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ORIGINAL PAPER

Usefulness of a composite electrode with a carbon surface modified by electrosynthesized polypyrrole for supercapacitor applications

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Abstract Thin polypyrrole (PPy) films (thickness = 5–10 nm) were electrochemically deposited in situ on a carbon paste (97% of graphite plus 3% of Teflon) by means of cyclic voltammetry (CV), from an acetonitrile solution of pyrrole (0.2 M) and $NaClO_4$ (0.1 M). The obtained PPy/graphite composite electrode was investigated by CV and chronopotentiometry in 0.3 M $NaClO_4$ aqueous electrolytic solution. The capacitance of a composite electrode, calculated by CV, was about 10 F g^{-1}. The capacitance value of the composite electrode was approximately nine times larger than that of pure graphite. The massic charge and discharge capacity (Q) values, calculated by chronopotentiometry, were considerably higher for the composite electrode—by more than 60 times—than for the pure graphite electrode. Electrochemical impedance spectroscopy (EIS) measurements, performed under stationary conditions, led to an interfacial capacitance value intermediate between that of pure graphite and that of the composite electrode.

Keywords Polypyrrole · Pseudo-capacitance · Capacitance · Composite electrode

1 Introduction

Nowadays, supercapacitors represent the most promising electrochemical systems for energy storage [1, 2]. Their advantages are mainly based on their interesting properties in terms of energy density and specific electrical power. Indeed, these particular devices, which are based, in most cases, on the use of nano-structured materials, nanotubes, and nanocomposites, generally possess electrical power values higher than those of the usual batteries, as well as energy density values larger than those of the traditional capacitors [2–6].

The conducting organic polymers (COP) often constitute the active matter of supercapacitors. COP are mostly applied to the surface modification of carbon-containing electrodes, essentially because of their interesting chemical characteristics for energy storage, low cost of production, good electrochemical reversibility during the charge-discharge phenomena, as well as their large charge density, and their relatively easy chemical and/or electrochemical synthesis [3, 4, 7–9].

Nevertheless, COP present some disadvantages due to their low specific capacity and a short life time related to the faradic reactions [10]. This low capacity can be considerably improved by building composite electrodes made of conducting polymer/carbonaceous substrate as graphite [11, 12], or by coupling conducting polymer with carbon nanotubes [4, 8, 13, 14]. In these conditions, COP can be

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easily deposited on the graphite or on other carbon substrates by a chemical or an electrochemical method [4, 9, 15, 16].

Indeed, graphite itself is an excellent candidate as an active matter for capacitors electrode, because of a good electronic conductivity and a good porosity, resulting into an excellent aptitude to accumulate electrical charges at the electrode/electrolyte interface [12]. The storage electrochemical capacity of graphite can be improved by increasing its specific surface, either by chemical activation or by addition of a pseudo-capacitance which consists to deposit a COP such as polypyrrole (PPy) on the graphite surface or within its structure [10, 16, 17]. Also, in a recent study, Woo et al. [9] prepared a composite electrode consisting of bimodal porous carbon and PPy, obtained by electropolymerization of pyrrole within the macropores of the bimodal porous carbon.

In this work, we have performed the in situ electrosynthesis of PPy thin films on graphite substrate, with the aim of covering the surface of graphite and of significantly increasing the electro-active surface of the substrate. The goals of this study were to investigate the performances and electrochemical activity of these newly obtained PPy/graphite composite electrodes as well as the improvement of their pseudo-capacitance properties, resulting from the use of a larger electro-active surface.

2 Experimental part

2.1 Materials

Graphite powder was obtained from Carbone-Lorraine. Pyrrole (purity: 98%), sodium perchlorate ($NaClO_4$), and acetonitrile were purchased from Sigma Aldrich, and used as received.

2.2 Electrode preparation, electrochemical cell, and procedures

A mixture, constituted of 97% of graphite carbon and of 3% of Teflon used as binder, was homogenized and compacted in a mold to obtain pellets which were prepared by pressing the mixture (100 or 200 mg) under a high pressures (0.5–1.0 ton cm^{-2}), using a KBr tablet mould in a Carver Laboratory press model S/N 3392-69.

These pellets presented the advantage to possess a good electronic conductivity and a relatively high porosity (corresponding to the amount of electrolyte retained in the pellet). Before each electrochemical measurement, the pellet mass was weighed, and then was introduced into a specially built electrochemical cell made in Teflon (Fig. 1). This cell included a counter-electrode (stainless steel grid), a reference electrode (saturated calomel electrode, SCE), and a gold plate which was connected to a wire, used as a collector allowing the electric current to flow. The pellet had to be well fixed on the gold surface, in order to avoid any direct polymer deposit on the gold plate. An acetonitrile solution containing pyrrole (0.2 M) and $NaClO_4$ (0.1 M) was then put into the electrochemical cell which was connected to a potentiostat. The pellets were immersed into this electrolytic solution during 8 h, in order to ensure a good impregnation before starting the PPy electrodeposition.

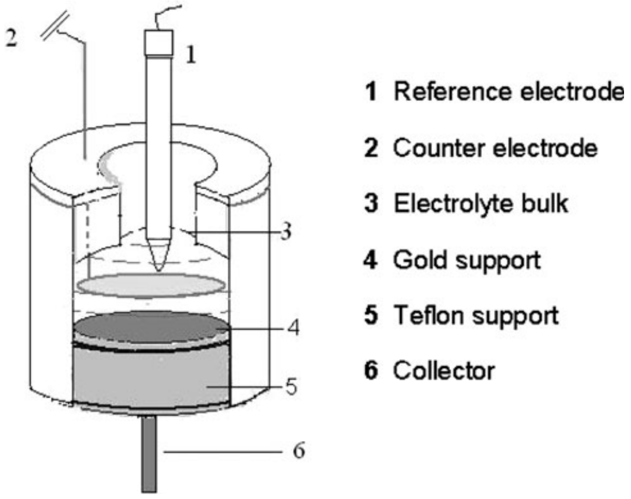

Fig. 1 The electrochemical cell

2.3 Electrochemical, microscopic, and impedance measurements

All electrochemical measurements were carried out on an EG & G potentiostat 362. The scanning electron microscopy (SEM) photos of the surface of composite material pellets were realized on a SEMFEG Zeiss Ultra 55 instrument. Impedance measurements were performed by using either a Radiometer analytical Voltalab PGZ 301 or a Solartron 1287/1250 electrochemical work station, in the typical frequency range 10 mHz–100 kHz. The amplitude of the AC signal was 10 mV.

3 Results and discussion

3.1 In situ electrodeposition of PPy

For the PPy electrodeposition, cyclic voltammograms (CVs) were recorded between −1.5 and 1.5 V/SCE in a 0.2 M pyrrole + 0.1 M $NaClO_4$ acetonitrile solution (Fig. 2). Wide anodic and cathodic waves occurred respectively at 0.75 and −1.25 V/SCE. The peak intensity

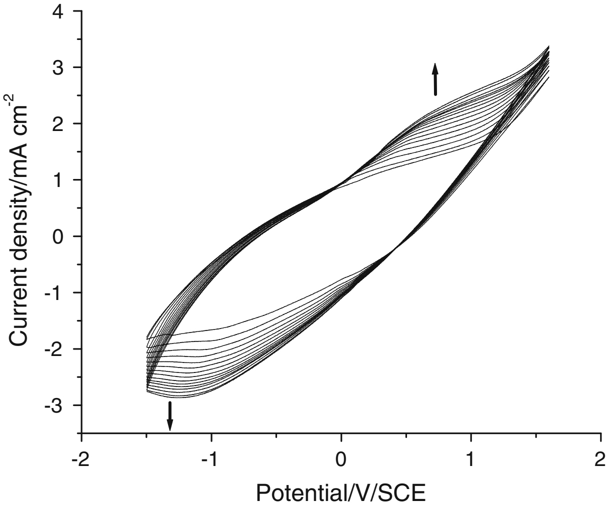

Fig. 2 Cyclic voltammograms for PPy electrodeposition on a graphite pellet in a 0.2 M pyrrole + 0.1 M $NaClO_4$ acetonitrile solution—15 cycles—scan rate: v = 100 mV s^{-1}

values increased with the number of cycles, which indicated the progressive PPy electrodeposition on the graphite pellets. The anodic current density values were found to increase from 1.5 to 2.5 mA cm^{-2}, and the cathodic current density ones from −1.7 to −2.8 mA cm^{-2}. Moreover, it appeared a dark coloration on the graphite pellets, confirming the formation of a polymer deposit at the electrode surface. The presence of only one anodic and one cathodic peak suggested that, as expected, the pyrrole electropolymerization took place solely at the 2,2′- position.

3.2 Morphology of PPy/graphite composite electrodes

The morphologic study of pure graphite and PPy–graphite composite electrodes was carried out by means of SEM. The SEM photos are presented in Figs. 3 and 4. As can be seen, the micrograph of pure graphite electrode surface shows the presence of regularly ordered graphite layers, whereas those of the PPy–graphite composite electrode surface present more heterogeneous microstructure, resulting from the insertion of PPy thin layers within graphite (Figs. 3, 4).

This PPy/graphite particular microstructure, which certainly corresponds to all the pellet surface, is representative of the porous nature of the electrode, and might explain to some extent the increased specific surface of the composite pellet PPy/graphite compared to that of graphite alone.

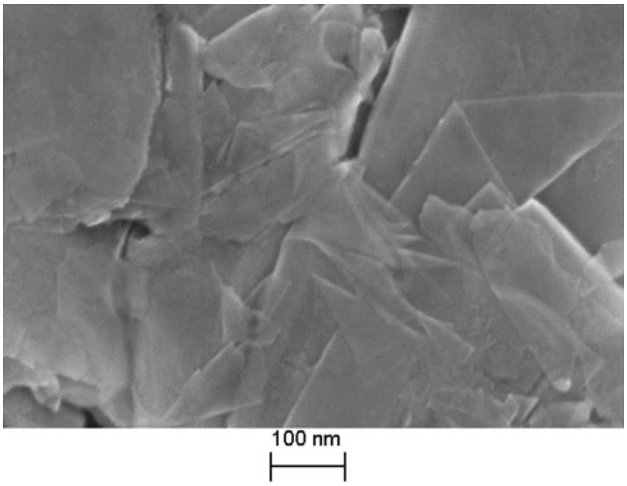

Fig. 3 SEM photo of a graphite pellet

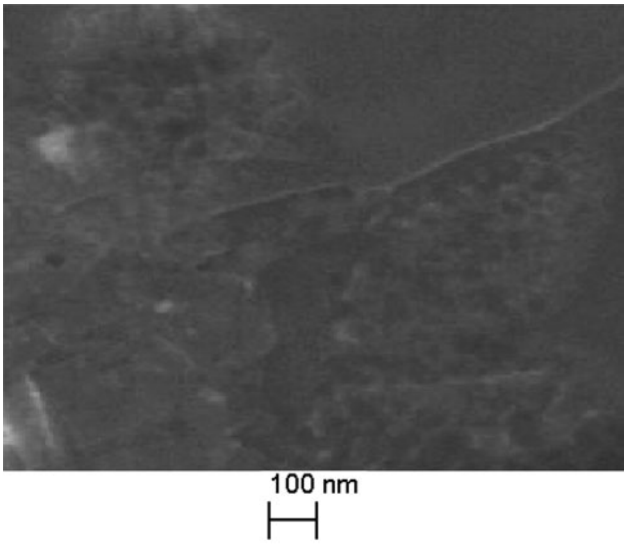

Fig. 4 SEM photo of a PPy/graphite composite electrode

3.3 Electrochemical study of PPy/ graphite composite electrodes

As already mentioned, one of the goals of this work was to electrochemically characterize the PPy/ graphite composite electrodes. For the sake of clarity, the results of both electrochemical techniques (cyclic voltammetry [CV] and chronopotentiometry) used for characterization of the composite electrodes are discussed separately in the following parts, but they can be considered as complementary.

3.3.1 Cyclic voltammetry

Before beginning the electrochemical study, the PPy/ graphite composite electrodes (1.0 cm diameter; 1 mm thickness), obtained by in situ PPy electrodeposition as above described, were initially stabilized during about 5 min in a monomer-free 0.3 M $NaClO_4$ aqueous electrolytic solution. Then, the CVs of the composite electrodes (obtained after a PPy electrodeposition of 15 cycles) were studied in a 0.3 M $NaClO_4$ aqueous electrolytic solution at

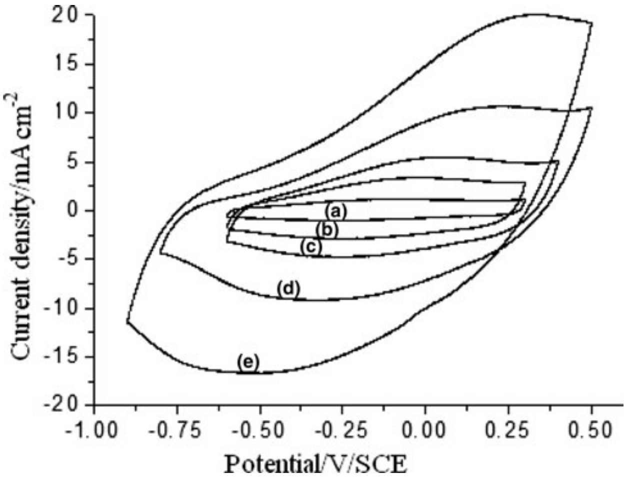

Fig. 5 Cyclic voltammograms of a PPy/graphite composite electrode, recorded in a 0.3 M $NaClO_4$ aqueous solution, at potential scan rate values of 1.0 mV s^{-1} (*a*), 3.0 mV s^{-1} (*b*), 5.0 mV s^{-1} (*c*), 10 mV s^{-1} (*d*), 20 mV s^{-1} (*e*)

various scanning rates ($v = 1.0$–20.0 mV s^{-1}) (Fig. 5). As can be seen, the oxidation and reduction peaks of the CV curves are rather poorly defined, and they are broad and asymmetric. Moreover, the separation between the peak potentials is relatively large ($\Delta E_p \approx 0.75$ V), and also depends on the scan rate. It has been previously suggested that the electrochemical charging/discharging process, i.e., the CV behavior of a redox composite electrode, might be influenced by the ohmic resistance [18, 19]. Moreover, the oxidation current limit is higher than the reduction current one, like observed in the case of chemically synthesized PPy incorporated into a composite graphite electrode [16].

As shown in Fig. 6, the current density of anodic and cathodic peaks linearly increased with the potential scan rate, which indicates the electrochemical reaction of surface-localized species, generally encountered in the case of conducting polymers [20]. It also indicates that the processes of doping and de-doping are controlled by capacitive and pseudo-capacitive phenomena, probably related to the specific structure of the PPy-containing graphite [10]. This is in contrast with the behavior of composite electrodes built with chemically synthesized PPy, for which the current density of anodic and cathodic peaks linearly increased with the square root of the potential scan rate [16].

Moreover, careful observation of the CV curves revealed the presence of capacitive current notable values remaining even after the redox reaction had taken place.

The fact that, at the end of the oxidation process, the current was not null and became constant, again demonstrated the capacitive character of the PPy/graphite composite electrodes [16]. The gravimetric capacitance values, calculated from the voltammograms of Fig. 5 for the PPy/graphite composite electrodes under study, were found to be

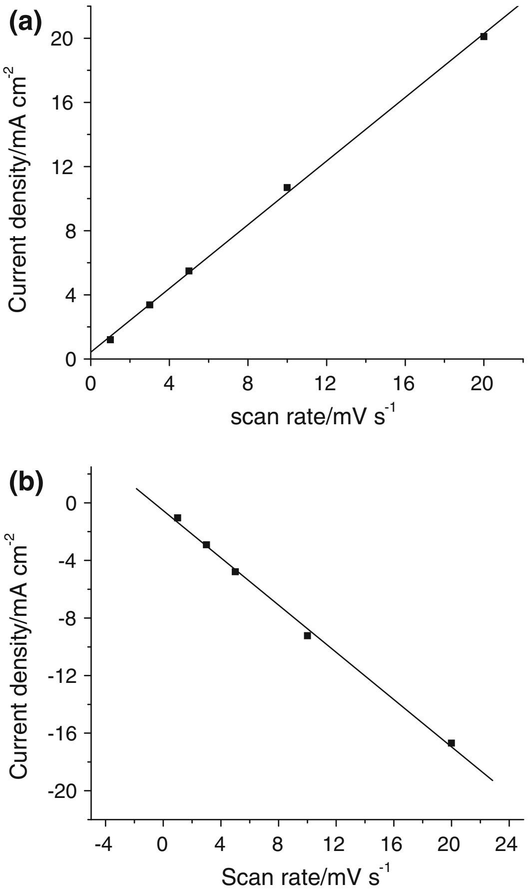

Fig. 6 Linear plots of the: **a** anodic peak current density and **b** cathodic peak current density versus the scan rate

about 10 F g^{-1}, comparable to those obtained very recently by Ruch et al. [6], using electrodes suitable for supercapacitors, made either of single-walled carbon nanotubes ($\sim$20 F g^{-1}) or of activated carbon ($\sim$34 F g^{-1}) in a non-aqueous electrolyte.

Moreover, the study of the electroactivity enabled us to compare the capacitance of a pure graphite electrode and of a PPy/graphite composite electrode. Indeed, the maximum capacitance value of the pellet formed from pure graphite was approximately 0.8 F g^{-1}, whereas a PPy/graphite composite electrode obtained after polymer electrodeposition presented a maximum capacitance value of about 7.3 F g^{-1} for a CV recorded after 15 cycles (Fig. 7). The capacitance of graphite was thus multiplied by about nine in the presence of active matter. This dramatic enhancement of the graphite capacitance can be explained by the composite electrode active surface increase. In fact, it can be assumed that the polymer pseudo-capacitance value is added to the graphite capacitance value [12].

Also, it is worthwhile to note that it appeared neither an oxidation peak, nor a reduction peak on the CV curve obtained with a pure graphite electrode. In contrast, the

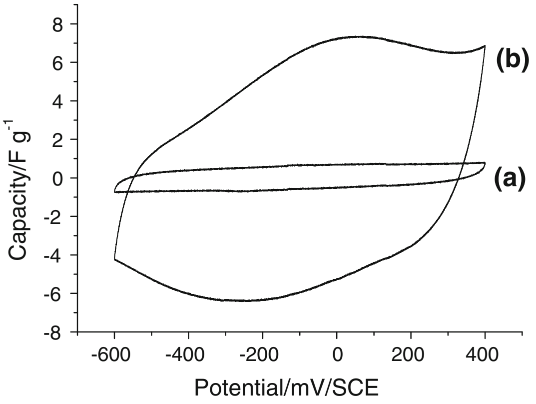

Fig. 7 Plots of the: (*a*) massic capacity of the pure graphite electrode and (*b*) massic capacity of the PPy/graphite composite electrode versus the electrode potential (*E*)—composite electrode prepared by CV with 15 cycles—scan rate: $v = 5$ mV s^{-1}

oxidation and reduction peaks were clearly visible in the CV curve of the PPy/graphite composite electrode (Fig. 7). These peaks can be considered as resulting from the superposition of the PPy faradic reaction and of the capacitor charge process (capacitive current), occurring at the interface between the electrode surface and the adjacent solution layer [10, 12].

3.3.2 Chronopotentiometry

Chronopotentiometric curves obtained at a constant current density value of 1 mA cm^{-2} were recorded in a 0.3 M $NaClO_4$ aqueous solution for a pure graphite electrode (Fig. 8a) and for a PPy/graphite composite electrode (Fig. 8b). The shape of these curves indicate the occurrence of charge and discharge processes, which confirms the presence of capacitive phenomena, already revealed by the above described electroactivity studies. The potential (*E*) value reached by the electrode was found to decrease quasi-linearly with time (*t*), suggesting that the whole electrode behaves like a capacitor, as previously observed [16]. This phenomenon, called pseudo-capacitance, can be related to the electrochemical double-layer developed by the graphite and PPy, but also to the faradic reactions which take place in PPy [10, 16]. Moreover, it is interesting to note that the discharge time value of the PPy/graphite composite electrode (approximately 8.9 min) was much longer than that of pure graphite (about 0.17 min). Consequently, a charge–discharge cycle using a PPy/graphite composite electrode will last approximately 24 min, whereas the duration of the corresponding cycle in the case of a pure graphite electrode will be only about 0.4 min.

The massic charge and discharge capacity (*Q*) values, calculated from the chronopotentiometric curves for a pure graphite electrode and for a PPy/graphite composite electrode, are presented in Table 1. As can be seen, the massic charge and discharge capacity values were, respectively, 1.70 and 1.53 mAh g^{-1} for a PPy/graphite composite electrode vs., respectively, 0.027 and 0.024 mAh g^{-1} for a pure graphite electrode. Therefore, *Q*-values were considerably larger for a PPy/graphite composite electrode—by more than 60 times for the charge as well as for the discharge phenomena—than for a pure graphite electrode. These results confirm those obtained with CV. We can thus conclude that the use of PPy as active matter increased considerably the capacitance of the graphite pellet.

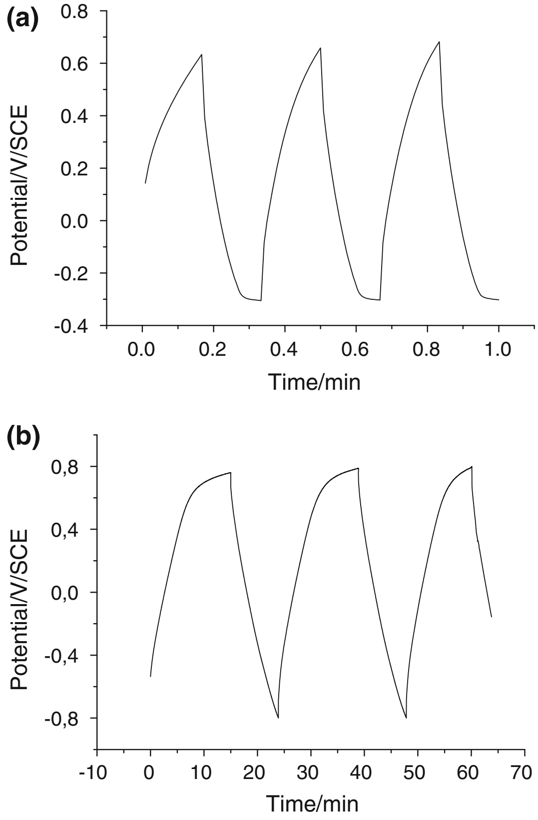

Fig. 8 Chronopotentiometric curves of **a** a pure graphite electrode and **b** a PPy/graphite composite electrode recorded in a 0.3 M $NaClO_4$ aqueous solution. Charge or discharge applied current density 1 mA cm^{-2}

3.3.3 Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy (EIS) is a powerful technique for studying the electrical response of complex systems, including conducting polymer films and three-dimensional composite electrodes [16, 17, 21]. However, a drawback of this technique is that EIS needs the system under study to be stationary. This means that the working conditions, including the dc potential and current, should be independent of time.

Table 1 Massic charge and discharge capacity values calculated from the chronopotentiometric curves for a pure graphite electrode and for a PPy/graphite composite electrode

Electrode	Massic charge capacity/mAh g^{-1}	Massic discharge capacity/mAh g^{-1}
Pure graphite	0.027	0.024
Composite PPy/graphite	1.70	1.53

As an example, Fig. 9a displays the Nyquist complex impedance diagram obtained for a Ppy/graphite composite electrode in a 0.3 M $NaClO_4$ aqueous electrolytic solution under galvanostatic conditions ($I = 0.5$ mA), and recorded between 0.01 Hz and 65 kHz. Roughly, two capacitance loops are observed. The high frequency one is strongly flattened, which can be interpreted as the signature of the porous structure of the composite electrode. The low frequency loop is governed by the large interfacial capacitance of the electrolyte/electrode interface in parallel with a finite transfer resistance [11, 17, 22]. The value of the interfacial capacitance can be more clearly evidenced by plotting the complex capacitance $C^* = C' - jC''$, defined by $C^* = (j\omega Z)^{-1}$, as shown in Fig. 9b. Below 10 mHz, the real part of C^* becomes constant and equal to 0.08 F. The mass of the active matter is 0.140 g, leading to a specific capacitance of about 0.6 F g^{-1}. Because of the constraints imposed by working under stationary conditions, EIS allows us to check the electrode status only in the fully charged or fully discharged state, in the present case. As a consequence, the interfacial capacitance determined by EIS is mainly representative of the graphite response, in agreement with the results of voltammetry for a pure graphite electrode. Its value is significantly lower than the value found by CV and chronopotentiometry, the latter ones being performed under transient conditions.

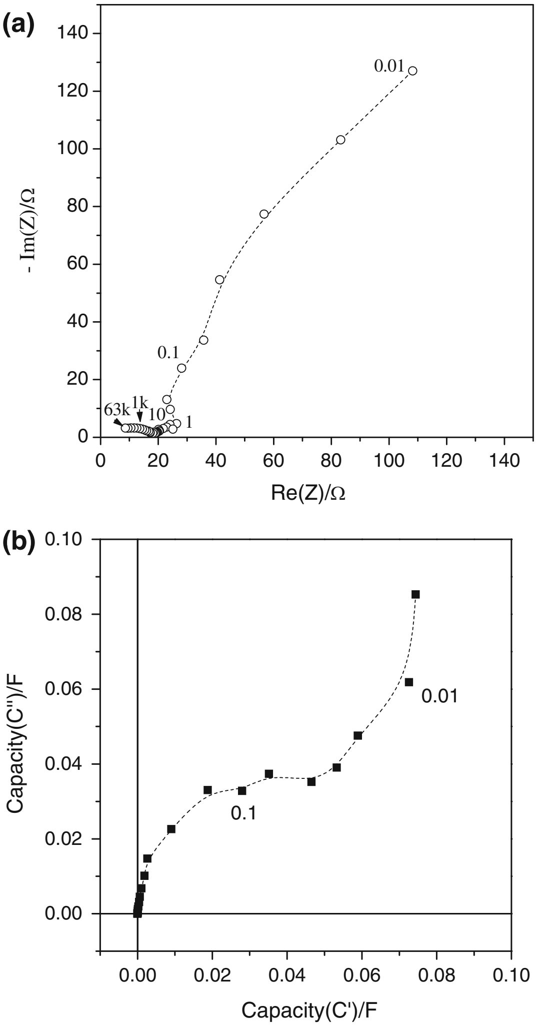

Fig. 9 Stationary impedance response of a PPy/graphite composite electrode in a 0.3 M $NaClO_4$ aqueous solution at the end of a charge sequence at a constant current of 0.5 mA: **a** in the Nyquist representation and **b** in the complex capacitance representation

This conclusion is independent of the mode of polarization used for the EIS diagrams. Indeed, Fig. 10 shows the Nyquist impedance diagram obtained for a PPy/graphite composite electrode under potentiostatic conditions at $E = +200$ mV, after a stabilization step of 160 s, much shorter than the charge–discharge time as depicted in Fig. 8b. The impedance diagram in Fig. 10 closely resembles the one in Fig. 9a. From the low frequency capacitive branch, one can estimate a value for the interfacial capacitance, i.e. 0.29 F leading to 2 F g^{-1}. The same results have been obtained after holding the composite electrode at +400 mV for 10 h; the real part of the complex capacitance measured between 63 kHz and 250 μHz, was found constant and equal to 2 F g^{-1} at frequencies below 1 mHz. Such a value is intermediate between that of pure graphite and that of the PPy/graphite composite electrode as determined by the CV technique.

4 Conclusion

In this study we have been able to manufacture and characterize a PPy/graphite composite electrode obtained by in situ electrodeposition of the polymer. Investigation of this composite electrode by various electrochemical methods, including CV and chronopotentiometry, showed that modification of the graphite surface by electrochemically depositing a conducting polymer such as PPy could generate

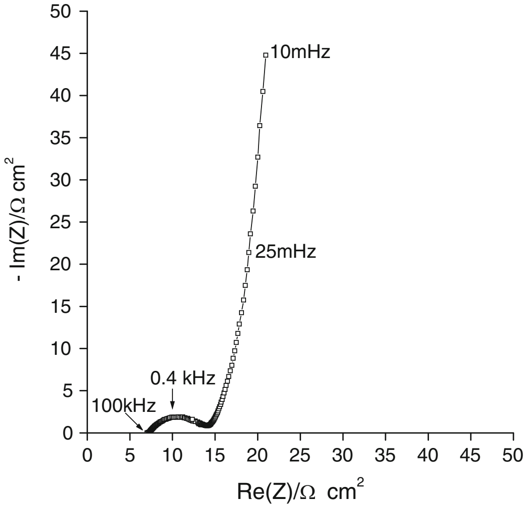

Fig. 10 Nyquist representation of an impedance diagram obtained for a PPy/graphite composite electrode under potentiostatic conditions at +200 mV, after a stabilization step of 160 s, measured between 100 kHz and 10 mHz

an important change of the electrode specific surface. Consequently, the capacitance of a PPy/graphite composite electrode was considerably increased—by a factor of nine—relative to that of a pure graphite electrode. We also found that the massic charge and discharge capacity values of a PPy/graphite composite electrode were considerably larger—by more than 60 times for the charge as well as for the discharge phenomena—than those of a pure graphite electrode. The EIS measurements, performed under stationary conditions on the pure graphite and the PPy/graphite composite electrodes, led to an interfacial capacitance value intermediate between that of pure graphite and that of the PPy/graphite composite electrode as determined under transient conditions by the CV and chronopotentiometry techniques. Also, in view of recent literature studies showing the considerable enhancement of the effective surface area and gravimetric capacitance values of commercial activated carbon for use in electrochemical capacitors by a simple treatment with KOH at 850 °C [23], and the increase of interfacial capacitance of C-cloth electrodes in acidic medium [24], we decided to orient our future research work towards the development of improved PPy/graphite composite electrodes of larger porosity, and possibly activated by KOH and/or used in acidic medium. Under these conditions, the interesting electrochemical properties of PPy/graphite composite electrodes, such as their capacitance and pseudo-capacitance ability, which have been revealed in the present paper, should be still improved in order to lead to the possibility of using this type of electrode for supercapacitor applications.

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