

Hydrogen Evolution Reaction at Zirconium and Si-Modified Zirconium Electrodes. Electrochemistry at Fractal Interfaces.

M. Hromadová^{1,*}, J. Kocábová¹, L. Pospíšil¹, S. Cichoň², V. Cháb², M. Novák³, J. Macák³

¹ J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 3, 182 23 Prague, Czech Republic

² Institute of Physics of the Czech Academy of Sciences, 182 21 Prague, Czech Republic

³ Department of Power Engineering, University of Chemistry and Technology, Technická 5, 166 28 Prague, Czech Republic

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In memory of Professor Zdravko Stoynov for his kind personality and innovative scientific contribution to electrochemistry

Hydrogen evolution reaction was studied by electrochemical impedance spectroscopy at a high purity grade zirconium and Si-modified zirconium electrode in borate buffer. Roughness factor and fractal dimension of the electrode surface were determined for both electrodes from topographic images obtained by atomic force microscopy. Electrochemical impedance spectra were fitted by a simple equivalent circuit containing constant phase element, which provided the exponent n that can be directly related to fractal dimension D_f of the electrode surface. For Zr electrodes a reasonable agreement between D_f values calculated from n exponent of the constant phase element and the experimentally-obtained fractal dimension was found, whereas this approach failed for Si-modified Zr electrodes. Further implication of this result for the determination of hydrogen evolution rate parameters is discussed.

Key words: zirconium, hydrogen evolution reaction, impedance, fractal dimension, atomic force microscopy

INTRODUCTION

This contribution is dedicated to the memory of Professor Zdravko Stoynov for his pioneering work in the field of electrochemical impedance analysis [1].

Presented work is focused on the interpretation of the constant phase element (CPE) by employing fractal analysis of the electrode|electrolyte interface. The nature of CPE has been discussed extensively in the past [2-15] and it is generally believed that the CPE behavior is a consequence of the current density distribution along the electrode|electrolyte interface due to the surface inhomogeneity. If the CPE is only the intrinsic property of the double layer, the fitting parameter Q is independent of the solution resistance R_s and there is no need to invoke the distribution function for the relaxation times [5]. In most of the experimental cases, however, this is not the case and several distribution models (ladder or other transmission line networks) have been assumed

leading to the effective capacitance value C_{eff} , which can be obtained from Q parameter by several different expressions that include not only the solution resistance but the charge transfer resistance values as well [5,6].

Another concept that explains the CPE behavior uses the description of the surface inhomogeneity by a fractal geometry [8,9]. Based on this approach Nyikos and Pajkossy [8] suggested a simple relationship $n = 1/(D_f - 1)$ between the CPE parameter n and the effective dimension of the electrode surface D_f , which was experimentally verified for fractal blocking electrodes [10]. Subsequently, Mulder and Sluyters [9] used the surface fractal properties to explain depressed semicircular arcs in impedance plots for irreversible electrode reactions. Several subsequent experimental works took up on this concept [16-18].

Hydrogen evolution reaction (HER) on two different types of zirconium-based interfaces, namely on pure zirconium and Si-modified zirconium electrode materials, has been used for this evaluation. Electrochemical impedance spectroscopy (EIS) measurements were obtained under the experimental conditions that enabled

To whom all correspondence should be sent:
E-mail: magdalena.hromadovajh-inst.cas.cz

simplification of the impedance response and subsequent spectra analysis by utilization of a simple $R_s(\text{CPE}-R_{ct})$ electric circuit, where R_s is the solution resistance, R_{ct} is the charge transfer resistance and CPE represents the constant phase element referring to the electrode capacitive behavior. This simplification was achieved by using a sufficiently negative applied potential with respect to the equilibrium potential (open circuit potential) [19] thus eliminating salient contribution from the charge transfer kinetics related to the oxide film formation. Two experimental parameters Q and n were obtained from the impedance corresponding to the CPE using the expression $Z_{\text{CPE}} = Q^{-1}(j\omega)^{-n}$. Parameter n represents a frequency-independent phase angle different from 90° . If the phase angle is 90° degrees, parameter n equals to 1. For smaller phase angles, n values are smaller than 1. The atomic force microscopy (AFM) was used for ex-situ imaging of the electrode surface topography, which allowed determination of two characteristic surface parameters, namely, a roughness factor R_f and a fractal dimension D_f . These experimental values were then used to interpret the CPE parameters Q and n obtained from the analysis of EIS spectra. We are not aware of any previous work that utilizes the AFM method for the interpretation of the CPE values as is presented in this communication.

EXPERIMENTAL

Zirconium samples were prepared from two types of Zr, wire and rod. Zirconium wire (Alfa Aesar, 0.25 mm diameter, 99.95% purity, metallic impurity 29 ppm Hf, 190 ppm Fe, 1.8 Cu, 8.4 ppm Cr and 4.1 ppm Ni) was soldered to a support copper wire, inserted in a thick walled tight glass capillary and fixed with a TorrSeal™ resin (Varian Inc., USA). The exposed part of the wire was polished with silicon carbide paper (5000, WS Flex 16 Waterproof, Hermes, Germany). Exposed geometric electrode area of thus prepared Zr microelectrode (mZr-5000) was $4.91 \times 10^{-4} \text{ cm}^2$. Zirconium rod (Alfa Aesar, 12.7 mm in diameter, annealed, 99.2+ % (metals basis excluding Hf), Hf 4.5% max.) was cut into small 4 mm thick pellets, which were consecutively polished on one side with the silicon carbide paper (WS Flex 16 Waterproof, Hermes, Germany) of increasingly smaller grit sizes (P1200, P2000, P2500 and 5000). Zr pellet electrode polished with 5000 grit paper is labelled as Zr-5000. Final step consisted of polishing with a diamond paste (particle size 3 μm , D3 Urdiamant polishing paste, Czech Republic). Thus prepared surface was rinsed copiously with water and

acetone, cleaned with ultrasound and dried. This electrode is labelled as Zr-D3. Zirconium pellets were then used for further surface modification. Si-modified Zr electrode (SiZr-D3) with approximately 1 to 1 ratio of Si to Zr atoms in the surface layer was prepared employing DC magnetron sputtering from pure Si and Zr targets in Ar plasma at 2 Pa. All targets were at least 3N purity. Composition was probed by the scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), X-ray photoelectron spectroscopy (XPS), glow-discharge optical emission spectroscopy (GD-OES) and Raman spectroscopy. Before the deposition, samples were annealed in-situ in an ultrahigh vacuum at 700°C for 30 min with the aim to prepare a clean surface for subsequent deposition. This step ensured the absence of detrimental oxide layer interface. Deposition was performed at 300°C . After the deposition, samples were annealed in-situ in Ar at 2 Pa at 700°C so as to promote alloying and silicide formation.

All ex-situ Atomic Force Microscopy (AFM) topography images were obtained in the contact mode regime using Agilent 5500 Scanning Probe Microscope (Agilent Technologies, USA). A large AFM scanner (100 $\mu\text{m} \times 100 \mu\text{m}$) and PPP-CONT cantilevers (Agilent Technologies, USA) of nominal force constant of 0.2 N/m and resonant frequency 13 kHz were used. The recording speed was in the range of 0.2–0.7 lines/s. AFM images were analyzed using the visualization and analysis software Gwyddion 2.35 from the Czech Metrology Institute [20]. Both the roughness factor R_f and the fractal dimension D_f (using cube counting algorithm [21]) were determined by this software. Ideally flat electrode surface has the roughness factor $R_f = 1$ (real electrode area equals to the geometric one) and the fractal dimension $D_f = 2$. All AFM images shown in this publication are plane-corrected.

EIS spectra were measured in the special electrochemical cell [22] that permits measurement on a selected sample area of $4.02 \times 10^{-2} \text{ cm}^2$ using a three-electrode setup and employing Autolab PGSTAT30 potentiostat/ galvanostat equipped with a frequency response module FRA (Metrohm, Switzerland). An aqueous borate buffer solution consisting of 0.2 M boric acid and 0.05 M sodium tetraborate decahydrate of pH 7.33 was used. Experimental procedure was similar to that reported for Zr microelectrode [19], when electrode was immersed in the solution under the potential control. In the case of pellet electrodes, the main compartment of the electrochemical cell was mounted on top of a dry-polished Zr pellet and the

electrode surface was always contacted with a deaerated electrolyte solution under the potential control reported. This step is extremely important for an achievement of sufficient experimental reproducibility of the EIS measurement. This procedure allowed local measurements on approximately 6 areas of the sample surface. EIS spectra were analyzed with Zview software, version 3.2b (Scribner Associate, Inc., North Carolina, USA).

RESULTS AND DISCUSSION

Figure 1 shows anodic polarization curves for Zr microelectrode (mZr-5000) and Zr pellet electrode (Zr-5000) that were dry-polished with the silicon carbide paper (5000 grit, WS Flex 16), and for Si-modified Zr pellet electrode (SiZr-D3) that was used as received.

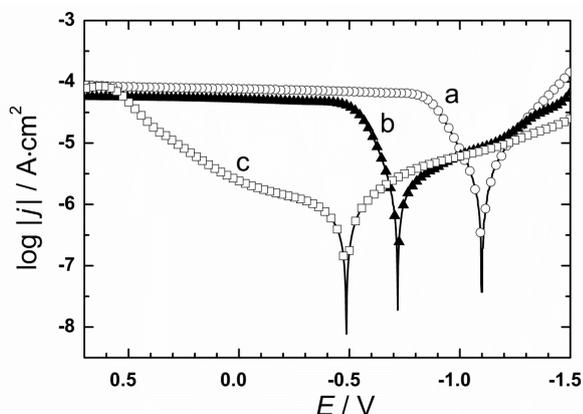


Fig. 1. Anodic polarization curves obtained in borate buffer solution (pH = 7.33) at potential scan rate 0.01 V/s and starting at -1.5 V for: a) mZr-5000, b) Zr-5000 and c) SiZr-D3 electrode.

Curves were obtained at pH = 7.33 after 120 seconds of waiting period at the open circuit potential (OCP). An equilibrium potential, at which the anodic and cathodic currents are equal (effectively the OCP value), amounts to -1.1V for mZr-5000, -0.72V for Zr-5000 and -0.48V for SiZr-D3 against the Ag|AgCl|1M LiCl reference electrode. Differences between the zirconium microelectrode and pellet electrode may be due to a higher content of metallic impurities in the latter case. Si-modified zirconium electrode (SiZr-D3) has the most positive OCP value of all three electrodes and gives the lowest value for the HER current at -1.5V.

Qualitatively the same result was obtained by a conventional voltammetric scan starting from potential -1.0V in the cathodic direction using the potential scan rate of 0.1 V/s (see Figure 2). In this case the cathodic current has lower value for SiZr-D3 electrode compared to Zr-5000 electrode.

Impedance spectra were obtained for all studied samples at -1.5V against the reference electrode using 5mV amplitude for AC component of the potential. The electrochemical cell was filled under the potential control at -1.1V with the electrolyte, which was previously bubbled with argon to minimize the amount of dissolved oxygen. Then the potential was stepped to -1.5V and the impedance spectra were measured. Representative EIS spectra for Zr-D3, Zr-5000 and SiZr-D3 pellet electrodes are shown in Figure 3. Fitting parameters for these individual curves are summarized in Table I, whereas Table II contains the average Q and n parameters from all measured curves under the same experimental conditions.

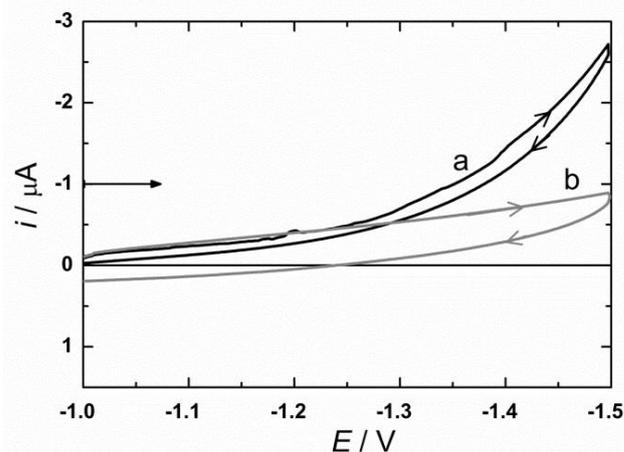


Fig. 2. Cyclic voltammogram for HER process in borate buffer solution (pH = 7.33) at potential scan rate 0.1 V/s on: a) Zr-5000 and b) SiZr-D3 electrode. Contact of the electrode with solution was done under potential control at -1.0 V.

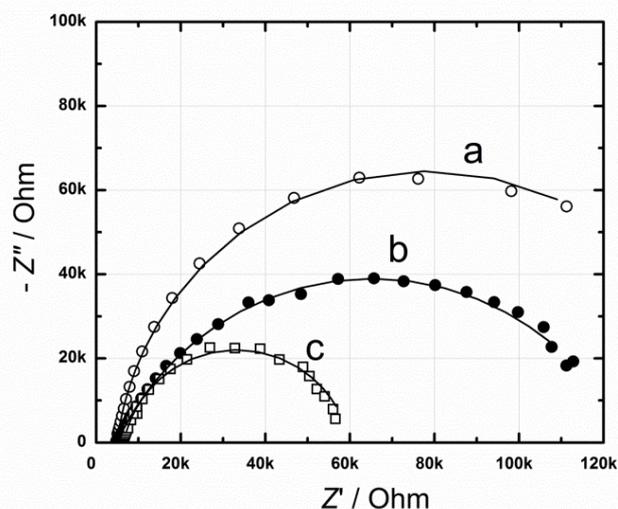


Fig. 3. The representative complex impedance plot for HER obtained at -1.5V on: a) Zr-D3, b) SiZr-D3 and c) Zr-5000 pellet electrode. Symbols indicate the experimental data and lines the best fit to the $R_s(CPE-Rct)$ equivalent circuit.

Table 1. EIS fitting parameters for data in Figure 3

Electrode	R_s / Ω	R_{ct} / Ω	n	$Q / \Omega^{-1} s^n$
Zr-5000	6 526	53 445	0.87	1.5×10^{-6}
Zr-D3	4 914	146 730	0.92	3.6×10^{-7}
SiZr-D3	4 961	120 680	0.73	1.8×10^{-6}

Surface structures of samples Zr-5000, Zr-D3 and SiZr-D3 were analyzed ex-situ employing the AFM technique. Topographic images from several areas of each sample were obtained. Only the largest one ($50 \times 50 \mu\text{m}^2$ area) was used for determination of the roughness factor R_f and fractal dimension D_f parameters. The cube counting algorithm implemented within the Gwyddion software was used for fractal analysis. [21].

Figure 4 shows the ex-situ AFM topography images ($50 \mu\text{m} \times 50 \mu\text{m}$) of the Zr pellet polished with a $3 \mu\text{m}$ diamond paste (Zr-D3) and the Si-modified zirconium (SiZr-D3) pellet electrodes. Left image represents Zr-D3 and right image SiZr-D3, whereas scale z of the left image is $0.48 \mu\text{m}$ and of the right image $1.2 \mu\text{m}$, respectively. Below the images are the height profiles obtained along the black line indicated in the image. Evidently, there is a large difference between the surface corrugations of these two samples. This observation is consistent with the differences of the roughness factor and fractal dimension values obtained from Gwyddion software and summarized in Table II. Similar analysis was done for Zr-5000 sample

and the corresponding R_f and D_f values are also shown in Table II. Due to the construction of mZr-5000 electrode, it was not possible to obtain the relevant topography information for this surface. Since the same surface treatment was used for both mZr-5000 and Zr-5000 electrodes, we assumed that R_f and D_f parameters are the same as those obtained for Zr-5000 electrode.

Atomic force microscopy technique was used also for analysis of the surface morphology before and after the HER process. Figure 5 shows the AFM topography images taken on the same electrode SiZr-D3 in the area that was not subjected to the HER (left) and inside the region subjected to HER (right). AFM measurement was done in contact mode; z scale is $1.5 \mu\text{m}$ (left) and $1.1 \mu\text{m}$ (right), respectively. The relevant region subjected to HER was identified by the O-ring imprint.

Large scale images shown in Figure 5 confirm that the surface morphology does not change significantly before and after HER process, but it is evident (also from the height profiles) that the surface becomes somewhat smoother.

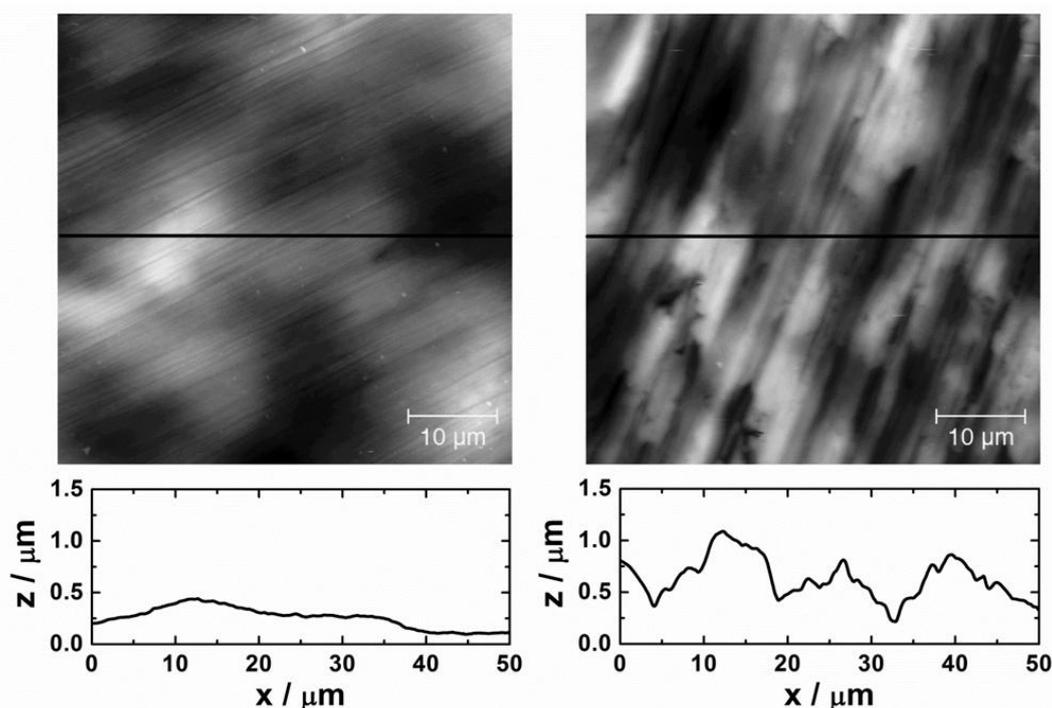


Fig. 4. Ex-situ AFM topography image of Zr-D3 (left) and SiZr-D3 (right) pellet electrode obtained before the HER. The height profile obtained along the black horizontal line is shown below.

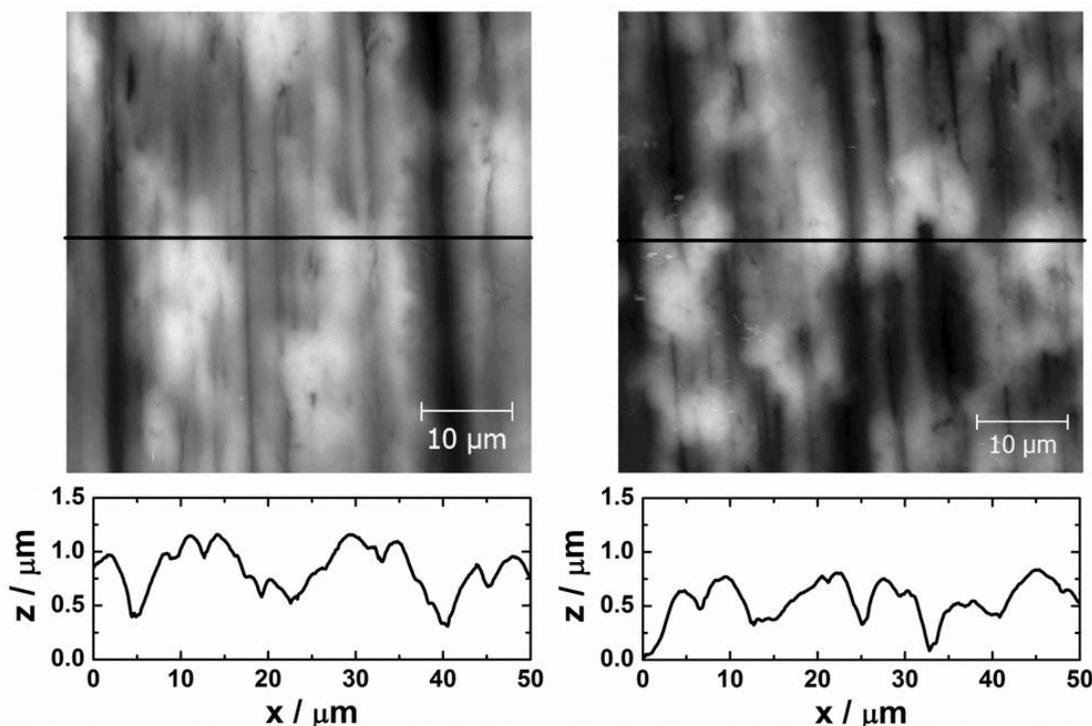


Fig. 5. Ex-situ AFM topography images of SiZr-D3 surface before (left) and after (right) HER studied by impedance spectroscopy at -1.5V . The height profile obtained along the black horizontal line is shown below.

Both, the roughness factor and fractal dimension decrease slightly. For this SiZr-D3 sample R_f changes from 1.015 to 1.011 and D_f changes from 2.19 to 2.17, respectively. These changes are small in view of the fact that from all of the imaged areas and SiZr-D3 samples the average R_f is 1.012 ± 0.001 (change from 1.015 ± 0.002) and the average D_f is 2.19 ± 0.02 (change from 2.18 ± 0.01), respectively.

Once all relevant information is summarized from the EIS and AFM experiments, we can put into the test a suggested interpretation of the CPE parameter n in terms of the fractal dimension D_f of the sample surface. As previously suggested and experimentally verified for fractal blocking electrodes [8,10], the relationship between these two parameters should follow a simple expression $n = 1/(D_f - 1)$. In this work we obtained experimentally fractal dimension D_f values from

which one can compute parameter n , which we label for the purpose of comparison as $n(D_f)$. Its values are summarized in Table II. Comparison of $n(D_f)$ with the experimentally obtained exponent n from the EIS spectra gives an excellent agreement for Zr-5000 and Zr-D3 samples. Interestingly, it also explains the n parameter obtained from impedance spectra analysis for mZr-5000 under the assumption that experimental D_f would be the same for both electrodes. These electrodes have different geometric area, but were subjected to the same pretreatment procedure before the HER measurement. The only time that we did not get a quantitative agreement between $n(D_f)$ and n values is in the case of Si-modified Zr pellet electrode, when experimentally obtained parameter n from EIS measurements was much lower than the $n(D_f)$ calculated one.

Table 2. Roughness factor R_f , fractal dimension D_f , CPE parameters Q and n for different electrode surfaces.

Electrode	R_f^a	D_f^a	$n(D_f)$	n	$Q / \Omega^{-1} s^n$
mZr-5000	–	–	–	0.82 ± 0.01	$(2.3 \pm 0.3) \times 10^{-8}$
Zr-5000	1.053 ± 0.004	2.24 ± 0.03	0.81 ± 0.02	0.82 ± 0.04	$(1.6 \pm 0.2) \times 10^{-6}$
Zr-D3	1.003 ± 0.001	2.08 ± 0.03	0.93 ± 0.03	0.91 ± 0.01	$(3.2 \pm 0.6) \times 10^{-7}$
SiZr-D3	1.015 ± 0.002	2.18 ± 0.01	0.85 ± 0.01	0.74 ± 0.01	$(1.8 \pm 0.2) \times 10^{-6}$

^acalculated for area $50 \times 50 \mu\text{m}^2$ (see for example Fig. 4)

This experiment suggests that the current distribution on SiZr-D3 electrode is not related primarily to the surface geometry, but rather to the fact that the electrode surface is heterogeneous and composed of the Si and Zr atoms, which have very different behavior with respect to the HER kinetics. This in turn leads to the surface distribution of time-constants [6]. One may invoke the fact that the surface of the SiZr-D3 electrode has approximately the same amount of Si and Zr atoms. However, we do not know from the AFM experiments alone the actual distribution of these chemical elements at the electrode|electrolyte interface. The experiment that correlates $n(D_f)$ and n values may give us a hint on the role of local surface inhomogeneities on the charge transfer kinetics. In the case of HER one should additionally consider the Volmer-Heyrovský-Tafel mechanism that includes hydrogen adsorption step [19].

CONCLUSIONS

The ex-situ AFM was used to characterize several zirconium-based electrode surfaces prior and after the HER at potentials negative of the open circuit potential value. Two main characteristic parameters were reported, namely, the roughness factor R_f and fractal dimension D_f of the studied surface. A reference zirconium system gave R_f and D_f values in accord with the expectation that the roughness factor and fractal dimension of the surface should decrease for the electrode consecutively polished with 5000 silicon carbide paper and subsequently with a 3 μ m diamond paste. Both parameters increase when zirconium surface is modified by Si adlayer in the ratio 1:1 with respect to zirconium. The effect of HER on the electrode surface morphology was found to be almost negligible leading to a small decrease in the roughness factor and surface fractal dimension. Experimental D_f values were obtained by the cube counting analysis of the ex-situ AFM topography images and were used successfully to explain the non-ideality of the interfacial capacitance (CPE) behavior for Zr-based electrodes.

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Реакция на отделяне на водород при циркониеви и Si-модифицирани циркониеви електроди.
Електрохимия на фрактални повърхности

М. Хромадова^{1,*}, Я. Кочабова¹, Л. Пошпишил¹, К. Кихон, В. Чаб², М. Нивак³, Я. Масак³

¹ *Институт по физикохимия „Я. Хейровски“ на Чешката академия на науките, Доляскова3, 182 23 Прага, Чешка република*

² *Институт по физика на Чешката академия на науките, 182 21 Прага, Чешка република*

³ *Катедра "Енергетика", Химически и технологичен университет, Техническа 5, 166 28 Прага, Чешка република*

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(Резюме)

В памет на проф. Здравко Стойнов, неговата любяща личност, иновативен и научен принос в електрохимията

Реакцията на отделяне на водород беше изследвана чрез електрохимична импедансна спектроскопия в цирконий с висока чистота и в циркониев електрод модифициран със силиции в боратен буфер. Коефициентът на грапавост и фракталният размер на повърхността на електрода са определени за двата електрода от топографски изображения, получени чрез атомно силова микроскопия. Електрохимичните импедансни спектри бяха анализирани с помоща на проста еквивалентна схема, съдържаща елемент с постоянна фаза, определящ коефициента n , който е непосредствено свързан с фракталния размер D_f на повърхността на електрода. За циркониеви електроди съотношението между стойностите на D_f , изчислени от експонентата n на елемента с постоянна фаза и експериментално получените фрактални измервания, е приемливо, от друга страна този подход не дава резултати при Zr електроди модифицирани със Si. Значението на този резултат за определяне на параметрите на скоростта на отделяне на водород се дискутира.