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Hydrogen Evolution Reaction at Ru-modified Carbon Fibre in 0.5 M H_2SO_4

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Present study covers a.c. impedance investigations of hydrogen evolution reaction (HER), carried-out on carbon fibre (CF) and Ru-modified CF tow materials. The HER was examined in 0.5 M H_2SO_4 solution for surface-activated CF and electrochemically deposited Ru on Hexcel 12K CF tow materials. Kinetics of the hydrogen evolution reaction were studied at room temperature, over the cathodic overpotential range: -100 to -800 mV vs. RHE. Corresponding values of the charge-transfer resistance, the exchange current-density for the HER and other electrochemical parameters for examined catalyst materials were recorded.

Keywords: carbon fibre; CF; Ru-modified CF; HER; impedance spectroscopy

1. INTRODUCTION

Cathodic evolution of hydrogen is one of the most important electrochemical processes, especially from the perspective of growing H importance for the world's economy [1]. Hydrogen evolution reaction (HER) has extensively been studied on noble metal catalysts, especially such as polycrystalline and single-crystal surfaces of Pt [2-6], as well as on numerous other metals and their alloys, for example on Ru [7-10], Co [11], Pb [12], Zn-Ni [13], Ni-P [14,15] and Ni-Mo [16]. Recently, nanostructured-type materials, such as carbon felt and glassy carbon have attracted major attention as catalyst supports, due to their outstanding physical and chemical properties [17-20].

The hydrogen evolution reaction leads to the generation of bulk H_2 species and proceeds at potentials negative to the H_2 reversible potential. The HER mechanism at metal (Me) electrode is based on a 2-step reaction that involves an adsorbed H intermediate, as shown for acidic media below [2]:

1. $H_3O^+ + e^- + Me \rightarrow MeH_{ads} + H_2O$ (*Volmer electrochemical discharge step*)
2. $MeH_{ads} + H_3O^+ + e^- \rightarrow H_2\uparrow + H_2O + Me$ (*Heyrovsky electrochemical desorption step*)

2'. $2MeH_{ads} \rightarrow H_2\uparrow + 2Me$ (*Tafel catalytic recombination step*)

Present work focuses on the impedance (kinetic) study of the HER, which is performed on carbon fibre (CF) and Ru-modified, 12,000-filament (12K) Hexcel AS4C CF tow electrodes in 0.5 M H_2SO_4 supporting electrolyte. It is a continuation of some earlier works published from this laboratory on the kinetic aspects of the hydrogen evolution reaction, studied on various carbon fibre and nickel-coated carbon fibre materials [21, 22].

2. EXPERIMENTAL

2.1. Solutions and chemical reagents

All solutions were made up using a Direct-Q3 UV ultra-pure water purification system from Millipore. This system gives a final H_2O product of 18.2 MΩ cm resistivity. Aqueous, 0.5 M H_2SO_4 solution was prepared from sulphuric acid of highest purity available (SEASTAR Chemicals, BC, Canada). Before each impedance experiment, atmospheric oxygen was removed from solution by bubbling with high-purity argon (Ar 6.0 grade, Linde). In addition, 0.1 M NaOH solution was prepared from AESAR, 99.996 % NaOH pellets in order to conduct oxidation pre-treatments to carbon fibre tow electrodes.

2.2. Electrochemical cell, electrodes and experimental methodology

During the course of this work an electrochemical cell (made of Pyrex glass) was used. The cell comprised three electrodes: a CF-based working electrode (WE) in a central part, a reversible Pd hydrogen electrode (RHE) as reference and a Pt counter electrode (CE), both placed in separate compartments. In this study, both heat-treated (for 4 hours at 330 ^oC, carried-out in a muffle furnace in order to remove organic sizing from the fibre), as well as electrochemically oxidized (in 0.1 M NaOH solution, at an anodic current-density of 0.3 mA cm^{-2} for 300 s) CF tow electrodes were employed. On the other hand, electrodeposition of Ru on CF tow samples was performed from $RuCl_3$ solution (10 g dm^{-3} and pH of 1.5), at a current-density of 0.2 mA cm^{-2} (on both types of the CF material) to produce catalyst deposits at below 1 wt.% Ru.

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 H_2SO_4, until H_2 bubbles in the electrolyte were clearly observed. The stability of the Pd reference electrode was occasionally checked by recording its potential shift in time. No significant potential shift was observed for such-prepared Pd reversible hydrogen electrode, up to 72 hours from its initial H charging. Therefore, all the potentials throughout this work are given on the RHE scale. 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 cleaned in hot sulphuric acid. In the same way, before each series of experiments, the electrochemical cell was taken apart and soaked in hot sulphuric acid for at least 2 hours. After having been cooled to about 40 ^{o}C, the cell was thoroughly rinsed with Millipore ultra-pure water.

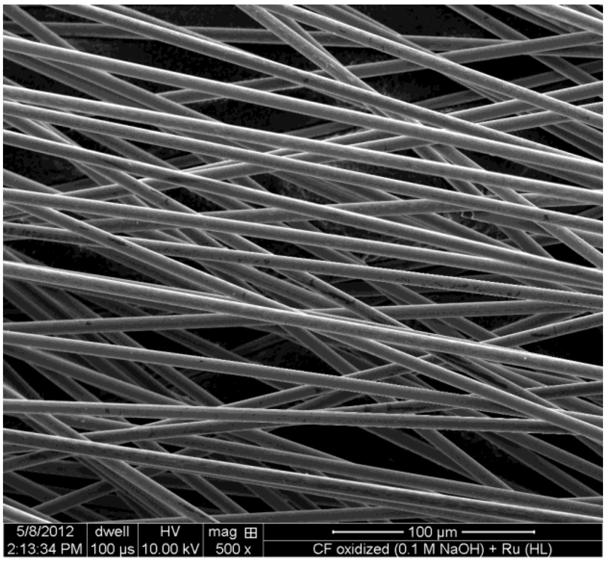
A.c. impedance spectroscopy was used during the course of this work. All measurements were conducted by means of the *Solartron* 12608W Full Electrochemical System, consisting of 1260 frequency response analyzer (FRA) and 1287 electrochemical interface (EI). For impedance measurements, the generator provided an output signal of known amplitude (5 mV) and the frequency range was typically swept between 1.0×10^{5} and 0.5×10^{-1} Hz. The instruments were controlled by *ZPlot 2.9* software for Windows (Scribner Associates, Inc.). Presented impedance results were obtained through selection and analysis of representative series of experimental data. Usually, three impedance measurements were carried-out at each potential value, independently at several catalyst electrodes. Reproducibility of such-obtained results was typically below 10 % from tow-to-tow. Data analysis was performed with *ZView 2.9* software package, where the impedance spectra were fitted by means of a complex, non-linear, least-squares immitance fitting program, *LEVM 6*, written by J.R. Macdonald [23].

In addition, spectroscopic characterization of Ru-modified CF tow electrodes was performed by means of Quanta FEG 250 scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1. SEM characterization of Ru-modified CF tow electrodes

A sample of Ru-modified (at *ca*. 40 wt.% Ru) Hexcel 12K CF (oxidized) tow is shown in SEM micrograph pictures of Figs. 1a and 1b. As can be observed in these micrographs, obtained metal deposit is quite regular and continuous throughout the CF tow.



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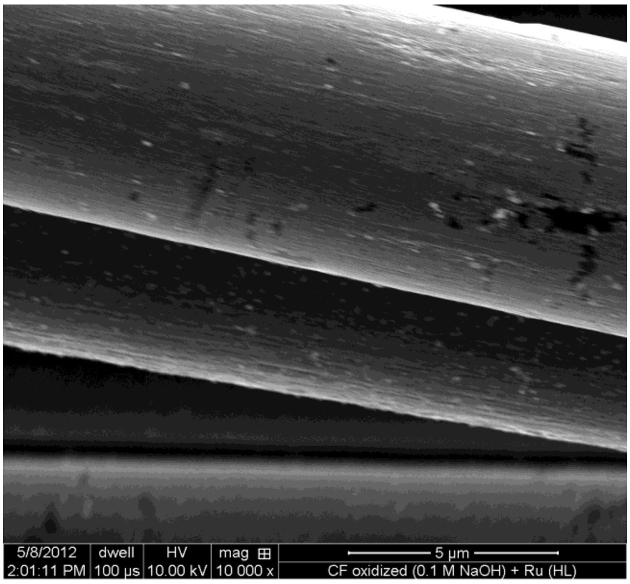

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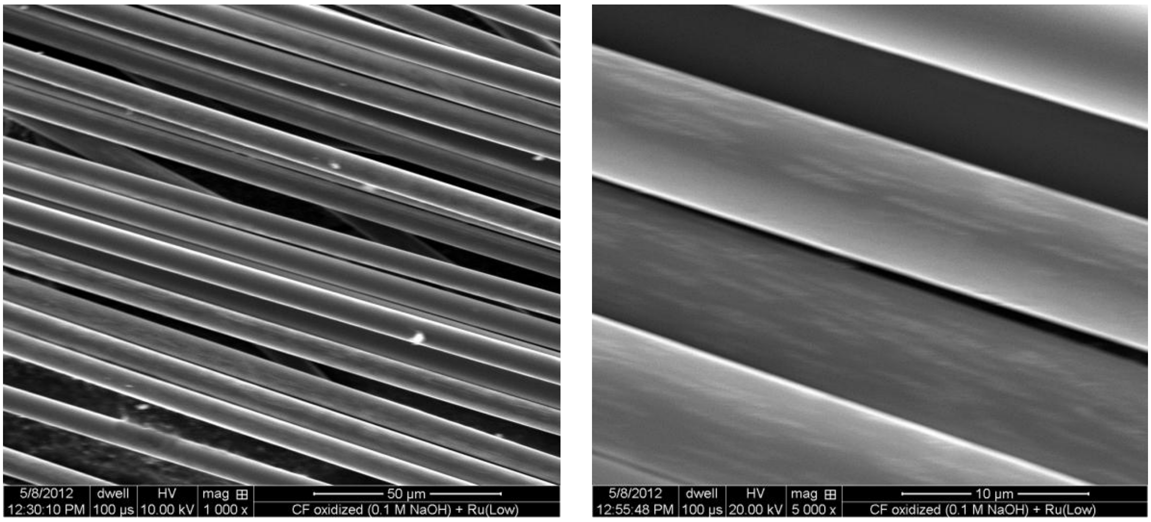
Figure 1. a) SEM micrograph picture of Ru-modified (*ca*. 40 wt.% Ru) Hexcel 12K AS4C CF-oxidized tow sample, taken at 500 magnification. b) As in (a), but taken at 10,000 magnification.



A B

Figure 2. a) SEM micrograph picture of Ru-modified (*ca*. 0.5 wt.% Ru) Hexcel 12K AS4C CF-oxidized tow sample, taken at 1,000 magnification. b) As in (a), but taken at 5,000 magnification.

For the HER experiments performed in this work, all Ru-modified CF tow electrodes contained only *ca*. 0.5 (± 0.1) wt.% Ru, where such-obtained catalyst deposits were practically undetectable on the carbon fibre tows (see the recorded SEM micrograph photos in Figs. 2a and 2b).

3.2. Hydrogen evolution reaction on heat-treated and oxidized CF tow electrodes in 0.5 M H_2SO_4

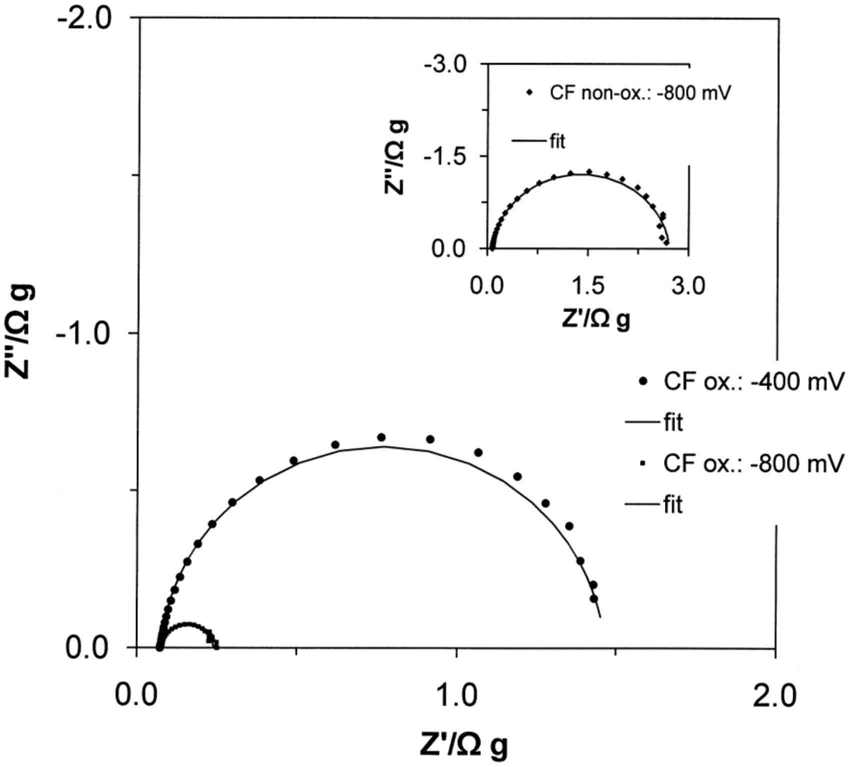


Figure 3. Complex-plane impedance plots for heat-treated (inset) and electrooxidized Hexcel 12K CF tow electrodes in contact with 0.5 M H_2SO_4, recorded at room temperature for the stated potential values (vs. RHE). The solid lines correspond to representation of the data according to the equivalent circuit shown in Fig. 4.

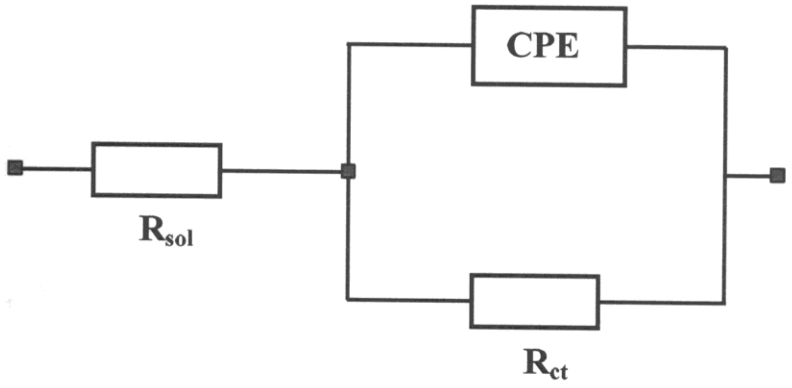


Figure 4. Equivalent circuit model used for fitting the impedance data for Hexcel 12K CF tow electrodes, obtained in 0.5 M H_2SO_4. The circuit includes a constant phase element (CPE) for distributed capacitance.

The a.c. impedance behaviour of the HER at heat-treated and electrooxidized Hexcel 12K carbon fibre tow electrodes in 0.5 M H_2SO_4 is presented in Fig. 3 and Table 1. Here, both fibre electrodes exhibited single and "depressed" semicircles (a single-step charge-transfer reaction) at all potentials, in the investigated frequency range (see examples of the recorded Nyquist impedance plots in Fig. 3).

Table 1. Electrochemical parameters for the HER, obtained at heat-treated and electrooxidized (in 0.1 M NaOH at j_a=0.3 mA cm^{-2}) Hexcel 12K CF tow electrodes, in contact with 0.5 M H_2SO_4. The results were obtained by fitting the CPE-modified Randles equivalent circuit (see Fig. 4) to the experimentally obtained impedance data (reproducibility usually below 10 %).

E/mV	R_{ct}/Ω g	C_{dl}/μF g^{-1}s$^{\varphi 1-1}$
Hexcel 12K CF$_{non\ ox.}$		
-100	191.14 ± 7.27	39,500 ± 138
-200	178.56 ± 6.53	39,700 ± 142
-400	147.10 ± 4.36	38,900 ± 140
-600	41.54 ± 0.39	36,600 ± 135
-800	2.64 ± 0.01	31,400 ± 345
Hexcel 12K CF$_{ox.}$		
-100	59.787 ± 1.477	95,926 ± 287
-200	46.587 ± 0.932	96,744 ± 290
-400	1.446 ± 0.010	84,602 ± 930
-600	0.283 ± 0.001	96,863 ± 1,307
-800	0.176 ± 0.001	111,068 ± 1,999

Furthermore, comparison of Faradaic reaction resistance (R_{ct}) and double-layer capacitance (C_{dl}) parameters for the HER at the heat-treated and oxidized CF tow electrodes (derived based on a constant phase element – CPE-modified Randles equivalent circuit model illustrated in Fig. 4) is shown in Table 1. The CPE element was used in the circuit in order to account for the capacitance dispersion effect [21, 22, 24, 25] (represented by distorted semicircles in the Nyquist plots).

For the basic (heat-treated) CF tow electrode, the recorded R_{ct} parameter becomes reduced from about 191 Ω g at -100 mV to reach 2.6 Ω g at the potential of -800 mV vs. RHE. Then, modification of the CF electrode by surface electrooxidation caused significant reduction of the charge-transfer resistance parameter by *ca*. 3.2 times at -100 mV and by 15 times at the overpotential of -800 mV (see Table 1 for details). Furthermore, the double-layer capacitance parameter for the heat-treated CF tow electrode somewhat diminished from 39,500 μF g^{-1} s$^{\varphi 1-1}$ at -100 mV to 31,400 μF g^{-1} s$^{\varphi 1-1}$ at -800 mV. The above is most likely a result of partial blocking of electrochemically active electrode surface by freshly formed hydrogen bubbles (easily envisaged for a complex 12K tow fibre electrode). In contrast, considerably increased C_{dl} parameter values were recorded for the electrooxidized CF electrode (95,926 and 111,068 μF g^{-1} s$^{\varphi 1-1}$ at -100 and -800 mV, respectively). The above strictly reflects a considerable increase of the electrochemically active surface area, achieved upon an electrooxidation treatment. At the same time, the dimensionless φ_1 parameter (φ determines the constant phase angle in the complex-plane plot and $0 \le \varphi \le 1$) of the CPE circuit (Fig. 4) varied between 0.77 and 0.95 (as similarly observed for both Ru-modified CF tow electrodes, see symbol φ_2 in Table 2).

Table 2. Electrochemical parameters for the HER, obtained at Ru-modified, heat-treated and electrooxidized (in 0.1 M NaOH at j_a=0.3 mA cm^{-2}) Hexcel 12K CF tow electrodes, in contact with 0.5 M H_2SO_4. The results were obtained by fitting the CPE-modified Randles equivalent circuit (see Fig. 4) to the experimentally obtained impedance data (reproducibility usually below 10 %).

E/mV	R_{ct}/Ω g	C_{dl}/μF $g^{-1}s^{\varphi2-1}$
Ru-modified Hexcel 12K $CF_{non-ox.}$		
-100	87.39 ± 1.55	41,881 ± 139
-200	58.03 ± 0.86	42,005 ± 168
-400	9.65 ± 0.05	39,541 ± 219
-500	4.70 ± 0.02	37,383 ± 190
-600	2.75 ± 0.01	35,957 ± 288
-800	0.73 ± 0.00	28,040 ± 785
Ru-modified Hexcel 12K $CF_{ox.}$		
-100	6.320 ± 0.040	124,508 ± 547
-200	0.747 ± 0.003	115,299 ± 1,325
-400	0.086 ± 0.000	162,384 ± 5,845
-500	0.048 ± 0.000	188,033 ± 6,957
-600	0.046 ± 0.000	153,542 ± 11,669
-800	0.018 ± 0.000	323,954 ± 17,490

3.3. Hydrogen evolution reaction on Ru-modified, heat-treated and electrooxidized CF tow electrodes in 0.5 M H_2SO_4

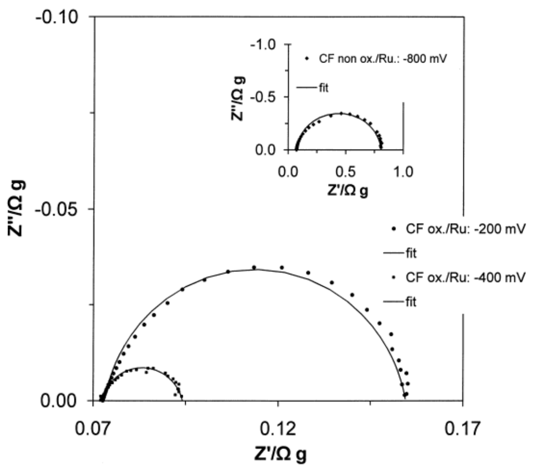


Figure 5. Complex-plane impedance plots for Ru-modified, heat-treated (inset) and electrooxidized Hexcel 12K CF tow electrodes in contact with 0.5 M H_2SO_4, recorded at room temperature for the stated potential values (vs. RHE). The solid lines correspond to representation of the data according to the equivalent circuit shown in Fig. 4.

The impedance characterization of the HER at Ru-modified (heat-treated and electrochemically oxidized) CF tow materials (at *ca*. 0.5 wt.% Ru) in 0.5 M H_2SO_4 is presented in Fig. 5 and Table 2. Again, both Ru-modified CF electrodes exhibited somewhat distorted semicircles in the Nyquist impedance plots (see examples in Fig. 5).

As a consequence of the catalyst electrodeposition, the heat-treated (non-oxidized) $CF_{non\text{-}ox.}$/Ru electrode exhibited significantly reduced values of the R_{ct} parameter; namely, 2.2 and 3.6 times at -100, and -800 mV, respectively, as compared to those of the heat-treated CF tow electrode (see Tables 1 and 2 for detail). Furthermore, when the electrooxidized carbon fibre is modified with ruthenium, the recorded ratios of the R_{ct} parameter ($CF_{ox.}$ vs. $CF_{ox.}$/Ru) come to about 9.4 and 9.8 at -100, and -800 mV vs. RHE, correspondingly. Then, significance of the employed oxidation treatment can conveniently be rationalized through comparison of the calculated R_{ct} ratios for the Ru-modified, heat-treated and electrooxidized CF tow electrodes, which amount to about 13.8 and 40.5 at -100, and -800 mV, respectively (Table 2).

In addition, the double-layer capacitance parameter for Ru-modified, heat-treated CF electrode becomes reduced from 41,881 $\mu F\ g^{-1}\ s^{\varphi 2-1}$ at the overpotential of -100 mV to reach 28,040 $\mu F\ g^{-1}\ s^{\varphi 2-1}$ at -800 mV (compare with the C_{dl} values recorded for the heat-treated CF electrode in Table 1). On the contrary, at the oxidized $CF_{ox.}$/Ru composite electrode, a significant increase of the double-layer capacitance was observed, where the C_{dl} ranged from 124,508 $\mu F\ g^{-1}\ s^{\varphi 2-1}$ at -100 mV to 323,954 $\mu F\ g^{-1}\ s^{\varphi 2-1}$ at -800 mV.

With respect to geometrical surface area, the recorded at -100 mV C_{dl} values account for *ca.* 12.9 and 38.5 $\mu F\ cm^{-2}\ s^{\varphi 2-1}$ for the $CF_{non\text{-}ox.}$/Ru, and $CF_{ox.}$/Ru electrodes, correspondingly (compare with an average double-layer capacitance of 20 $\mu F\ cm^{-2}$ for a smooth and homogeneous metal surface [26]). Such low C_{dl} values recorded for the heat-treated $CF_{non\text{-}ox.}$/Ru electrode could imply incomplete removal of polymeric sizing (typically present in the amount of 0.2 wt.% for “as received” Hexcel CF material) from the surface of CF filaments upon the conducted heat-treatment (also compare with the recorded low values of the C_{dl} parameter for pure, heat-treated CF tow electrode in Table 1). On the other hand, superior electrocatalytic activity of Ru towards the HER could be validated by eliminating/compensating the effect of CF surface roughness. Thus, for the $CF_{ox.}$ vs. $CF_{ox.}$/Ru electrode pair, the R_{ct} ratio (for -100 mV) comes to 9.4 for the corresponding surface area ratio of 0.77 (calculated based on the recorded values of the C_{dl} parameter at this overpotential).

Moreover, a plot of –log R_{ct} vs. overpotential (see Fig. 6 below) shows a fairly good linear dependence for the three examined CF tow electrodes, over the studied overpotential range (agreement with the kinetically-controlled process [27-30] that proceeds via the Volmer-Heyrovski route: equations 1 and 2 above). The exchange current-densities for the HER in Fig. 6 were calculated based on the well-known Butler-Volmer equation and through utilization of the relation between the exchange current-density (j_0) and the R_{ct} parameter for $\eta \rightarrow 0$ (equation 3 below):

$$j_0 = \frac{RT}{zFR_{ct}} \qquad 3.$$

Thus, the highest value of the exchange current-density (j_0= 3.0x10^{-6} A cm^{-2}) was exhibited by the Ru-modified, electrooxidized CF tow electrode, whereas dramatically reduced (by *ca*. 2 orders in magnitude, see Fig. 6) and comparable values of j_0 were recorded for the heat-treated and Ru-modified heat-treated CF materials.

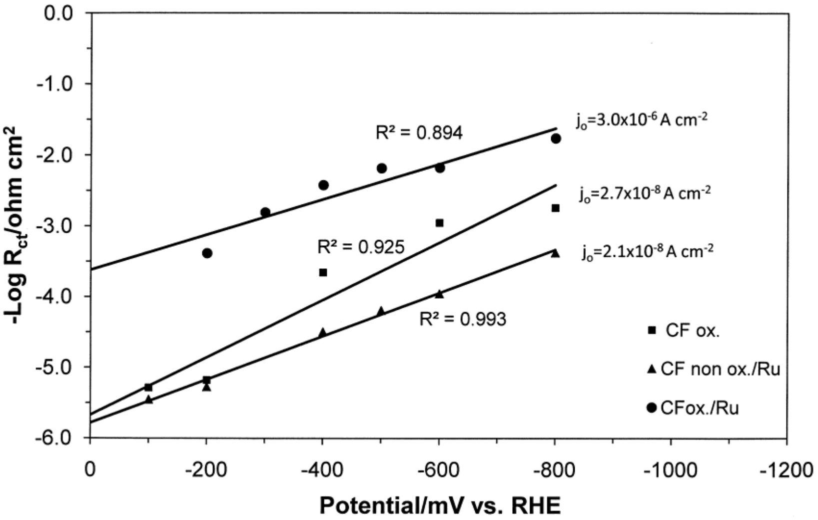


Figure 6. –log R_{ct} vs. overpotential relationship, obtained for the HER in 0.5 M H_2SO_4 solution, for the stated Hexcel 12K CF tow electrodes. Symbols stand for experimental results and lines are data fits.

In other words, catalytic properties of ruthenium, electrodeposited at nearly a trace amount on the CF tow material, can only be revealed on properly functionalized and roughened surface of carbon fibre filaments (achieved via electrochemical oxidation treatments).

4. CONCLUSIONS

a) Electrodeposition of ruthenium at nearly a trace amount (*ca*. 0.5 wt.% Ru) on electrooxidized surface of 12,000-filament carbon fibre tow electrode dramatically enhanced catalytic activity of the CF base material towards cathodic evolution of hydrogen.

b) Surface oxidation treatment proves to play a key role in enhancing catalytic activity of a metal catalyst.

c) Electrochemical oxidation makes a very convenient way not only to activate the CF tow's entity (via its surface functionalization), but also to remove any organic residue, such as incompletely stripped off sizing or other surface contaminants.

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