Int. J. Electrochem. Sci., 8 **(2013)** 11823 - 11831

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Influence of Electrochemical Oxidation of Carbon Fibre on Cathodic Evolution of Hydrogen at Ru-Modified Carbon Fibre Material Studied in 0.1 M NaOH

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Received: 9 July 2013 / *Accepted:* 17 August 2013 / *Published:* 10 September 2013

In this study, the influence of electrochemical oxidation treatments of carbon fibre (CF) tow material on the kinetics of hydrogen evolution reaction (HER) at Ru-modified CF catalysts was investigated. Examinations were performed on electrochemically pretreated CF, as well as on Ru-deposited carbon fibre tow materials. Kinetics of the hydrogen evolution reaction were investigated at room temperature in 0.1 M NaOH solution, over the cathodic overpotential range: -100 to -1000 mV vs. RHE. Corresponding values of charge-transfer resistance, exchange current-density for the HER and other electrochemical parameters for the examined catalyst materials were recorded.

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

1. INTRODUCTION

Carbon fibre (CF) materials have been used for many years by various industries, especially being utilized by general engineering, chemistry, computer and telecommunication markets. In fact, CFs are often applied as reinforcing materials during the production process of motor vehicles, boats, ships, bicycle frames, etc. Extensive industrial application of carbon fibre materials results from their unique chemical and physical properties, namely: high thermal and electrical conductivities, strong resistance to chemicals and superior mechanical properties. In addition, for CF-based composite materials, carbon fibre filler could significantly suppress mechanical vibrations, as well as electromagnetic interference phenomena that these materials are susceptible to [1-8]. At the same time, some of the CF materials allow to make effective catalysts for electrochemical processes with highly modifiable active surfaces. Here, 12K carbon fibre ribbon (12,000 individual filaments with a diameter of 7 microns each) has a geometrical area of about 26 cm^2 per 1 cm long ribbon. Specific catalytic properties of the CF tow material could significantly be improved through the application of electrochemical oxidation treatments, in addition to surface electrodeposition of small amounts of noble metals.

Present work is a continuation of some earlier papers published from this laboratory on the kinetic aspects of the hydrogen evolution reaction, studied on various carbon fibre and nickel-coated carbon fibre materials [9-12]. This study focuses on a.c. impedance evaluation of the HER, performed on a number of pure CF and Ru-modified CF tow electrodes, examined in 0.1 M NaOH supporting electrolyte.

2. EXPERIMENTAL

2.1. Materials and sample preparation

Hexcel 12K AS4C carbon fibre tow was used to prepare electrodes in this work. All supporting electrolytes were prepared by means of a Direct-Q3 UV ultra-pure water purification system from Millipore. 0.1 M NaOH solution was prepared from AESAR, 99.996% (semiconductor grade) NaOH pellets, whereas 0.5 M H_2SO_4 was made from ultra-pure sulphuric acid supplied by SEASTAR Chemicals (BC, Canada). Atmospheric oxygen was removed from solution before each electrochemical experiment by bubbling with high-purity argon (Ar 6.0 grade, Linde). In addition, during the experiments, the argon gas flow was kept above the solution.

In order to remove a protective organic sizing from “as received” carbon fibre, the tow electrodes were initially heat-treated in a muffle furnace (for 4 hours at 350 ^{o}C). Such pretreated CF electrodes were then electrochemically oxidized in 0.1 M NaOH solution, at an anodic current-density of 0.3 mA cm^{-2} ($CF_{ox.1}$: 300 s and $CF_{ox.2}$: 600 s) and in 0.5 M H_2SO_4 at 0.3 mA cm^{-2} ($CF_{ox.3}$: 300 s and $CF_{ox.4}$: 600 s). Another, complementary CF electrode was prepared from unoxidized fibre specimen ($CF_{non\text{-}ox.}$). Then, electrodeposition of Ru on the CF tow samples was made from $RuCl_3$ solution (10 g dm^{-3} and pH = 1.5), at a current-density of 0.4 mA cm^{-2} to produce catalyst deposits at *ca*. 1 wt.% Ru.

2.2. Electrochemical cell, electrodes and experimental methodology

An electrochemical cell used in this study was made of Pyrex glass, which contained 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. 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 flame-annealed, followed by cathodic charging with hydrogen in 0.5 M H_2SO_4 until H_2 bubbles in the electrolyte were observed. The potential shift in time was occasionally checked to determine stability of the Pd reference electrode. The counter electrode was made of a coiled Pt wire (1.0 mm diameter, 99.9998% purity, Johnson Matthey, Inc.). Before its use, the counter electrode was cleaned in the same way as the RHE. The electrochemical cell before each series of experiments was taken apart and soaked in hot sulphuric acid for at least 2 hours. After having been cooled to about 30 ºC, the cell was thoroughly rinsed with Millipore ultra-pure water.

A.c. impedance spectroscopy technique was employed during the course of this work. All measurements were performed by means of the *Solartron* 12.608 W Full Electrochemical System, consisting of 1260 frequency response analyzer (FRA) and 1287 electrochemical interface (EI) units. For impedance measurements, the generator provided an output signal of known amplitude (5 mV) and the frequency range was usually swept between 1.0×10^{5} and 0.2×10^{-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, impedance measurements were carried-out at each potential value, independently at three catalyst tow 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 [13].

3. RESULTS AND DISCUSSION

3.1. Hydrogen evolution reaction on "as received" and electrooxidized CF tow electrodes in 0.1 M NaOH

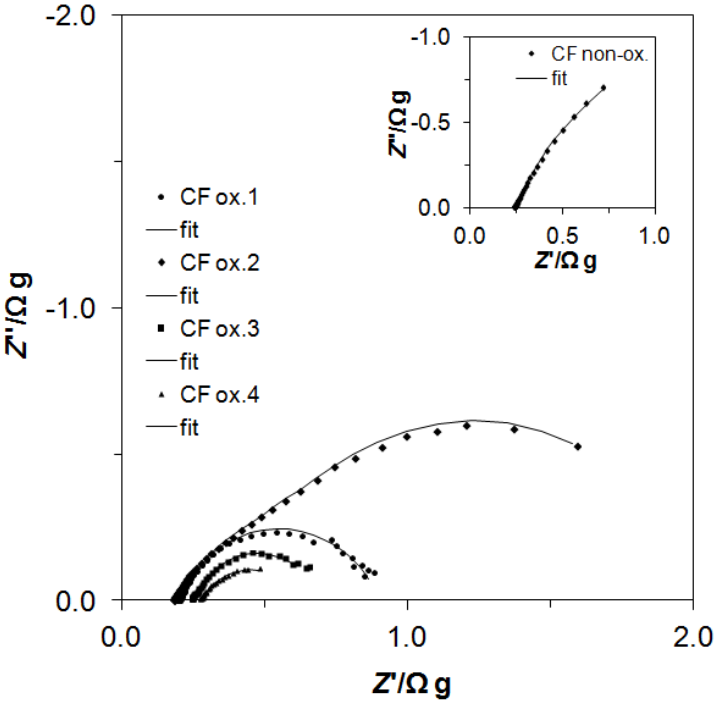

Figure 1. Complex-plane impedance plots for "as received" (inset) and electrochemically oxidized CF tow electrodes in contact with 0.1 M NaOH, recorded at room temperature for the potential of -1000 mV (vs. RHE). The solid lines correspond to representation of the data according to equivalent circuit shown in Fig. 2.

Experimentally obtained HER impedance results for “as received” and electrooxidized CF tow electrodes, examined in 0.1 M NaOH solution, are given in Fig. 1 and Table 1 below. In the explored frequency range, all fibre electrodes exhibited two partial and somewhat “depressed” semicircles in the Nyquist impedance plots (see examples of the recorded impedance behaviour in Fig. 1). An equivalent circuit model used for fitting the impedance data is illustrated in Fig. 2.

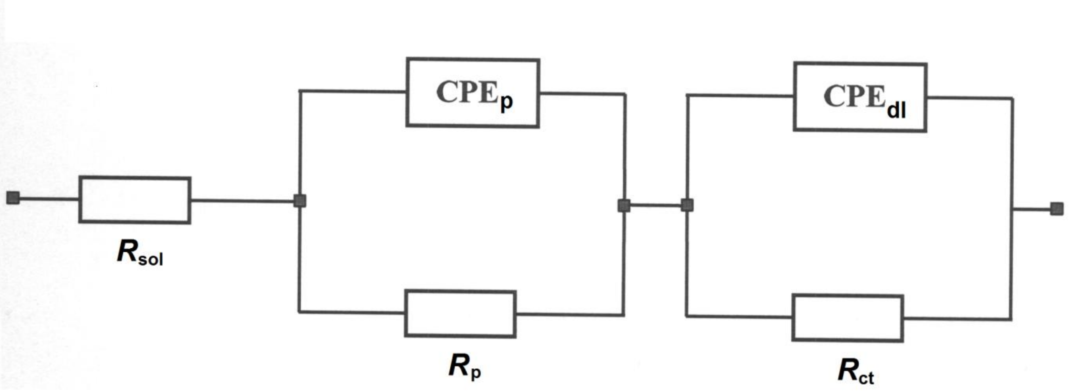

Figure 2. Two CPE-*R* element equivalent circuit model used for fitting the impedance data for CF tow electrodes, obtained in 0.1 M NaOH. The circuit includes two constant phase elements (CPEs) to account for distributed capacitance; R_{ct} and C_{dl} (CPE$_{dl}$) elements correspond to the HER charge-transfer resistance and double-layer capacitance components; R_p and C_p (CPE$_p$) elements refer to the resistance and capacitance components of an electrode porosity response; R_{sol} is solution resistance.

The circuit contains two constant phase elements (CPEs) in order to account for the capacitance dispersion effect (see e.g. Refs. 9-11 for details). The first, high-frequency semicircle (C_p-R_p elements in Fig. 2) corresponds to the electrode porosity response, while the second, intermediate/low frequency loop (C_{dl}-R_{ct} elements) represents the HER kinetics [14-17].

Hence, the recorded R_{ct} parameter for CF$_{non\text{-}ox.}$ electrode diminished from 200.50 Ω g at -100 mV to reach 6.12 Ω g at the potential of -1000 mV vs. RHE (Table 1). All electrochemical oxidation treatments applied to the CF tow caused considerable reduction of the charge-transfer resistance parameter (from about 1.8× for CF$_{ox.1}$ and CF$_{ox.2}$ to 100× for CF$_{ox.3}$ and 118× for CF$_{ox.4}$ at -100 mV, comparatively to the non-oxidized CF tow electrode). On the other hand, at the overpotential of -1000 mV, the R_{ct} parameter for electrooxidized electrodes became (comparatively) reduced by *ca.* 9.4, 3.9, 14.2 and 32.2× for the CF$_{ox.1}$ through CF$_{ox.4}$ specimens, respectively.

Furthermore, double-layer capacitance parameter for “as received” CF tow electrode dramatically increased from 238,191 μF g^{-1} $s^{\varphi 1-1}$ at -100 mV to reach 1,356,125 μF g^{-1} $s^{\varphi 1-1}$ at -1000 mV (likely the result of severe surface inhomogeneity, existing for untreated carbon fibre tow electrode). Similar effect was also recorded for the CF$_{ox.1}$ and CF$_{ox.2}$ tow electrodes. In contrast, for the CF$_{ox.3}$ and CF$_{ox.4}$ tow electrodes, the C_{dl} parameter tends to significantly decline with rising overpotential (see Table 1 for details). The above is most certainly caused by partial blocking of electrochemically active electrode surfaces by freshly formed hydrogen bubbles (clearly visible at the

$CF_{ox.}$ electrodes upon the HER experiments). In addition, these results prove that electrochemical oxidation performed in sulphuric acid presents much more severe reaction conditions than the corresponding sodium hydroxide treatment.

Table 1. Electrochemical parameters for the HER, obtained at "as received" and surface-electrooxidized CF tow electrodes, in contact with 0.1 M NaOH. The results were obtained by fitting the two CPE-*R* element (Fig. 2) equivalent circuit to the experimentally obtained impedance data (reproducibility usually below 10-15%, $\chi^2 = 5\times10^{-5}$ to 9×10^{-4}).

E/mV	R_{ct}/Ω g	C_{dl}/μF g^{-1} s$^{\varphi1-1}$	R_p/Ω g	C_p/μF g^{-1} s$^{\varphi2-1}$
$CF_{non\text{-}ox.}$				
-100	200.50 ± 34.64	238,191 ± 561	0.02 ± 0.00	903,250 ± 22,517
-200	154.27 ± 41.65	544,500 ± 3,446	0.56 ± 0.04	563,666 ± 20,285
-400	123.24 ± 3.30	741,666 ± 21,337	0.66 ± 0.18	1,658,875 ± 83,190
-600	84.16 ± 2.52	854,416 ± 3,331	0.59 ± 0.11	1,792,750 ± 136,682
-800	32.04 ± 2.04	1,052,958 ± 21,741	0.35 ± 0.06	1,909,375 ± 140,157
-1000	6.12 ± 0.14	1,356,125 ± 19,134	0.23 ± 0.03	1,310,875 ± 121,662
$CF_{ox.1}$				
-100	112.12 ± 4.33	126,812 ± 140	0.02 ± 0.00	865,764 ± 169,334
-200	116.86 ± 4.32	126,791 ± 131	0.03 ± 0.00	1,015,972 ± 176,196
-400	54.43 ± 2.70	134,632 ± 170	0.02 ± 0.00	696,736 ± 99,939
-600	14.72 ± 0.47	147,780 ± 137	0.01 ± 0.00	659,569 ± 115,279
-800	2.50 ± 0.02	175,347 ± 308	0.01 ± 0.00	322,538 ± 59,662
-1000	0.65 ± 0.00	185,565 ± 1,434	0.01 ± 0.00	247,756 ± 56,948
$CF_{ox.2}$				
-100	113.60 ± 11.06	196,300 ± 81	0.38 ± 0.01	518,150 ± 19,785
-200	93.00 ± 7.72	204,190 ± 397	0.30 ± 0.02	513,600 ± 12,507
-400	61.18 ± 4.30	261,760 ± 978	0.45 ± 0.03	434,55 ± 8,747
-600	35.98 ± 2.16	228,130 ± 630	0.51 ± 0.03	357,590 ± 6,955
-800	8.79 ± 0.30	325,340 ± 3,565	0.62 ± 0.04	303,680 ± 7,001
-1000	1.57 ± 0.07	557,750 ± 18,579	0.56 ± 0.04	269,830 ± 5,688
$CF_{ox.3}$				
-100	2.00 ± 0.02	427,569 ± 21,431	0.04 ± 0.00	517,243 ± 90,265
-200	1.12 ± 0.07	142,736 ± 3,305	0.13 ± 0.01	1,027,292 ± 102,325
-400	0.75 ± 0.01	174,528 ± 1,550	0.25 ± 0.01	2,414,097 ± 251,684
-600	0.78 ± 0.02	229,000 ± 6,617	0.02 ± 0.00	218,701 ± 37,986
-800	0.53 ± 0.10	126,916 ± 14,698	0.31 ± 0.07	778,472 ± 24,303
-1000	0.43 ± 0.01	228,458 ± 5,300	0.01 ± 0.00	134,590 ± 1,681
$CF_{ox.4}$				
-100	1.70 ± 0.02	509,736 ± 16,885	0.02 ± 0.00	187,257 ± 34,649
-200	1.23 ± 0.01	424,833 ± 4,970	0.04 ± 0.00	399,652 ± 67,483
-400	0.49 ± 0.01	183,937 ± 7,543	0.14 ± 0.02	574,625 ± 7,543
-600	0.34 ± 0.04	444,348 ± 596	0.27 ± 0.02	751,905 ± 105,252
-800	0.19 ± 0.01	132,312 ± 1,225	0.23 ± 0.01	1,124,930 ± 12,510
-1000	0.19 ± 0.01	139,020 ± 1,987	0.11 ± 0.01	895,763 ± 145,821

Table 2. Electrochemical parameters for the HER, obtained at Ru-modified CF tow electrodes, in contact with 0.1 M NaOH. The results were obtained by fitting the two CPE-*R* element (Fig. 2) equivalent circuit to the experimentally obtained impedance data (reproducibility usually below 10-15%, $\chi^2 = 9\times10^{-5}$ to 4×10^{-4}).

E/mV	R_{ct}/Ω g	C_{dl}/μF g^{-1} s$^{\varphi3-1}$	R_p/Ω g	C_p/μF g^{-1} s$^{\varphi4-1}$
		Ru-modified CF$_{\text{non-ox.}}$		
-100	1.00 ± 0.07	512,394 ± 28,591	0.56 ± 0.06	417,258 ± 9,816
-200	0.63 ± 0.10	574,135 ± 80,666	0.41 ± 0.09	387,952 ± 20,554
-250	0.22 ± 0.05	1,079,529 ± 215,905	0.46 ± 0.06	360,417 ± 7,552
-300	0.21 ± 0.01	316,288 ± 25,303	0.24 ± 0.01	180,309 ± 27,046
		Ru-modified CF$_{\text{ox.1}}$		
-100	0.31 ± 0.02	129,494 ± 12,272	0.06 ± 0.01	2,762,204 ± 521,568
-200	0.15 ± 0.01	143,006 ± 4,561	0.03 ± 0.01	1,261,438 ± 227,262
-250	0.12 ± 0.01	136,986 ± 6,706	0.03 ± 0.01	1,240,537 ± 233,404
-300	0.10 ± 0.01	143,835 ± 5,704	0.02 ± 0.01	139,698 ± 34,924
		Ru-modified CF$_{\text{ox.2}}$		
-100	0.80 ± 0.06	448,618 ± 30,271	0.44 ± 0.05	254,009 ± 8,486
-200	0.49 ± 0.01	686,237 ± 61,761	0.43 ± 0.03	213,886 ± 4,063
-250	0.33 ± 0.03	278,544 ± 11,977	0.03 ± 0.00	259,722 ± 43,893
-300	0.20 ± 0.00	151,396 ± 6,055	0.03 ± 0.00	16,647 ± 2,524
		Ru-modified CF$_{\text{ox.3}}$		
-100	0.84 ± 0.04	165,198 ± 6,607	0.05 ± 0.01	632,815 ± 183,250
-200	0.46 ± 0.01	162,965 ± 1,955	0.03 ± 0.00	412,589 ± 20,629
-250	0.21 ± 0.00	163,842 ± 4,088	0.02 ± 0.00	158,726 ± 20,634
-300	0.16 ± 0.00	155,609 ± 7,220	0.01 ± 0.00	109,048 ± 14,176
		Ru-modified CF$_{\text{ox.4}}$		
-100	0.19 ± 0.00	216,061 ± 7,517	0.01 ± 0.00	96,575 ± 12,070
-200	0.14 ± 0.00	156,306 ± 2,105	0.03 ± 0.00	93,198 ± 2,697
-250	0.11 ± 0.00	196,220 ± 14,245	0.01 ± 0.00	66,078 ± 7,268
-300	0.08 ± 0.00	214,636 ± 15,453	0.02 ± 0.00	99,815 ± 4,174

On the other hand, the surface-porosity related charge-transfer resistance (R_p) parameter exhibited significantly less overpotentially-dependent behaviour than that recorded for the R_{ct} parameter for both unmodified and the Ru-modified CF tow electrodes. Also, the corresponding pseudocapacitance, C_p parameter demonstrated considerable oscillation over the examined potential range (see Tables 1 and 2). Nevertheless, it should be stated that the CF tow's entity cannot be treated as a "static" porous electrode system, especially when the experiments are performed over a large range of overpotentials. In fact, the tows's entity undergoes considerable modification as the cathodic overpotential changes, thus causing significant oscillations of the recorded R_p and C_p parameters.

In addition, the dimensionless φ_1 and φ_2 parameters (φ determines the constant phase angle in the complex-plane plot, where $0\leq\varphi\leq1$) of the CPE circuit (see Fig. 2 and Table 1) varied between 0.70-0.99 and 0.46-0.96, correspondingly (as similarly observed for the Ru-modified CF tow electrode parameters φ_3 and φ_4 in Table 2).

3.2. Hydrogen evolution reaction on Ru-modified CF tow electrodes in 0.1 M NaOH

Fig. 3 and Table 2 present a.c. impedance characterization of the HER, at Ru-modified CF tow electrodes (at *ca.* 1 wt.% Ru), examined in 0.1 M NaOH supporting electrolyte. As a result of electrodeposition of ruthenium, the R_{ct} parameter became significantly reduced, as compared to that recorded for the unmodified CF electrodes. Hence, for the Ru-modified $CF_{non\text{-}ox.}$ fibre electrode, the R_{ct} diminished (comparatively) by about 200× at -100 mV, where for a sequence of electrooxidized carbon fibre tow electrodes ($CF_{ox.1}$, $CF_{ox.2}$, $CF_{ox.3}$ and $CF_{ox.4}$), the R_{ct} reduced by *ca.* 362, 142, 2 and 9×, correspondingly. As for the ruthenium-modified CF tow electrodes the HER got excessively vigorous, electrochemical investigations for this type of fibre electrodes were limited to the overpotential of -300 mV (Table 2). Thus, at -300 mV, the highest value of the R_{ct} parameter was recorded for the $CF_{non\text{-}ox.}$/Ru electrode (0.21 Ω g), whereas the lowest R_{ct} value (0.08 Ω g) at this potential was exhibited by the $CF_{ox.4}$/Ru composite electrode.

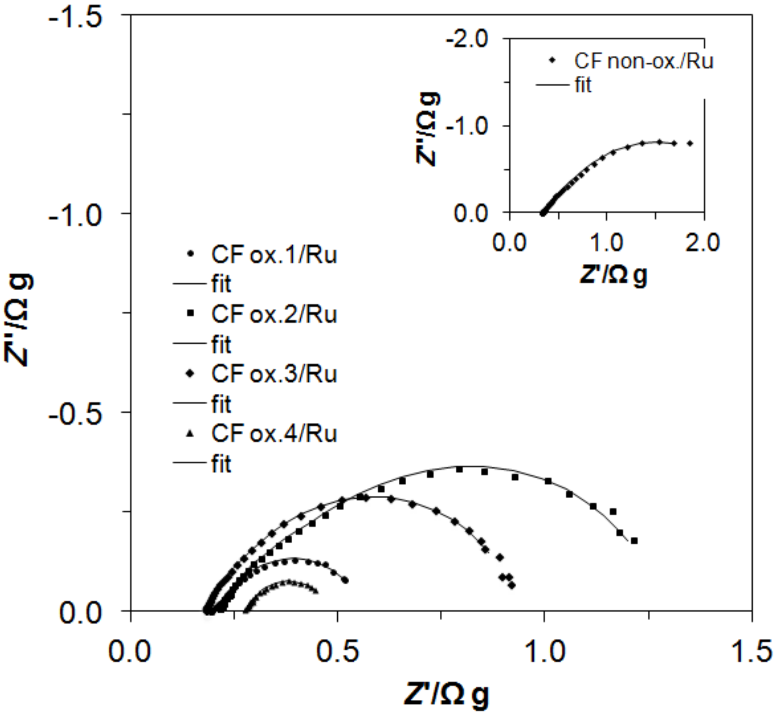

Figure 3. Complex-plane impedance plots for Ru-modified, pretreated CF tow electrodes (see Fig. 1) in contact with 0.1 M NaOH, recorded at room temperature for -100 mV (vs. RHE). The solid lines correspond to representation of the data according to equivalent circuit shown in Fig. 2.

On the other hand, the double-layer capacitance parameter for the Ru-modified $CF_{non\text{-}ox.}$ electrode increased by about 2.2× at the overpotential of -100 mV (as compared to the C_{dl} value recorded for a baseline $CF_{non\text{-}ox.}$ substrate). Furthermore, electrodeposition of ruthenium onto electrooxidized CF tow materials generally did not increase the electrochemically active surface area for a sequence of carbon fibre tow substrates: $CF_{ox.1}$ through $CF_{ox.4}$. Thus, facilitation of the HER kinetics for the Ru-modified $CF_{ox.}$ composite electrodes could predominantly be attributed to the catalytic activity of ruthenium electrodeposit.

Furthermore, plots of –log R_{ct} vs. overpotential (Figs. 4a and b) showed a fairly good linear dependence for all examined fibre electrodes, over the studied overpotential range. The above is consistent with the kinetically-controlled reaction [18-21], which proceeds via the Volmer-Heyrovsky path [22]. The exchange current-densities (j_0) for the HER were calculated based on the Butler-Volmer equation (see e.g. Ref. 9). Hence, the ruthenium-modified CF electrodes demonstrated substantially increased values of the j_0 parameter by *ca.* 170× for “as received”, 592× for the $CF_{ox.1}$ and 5× for the surface-electrooxidized $CF_{ox.4}$ electrode, as compared to those of unmodified CF tow samples (see Figs. 4a and b, again).

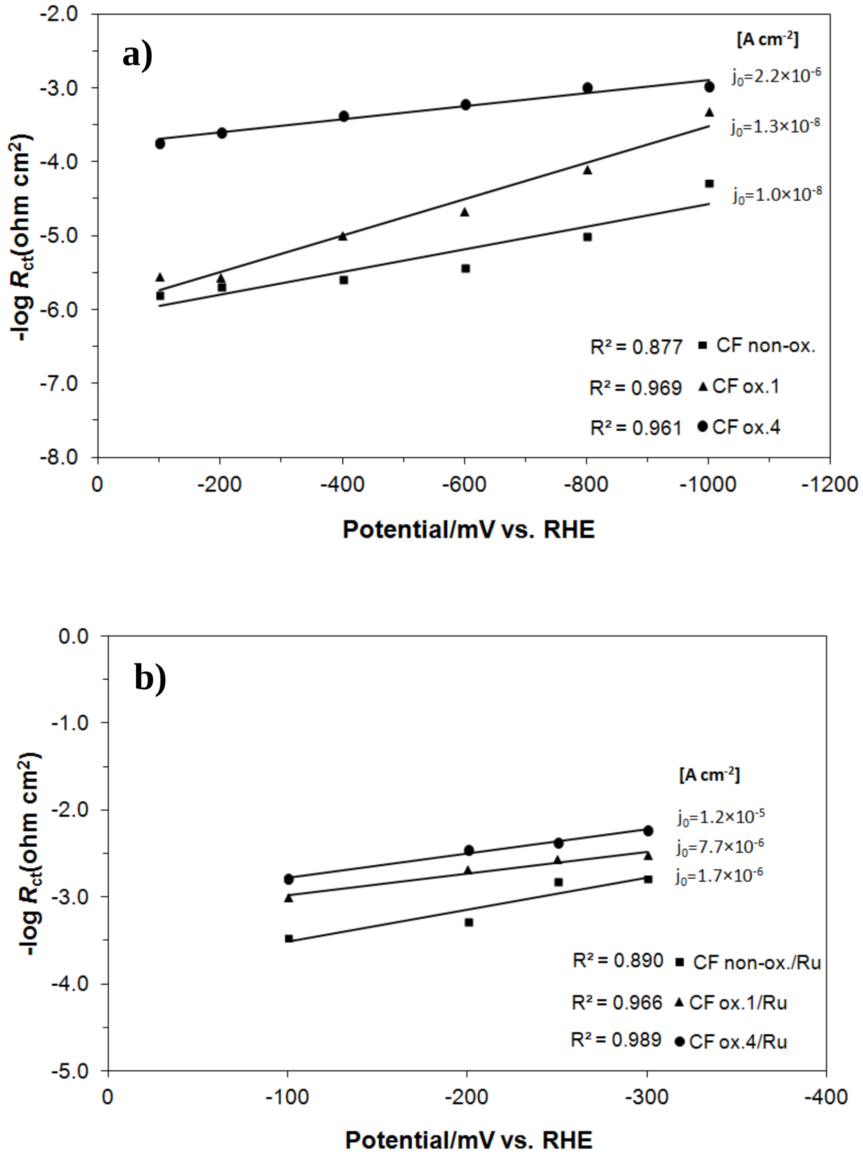

Figure 4. a) –log R_{ct} vs. overpotential relationship, obtained for the HER in 0.1 M NaOH solution, for “as received” and electrochemically oxidized CF tow electrodes. Symbols stand for experimental results and lines are data fits. b) As above, but for Ru-modified CF tow electrodes.

4. CONCLUSIONS

Specific electrochemical surface oxidation treatments could induce dramatic changes to electrochemically accessible surface area of carbon fibre, baseline 12,000-filament tow material. The above might result in significant enhancement of catalytic properties of carbon fibre towards cathodic evolution of hydrogen. Electrodeposition of ruthenium (at *ca*. 1 wt.%) on the surface of 12K CF tow material results in further, considerable improvement of its catalytic HER properties.

In conclusion, obtained considerable enhancement of catalytic HER behaviour for ruthenium-modified CF-oxidized tow materials, indicated substantial opportunities for this type of cathode materials in industrial water electrolysers.

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