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Pseudocapacitance effects for enhancement of capacitor performance

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Abstract

We report on the pseudo-capacitance induced by a nitrogen substituted in the carbon network composite prepared by a simple carbonization (750⁰C) of formaldehyde and melamine in the presence of carbon nanotubes. Nitrogen content in the composites varied from 7.4 to 21.7 wt%. Such materials have a higher density than activated carbons, hence, they can supply better volumetric capacity. N-rich composites show an excellent charge propagation at current loads from 500 mA g⁻¹ to 50 A g⁻¹ because of multiwalled nanotubes which play a conducting as well as a supporting role. The electrochemical performance of various composites was investigated in two and three electrode cells using acidic (1 mol L⁻¹ H₂SO₄), alkaline (6 mol L⁻¹ KOH), neutral (1 mol L⁻¹ Na₂SO₄) and organic electrolytes (1 mol L⁻¹ TEABF₄ in acetonitrile). Organic and neutral medium is not adapted for N-rich carbon electrodes of supercapacitor. The detailed electrochemical characterization pointed out the differences of charge propagation of electrodes with the different polarity.

Keywords: Supercapacitor, Pseudocapacitance, Doped Carbon, Nitrogen, Melamine

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1 Introduction

The most commonly used electrode materials for electrochemical capacitors are activated carbons, because they are commercially available and they can be produced with large specific surface area [1-9]. However, only their electrochemically available surface area is useful for charging the electrical double layer (EDL). The EDL formation is especially efficient in carbon pores of size below 1 nm because of the lack of space charge and a good attraction of ions along pore walls [10-12]. Taking into account the size of solvated cations and anions, most of such ions are definitively in this range. However, during formation of EDL a solvating cloud surrounded ions could be partially lost under polarization [10, 12]. On the other hand, for quick transportation and better charge propagation, some small mesopores are useful. Obviously interconnectivity of pores as well as a good wettability are also important parameters for an efficient EDL performance.

Lately, it has been shown that some carbons even with a moderate surface area can supply interesting capacitance values because of heteroatom presence in the carbon network. In this case pseudocapacitance phenomena connected with a quick faradaic reactions take place. The most often heteroatoms present in the carbon network are oxygen, nitrogen, hydrogen. Especially nitrogen and oxygen are of great interest for capacitance enhancement. The profitable effect of these heteroatoms in carbon network has been already documented [13-25]. The type of surface groups is crucial for a good cycling performance of supercapacitor. Especially, in the case of nitrogen atoms the various groups such as pyridinic, pyrrolic, quaternary, pyridonic and pyridine N-oxide are commonly distinguished among N atoms substituted for carbon in a ring system [26]. The variety of surface functionality results both from the position occupied in the ring system and from the extent of association with oxygen that hardly can be avoided during a synthesis. The surroundings of nitrogen atom in graphene layer obviously affect its charge, electron donor/acceptor properties and the contribution to the delocalized π electron system.

Generally, presence of nitrogen in carbon material can enhance capacitance due to faradaic redox reactions but also because of the modification of its electronic character as well as improvement of electrode wettability.

Enrichment in nitrogen can be realized by a few ways such as ammoxidation, i.e. the reaction with ammonia/air mixture applied at various stages of preparation of porous material (by treatment of raw material as well as performed before or after activation) [17]. Another

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3 procedure is carbon activation by nitrogen oxide. However, carbonization of suitable
4 precursors rich in heteroatoms is the most popular method. It has been already proved that
5 through the carbonisation of organic precursors rich in nitrogen some carbon materials
6 adapted for supercapacitor can be obtained [15,16, 18-24]. The porosity of final carbons
7 depends often on the type and amount of gases evolved during carbonisation, sometimes a
8 profitable autoactivation of carbon can take place. In this case adding of nanotubes to the
9 substrate before carbonisation is useful and gives exceptional properties of composite. It is
10 well known that pure carbon nanotubes supply moderate capacitance values but they have a
11 great interest for electrochemical use because of their extraordinary physical characteristics.
12 Especially, their electrical conductivity and mechanical properties (high resiliency) as well as
13 mesoporous character are profitable for formation of various electrode composites with
14 conducting polymers, transition metal oxides but also carbon/carbon nanocomposites from
15 polymer rich in nitrogen [15, 16, 24]. For the preparation of carbon composites with various
16 N content, a melamine has been often used as an attractive carbon precursor rich in nitrogen
17 (45 wt%). Such nitrogenated composites appear to be interesting materials for supercapacitors
18 [24].

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21 High power supercapacitor is able to supply or collect a charge in a short time, e.g. for
22 starting vehicle or recovery energy from braking. It is an attractive power source of long-
23 durability mainly for hybrid application. Hence, for this application, the electrode materials
24 with a quick charge propagation and a good cyclability is demanded.

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27 In this paper, our aim is to investigate the beneficial effect of nitrogen in the composite
28 with incorporated nanotubular backbone taking into account a polarity of electrode. For this
29 target most of experiments are performed in a three electrode cell to see the behaviour of
30 positive and negative electrode separately. The role of electrolytic solution on capacitance
31 properties of N-rich carbons was also investigated.

32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 **2 Experimental**

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55 Carbon composites have been prepared by a polymerisation of melamine with
56 formaldehyde in the presence of controlled amount of multiwalled carbon nanotubes. Carbon
57 nanotubes were obtained by catalytic method using $\text{Co}_x\text{Mg}_{1-x}\text{O}$ solid state catalyst and
58 acetylene as a carbon source [27]. Hydrogen evolved during acetylene decomposition could
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3 easily reduce cobalt oxide supplying *in situ* Co catalyst particles, in turn, multiwalled carbon
4 nanotubes were formed with a very high efficiency. For the nanotubes purification a
5 concentrated HCl has been used. Procedure of composite preparation was described elsewhere
6 [24]. Briefly, the polymerised blend was carbonised at 750 °C for one hour. The final
7 carbonisation product was named M+F (i.e. melamine and formaldehyde without carbon
8 nanotubes) whereas N+M+F means composite with carbon nanotubes. 2M and 3M stands for
9 a twofold and threefold melamine proportion in the blend.

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16 The elemental analysis performed on CHNS VARIO EL3 showed that nitrogen content
17 varied in the final product from 7.4 to 21.7 wt%. Oxygen content was calculated by difference
18 and its amount was comparable in all the samples varying from 5.9 to 7.8 wt%. X-ray
19 Photoelectron Spectroscopy (XPS) technique was selected to analyse the surface chemistry of
20 samples using VSW Ltd England. For the observation of the composite texture, transmission
21 electron microscopy (TEM) with a JEM3010 apparatus was used.

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28 Electrochemical characterization was performed on the electrodes in the shape of pellets.
29 They contained 85 wt.% of composite, 10 wt% of polyvinylidene fluoride (PVDF Kynar Flex
30 2801) and 5 wt% of acetylene black. The mass of electrodes were in the range of 8 to 14 mg
31 and a geometric surface area of one electrode was 0.8 cm². Different types of electrolyte was
32 used for electrochemical investigation, i.e. 1 mol L⁻¹ H₂SO₄, 6 mol L⁻¹ KOH, 1 mol L⁻¹
33 Na₂SO₄ and 1 mol L⁻¹ TEABF₄ in acetonitrile. The capacitance properties of the composite
34 materials (expressed per mass of one electrode) were investigated by galvanostatic (50 mA g⁻¹
35 – 50 A g⁻¹) and potentiodynamic cycling (1 mV s⁻¹ to 1000 mV s⁻¹) and by impedance
36 spectroscopy (100 kHz-1 mHz) using ARBIN Instruments BT2000 – USA, VMP2/Z Biologic
37 - France and AUTOLAB 30 FRA2-Netherlands potentiostat-galvanostats.

3 Results and Discussion

3.1 Physicochemical characterization

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The detailed physicochemical characterization allows to correlate the electrochemical
behaviour with physical properties (Table 1). For the description of morphology and texture,
the nanotubular composites were observed by transmission electron microscopy (TEM). The
selected images of composite N+2M+F with 11% content of nitrogen and composite
N+3M+F with 14 wt% of N are shown in Fig. 1a, b, respectively. It is well seen that

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3 nanotubes play a template effect where a composite reflects entangled morphology of
4 nanotubes preserving presence of mesopores. A good adhesion of homogeneously distributed
5 polymer to Nts is demonstrated. Increasing the melamine content, in the case of N+3M+F, a
6 gradual change in composite morphology takes place and a compact texture together with
7 some agglomerates is observed. On the other hand, a simple carbonisation product of
8 melamine and formaldehyde (M+F) blend without nanotubes gives an amorphous and less
9 porous texture.

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16 Three main peaks N1s have been observed by XPS analysis, however, pyridinic with
17 binding energy of 398.7 eV and quaternary (400.9 eV) are dominant. The amount of pyridinic
18 groups is the same, i.e. 4.9 at.% in composites N+2M +F and N+3M+F whereas it reaches
19 10.2 at.% for M+F and only 2.7 at% for N+M+F composite. The quaternary nitrogen
20 gradually decreases from 13.4 at% for M+F composite to 4.8 at% for N+M+F whereas it is
21 almost the same, i.e. 7.9 at% and 7.3 at% for N+3M+F and N+2M+F, respectively. The
22 elemental analysis performed on CHNS VARIO EL3 showed that nitrogen content in
23 composites varied from 7.4 to 21.7 wt%. It is important to stress that values from elemental
24 analysis and XPS are very comparable that is a proof of the same perfect distribution of
25 nitrogen in the bulk of carbon network as well as on the surface. On the other hand, the
26 amount of oxygen was almost the same in all the samples giving values from 5.9 to 7.8 wt%.

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35 Nitrogen sorption/desorption isotherms allow to estimate the specific surface area, pore
36 size distribution as well as micro/meso ratio. Total surface area is quite similar for the
37 investigated samples and it ranges from 329 to 403 m² g⁻¹ being the most developed for
38 N+3M+F composite (Table 1). Nitrogen sorption isotherms showed that carbon materials are
39 typically mesoporous (apart from material M+F, i.e. without nanotubes) and the amount of
40 micropores is very moderate. The micropore volume values for all the samples is comparable
41 varying from 0.152 to 0.174 cm³ g⁻¹. For sample (N+2M+F) a very accurate method to
42 monitor only the amount of ultramicropores, i.e. the pores smaller than 0.8 nm was realized
43 by sorption of carbon dioxide at 273 K. The value of pore volume was 0.118 cm³ g⁻¹ that
44 gives 409 m² g⁻¹. It can be assumed that small ultramicropores are also dominant in other
45 composites.

56 3.2 Electrochemical measurements

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60 The electrochemical performance of nitrogen enriched composites used as electrodes in
supercapacitor were partly determined by the porosity development. However, the surface

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3 chemistry being related primarily to the type and concentration of nitrogen containing groups
4 plays also an important role. It is also well known that presence of nitrogen improves
5 wettability of carbon matrix, hence, it can be predicted that aqueous electrolytic solution will
6 be preferable.
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10 Electrochemical properties of nitrogen enriched composites have been carefully
11 investigated by three electrochemical techniques (voltammetry cycling, galvanostatic
12 charge/discharge and impedance spectroscopy). Fig. 2 presents voltammetry characteristics at
13 potential scan rate of 10 mV s^{-1} for all the composites in $1 \text{ mol}^{-1} \text{ H}_2\text{SO}_4$. The curves show a
14 mirror-like behaviour typical for ideal capacitor. Only the composite M+F without nanotubes
15 containing 21.7 wt% nitrogen presents definitively worse characteristic the most probably
16 because of higher resistance. The capacitance values estimated by the integration of charge
17 are the following: composite (M+F) – 86 F g^{-1} , (N+M+F) – 101 F g^{-1} , (N+2M+F) – 157 F g^{-1} ,
18 and (N+3M+F) – 141 F g^{-1} . Typically for pseudofaradaic reactions the accessibility of ions to
19 the bulk of electrode material is crucial, however, in the case of M+F the porosity is less
20 developed due to the lack of nanotubes. The voltammetry at various scan rate (from 1 mV s^{-1}
21 until 1 V s^{-1}) for the best selected sample N+2M+F in $1 \text{ mol}^{-1} \text{ H}_2\text{SO}_4$ is presented in Fig. 3. It
22 is noteworthy that the registration of potentiodynamic characteristic at so high regime of 1 V
23 s^{-1} is extremely rare and proves an exceptional charge propagation. Obviously at so quick scan
24 rate an ideal square shape is not possible, however, the obtained characteristic is acceptable.
25 The galvanostatic charge/discharge is the most reliable method for estimation capacitor
26 performance in real application. The various current loads have been selected from 50 mA g^{-1}
27 to 50 A g^{-1} . The ability of charge accumulation diminishes with a load but still the sample
28 N+2M+F is able to supply capacitance of 60 F g^{-1} at 50 A g^{-1} current density. The impedance
29 spectroscopy can be also extremely useful for capacitor characterization. For example
30 expressing an increment of capacitance vs logarithm of frequency one can find so called
31 “frequency limit” after which a rapid capacitance drop is observed (Fig. 4). Generally the
32 higher this value the better charge propagation. For the sample N+2M+F the frequency limit
33 reaches a high value of 6.3 Hz.
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53 Detailed investigation were undertaken to explain what is the electrochemical behaviour
54 of both electrodes separately. For that, the galvanostatic charge/discharge in a two electrode
55 capacitor was performed with a simultaneous control of potential for both electrodes. Such
56 characteristics for N+2M+F composite operating in acidic medium is shown in Fig. 5.
57 Galvanostatic charge/discharge of capacitor was performed at 1 A g^{-1} current load. It is
58 interesting to note that the capacitance of total capacitor is equal to 148 F g^{-1} whereas positive
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3 electrode shows 133 F g^{-1} and negative 166 F g^{-1} . It shows that both electrodes have a
4 different contribution to the total capacitance. The same procedure was done for voltammetry
5 experiments at scan rate of 5 mV s^{-1} in acidic medium (Fig. 6). During this investigation a
6 higher discrepancy between capacitance behavior of both electrodes was found and positive
7 electrode showed higher capacitance values. We could assume that different functional groups
8 play role in both cases. But other parameters should be also taken into account e.g.
9 conductivity.

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16 Impedance spectroscopy seems to be the most adapted method for explanation of this
17 behavior because allows the study of the effect of frequency on the electrode series resistance
18 and on specific capacitance. Studying the dependence of capacitance versus frequency for
19 total two electrode capacitor built from N+2M+F material and for both electrodes separately,
20 an anomalous behavior is observed (Fig. 7). At 1mHz frequency the capacitance of negative
21 electrode is strikingly high (227 F g^{-1}) and positive electrode (151 F g^{-1}) is similar to total
22 capacitor (162 F g^{-1}). On the other hand, anomalous increase of capacitance is observed for
23 the positive electrode in the range of higher frequency (from 0.1 Hz to 100 Hz). To explain
24 this behavior, a very useful information can be obtained from Fig. 8 where the real part of
25 impedance is shown versus frequency. The original interpretation of this dependence has been
26 proposed by authors in Ref. [28]. According to them the first drop in the range of frequency
27 from 1 to 10 mHz is driven by the series and the parallel resistance. This latter is due to the
28 electronic leakage current through the separator, to the charge redistribution inside the
29 electrode and to the self-discharge. At very low frequency the parallel resistance contribution
30 is dominant. In the range of frequency from 10 mHz to 10 Hz the information on the series
31 resistance due to electronic resistance in the conductors and to the ionic resistance in the
32 electrolyte is supplied. Generally in this frequency region the parallel resistance is negligible.
33 At lower frequency the ions are able to reach electrode deeper in the pores of activated
34 carbon. Then, from 10 Hz to 1 kHz electronic resistance because of all the connections, the
35 contact resistance between the activated carbon and the current collector as well as the
36 minimal resistance of the electrolyte are observed. The region above 1 kHz reflects
37 supercapacitor inductance and the parasitic inductance of electrical cable which is negligible
38 in our case. Taking into account all above mentioned explanation [28] some anomalies of rich
39 in nitrogen composites could be reasonably elucidated. High capacitance at 1 mHz (Fig. 7)
40 proves that redox reactions of nitrogenated groups on negative electrode are extremely
41 efficient, on the other hand electronic structure/density of electronic states due to nitrogen are
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3 dominant for positive electrode. We can assume that both these effects are responsible for
4 excellent charge propagation of composite N+2M+F.
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7 Apart of capacitance properties of composite measured in acidic electrolyte some attention
8 has been also devoted to alkaline medium 6 mol l⁻¹ KOH, neutral solution 1 mol l⁻¹ Na₂SO₄
9 and organic electrolyte 1 mol l⁻¹ tetraethylammonium tetrafluoroborate (TEABF₄) in
10 acetonitrile (ACN). Fig. 9 shows voltammetry characteristics at 10 mV s⁻¹ in all these
11 electrolytic solutions using N+M+F composite with 7.4 wt% of nitrogen. The best
12 performance was observed in acidic medium (101 F g⁻¹). Comparable values (92 F g⁻¹) were
13 obtained in alkaline medium. As expected, in organic solution the moderate capacitance
14 values of 35 F g⁻¹ have been reached. In this case the low values are justified by lack of
15 protons in organic electrolyte but also size of ions in organic solutions are bigger. The lowest
16 values were reached for neutral medium (26 F g⁻¹).
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19 Surely the nitrogen presence has a profitable effect on capacitance values as well as for
20 good capacitor performance at drastic current loads especially in aqueous electrolyte,
21 however, the excess of nitrogen (presumably over 15%) will definitively aggravate
22 conducting properties, in turn, capacitance characteristics and supercapacitor cyclability. The
23 form in which N participates in carbon network is especially important. It seems that effect of
24 NH₂- groups being outside of matrix where N is chemically bound to organic molecules
25 (“chemical nitrogen”) will be of less importance and most probably such groups could block
26 entrance to pores. Substituted to carbon (“lattice nitrogen”) in the peripheral pyridinic groups
27 could play some useful role according to reversible redox reactions [24]. A great difference
28 between a “top” and a “valley” nitrogen position is expected, the latter being more profitable
29 because of stronger donor electron character. Quaternary nitrogen seems to be the most useful
30 position having a significant effect on the carbon electronic structure through decreasing an
31 energy gap between lowest unoccupied molecular orbitals (LUMO) and the highest occupied
32 molecular orbitals (HOMO). Donor properties are responsible for filling a conduction band by
33 electrons, hence, more ions can be sorbed in electrical double layer, especially for composites
34 where carbon is optimally substituted by nitrogen. However, it was confirmed experimentally
35 that the higher amount of nitrogen (over 15%) could be at the origin of significant aggravation
36 of conductivity. Effect of N content in the electrode on the conductivity is clearly proved by
37 impedance spectroscopy and it is shown in Fig. 8. Moreover, the loss of conductivity for
38 samples with a higher N content has been also found by molecular calculation. Apart from
39 nitrogen effect a high charge propagation can be partly explained by exceptional electronic
40 transport in carbon nanotubes which are still preserved after carbonisation process. Some
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3 further improvement of conductivity could be reached by increasing of the carbonization
4 temperature to 900⁰C, however, a significant decrease of periphery nitrogen functionalities
5 would drastically appear. Presence of nitrogen affects self-discharge of electrodes. For
6 instance, in the case of higher N content (21.7%) in the composite, the voltage of capacitor
7 drops to 0.33 V after 20 h at open circuit voltage whereas a slightly higher voltage (0.42V) is
8 maintained for 11.7 % N content. The higher nitrogen content, the higher self-discharge.
9 Taking into account cyclability tests, the capacitors with optimal N content (ca. 11%) could
10 be cycled over 5000 cycles at 0.5 A g⁻¹ current load in acidic medium with only moderate loss
11 of capacity (7%). On the other hand, the capacity loss for sample with 21.7% N content,
12 cycled in the same conditions, was definitively higher 30%.

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15 It is noteworthy that these N-rich composites obtained without activation process
16 present interesting values of specific surface capacitance from 30 to 42 μF cm⁻². Additionally,
17 because the composites have a moderate surface area, their volumetric capacitance is high.
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4 Conclusions

A series of nitrogen-rich composites with a wide range of N content from 7.4 to 21.7 wt.% has been synthesized by carbonization of melamine/ formaldehyde polymer blends in the presence of carbon nanotubes. Exceptional conducting and mechanical properties of multiwalled carbon nanotubes used for carbonisation of a polymer blend, without any activation process, allowed to prepare unique composites with a comparable texture (surface area of ca. 400 m²g⁻¹) but variable nitrogen content. Pseudocapacitance effects related to the nitrogen presence in carbon composite, where nanotubes played a role of a three dimensional conducting support, have been efficiently used in electrodes of supercapacitor. The useful effect of nitrogen is connected with faradaic reactions partly due to the presence of pyridinic groups but also because of the presence of quaternary nitrogen which could be responsible for significant modification of the electronic states density. Exceptionally good dynamic of charge was obtained especially for composite with ca. 11 wt% of N. The capacitance values of 160 F g⁻¹ at 1mHz frequency diminish only to 120 F g⁻¹ at 1 Hz and remain equal to 55 Fg⁻¹ at 10 Hz. Such behaviour was correlated with the impedance real part versus frequency plot. The detailed investigation of real part of impedance in two and three electrode cell shows elucidation of possible effect of redox reactions, electronic resistance and other parameters.

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3 N+2M+F composite could be loaded at high current density of 50 A g⁻¹ because
4 mesoporous network allowed a pseudocapacitance effect of nitrogen to be efficiently used.
5 Taking into account that presence of protons is necessary for extraction of pseudocapacitance
6 effects, neutral and organic electrolytes should be excluded for N-rich composites.
7 Substitutional heteroatoms in the carbon network are a promising way to improve capacitor
8 performance. Suitable amount of nitrogen (below 15%) without conductivity aggravation is
9 able to enhance capacitance but also to improve electrode wettability. The beneficial effect
10 induced by N groups depends strongly on the electrode polarity.
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Captions of table and figures

Table 1. Physicochemical and capacitance properties of composites. Capacitance values measured at 5A g^{-1}

Fig. 1a, b Transmission Electron Microscopy images of (a) composite with ca. 11 wt% of nitrogen (N+2M+F) and (b) composite with 14 wt% of N (N+3M+F)

Fig. 2 Voltammetry characteristics at 10 mV s^{-1} for different composites in acidic medium

Fig. 3 Voltammetry characteristics at various scan rates for N+2M+F composite (acidic electrolyte)

Fig. 4 Increment of capacitance versus logarithm of frequency for N+2M+F composite. Acidic medium.

Fig. 5 Galvanostatic charge/discharge of capacitor (1A g^{-1} current load) built from N+2M+F composite with a detailed potential control of positive and negative electrode. Acidic medium.

Fig. 6 Voltammetry characteristics (5mV s^{-1}) for N+2M+F composite operating as positive and negative electrode. Acidic medium.

Fig. 7 Capacitance versus frequency dependence for two electrode cell built from N+2M+F composite and for both electrodes (+) and (-) separately. For 1 mHz total capacitor 162 Fg^{-1} , positive electrode 151 Fg^{-1} , negative electrode 227 Fg^{-1} . Acidic medium.

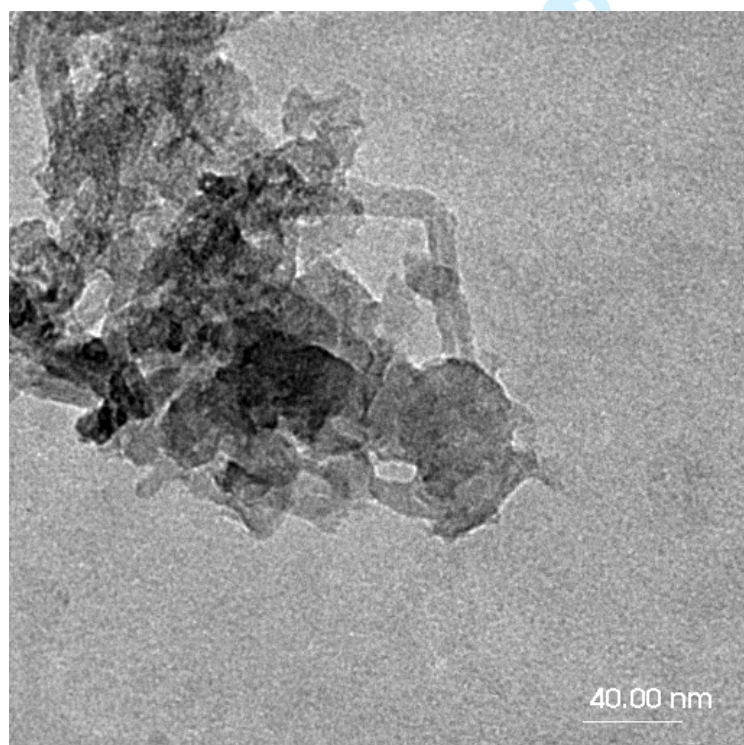
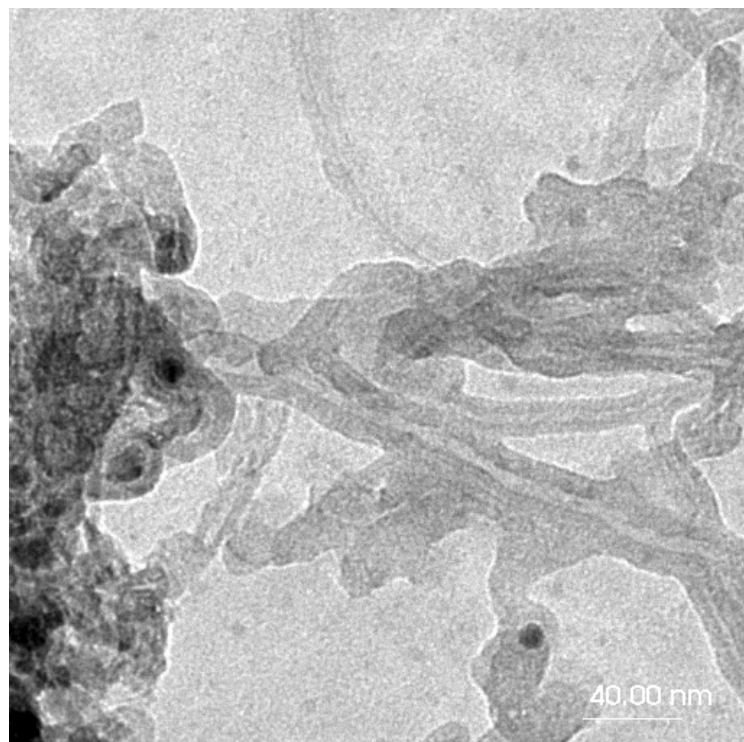
Fig. 8 Real part of impedance as a function of frequency for all the composites investigated in two electrode cells (acidic medium).

Fig. 9 Voltammetry characteristics at 10 mV s^{-1} scan rate for the nitrogen enriched composite (N+M+F). Various aqueous electrolytic solutions and organic medium.

Table 1. Physicochemical and capacitance properties of composites. Capacitance values measured at 5A g⁻¹

Sample	S _{BET} (m ² g ⁻¹)	V _t (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	N (wt%)	C (Fg ⁻¹)
M+F	329	0.162	0.152	21.7	4
N+3M+F	403	0.291	0.174	14.0	100
N+2M+F	393	0.321	0.167	11.7	126
N+M+F	381	0.424	0.156	7.4	83

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Fig. 1 a, b Transmission Electron Microscopy images of (a) composite with ca. 11 wt% of nitrogen (N+2M+F) and (b) composite with 14 wt% of N (N+3M+F)

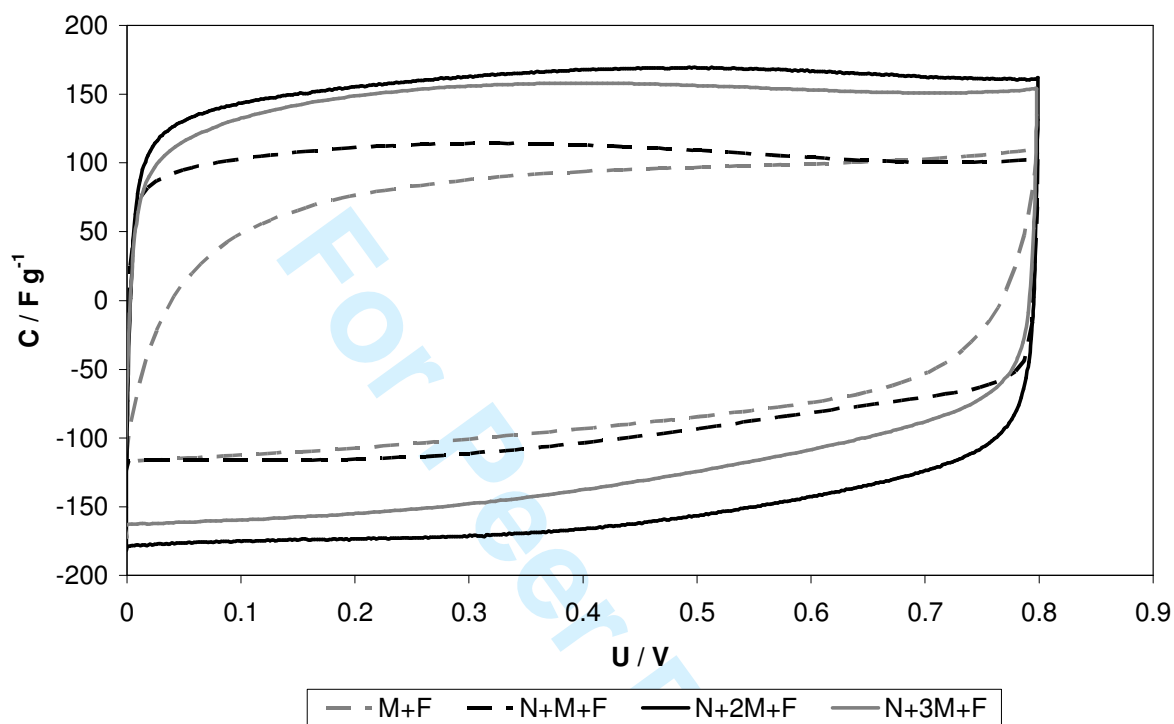


Fig. 2 Voltammetry characteristics at 10 mV s^{-1} for different composites in acidic medium

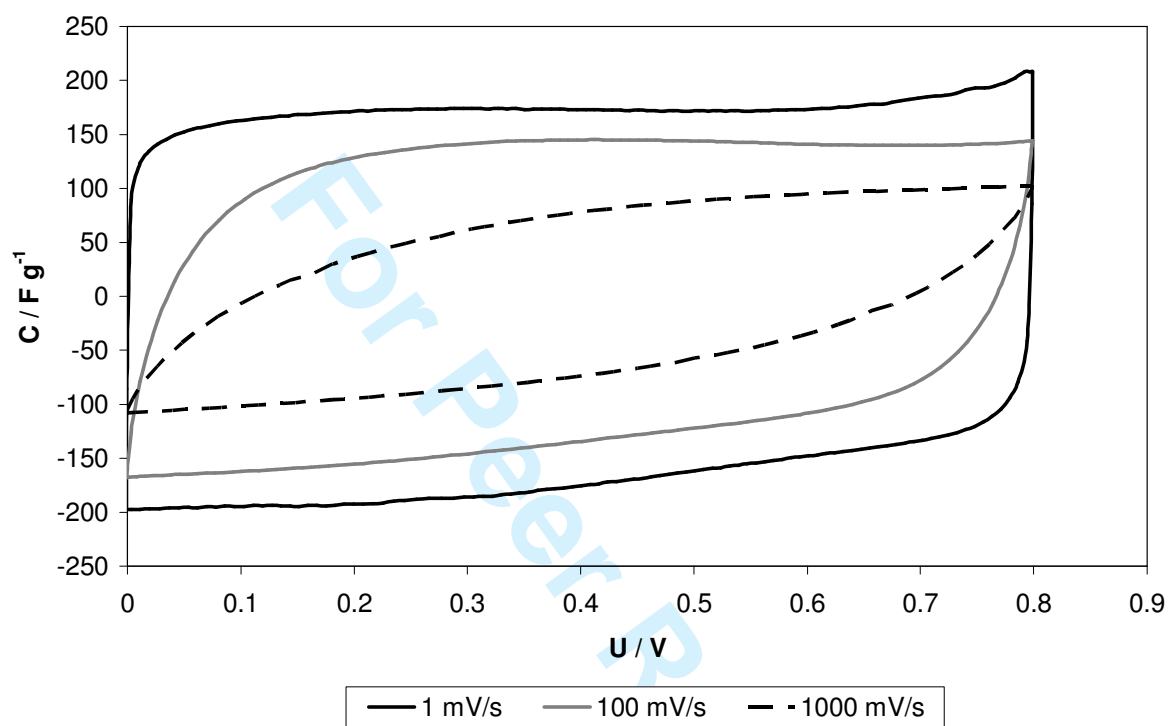


Fig. 3 Voltammetry characteristics at various scan rates for N+2M+F composite (acidic electrolyte)

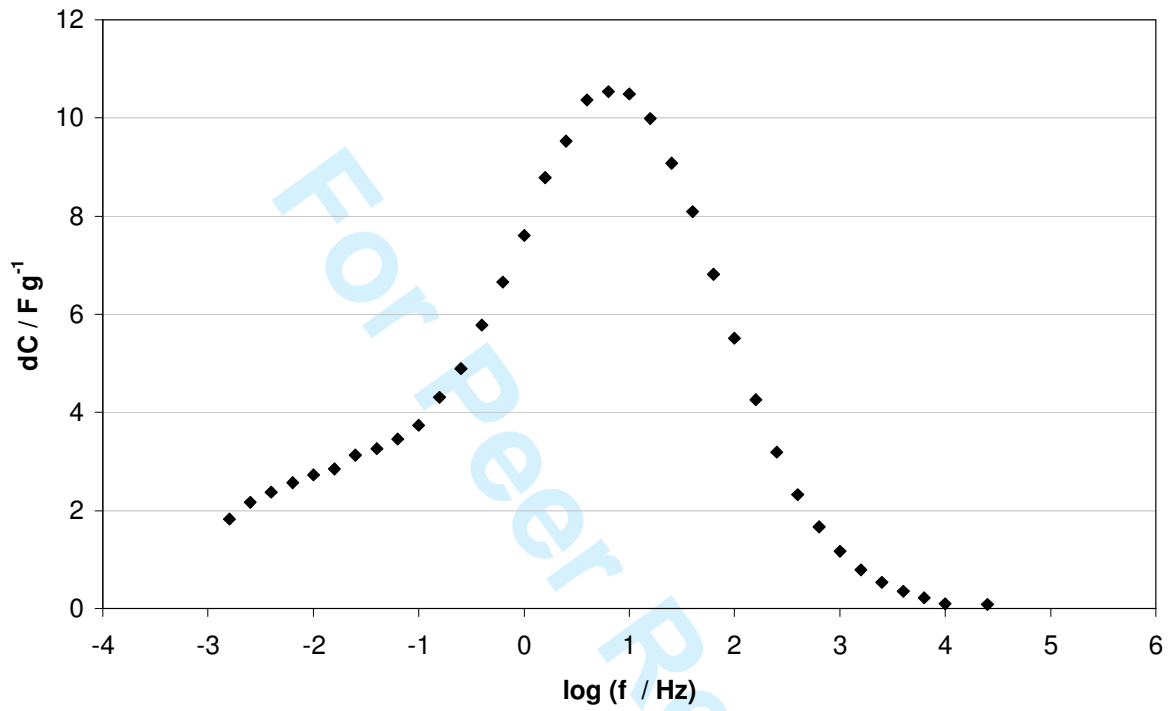


Fig. 4 Increment of capacitance versus logarithm of frequency for N+2M+F composite.
Acidic medium.

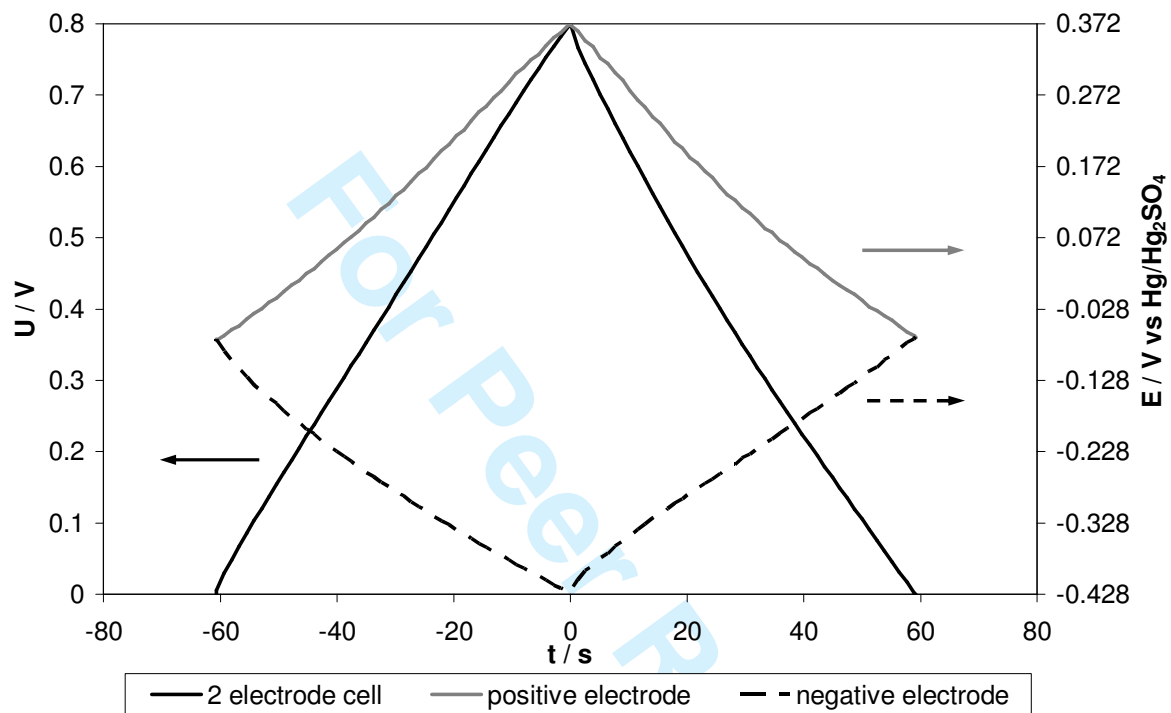


Fig. 5 Galvanostatic charge/discharge of capacitor (1A g^{-1} current load) built from N+2M+F composite with a detailed potential control of positive and negative electrode. Acidic medium.

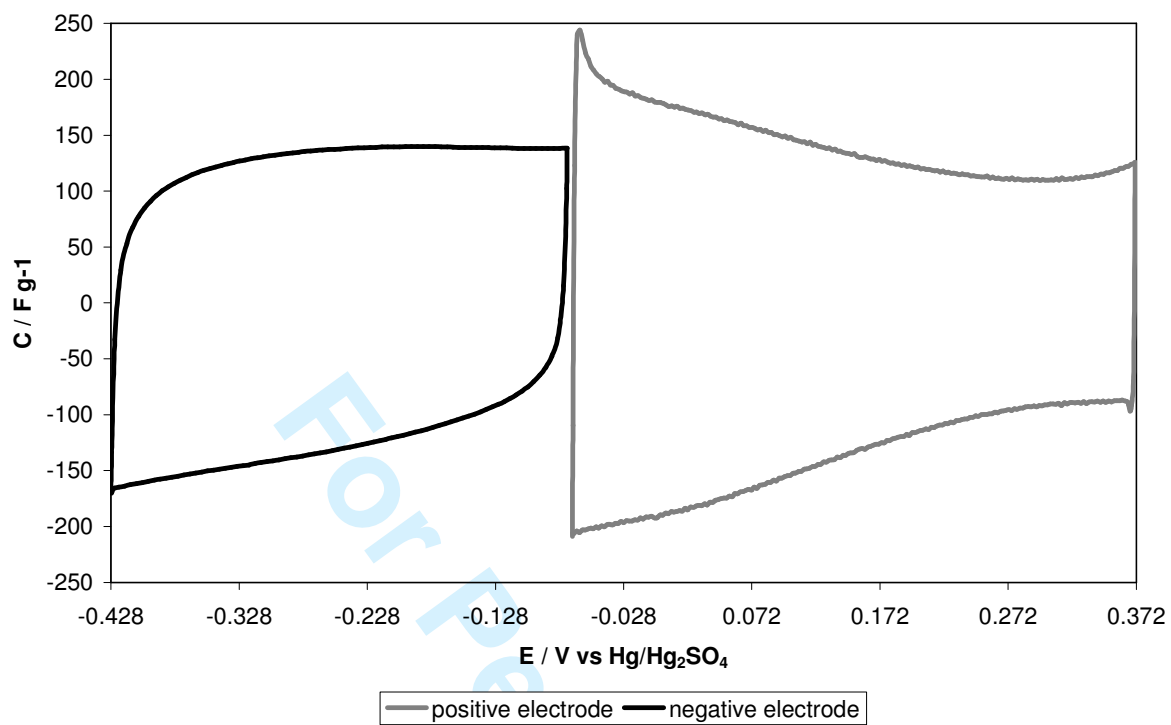


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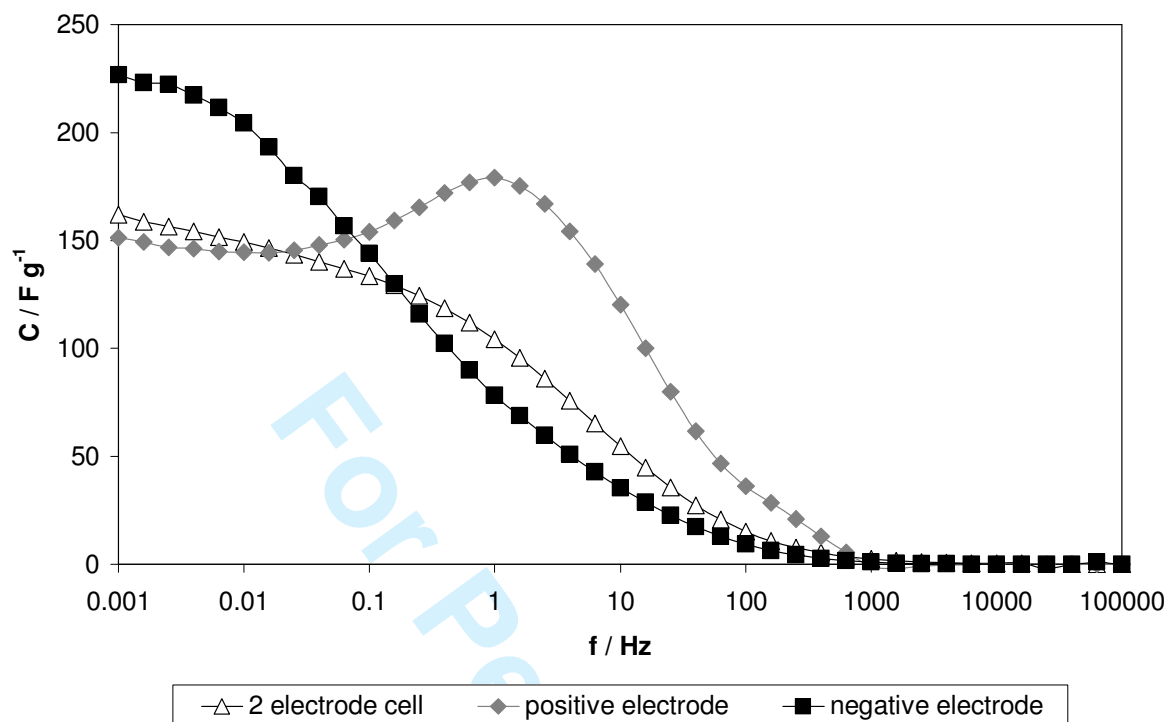


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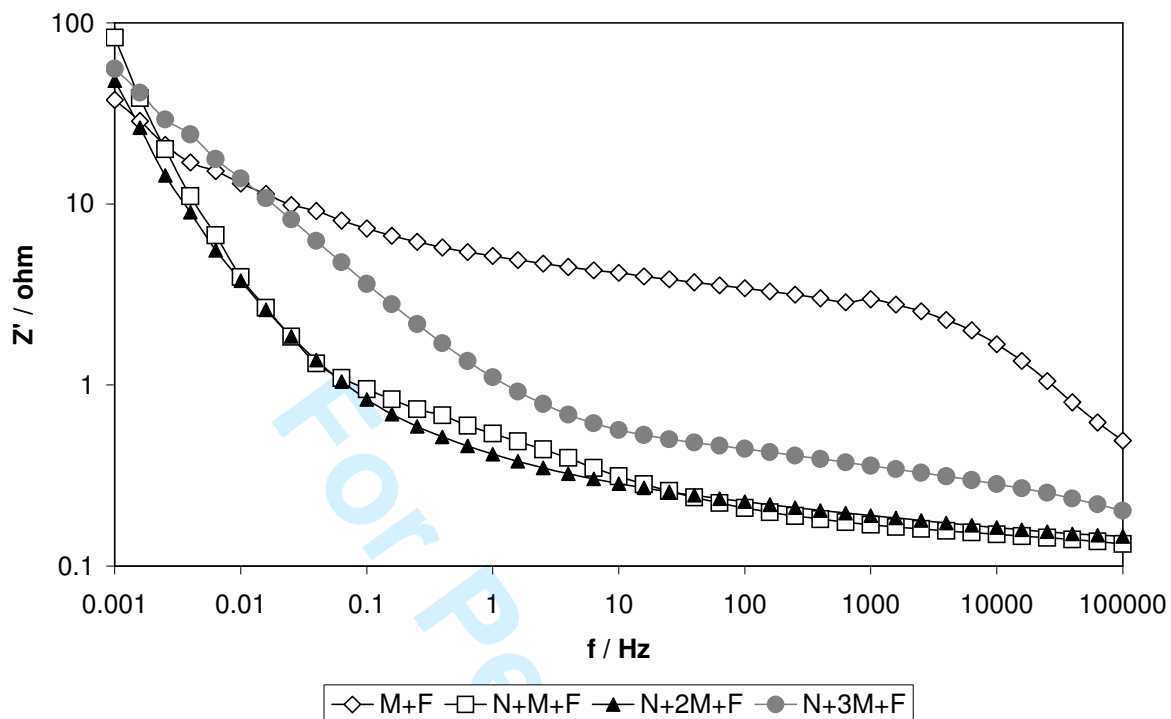


Fig. 8 Real part of impedance as a function of frequency for all the composites investigated in two electrode cells (acidic medium).

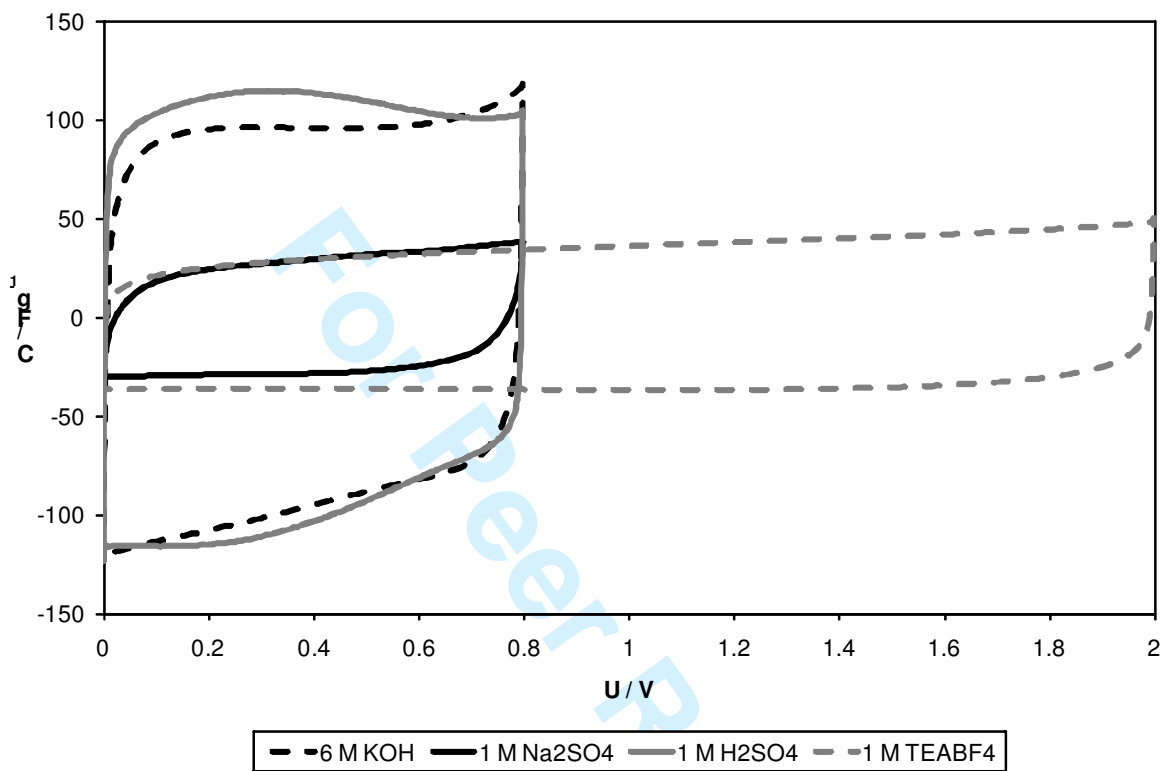


Fig. 9 Voltammetry characteristics at 10 mV s^{-1} scan rate for the nitrogen enriched composite (N+M+F). Various aqueous electrolytic solutions and organic medium.

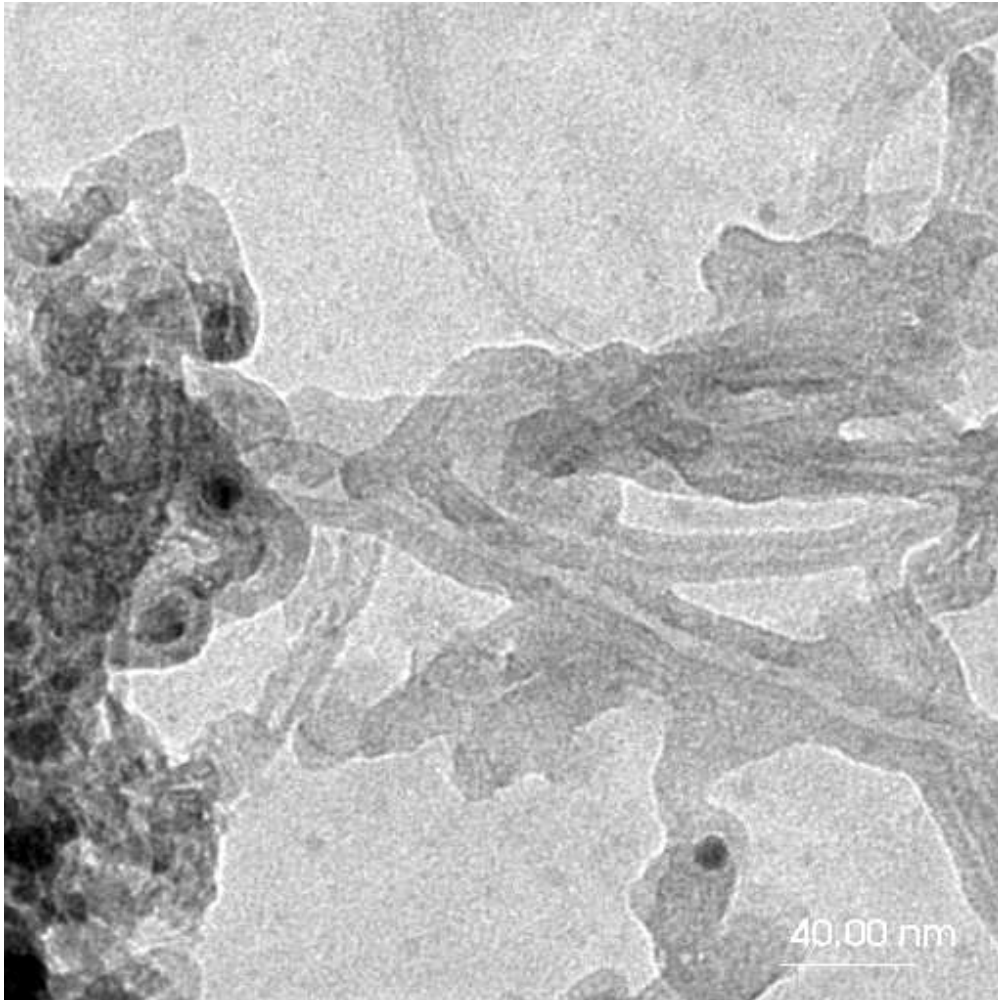


Fig. 1a Transmission Electron Microscopy image of composite with ca. 11 wt% of nitrogen
(N+2M+F)
135x135mm (96 x 96 DPI)

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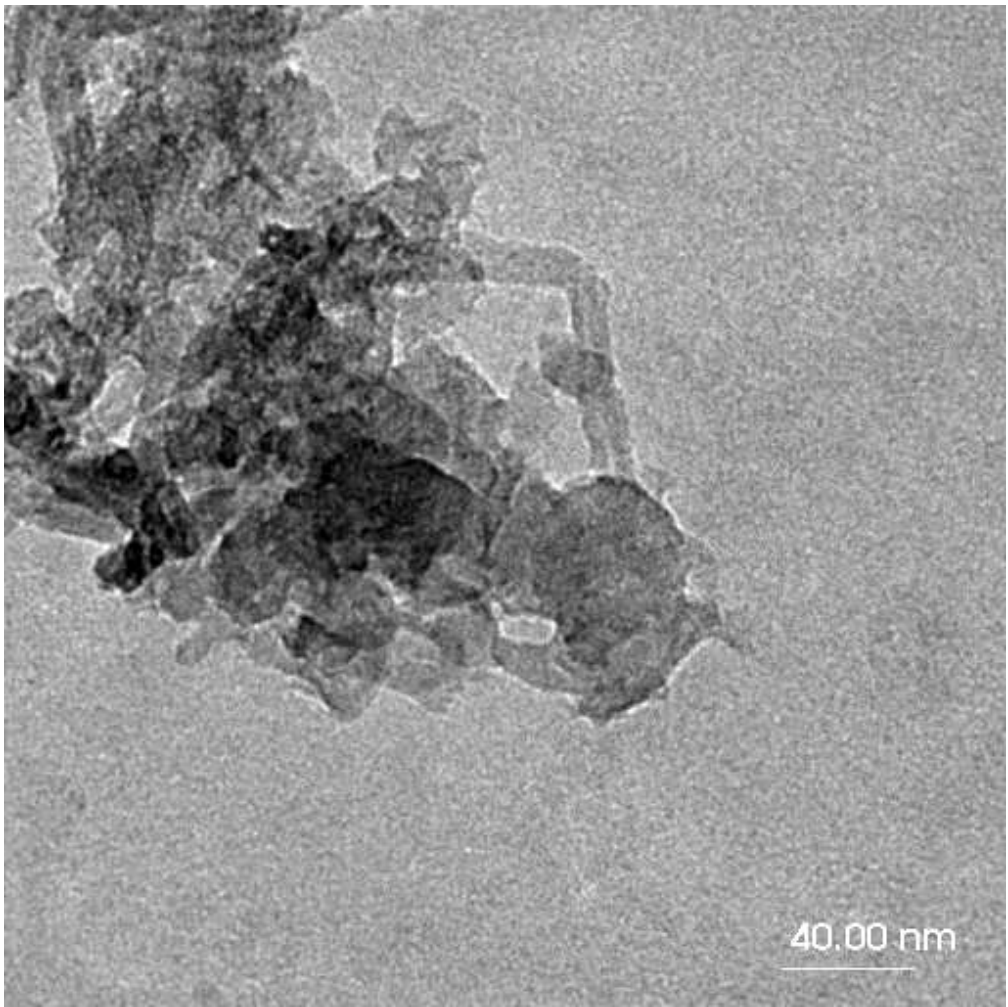


Fig. 1 b Transmission Electron Microscopy image of composite with 14 wt% of N (N+3M+F)
135x135mm (96 x 96 DPI)

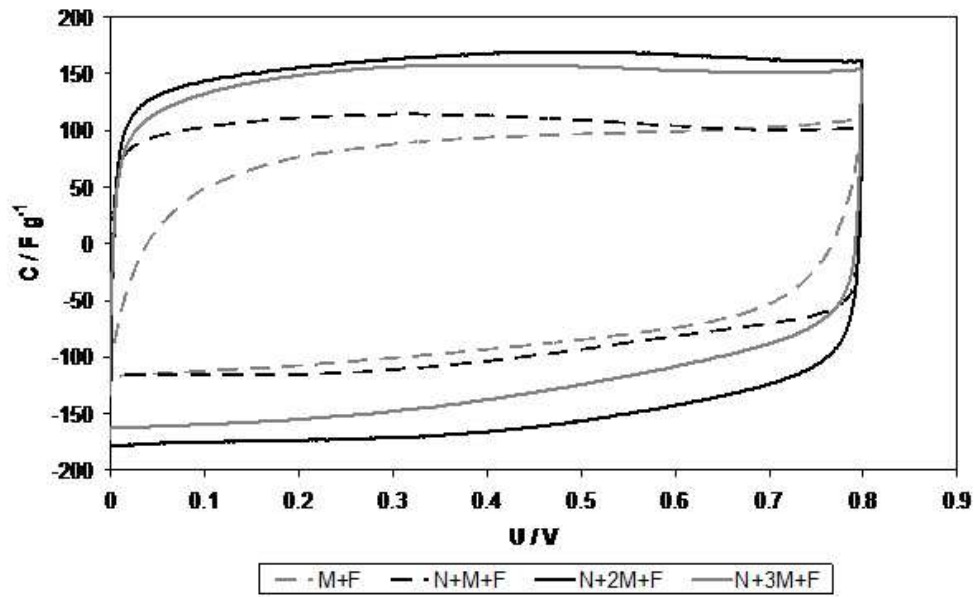


Fig. 2 Voltammetry characteristics at 10 mV s^{-1} for different composites in acidic medium
160x99mm (96 x 96 DPI)

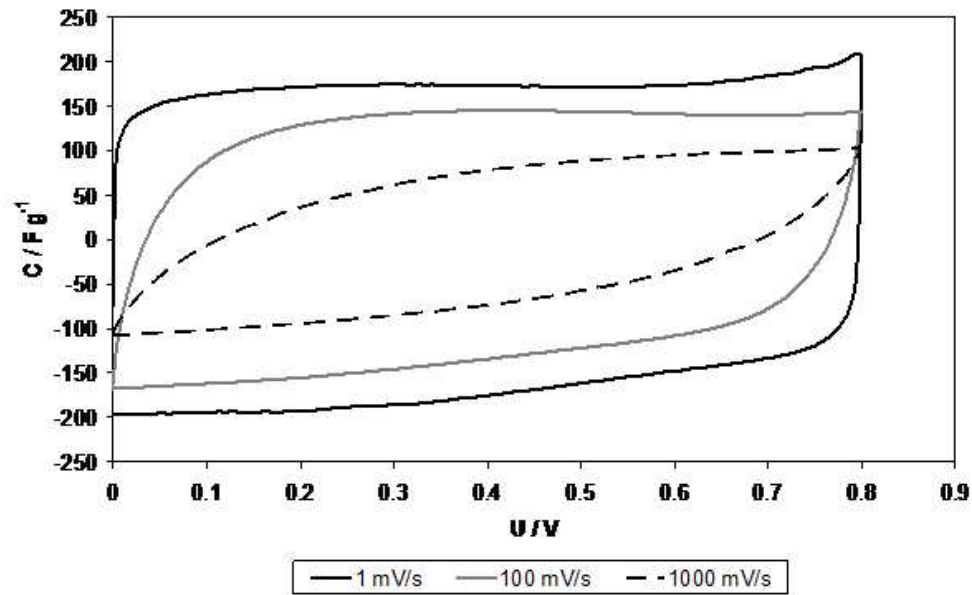


Fig. 3 Voltammetry characteristics at various scan rates for N+2M+F composite (acidic electrolyte)
160x99mm (96 x 96 DPI)

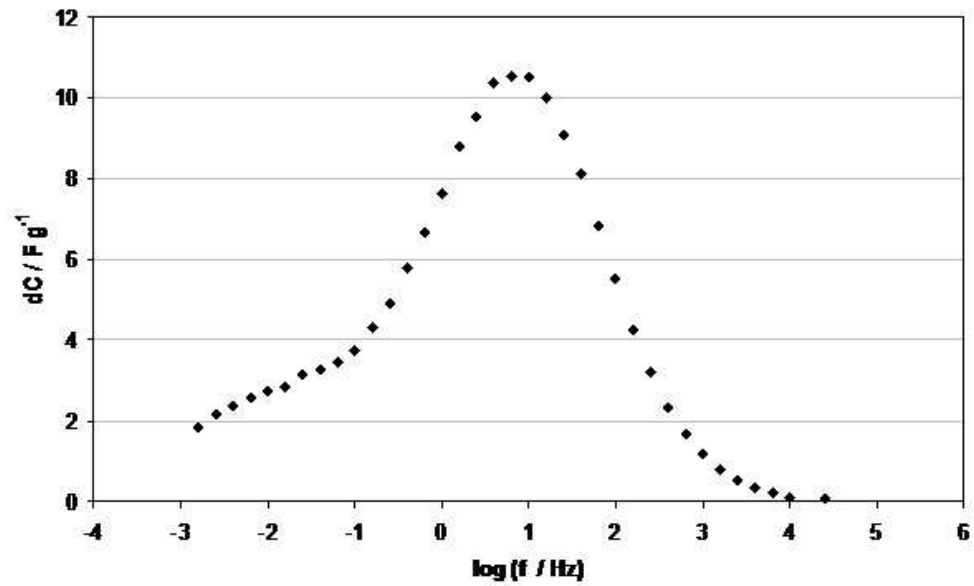


Fig. 4 Increment of capacitance versus logarithm of frequency for N+2M+F composite. Acidic medium.
160x99mm (96 x 96 DPI)

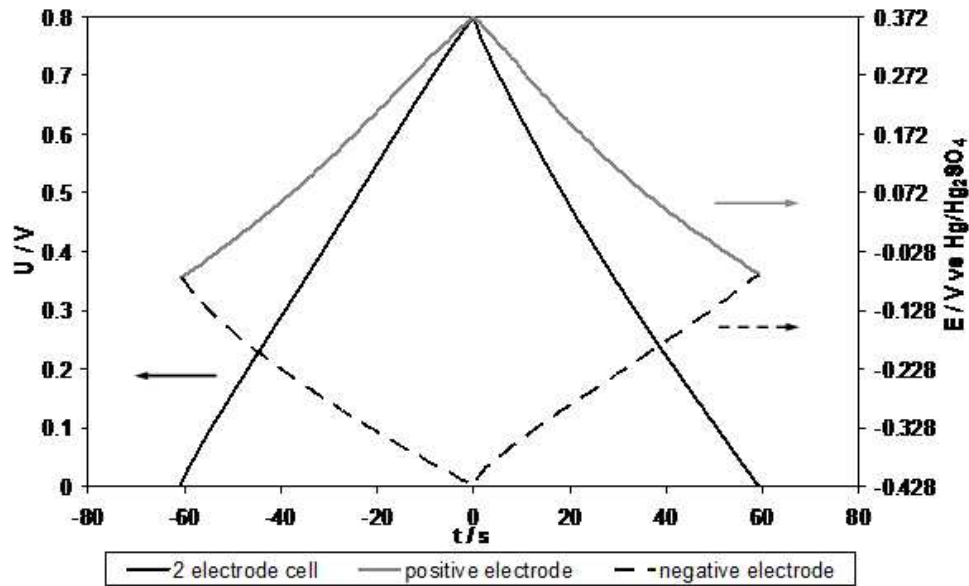


Fig. 5 Galvanostatic charge/discharge of capacitor (1A g-1 current load) built from N+2M+F composite with a detailed potential control of positive and negative electrode. Acidic medium. 160x99mm (96 x 96 DPI)

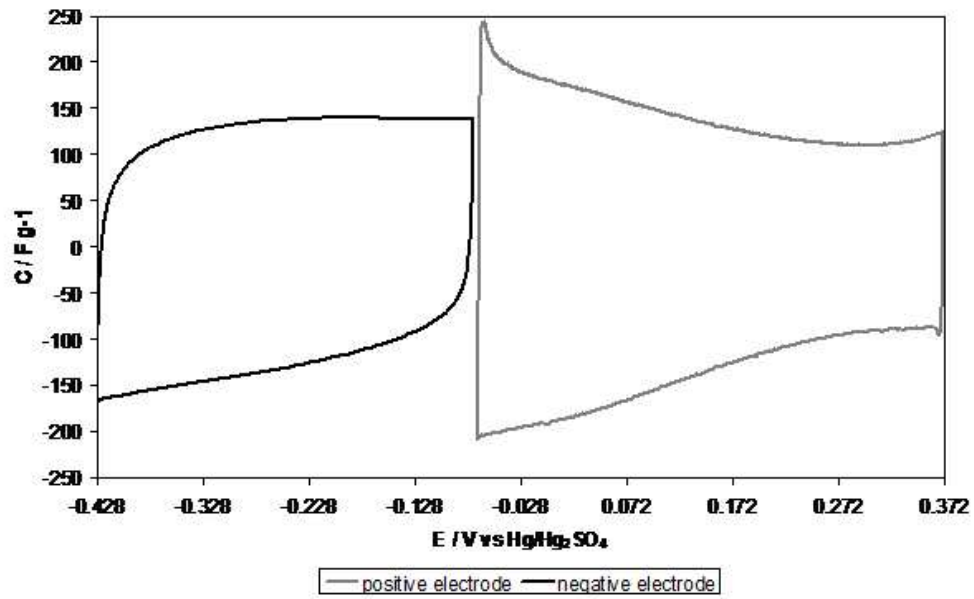


Fig. 6 Voltammetry characteristics (5mV s^{-1}) for N+2M+F composite operating as positive and negative electrode. Acidic medium.
160x99mm (96 x 96 DPI)

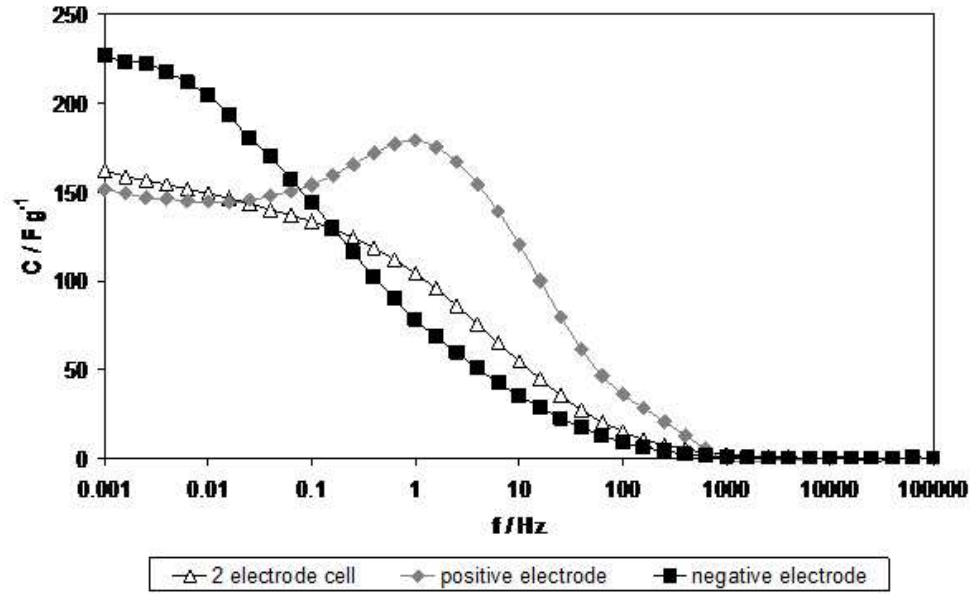


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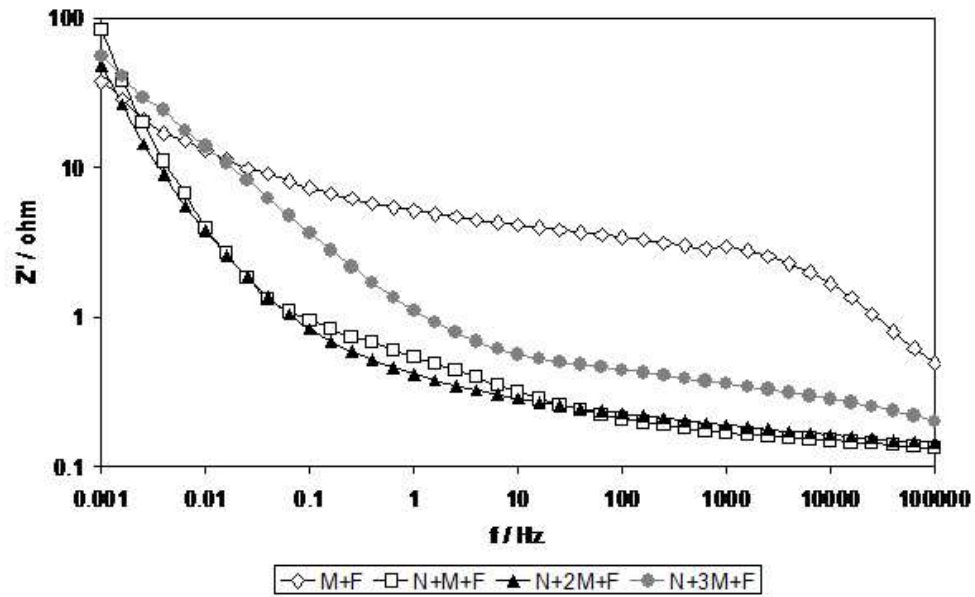


Fig. 8 Impedance real part as a function of frequency for all the composites investigated in two electrode cells (acidic medium).
160x99mm (96 x 96 DPI)

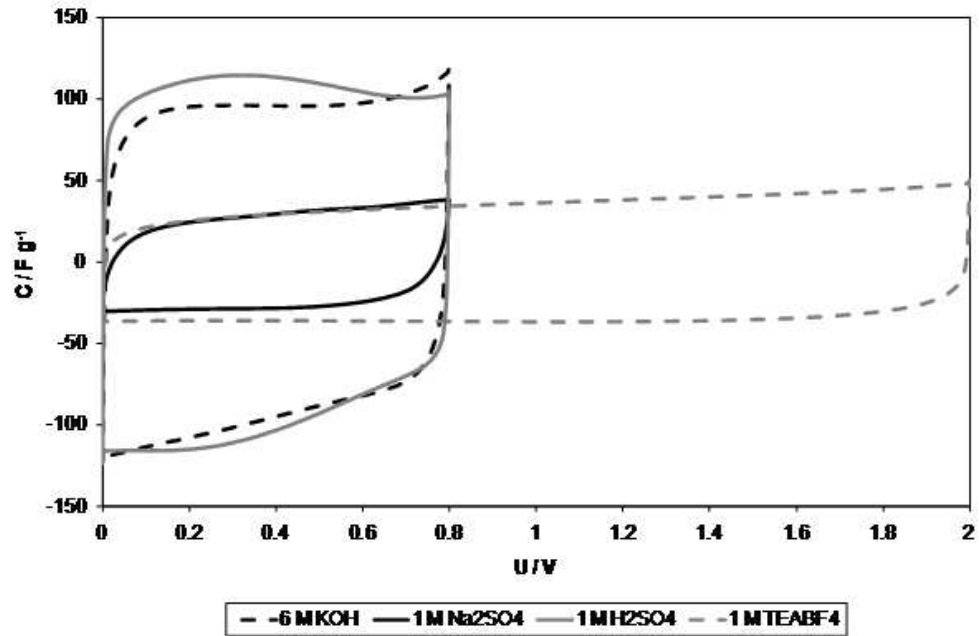


Fig. 9 Voltammetry characteristics at 10 mV s^{-1} scan rate for the nitrogen enriched composite (N+M+F). Various aqueous electrolytic solutions and organic medium.

160x104mm (96 x 96 DPI)