts because of its moderate activity for O\(_2\) electrode reduction in a wide potential region in acid media.

Using the RDE method, at more negative potentials than \(-0.23 \) V vs. MSE, the number of electrons \( n \) transferred per one O\(_2\) molecule electrode reduction calculated was (\( \geq 2.6 \)) being in a good agreement with literature data. However, analysis of impedance spectra shows nearly pseudocapacitive behaviour for C(WC) electrodes at low ac frequency region (\( f < 1 \) Hz), where probably the O\(_2\) electrode reduction reaction rate is limited by the rate of intermediate (H\(_2\)O\(_2\)) or final product adsorption step. In the electrode potential region from 0 V to 0.4 V vs. MSE, the very high series and parallel capacitance values (\( \sim 70–90 \) F g\(^{-1}\)) (calculated per active material weight) have been established for C(WC) 1100 °C. At all electrode potentials studied, series and parallel capacitance values coincide at frequency \( f < 0.05 \) Hz, demonstrating the nearly so-called pseudocapacitive behaviour. Thus, C(WC) catalysts are inter-

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**Fig. 11.** Dependencies of \( C_s \) and \( C_p \) on log f plots for various C(WC)|GCDE systems (noted in figure) in 0.5 M H\(_2\)SO\(_4\) solution, saturated with O\(_2\) (at different E, noted in figure).
testing electrode materials or catalyst supports for polymer electrolyte fuel cells and hybrid supercapacitor systems.

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