Accepted Manuscript

Title: Polyaniline/porous carbon electrodes by chemical polymerization: Effect of carbon surface chemistry

Authors: M.J. Bleda-Martínez, E. Morallón, D. Cazorla-Amorós

PII: S0013-4686(07)00191-0
DOI: doi:10.1016/j.electacta.2007.01.073
Reference: EA 12331

To appear in: *Electrochimica Acta*

Received date: 13-10-2006
Revised date: 13-12-2006
Accepted date: 25-1-2007

Please cite this article as: M.J. Bleda-Martínez, E. Morallón, D. Cazorla-Amorós, Polyaniline/porous carbon electrodes by chemical polymerization: Effect of carbon surface chemistry, *Electrochimica Acta* (2007), doi:10.1016/j.electacta.2007.01.073

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**POLYANILINE/POROUS CARBON ELECTRODES BY CHEMICAL
POLYMERIZATION: EFFECT OF CARBON SURFACE CHEMISTRY**

M.J. Bleda-Martínez, E. Morallón^{a*}, D. Cazorla-Amorós

Departamento de Química Inorgánica. Universidad de Alicante. Ap. 99, E-03080.

Alicante. Spain

^a Departamento de Química-Física. Universidad de Alicante. Ap. 99, E-03080.

Alicante. Spain

* Corresponding author: e-mail: morallon@ua.es

FAX: (+34) 965 903537

TEL: (+34) 965 909590

ABSTRACT

Polyaniline/porous carbon composite electrodes were prepared by chemical polymerization and characterized in terms of porosity and performance as electrochemical capacitors

To obtain the composite electrodes two methods were used. The first method consisted of mixing, directly, the activated carbon with chemically polymerized polyaniline. The second one consisted of mixing the activated carbon with aniline and subsequent chemical polymerization. Additionally, the second process was carried out with the porous carbon previously thermally treated in N₂ up to 900°C in order to remove surface oxygen groups.

Changes in porosity with the polyaniline addition were analysed. It has been proved that the method used strongly affects the porous structure. Dealing with the electrochemical performance, polyaniline and carbon mechanically mixed seem to work independently, being the composite behaviour a combination of the corresponding performance of both materials separately. The composites prepared by the second method (polymerization over carbon) reveal the key role of surface chemistry in polyaniline coating. Aniline reacts with the oxygen complexes and their positive effect in capacitance is not observed.

The second method (polymerization over carbon) using a thermally treated carbon seems to be the best one since a more porous (or thinner) polyaniline film is produced.

Keywords: Activated carbon; Polyaniline; Surface oxygen complexes; Capacitance; Chemical polymerisation

1. INTRODUCTION

Porous carbons are extensively studied as electrode materials for double layer capacitors due to their large surface area, chemical stability, easy processability and long cycle life [1, 2]. These porous materials can store electrical energy mainly in an electrostatic way, similarly to negative or positive electric charges on the plates of a capacitor. As a result they present high power density. However, they can not provide as much energy density as faradaic pseudocapacitors, because of the relatively low specific capacitance of the electrical double layer [3]. It is important to remark that porous carbon materials can also present a pseudocapacitive behaviour due to redox processes undergone by surface functional groups, but this contribution is not as important as the one related to the double layer charge.

On the other hand, conducting polymers are able to store energy through their redox processes. These polymers can be considered as potential candidates for electrochemical capacitor materials because they present a continuous range of oxidation states with increasing electrode potential, thus presenting a pseudocapacitive behaviour [1]. Moreover, they exhibit a three dimensional mechanism of charge storage, that is, the mechanism involving the conducting polymer is a bulk process, leading to large values of energy density [4-6]. Nevertheless, conducting polymers have also disadvantages. Cycle life is lower than that provided by porous carbon materials because redox sites in the polymer chain are not stable enough for many repeated redox processes [7]. Apart from that, swelling and shrinkage of conducting polymers occurring with insertion/deinsertion of counter ions produce mechanical stress which also causes a minor long-term stability [8].

Taking into account the positive and negative features shown by both porous carbon materials and conducting polymers, it is reasonable to develop a carbon/conducting polymer composite which could improve the performance of supercapacitors, taking advantage from both, the double layer mechanism provided by porous carbon materials and the pseudocapacitive contribution from conducting polymers. Besides, carbon materials improve mechanical properties and stability of the original polymer matrix [9], and conducting polymers can also supply an increased electrical conductivity [10, 11].

Among all conducting polymers, p-dopable ones are more stable against degradation than n-dopable [12]. Polyaniline is one of the most important ones due to its easy polymerisation in aqueous media, good stability in air and easiness in doping/dedoping [13, 14]. Additionally, its preparation costs are competitive [14-16] and it has a high conductivity close to 2 S/cm [14]. The PANI doping level, which is the main controlling factor of the electrical conductivity, will depend on the thickness of the PANI layer, since it involves ions diffusion through the bulk of the polymer [17]. Dealing with the capacitance values, polyaniline electrodes can reach capacitance values about of 700-800 F/g [16, 18, 19]. Moreover, the electrochemical behaviour of polyaniline electrochemically polymerised has been extensively studied [20-26].

Composites preparation from carbon materials and electrochemically polymerised polyaniline was extensively studied [10, 11, 13, 27-31]. However, the electrochemical method to prepare polyaniline is limited in terms of mass production [7, 8]. In spite of the fact that chemical polymerisation is easier than the electrochemical one [32], composites from carbon and chemically polymerised polyaniline was rarely studied and

most of them use carbon nanotubes [6- 9, 32, 33]. Very little work has been done dealing with activated carbon and chemically polymerised polyaniline [34, 35].

In this research, we prepared composites using a chemically activated carbon (AC) with a high development of porosity and chemically polymerised polyaniline (PANI) following different methods. The first one consists of the mechanical mixing of the activated carbon and polyaniline in different amounts. The second one consists of mixing the carbon with aniline in different amounts and carrying out a subsequent chemical polymerisation in acidic media. Changes in porosity and electrochemical behaviour with the polyaniline addition were analysed and interpreted in terms of the relevance of the carbon surface chemistry on the resulting PANI coating.

2. EXPERIMENTAL

2.1. Chemicals

Chemicals used such as KOH, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, HCl, NH_4OH and aniline were from Merck p.a., acetylene black was from Strem Chemicals and binder (poly(vinylidene)chloride – PVDC- copolymer) from Sutcliffe Speakman. All these chemicals were used as received except aniline which was freshly distilled three times by refluxing before use

2.2. Samples preparation

2.2.1. Electrode preparation by the first method (i.e., mechanical mixing of AC and PANI).

An anthracite was chemically activated using KOH as activating agent. The activating agent/carbon ratio employed was 3:1. The activation temperature (750°C) was kept for 1 hour in inert atmosphere (800 ml/min N₂). Details of the activation process are available elsewhere [36].

In order to obtain polyaniline, a 0.1M aniline and 1M HCl solution was placed in a polymerisation reactor at 0°C. Ammonium persulphate dissolved in 1M HCl solution and at the same temperature was added to the reactor. The aniline:ammonium persulphate molar ratio was 1:1. The polymerisation started with the oxidant addition and finished in two hours time, approximately. The resultant polymer was then washed with 1M HCl to remove oligomers. Subsequently it was washed with 1M NH₄OH in order to obtain the polymer in its base state. The polymer was dried in dynamic vacuum for 24 hours. Details of the process are available elsewhere [37]. The scheme of the polymerization is included below.

Composite electrodes were prepared by mixing the chemically activated anthracite, polyaniline, acetylene black and binder (PVDC copolymer), in different amounts. Table 1 shows these percentages.

Table 1. Preparation conditions for electrodes prepared by mechanical mixing of AC and PANI.

Electrode	% Activated carbon	% Polyaniline	% Acetylene Black	% Binder
A	75%	0%	9%	15%
AM1	59%	15%	9%	17%
AM2	53%	23%	9%	15%
AM3	45%	30%	9%	16%
PANI	0%	100%	0%	0%

2.2.2. Electrode preparation by the second method (i.e., polymerisation over carbon:

AC and aniline mixing and subsequent polymerisation)

In order to develop electrodes following the second method, composites were prepared as in the first one but employing pure aniline instead of the previously polymerised polyaniline. The compositions are shown in Table 2. Once prepared, these composites were introduced for an hour in an ammonium persulphate solution in 1M HCl. The oxidant amount was calculated in order to obtain an aniline:ammonium persulphate molar ratio equal to 1:1. A polyaniline coating is then obtained over the carbon material. The composites were then washed with 1M HCl.

To analyse the effect of surface chemistry in polyaniline coating, the same process was carried out with the activated carbon previously treated up to 900°C in an inert atmosphere (N₂) (Sample ATT). After this thermal treatment, the activated carbon loses most of its surface oxygen complexes (from 3413 $\mu\text{mol/g}$ in the pristine AC to 366

$\mu\text{mol/g}$ in the heat treated sample [38]). The composition of these composites is also included in Table 2.

Table 2. Preparation conditions for electrodes prepared by chemical polymerisation of aniline in presence of AC.

Electrode	% Activated carbon	% Aniline	% Acetylene Black	% Binder
AP1	61%	11%	9%	19%
AP2	59%	18%	10%	13%
ATT	77%	0%	10%	13%
ATTP1	66%	12%	10%	12%
ATTP2	58%	18%	10%	13%

2.3. Porous texture characterization

Porous texture of all samples was determined by physical adsorption (N_2 at 77 K and CO_2 at 273 K) using an automatic adsorption system (Autosorb-6, Quantachrome) after samples out-gassing at 523 K under vacuum for 4 h. The total micropore volume (pore size smaller than 2 nm) was calculated from the application of the Dubinin-Radushkevich equation to the N_2 adsorption at 77K. The narrow micropore volume (pore size smaller than around 0.7 nm) was assessed from CO_2 adsorption at 273 K using the DR equation [39]. The densities of the adsorbed phase used for the calculations, were 0.808 and 1.023 g/ml for N_2 and CO_2 [39], respectively. The apparent surface area was calculated by the BET equation.

2.4. XPS and Elemental analysis

XPS on the samples were obtained by using a VG-Microtech Multilab electron spectrometer. The source employed was the Mg Ka (1253.6 eV) radiation of twin anode

in the constant analyser energy mode. Pressure of the analysis chamber was maintained below $1.33 \cdot 10^{-7}$ Pa. The binding energy scale was regulated by setting the C1s transition. Peak areas were estimated by calculating the integral of each peak after subtraction of the background and fitting the experimental peak by a Gaussian–Lorentzian (70:30) curve.

A Carlo Erba model CHNS-O EA1108 elemental analyzer was also used.

2.5. *Electrochemical characterization.*

The composite electrodes prepared were pressed in a stainless steel mesh as a current collector. The electrochemical characterization of the electrodes was done using a standard three electrode cell configuration. Reversible hydrogen electrode (RHE), immersed in the same solution, was used as reference and a spiral of platinum wire was employed as a counter electrode. 1M H₂SO₄ was used as aqueous electrolyte.

The redox behaviour of the samples was assessed by cyclic voltammetry in 1M H₂SO₄ solution at 0.5 mV s^{-1} . The capacitance values were calculated from the integration of the area of the voltammograms. The result is expressed in F g^{-1} taking into account the weight of the active part of the composite, that is, carbon and polyaniline. The weight of the electrodes used was of about 80 mg of active material. The geometric surface was about 2 cm^2 .

All electrochemical measurements were carried out with an EG&G Potentionstat/Galvanostat model 273 controlled by software EChem M270. All the

solutions were prepared with ultrapure water (Purelab ELGA) with a resistivity of 18 M Ω cm.

3. RESULTS AND DISCUSSION

3.1 Porous texture characterization

Table 3 contains the BET surface areas and the micropore volumes calculated from N₂ adsorption data at 77 K [$V_{DR}(N_2)$] and CO₂ adsorption data at 273 K [$V_{DR}(CO_2)$] for each sample. The pristine AC is an essentially microporous material [36], which porosity decreases somewhat after the thermal treatment (compare sample A and ATT). Regarding the PANI-containing composites, the porosity of the materials depends on the preparation method. Thus, the porosity decreases for the materials prepared by mechanical mixing of the PANI and AC (samples AM in Table 3) and, specially, for the samples prepared by polymerization of the aniline and the pristine AC (samples AP in Table 3). However, porosity remains unchanged for the composites prepared with the heat treated AC (samples ATT in Table 3).

Table 3. Textural characterization and capacitance values for all the samples.

Sample	BET (m ² /g)	$V_{DR}(N_2)$ (cm ³ /g)	$V_{DR}(CO_2)$ (cm ³ /g)	C (F/g)
PANI	46	0.02	0.05	226
A	1442	0.68	0.43	228
AM1	1127	0.53	0.33	273
AM2	1075	0.52	0.33	316
AM3	920	0.44	0.31	296
AP1	921	0.44	0.27	187
AP2	903	0.43	0.28	182
ATT	1110	0.53	0.34	125
ATTP1	1021	0.49	0.29	133
ATTP2	1101	0.53	0.30	148

In order to deepen into the influence of polyaniline coating in the textural properties of the composites, a theoretical BET surface area was calculated for each sample considering that the composite BET surface area should be a lineal combination of both the carbon material and the polyaniline surface area. In this calculation, it was supposed that acetylene black and binder do not contribute to surface area. The results obtained are shown in Fig. 1. In this figure, experimental BET surface area values have been plotted vs. calculated BET surface area. Composites placed on the diagonal straight line have the theoretical BET value. If points are located over this line, they show a BET value higher than expected and vice versa. It can be seen that the points corresponding to samples prepared by mechanical mixing (samples AM) are situated approximately on the straight line, that is to say, they follow the mixtures rule. However, samples prepared by chemical polymerisation over the pristine AC (samples AP) show a lower BET surface area than expected. In this case, polyaniline seems to block part of the porosity. Composites prepared by chemical polymerisation over the thermally treated carbon material (samples ATT), follow the opposite trend, that is, they are over the straight line of Figure 1. This means that PANI is positively contributing to the porosity of the composites, what indicates that it has higher porosity than the pure PANI. Thus, it can be concluded that the AC can contribute to obtain a more porous polyaniline using this preparation method.

3.2 *Electrochemical characterization*

The capacitance values of the composite electrodes, measured by cyclic voltammetry, are shown in Table 3. The capacitance values for the AC (sample A) and the thermally

treated (sample ATT), were previously discussed [38]. The differences in capacitance between both samples result from the differences in porosity and surface chemistry. Both, a larger surface area and amount of surface oxygen groups, contribute positively to the capacitance value [38,40].

Regarding the composites, it can be observed that those prepared by mechanical mixing with polyaniline (samples AM) and after aniline polymerisation over the thermally treated carbon (samples ATT), have higher capacitance than their corresponding AC (i.e., sample A and ATT, respectively). However, the capacitance values of the composites prepared after aniline polymerisation over the pristine AC (sample A), which contains an important concentration of surface oxygen groups, are lower than for the AC alone (compare sample A and samples AP).

The voltammograms in 1M H₂SO₄ for the samples prepared by direct mixing are shown in Fig 2. It can be observed that the activated carbon (sample A) presents a quasi-rectangular voltammogram shape, indicating that the charge of the double layer is the main contribution to capacitance. Samples AM1, AM2, also present the double layer contribution and a redox peak at approximately 0.45V related to the leucoemeraldine-emeraldine transition [14, 21, 24, 26]. Moreover, as the amount of polyaniline increases (AM3 sample), a noticeable change in the voltammogram shape appears. This change in the voltammogram is more marked for pure polyaniline and it is attributed to limited ions diffusion-migration process in the bulk of the polymer and to the ohmic drop within the thick polymer layer [26]. The integration of the curves, taking into account the scan rate and the double layer contribution has allowed us to estimate the ratio charge-to-mass for chemically polymerised polyaniline.

Dealing with samples prepared by the second method (polymerization over carbon), voltammograms are shown in Fig. 3 and Fig. 4, for the composites made from the pristine carbon (sample A) and the thermally treated one (sample ATT), respectively. The amount of polyaniline in these samples was estimated from the charge of the voltammogram peaks at approximately 0.39V, subtracting the double layer contribution and considering the ratio charge-to-mass for polyaniline calculated previously. The estimated percentage of polyaniline in these samples is shown in Table 4.

Table 4. Percentage of polyaniline in samples prepared by chemical polymerisation of aniline in presence of AC

Sample	% PAni
AP1	2 %
AP2	3 %
ATTP1	2 %
ATTP2	6 %

As it can be seen in Table 4, the amount of polyaniline in samples prepared by the second method (polymerization over carbon) is much lower than the initial aniline amount in the composites. Thus, it can be concluded that the polymerisation reaction has not produced the total conversion of aniline, that is, the polymerisation has not been complete. Apart from that, it can be observed that the yield is better for the samples polymerised over the thermally treated carbon.

Figure 3 shows that the contribution related to double layer charge decreases with increasing the amount of polyaniline. The opposite trend is shown for the redox contribution (peak at about 0.35V), which increases with the polyaniline content. Apart from that, the broad redox peak located at 0.5-0.7 V in the activated carbon sample has

almost disappeared in the carbon-polyaniline composites. This broad peak has been assigned to the surface redox processes undergone by surface oxygen complexes [38]. These results suggest that part of the available surface area has decreased with the polyaniline coating (in agreement with the BET surface area) and some surface oxygen groups have been partially removed by reaction with aniline, as it has been confirmed by XPS and will be shown later.

Figure 4 shows that the double layer contribution does not decrease with the amount of polyaniline (again in agreement with the porosity data) but that the capacitance of the samples prepared with the thermally treated AC, increases. This is the opposite of what was observed with samples obtained from the pristine activated carbon (Figure 3). Apart from that, redox processes related to surface oxygen complexes are present neither in the ATT sample nor in the polyaniline coated ones.

It is suggested that if there are surface oxygen complexes in the carbon material, aniline can react with them. If these oxygen complexes are located near the pores entrance, then, their reaction with aniline and subsequent polymerisation would block some of the porosity. However, if there are not surface oxygen complexes, aniline does not have specific sites to react, and then, it settles homogeneously within the activated carbon pores and will not block the porosity, considering that the amount of PANI is small.

Interestingly, the redox process related to leucoemeraldine-emeraldine transition in polyaniline is more reversible for samples prepared by the second method (polymerization over carbon). This phenomenon was previously reported for composites made from electrochemically synthesised polyaniline and single walled

nanotubes (SWNTs). A slight negative shift in this oxidation peak, compared with pure polyaniline, occurs when SWNT are added, improving reversibility [31]. It seems that the carbon material helps polyaniline to be rougher and thinner and, consequently, to give better redox kinetics [13]. This statement from the literature is corroborated if the capacitance associated to the PANI in sample ATTP2 is estimated. A capacitance value of 400 F/g is obtained, which is much higher than that for the chemically polymerized PANI (226 F/g in Table 3).

3.3 XPS and elemental analysis results

In order to verify the former hypothesis (reaction of surface oxygen complexes with aniline), 1.5 g of the original carbon (sample A) was oxidized by mixing with concentrated nitric acid during 3 h at room temperature to increase the content in surface oxygen groups. After this treatment, the sample was washed several times with hot distilled water until the pH of the filtrate was the same as the washing water. Then, the sample was dried at 100°C (sample AO). Aniline was added to this oxidised carbon material (sample AOAni) in an amount of approximately 40 wt%.

The elemental analysis and XPS results for samples A, AO and AOAni are shown in Table 5. Both XPS and elemental analysis show that the oxidation treatment in nitric acid is very efficient to increase the oxygen content of the activated carbon, as it is well known. Interestingly, aniline addition produces an important decrease in the oxygen content as clearly observed in the O/C ratio included in Table 5. Thus, it is confirmed that aniline incorporation removes surface oxygen complexes by reaction with them.

Table 5. Elemental analysis and XPS results.

Sample	% Carbon		% Nitrogen		% Hydrogen	% Oxygen		O/C (ratio)	
	EA	XPS	EA	XPS	EA	EA	XPS	EA	XPS
A	82.98	86.89	0.00	0.00	0.56	16.46	13.11	0.20	0.15
AO	74.25	80.11	0.61	0.00	0.92	24.22	19.89	0.33	0.25
AOAni	81.91	84.76	5.40	4.69	2.14	10.55	10.55	0.13	0.12

Figure 5 shows the N1s spectrum for sample AOAni to analyse the state of aniline after the chemical polymerization in the oxidised sample. Nitrogen in samples A and AO was undetectable by XPS. The N1s spectrum consists of a broad peak that can be deconvoluted into three components at 398.7 ± 0.3 eV, 399.4 ± 0.3 eV and 400.5 ± 0.3 eV. The peak at 398.7 can be attributed to the neutral imine nitrogen ($-N=$) [41-47]. The peak at 399.4 ± 0.3 eV corresponds to neutral amine nitrogen ($-NH-$) [41-43, 45]. These peaks are in agreement with the formation of polyaniline, thus corroborating the voltammetric results. The peak at 400.5 ± 0.3 eV is usually assigned to pyrrolic nitrogen [41-45] and could be associated to the reaction products of aniline and surface oxygen groups on the carbon surface [41].

4. CONCLUSIONS

Different activated carbon/polyaniline composite electrodes have been developed in order to study their electrochemical behaviour and performance as supercapacitors. The preparation method of these composites has turned out to be very important. The first method used consisted of mechanical mixing polyaniline with the activated carbon. The results suggest that polyaniline and the carbon material work independently, and the performance of the composite electrode can be considered as a combination of the two components separately. On the other hand, the results dealing with the second method

used (chemical polymerisation over carbon) suggest that the polyaniline coating strongly depends on surface chemistry. Aniline reacts with surface oxygen groups, thus eliminating their positive effect on capacitance and producing important changes in porosity. In this sense, the polymerisation of aniline over a carbon material containing surface oxygen groups does not improve capacitance values.

Taking into account the results of this experimental work, carbon/polyaniline composites are more effective as capacitors if the two components are mixed directly or polymerised over a carbon material with a low content in surface oxygen complexes. This last method is very efficient to improve PANI contribution to the total capacitance of the material compared to the pure PANI. It is remarkable that small additions of PANI (about 6 wt%) can produce an increase in capacitance of about 20% of the pristine activated carbon (from 125 F/g to 148 F/g).

ACKNOWLEDGEMENTS. The authors thank MEC for financial support (Project PPQ2003-03884 and MAT 2004-01479). M.J.B.-M. thanks MEC for the thesis grant.

REFERENCES

- [1] Conway BE. Electrochemical Capacitors. Kluwer Academic/Plenum Publishers, New York, 1999
- [2] Frackowiak E, Béguin F. Carbon 39 (2001) 937
- [3] Zhou Z, Cai N, Zhou Y. C. Materials Chemistry and Physics 94 (2005) 371
- [4] Burke A. Journal of Power Sources 91 (2000) 37
- [5] Girija TC, Sangaranarayanan MV. Synthetic Metals 156 (2006) 244
- [6] Deng M, Yang B, Hu Y. Journal of Materials Science (2005) Letters.
- [7] Park HJ, Ko JM, Park OO, Kim DW. Journal of Power Sources 105 (2002) 20.
- [8] Khomenko V, Frackowiak E, Béguin F. Electrochimica Acta 50 (2005) 2499
- [9] Zhou YK, He BL, Zhou WJ, Huang J, Li XH, Wu B, Li HL. Electrochimica Acta 49 (2004) 257
- [10] Jang J, Bae J, Choi M, Yoon SH. Carbon 43 (2005) 2730
- [11] Sivakumar C, Nian JN, Teng H. Journal of Power Sources 144 (2005) 295
- [12] Ryu KR, Lee Y, Han KS, Park YJ, Kang MG, Park NG, Chang SH. Solid State Ionics 175 (2004) 765
- [13] Ko JM, Song RY, Yu HJ, Yoon JW, Min BG, Kim DW. Electrochimica Acta 50 (2004) 873
- [14] Hu CC, Lin JY. Electrochimica Acta 47 (2002) 4055
- [15] Gupta V, Miura N. Electrochemical and Solid-State Letters 8 (2005) A630
- [16] Ryu KS, Kim KM, Park NG, Park YJ, Chang SH. Journal of Power Sources 103 (2002) 305
- [17] Zhou H, Chen H, Luo S, Lu G, Wanzhi W, Kuang Y. Journal Solid State Electrochemistry 9 (2005) 574.

- [18] Rajendra Prasad K, Munichandraiah N. Journal of The Electrochemical Society 149 (2002) A1393
- [19] Zhou H, Chen H, Luo S, Lu G, Wei W, Kuang Y. Journal Solid State Electrochemistry 9 (2005) 574
- [20] Mondal SK, Rajendra Prasad K, Munichandraiah N. Synthetic Metals 148 (2005) 275
- [21] Aoki K, Tano S. Electrochimica Acta 50 (2005) 1491
- [22] Leinad Gnana Lissy S, Pitchumani S, Jayakumar K. Materials Chemistry and Physics 76 (2002) 143
- [23] Roßberg K, Paasch G, Dunsch L, Ludwig S. Journal of Electroanalytical Chemistry 443 (1998) 49
- [24] Santiago EI, Pereira EC, Bulhões LOS. Synthetic Metals 98 (1998) 87
- [25] Clemente A, Panero S, Spila E, Scrosati B. Solid State Ionics 85 (1996) 273
- [26] Fusalba F, Gouérec P, Villers D, Bélanger D. Journal of The Electrochemical Society 148 (2001) A1
- [27] Chih W, Wen TC, Teng H. Electrochimica Acta 48 (2003) 641
- [28] Lin YR, Teng H. Carbon 41 (2003) 2865
- [29] Talbi H, Just PE, Dao LH. Journal of Applied Electrochemistry 33 (2003) 465
- [30] Hu CC, Li WY, Lin JY. Journal of Power Sources 137 (2004) 152
- [31] Zhou YK, He BL, Zhou WJ, Li HL. Journal of The Electrochemical Society 151 (2004) A1052
- [32] Frackowiak E, Khomenko V, Jurewicz K, Lota K, Béguin F. Journal of Power Sources 153 (2006) 413
- [33] Wu, M, Snook, GA, Gupta, V, Shaffer, M, Fray, D.J , Chen, GZ. Journal of Materials Chemistry 23 (2005) 2297

- [34] Ryu KS, Lee YG Kim KM, Park YJ, Hong YS, Wu X, Kang MG, Song RY, Ko JM. *Synthetic Metals* 153 (2005) 89
- [35] Zhou ZH, Cai N, Zeng Y, Zhou YH. *Chinese Journal of Chemistry* 24 (2006) 13
- [36] Lozano-Castelló D, Lillo-Ródenas MA, Cazorla-Amorós D, Linares-Solano A. *Carbon* 39 (2001) 741
- [37] Salavagione HJ. Ph Thesis, Universidad Nacional de Río Cuarto. (2003).
- [38] Bleda-Martínez MJ, Lozano-Castelló D, Morallón E, Cazorla-Amorós D, Linares-Solano A. *Carbon* 44 (2006) 2642
- [39] Cazorla-Amorós D, Alcaniz-Monge J, De la Casa-Lillo MA, Linares-Solano A. *Langmuir* 14 (1998) 4589
- [40] Bleda-Martínez MJ, Macia-Agullo JA, Lozano-Castelló D, Morallón E, Cazorla-Amorós D, Linares-Solano A. *Carbon* 43 (2005) 2677
- [41] Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A, Find J, Wild U, Schlögl J. *Carbon* 40 (2002) 597
- [42] Cagniant D, Gruber R, Boudou JP, Bilem C, Bimer J, Salbut PD. *Energy & Fuels* 12 (1998) 672
- [43] Cansen RJJ, van Bekkum H. *Carbon* 33 (1995) 1021
- [44] Li F, Qian Q, Yan F, Yuan G. *Carbon* 44 (2006) 128
- [45] Pels JR, Kapteijn F, Moulijn JA, Zhu Q, Thomas KM. *Carbon* 33 (1995) 1641
- [46] Matter PH, Zhang L, Ozkan US. *Journal of Catalysis* 239 (2006) 83
- [47] Lota G, Gryzyb B, Machnikowska H, Machnikowski J, Frackowiak E. *Chemical Physics Letters* 404 (2005) 53

FIGURE CAPTIONS

Figure 1. Experimental BET surface area vs. calculated BET surface area

Figure 2. Cyclic voltammograms for electrodes prepared by the first method (mechanical mixing) in 1M H₂SO₄ solution. 0.5 mV s⁻¹. Room temperature

Figure 3. Cyclic voltammograms for electrodes prepared by the second method (polymerization over carbon) in 1M H₂SO₄ solution. 0.5 mV s⁻¹. Room temperature

Figure 4. Cyclic voltammograms for electrodes prepared by the second method (polymerization over carbon) with the carbon thermally treated in 1M H₂SO₄ solution. 0.5 mV s⁻¹. Room temperature

Figure 5. N1s XPS spectrum for sample AOAni

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5