



Short communication

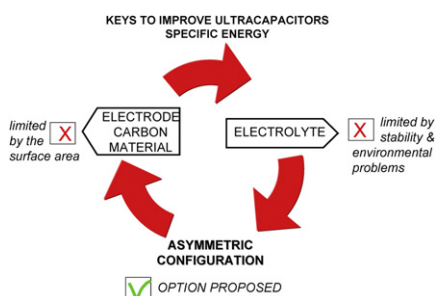
High energy ultracapacitor based on carbon xerogel electrodes and sodium sulfate electrolyte

P. Staiti^{a,*}, A. Arenillas^b, F. Lufrano^a, J.Á. Menéndez^b^aCNR-ITAE, Via Salita S. Lucia 5, 98126 Messina, Italy^bINCAR-CSIC, Apartado 73, 33080 Oviedo, Spain

HIGHLIGHTS

- ▶ An ultracapacitor based on carbon electrodes and sodium sulfate electrolyte was tested in the voltage range 0–1.8 V.
- ▶ The UCap exhibited good capacitance, high specific energy and excellent cycling stability.
- ▶ The UCap had specific energy (17.5 Wh kg^{-1}) remarkably higher than similar UCaps reported in literature.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 February 2012

Received in revised form

13 April 2012

Accepted 22 April 2012

Available online 3 May 2012

Keywords:

Ultracapacitors

Energy storage

Carbon xerogel

Aqueous electrolyte

Specific energy

ABSTRACT

An ultracapacitor (UCap) based on carbon xerogel electrodes and sodium sulfate electrolyte was investigated in the voltage range between 0 and 1.8 V. Notwithstanding the high value of maximum voltage (1.8 V) the UCap exhibited excellent stability during 20000 of cycling test. Moreover, the achievement of this high voltage made possible to obtain high value of specific energy. The stability was possible because the potential limits of electrode–electrolyte decomposition at positive and negative electrodes were never achieved. This is because an asymmetric UCap with different amounts of carbon xerogel in the electrodes was used. The UCap with the carbon xerogel of BET specific surface area of $3100 \text{ m}^2 \text{ g}^{-1}$ demonstrated a specific energy of 17.5 Wh kg^{-1} and a specific capacitance of 156 F g^{-1} and, retained 91% of initial capacitance after 20000 cycles of duration test.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Ultracapacitors (UCaps) based on electrochemical double layer capacitance (EDLC) are electrical energy storage devices releasing energy in faster way than rechargeable batteries and fuel cells. This is because the capacitance is ruled by a fast physical process of charge-separation at the electrode–electrolyte interface [1, 2]. Furthermore, UCaps show some other advantages over more traditional energy storage devices such as high power rate, lower

cost, major safety and durability, as well as the possibility to make maintenance-free flexible packaging [3]. Unfortunately the low specific energy demonstrated from these devices, that notwithstanding is higher than traditional capacitors, remains much lower than batteries or even fuel cells [4] and is the main drawback that limits their application on large scale. Due to these reasons UCaps are not frequently used alone [3, 5, 6] but usually together with the aforementioned devices which can release larger amounts of electric energy [7–10]. However, UCaps are ideal devices for those applications requiring high power for short times, short load cycles and high reliability requirement, such as load cranes, forklifts, emergency doors, emergency valves, and for boosting and

* Corresponding author. Tel.: +39 (0)90624226; fax: +39 (0)90624247.

E-mail address: staiti@itae.cnr.it (P. Staiti).

regenerative braking of electric vehicles [11]. Due to their high rate of storing and releasing energy they are applied as power leveling for electric grid-connected utilities and for factory power backup. With a bank of UCaps, for example, it is possible to bridge the short time duration between the power failure and the startup of backup power generators. Therefore, there is a strong interest worldwide on improvement of performance of UCaps and especially on increasing of the specific energy of UCaps to a level comparable with secondary batteries. A high energy can be achieved by (i) finding a breakthrough active material for the electrodes, (ii) by finding electrolytes of high conductivity and wide voltage window, or (iii) by optimizing the UCap configuration. There are already works reported in the current literature regarding to the optimized properties of carbon materials used in EDLC [12,13] or the use of other kind of materials such as metal oxides and conducting polymers [14,15]. It seems difficult to improve these materials characteristics to reach the targets fixed. On the other hand, there are some works regarding to the use of organic and ionic liquid electrolytes in order to increase the specific energy of UCaps [16], but often they are far from the prefixed objectives because of environmental problems, degradability or high costs associated. It seems that the strategic way to increase the performance and the practical acceptability of UCaps is to find optimal active material, to use friendly electrolytes and to find a convenient configuration. Recently, Fic et al. found very interesting results in neutral electrolyte obtaining stable performance in a UCap with lithium sulfate electrolyte and carbon based electrodes [17]. Their UCap was made to work in a wide voltage range, i.e. even 2.2 V, without any significant capacitance fade during 15000 cycles.

The present work reports results obtained from UCap with electrodes containing carbon xerogel tested with sodium sulfate electrolyte. This work has as principal aim to fill the gap of information on high voltage UCap with sodium sulfate electrolyte that is a low cost and eco-friendly material. Then it may be considered complimentary to that of Fic et al. who have deeply studied the device in lithium sulfate electrolyte but gave a few information on UCap with sodium sulfate and potassium sulfate. In fact, stable capacitance values of 75 and 50 F g⁻¹ were clearly reported for the UCaps with sodium sulfate and potassium sulfate, respectively, as obtained from charge–discharge test while remained unclear the voltage range in which these values were obtained and the number of cycles carried out during the test.

It is well known that the capacitance of UCaps increases with the effective specific surface area of the electrodes wetted with the electrolyte and decreases with the thickness of the formed double layer. Therefore, the use of highly porous carbon materials of high surface area is a significant factor strongly desiderated for obtaining high capacitance values [18–21] as well as thinner double layers. Thinner double layers would mean that a larger amount of smaller pores of material could be occupied by the electrolyte for the capacitive process. However, it is clear that is not possible to increase the specific surface area of carbon materials without a limit and the thickness of double layer is a characteristic of the specific electrolyte and solvent used.

It is also known that the energy of UCap increases by increasing the capacitance (C) and even more by increasing the maximum voltage (V) of operation of device, according to equation:

$$E_{\max} = 1/2 CV^2.$$

Therefore, it is evident that once the material has a considerable specific surface area it is possible to increase the energy of the UCap by regulating the maximum voltage up to values at which the electrode–electrolyte couples still maintain their stability.

In the present work, it has to be taken into account that the electrochemical performance of aqueous UCaps is usually limited

by the irreversible electrochemical processes occurring at potentials above 0.95 V for the positive electrode and below –1.0 V for the negative electrode in neutral electrolyte [12]. These limits were confirmed in this study with the carbon xerogel-based electrodes in sodium sulfate electrolyte through electrochemical tests carried out in three-electrode test cell.

Taking into account this consideration, an UCap in asymmetric configuration has been designed, that contained electrodes with different carbon loadings in order to avoid that the potentials of single electrodes overcame the own electrochemical limit of stability. In the present paper the results obtained by the asymmetric UCap will be reported and discussed and indication on the more appropriate loading of carbon for the positive and negative electrodes will be given.

2. Experimental

2.1. Preparation of carbon xerogel

The active material (i.e., carbon–xerogel) was synthesized by controlled polymerization of resorcinol and formaldehyde using microwaves for the polymerization, curing and drying steps. The variation of the pH in the precursor solution allows controlling the porosity of the final carbon [22]. In this case, a pH of 6.5 was used in order to create mesopores of narrow size. The specific surface area of the resultant material was measured by application of the BET equation to the adsorption–desorption N₂ isotherms at –196 °C, resulting in 3100 m² g⁻¹. The material is practically pure carbon (>95 wt% C) with some H and O content (c.a. 1 and 3 wt%, respectively).

2.2. Preparation of electrodes

The electrodes were prepared by spreading a slurry of carbon xerogel, polymer binder (PVDF) and dimethylacetamide on a supporting titanium net disk ($\varphi = 1.5$ cm). The binder and the titanium net (200 mesh) gave optimal mechanical properties to the active layer when the composition was 90 wt% of carbon and 10 wt% of binder. A carbon loading of 8.65 mg cm was used for studying both positive and negative electrodes in three-electrode test cell. On the other side, in the two-electrode test cell a load of 9.07 mg cm of carbon in positive electrode and of 4.13 mg cm in negative electrode were used. Thus, the ratio of carbon loading between positive and negative electrode was 2.13 and this allowed the UCap to work up to 1.8 V of maximum potential without the appearance of any electrochemical decomposition process.

2.3. Electrochemical characterization

Active electrode materials were characterized in both two and three-electrode test-cells. The latter allows to identify the limits of potential of positive and negative electrodes, beyond which the electrodes and electrolyte became unstable. On the other hand, the use of the two-electrode test cell (single cell) allowed to investigate the electrochemical performance of full device in the real operative condition.

In all the electrochemical tests an 1 M Na₂SO₄ aqueous solution was used as electrolyte. The limits of stability of the single electrodes were determined in the three-electrode cell through cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements carried out at voltage sweep rate (vsr) of 10 mV s⁻¹ and current density of 10 mA cm⁻², respectively. The endurance test was carried out in two-electrode test cell by a large number of repeated cycles conducted in cyclic voltammetry mode in the voltage window between 0 V and 1.8 V and at the vsr of 30 mV s⁻¹

while a few of cycles of CVs carried out at the beginning and at the end of the cycling test were made at the vsr of 20 mV s^{-1} . The latter cycles were made to evidence the modifications of UCap and electrodes performances caused by the 20000 cycles test.

The two-electrode test-cell was equipped with a supplementary saturated calomel electrode (SCE) that allowed to separately determine the potentials of positive and negative electrodes. Fig. 1 shows a schematic view of the two-electrode test-cell.

3. Results and discussion

The cyclic voltammograms of Fig. 2 obtained from the test carried out at different extension of voltage windows evidence the electrochemical stability limits of positive (right side of figure) and negative (left side of figure) electrodes. From the figure it is possible to affirm that the positive electrode is stable in the increasing electrode potential windows up to the maximum potential of about 0.95 V. Above this potential a pronounced current peak appears. For the negative electrode, evident effects of electrochemical decomposition are not present also in the maximum investigated voltage window between 0.135 V and -0.960 V .

The confirmation of the range of potential within which positive and negative electrodes maintain their stability was obtained by calculating the coulomb efficiency from the data obtained by the galvanostatic charge-discharge test. The curves obtained from the GCD test is reported in the Fig. 3 and the coulombic efficiencies and specific capacitances referred to the different investigated ranges of potential in Table 1.

From these tests it was evidenced that at potentials $\geq 1.0 \text{ V}$ a decomposition process on the positive electrode occurs, that is displayed by the shape of CV and GCD curves and is confirmed by the low coulombic efficiency (CE) obtained by the galvanostatic charge-discharge measurements. The value of CE was simply calculated as ratio between the released charge (Q_d) and the stored charge (Q_c) $\times 100$. A low value of CE suggests that charges stored during the charging process are used for some irreversible electrochemical process and then not more released during the discharging process.

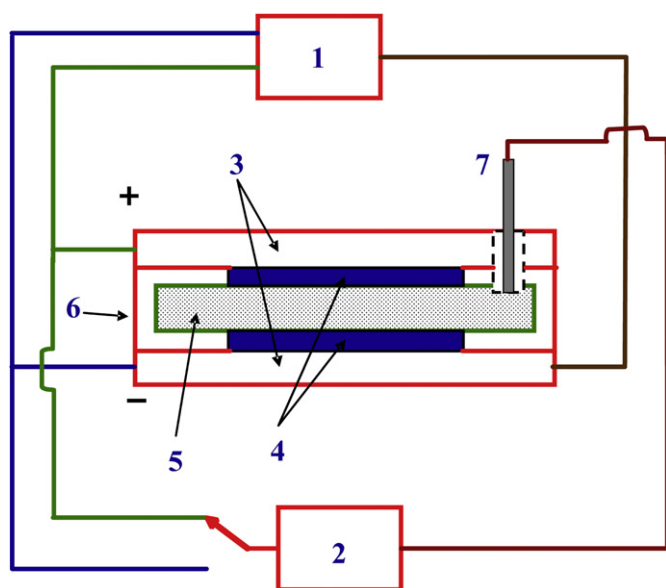


Fig. 1. Schematic view of ultracapacitor test cell. 1, 2 – Electrochemical instruments; 3 – External current collectors; 4 – Electrodes; 5 – Separator with electrolyte; 6 – Insulating gasket; 7 – Reference electrode.

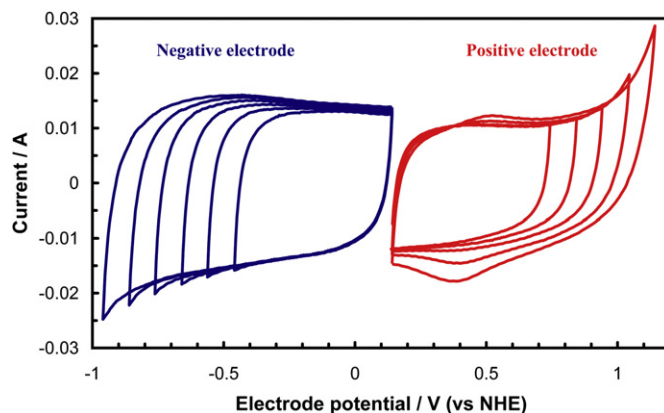


Fig. 2. Cyclic voltammograms of positive and negative electrodes from three-electrode test-cell. V.s.r.: 10 mV s^{-1} .

In Table 1, the coulombic efficiencies and the specific capacitances of the single electrodes as obtained from the three-electrode test-cell are reported. It is evident from the data that the positive electrode working in the range of potential 0–0.9 V is still stable (CE = 93%) while in the range 0–1 V the stability drops down (CE = 78 %). The specific capacitances reported in Table 1 were calculated from the discharge branches of GCD measurements considering the weights of carbon in the electrodes.

It is well known that in a symmetric carbon-based ultracapacitor, i.e. an UCap with the same carbon loading in positive and negative electrodes, that uses sodium sulfate electrolyte, it is the positive electrode that limits the stability of the full device [12]. This is because this electrode first reaches the potential of instability for two reasons: 1) the polarization of the positive electrode is faster than that of the negative electrode; 2) the E_{0V} potential (i.e. the potential of electrodes when the UCap is completely discharged) is closer to the limit of stability of the positive electrode (see Fig. 4). The first point is explained by the higher sterical hindrance of hydrated sulfate anions which accumulate on the positive electrode during the charging phase respect to the sodium cations which accumulate on the negative electrode; it is obvious that if two electrodes have the same surface available for the formation of the double layer the polarization is faster for the electrode than finds more difficulty to store ions on its surface area. The second point is explained by the fact that the E_{0V} potential is the results of mixed potentials between positive and negative electrodes. It is verisimilar, that little amounts of oxygen and

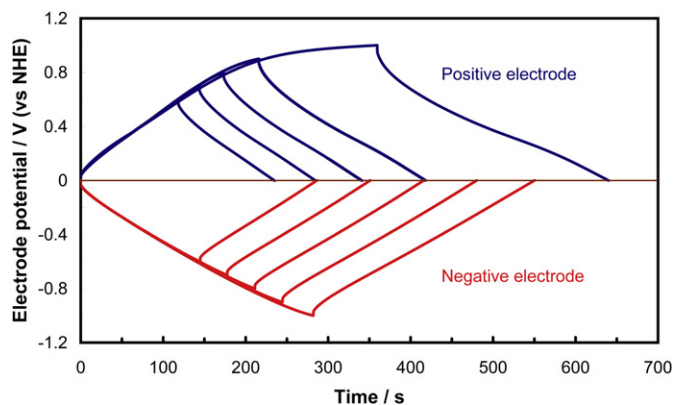


Fig. 3. Galvanostatic charge-discharge curves of positive and negative electrodes from three-electrode test-cell. Current density: $\pm 10 \text{ mA cm}^{-2}$.

Table 1
Coulombic efficiency and specific capacitance of positive and negative electrodes obtained by GCD in the three-electrode test-cell.

Positive electrode			Negative electrode		
Range of potential (V vs NHE)	Coulombic efficiency (%)	Specific capacitance (Fg ⁻¹)	Range of potential (V vs NHE)	Coulombic efficiency (%)	Specific capacitance (Fg ⁻¹)
0–0.6	99	225	0 – -0.6	98	273
0–0.7	97	232	0 – -0.7	98	286
0–0.8	96	242	0 – -0.8	97	296
0–0.9	93	260	0 – -0.9	96	302
0–1.0	78	(320)	0 – -1.0	95	310

hydrogen might form at the positive and negative electrodes, respectively, during the charging process remaining entrapped in the smaller pores. An electrochemical equilibrium forms at the three phase regions (gas, electrolyte, carbon) of each electrode that is responsible for the voltage of the discharged UCap (E_{0V}).

In this work, we have designed an UCap in asymmetric configuration, in which the carbon loading in positive electrode is fixed in such an amount that the own polarization during UCap charging is slower than that of negative electrode and, its maximum potential reaches values lower than 0.9 V. This configuration of UCap was electrochemically investigated in a two-electrode cell configuration in which also a reference electrode is connected (see Fig. 1). By following the potential of the cell and those of two electrodes it was possible to determine the electrical features of whole capacitor and to have information on the behavior of each electrode.

Fig. 4 shows the voltage of full UCap that varies from 0 to 1.8 V and the potentials of positive and negative electrodes, which remain within the prefixed limit of +0.9 V and -1.0 V, respectively. This result demonstrates that the UCap is working up to 1.8 V without appreciable faradaic irreversible processes. The stability of the UCap that is a main concern was investigated in cycling charge–discharge measurement carried out in CV mode in the voltage range from 0 to 1.8 V and at voltage sweep rate of 30 mV s⁻¹. After 20000 of charge–discharge cycles, the UCap retained up to 91% of the initial capacitance. This result demonstrates that UCap can work reversibly until 1.8 V in aqueous sodium sulfate electrolyte maintaining almost stable performance, and with the advantage of the achievement of higher values of specific energy ($E = 1/2CV^2$).

In Table 2, the results of electrochemical characteristic of UCap at the start and after 20000 cycles are reported. The specific capacitance (C_s) referred at one single electrode after 20000 cycles, as calculated from the equation $C_s = 4 \times C_{UCap}$, where C_{UCap} is the capacitance of complete UCap for the total weight of carbon in the

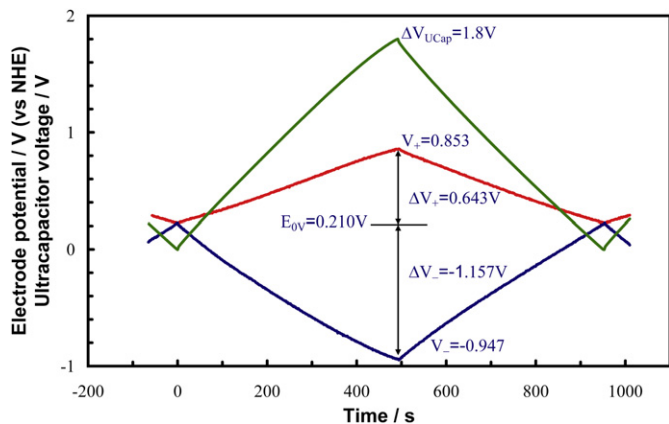


Fig. 4. Galvanostatic charge–discharge curves of UCap and electrodes. Current density: 2 mA cm⁻². Electrolyte: 1 M Na₂SO₄ aqueous solution.

Table 2
Results of electrochemical performances of UCap and of single electrodes before and after cycling test.

	Carbon loading	At the beginning	After 20000 cycles
Supercapacitor	13.20 mg cm ⁻²		
Maximum voltage		1.8 V	1.8 V
Specific capacitance, C_s		156 Fg ⁻¹	143 Fg ⁻¹
Coulombic efficiency		94%	94%
Equilibrium potential, E_{0V}		0.210 V	0.187 V
Positive electrode	9.07 mg cm ⁻²		
Maximum potential		0.853 V	0.945 V
Maximum polarization		0.643 V	0.758 V
Specific capacitance, C_{Pos}		159 Fg ⁻¹	123.9 Fg ⁻¹
Negative electrode	4.13 mg cm ⁻²		
Minimum potential		-0.947 V	-0.855 V
Maximum polarization		1.157 V	1.042 V
Specific capacitance, C_{Neg}		186 Fg ⁻¹	197.7 Fg ⁻¹

Note: all the potentials refer to the NHE.

electrodes, decreases from 156 to 143 Fg⁻¹. This is due to the decrease of the capacitance of the positive electrode that changes from 159 to 123.9 Fg⁻¹. In the same period, the maximum potential of positive electrode increases from 0.853 V to 0.945 V indicating that it is now closer to the potential at which irreversible reactions appear (1 V). It is worth to remark the high cycling stability of UCap that reached 20000 cycles of charge–discharge with a limited decay. This may be attributed to both the high quality of carbon xerogel material and the accurate control of the range of potential of the positive electrode. Previous results reported by Demarconay [12] and Yang [23] for symmetric UCap, cycled between 0 and 1.6 V showed relatively low stability after 10000 and 2000 cycles, respectively. The specific energy of our UCap varied from the initial 17.5 Wh kg⁻¹ to 16.1 Wh kg⁻¹ after 20000 cycles. Eskusson [24] recently reported specific energy of 5.7 Wh kg⁻¹ in a 6 M KOH aqueous UCap. Thus our values are about twice than those reported in literature for similar laboratory UCaps. The results reported by Fic et al. [17] are effectively very interesting for the maximum operational voltage obtained during experiments, their UCap was able to operate up to 2.2 V, and for the high cycling stability, 15000 cycles without any significant capacitance fade, nevertheless, these results were obtained with lithium sulfate electrolyte and in symmetric ultracapacitor, whereas we obtained our results with the cheaper and more eco-friendly sodium sulfate electrolyte in an asymmetric ultracapacitor.

4. Conclusions

An UCap in asymmetric configuration, i.e. with different carbon loadings in the positive and negative electrodes was designed and tested with sodium sulfate electrolyte. The specific configuration made possible to increase the voltage of operation upto 1.8 V without the appearance of instability processes at the electrodes. The UCap was successfully investigated for 20000 cycles obtaining at the end of the test a retention of 91% of the initial capacitance and a specific energy of 16.1 Wh kg⁻¹. These results, besides the point of using low cost and environmental friendly materials (i.e. carbon xerogel material and aqueous sodium sulfate electrolyte) in the UCap, make this system very interesting if compared with other literature results obtained in similar devices.

Acknowledgements

The support from the Ministerio de Ciencia e Innovación (Ref. MAT2011-23733) is greatly acknowledged. The authors of CNR-ITAE of Messina acknowledge the Ministero dello Sviluppo

Economico (Italy) for financial support in the frame of “Accordo di programma CNR-MSE” project “Sistemi elettrochimici per l’accumulo dell’energia” (Ref. Decreto MAP del 23 March 2006)

References

- [1] B.E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Plenum Publishers, New York, 1999.
- [2] P. Simon, Y. Gogotsi, *Nature Mater.* 7 (2008) 845–854.
- [3] R. Kotz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483–2498.
- [4] M. Winter, R.J. Brodd, *Chem. Rev.* 104 (2004) 4245–4269.
- [5] F. Simjee, P.H. Chou, *Proceedings of the 2006 International symposium on low power electronics and design (ISLPED'06)*, October 4–6, 2006, pp. 197–202.
- [6] T. Zhu, Z. Zhong, Y. Gu, T. He, Z. Zhang, *Proceedings of the 7th International conference on mobile systems, applications, and services (MobiSys'09)*, June 22–25, 2009, pp. 319–332.
- [7] J. Alberola, J. Pelegri, R. Lajara, J.J. Perez, *Proceedings of the IEEE Instrumentation and measurement technology conference (I2MTC'08)*, May 12–15, 2008, pp. 657–662.
- [8] J. Jeong, X. Jiang, D. Culler, *Proceedings of the 5th International Conference on networked sensing systems (INSS'08)*, June 17–19, 2008, pp. 181–188.
- [9] H. Yang, Y. Zhang, *Proceedings of SPIE, Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems 2010*, 7647 (2010) 76472U.
- [10] P. Thounthong, S. Rael, B. Davat, *J. Power Sources* 193 (2006) 376–385.
- [11] J.R. Miller, P. Simon, *Science* 321 (2008) 651–652.
- [12] L. Demarconnay, E. Raymundo-Pinero, F. Beguin, *Electrochem. Commun.* 12 (2010) 1275–1278.
- [13] V. Khomenko, E. Raymundo-Pinero, F. Beguin, *J. Power Sources* 195 (2010) 4234–4241.
- [14] L. Demarconnay, E. Raymundo-Pinero, F. Beguin, *J. Power Sources* 196 (2011) 580–586.
- [15] G.A. Snook, P. Kao, A.S. Best, *J. Power Sources* 196 (2011) 1–12.
- [16] A. Lewandowski, A. Olejniczak, M. Galinski, I. Stepniak, *J. Power Sources* 195 (2010) 5814–5819.
- [17] K. Fic, G. Lota, M. Meller, E. Frackowiak, *Energy Environ. Sci.* 5 (2012) 5842–5850.
- [18] A.G. Pandolfo, A.F. Hollenkamp, *J. Power Sources* 157 (2006) 11–27.
- [19] T.A. Centeno, F. Stoeckli, *J. Power Sources* 154 (2006) 314–320.
- [20] G. Lota, T.A. Centeno, E. Frackowiak, F. Stoeckli, *Electrochim. Acta* 53 (2008) 2210–2216.
- [21] M. Inagaki, H. Konno, O. Tanaike, *J. Power Sources* 195 (2010) 7880–7903.
- [22] L. Zubizarreta, A. Arenillas, A. Dominguez, J.A. Menendez, J.J. Pis, *J. Non-Cryst. Solids* 354 (2008) 817–825.
- [23] X. Yang, Y.-S. He, G. Jiang, X.-Z. Liao, Z.-F. Ma, *Electrochem. Commun.* 13 (2011) 1166–1169.
- [24] J. Eskusson, A. Janes, A. Kikas, L. Matisen, E. Lust, *J. Power Sources* 8 (10) (2011) 4109–4116 196.