

Short communication

## Poly(3-methylthiophene)/MnO<sub>2</sub> composite electrodes as electrochemical capacitors

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### Abstract

Composite electrodes prepared by electrodeposition of manganese oxide on titanium substrates modified with poly(3-methylthiophene) (PMeT) were investigated and compared with Ti/MnO<sub>2</sub> electrodes. The polymer films were prepared by galvanostatic deposition at 2 mA cm<sup>-2</sup> with different deposition charges (250 and 1500 mC cm<sup>-2</sup>). The electrodes were characterized by cyclic voltammetry in 1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> and by scanning electron microscopy. The results show a very significant improvement in the specific capacitance of the oxide due the presence of the polymer coating. For Ti/MnO<sub>2</sub> the specific capacitance was of 122 F g<sup>-1</sup>, while Ti/PMeT<sub>250</sub>/MnO<sub>2</sub> and Ti/PMeT<sub>1500</sub>/MnO<sub>2</sub> displayed values of 218 and 66 F g<sup>-1</sup>, respectively. If only oxide mass is considered, the capacitances of the composite electrode increases to 381 and 153 F g<sup>-1</sup>, respectively. The micrographs of samples show that the polymer coating leads to very significant changes in the morphology of the oxide deposit, which in consequence, generate the improvement observed in the charge storage property.

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### 1. Introduction

Growing demands for systems and devices that require high-performance power sources have stimulated research fields related to energy storage. Moreover, the growing environmental and economic impact of the production and use of fossil fuels have stimulated the search for alternative energy sources, such as electrochemical energy. Batteries, fuel cells, and more recently, electrochemical capacitors have been extensively studied in recent decades.

Electrochemical capacitors are unique materials, since they combine characteristics of dielectric capacitors and of rechargeable batteries, such as high power density for low energy density, high charge–discharge cycle life, and high discharge efficiency [1–4]. The interest in electrochemical capacitors is related mainly to the development of hybrid systems for electric vehicles to complement batteries [5–7] and portable

electronic displays that require compact high energy power sources.

There are two electrochemical charge storage mechanisms. The first one is called double layer capacitance and occurs at the solid/electrolyte interface by charge accumulation at the surface of the solid electrode. The second mechanism occurs due to reversible faradaic processes at the surface and in the bulk of the electrode and is named pseudocapacitance [1–4]. Double layer capacitors are, in general, made with carbon compounds [8–11], while pseudocapacitors can be produced using certain transition metal oxides, such as RuO<sub>2</sub> [12–16], IrO<sub>2</sub> [17,18], MnO<sub>2</sub> [19–29], NiO<sub>x</sub> [30,31], Co<sub>3</sub>O<sub>4</sub> [32], and conducting polymers, such as polyaniline [33–35], polypyrrole [35,36] and polythiophenes [37–39]. The capacitance values can be a 100 times higher for pseudocapacitive electrodes than for carbon electrodes, since the redox reactions occur both at the surface and in the bulk of the electrode. For this reason, in the latter case the specific capacitance is expressed in terms of capacitance per interfacial area unit. It is customary to adopt capacitance per unit mass (F g<sup>-1</sup>).

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Although RuO<sub>2</sub> is the material that presents the highest specific capacitance values (720 F g<sup>-1</sup>) [12,13], it is expensive, which limits its commercial use. MnO<sub>2</sub> has shown to be a promising alternative for commercial application due to advantages, such as non-toxicity and, mainly, low cost. In this sense, electrodes of MnO<sub>2</sub> have been prepared by different methods [19–29]. As in RuO<sub>2</sub>, the charge storage mechanism in MnO<sub>2</sub> is related not only to charge separation at the electrolyte/electrode interface but also to pseudocapacitance. And in the same way, the best results have been obtained with hydrous and amorphous oxides, as in the case of RuO<sub>2</sub> electrodes.

Reddy and Reddy [24,25] have prepared MnO<sub>2</sub> by a sol–gel method. The electrodes, produced with 23 wt% of the carbon black and 9 wt% of poly(tetrafluoroethylene) (PTFE) binder and with specific capacitances on the order of 110–130 F g<sup>-1</sup> were obtained at scan rate 5 mV s<sup>-1</sup> in 2 mol L<sup>-1</sup> NaCl. Lee et al. [26] obtained specific capacitances of 243 F g<sup>-1</sup> in 2 mol L<sup>-1</sup> KCl with electrodes containing K<sub>0.31</sub>MnO<sub>2.12</sub>·0.63H<sub>2</sub>O prepared by thermal decomposition of KMnO<sub>4</sub> at 550 °C. For amorphous MnO<sub>2</sub> prepared by reduction of KMnO<sub>4</sub> with Mn<sup>2+</sup> the specific capacitance was of 198 F g<sup>-1</sup>. In both cases the electrodes were prepared with 25 wt% of acetylene black and 5 wt% of PTFE. The best results were obtained with electrodeposited electrodes. Using a factorial fractional design, Hu and Tsou [23] optimized the conditions of preparation for hydrous and amorphous MnO<sub>2</sub> deposited onto a graphite substrate from MnSO<sub>4</sub> solution by anodic deposition. A 220 F g<sup>-1</sup> were obtained for an electrode produced at 3.7 mA, deposition charge of 0.3 C cm<sup>-2</sup>, in 0.16 mol L<sup>-1</sup> MnSO<sub>4</sub> and pH 5.6. MnO<sub>2</sub> was deposited on stainless steel by cyclic voltammetry in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + 0.5 mol L<sup>-1</sup> of MnSO<sub>4</sub>·5H<sub>2</sub>O at several scan rates by Prasad and Miura [27]. The highest specific capacitance was of 482 F g<sup>-1</sup> in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> at  $v = 10$  mV s<sup>-1</sup> for an electrode deposited at 200 mV s<sup>-1</sup>. The same authors prepared nickel–manganese (NMO) oxide and cobalt–manganese (CMO) oxide using the same methodology [28] and obtained specific capacitances of 621 and 498 F g<sup>-1</sup> for NMO and CMO, respectively.

Conductor polymers are also promising class of materials for electrochemical capacitors. Fast kinetic to the doping/undoping mechanisms and their ability to undergo both n- and p-doping are the main advantages. These materials have been used along with carbon and oxides in pseudocapacitive electrodes [40–43]. Poly(3-methylthiophene), particularly, it is an interesting material due to facility of synthesis, reversibility and stability. Moreover, previous studies [44,45] pointing for a granular morphology of high surface area controlled by synthesis conditions. In this sense, the use of the PMeT as substrate could be leads to improve of the capacitive properties of another materials deposited onto them.

In this work, we report studies of the preparation of MnO<sub>2</sub> by electrodeposition using the cyclic voltammetry technique in MnSO<sub>4</sub> medium. The aim of the present work was to investigate the effect of the modification of the titanium substrate using another pseudocapacitive material, PMeT, which was galvanostatically deposited onto Ti, with different deposition charges.

## 2. Experimental

### 2.1. Substrate previous treatment

Metal titanium plates with 99.7% purity (TiBrazil) with working areas of 1 cm<sup>2</sup> were used as substrates to prepare the PMeT–MnO<sub>2</sub> electrodes. Substrates were treated by sandblasting, followed by a chemical treatment in hot 10% (w/w) oxalic acid solution for 10 min. Finally, the electrodes were washed with Milli-Q water and dried at 150 °C.

### 2.2. Preparation of the PMeT coating

The PMeT deposits were galvanostatically synthesized on titanium electrodes from a 0.1 mol L<sup>-1</sup> 3-methylthiophene and 0.02 mol L<sup>-1</sup> (CH<sub>3</sub>)<sub>4</sub>NBF<sub>4</sub> in acetonitrile solution. Two different samples were prepared. The synthesis was carried out at 2 mA cm<sup>-2</sup> and the deposited charges were of 250 mC cm<sup>-2</sup> (PMeT<sub>250</sub>) and 1500 mC cm<sup>-2</sup> (PMeT<sub>1500</sub>). For this process a one-compartment cell and the three-electrode configuration were used. The Ti substrates were used as working electrodes and a Pt plate and an Ag wire were used as counter- and pseudo-reference electrodes, respectively. Following the PMeT deposition, the Ti/PMeT electrodes were washed with acetonitrile and dried in air.

### 2.3. Preparation of the MnO<sub>2</sub> coating

The MnO<sub>2</sub> was deposited on Ti and Ti/PMeT electrodes by cyclic voltammetry between the potential limits of 0.0 and 1.5 V and scan rate of 200 mV s<sup>-1</sup>. Three hundred cycles were performed in order to achieve proper deposited thickness. A 0.4 mol L<sup>-1</sup> MnSO<sub>4</sub> solution was used as electrolyte. For this deposition step, a Pt plate and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode. Subsequent to deposition, these electrodes were cleaned in distilled water and dried at 40 °C. The mass of the electrodes was determined before polymer deposition and after the polymer and oxide depositions to allow specific capacitance calculations.

### 2.4. Electrodes characterization

Cyclic voltammetry measurements were performed using a PGSTAT 30 model Autolab potentiostat/galvanostat. Measurements were performed in a three-electrode cell. As a counter electrode and reference electrode, a Pt plate and a saturated calomel electrode were used. The Ti/MnO<sub>2</sub> and Ti/PMeT/MnO<sub>2</sub> electrodes were used as working electrodes. The measurements were performed at room temperature in 1.0 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The surface morphology was analyzed with a JEOL-JSM-6306LZ scanning electron microscope.

## 3. Results and discussion

Fig. 1 shows the cyclic voltammograms during 300th deposition cycle of MnO<sub>2</sub> for oxide deposited on Ti, on Ti/PMeT<sub>250</sub> and on Ti/PMeT<sub>1500</sub>. The same profile was observed for all three

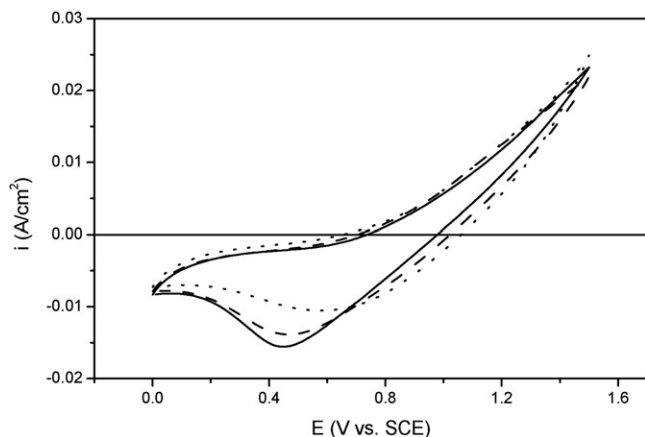


Fig. 1. 300th cyclic voltammograms of the  $\text{MnO}_2$  deposition on: (—) Ti, (---) Ti/PMeT<sub>250</sub> and (···) Ti/PMeT<sub>1500</sub> electrodes,  $\text{MnSO}_4$  0.4 M solution and  $v = 200 \text{ mV s}^{-1}$ .  $T = 25^\circ\text{C}$ .

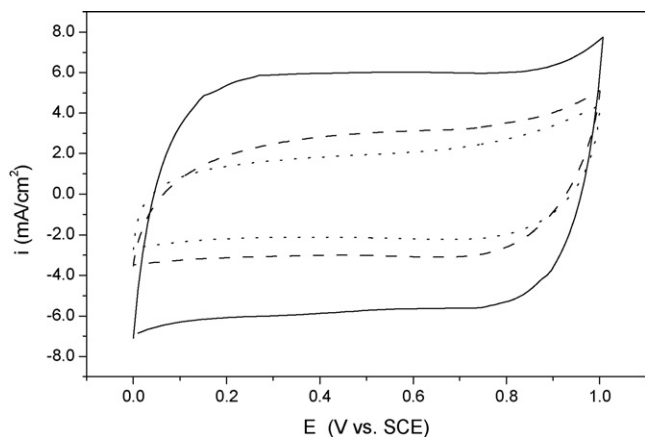


Fig. 2. Cyclic voltammograms of the electrodes: (—) Ti/ $\text{MnO}_2$ , (---) Ti/PMeT<sub>250</sub>/ $\text{MnO}_2$  and (···) Ti/PMeT<sub>1500</sub>/ $\text{MnO}_2$ ,  $\text{Na}_2\text{SO}_4$  1.0 M solution and  $v = 20 \text{ mV s}^{-1}$ .  $T = 25^\circ\text{C}$ .

samples. The oxidation of the  $\text{MnSO}_4$  began at 0.75 V and the anodic current increases up to the inversion potential. In the cathodic scan, a reduction peak is observed around 0.5–0.6 V. In the initial cycles the anodic and cathodic charges increase. They subsequently decrease for higher numbers of cycles and then practically become stable. A displacement of the cathodic peak to more negative potentials is also observed with cycling of the electrodes. The  $\text{MnO}_2$  deposition charges on Ti/PMeT electrodes were lower than the deposition charges on the Ti electrode. As a consequence, the mass of the oxide coating was lower. The

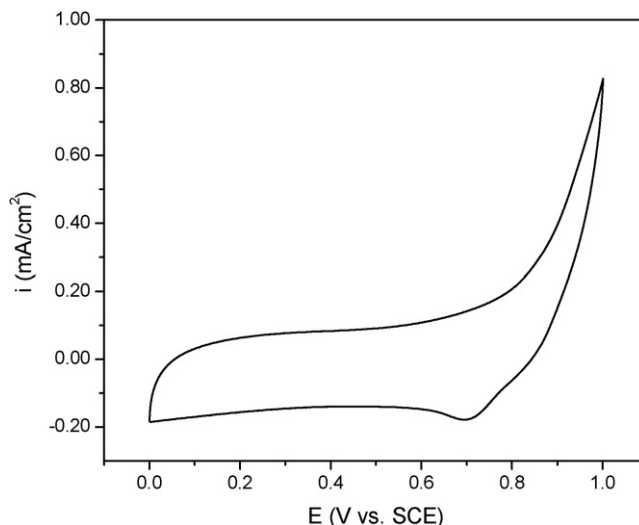


Fig. 3. Cyclic voltammograms of the Ti/PMeT<sub>250</sub> electrode in  $\text{Na}_2\text{SO}_4$  1.0 M solution and  $v = 20 \text{ mV s}^{-1}$ .  $T = 25^\circ\text{C}$ .

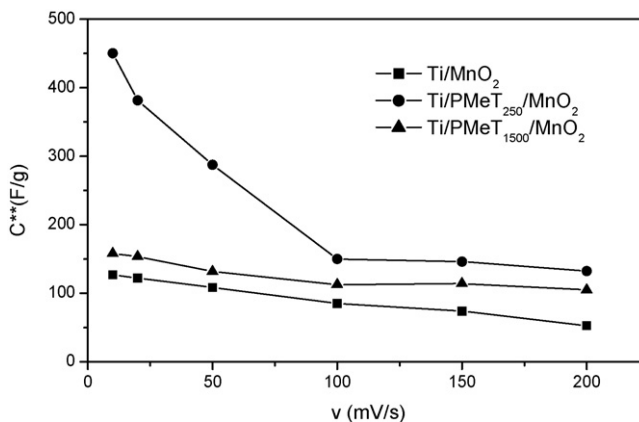


Fig. 4. Specific capacitance as a function of the scan rate.

mass of  $\text{MnO}_2$  deposited directly on Ti was of around 2.5 mg, while the mass deposited on Ti/PMeT electrodes was between 0.4 and 0.6 mg. This fact is probably related to higher resistivity of the polymeric film compared to the titanium electrode.

The electrochemical characterization of the electrodes was performed by cyclic voltammetry measurements in  $1.0 \text{ mol L}^{-1}$   $\text{Na}_2\text{SO}_4$  solution. The voltammetric behavior of  $\text{MnO}_2$  deposited on PMeT is the same as for the oxide deposited directly on Ti, as seen in Fig. 2. The curves show a rectangular shape and no peaks. Although the current increases near the limit potentials

Table 1

Mass and specific capacitances of the electrodes

Electrodes	Mass electrodes (mg)		Specific capacitance <sup>a</sup> ( $\text{F g}^{-1}$ )	
	PMeT + $\text{MnO}_2$	Only $\text{MnO}_2$	$C^*$	$C^{**}$
Ti/ $\text{MnO}_2$	—	2.5	—	122
Ti/PMeT <sub>250</sub> / $\text{MnO}_2$	0.7	0.4	218	381
Ti/PMeT <sub>1500</sub> / $\text{MnO}_2$	1.4	0.6	66	153

<sup>a</sup> Specific capacitances obtained by cyclic voltammetry at  $20 \text{ mV s}^{-1}$ .

\* Based on PMeT– $\text{MnO}_2$  composite mass.

\*\* Based on  $\text{MnO}_2$  mass.



due to polarization resistance, high magnitude and practically constant currents are observed over an extensive potential window, characterizing the capacitive nature of these materials.

The large values of current in voltammograms could not be associated with double layer charging, but should be the result of the pseudocapacitance attributed to the Mn(III)/Mn(II), Mn(IV)/Mn(III) and Mn(VI)/Mn(IV) redox transitions [22,46,47].

When the voltammograms of different electrodes are compared, it is observed that the MnO<sub>2</sub> on Ti has higher current density values than the composite electrodes and so its charge density is also higher. However, the oxide mass deposited in the former case is significantly larger. Therefore, in comparing the charge storage property, the mass of electrodes should be taken into consideration. Cathodic or anodic charges integrated

from cyclic voltammetry were used to determine the specific capacitance of the electrodes estimated according to Eq. (1).

$$C = \frac{Q}{\Delta E m} \quad (1)$$

where  $C$  is the specific capacitance ( $\text{F g}^{-1}$ ),  $Q$  the voltammetric charge (C),  $\Delta E$  the potential window (V) and  $m$  is the mass of material (g).

The specific capacitance measured at  $20 \text{ mV s}^{-1}$  and the mass of the electrodes are presented in Table 1. In this table it is clear that the Ti/PMeT<sub>250</sub>/MnO<sub>2</sub> electrode has a storage charge capacity that is much higher than the others electrodes. When the total mass of the composite electrode is considered, the specific capacitance ( $C^*$ ) is 1.8 times higher than the specific capacitance of the Ti/MnO<sub>2</sub> electrode. On the other hand, when only

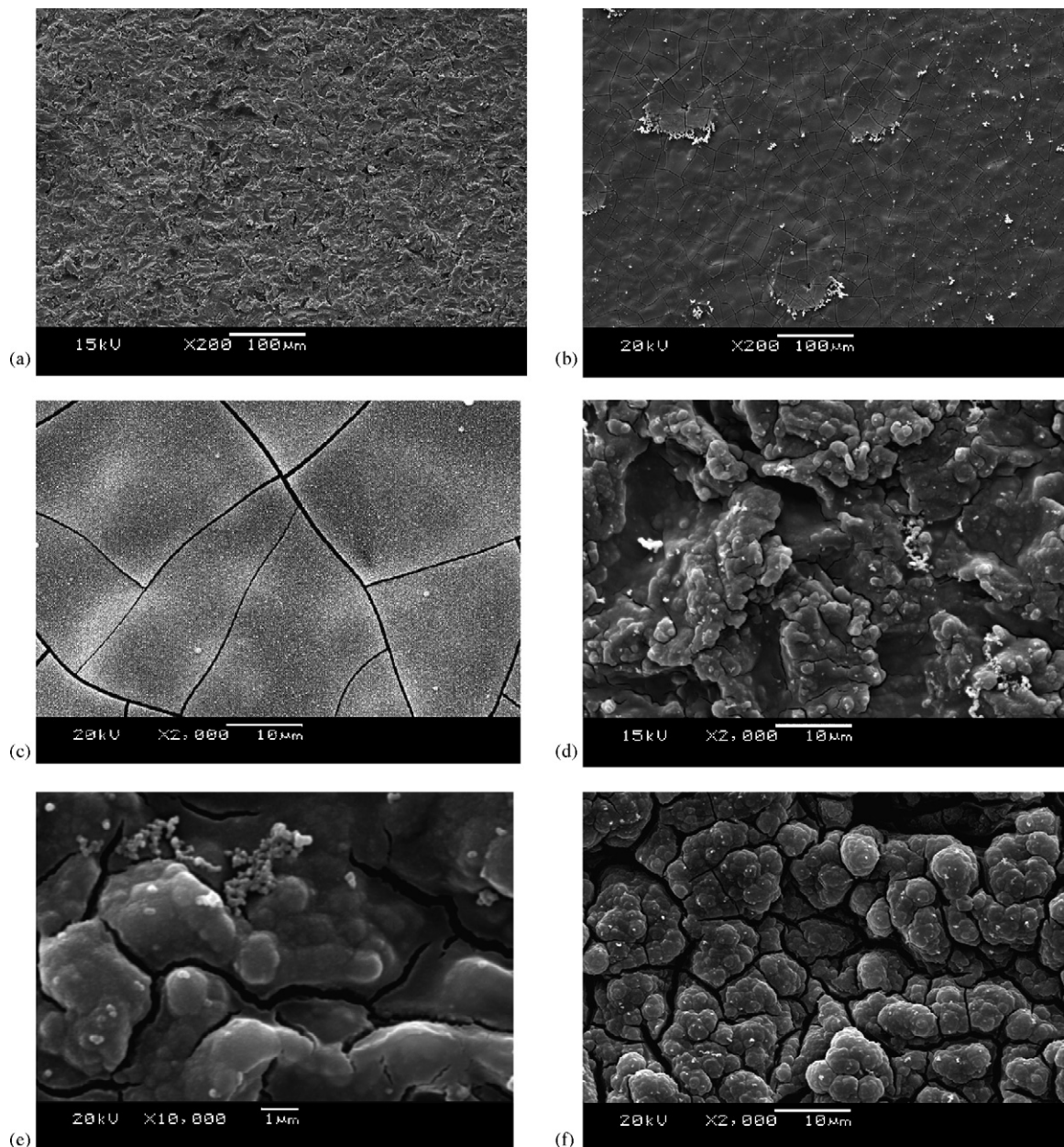


Fig. 5. Scanning electron micrographs of the electrodes: (a) Ti/PMeT<sub>250</sub>, (b and c) Ti/MnO<sub>2</sub>, (d and e) Ti/PMeT<sub>250</sub>/MnO<sub>2</sub> and (f) Ti/PMeT<sub>1500</sub>/MnO<sub>2</sub>.

MnO<sub>2</sub> mass is considered, the specific capacitance ( $C^{**}$ ) is 3.0 times higher for Ti/PMeT<sub>250</sub>/MnO<sub>2</sub> and 1.3 times higher for Ti/PMeT<sub>1500</sub>/MnO<sub>2</sub> in comparing to the Ti/MnO<sub>2</sub> electrode.

It is important to point out that the PMeT is also a capacitive material. However, as seen in Fig. 3, the current densities of the Ti/PMeT electrodes in Na<sub>2</sub>SO<sub>4</sub> electrolyte are much smaller than the MnO<sub>2</sub> deposits. Previous studies in the literature [48,49], show that the PMeT has a better performance in non-aqueous solvents, such as, acetonitrile. Specific capacitances on the order of 270 F g<sup>-1</sup> are reported in the literature [50] for PMeT electrodes electrochemically deposited and characterized in 1 mol L<sup>-1</sup> NEt<sub>4</sub>BF<sub>4</sub>/propylene carbonate. The low response of the polymeric electrode in Na<sub>2</sub>SO<sub>4</sub> solution indicates that the capacitance of the polymer coating should not have an important contribution to the total capacitance of the composite electrode. However, electrochemical impedance spectroscopy studies with electrodes made by deposition of RuO<sub>x</sub> on poly(3,4-ethylenedioxythiophene) show that they have a pseudocapacitive component associated with the PEDT [40].

Fig. 4 presents a specific capacitance of MnO<sub>2</sub> ( $C^{**}$ ) as a function of the scan rate. As expected, the capacitance decreases with increasing scan rate. Nevertheless, this decrease is more pronounced to Ti/PMeT<sub>250</sub>/MnO<sub>2</sub>. When the scan rate was increased from 10 to 200 mV s<sup>-1</sup>, the  $C^{**}$  of Ti/PMeT<sub>250</sub>/MnO<sub>2</sub> was reduced to 70%. In the same way, decreases of 60 and 34% were observed for Ti/MnO<sub>2</sub> and Ti/PMeT<sub>1500</sub>/MnO<sub>2</sub>, respectively. This occurs because the charge is dependent not only on the potential, but also of the scan rate, since the adsorption and/or insertion process is limited by the cation diffusion to active sites of the electrode.

All electrochemical results show that the PMeT coating has a primary importance on the properties of the oxide film. Changes in the PMeT deposition conditions should lead to improving the capacitive property of the composite electrode. Nonetheless, although there is a possibility of a capacitive contribution from the polymeric coating, we shall see in what follows that improvements in the charge storage property of the electrodes occur mainly due to morphologic effects.

The surface morphology analysis is shown in Fig. 5. The first micrograph shows the surface of the Ti/PMeT<sub>250</sub> electrode. A compact and porous deposit is observed, similar to the Ti/PMeT<sub>1500</sub> electrode surface. The Ti/MnO<sub>2</sub> electrode (Fig. 5b and c) has a compact granular structure and presents cracks: both are characteristics of this oxide category. When the MnO<sub>2</sub> is deposited on the PMeT coating its surface undergoes very visible modifications. In both cases for composite electrodes, an increase in the grain size was observed, as well as a very irregular surface with granular agglomerates and deep cracks. A more irregular surface and smaller grain sizes are present in Ti/PMeT<sub>250</sub>/MnO<sub>2</sub> electrodes (Fig. 5d and e) when compared to Ti/PMeT<sub>1500</sub>/MnO<sub>2</sub> electrodes (Fig. 5f). The cracks are present in Ti/PMeT<sub>250</sub>/MnO<sub>2</sub> surface and can be observed in the amplification of the Fig. 5e.

Therefore, the effect of polymer on the electrode properties is obvious. Compact structures such as the Ti/MnO<sub>2</sub> electrode should significantly reduce the mobility of the ions in the oxide compared to the structure shown for the Ti/PMeT/MnO<sub>2</sub> elec-

trodes. The PMeT deposit leads to changes in the morphology of the oxide coating. An irregular surface produced by oxide on polymer leads to more sites that are susceptible to redox reactions, a greater active area and consequently, higher capacitance. In the same way, the Ti/PMeT<sub>250</sub> produced oxide with smaller grain size than the Ti/PMeT<sub>1500</sub>. The smaller grain size also leads to a higher number of active sites. A possible justification for such a large effect could be a change in the mechanism for the nucleation kinetics of the MnO<sub>2</sub>. The increase in surface area is possibly due to inhibited grain growth or an increase in the oxide growth rate.

#### 4. Conclusions

MnO<sub>2</sub> electrochemically deposited on titanium covered by PMeT presents a voltammetric profile that is the same as for oxide deposited directly on titanium. However, the PMeT coating leads to an increase in the capacitive property of the oxide. Although the polymer may contribute to the specific capacitance of the electrode, since it is also a pseudocapacitive material, we believe that the improved charge storage property of the electrodes is related mainly to changes in the morphology of the manganese oxide deposit due to the presence of the polymeric film. The maximum specific capacitance value was of 218 F g<sup>-1</sup> ( $v = 20$  mV s<sup>-1</sup>) for the sample prepared on Ti/PMeT<sub>250</sub> as a substrate, and this value is three times larger if only the mass of the MnO<sub>2</sub> is considered.

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#### References

- [1] R. Kotz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483–2498.
- [2] B.E. Conway, *J. Electrochem. Soc.* 138 (1991) 1539–1548.
- [3] B.E. Conway, V. Birss, J. Wojtowicz, *J. Power Sources* 66 (1997) 1–14.
- [4] R.A. Huggins, *Solid State Ionics* 134 (2000) 179–195.
- [5] W.G. Pell, B.E. Conway, W.A. Adams, J. de Oliveira, *J. Power Sources* 80 (1999) 134–141.
- [6] E. Faggioli, P. Rena, V. Danel, X. Andrieu, R. Mallant, H. Kahlen, *J. Power Sources* 84 (1999) 261–269.
- [7] A. Du Pasquier, I. Plitz, J. Gural, S. Menocal, G. Amatucci, *J. Power Sources* 113 (2003) 62–71.
- [8] X. Liu, T. Osaka, *J. Electrochem. Soc.* 143 (1996) 3982–3986.
- [9] A. Celzard, F. Collas, J.F. Maréché, G. Furdim, I. Rey, *J. Power Sources* 108 (2002) 153–162.
- [10] H. Pröbstle, C. Schmitt, J. Fricke, *J. Power Sources* 105 (2002) 189–194.
- [11] A. Lewandowski, M. Zajder, E. Frackowiak, F. Béguin, *Electrochim. Acta* 46 (2001) 2777–2780.
- [12] J.P. Zheng, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) L6–L8.
- [13] J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699–2703.
- [14] I.-H. Kim, K.-B. Kim, *Electrochem. Solid State Lett.* 4 (2001) A62–A64.
- [15] C.-C. Hu, K.-H. Chang, *J. Power Sources* 112 (2002) 401–409.
- [16] B.-O. Park, C.D. Lokhande, H.-S. Park, K.-D. Jung, O.-S. Joo, *J. Power Sources* 134 (2004) 148–152.
- [17] J. Mozota, B.E. Conway, *Electrochim. Acta* 28 (1983) 1–8.

- [18] B.E. Conway, J. Mozota, *Electrochim. Acta* 28 (1983) 9–16.
- [19] J. Jiang, A. Kucernak, *Electrochim. Acta* 47 (2002) 2381–2386.
- [20] M. Toupin, T. Brousse, D. Bélanger, *Chem. Mater.* 14 (2002) 3946–3952.
- [21] M. Toupin, T. Brousse, D. Bélanger, *Chem. Mater.* 16 (2004) 3184–3190.
- [22] C.-C. Hu, T.-W. Tsou, *Electrochem. Commun.* 4 (2002) 105–109.
- [23] C.-C. Hu, T.-W. Tsou, *J. Power Sources* 115 (2003) 179–186.
- [24] R.N. Reddy, R.G. Reddy, *J. Power Sources* 124 (2003) 330–337.
- [25] R.N. Reddy, R.G. Reddy, *J. Power Sources* 132 (2004) 315–320.
- [26] Y. Lee, V. Manivannan, J.B. Goodenough, *C.R. Acad. Sci. Ser. II* 2 (1999) 565–577.
- [27] K.R. Prasad, N. Miura, *J. Power Sources* 135 (2004) 354–360.
- [28] K.R. Prasad, N. Miura, *Electrochem. Commun.* 6 (2004) 1004–1008.
- [29] J.N. Brogton, M.J. Brett, *Electrochim. Acta* 50 (2005) 4814–4819.
- [30] K.W. Nan, K.B. Kim, *Electrochemistry* 69 (2001) 467–472.
- [31] K.R. Prasad, N. Miura, *Appl. Phys. Lett.* 85 (2004) 4199–4201.
- [32] H.-K. Kim, T.-Y. Seong, J.-H. Lim, W.I. Cho, Y.S. Yoon, *J. Power Sources* 102 (2001) 167–171.
- [33] F. Fusalba, P. Gouérec, D. Villers, D. Bélanger, *J. Electrochem. Soc.* 148 (2001) A1–A6.
- [34] K.S. Ryu, K.M. Kim, N.-G. Park, Y.J. Park, S.H. Chang, *J. Power Sources* 103 (2002) 305–309.
- [35] A. Clémente, S. Panero, E. Spila, B. Scrosati, *Solid State Ionics* 85 (1996) 273–277.
- [36] S.A. Hashmi, A. Kumar, S.K. Tripathi, *Eur. Polym. J.* 41 (2005) 1373–1379.
- [37] A. Laforgue, P. Simon, C. Sarrazin, J.-F. Fauvarque, *J. Power Sources* 80 (1999) 142–148.
- [38] A. Laforgue, P. Simon, J.-F. Fauvarque, *Synth. Met.* 123 (2001) 311–319.
- [39] C. Arbizzani, M. Mastragostino, F. Soavi, *J. Power Sources* 100 (2001) 164–170.
- [40] J. Hong, I.-H. Yeo, W. Paik, *J. Electrochem. Soc.* 148 (2001) A156–A163.
- [41] P. Gómez-Romero, M. Chojak, K. Cuentas-Gallegos, J.A. Asensio, P.J. Kulesza, N. Casan-Pastor, M. Lira-Cantú, *Electrochem. Commun.* 5 (2003) 149–153.
- [42] K.H. An, K.K. Jeon, J.K. Heo, S.C. Lim, D.J. Bae, Y.H. Lee, *J. Electrochem. Soc.* 149 (2002) A1058–A1062.
- [43] Z. Zhou, N. Cai, Y. Zhou, *Mater. Chem. Phys.* 94 (2005) 371–375.
- [44] L. Micaroni, D. Dini, F. Decker, M.-A. De Paoli, *J. Solid State Electrochem.* 3 (1999) 352–356.
- [45] L. Micaroni, M.-A. De Paoli, *Sol. Energy Mater. Sol. Cells* 43 (1996) 79–81.
- [46] J.P. Zheng, J. Huang, T.R. Jow, *J. Electrochem. Soc.* 144 (1997) 2026–2031.
- [47] S.-C. Pang, M.A. Anderson, T.W. Chapman, *J. Electrochem. Soc.* 147 (2000) 444–450.
- [48] J. Roncali, *Chem. Rev.* 92 (1992) 711–738.
- [49] F.-J. Pern, A.J. Frank, *J. Electrochem. Soc.* 137 (1990) 2769–2777.
- [50] A. Du Pasquier, A. Laforgue, P. Simon, *J. Power Sources* 125 (2004) 95–102.