

Electrooxidation of Ethanol on Pd-Modified Carbon Fibre Tow Material

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Received: 29 October 2012 / *Accepted:* 27 November 2012 / *Published:* 1 January 2013

Present work reports cyclic voltammetric and a.c. impedance spectroscopy investigations of ethanol electrooxidation on palladium-modified (via Pd electrodeposition) carbon fibre tow catalyst material, carried-out in 0.5 M H₂SO₄ and 0.1 M NaOH solutions. The kinetics of ethanol electrooxidation were examined at room temperature through evaluation of the impedance-recorded resistance and capacitance parameters. Also, comparison of ethanol oxidation kinetics with those of underpotential deposition of hydrogen (UPD of H) in 0.1 M NaOH, was made.

Keywords: Ethanol electrooxidation, CF, Pd-modified CF, impedance spectroscopy.

1. INTRODUCTION

Electrooxidation of ethanol on a catalyst surface is a complex anodic reaction, which involves generation of numerous, surface-adsorbed reaction intermediates. It is widely accepted [1-3] that following the surface electrosorption step, ethanol molecule can either dissociate to surface-adsorbed CO_{ads} species or else it could become oxidized to form acetaldehyde. Then, in the presence of adsorbed OH, consecutive oxidation steps lead to the formation of CO₂ or acetic acid, following their desorption from the catalyst surface.

Platinum, due to its outstanding properties, makes one of the most widely used catalyst material in electrochemistry. Therefore, Pt [3-6] and Pt-based materials (e.g. PtRu [1, 7], PtRh [1, 2], PtSn [1, 6, 8-11] and PtPd [12]) have extensively been examined towards their electrochemical behaviour for ethanol oxidation (especially with respect to their application in direct ethanol fuel cells: DEFCs). Nevertheless, Pt-based bulk materials are extremely expensive; thus, development of efficient and price-competitive anode electrocatalyst materials for DEFC systems is of significant importance from both the technical and scientific points of view.

This work constitutes an electrochemical study of the process of ethanol oxidation on Pd-modified carbon fibre (CF) catalyst material, studied in 0.5 M H₂SO₄ and 0.1 M NaOH solutions. Carbon fibre could possibly offer attractive, large surface-area catalyst materials, suitable to a number of electrochemical applications. This is because properties of CF (including its electrochemically active surface area) could extensively be modified, e.g. during CF surface pre-treatment, as well as catalyst (electro)deposition processes.

Electrooxidation of ethanol on Pd-based catalysts was studied in the past, especially by means of cyclic voltammetry technique for Pd bulk [13-15], as well as Pd-nanoparticle [16-18] electrodes. Interestingly, palladium was found to exhibit very high catalytic activity towards ethanol oxidation reaction in alkaline media [13-18], while it was practically inactive in acidic solutions [15, 17]. However, the latter finding was principally concluded through comparative, i.e. carried-out in the absence of ethanol, CV experiments.

2. EXPERIMENTAL

2.1. Solutions and solutes

High-purity acidic and alkaline solutions were prepared from water delivered by an 18.2 M Ω Direct-Q3 UV ultra-pure water purification system from Millipore. Aqueous 0.5 M H₂SO₄ solution was made up from sulphuric acid of highest purity available (SEASTAR Chemicals, BC, Canada). Also, 0.1 M NaOH electrolyte was prepared from AESAR, 99.996 % NaOH pellets. Ethanol (Stanlab, pure, p.a., Poland) was used to prepare acidic and alkaline solutions, at a concentration of 1.0 M C₂H₅OH. Before conducting experiments, all solutions were de-aerated with high-purity argon (Ar 6.0 grade, Linde), the flow of which was also maintained above the solutions during the cyclic voltammetry and impedance spectroscopy measurements.

2.2. Electrochemical cell, reference and counter electrodes

An electrochemical cell, made of Pyrex glass, was used during the course of this work. The cell comprised three electrodes: a Pd-modified CF working electrode (WE), equipped with flexible adjustment (in a central part), a reversible Pd hydrogen electrode (RHE) as reference and a Pt counter electrode (CE), both in separate compartments. Prior to each series of experiments, the electrochemical cell was taken apart and soaked in hot sulphuric acid for at least 3 hours. After having been cooled to about 30 °C, the cell was thoroughly rinsed with Millipore ultra-pure water. An identical procedure was applied for cleaning all the glassware used to prepare supporting electrolytes.

The palladium hydrogen electrode, acting as a reversible hydrogen electrode (RHE) was used throughout this work. Hence, all the potentials are given on the RHE scale. The palladium RHE was made of a coiled Pd wire (0.5 mm diameter, 99.9 % purity, Aldrich) and sealed in soft glass. Before its use, this electrode was cleaned in hot sulphuric acid, followed by cathodic charging with hydrogen in 0.5 M H₂SO₄ (at current, I_c= 10 mA), until H₂ bubbles in the electrolyte were clearly observed. A

counter electrode was made of a coiled Pt wire (1.0 mm diameter, 99.9998 % purity, Johnson Matthey, Inc.). Prior to its use, the counter electrode was either cleaned in hot sulphuric acid or was flame-annealed.

2.3. Equipment and Pd-based CF catalyst material

Cyclic voltammograms were recorded at 293 K (room temperature), at a sweep-rate of 50 mV s⁻¹ by means of the *Solartron* 12,608 W Full Electrochemical System, consisting of 1260 frequency response analyzer (FRA) and 1287 electrochemical interface (EI). For a.c. impedance measurements (also carried-out at room temperature), the 1260 FRA generator provided an output signal of known amplitude (5 mV) and the frequency range was typically swept between 1.0x10⁵ and 0.5x10⁻¹ Hz. The instruments were controlled by *ZPlot 2.9* or *Corrware 2.9* software for Windows (Scribner Associates, Inc.). Presented here impedance results were obtained through selection and analysis of representative series of experimental data. Usually, three impedance measurements were conducted at each potential value. Reproducibility of such-obtained results was typically below 10 % from one measurement to another. The impedance data analysis was performed with *ZView 2.9* software package, where the spectra were fitted by means of a complex, non-linear, least-squares imittance fitting program, *LEVM 6*, written by Macdonald [19]. Two equivalent circuits employed for the analysis of the recorded impedance results would later be shown in Figs. 4a and 4b. Both circuits contain constant-phase elements (CPEs) in order to account for a distributed capacitance phenomenon.

Additionally, spectroscopic characterization of Pd-modified CF fibre composites was performed by means of Quanta FEG 250 scanning electron microscope (SEM).

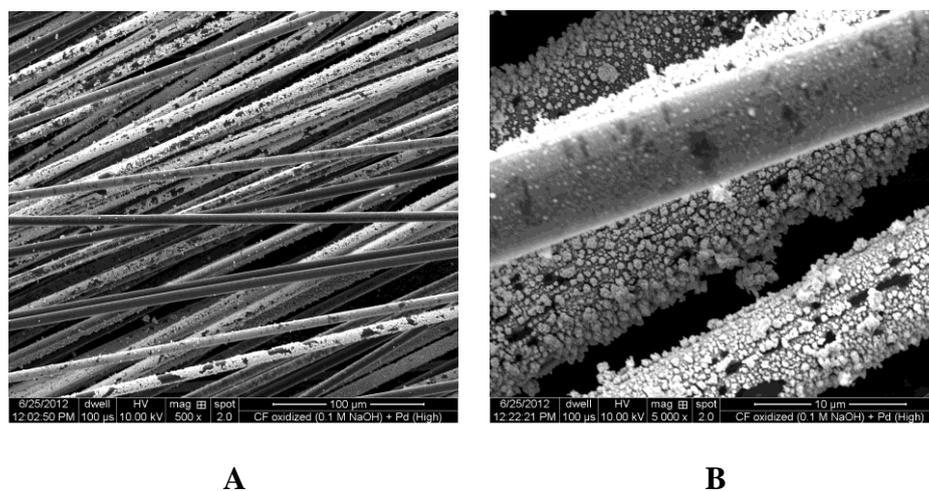


Figure 1. a) SEM micrograph picture of Pd-modified (*ca.* 50 wt.% Pd) CF-oxidized Hexcel 12K AS4C carbon fibre tow sample, taken at 500 magnification. b) As in (a), but taken at 5,000 magnification.

Hexcel 12K (12,000 single filaments of 7 μm diameter each) AS4 (PAN: polyacrylonitrile based) carbon fibre tow product [20] was employed as a base catalyst material. The Hexcel fibre tow is

typically sized by the manufacturer with an epoxy resin (0.21 wt. % on average), in order to ease fibre handling and thus to reduce damage to the material. Hence, initially, this organic sizing was removed from the fibre samples by applying heat-treatment, carried-out in a muffle furnace at low oxygen atmosphere (with fibre residence time of 4 hours at 350 °C). Then, CF tow samples were subjected to electrooxidation treatment, carried-out in 0.1 M NaOH solution, at an anodic current-density of 0.2 mA cm⁻² for 300 s. Electrodeposition of Pd on CF tow electrodes was performed from PdCl₂ (2 g dm⁻³) solution of pH 1.5, at a cathodic current-density of 5.0 mA cm⁻² in order to produce *ca.* 50 wt.% Pd loadings (see SEM micrograph pictures in Figs. 1a and 1b above).

3. RESULTS AND DISCUSSION

3.1. Electrooxidation of ethanol on Pd-modified CF catalyst in 0.5 M H₂SO₄

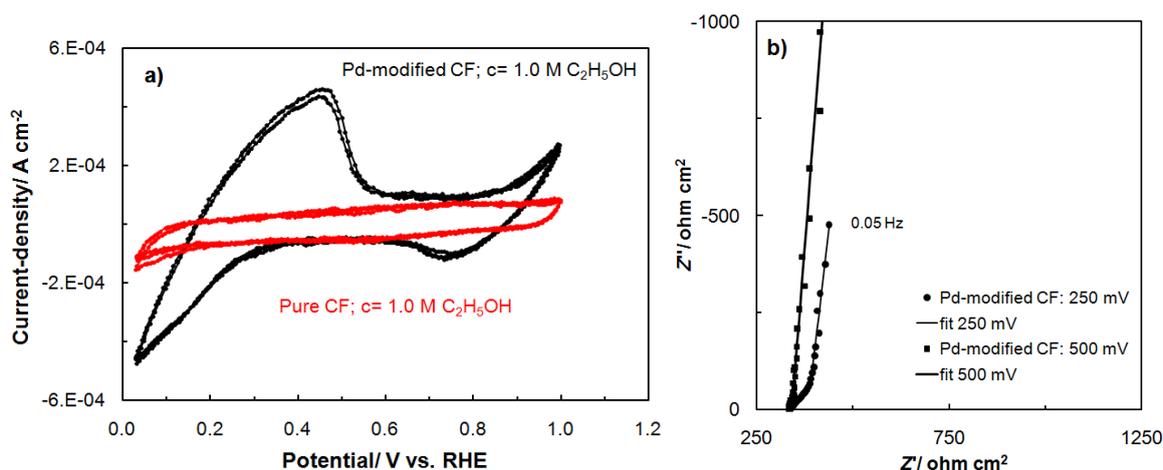


Figure 2. a) Cyclic voltammograms for Pd-modified and pure Hexcel 12K CF tow materials, carried-out in 0.5 M H₂SO₄, at a sweep-rate of 50 mV s⁻¹ and in the presence of 1.0 M C₂H₅OH (three consecutive cycles were recorded for each CV run). b) Complex-plane impedance plots for Pd-modified CF electrode in contact with 0.5 M H₂SO₄, in the presence of 1.0 M C₂H₅OH, recorded at 250 and 500 mV vs. RHE (at 293 K). For the plot recorded at 250 mV, a solid line corresponds to representation of the data according to the equivalent circuit shown in Fig. 4a.

The cyclic voltammetric behaviour of the process of electrooxidation of ethanol (at 1.0 M C₂H₅OH) on Pd-modified (at *ca.* 50 wt. % Pd) carbon fibre electrode surface in 0.5 M H₂SO₄ is shown in Fig. 2a above. Thus, two oxidation regions can clearly be observed in the voltammetric profile for the Pd-modified carbon fibre electrode. The first, broad anodic peak (centred at *ca.* 0.45 V/RHE) could most likely be attributed to oxidation of Pd-electrosorbed hydrogen from the catalyst surface, i.e. the so-called *underpotentially deposited hydrogen* (or UPD of H) [21-23]. Respectively, a reduction region that emerges over the potential range 0.30 to *ca.* 0.05 V (Fig. 2a) corresponds to reductive deposition of hydrogen on the Pd surface.

Another oxidation process commences on the CF/Pd surface, as the electrode potential approaches 1.0 V (see Fig. 2a again). The latter process most probably proceeds with active participation of surface-adsorbed, oxygen-like species (compare with the corresponding reductive peak centred at *ca.* 0.75 V). Please note however that the observed high-potential oxidation process is not associated with any degradative oxidation of the CF surface. The above can be supported by comparing the recorded cyclic voltammogram for the Pd-modified CF electrode with that obtained for pure, unmodified carbon fibre material in Fig. 2a.

Table 1. Resistance and capacitance parameters for the process of UPD of H on Pd-modified CF electrode in 0.5 M H₂SO₄ (recorded at 293 K in the presence of 1.0 M C₂H₅OH), obtained by finding the equivalent circuit which best fitted the impedance data, as shown in Fig. 4a.

E/ mV	R _H / Ω cm ²	×10 ⁶ C _{pH} / F cm ⁻² s ^{φ¹-1}	×10 ⁶ C _{dl} / F cm ⁻² s ^{φ²-1}
200	41.1 ± 4.6	4,586 ± 649	1,146 ± 137
250	103.9 ± 8.1	3,889 ± 377	1,106 ± 105
300	202.2 ± 17.2	2,035 ± 218	1,390 ± 103
350	6,841 ± 1,026	123.2 ± 14.4	1,595 ± 60

The a.c. impedance behaviour of the Pd-modified CF electrode surface in 0.5 M H₂SO₄ (recorded in the presence of 1.0 M C₂H₅OH) is presented in Table 1 and in Fig. 2b above. Hence, the recorded Nyquist impedance spectra exhibit a single partial, distorted semicircle and a capacitive line, at an inclination to the Z' axis different from 90°, over the potential range: 200-350 mV (see an example of the behaviour at 250 mV in Fig. 2b). This partial semicircle clearly corresponds to the process of UPD of H at Pd (refer to Fig. 2a). The recorded minimum value of the charge-transfer resistance parameter (R_H) for the process of UPD of H comes to 41.1 Ω cm² at 200 mV, which then dramatically rises to reach the value of 6,841 Ω cm² at 350 mV (see Table 1). These values of the R_H parameter are dramatically increased (*ca.* 2-3 orders in magnitude), as compared to those previously reported in literature for Pt-bulk single-crystal planes in 0.5 M H₂SO₄ [22, 23]. Please note however that all calculations for the Pd-modified fibre catalyst refer to geometrical surface area of unmodified CF electrode, whereas electrochemically active surface (available for the process of UPD of H) covers only that part of the metallic Pd deposit, which is apparently unknown. Nevertheless, some interference from adsorption of ethanol molecules over the potential range for UPD of H can be observed. Thus, in the absence of ethanol, the recorded charge-transfer resistance value at 300 mV came to 77.0 Ω cm², which translates to *ca.* 2.6× slower kinetics of UPD of H (at this potential) in the presence of alcohol in solution. Furthermore, the recorded values of adsorption pseudocapacitance (C_{pH}) parameter: 4,586 and 123.2 μF cm⁻² s^{φ¹-1} at 200, and 350 mV, respectively follow the reported changes of the R_H parameter.

On the other hand, the recorded in Table 1 double-layer capacitance values (C_{dl}) showed significant fluctuation (from 1,106 to 1,595 $\mu\text{F cm}^{-2} \text{ s}^{\varphi_2-1}$). Dramatically increased C_{dl} (55-80 \times above that commonly used value of 20 $\mu\text{F cm}^{-2}$ in literature for smooth and homogeneous surfaces [24, 25]) is a consequence of extensive surface electrooxidation pre-treatment applied to carbon fibre (e.g. refer to Ref. 26 for details), as well as electrodeposition of palladium, carried-out on such pre-treated carbon fibre material.

Furthermore, a deviation from the purely capacitive behaviour (which demanded the use of the CPE components in the equivalent circuits, see later Figs. 4a and 4b) corresponds to distribution of capacitance. The above is the characteristic behaviour of irregular and porous electrode geometry, such as that of a complex 12K CF tow electrode [24-27]. In this work, values of dimensionless parameters φ_1 and φ_2 (for the CPE components) oscillated between 0.79 and 0.97. Please note that $0 \leq \varphi \leq 1$ and when $\varphi=1$, the CPE acts just like a pure capacitor.

Then, for potentials beyond 350 mV, the impedance behaviour is characterized by a vertical, capacitive line with some dispersion of C (see an example recorded at 500 mV in Fig. 2b). Absence of any ongoing surface Faradaic process for the potential range: 400-600 mV gives kinetic evidence that ethanol does not undergo electrooxidation on Pd in sulphuric acid solution.

3.2. Electrooxidation of ethanol on Pd-modified CF catalyst in 0.1 M NaOH

On the other hand, electrooxidation of ethanol on the CF/Pd electrode surface in 0.1 M NaOH is characterized (see Fig. 3a) by the presence of a single, broad oxidation peak (centred at *ca.* 0.35 V/RHE), which then follows with a continuous increase of the recorded anodic current-density, already beyond the potential of about 0.55 V.

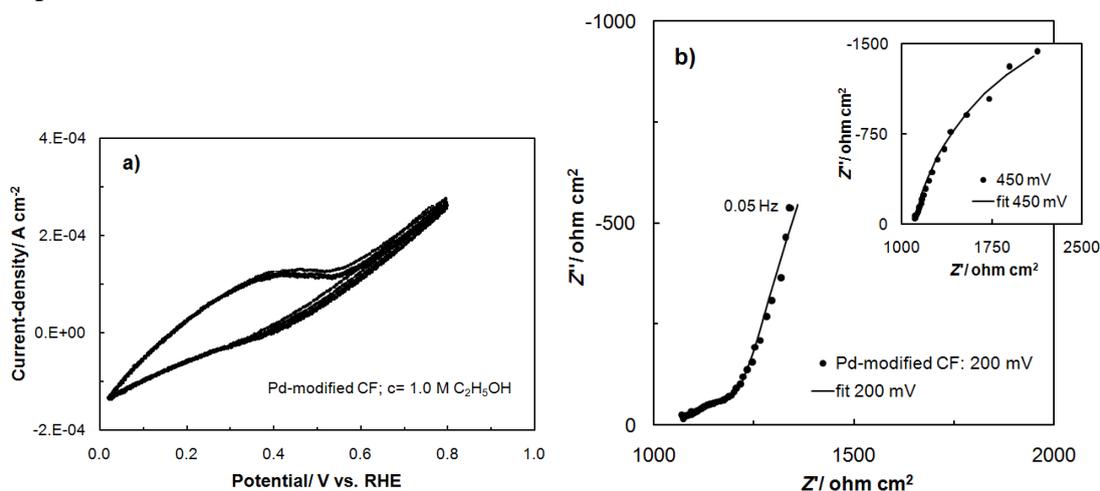


Figure 3. a) Cyclic voltammograms for ethanol electrooxidation on Pd-modified Hexcel 12K CF tow material, carried-out in 0.1 M NaOH, at a sweep-rate of 50 mV s^{-1} and in the presence of 1.0 M $\text{C}_2\text{H}_5\text{OH}$ (three consecutive cycles were recorded). b) Complex-plane impedance plots for Pd-modified CF electrode in contact with 0.1 M NaOH, in the presence of 1.0 M $\text{C}_2\text{H}_5\text{OH}$, recorded at 200 and 450 mV (inset) vs. RHE (at 293 K). Solid lines correspond to representation of the data according to the equivalent circuits shown in Figs. 4a (200 mV) and 4b (450 mV).

Table 2. Resistance and capacitance parameters for the process of UPD of H and electrooxidation of ethanol on Pd-modified CF electrode in 0.1 M NaOH (recorded at 293 K in the presence of 1.0 M C₂H₅OH), obtained by finding the equivalent circuits which best fitted the impedance data, as shown in Figs. 4a^a and 4b^b.

E/ mV	R _H / Ω cm ²	×10 ⁶ C _{pH} / F cm ⁻² s ^{φ¹-1}	×10 ⁶ C _{dl} / F cm ⁻² s ^{φ²-1}	R _{ct} / Ω cm ²
200 ^a	208.6 ± 13.9	3,558 ± 238	853.6 ± 86.9	-----
250 ^a	310.6 ± 33.3	2,035 ± 250	888.9 ± 92.9	-----
300 ^a	778.9 ± 92.3	604.2 ± 45.3	1,045 ± 76	-----
400 ^b	-----	-----	906.5 ± 9.5	6,084 ± 371
450 ^b	-----	-----	890.2 ± 7.8	4,040 ± 137
500 ^b	-----	-----	856.3 ± 12.0	2,228 ± 93
600 ^b	-----	-----	1,016 ± 26	1,250 ± 84

The impedance behaviour of ethanol oxidation reaction (at 1.0 M C₂H₅OH) on the Pd-modified CF electrode surface in 0.1 M NaOH solution is shown in Table 2 and in Fig. 3b. Thus, for the potential range: 200-300 mV, the recorded Nyquist impedance spectra exhibit a single partial, somewhat distorted semicircle and a capacitive line, at an inclination to the Z' axis different from 90° (see an example of the behaviour at 200 mV in Fig. 3b). This semicircle corresponds to the process of UPD of H at Pd (also refer to Fig. 3a). The recorded minimum value of the charge-transfer resistance parameter (R_H) for the process of UPD of H comes to 208.6 Ω cm² at 200 mV, which then dramatically increases to reach the value of 778.9 Ω cm² at 300 mV (see Table 2). Again, the recorded values of adsorption pseudocapacitance (C_{pH}) parameter: 3,558 and 604.2 μF cm⁻² s^{φ¹-1} at 200, and 300 mV, correspondingly follow the reported changes of the R_H parameter. Moreover, it should be noted that the kinetics of UPD of H in alkaline medium are significantly slower than those recorded above for acidic electrolyte (compare the respective R_H parameter values in Table 2 with those reported in Table 1).

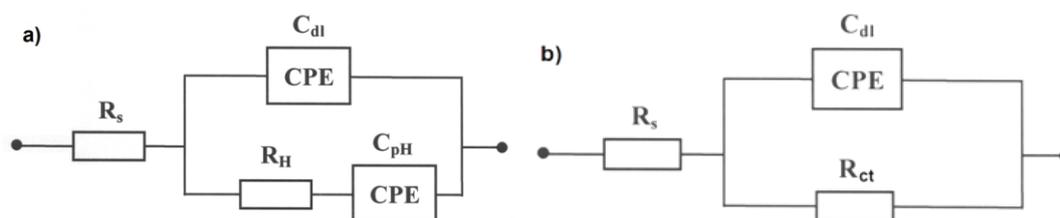


Figure 4. Two equivalent circuits, used for fitting the obtained a.c. impedance spectroscopy data in this work, where: R_s is solution resistance, C_{dl} is double-layer capacitance, R_H and C_{pH} are resistance and pseudocapacitance parameters for the process of UPD of H, R_{ct} is charge-transfer resistance parameter for electrooxidation of ethanol. The circuits include two constant phase elements (CPEs) to account for distributed capacitance.

Then, for the potential range: 400-600 mV, the impedance behaviour is characterized by the presence of a single, large-diameter partial semicircle in the Nyquist plot (see an example recorded at 450 mV in inset to Fig. 3b). The corresponding charge-transfer resistance: R_{ct} parameter reported in Table 2 is associated with the process of ethanol oxidation on the CF/Pd electrode surface. Minimum of the R_{ct} parameter ($1,250 \Omega \text{ cm}^2$) was recorded at 600 mV, a potential value which matches a rapid increase of the anodic current-density in Fig. 3a (compare the reported R_{ct} values in Table 2 with those produced for ethanol oxidation on bulk Pt electrode, carried-out in 0.1 M NaOH solution in Ref. 28). Additionally, the recorded here rates of ethanol oxidation in NaOH were considerably slower than those derived for UPD of H in this medium (compare the reported values of the R_{ct} with those of the R_H parameter in Table 2).

Furthermore, the C_{dl} parameter exhibited (again) significant fluctuation (from about 850 to *ca.* 1,050 $\mu\text{F cm}^{-2} \text{ s}^{\varphi_2-1}$). As for the results obtained in sulphuric acid, the recorded C_{dl} values in alkaline solution are radically (*ca.* 40-50 \times) increased beyond that generally expected C_{dl} value for smooth/homogeneous surfaces (Table 2). In addition, values of dimensionless parameters φ_1 and φ_2 oscillated between 0.70 and 0.89.

4. CONCLUSIONS

The kinetic results obtained through application of a.c. impedance spectroscopy showed that Pd (employed as a composite: carbon fibre/Pd catalyst) exhibited no catalytic activity towards ethanol oxidation in acidic medium. On the contrary, palladium employed in a composite form, proved to be a valuable electrocatalyst for ethanol oxidation reaction in alkaline solution (0.1 M NaOH supporting electrolyte).

The presence of ethanol molecules on the surface of CF/Pd catalyst material significantly affects the rates for UPD of H, as compared to those obtained in the absence of ethanol in the supporting electrolyte. The rates of UPD of H in 0.1 M NaOH are considerably faster than those of ethanol oxidation reaction in this medium.

ACKNOWLEDGEMENTS

This work has been financed by the strategic program of the National (Polish) Centre for Research and Development (NCBiR): „Advanced Technologies for Energy Generation. Task 4: Elaboration of Integrated Technologies for the Production of Fuels and Energy from Biomass, Agricultural Waste and other Waste Materials”.

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