Determination of Pseudocapacitance Changes of Nickel Oxide NiO Electrode with the Use of Dynamic Electrochemical Impedance Spectroscopy

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The electrochemical capacitors (ECs) are attractive energy storage devices which can be applied in many electronic products (e.g., cameras, laptops, cell phones) or hybrid electric vehicles (HEV). The energy storage in ECs is based on capacitive (the electrical double layer charging/discharging) and pseudocapacitive (additional charge provided by faradic reaction) phenomena. Considering the electrodes exhibiting pseudocapacitance, examination of their capacitance value is usually complicated, mainly because of its dependence on applied potential. This paper presents the results of evaluating the capacitance of the nickel oxide electrode material by the analysis of the impedance spectra obtained by Dynamic Electrochemical Impedance Spectroscopy (DEIS). The proposed solution allows to acquire the detailed information about capacitance changes as a function of applied potential. Another applied technique, i.e. Atomic Force Microscopy (AFM) revealed no significant changes of electrode topography during polarization.

1. INTRODUCTION

Dynamic science and technology development in last decades caused dramatic increase of power demand. The main reason of this phenomenon is modern style of life, where such devices as

laptops, mobile phones etc. are rather indispensable; the increasing rate of industrial activities also requires portable power sources which are able to supply energy at any place and for a very long time.

Batteries, capacitors and supercapacitors are today the main energy storage devices. First electrochemical capacitor was described by Becker in 1957; however, electrochemical researches on electrochemical capacitors have been intensively developed in last decade of the 20th century. These devices appeared again as some kind of answer for the increasing demand for power sources, especially in the automotive industry, where high power rates are strongly needed, particularly during the start, movement and acceleration of electric vehicles [1].

Supercapacitors, called also ultracapacitors or electrochemical capacitors, provide capacitance in order of several hundred farads. When compared to batteries, they possess high power density, exhibit excellent pulse charge/discharge property, high electric efficiency, long shelf- and cycle life (up to million cycles) but they suffer from low energy density. Taking into account aforementioned features, supercapacitors can be considered as an alternative to pulse batteries, to provide high power density in a short period of time [2,3].

Energy storage in capacitor is usually attributed to two phenonema: always to simple charging/discharging of the electrical double layer (on the electrodes with high specific surface area, e.g. from activated carbon, carbon aerogels, foams etc.) and additionally to pseudocapacitance, being described as additional useful charge coming from faradic reactions occuring on electrode/electrolyte interface as well as in electrode or electrolyte bulk. The most often electrode materials which reveal pseudocapacitive behaviour are transition metal oxides, i.e. RuO_2, IrO_2, NiO, CoO, or MnO_2 [4].

The capacitance is the main parameter which determines the usability of supercapacitor material. Considering the energy which might be stored or released by these devices, it is also important to specify precisely the operational potential range of electrode material as well as electrolyte, within supercapacitor can operate without self-destruction (electrode oxidation, electrolyte decomposition) and which guarantees the highest energetic efficiency.

To determine the supercapacitor capacitance, three electrochemical methods are usually applied: Linear Sweep Voltammetry (LSV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). For LSV [5,6] specific capacitance (i.e. capacitance per mass unit) is calculated as follows:

$$C = \frac{\int_{Vi}^{Vf} I(V)dV}{\frac{dE}{dt} m \cdot (V_f - V_i)} \qquad (1)$$

where dE/dt is the sweep rate (V/s), V_i and V_f are the initial and the final voltages (V) respectively, m is the mass of electroactive material and expression $\int_{Vi}^{Vf} I(V)dV$ means integrated current in potential window.

In chronopotentiometric mode [7-10] the capacitance can be calculated as follows:

$$C = \frac{I}{\dfrac{dE}{dt} m}$$ (2a)

or equivalently:

$$C = \frac{I \Delta t}{m \Delta V}$$ (2b)

where I is the charging/discharging current (A), dE/dt indicates the slope of the discharge curve on the E=f(t) plot, m is the mass of electroactive materials, ΔV is the potential window and Δt is the time of discharge process.

These methods are readily used in practice. However, all of them have a considerable drawback: the potential range for the investigated capacitance is not unequivocally specified and the choice of the potential window is very often not well grounded. It is generally known that nickel oxide effectively operates in potential range of 0.5 V [11]. However, many authors comparing capacitances (for different additives, annealing temperatures, sweep rates, etc.) limit the potential window to 0.3 V [12], 0.35 V [13,14], 0.46 [7], 0.5 V [11,15], 0.7 V [16] etc, without giving any reasonable grounds for such a choice.

Moreover, it is worth to note, that capacitance value strongly depends on applied potential. This fact is very significant for supercapacitors, especially when keeping in mind that pseudocapacitance is the effect of faradaic reaction. Hence, capacitance value also depends on applied scan rate, therefore, increase of dE/dt value causes capacitance decrease [16,17].

Apart from voltamperometry and chronopotentiometry techniques, the capacitance of EC can be also determined using Electrochemical Impedance Spectroscopy (EIS) [1]. These methods have received tremendous increase in popularity in recent years. First application of them was determination of the double-layer capacitance and in ac polarography. Presently, EIS is mainly applied to the characterization of the electrode processes and complex interfaces. Briefly, impedance spectra reveals the electrode response to the application of a periodic, small amplitude alternate current signal. The capacitance is then calculated as follows:

$$C = \frac{1}{2\pi f \cdot \mathrm{Im}(Z)}$$ (3)

where f is the charging/discharging current frequency and Im(Z) is the imaginary part of impedance at frequency f.

However, the results obtained with this method are usually quite lower than for the other techniques mentioned above and preferably should not be compared with each other [18, 19]. Additionally, the time of frequency response measurement is relatively longer than for the others, therefore, some unpredictable changes of electrode physicochemical properties may occur during the experiment.

Due to the fact that measured impedance is a complex value, also capacitance value calculated with this method is characterised with real Re(C) and imaginary Im(C) part [20].

$$C(\omega) = \mathrm{Re}(C)\omega - j\,\mathrm{Im}(C)\omega \qquad (4a)$$

Where

$$\mathrm{Re}(C) = \frac{\mathrm{Im}(Z) \cdot \omega^{-1}}{(\mathrm{Re}(Z) \cdot \omega)^2 + (\mathrm{Im}(Z) \cdot \omega)^2} \qquad (4b)$$

$$\mathrm{Im}(C) = \frac{\mathrm{Re}(Z) \cdot \omega^{-1}}{(\mathrm{Re}(Z) \cdot \omega)^2 + (\mathrm{Im}(Z) \cdot \omega)^2} \qquad (4c)$$

where $\omega = 2\pi f$, C and Z are the appropriately imaginary and real part of capacitance and impedance, respectively.

Assuming that in (4c) $\mathrm{Re}(Z) \ll \mathrm{Im}(Z)$ it is possible to reduce the Equation to (3).

The results reported by Ganesh et al. [12,20] indicate that even for small frequencies the imaginary part of capacitance is considerably large. This implies that evaluating the capacitance of capacitors in this frequency range, the real part of the impedance should be also considered. The impedance results obtained for supercapacitors at low frequencies and transposed to $\mathrm{Im}(C) = f(\mathrm{Re}(C)(\omega))$ system, usually take on the form of a semicircle or at least a part of it (Fig. 1 and Fig. 2). According to this, using extrapolation is it possible to estimate the capacitance $\mathrm{Re}(C)_{\omega \to 0}$, if Im(C) can be omitted. Such method is commonly used for evaluating the resistance of simple equivalent circuits from incomplete impedance spectra [21].

Evaluating the capacitance through extrapolation should not cause any difficulties when applied to double layer capacitors. However, in case of capacitors exhibiting the pseudocapacitance effect, impedance measurements can lead to ambiguities in obtained results since impedance analysis requires stationary conditions [22].

Stability of physicochemical properties of electrode material forming the electrochemical capacitors is very difficult, sometimes even impossible to obtain. Impedance measurements in range of low frequencies takes usually several hours. During this period, considerable changes may occur on the electrode, probably as the result of electrochemical reactions. It is the main reason of ambiguities in the obtained results. The initial and final values of impedance represent different states of the electrode and the obtained spectra are rather impossible to be correctly interpreted.

In this paper we present a novel method for determining the capacitance that changes with applied potential using Dynamic Electrochemical Impedance Spectroscopy (DEIS). This technique might be considered as a variant of commonly used Electrochemical Impedance Spectroscopy (EIS). Theoretical backgrounds of this method have been reported by Darowicki [23-26].

The advantage of DEIS in comparison with other techniques is the possibility to conduct the measurements in non-stationary conditions, e.g., in dynamic systems. DEIS method was used to evaluate the capacitance of nickel oxide electrode with potential changing in time. The results of this experiment will give the grounds for choosing a proper potential window and in the future will help to optimize the potential ranges for other electrode materials used in supercapacitors.

The paper describes methodology for evaluating the capacitance of supercapacitors as the function of potential, using the porous NiO as an example. The method is based on DEIS technique and the analysis of complex impedance spectra.

2. EXPERIMENTAL PART

The chosen material for experiments was nickel oxide, being an attractive material for supercapacitors, mainly due to low price and relatively high value of specific capacitance. Nickel oxide was prepared by chemical precipitation of nickel hydroxide from the $Ni(NO_3)_2$ solution. NaOH solution was slowly dropped into salt; the molar ratio of $Ni(NO_3)_2$:NaOH was 1:2. The precipitated hydroxide was washed with distilled water and then dried at 80°C. After that nickel hydroxide was heated in the air at 300°C for 2 hours in order to obtain the highest capacitance [14,16]. The capacitor electrodes were formed as pressed pellets (15-18 mg) consisting of 85% active material, 10% binder (PVDF, Kynar Flex 2801) and 5% acetylene black (to ensure good conductivity).

The investigations on nickel oxide were performed in three-electrode system in 6 M KOH. The reference electrode in voltammetric and impedance measurements was Hg/HgO (MOE), counter electrode was a platinum sheet. All measured potentials mentioned in this paper refer to MOE electrode. Linear sweep voltammetry (LSV) measurements were performed at 0.1 mVs^{-1} sweep rate in 6 M KOH on Princeton Parstat 2263 device. In potentiodynamic method (DEIS) ac perturbation signal, composed of sinusoids of frequencies ranging from 0.07 Hz to 4.5 kHz, was generated by National Instruments PXI 6120 card. For dc perturbation, 33120 Agilent generator was used. Furthermore KGL103-stat v.4.1. (potentiostat) was used in order to apply the signals on the investigated system. Acquisition, analysis and decomposition of signals were performed in Labview 7.1. The AFM microscope from NT-MDT company was used to evaluate the surface of the electrode.

The working electrode (NiO) was put into an electrochemical cell filled with 6 M KOH solution, where the reference electrode was a nickel rod and the platinum sheet was a counter one. The surface was scanned with silicon probe NSG01. The probe parameters were as follows: chip size: 3.6 X 1.6 X 0.4 mm, reflective side: Au, cantilever number: 1, rectangular, tip height: $10 - 15$ µm, tip cone angle ≤ 22 °, tip curvature radius 10 nm. The scan point size was 256 X 256, the scan velocity 39.80 µm/s. First 5 cycles were performed from -0.6 to 0.55 vs Hg/HgO, then at eight different potentials (15 min per each one) the topography of the surface in the tapping mode was done.

3. RESULTS AND DISCUSSIONS

The voltammogram obtained at 0.1 mVs^{-1} is shown in Fig. 1. Very similar one was obtained by Wang [27]. According to literature data, peak A/B corresponds to redox reaction:

$$NiO + OH^- \rightarrow NiOOH + 1e^-$$
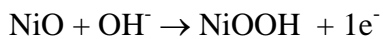
and seems to be an electrochemical response of surface quasi-reversible redox reaction responsible for the pseudocapacitive behaviour of NiO based supercapacitors [7,13,27].
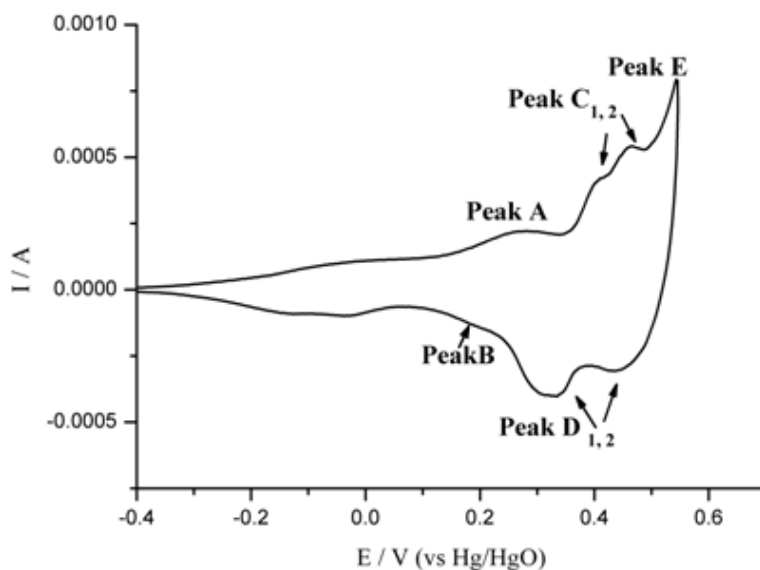

Figure 1. Voltammogram for nickel oxide in 6 M KOH at 0.1 mVs^{-1} sweep rate.

It should be noted that nickel oxide might have also a non-stoichiometric nature; such behaviour was noticed especially for annealing temperature at 300 °C [16].
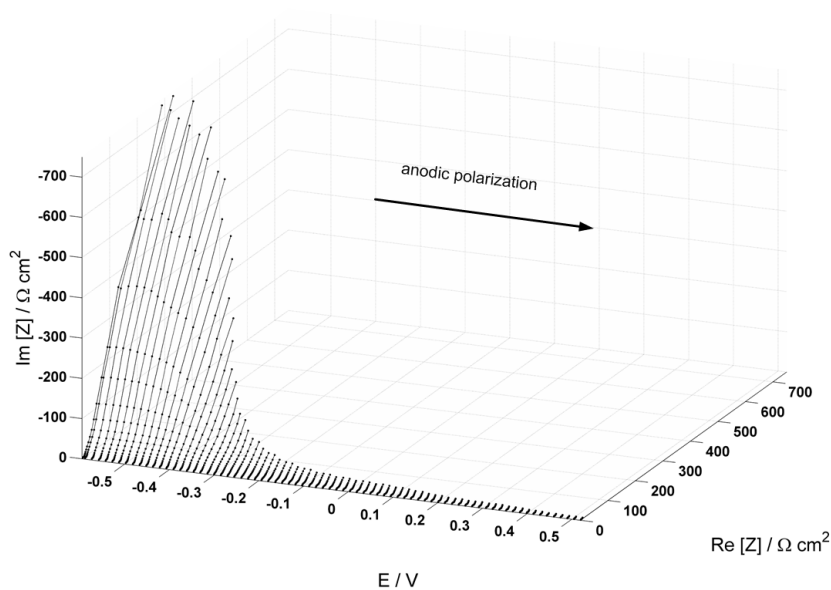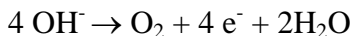

Figure 2a. Impedance spectrogram obtained for anodic polarization (potential range: from -0.4 V to 0.55 V).

Peaks C1/D1 and C2/D2 may correspond to oxidation/reduction of $Ni(OH)_2$ to NiOOH in different crystallographic forms (α-, β-). Taking into account that β-NiOOH can be irreversibly converted to γ-NiOOH D2 can be also responsible for the reduction of $NiOO_2$ (form which contributes in oxygen evolution) [28-30].

Peak E is related to the oxygen evolution:

$$4\ OH^- \rightarrow O_2 + 4\ e^- + 2H_2O$$

The potentiodynamic method allowed to obtain the impedance spectra as a function of changing potential, both for anodic and cathodic polarization. They are presented in Fig. 2a and Fig. 2b, respectively.
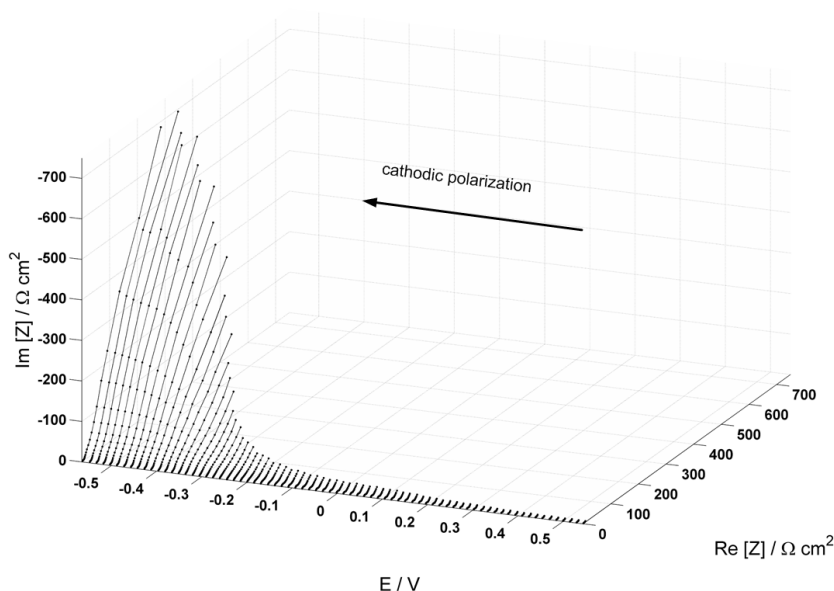
Figure 2b. Impedance spectrogram obtained for cathodic polarization (potential range: from 0.55 V to -0.4 V).
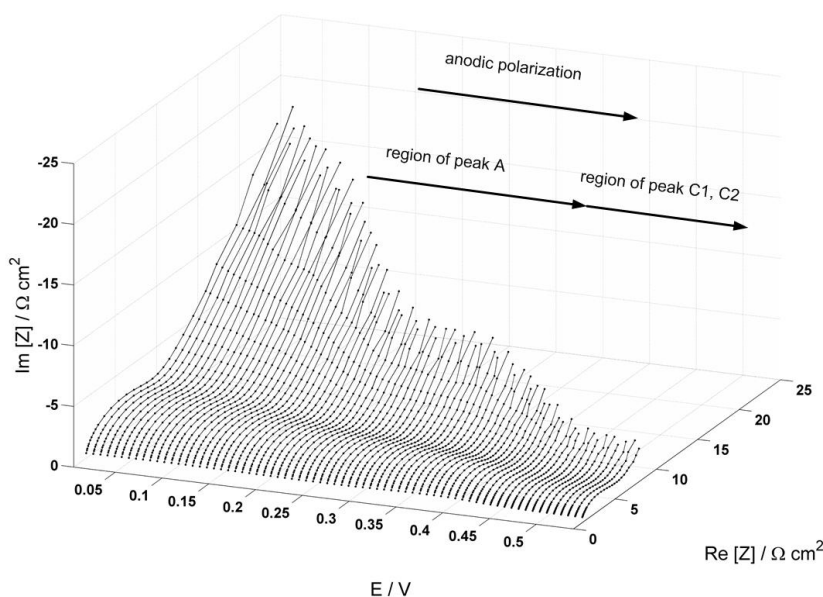

Figure 3a. Magnification of impedance spectrogram for anodic polarization.
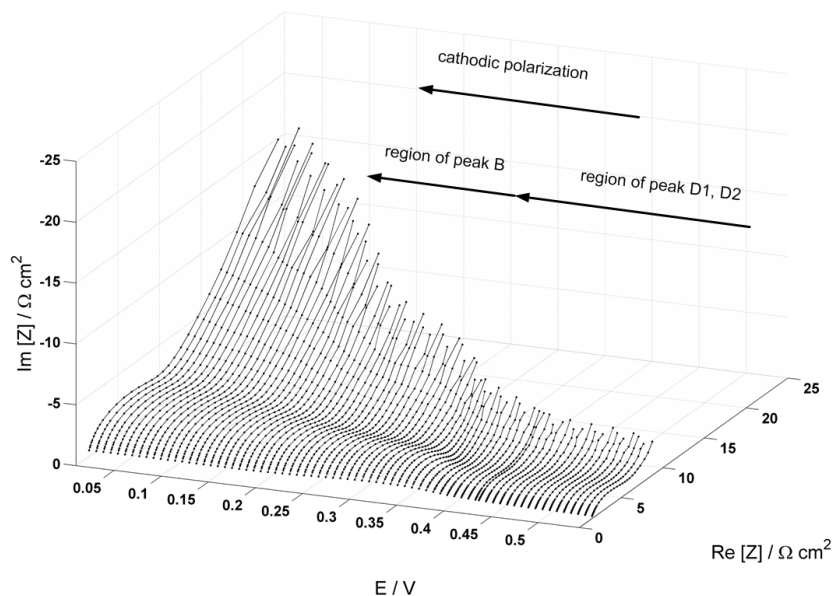
Figure 3b. Magnification of impedance spectrogram for cathodic polarization.

In both figures the increase of impedance at -0.1 V is observed. It suggests that the region below -0.1 V is definitely unfavourable as working potential window for supercapacitors made of nickel oxide, because the faradaic reaction is impeded. The changes of impedance in potential area recommended for supercapacitors are presented in Fig.3a and Fig. 3b.

It can be observed, that at 0.1 V the impedance decreases rapidly (Fig. 3a and Fig. 3b), which corresponds to the quasi-reversible reaction of nickel oxide - peak A/B. Changes in complex capacitance as a function of applied potential were recalculated directly from impedance data using Eq. 1 and Eq. 2. Obtained complex capacitance spectra are presented in Fig. 4a and Fig. 4b, both for anodic and cathodic polarization, respectively.
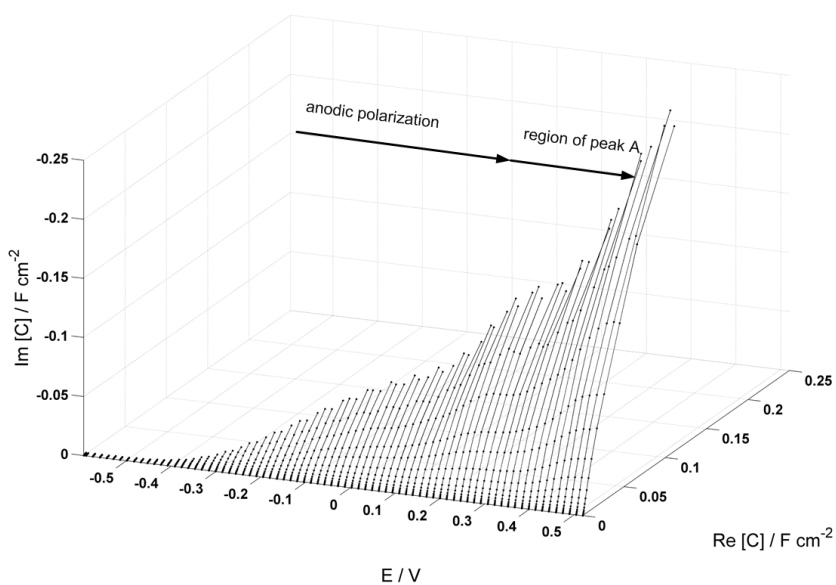

Figure 4a. Capacitance spectrogram obtained for anodic polarization .
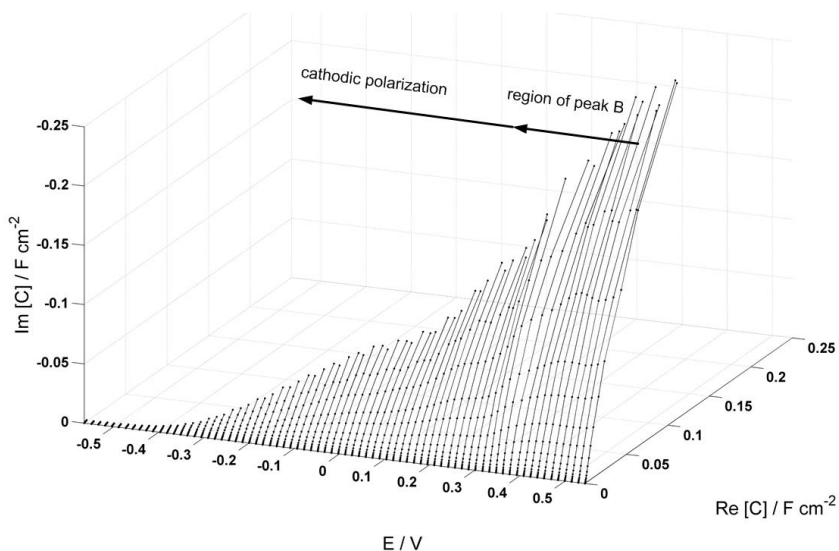
Figure 4b. Capacitance spectrogram obtained for cathodic polarization .

During anodic polarization the capacitance increases (Fig. 4a). The raise of capacitance is much faster in the region of oxidation of NiO to NiOOH (Peak A). However, at higher anodic potentials the capacitance still increases. Similar behaviour can be observed for cathodic polarization (Fig. 4b). Capacitance semicircles were extrapolated and the real part of capacitance at $\text{Re}(C)_{\omega \to 0}$ was estimated for each potential (Fig.5 a, b).
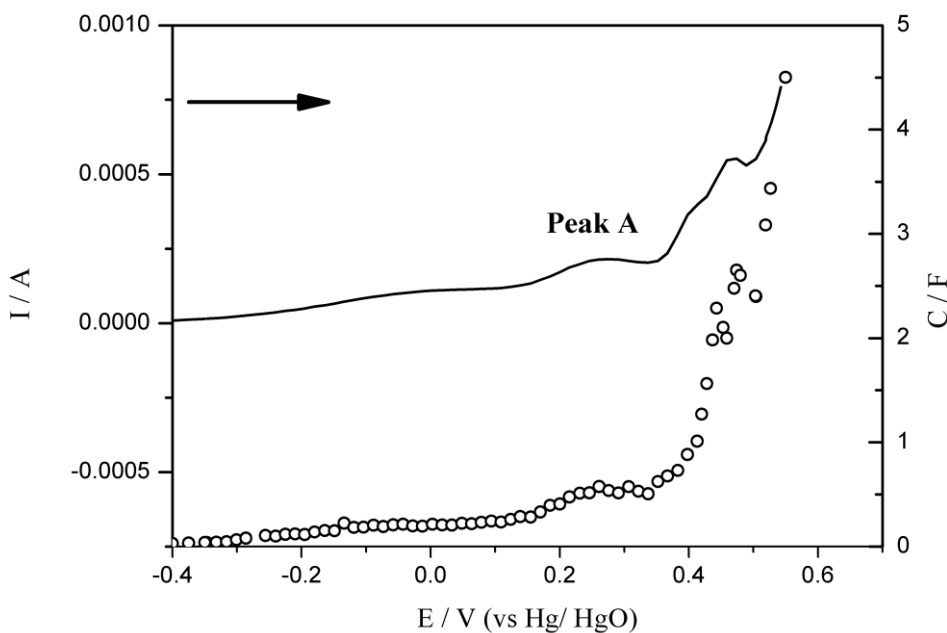

Figure 5a. Changes of capacitance as a function of potential for anodic polarization, where: − current, -○- capacitance.
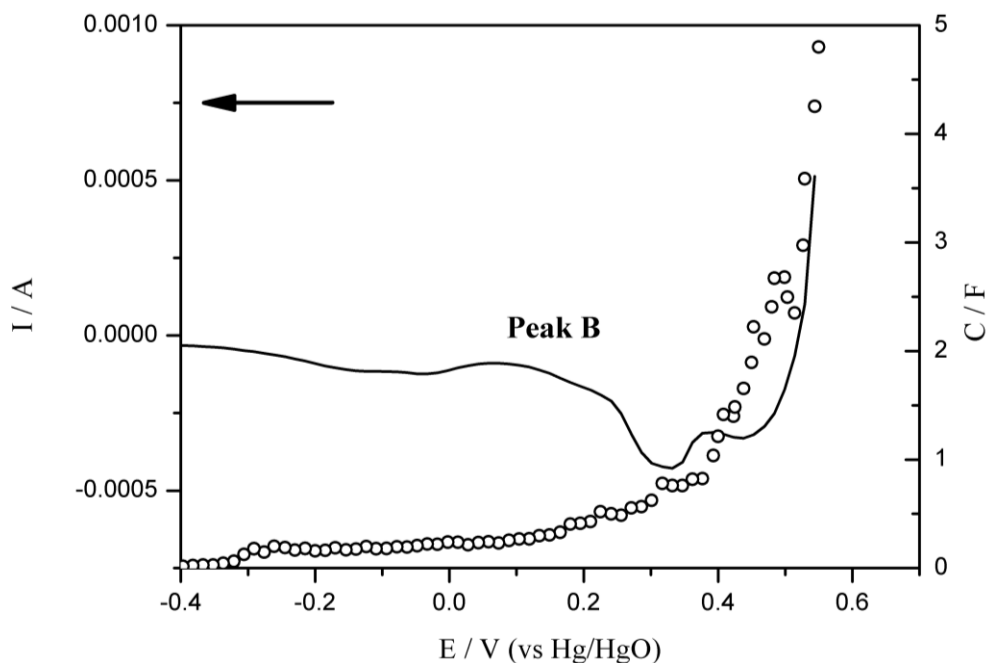
Figure 5b. Changes of capacitance as a function of potential for cathodic polarization, where: − current, -○- capacitance.

Further capacitance increase may be the result of higher current values (what means also lower impedance values, according to Eq.3) or another faradic reaction. According to Nam [11] pseudocapacitance may be the result of surface reaction $NiO \rightarrow NiOOH$ as well as bulk transition reaction of $Ni(OH)_2 \rightarrow NiOOH$ [31].

Nam's assumption is in agreement with the results obtained by DEIS method; this technique also revealed and confirmed the capacitance increase in the region of bulk reaction $Ni(OH)_2 \rightarrow NiOOH$.

If the dependence of capacitance on potential region is known, the question of electrode topography changes followed by capacitance changes should be explained.

According to this question, the topographies of nickel oxide samples at different applied potentials are shown. Because no significant change was observed, only images obtained at - 0.25; 0.2; 0.45 V *vs.* Hg/HgO in 0.6 M KOH are present here, in Fig. 6a - c.

Anyway, taking into account the suggestion proposed in the literature [11] and considering obtained voltammogram (Fig. 1) at -0.25 V, the nickel oxide surface should be covered (but not fully) by $Ni(OH)_2$ and at 0.2 V the surface redox reaction should begin ($NiO \rightarrow NiOOH$); furthermore, at 0.45 V $Ni(OH)_2$ should change into NiOOH in the bulk reaction. However, the results based on electrochemical AFM reveals no significant changes on the surface in the selected area. It may be explained by the same hexagonal crystallographic structure of $Ni(OH)_2$ and NiOOH [32] with discrete changes in c-axis, which could not be observed at applied magnification
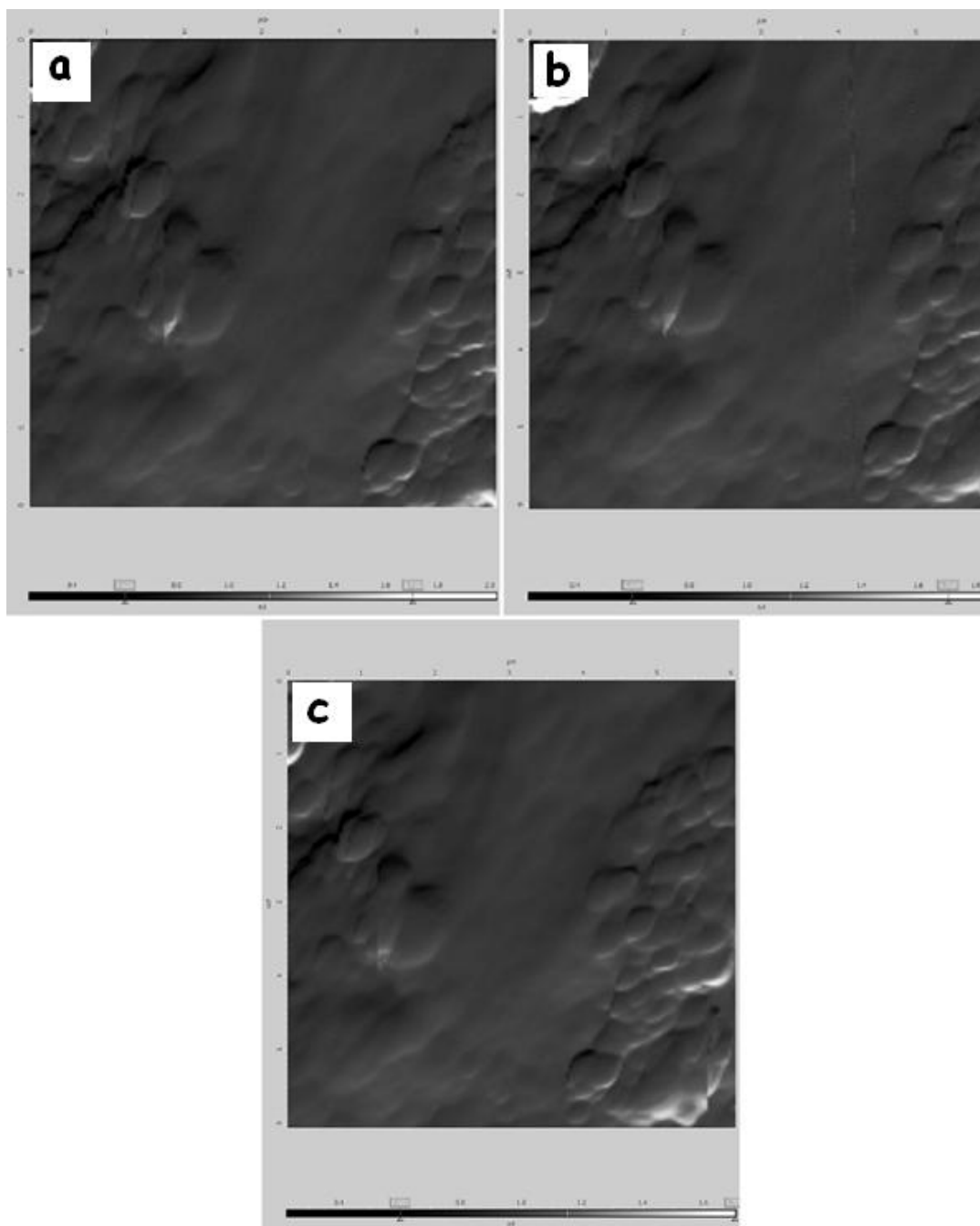
Figure 6. Topography of nickel oxide a: (a) -0.25 V; (b) at 0.2 V and (c) at 0.45 V vs Hg/HgO, respectively.

4. CONCLUSIONS

Using Dynamic Electrochemical Impedance Spectroscopy technique, the changes of capacitance *vs.* potential can be measured, therefore, it also possible to investigate the contribution of pseudocapacitance on total capacitance. This is completely novel approach in investigations on energy storage systems. The results clearly show that the capacitance of supercapacitor increases with anodic polarization. This information strictly confirmed the assumption of Nam et al. [11] that pseudocapacitance is the result of redox reaction $NiO \rightarrow NiOOH$, as well as $Ni(OH)_2 \rightarrow NiOOH$.

According to Conway [19], if faradaic resistance becomes small at high potentials or in case of porous electrode, the double layer capacitance and pseudocapacitance cannot be distinguished. Firstly, the capacitance slowly arises, which in our opinion, can be connected to the capacitance of the double layer, and that value does not change significantly, till the potential of 0.1 V is reached. At this potential the faradaic surface reaction of nickel oxide to nickel oxyhydrooxide proceeds (which is attributed to be responsible for pseudocapacitance), therefore the influence of pseudocapacitance is observed. However, at higher anodic potentials capacitance still increases, even at regions where the nickel hydrooxide transfers to oxyhydrooxides of different structures.

However, based on the obtained results, it is difficult to determine the influence of expanding the potential window towards the values with higher capacitance on supercapacitor efficiency and lifetime. Probably, it could be caused by irreversible reactions which might occur in discussed potential range. Additionally, another consequence could be the decrease of rate capability, being the most important feature of supercapacitors.

This leads us to a conclusion that further research in galvanostatic mode for different potential windows are required. Topographic images did not show any visible changes on the surface of nickel oxide. For the investigated area the reaction of $Ni(OH)_2$ into $NiOOH$ was not observed. This can be the result of very similar hexagonal structure of both compounds (the difference of about 0.1 angstrom could not be observed).

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