

# Deposition of polyaniline on RVC electrodes: effect of substrate thickness

Carla Dalmolin · Sonia R. Biaggio ·  
Romeu C. Rocha-Filho · Nerilso Bocchi

Received: 15 April 2006 / Revised: 28 June 2006 / Accepted: 11 July 2006 / Published online: 23 September 2006  
© Springer-Verlag 2006

**Abstract** Polyaniline films, obtained by either chemical or electrochemical deposition on reticulated vitreous carbon (RVC), were investigated as a function of the substrate thickness. The electrochemical properties of these RVC/Pani electrodes were assessed by cyclic voltammetry and electrochemical impedance spectroscopy (EIS), whereas the morphology of the Pani films on RVC was analyzed by scanning electron microscopy (SEM). The cyclic voltammetric results revealed that the oxidation/reduction charges for electro-deposited polyaniline decrease as the RVC thickness is increased. Conversely, the charge densities for the chemically deposited films do not present a significant dependence on the substrate thickness. Two time constants, appearing in all the EIS spectra, indicate that an ohmic drop effect within the RVC substrate affects the polymer electrodeposition and the electrochemical behavior of the obtained electrodes. Therefore, an electric equivalent circuit considering the different electrochemical environments at the outer and inner RVC surfaces was proposed to analyze the EIS data.

**Keywords** Polyaniline electrodeposition · Reticulated vitreous carbon · Impedance spectroscopy · Tridimensional electrodes · RVC thickness

## Introduction

Wang [1] originally introduced reticulated vitreous carbon (RVC) as a promising material for electrochemical applications. RVC (also referred to as carbon foam) is described as

an open-pore material having a honeycomb or foamy structure, composed of non-porous vitreous carbon. This tridimensional (3-D) porous structure leads to a high macroscopic surface area and a low density. The RVC surface is easily modified by various materials, including conducting polymers [2]. In the last decades, RVC was used for many electrochemical purposes, especially as modified electrodes for batteries and electroanalysis [2–6]. Recently, Friedrich et al. [7] presented an illustrated review of RVC as an electrode material, encompassing applications such as electroanalytical studies and sensors, metal ion removal, synthesis of organics and Fenton's reagent, H<sub>2</sub>O<sub>2</sub> production and batteries/fuel cells. They also analyzed the physical structure of RVC by using scanning electron microscopy.

In spite of all the advantages presented by RVC electrodes, it was only in this decade that this material was employed as a substrate for conducting polymer deposition, especially in applications where a high surface area is intended. The effect of the electrodeposition conditions of polypyrrole (PPy) and polyaniline (Pani) films onto RVC substrates on the remediation of Cr(VI) by its reduction in aqueous media was analyzed by Rodriguez et al. [8] and by Ruotolo et al. [9, 10]. RVC/PPy composites were prepared either to recover Cu(II) from diluted acidic solutions [11] or to separate and recover gold and other metal ions with a high degree of efficiency and selectivity [12]. RVC electrodes were also employed as host substrates for the electrochemical deposition of heparin-doped polypyrrole, resulting in a new method for purification of thrombin [13]. Tsutsumi et al. [14] developed an electrode for lithium ion batteries using chemically prepared polyaniline deposited onto reticulated vitreous carbon. This electrode showed good performance during the first cycles, although a capacity fade was observed due to peeling of the polymer from the substrate. Furthermore, RVC–polyaniline–Pd electrodes were investigated for hydrogen sorption [15].

C. Dalmolin · S. R. Biaggio (✉) · R. C. Rocha-Filho · N. Bocchi  
Departamento de Química, Universidade Federal de São Carlos,  
C.P. 676, 13560-970 São Carlos-SP, Brazil  
e-mail: biaggio@power.ufscar.br

Polyaniline itself has received much attention for a wide range of technological applications, such as sensors, electrochromic displays, supercapacitors and batteries [16, 17], where its high surface area is an important advantage. Dinh and Birss [18] investigated the effect of the substrate (glassy carbon, Au and Pt) on the properties of electrochemically deposited Pani films and found that the film's growth rate, electrochemical properties and morphological characteristics are significantly affected by the substrate. Moreover, since RVC electrodes are tridimensional, their properties are critically dependent on the potential distribution generated within their structure [19, 20].

Although various studies using RVC as substrate for electropolymerization were reported, not many concern the dependence of the final electrode properties on the substrate 3-D features. Recently, we have reported some differences between the Pani electropolymerization process onto carbon fiber (CF), a 2-D substrate, and onto RVC [21]. The electrochemical properties of CF/Pani and RVC/Pani electrodes were investigated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS); the differences between the two electrodes were analyzed based on the substrates' geometry, since for a 3-D electrode a potential gradient across its thickness should be considered. In this context, Lassia [22] reported some EIS analyses of porous electrodes, based on de Levie's models for bidimensional and microporous electrodes [23], where a concentration gradient of the electroactive species inside the pores is always considered. However, this assumption does not hold for the macroporous 3-D RVC electrodes, since the homogeneous macropores do not hinder the influx of the electroactive species; nevertheless, a limited current penetration depth is always observed [19] and a new approach to the EIS analysis should be envisaged.

Thus, taking into account that RVC can be considered as a substrate to prepare high surface area Pani electrodes and that a more detailed analysis of the previously reported results [21] was intended, in this work polyaniline deposition is carried out as a function of the RVC thickness, aiming at understanding and minimizing the ohmic drop effect in the RVC/Pani electrodes. The electrochemical and morphological properties of Pani films produced via electropolymerization or chemical synthesis are analyzed by means of cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy.

## Materials and methods

The substrate (80-ppi RVC from ERG, USA) was cut into pieces ~1.0-cm high, ~0.5-cm wide (or ~1.5-cm wide for the two thicker electrodes), of various thicknesses: 1/16 in.

(0.19 cm), 1/8 in. (0.38 cm), 1/4 in. (0.76 cm) and 3/8 in. (1.14 cm). The corresponding specific surface areas for each RVC electrode were calculated based on the ratio surface area/volume reported by Friedrich et al. [7] for 80-ppi RVC, that is,  $50 \text{ cm}^{-1}$ . Before any electrochemical measurement, the RVC pieces were left in contact with the working electrolyte for at least 24 h to ensure their complete wetting. The Pani electrosynthesis were carried out potentiodynamically for 300 voltammetric cycles in a 0.5 M  $\text{H}_2\text{SO}_4$ /0.1 M aniline solution, according to a previously reported procedure [21, 24]. The initial 3 cycles were imposed at a slower sweep rate over a wider potential range, to activate a higher number of anilinium radical cations necessary to initiate the polymerization.

To analyze Pani films whose substrate thicknesses would not affect the polymer deposition, chemical depositions were also performed. Thus, the emeraldine salt of polyaniline was chemically synthesized by oxidative polymerization of aniline in aqueous 1 M  $\text{H}_2\text{SO}_4$  containing ammonium persulfate at  $-2.0 \text{ }^\circ\text{C}$ , based on a procedure carried out by a group of laboratories [25] using excess HCl (instead of  $\text{H}_2\text{SO}_4$ ). The obtained green powder was treated with 1 M  $\text{NH}_4\text{OH}$  and the resulting emeraldine base was then dissolved in *N*-methylpyrrolidinone (NMP). The RVC substrates were immersed in the Pani/NMP solution for about 5 min; after, the obtained RVC/Pani electrodes were kept at  $80 \text{ }^\circ\text{C}$  under vacuum for 48 h so the NMP evaporated.

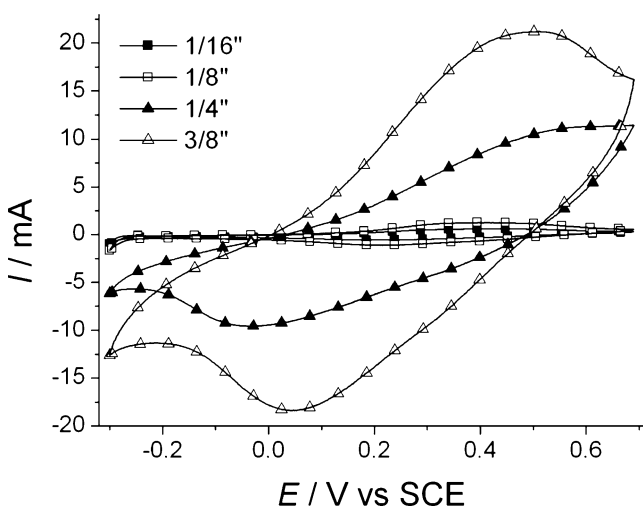
The electrochemical experiments were carried out in a conventional three-electrode Pyrex-glass cell containing RVC/Pani as working electrode, a Pt cylindric grid as counter electrode and a saturated calomel electrode (SCE) as reference, which were connected to an ECOCHEMIE PGSTAT 20 general purpose electrochemical system and frequency response analyzer. Both the voltammetric and the EIS measurements were made in a 0.5 M  $\text{H}_2\text{SO}_4$  solution kept at room temperature (ca.  $25 \text{ }^\circ\text{C}$ ). In the voltammetric tests, the electrode potential was scanned for up to 200 cycles between  $-0.3 \text{ V}$  and  $0.69 \text{ V}$  (SCE) at  $100 \text{ mV s}^{-1}$  and the corresponding electrical charges were measured. The impedance spectra were obtained potentiostatically, from  $-0.20 \text{ V}$  to  $0.60 \text{ V}$  (SCE) in steps of  $0.10 \text{ V}$ . The frequency of the ac signal with an amplitude of  $10 \text{ mV}$  (rms) was varied in the  $10 \text{ mHz}$  to  $10 \text{ kHz}$  frequency range. An equilibration time of  $600 \text{ s}$  was set at each dc potential before the EIS measurements were started. A non-linear least square (NLLS) method was used to fit an electrical equivalent circuit to the obtained data [26].

The morphological characteristics of the RVC/Pani electrodes were investigated using a 960 DSM Zeiss scanning electron microscope. The inner surface of the RVC substrates was accessed by a sectional cut along the center of the electrode.

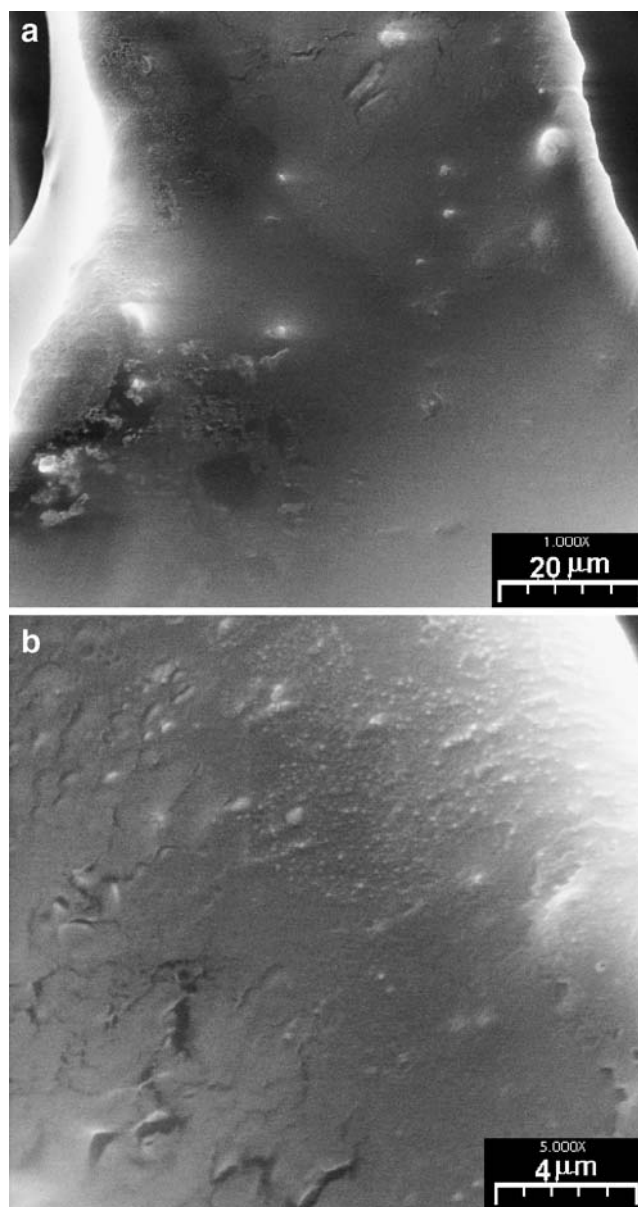
## Results and discussion

### Voltammetric profiles and morphology

Voltammetric profiles for the chemically prepared polyaniline deposited onto RVC with different thicknesses are shown in Fig. 1. The electrochemical behavior is quite similar for all thicknesses, although the current intensities increase with the substrate thickness due to the increase of the substrate real area. A faradaic process is observed in the anodic scan, corresponding to the oxidation process of the insulating form of polyaniline (leucoemeraldine) to its conducting form (emeraldine). On the reverse scan, a cathodic faradaic process indicates the reduction of emeraldine. The subsequent transition (emeraldine to pernigraniline) is not evident due to the low positive potential limit, as required for better film properties to be used as electrodes in batteries [24]. The Pani deposited films showed good stability and adherence to the RVC substrate, since the electrical charge associated to the respective voltammograms did not change significantly even after 200 cycles. For thicker substrates the potential separation between the anodic and cathodic peaks is larger. This feature is usually found for thick polyaniline films, since electrolyte access to the polymer is hindered and therefore the redox processes are slowed down [24]. However, this should not be the case for the films presently analyzed. In the chemical depositions where electrodes are immersed in the polymer solution, the thickness of the Pani films should be dependent only on the polymer concentration and the immersion time, regardless of the substrate thickness. Scanning electron micrographs of chemically synthesized polyaniline films deposited on 1/8 in.-thick RVC (see Fig. 2) reveal the formation of a uniform, compact film. These film



**Fig. 1** Voltammetric profiles for the 200th cycle between  $-0.3$  V and  $0.69$  V, at  $100$   $\text{mV s}^{-1}$ , in a  $0.5$  M  $\text{H}_2\text{SO}_4$  aqueous solution for the RVC/Pani electrodes prepared by casting on RVC substrates of various thicknesses (indicated in the figure)



**Fig. 2** SEM micrographs of the inner region of chemically prepared RVC/Pani deposited on the 1/8 in.-thick substrate. Magnification: (a)  $1,000\times$  and (b)  $5,000\times$

micrographs along with the voltammetric responses (see below) indicate that the amount of chemically deposited polyaniline is very low, thus leading to the formation of very thin films. Hence, the larger potential peak separation that occurs as the substrate thickness is increased cannot be attributed to the film thickness. The same morphological features were found for Pani deposited on the substrates of other thicknesses. Therefore, it is believed that the RVC thickness is, in some way, unsettling the polyaniline electrochemical processes during cyclic voltammetry.

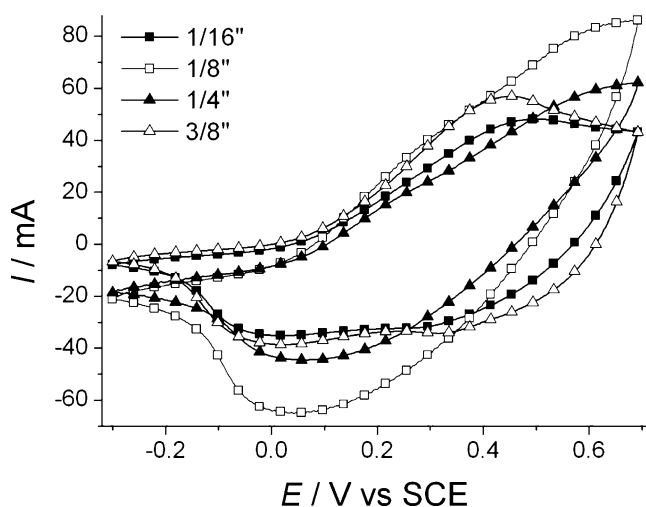
The cyclic voltammograms (200th cycle) for polyaniline electro-synthesized onto RVC of different thicknesses are

shown in Fig. 3. Differently from the just analyzed case, the variations of the current intensities of the anodic/cathodic peak-potentials do not suggest a clear dependence on the substrate thickness, although higher potential peak separations are observed when compared to those for the thinner chemically prepared electrodes. The increase of the peak-potential separation, understood as an increase of film resistance, was already expected since polyaniline films grown potentiodynamically tend to be thicker and porous [24]. Scanning electron micrographs of such films (Fig. 4) show a very porous morphology and will be further analyzed below.

Analyzing more closely the current intensities of the voltammetric profiles presented in Fig. 3, an interesting effect can be noted. Although the thicker substrates have higher areas, the current intensities do not increase as expected and already observed for chemically deposited polyaniline (Fig. 1). From the results reported by Lanza and Bertazzoli [20], it is known that the real area of a tridimensional electrode is different from its active area, since current penetration decreases for thicker electrodes. Taking this fact into account, the anodic and cathodic charges obtained from the voltammetric profiles presented in Figs. 1 and 3 were normalized with respect to the specific surface area of the substrate (see Table 1). Comparing the charge density values in Table 1, it is clear that the potentiodynamically grown Pani films are much thicker than the chemically deposited ones. However, in the former case the charge densities decrease with the substrate thickness indicating that different effects occurring at the RVC inner and outer regions hinder current penetration and, consequently, Pani formation and its redox processes. For the chemically deposited Pani, the charge densities do not

present a significant dependence on the RVC thickness; the fact that the charge density for the 3/8 in. substrate is somewhat smaller than the one for the 1/4 in. substrate again suggests hindrance of the current penetration.

Scanning electron microscopy (SEM) was used to assess information about Pani formation and its morphology along the RVC thickness. Figure 4 shows the SEM micrographs for the outer and inner regions of electrodeposited RVC/Pani electrodes, for different substrate thicknesses. For the 1/16 in. and 1/8 in.-thick substrates, the Pani films appear very porous, in agreement with the thick films produced potentiodynamically on other substrates such as carbon fiber or platinum [21, 24]. The higher current values observed in the voltammetric profile for the 1/8 in.-thick RVC when compared to that for the 1/16 in.-thick RVC (Fig. 3) does not match with the higher charge densities found for the latter. The higher real area of the 1/8 in.-thick RVC explains the higher current values. However, its lower charge density may indicate a loss of active area in its inner region. Indeed, Fig. 4d shows a less porous polyaniline film deposited in the inner region of this substrate. For the thicker electrodes (1/4 in. and 3/8 in.), the differences in the Pani morphology between the outer and inner regions are more drastic, supporting the idea that their lower charge densities (Table 1) are related to a loss of their active area. A porous film can be seen in the outer region while the film formed in the inner region is compact (Fig. 4e–h). These results were explained in a preceding paper [21] as due to a change in the aniline oxidation rate at the inner surface of the tridimensional electrodes. It is known that the rate of the monomer oxidation affects the polymer chain formation, i.e., the slower the monomer oxidation rate, the more packed the polymer chain will be and, hence, the more compact the morphology will seem [27, 28]. Then, the occurrence of Pani films with different morphologies along the RVC substrate might be an indication that there were different oxidation rates due to a potential distribution within the RVC structure and that this effect is more



**Fig. 3** Voltammetric profiles for the 200th cycle between  $-0.4$  V and  $0.69$  V, at  $100$   $\text{mV s}^{-1}$ , in a  $0.5$  M  $\text{H}_2\text{SO}_4$  aqueous solution for the RVC/Pani electrodes prepared by electrodeposition on RVC substrates of various thicknesses (indicated in the figure)

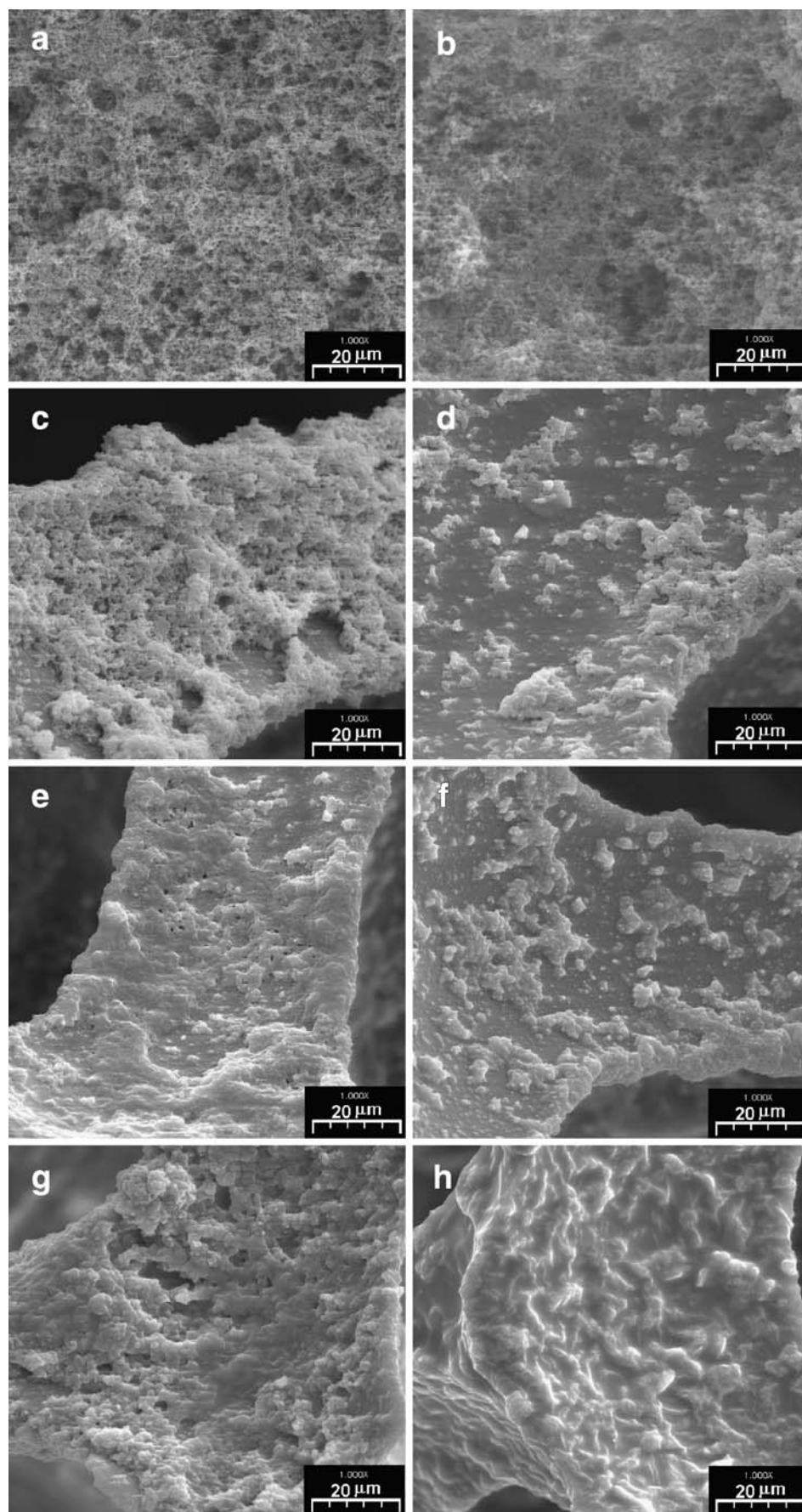
**Table 1** Charge densities (in  $\text{mC cm}^{-2}$ ) obtained from the voltammograms shown in Figs. 1 and 3, taking into account the RVC specific surface areas\*

RVC thickness		1/16 in.	1/8 in.	1/4 in.	3/8 in.
Charge density for electrodeposited RVC/Pani	Anodic	82.1	47.9	11.7	7.43
	Cathodic	82.0	47.6	11.7	7.40
Charge density for chemically deposited RVC/Pani	Anodic	0.752	1.02	1.57	1.31
	Cathodic	0.912	1.18	1.63	1.36

\* See details in the “Materials and methods” section



**Fig. 4** SEM micrographs of the outer (left) and inner (right) regions of the electrodeposited RVC/Pani electrodes. RVC thickness: 1/16 in. (**a, b**); 1/8 in. (**c, d**); 1/4 in. (**e, f**); 3/8 in. (**g, h**)



pronounced for thicker electrodes. The lower current values and charge densities as the RVC thickness increased also indicate a loss in the active area of the tridimensional substrate. Consequently, when more homogenous and porous films are intended, whose electrochemical properties will not be influenced by the potential distribution inside the substrate structure, undoubtedly the polyaniline electro-deposition should be carried out on the thinner RVC substrate. For applications where thicker substrates are needed, chemically synthesized polyaniline seems to be more suitable, though its electrochemical activity will be still compromised by lower current penetration in the tridimensional electrodes.

### Electrochemical impedance spectroscopy

The electrical properties of RVC/Pani electrodes were analyzed by EIS to elucidate processes like electrolyte diffusion and electronic conduction as a function of electrode thickness. The spectra, acquired at different increasingly positive dc potentials, showed profiles that gradually changed from resistive to capacitive as the potential was increased, i.e., as polyaniline changed from the reduced (insulating) to the oxidized (conducting) state. For polyaniline electrodes, the impedance data are commonly analyzed using an electric equivalent circuit as the one shown in Fig. 5 [29], consisting of the following elements:

- A resistor,  $R_1$ , related to the resistive behavior of the electrode, polymer and electrolyte, also known as ohmic resistance.
- A constant phase element,  $Q$ , related to the charge accumulation at the electrolyte/polymer interface. In an ideally flat electrode, this element would be replaced by a pure capacitor.
- Another resistor,  $R_2$ , related to the electron charge-transfer resistance between electrolyte and electrode.
- A diffusion element,  $T$ , related to the diffusion inside the polymer, where the polymer/substrate interface precludes the flow of the species promoting another charge accumulation at this interface [30, 31].

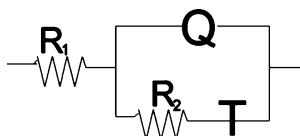
Actually, the equivalent circuit shown in Fig. 5 is a general model, since the impedance profiles change with the polarization potential. For reduced Pani, the spectra present well-defined semicircles and the equivalent circuit

can be simplified by removing the  $T$  element. On the other hand, for oxidized Pani, diffusion within the polymer is observed and the diffusion element has to be considered. This behavior is well-known for polyaniline deposited on bidimensional electrodes. EIS analyses for tridimensional electrodes are not commonly found, and, as previously reported [21], thicker RVC/Pani electrodes present different electrochemical environments, which result in more complex EIS spectra. Thus a variation of the above general circuit becomes necessary to fit the experimental data. This more complex electric equivalent circuit (see Fig. 6), with an additional parallel  $RQ$  combination coupled to the  $T$  element, consists of the following elements:

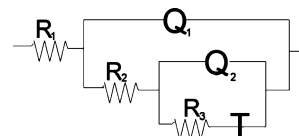
- $R_1$ , the ohmic resistance, which for positive potentials (conducting polyaniline) is simply the solution resistance.
- $Q_1$ , the charge accumulation at the solution/polymer interface in the outer regions of the electrode.
- $R_2$ , also related to the solution resistance, but this time in the inner regions of the electrode. As the electrolyte solution penetrates into the inner regions of the RVC substrate, its effective conductivity decreases due to the tortuosity of the porous media [32, 33], generating a different environment for the charge-transfer reactions.
- $Q_2$ , the charge accumulation at the solution/polymer interface in the inner regions of the electrode, which is also affected by the decreased conductivity of the electrolyte.
- $R_3$ , the charge-transfer resistance associated with the polymer/substrate interface, which is inversely proportional to the electron transfer rate and can be used as a kinetics indicator.
- $T$ , the element related to diffusion inside the polymer.

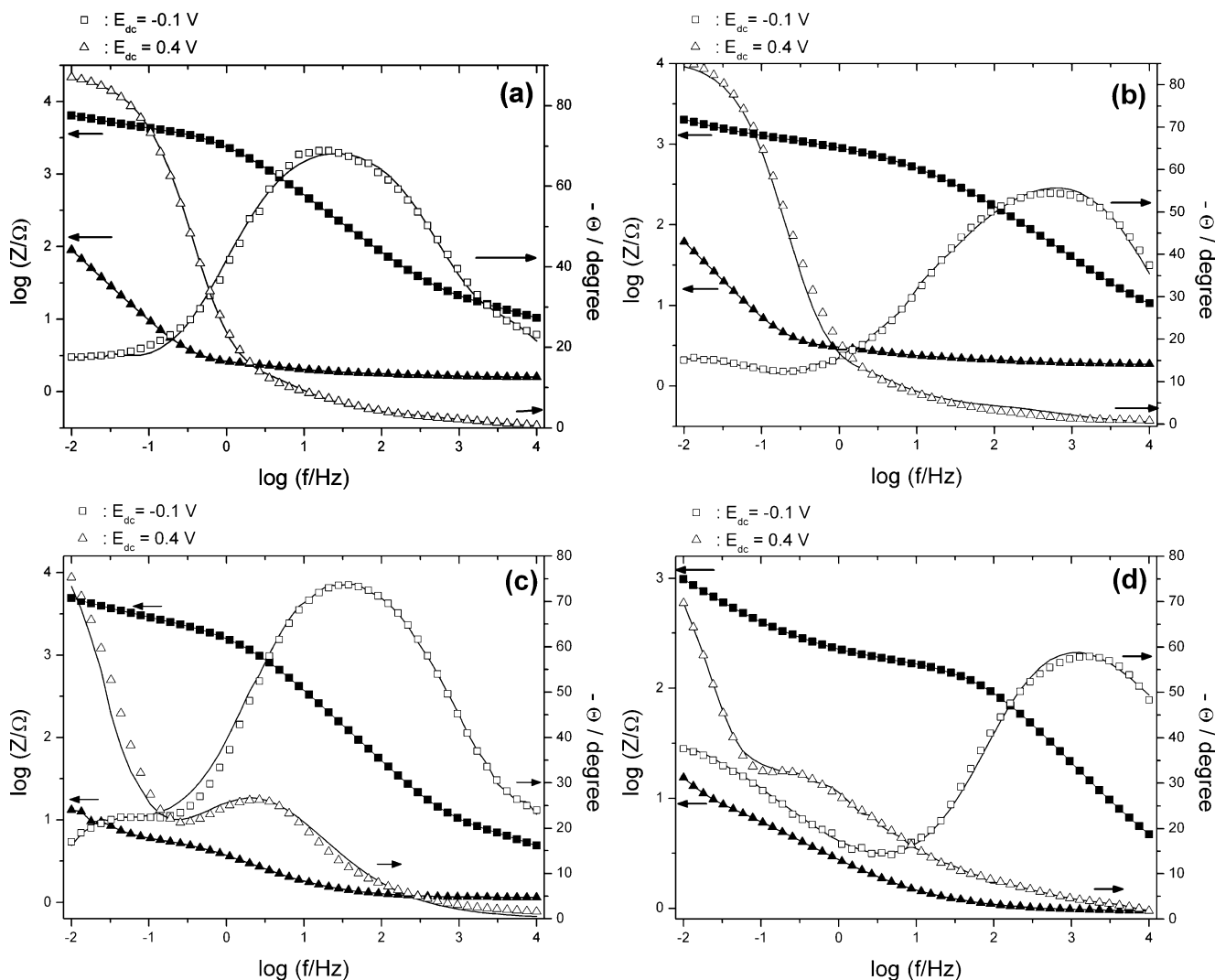
Typical Bode plots obtained at  $-0.1$  V and  $0.4$  V (for insulating and conducting Pani, respectively), for both preparation methods and various RVC thicknesses, are presented in Figs. 7 and 8. The curves obtained by fitting the more complex equivalent circuit (Fig. 6) to the experimental data are also included in the plots with good agreement between the experimental and fitted data. The values of the quantities related to the inner region of the electrode ( $R_2$ ,  $Q_2$ ,  $R_3$  and  $T$ ) obtained in the fitting are presented in Tables 2 and 3, for electrochemically and chemically synthesized polyaniline, respectively. It should be noted that the values of  $R_1$  and  $Q_1$  (not shown) follow the

**Fig. 5** Electric equivalent circuit commonly used to fit the electrochemical impedance data for polyaniline electrodes



**Fig. 6** Electric equivalent circuit model used to fit the electrochemical impedance data for the RVC/polyaniline electrodes





**Fig. 7** Bode plots for the electrochemically synthesized RVC/polyaniline electrodes in a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. Experimental data (points) and fitted curves for different RVC thicknesses: **(a)** 1/16 in., **(b)** 1/8 in., **(c)** 1/4 in. and **(d)** 3/8 in.

same trend as those of  $R_2$  and  $Q_2$ , respectively. However, the values of  $R_2$  are higher than those of  $R_1$ , indicating that electrolyte conductivity is indeed affected by the porous medium. This means that an environment in the inner RVC surfaces differs from that at the outer RVC surfaces.

The values of  $R_3$  obtained for electrodes polarized at  $-0.1$  V refer to the charge-transfer resistance of the insulating Pani film. The higher  $R_3$  values for chemically prepared polyaniline can be due to its more compact morphology, which hinders the mobility of the counterions across the film for charge compensation. As it can be seen in Tables 2 and 3, the fitting of the EIS data yielded values for the diffusion element  $T$  even at potentials where polyaniline is insulating. As stated earlier, the diffusion element  $T$  is related to finite diffusion in a medium where one interface precludes diffusion, creating saturation zones,

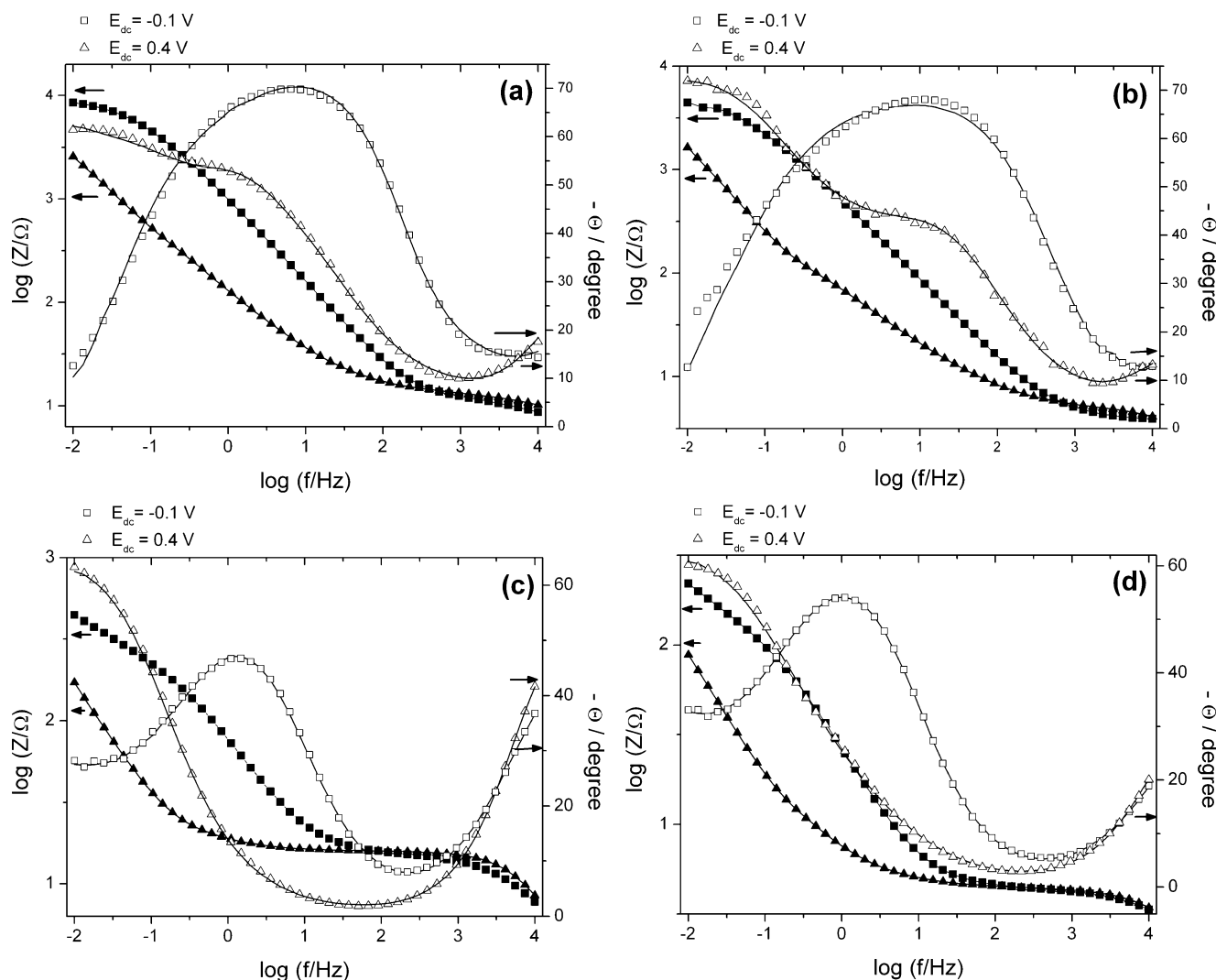
as it may occur, for example, at the polymer/substrate interface. Thus, its impedance is related to a hyperbolic tangent function, defined as [34]:

$$Z(T) = \frac{\tanh [B(j\omega)^{1/2}]}{Y_0(j\omega)^{1/2}}$$

where

$$B = \sqrt{\frac{L^2}{D}}$$

$L$  being the film thickness and  $D$  a combination of the diffusion coefficients of the ionic species ( $D_i$ ) and the electrons ( $D_e$ ) [34]. Then, the high values obtained for  $B$  indicate a low diffusion coefficient, as expected for Pani insulating films. For chemically prepared polyaniline,



**Fig. 8** Bode plots for the chemically synthesized RVC/polyaniline electrodes in a 0.5 M  $\text{H}_2\text{SO}_4$  aqueous solution. Experimental data (points) and fitted curves for different RVC thicknesses: **(a)** 1/16 in., **(b)** 1/8 in., **(c)** 1/4 in. and **(d)** 3/8 in.

deposited on the thinner 1/16 in. or the 1/8 in. RVC, the fitting of the data did not yield a diffusion element. This suggests that for these RVC thicknesses, the Pani film is much more compact, something that is confirmed by comparing the SEM micrographs for the chemically (Fig. 2) and electrochemically prepared (Fig. 4a and d) Pani films on the 1/8 in. RVC.

Differences in the EIS spectra are more pronounced when polyaniline is conducting. For chemically prepared polyaniline (Fig. 8), two time constants are always seen, independent of the RVC thickness. This can be explained by the deposition of a compact, thin and homogeneous Pani film both on the outer and the inner RVC surfaces. However, two electrochemical environments are present due to the ohmic loss at the inner region of the electrodes and, therefore, the circuit presented in Fig. 6 had to be used for the fitting of the data. On the other hand, for the electrosynthesized polyaniline,  $R_1$  and  $Q_1$  were not defined

for the 1/16 in. or the 1/8 in. RVC, indicating that for these thinner electrodes the effect of the ohmic drop inside the substrate is minimized due to the highly porous Pani film on the RVC macroporous structure (see Fig. 4a–d). In these cases, the RVC/Pani behaves as if it was a bidimensional electrode and no differences between the outer and the inner regions are observed. When the RVC thickness increases, different Pani morphologies within the electrode (see again Fig. 4) yield different electrochemical environments, leading to different impedance behaviors.

Values calculated for  $R_3$  and  $T$  for chemically prepared Pani (Table 3) confirm the above analysis. When the polymer is conducting,  $D_e \gg D_i$  and  $D_i$  is the rate determining factor for the charge-carrier diffusion [34]. The decrease in the value of  $B$  as the potential is increased indicates that the diffusion coefficients of the moving counter-ions are becoming larger. However, for electrosynthesized films (Table 2), the values of  $B$  increase with the electrode



**Table 2** Values of different parameters obtained by fitting the response of the equivalent circuit shown in Fig. 6 to the impedance data for the electrodeposited RVC/Pani electrodes, as a function of the applied potential and substrate thickness

E/V vs SCE	RVC thickness/in.	$R_2/\Omega$	$R_3/\Omega$	$Q_2/\Omega^{-1} s^n$	$n_{Q_2}$	$Y_0/\Omega^{-1} s^{0.5}$	$B/s^{0.5}$
-0.1	1/16	14.8	3893	$4.52 \times 10^{-5}$	0.820	$1.16 \times 10^{-3}$	9.07
	1/8	8.48	1309	$2.39 \times 10^{-5}$	0.780	$2.99 \times 10^{-3}$	9.25
	1/4	4.75	237	$3.36 \times 10^{-5}$	0.876	$2.72 \times 10^{-3}$	10.2
	3/8	2.95	154	$3.26 \times 10^{-5}$	0.741	$4.63 \times 10^{-3}$	15.2
0.2	1/16	1.87	0.330	$1.79 \times 10^{-2}$	0.700	$2.40 \times 10^{-1}$	0.790
	1/8	1.34	0.433	$2.20 \times 10^{-2}$	0.758	$3.14 \times 10^{-1}$	0.873
	1/4	1.14	11.0	$4.11 \times 10^{-2}$	0.753	$4.31 \times 10^{-1}$	1.67
	3/8	0.927	11.5	$1.15 \times 10^{-1}$	0.719	$2.39 \times 10^{-1}$	2.60
0.4	1/16	1.59	0.160	$9.54 \times 10^{-3}$	0.790	$2.70 \times 10^{-1}$	0.590
	1/8	1.87	0.332	$1.60 \times 10^{-3}$	0.730	$2.93 \times 10^{-1}$	0.776
	1/4	1.09	5.52	$2.83 \times 10^{-2}$	0.766	$4.51 \times 10^{-1}$	1.52
	3/8	0.884	8.52	$1.13 \times 10^{-1}$	0.692	$3.42 \times 10^{-1}$	2.38

thickness, indicating that the diffusion coefficient is becoming smaller. For the chemically prepared electrodes, the values of  $B$  are not affected by the RVC thickness. Therefore, the differences observed in the  $T$  element for the electrosynthesized Pani may be related to the polymer morphology, which is affected by the substrate thickness.

The data in Tables 2 and 3 also suggest that the charge-transfer resistance ( $R_3$ ) is affected by the RVC thickness, especially in the case of the electrosynthesized polyaniline. High  $R_3$  values are observed at  $-0.1$  V, decreasing as the electrode area increases, i.e., RVC thickness increases. For conducting Pani, an opposite effect is observed as the electrode area increases, showing again that its redox reactions are negatively affected. However, this behavior is not observed for the chemically prepared RVC/Pani electrodes, thus indicating that its cause is not the RVC thickness itself, but the different film morphologies obtained during the electrochemical polymerization of polyaniline onto the thicker RVC substrates.

### Conclusions

Electrochemical and morphological aspects of RVC/Pani electrodes produced by both chemical and electrochemical methods were investigated as a function of the RVC thickness. Although high surface area electrodes are obtained when tridimensional electrodes are used as the substrate for the polyaniline electropolymerization, its redox reactions are affected by the substrate thickness. For chemically prepared electrodes, whose deposition is not affected by the substrate thickness, the voltammetric results show only a slight dependence of the Pani electrochemical behavior upon the RVC thickness. Thicker substrates still present high active areas, although with higher peak-potential separations, indicating slower electrochemical reaction rates, something not observed for the thinner substrates. Indeed, EIS measurements showed that the electrolyte conductivity decreases at the inner surfaces and this could be an explanation for those higher peak-potential separations.

**Table 3** Values of different parameters obtained by fitting the response of the equivalent circuit shown in Fig. 6 to the impedance data for chemically prepared RVC/Pani electrodes, as a function of applied potential and substrate thickness

E/V vs SCE	RVC thickness/in.	$R_2/\Omega$	$R_3/\Omega$	$Q_2/\Omega^{-1} s^n$	$n_{Q_2}$	$Y_0/\Omega^{-1} s^{0.5}$	$B/s^{0.5}$
-0.1	1/16	8.17	9620	$1.08 \times 10^{-4}$	0.889	–	–
	1/8	11.5	5473	$4.54 \times 10^{-4}$	0.725	–	–
	1/4	14.3	247	$3.09 \times 10^{-3}$	0.774	$1.41 \times 10^{-2}$	9.58
	3/8	3.98	126	$8.67 \times 10^{-3}$	0.801	$2.67 \times 10^{-2}$	10.1
0.2	1/16	12.4	2993	$1.58 \times 10^{-3}$	0.677	$2.07 \times 10^{-4}$	4.67
	1/8	2.20	19.0	$3.29 \times 10^{-3}$	0.684	$2.66 \times 10^{-2}$	1.48
	1/4	14.0	5.90	$3.51 \times 10^{-2}$	0.605	$1.24 \times 10^{-2}$	1.96
	3/8	2.98	0.548	$6.24 \times 10^{-2}$	0.605	$9.58 \times 10^{-3}$	2.05
0.4	1/16	13.8	82.1	$2.15 \times 10^{-3}$	0.662	$3.12 \times 10^{-4}$	1.87
	1/8	2.14	10.0	$2.23 \times 10^{-3}$	0.633	$3.16 \times 10^{-3}$	1.23
	1/4	14.6	5.90	$4.02 \times 10^{-2}$	0.726	$1.43 \times 10^{-2}$	0.934
	3/8	3.71	4.86	$6.11 \times 10^{-2}$	0.651	$2.09 \times 10^{-2}$	1.32

Conversely, the electrodeposition of Pani is strongly dependent upon the substrate thickness, as showed by the SEM micrographs. Thus, high peak-potential separations in the voltammetric profiles were already expected due to the polymer porous morphology, although a direct relationship between substrate thickness (specific surface area) and active area could not be obtained.

An equivalent electric circuit model was proposed for the analysis of the EIS data, taking into account the different electrochemical environments at the outer and inner RVC surfaces. The values obtained for the different parameters indicate that electrochemically prepared electrodes are more susceptible to an ohmic drop across the RVC structure since the morphologies of the obtained Pani are different. Finally, when more homogenous and porous polyaniline films are required, the obtained results indicate that electropolymerization onto thinner substrates might be the best choice. On the other hand, for applications where a high tridimensional surface area is intended (thicker substrates), chemical deposition seems to be the best choice.

**Acknowledgements** The authors are grateful to FAPESP, CAPES and CNPq for the scholarships and grants that made this work possible. C.D. is grateful to FAPESP for her doctoral scholarship.

## References

- Wang J (1980) *Electrochim Acta* 26:1721
- Czerwinski A, Dmochowska M, Grden M, Kopczyk M, Wojcik G, Mlynarek G, Kolata J, Skowronski JM (1999) *J Power Sources* 77:28
- Czerwinski A, Zelazowska M (1997) *J Power Sources* 64:29
- Gyenge E, Jung J, Mahato B (2003) *J Power Sources* 113:388
- Alvarez-Gallegos A, Pletcher D (1998) *Electrochim Acta* 44:853
- Tang X, Xie B, Larsson P, Danielsson B, Khayyami M, Johansson G (1998) *Anal Chim Acta* 374:185
- Friedrich JM, Ponce-de-Léon C, Reade GW, Walsh FC (2004) *J Electroanal Chem* 561:203
- Rodriguez FJ, Gutiérrez S, Ibañez JG, Bravo JL, Batina N (2000) *Environ Sci Technol* 34:2018
- Ruotolo LAM, Liao AA, Gubulin JC, *J Appl Electrochem* 34:1259
- Ruotolo LAM, Gubulin JC (2005) *React Funct Polym* 62:141
- Piatnicki CMS, Azambuja DS, Hasse EES, Castagno KRL, Guterres SB (2002) *Sep Sci Technol* 37:2459
- Price WE, Ralph SF, Wallace GG (2001) *Aust J Chem* 54:615
- Yang X, Too CO, Sparrow L, Ramshaw J, Wallace GG (2002) *React Funct Polym* 53:53
- Tsutsumi H, Yamashita S, Oishi T (1997) *Synth Met* 85:1361
- Frydrychewicz A, Vassiliev SY, Tsirlina GA, Jackowska K (2005) *Electrochim Acta* 50:1885
- Bhattacharya A, De A (1996) *Prog Solid State Chem* 24:141
- Gospodinova N, Terlemezyan L (1998) *Prog Polym Sci* 23:1443
- Dinh HN, Birss VI (2000) *J Electrochem Soc* 147:3775
- Doherty T, Sunderland JG, Roberts EPL, Pickett DJ (1996) *Electrochim Acta* 41:519
- Lanza MRV, Bertazzoli R (2000) *J Appl Electrochem* 30:61
- Dalmolin C, Canobre SC, Biaggio SR, Rocha-Filho RC, Bocchi N (2005) *J Electroanal Chem* 578:9
- Lasia A (1995) *J Electroanal Chem* 397:27
- de Levie R (1963) *Electrochim Acta* 8:751
- Andrade GT, Aguirre MJ, Biaggio SR (1998) *Electrochim Acta* 44:633
- Stejskal J, Gilbert RG (2002) *Pure Appl Chem* 74:857
- Boukamp BA (1995) Software EQUIVCRT, Version 4.51
- Nunziante P, Pistoia G (1989) *Electrochim Acta* 34:223
- Tang H, Kitani A, Shiotami M (1996) *Electrochim Acta* 41:1561
- Gazotti WA Jr, Matencio T, De Paoli M-A (1998) *Electrochim Acta* 43:457
- Boukamp BA (1986) *Solid State Ion* 20:31
- Skinner NG, Hall EAH (1994) *Synth Met* 63:133
- Ruotolo LAM, Gubulin JC (2002) Proceedings of 30th ENEMP: Congresso Brasileiro de Sistemas Particulados, São Carlos, SP. (<http://www.ufscar.br/~enemp2002/pi32.pdf>)
- Gonzalez-Garcia J, Bonete P, Exposito E, Montiel V, Aldaz A, Torregrosa-Macia R (1999) *J Mater Chem* 9:419
- Vorotynev MA, Daikhin LI, Levi MD (1994) *J Electroanal Chem* 364:37