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Preparation and characterization of RuO$_2$/polyaniline composite electrodes

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Abstract RuO$_2$–polyaniline (PANI) composites have been prepared by a novel method resulting in a composite material at the electrode surface. The method is based on the utilization of the chemical oxidation of aniline by the RuO$_2$ attached to the gold substrate in acid media. Electrochemical quartz crystal nanobalance combined with cyclic voltammetric and chronoamperometric measurements was used to study the oxidative deposition process as well as the exchange of ions and solvent molecules during cycling. The chemical reaction between RuO$_2$ and aniline results in a surface mass increase at the open circuit, and it also manifests itself in the substantial decrease of the open-circuit potential after addition of aniline into the supporting electrolyte. The potential range, the nature of the electrolyte, and the pH have been varied. The results of the piezoelectric nanogravimetric studies obtained for the redox transformation of RuO$_2$ and the composites are elucidated by the transport of ions and water molecules. It has been shown that the behavior of RuO$_2$ as well as of the composites strongly depends on the spontaneous and potential-dependent solvent sorption, the nature of the electrolyte, and the potential range. It has been found that the value of the specific capacitance was substantially increased by the polyaniline present without any significant deterioration of stability of the capacitor.

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Introduction

Supercapacitors are mostly used as complementary devices to batteries and fuel cells which have high energy densities but cannot supply a high power during short time scale. Because these energy-oriented power sources have been increasingly employed in electric and hybrid vehicles, where during acceleration a high power density is needed or in backup power devices where the fast response is crucial, the application of another unit is inevitable for providing high power for a short time. Supercapacitors [1] are ideal for these purposes, and that is the very reason for the intense quest regarding stable, reversible, and effective electrode materials which can meet the requirements of reversibility, long-term stability, the high storage capacity, and the fast charging/discharging characteristics. Among the different metal oxides, the properly prepared hydrous RuO$_2$, which shows the best properties [2–15], has been proposed for this purpose. Its commercial use is, however, hindered due the its high cost and limited availability. Very different values of the specific capacitance of ruthenium oxide have been found, e.g., 380 F/g obtained for thermally prepared anhydrous form of ruthenium oxide [9], while 600–900 F/g for amorphous hydrated form [7, 15].

Another class of materials which in principle are suitable for supercapacitor applications are the electrically conducting polymers. These materials are cheap and show reversible redox behavior and high capacitance, but their long-term stability is not good enough [16]. The combinations of RuO$_2$ with conducting polymers seem to be a promising attempt to have a possible synergic effect, i.e.,

simultaneously improving the stability and decreasing the cost. Such investigations have been started by using RuO_2 and polyaniline in combination with Nafion [11]. Ir oxide–polyaniline composites have also been studied [12]. The following techniques have been used so far to prepare such composites. Casting chemically prepared polyaniline and Nafion on the electrode surface which was covered by hydrous RuO_2 deposited electrochemically from $RuCl_3 \cdot xH_2O$ solutions [11] or deposition of polyaniline (PANI) by electropolymerization in the pores of IrO_x [12]. Recently, the preparation of RuO_2–poly(3,4-ethylenedioxythiophene) nanocomposite for supercapacitor purpose has been reported [13]. In this case, the precursors were mixed, and a chemical oxidation was applied. It is also possible to mix chemically prepared polyaniline with RuO_2 and then coating the electrode by this composite. Albeit we have tried both the latter methods as well as the electropolymerization of aniline on the top of RuO_2, we will present a third technique which is simple, easily controlled, and resulting in a well-defined, well-dispersed RuO_2–polyaniline composite on the electrode surface. Its essential feature is the use of the oxidation power of Ru(IV), which is the ability of RuO_2 crystals attached to the electrode surface to oxidize the aniline which process resulting in the formation of PANI on the external and internal surfaces of RuO_2 crystals. The reduced ruthenium sites were regenerated by using short potential pulses.

Experimental

H_2SO_4, Na_2SO_4 (Merck, analytical grade), RuO_2 hydrate (Aldrich), and distilled aniline were used. Solutions were prepared with doubly distilled water. All solutions were purged with oxygen-free argon, and an inert gas blanket was maintained throughout the experiments.

Five megahertz AT-cut crystals of 1-in. diameter (Stanford Research Systems, SRS, USA) were used in the electrochemical quartz crystal nanobalance (EQCN) measurements. Each side of the crystals was coated with titanium underlayer and platinum. Only one side of the crystals with a projected surface area of $A=1.22$ cm^2 was exposed to the electrolyte solution. The piezoelectrically active area was equal to 0.33 cm^2. The crystals were mounted in the holder made from Kynar and connected to a SRS QCM100 unit. The polished crystals were optically clear; according to the SRS certification, their average surface roughness was ca. 5 nm. The reference electrode was a sodium chloride-saturated calomel electrode. The Sauerbrey equation was used for estimation of the surface mass changes (Δm) from the frequency changes (Δf), with an integral sensitivity, $C_f = 3.43 \times$

10^7Hzcm^{2}g^{-1} at 20 °C. The value of the integral sensitivity has been determined by using electrochemical silver deposition/dissolution from solutions containing 5×10^{-2} $AgNO_3$. An immersion test, i.e., monitoring the frequency decrease after the complete immersion of the crystal from air in water or H_2SO_4 solutions was also applied to monitor the proper functioning of the crystal. Pt wire was used as a counter electrode.

The RuO_2 particles were attached to the gold surface by wiping the electrode with a cotton swab containing the material [17], and then making use of a drop of distilled water, the microcrystals were fixed. By the help of this procedure, the crystals can be "glued" to the metal. This method of preparing the electrode produces a randomly distributed ensemble of the material on the gold; however, the distribution of particles was more or less uniform according to visual inspection. Although the requirements (uniform and homogeneous surface layer) for the application of Sauerbrey equation are not perfectly met, on the basis of measured frequency values (Δf), a rough estimation can be done. The relative values of Δf obtained for the incorporation of different ions and solvent molecules, however, should be approximately correct. Usually 1–20 μg RuO_2 was deposited and used in these studies. The amount of RuO_2 was determined by measuring the frequency changes caused by the deposition of RuO_2 in dry state. After the treatment described above, the samples remain stably attached to the gold surface, i.e., there was no falling even in dry state.

For the calculation of the apparent molar mass (M) of the species exchanged during the redox processes, the following equations were used:

$$M = \frac{nFA\,\Delta f}{C_f\,Q} \tag{1}$$

where n is the number of electrons transferred in the reaction, F is Faraday constant, A is the acoustically active surface area, and Q is the corrected charge taking into account the ratio of the piezoelectrically active surface area and the geometric surface area exposed to the solution. The values of specific capacitance, C_s, were determined from the cyclic voltammetric curves by using the equation as follows:

$$C_s = Q_{meas}/\Delta Em \tag{2}$$

where Q_{meas} is the charge consumed in the potential interval ΔE and m is the mass of the deposited $RuO_2 \cdot xH_2O$.

An Elektroflex 453 potentiostat and a Universal Frequency Counter TR-5288 connected with an IBM personal computer were used for the control of the measurements and for the acquisition of the data.
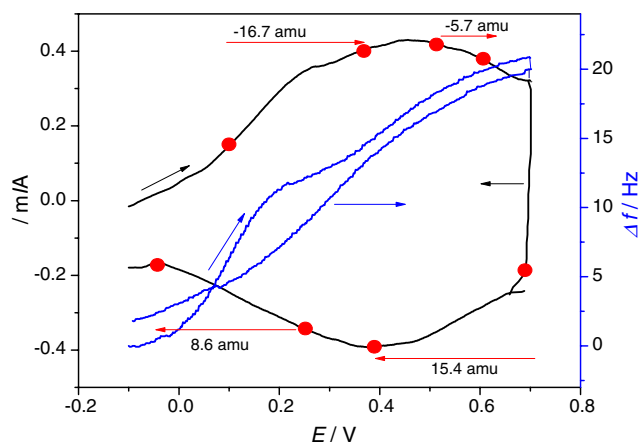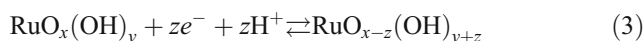
Fig. 1 Cyclic voltammogram and the simultaneously obtained EQCN frequency response for an Au|RuO$_2$ electrode in contact with 0.5 M H$_2$SO$_4$. Scan rate 20 mV s^{-1}. Abbreviation *amu* means atomic mass units
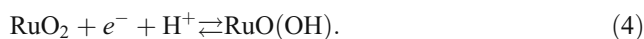
Results and discussion

It is well known that the cyclic voltammetric responses of RuO$_2$ substantially depend on the method of the preparation of the sample [1–10]. While the shapes of the voltammograms are more or less similar, the capacitances may differ by orders of magnitude. The EQCN responses, which have been reported so far in the literature [1, 3, 7], are also different. This phenomenon has been interpreted in terms of crystallinity, structure, and water content of RuO$_2$. Figure 1 shows the characteristic cyclic voltammetric response of the hydrous RuO$_2$ investigated in this work, together with the quartz crystal frequency change during the potential cycling. High anodic and cathodic currents registered throughout the whole potential window investigated con-

firm the suitability of this material in supercapacitor applications. The broad current peak pair in the middle of the potential window is frequently encountered with this type of material and is usually attributed in the literature to the reversible redox processes accompanied by the sorption of H$^+$ ions and water molecules [18, 19]. The quartz crystal oscillating frequency continuously increases during the anodic sweep indicating that the mass release accompanies the oxidation of ruthenium oxide. These results are in accordance with the redox reaction of ruthenium oxide which is in this potential region usually described as follows:

$$RuO_x(OH)_y + ze^- + zH^+ \rightleftarrows RuO_{x-z}(OH)_{y+z} \qquad (3)$$

or simply,

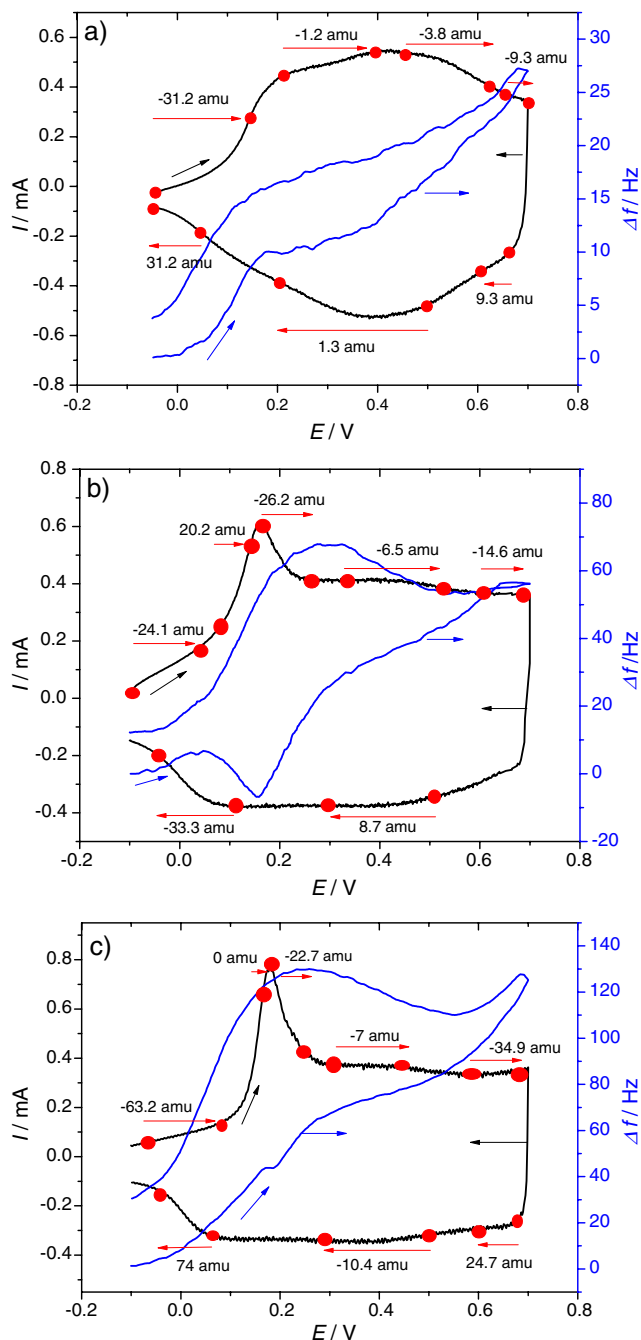$$RuO_2 + e^- + H^+ \rightleftarrows RuO(OH). \qquad (4)$$

The molar masses calculated for the species exchanged during this redox transformation are indicated in Fig. 1 in the corresponding potential regions. The molar mass values are much higher than what is expected for the sorption/desorption of H$^+$ ions. It follows that, beside H$^+$ ions, water molecules also enter/leave the solid phase. In the literature, very diverse values have been reported for the molar mass, from $M=3.2$ [7] to $M=56.3$ g mol^{-1} [1]. In our studies, molar masses ranging from $M=5$ to $M=40$ g mol^{-1} have been found depending not only on the potential range but also on the preconditioning of RuO$_2$ (duration of the swelling in the electrolyte at open-circuit potential or at a given potential, number of cycling) and the scan rate. This is an evidence that the water and ion dynamics during the course of redox reaction of ruthenium oxide are considerably influenced by its structure and hydration.
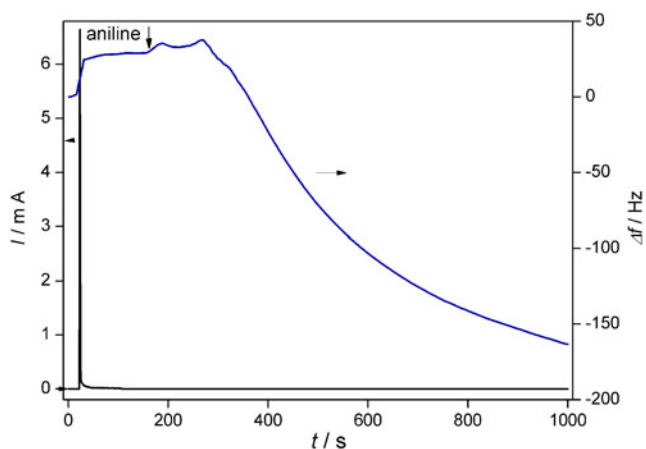
Fig. 2 The EQCN frequency change vs time curve observed for an Au|RuO$_2$ electrode after the addition of aniline into 0.5 M H$_2$SO$_4$ solution at open-circuit potential (0.85 V). The Ru has been oxidized previously (*current peak*); the addition of aniline is indicated by an *arrow*
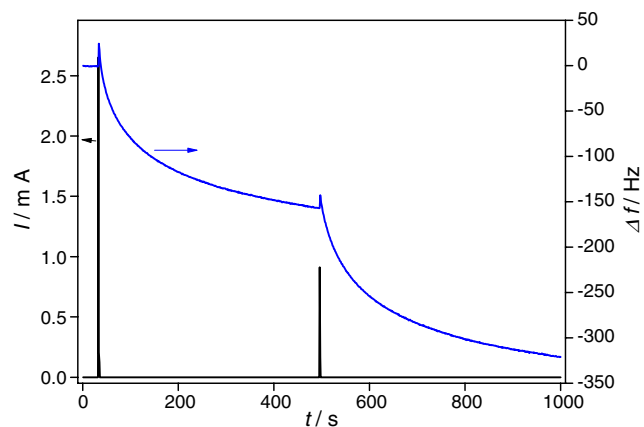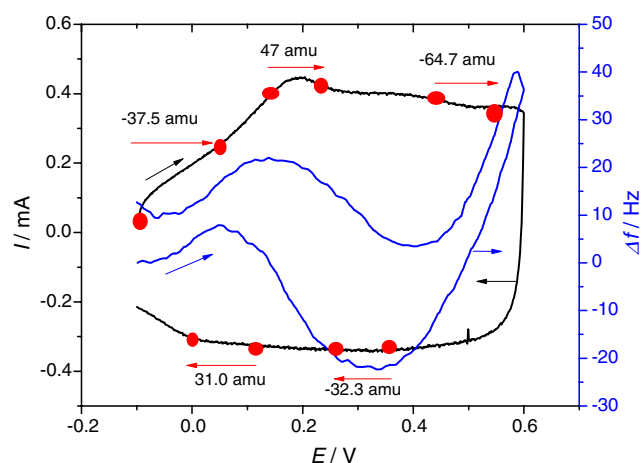

Fig. 3 The continuation of the experiment presented in Fig. 2. The EQCN frequency change vs time curve observed for the Au|RuO$_2$ electrode after two additional reoxidation pulses up to 0.8 V

Fig. 5 Cyclic voltammogram and the simultaneously obtained EQCN frequency response for the Au|RuO$_2$ + PANI described in Fig. 4b at pH 3.5 after addition of Na$_2$SO$_4$ in H$_2$SO$_4$ solution. Scan rate 20 mV s^{-1}. Abbreviation *amu* means atomic mass units

reaction, the equilibrium potential decreases from ca. 0.85 V to a low positive value (0.5 V) where the oxidation of aniline cannot take place. Figure 2 shows the results of such experiments. After addition of aniline (indicated by an arrow) to the acidic solution, a deposition of polyaniline on the previously oxidized RuO$_2$ attached to the gold surface starts. The rate of the deposition decreases as the equilibrium electrode potential decreases as a consequence of the conversion of Ru(IV) sites to Ru(III) or Ru sites of even lower valency. The deposition rate can be enhanced again and repeated several times by short potential pulses (2–3 s) up to 0.7–0.8 V as shown in Fig. 3. Figure 4a–c show the cyclic voltammograms of the resulting RuO$_2$/PANI composite after three successive deposition cycles. The current peaks characteristic of leucoemeraldine/emeraldine
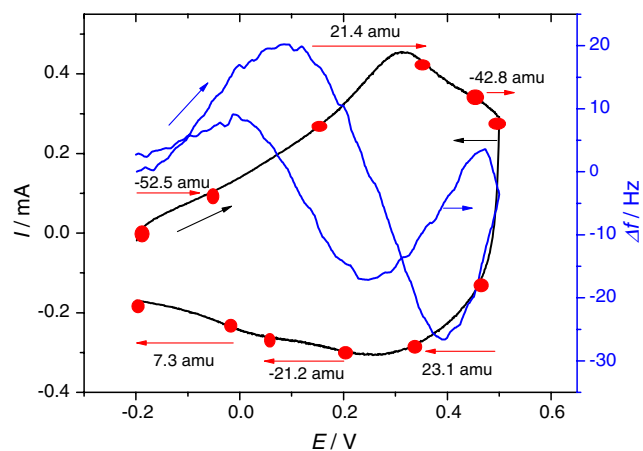

Fig. 4 Cyclic voltammograms and the simultaneously obtained EQCN frequency responses for the Au|RuO$_2$ + PANI electrode prepared by the procedure described above after **a** one, **b** three, and **c** five activation pulses. Scan rate 20 mV s^{-1}. Electrolyte 0.5 M H$_2$SO$_4$. Abbreviation *amu* means atomic mass units

Fig. 6 Cyclic voltammogram and the simultaneously obtained EQCN frequency response for the Au|RuO$_2$ + PANI described in Fig. 4b at pH 7 in 0.5 M Na$_2$SO$_4$ solution. Scan rate 50 mV s^{-1}. Abbreviation *amu* means atomic mass units

Spontaneous deposition of PANI on RuO$_2$ could be achieved by heterogenous redox reaction between RuO$_2$ and aniline dissolved in acidic solutions. Due to its high positive standard potential, RuO$_2$ [20] is able to oxidize aniline resulting in the formation of polyaniline on the surface of RuO$_2$. As a consequence of the chemical redox

redox transformation are clearly visible confirming the deposition of PANI. Also, from the Fig. 4, it could be inferred that the amount of polyaniline on the surface increases with each successive deposition cycle.

The deposition of PANI affects also the overall mass change during the redox transformations of RuO_2/PANI composite. After the potentials of leucoemeraldine/emeraldine transition, the quartz crystal oscillator frequency changes its slope (Fig. 4a) and at higher PANI loadings even a frequency decrease, ie., a mass increase appears. The mass increase for PANI in these potential ranges is a well-known phenomena due to anion uptake upon oxidation of the polymer backbone [16]. The apparent molar masses were indicated on the corresponding cyclic voltammograms, and their values in this case are the result of the combination of the two processes, the expulsion of protons and water from ruthenium oxide leading to mass decrease and anion uptake into the PANI film resulting in the mass increase.

One of the crucial features of the resulting RuO_2/PANI composite is that the electrochemical activity of the polyaniline is remarkably preserved even at higher pH values. Figure 5 shows the results obtained at pH 3.5 for the same electrode by adjusting the pH using Na_2SO_4. In accordance with the known behavior of PANI [16], there is only a slight shift of the leucoemeraldine/emeraldine wave. The EQCN frequency response shows the increased effects of the incorporation of anions at the first oxidation peak, and the desorption of these species at the second one since at this pH value, neither forms of PANI are protonated, and the charge compensating ions are anions, the deprotonation mentioned above plays a minor role if any.

Polyaniline usually does not show any electrochemical activity at pH values higher than 5; however, in this composite, albeit due to the shift of the second pair of waves, the two pairs of waves almost merge; the anion sorption and desorption processes are clearly seen in the region of the oxidation of the reduced and half-oxidized forms of PANI (Fig. 6). In the beginning of the scans, i.e., in the potential region between −0.2 and 0 V, the reversible EQCN frequency response characteristic to the response accompanying the redox transformation of the ruthenium sites also appears. The original responses have been observed again when the electrolyte was replaced by H_2SO_4. The composites show remarkable stability; their reponse do not change during extensive cycling in different media.

Another important feature of the formed RuO_2/PANI composites are their promising properties for supercapacitor applications. For the RuO_2 samples used in this study in contact with 0.5 M H_2SO_4 solution, the specific capacitance was found to be 540 ± 40 F g^{-1} in the potential range of −0.1 and 0.85 V at a scan rate of 20 mV s^{-1}. By PANI deposition, the specific capacitance can be increased as high as by 50% without practical deterioration of the response time or stability. Preliminary experiments showed that after successive cycling in sulfuric acid, the capacitance loss is not higher than 10–15% after 1,000 cycles. Even in some cases, there is an increase of capacitance during cycling which is most likely due to the completion of hydration and sorption of electrolyte which enhances the ionic charge transfer in the pores of RuO_2 and polyaniline. The more detailed study about the capacitive performances of RuO_2/PANI composites is underway.

Conclusions

A new, simple method has been suggested to prepare RuO_2–PANI composite electrodes for supercapacitor applications. The protocol is based on the reaction between Ru (IV) sites of the RuO_2 attached to the electrode surface and aniline added to an acid solution. The Ru sites that had been reduced due to the reaction have been regenerated by the application of short positive potential pulses. This procedure can be carried out as many times as necessary in order to achieve the desirable RuO_2–PANI ratio in the composites. In this way, the capacitance of the supercapacitors can be substantially increased. Furthermore, the stability problem, which is a serious hindrance in respect to the application of conducting polymers in supercapacitors, can be overcomed since this system shows a good long-term stability. It is remarkable that in these composites, the electrochemical activity of polyaniline is preserved even at higher pH values.

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