J. Electrochem. Sci. Eng. **2(1)** (2012) 41-52; doi: **10.5599/jese.2012.0010**

Open Access : : ISSN 1847-9286
www.jESE-online.org

Original scientific paper

Preparation and characterization of RuO_2/polyaniline/polymer binder composite electrodes for supercapacitor applications

SUZANA SOPČIĆ, MARIJANA KRALJIĆ ROKOVIĆ and ZORAN MANDIĆ✉

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, HR-10000 Zagreb, Croatia

✉Corresponding Author: E-mail: zmandic@fkit.hr; Tel.: +385-1-4597164

Received: January 4, 2012; Revised: February 23, 2012; Published: March 22, 2012

Abstract

The composite electrodes consisting of amorphous and hydrous RuO_2, polyaniline and polymeric binder, Nafion® or poly(vinilydene fluoride) were prepared. The electrochemical and pseudocapacitive properties of the prepared electrodes were investigated by cyclic voltammetry and electrochemical impedance spectroscopy. The results show that the responses of composite electrodes are very sensitive to the presence of individual components and their respective ratio in the mixture. The difference in the electrochemical behavior was explained by the different physico-chemical properties of the polymeric binders.

Keywords

RuO_2; polyaniline; supercapacitors, composite electrodes, Nafion®.

Introduction

Transition metal oxides such as ruthenium and manganese oxides are increasingly investigated as active electrode materials for electrochemical supercapacitors. Due to variety of different solid forms and a range of oxidation states they usually show almost flat current profile during linear polarization experiments. Among transition metal oxides showing this type of behavior, ruthenium(IV) oxide, RuO_2, stands out since it exhibits very reversible and reproducible solid state reactions involving redox transitions between Ru(III) and Ru(IV) redox states. The redox response is stable enough allowing the oxide to undergo several thousands of charging/discharging cycles without significant deterioration of its charge storage ability and kinetics [1]. However, the gravimetric capacitance of RuO_2 is very sensitive to the degree of its hydration and crystallinity and in order to be used in widespread applications of Ru-based supercapacitors, its utilization should be maximized.

It has recently been demonstrated that Ru(III)-Ru(IV) solid state redox transition of RuO_2 consists at least of two redox reactions taking place at different rates during its charging and discharging [2]. Fast reaction includes the simultaneous proton/electron exchange according to the generally accepted mechanism:

$$RuO_x(OH)_y + ze^- + zH^+ \Leftrightarrow RuO_{x-z}(OH)_{y+z} \tag{1}$$

whereas additional reaction was proposed to proceed with the incorporation of oxygen into the hydrous RuO_2 matrix during oxidation (Equation 2). The latter reaction was recently defined as dissociative adsorption of water [3].

$$2RuO_2 + 2e^- + 2H^+ \Leftrightarrow Ru_2O_3 + H_2O. \tag{2}$$

Equations (1) and (2) stipulate that both electronic conductivity and proton availability are necessary for good performance of ruthenium oxide in supercapacitor applications. Since the hydration of ruthenium oxide promotes the proton conductivity, while at the same time it hinders the electron transport especially among the ruthenium oxide particles, it is obvious that the compromise between these two effects has to be made. Crystalline forms of RuO_2 give very low gravimetric capacitances due to insufficient hydration and limited rates of proton transport into the deeper layers of oxide, whereas on the other hand, the capacitances up to 720 F/g were achieved with hydrous and amorphous RuO_2 prepared by the sol-gel synthesis method [4]. It is now well established and confirmed by several authors that, in order to achieve the maximal utilization of ruthenium oxide and extract as much charge as possible, two parameters, electronic and protonic conductivity, should be optimized. This is usually done by annealing the amorphous $RuO_2 \cdot xH_2O$ at appropriate temperatures [5-13].

Several strategies were attempted to improve further the RuO_2 utilization and to increase its gravimetric capacitance. One strategy includes the different RuO_2 preparation methods [4, 8-11,14-23], whereas several authors recognized the importance of both intra- and inter-particle electronic conductivities and prepared the composite materials of RuO_2 with various forms of carbon [6,18,19,27-28]. It was observed that nano-structured RuO_2 particles were decisive factor in achieving the high gravimetric capacitance [29,30]. Carefully prepared electrodes with low RuO_2 loadings and good electric contact between RuO_2 and underlying conductive support gravimetric capacitances of RuO_2 as high as 1500 F/g and even higher can be achieved [6,7,13].

Another class of materials showing the promising pseudocapacitive properties is conducting polymers. In contrast to redox mechanism of the transition metal oxides, electrochemical reactions of conducting polymers are usually accompanied by the exchange of anions with surrounding medium. Among these materials, polyaniline (PANI) is the most frequently investigated due to simple synthesis, rich chemistry and electrochemistry along with the stable and reproducible behavior. The gravimetric capacitance of PANI can reach up to 400 F/g and higher comprising a combination of pseudocapacitance and double layer capacitance [31]. Although the potential range of pseudocapacitive behavior of PANI is limited between the two redox transitions, leucoemeraldine/emeraldine and emeraldine/pernigraniline, it could nevertheless be expected that the combination of PANI with RuO_2 might lead to the possible synergic effects resulting in the composite material with improved characteristics for supercapacitor applications.

Several routes for the preparation of RuO_2/PANI composite materials were attempted. Song *et al* [32] deposited electrochemically the hydrous RuO_2 from $RuCl_3$ solutions on the casted PANI/Nafion® support. Deposition of PANI by electropolymerization in the pores of IrO_x [33] was also carried out. The preparation of RuO_2–poly(3,4-ethylenedioxythiophene) nanocomposite for supercapacitor purpose was reported [34]. Recently, the procedure based on the chemical reaction between RuO_2 attached at the electrode surface and aniline from the solution has been developed [35]. This system showed good long-term stability and preserved electrochemical activity at higher pH values.

In this paper, we describe the preparation of the RuO_2/PANI composite by slightly different approach. Electrochemical deposition of PANI was carried out from aniline solution onto the glassy carbon (GC) electrode covered by casted hydrous RuO_2 particles. PANI was deposited in the pores of and between RuO_2 particles, what should lead to an increase in overall capacitance of the RuO_2 electrode by the contribution of the PANI pseudocapacitance. Equally important should be the expected effective increase in the inter-particle electronic conductivity which was shown in some cases to be the limiting factor in achieving high capacitance of high-power supercapacitors. To be as close as possible to practical applications, RuO_2 electrodes were made by mixing the oxide with the polymeric binder of variable amount. Two frequently encountered polymer binders, Nafion® and poly(vinylidene fluoride) (PVDF) were used. Due to their different physico-chemical properties, it is expected that the binders should affect the overall performance of the composite GC/RuO_2/binder/PANI electrodes differently.

Thus, the aim of this work was to prepare the composite electrodes with variable amounts of RuO_2, PANI and binders and to investigate their electrochemical and supercapacitor properties. The optimization of the composition of the composite electrode to achieve maximum capacitance and power was also attempted. The intention was to reveal the role of the individual components in the overall behavior of the composite electrode.

Experimental

Chemicals and materials

The following analytical grade chemicals were purchased: RuO_2 in hydrated and amorphous form, Nafion® 117 (5 % solution in isopropyl alcohol) and poly(vinylidene fluoride) (PVDF) from Aldrich Chemie, N-methyl pyrrolidone (NMP) from Merck, isopropyl alcohol from T.T.T. (Croatia), aniline and H_2SO_4 from Fluka. All solutions were prepared from bi-distilled water. X-ray diffraction and thermogravimetric analysis of the RuO_2 sample were published elsewhere [13].

Preparation of composite electrodes

Particles of the hydrous ruthenium oxide, $RuO_2 \cdot xH_2O$, were dispersed in corresponding binder solution using an ultrasonic bath. Two binders were used, Nafion® in isopropyl alcohol and PVDF in NMP. Homogenized suspensions were casted on the glassy carbon electrode (GC), which was previously polished by Al_2O_3 slurry, washed by bi-distilled water and degreased in ethanol. The electrodes were dried 24 h at room temperature in open air in the case of Nafion® and in vacuum in the case of PVDF. Various quantities of polyaniline (PANI) were electrodeposited onto the composite electrodes by cyclic voltammetry from the solution of 0.1 M aniline in 0.5 M H_2SO_4, in the potential range from -100 to 900 mV vs. Ag/AgCl reference electrode with the scan rate of v = 50 mV/s. The exact compositions of electrodes and their assignations are given in Tables 1 and 2. The same electrode compositions were achieved only in two cases (electrodes XX22 and XX23) since it was not possible to obtain compact composite layer with amount of PVDF higher than 0.05 mg and with amount of Nafion® smaller than 0.025 mg.

Table 1. *Composition of composite electrodes with Nafion® as a binder.*

Electrode	m(RuO$_2$) / mg	m(Nafion®) / mg	Nafion®/RuO$_2$ ratio
RN14	0.04	0.10	2.50
RN15	0.04	0.40	10.0
RN22	0.10	0.025	0.25
RN23	0.10	0.05	0.50
RN24	0.10	0.10	1.00
RN25	0.10	0.40	4.00
RN35	0.46	0.40	0.86

Table 2. *Composition of composite electrodes with PVDF as a binder.*

Electrode	m(RuO$_2$) / mg	m(PVDF) / mg	PVDF/RuO$_2$ ratio
RP11	0.04	0.01	0.25
RP21	0.10	0.01	0.10
RP22	0.10	0.025	0.25
RP23	0.10	0.05	0.50
RP31	0.46	0.01	0.02

Electrochemical characterization of composite electrodes

Two electrochemical methods, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were used to investigate the electrochemical and capacitive properties of prepared composite electrodes. The measurements were done in three-electrode system where the working electrode was as prepared composite on GC substrate, the counter electrode was a Pt-foil and the reference electrode was Ag/AgCl (3M KCl). CV experiments were carried out in an one-compartment cell by the Potentiostat/Galvanostat PAR, model 263A whereas EIS measurements were carried out with lock-in amplifier EG&G PAR, model 5210, connected to the potentiostat.

Electrochemical properties of the prepared composite electrodes were investigated in 0.5 M H_2SO_4 in the potential range from -100 to 1000 mV with the scan rate of v = 50 mV/s. EIS measurements were carried out at dc potential of E_{dc}=0.45 V *vs.* Ag/ AgCl, with the amplitude of 5 mV in the frequency range from 100 kHz to 10 mHz.

Gravimetric capacitances were determined on the basis of RuO$_2$ content.

Results and Discussion

The results obtained indicate that the responses of the composite electrodes are very sensitive not only to their constituents but also to the quantities of the individual components as well as to their ratios.

Figures 1a and 1b show cyclic voltammograms of RuO$_2$/Nafion® composite electrodes of different compositions, RN15 and RN23, respectively, during several cycles of PANI electrodeposition. A brief inspection of the Figures 1a and 1b reveals the importance of Nafion® on the characteristics of composite electrodes. The specific currents and consequently the charge extracted from RN23 electrode are at least an order of magnitude higher than currents obtained for RN15 electrode. In addition, RN15 composite electrode shows close to rectangular shape prior to the PANI deposition (Fig. 1a, black line), which is characteristic for capacitive behavior. As the amount of RuO_2 is increased in RN23 with respect to RN15 electrode, larger deviations from rectangular shape were observed (Figure 1b). These deviations might be the consequence of the poor interparticle contacts among oxide particles of the RN23 electrode since it contains lower Nafion® content comparing to the RN15 electrode (Table 1) leading to the increased overall ohmic resistance. PANI deposition is also influenced by the composition of the composite electrode. The PANI growth seems to be much faster in the case of RN15 compared to RN23 composite electrode with well resolved current peaks corresponding to the well known leucoemeraldine/emeraldine and emeraldine/pernigraniline redox transitions superimposed onto the RuO_2 capacitive current. In the case of RN23 electrode, the PANI deposition causes only negligible change in cyclic voltammograms (Figure 1b).

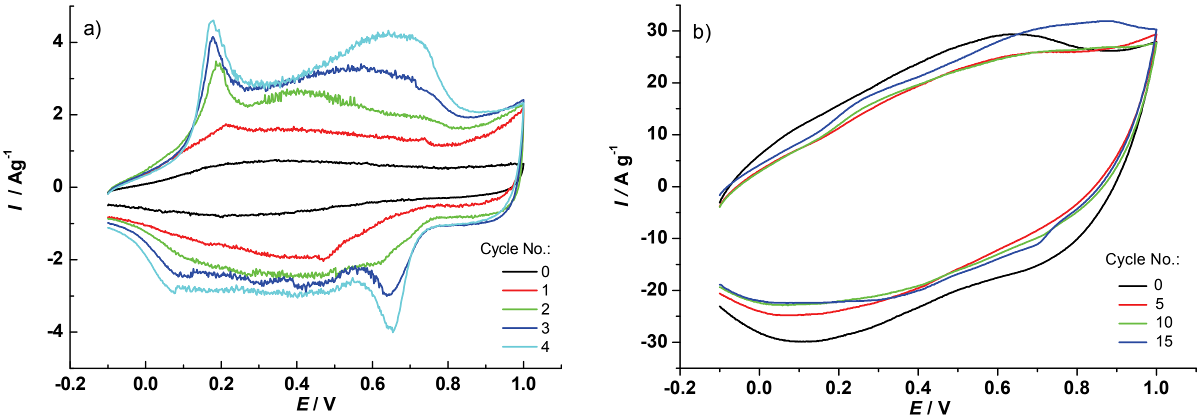

Figure 1. *Cyclic voltammograms of a) RN15 and b) RN23 composite electrode during several voltammetric cycles of the PANI electrodeposition. Scan rate = 50 mV/s.*

Cyclic voltammograms of the composite electrodes with PVDF (Figure 2, black lines) as a binder show very broad anodic peak at about 0.5 V, which is commonly observed in the cyclic voltammograms of hydrous $RuO_2 \cdot xH_2O$ [6-8,25]. It is usually explained by the reversible processes which accompany the sorption of protons and water molecules [38,39]. In contrast to the composite electrodes prepared with Nafion® as a binder, PVDF influences the specific currents in the opposite way. With the decrease in RuO_2 content relative to the PVDF, an increase of specific currents was achieved.

Cyclic voltammograms recorded during the deposition of PANI through several voltammetric cycles are also shown in Figures 2a and 2b. In the first few cycles of PANI deposition the specific current was somewhat decreased, while at later stages the continuous specific current increase was observed. The effect of PANI deposition is even more pronounced for RP21 electrode since high currents characteristic for RuO_2 disappear at the potentials higher than 850 mV, at which the conductive emeraldine form of PANI transforms into the non-conductive pernigraniline state. It seems that in this case non-conductive pernigraniline form increases inter-particle resistance and resistance between particles and the current collector resulting in the sudden current decrease in the pernigraniline potential region. It is interesting to note that such behavior was not obtained in the case when Nafion® was used as a binder (Figure 1). Further synthesis of PANI leads for all compositions of PVDF electrodes to the overall current increase due to the contribution of PANI redox reactions. Obviously, the polymerization process as well as the resulting properties of the electrodes with PVDF binder is different from those obtained when Nafion® is used.

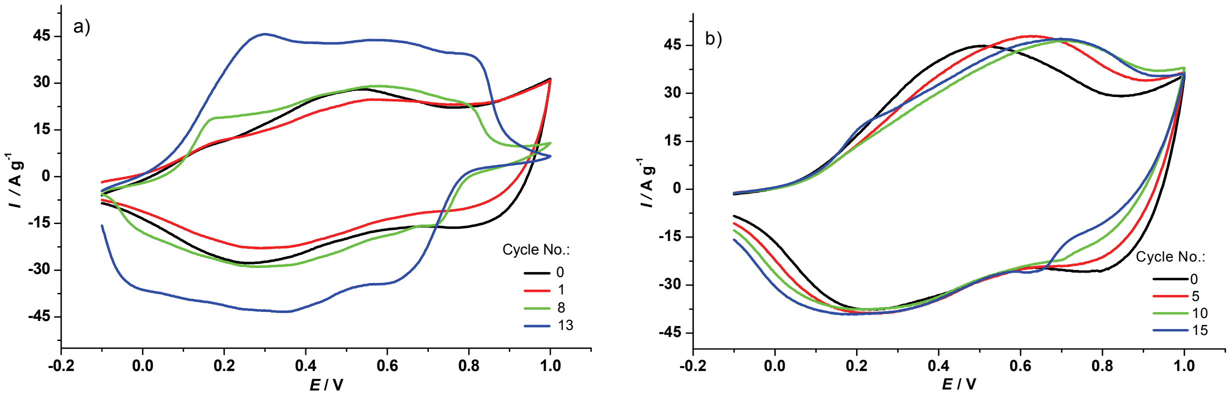

***Figure 2**. Cyclic voltammograms of (a) RP21 and (b) RP23 composite electrodes during several cycles of PANI deposition. Scan rate = 50 mV/s.*

Although the shape of cyclic voltammograms and current heights can reveal important information about the system studied, in the investigations aimed to the development of electrodes for supercapacitor applications more important quantity is the gravimetric capacitance, C_s. The gravimetric capacitance for the investigated composite electrodes could be determined from the cyclic voltammograms according to the Equation 1. The results obtained for the Nafion® and PVDF composite electrodes are shown in Figures 3a and 3b, respectively, as plots of gravimetric capacitance versus voltammetric cycles of PANI deposition.

$$C_s = \frac{Q}{(2\Delta E m)} \tag{1}$$

Q is the sum of anodic and catodic charges obtained by the integration of cyclic voltammograms in the potential interval ΔE, and *m* are the mass of casted RuO_2.

The data shown on Figure 3 could be analyzed from two different standpoints. The data values belonging to y-axis correspond to the gravimetric capacitances of electrodes composed of various RuO_2/Nafion® (Figure 3a) and RuO_2/PVDF (Figure 3b) ratios. The curves representing the dependence of gravimetric capacitance on the number of voltammetric cycles reveal the influence of PANI on the overall capacitance of the particular composite electrode. The analysis of the obtained results indicates the significant influence of the binder, its chemical structure or/and its physico-chemical properties on the overall behavior of RuO_2 composite electrode. While Nafion® exerts a negative influence, *i.e*. gravimetric capacitance decreases with the increase of Nafion® content relative to RuO_2, the gravimetric capacitance of RuO_2/PVDF composite electrodes shows completely opposite behavior (Figure 3c). With the increase of PVDF content relative to RuO_2 the overall capacitance increases. The highest RuO_2 gravimetric capacitance of 526 F g^{-1} was obtained for the RP11 composite electrode.

The formation of PANI on the surface and inside the pores of RuO_2/Nafion® composite electrodes contributes to the gravimetric capacitances although for some composite electrodes (RN22, RN23, RN24, RN35) slight decrease of the overall charge was observed after a few voltammetric cycles. The trend depends on Nafion®/RuO_2 ratio and decrease in charge is obtained in the cases when this ratio was less than 1.

In contrast to the RuO_2/Nafion® composite electrodes, deposition of PANI on RuO_2/PVDF electrode leads to the capacitance decrease in the first few voltammetric cycles but later on the capacitances steadily increase indicating the contribution of PANI redox reactions to the total charge of the composite electrodes.

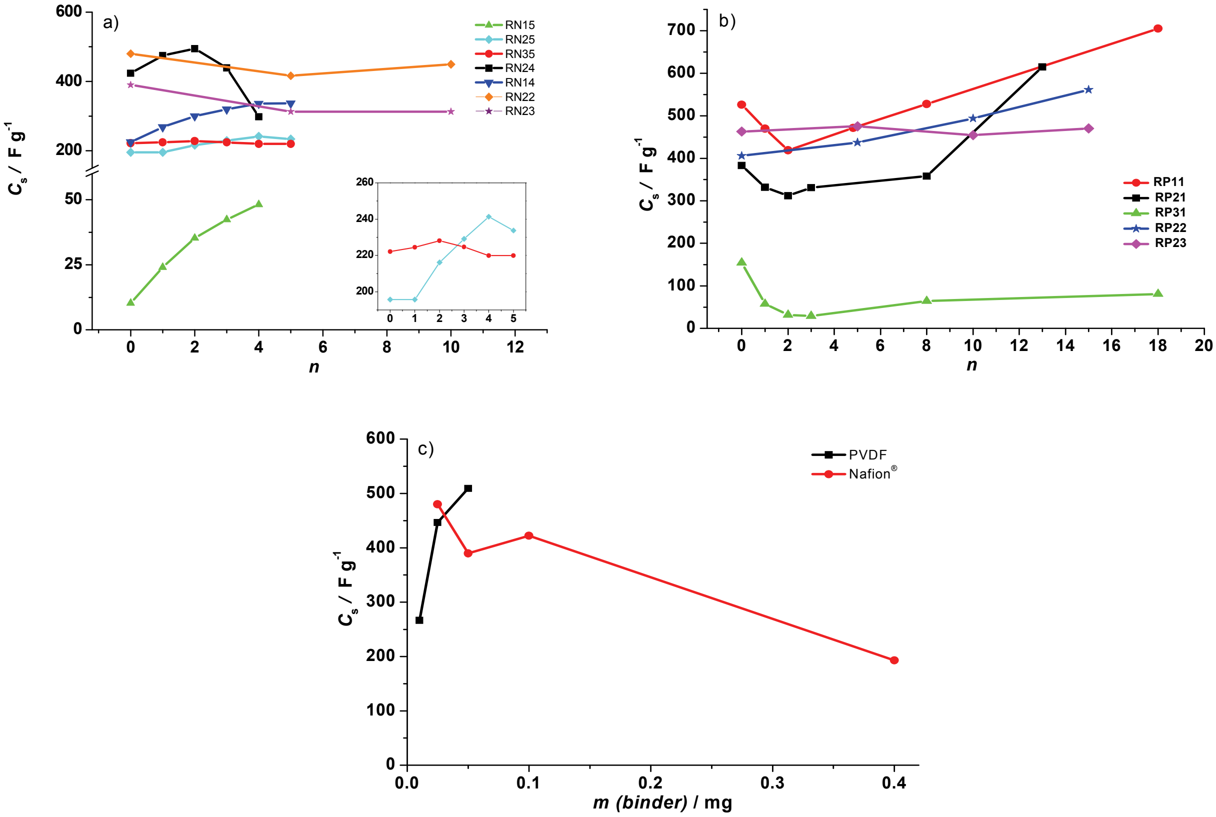

***Figure 3**. Dependence of the specific capacitance,* C_s*, on the number of voltammetric cycles of PANI deposition,* n*, for a)* RuO_2*/Nafion® composite electrodes, b)* RuO_2*/PVDF composite electrodes, c) the comparison of* C_s *dependence for the two composite electrodes* (n = 0)*,* m(RuO_2) = 0.1 mg

In order to get a deeper insight into the origins of such a peculiar behavior of the RuO_2 electrode and the role individual components play in the electrochemical properties of the composite electrodes, further investigations by the electrochemical impedance spectroscopy (EIS) were carried out. In Figures 4a and 4b Bode plots for the various compositions of RuO_2/Nafion® and RuO_2/PVDF electrodes are shown, respectively. Depending on the frequency range three regions of impedance response could be distinguished, resistive behavior at high frequencies, capacitive-like response at low frequencies and, in some cases, diffusion-like behavior in the intermediate frequency range. These impedance responses were usually observed for the porous electrodes involving RuO_2 pseudocapacitive behavior [9,38,39]. Diffusion characteristics are frequently explained by the rate-limiting transport of ions, mainly protons, into the deeper layers of porous and hydrous RuO_2.

Figure 4a displays impedance spectra of three composite electrodes prepared with Nafion® as a binder with the same amount of Nafion® and various amounts of RuO_2. Depending on the composite, various processes dominate the impedance spectra. All three composites show capacitive response at low frequencies. However, for the electrodes with relatively low RuO_2 content, the onset of the capacitive responses falls in the range of 1-10 Hz. For RN35 electrode, the electrode with very high RuO_2 and low Nafion® content, in the same frequency range a process controlled by diffusion appears and the onset of the capacitive response is shifted toward lower frequencies. On the other hand, the electrodes with very low RuO$_2$ content (RN15) exhibit in the high frequency range a behavior which could be modeled with parallel resistive/capacitive combination. This is probably due to increased inter-particle resistance caused by their separation by Nafion® chains or poor contact between oxide particles and GC support.

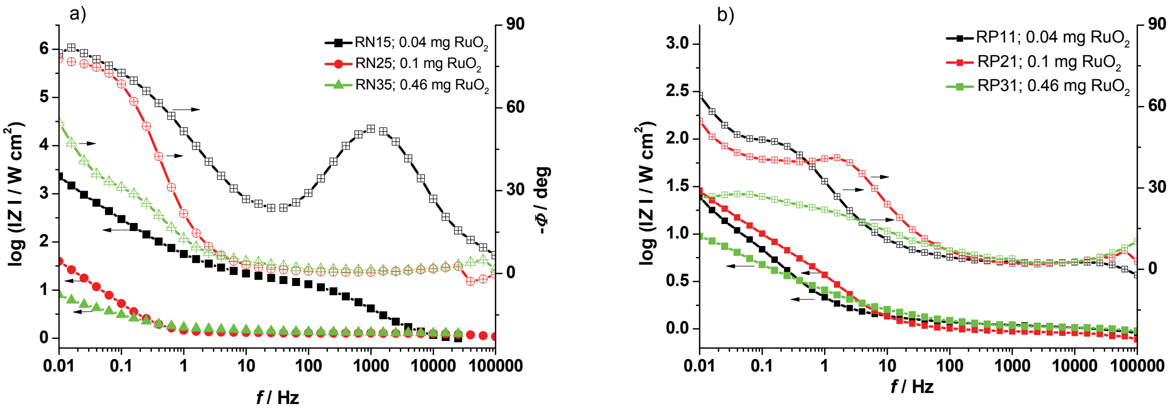

***Figure 4**. Bode plots of a) RuO$_2$/Nafion® and b) RuO$_2$/PVDF composite electrodes*

As impedance spectra were concerned, composite electrodes with PVDF as a binder (Figure 4b) behaved differently from the RuO$_2$/Nafion® composites. None of the RuO$_2$/PVDF composites showed resistive/parallel combination in high-frequency region of impedance spectra similar to RN15 electrode. However, diffusional process in the intermediate frequency range was observed for almost all composites.

PANI deposition causes the EIS spectra of RuO$_2$/Nafion® and RuO$_2$/PVDF composite electrodes to change. The changes in the impedance spectra during each successive voltammetric cycle are shown in Figures 5a and 5b, respectively. The changes depicted in the Figure 5 are mostly located in the medium, diffusion region of the frequency range. However, surprising observation was that in the case of RuO$_2$/Nafion® composite, each successive cycle of PANI deposition promotes diffusion process (Figure 5a), while on the other hand, diffusion process usually observed for RuO$_2$/PVDF electrode is hindered and starts to disappear with PANI deposition (Figure 5b).

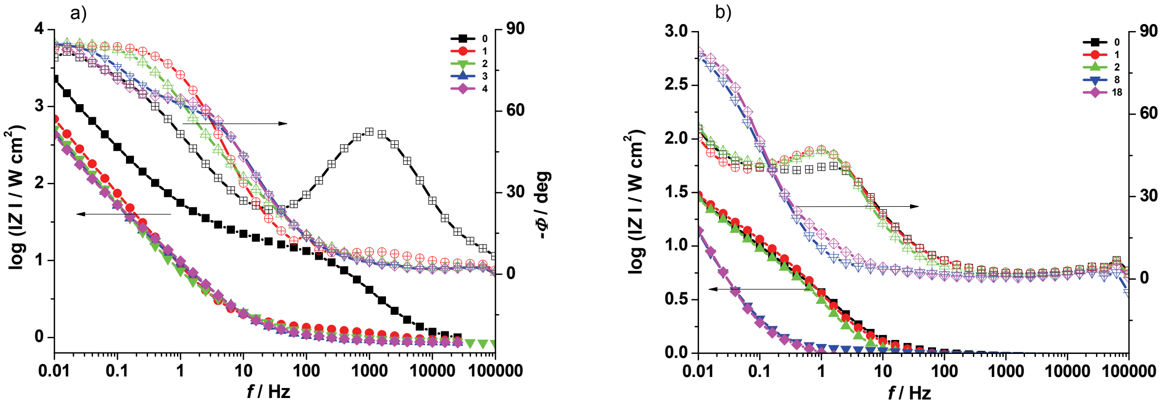

***Figure 5.** Bode plots of the composite electrodes, a) RN15 and b) RP21 at different voltammetric cycles of PANI deposition*

Specific capacitance values obtained from EIS (Table 3) are in a very good agreement and indicate the same trend as C_S values obtained from cyclic voltammetry. From the Table 3 it is also evident that C_S values obtained from EIS are higher compared to cyclic voltammetry values. These values are obtained using complex non-linear least square (CNLS) fitting of data in ZsimpWin program. The electrical equivalent circuit used in modeling procedure consisted of the parallel combination of Warburg diffusion impedance, Z_W, and constant phase element, Q, all in series with the solution resistance, R_s. Some C_s are estimated from $C=1/\omega Z''$ at 0.01 Hz, and for the two results (RN35 and RP11) it was not possible to obtain good fit or to estimate C_s. This could be explained by the fact that diffusion behavior which dominates in wide frequency range influences capacitive response in the low frequency range.

***Table 3**. C_s values obtained from CV and EIS of the RuO_2/binder electrodes for various compositions*

Electrode	C_s / F g^{-1} (CV)	C_s / F g^{-1} (EIS)
RN14	224	275
RN15	10.4	12.4
RN22	482	687
RN23	391	446
RN24	423	519
RN25	199	219
RP21*	381	671
RP22	409	526
RP23	437	770
RP31*	155	330

*C_s (EIS) values are estimated from $C = 1/\omega Z''$ at 0.01 Hz.

The reason for such an unusual behavior of the RuO_2/binder/PANI electrodes is obviously due to the specific inter-molecular interactions among various components. Although at the first glance two binders have similar chemical structure, there is, in fact, a tremendous difference in physico-chemical properties between them. Nafion® consists of two distinct domains, hydrophilic one around sulphonic groups, which exist at the end of the side chains of the hydrophobic polymer backbone. This is in contrast to the PVDF composed of completely hydrophobic chains. The sulphonic groups in Nafion® are able to interact with charged species and hydrophilic environment. When the RuO_2/Nafion® composite is formed, it is reasonable to assume that the sulphonic groups are oriented toward the hydrous RuO_2 surface effectively enveloping and blocking the solid particles with Nafion® chains, as depicted in Figure 6. The blocking effect of Nafion® is demonstrated by the decrease of gravimetric capacitance (Figures 3a and 3c) as well as by the disappearance of processes related to the diffusion of ions into the deeper layers and pores of RuO_2 (Figure 4a). The deposition of PANI on the RuO_2/Nafion® composite electrode removes Nafion® from the surface of RuO_2 due to energetically more favored ionic attraction between positive PANI backbone and sulphonic groups. In fact, sulphonic groups might play a role of counter-ions during PANI synthesis as well. The result is the liberation of the RuO_2 surface by PANI deposition enabling its unhindered oxidation and reduction including the transport of species into deeper layers what is manifested as a diffusion appearing in the middle frequency range during PANI deposition (Figure 5a).

PVDF binder, due to its hydrophobicity, forms separate isolated domains within its composite with RuO_2 and does not hinder the reactions of RuO_2 active sites by blocking the oxide surface (Figure 6). PVDF has no affinity toward PANI either and the deposition of PANI leads to the coverage of RuO_2 surface interfering with the RuO_2 redox reactions, especially those requiring transport of ionic species. As a result, the disappearance of diffusion characteristic was observed (Figure 5b) and total charge extracted after the initial decrease continuously increases due to the contribution of PANI redox reactions.

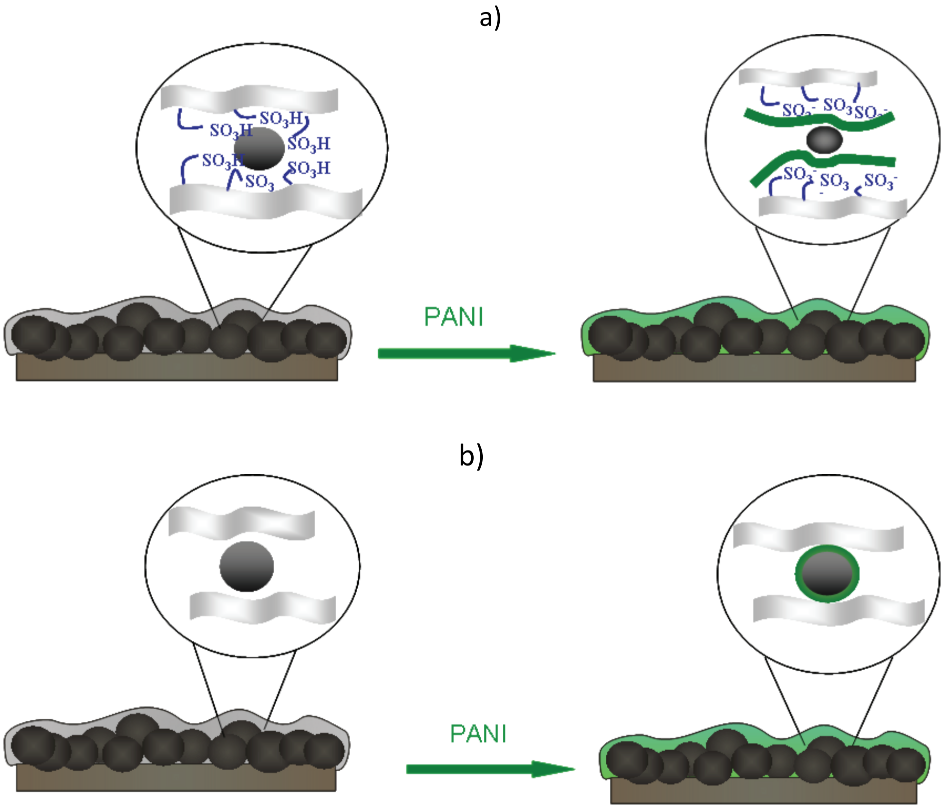

***Figure 6**. Schematic view of PANI growth within the composite electrodes of:*
a) RuO$_2$/Nafion$^{®}$ and b) RuO$_2$/PVDF.

The data presented in this paper reveal the importance of understanding of all properties of the components involved and interactions they undergo with each other in construction of the RuO$_2$ electrode with desired properties for supercapacitor applications. In order to prepare efficient capacitive electrode, one has to keep in mind its particular application. If high power supercapacitors are aimed, the electrodes exhibiting no diffusion processes, such as RN15 and RN25, are favorable. On the other hand, if high energy devices are needed, RuO$_2$/PDVF/PANI composite electrodes are preferable. Finally, in high energy devices for the applications with intermittent high current demand, the electrodes with the low Nafion$^{®}$ contents would be the composition of choice.

Conclusions

For the construction of active electrodes for supercapacitor applications consisting of hydrous ruthenium oxide, with or without polyaniline, one has to pay particular attention to the exact composition and amount of additives used in the manufacturing process. Different physico-chemical properties of polymeric binders influence the overall behavior of composite electrodes differently. Nafion consisting of perfluorinated chains having hydrophilic sulphonic groups attached on side-chains tends to block the surface of RuO$_2$, preventing deeper layers charging/discharging reactions. This decreases the overall capacitance of the RuO$_2$ but on the other hand enables its applications in the high-power devices.

Poly(vinlydene fluoride) forms separate domains within the composite electrode leaving the surface of RuO_2 free for the ionic transport which accompanies charging/discharging reactions. As a result, higher amount of RuO_2 material is utilized and consequently higher energy electrodes can be constructed, but with limited ability for high power applications.

Acknowledgements: *This work is supported by the national research project No 125-1252973-2576 from the Ministry of Science, Education and Sports of the Republic of Croatia. The authors wish to thank Višnja Horvat Radošević and Krešimir Kvastek for fruitful discussion related to this work.*

References

[1] K.H. Chang, C.C. Hu, *Appl. Phys. Lett.* **88** (2006) 193102
[2] S. Sopčić, M. Kraljić Roković, Z. Mandić, A. Róka, G. Inzelt, *Electrochim. Acta* **56** (2011) 3543-3548
[3] P. Kurzweil, *J. Power Sources* **190** (2009) 189-200
[4] J. P. Zheng , T.R. Jow, *J. Electrochem. Soc.* **142** (1995) L6-L8
[5] J. P. Zheng , P.J. Cygan, T. R. Jow, *J. Electrochem. Soc.* **142** (1995) 2699-2703
[6] C.C. Hu, W. C. Chen, K. H. Chang, *J. Electrochem. Soc.* **151** (2004) A281-A290
[7] O. Barbieri, M. Hahn, A. Foelske, R. Kötz, *J. Electrochem. Soc.* **153** (2006) A2049-A2054
[8] K. H. Chang, C. C. Hu, *J. Electrochem. Soc.* **151** (2004) A958-A964
[9] C. C. Hu, Y. H. Huang, K.H. Chang, *J. Power Sources* **108** (2002) 117-127
[10] I. H. Kim, K. B. Kim, *J. Electrochem. Soc.* **153** (2006) A383-A389
[11] J.H. Jang, A. Kato, K. Machida, K. Naoi, *J. Electrochem. Soc.* **153** (2006) A321-A328
[12] A. Foelske, O. Barbieri, M. Hahn, R. Kötz, *Electrochem. Solid St. Lett.* **9** (2006) A268-A272
[13] S. Sopčić, Z. Mandić, G. Inzelt, M. Kraljić Roković, E. Meštrović, *J. Power Sources* **196** (2011) 4849-4858
[14] V. Horvat Radošević, K. Kvastek, M. Vuković, D. Čukman, *J. Electroanal. Chem.* **482** (2000) 188-201
[15] C. C. Hu, Y. H. Huang, *J. Electrochem. Soc.* **146** (1999) 2465-2471
[16] K. Kvastek, V. Horvat-Radošević, *J. Electroanal. Chem* **511** (2001) 65-78
[17] T.R. Jow, J.P. Zheng, *J. Electrochem. Soc.* **145** (1998) 49-52
[18] J. Zhang, D. Jiang, B. Chen, J. Zhu, L. Jiang, H. Fang, *J. Electrochem. Soc.* **148** (2001) A1362-A1367
[19] V. Panić, T. Vidaković, S. Gojković, A. Dekanski, S. Milonjić, B. Nikolić, *Electrochim. Acta* **48** (2003) 3805-3813
[20] V. Panić, A. Dekanski, S. Gojković, V. Mišković-Stanković, B. Nikolić, *Mater. Sci. Forum* **453-454** (2004) 133-138
[21] V. Panić, A. Dekanski, S. Milonjić, R. Atanasoski, B. Nikolić, *Electrochim. Acta* **46** (2000) 415-421
[22] I. H. Kim, K. B. Kim, *Electrochem. Solid St. Lett* **4** (2001) A62-A64
[23] K. H. Chang, C. C. Hu, *Electrochem. Solid St. Lett* **7** (2004) A466-A469
[24] V. Panić, A. Dekanski, S. Gojković, S. Milonjić, V. Mišković-Stanković, B. Nikolić, *Mater. Sci. Forum* **494** (2005) 235-240
[25] I.H. Kim, J.H. Kim, Y.H. Lee, K.B. Kim, *J. Electrochem. Soc.* **152** (2005) A2170-A2178
[26] M. Min, K. Machida, J.H. Jang, K. Naoi, *J. Electrochem. Soc.* **153** (2006) A334-A338
[27] M. Ramani, B. Haran, R. White, B. Popov, *J. Electrochem. Soc.* **148** (2001) A374-A380
[28] V.V. Panić, A.B. Dekanski, R.M. Stevanović, *J. Power Sources* **195** (2010) 3969-3976
[29] V. Barranco, F. Pico, J. Ibanez, M.A. Lillo-Rodenas, A. Linares-Solano, M. Kimura, A. Oya, R.M. Rojas, J.M. Amarilla, J.M. Rojo, *Electrochim. Acta* **54** (2009) 7452–7457.

[30] F. Pico, J. Ibanez, M.A. Lillo-Rodenas, A. Linares-Solano, R.M. Rojas, J.M. Amarilla, J.M. Rojo, *J. Power Sources* **176** (2008) 417–425.

[31] Z. Mandić, M. Kraljić Roković, T. Pokupčić, *Electrochim. Acta*, **54** (2009) 2941-2950

[32] R.Y. Song, J.H. Park, S.R. Sivakkumar, S.H.Kim, J.M. Ko, D.-Y Park, S.M. Jo, D.Y. Kim, *J. Power Sources* **166** (2007) 297- 301

[33] K.-M. Lin, K.-H. Chang, C.-C Hu, Y.-Y Li, *Electrochim. Acta* **54** (2009) 4574-4581

[34] L. Chen, C. Yuan, B. Gao, S. Chen, X. Zhang, *J. Solid State Electr.* **13** (2009) 1925-1933

[35] S. Sopčić, M. Kraljić Roković Z. Mandić, G. Inzelt, *J. Solid State Electr.* **14** (2010) 2021-2026

[36] W. Sugimooto, T. Kizaki, K. Yokoshima, Y. Murakami, Y. Takasu, *Electrochim. Acta* **49** (2004) 313-320

[37] S. Trasatti, G. Buzzanca, *J. Electroanal. Chem.* **29** (1971) A1-A5

[38] R. Kötz, M. Carlen, *Electrochim. Acta* **45** (2000) 2483-2498

[39] X. Liu, P. G. Pickup, *J. Power Sources* **176** (2008) 410-416