

Electrical Double-Layer Capacitance of Zeolite-Templated Carbon in Organic Electrolyte

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Porous carbon materials have been prepared using chemical vapor deposition of ethylene and acetonitrile on zeolite Y templates with the subsequent removal of the template. The use of zeolite templates enabled tuning of the carbon chemistry, microstructure, and specific surface area while maintaining ordered pores and similar pore-size distribution. Evaluation of the performance of the templated carbons in electrochemical capacitors with tetraethylammonium tetrafluoroborate salt solution in acetonitrile showed a high gravimetric capacitance of up to 146 F/g and a short time constant of up to 3 s, indicating fast charge/discharge capability. Nitrogen doping limited the capacitor performance at high current densities without enhancing the energy-storage characteristics at low current densities. Specific capacitance at a constant pore size was found to linearly depend on the surface area, suggesting a potential for further improvements. Carbons produced by zeolite-templating method are promising for use in high-energy, high-power electrochemical capacitors employing organic electrolytes. © 2008 The Electrochemical Society. [DOI: 10.1149/1.3002375] All rights reserved.

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Electric double-layer capacitors (EDLCs), also called ultra- or supercapacitors, are rechargeable electrochemical energy-storage devices like batteries¹ but with different storage mechanisms and performance characteristics. The charge-storage mechanism in EDLCs is purely electrostatic in nature. During charging and discharging of EDLCs, no electron transfer takes place at the carbon electrode/ electrolyte interface. Due to the nature of the storage, one of the most interesting characteristics of EDLCs is their practically unlimited cycling life. The energy storage of an EDLC is determined by the maximum charge voltage and the capacitance of its electrodes or the amount of charge accumulated on the electrode per unit voltage. The power characteristic of an EDLC is mostly determined by the electrode capacitance and the ability of the electrolyte ions to rapidly move through the porous electrodes.

EDLCs possess much higher energy density than conventional capacitors due to the large surface area of the porous carbon electrode film. EDLCs can often store more power in a smaller volume¹ and at a lower cost^{1,2} than batteries and fuel cells. Their unique characteristics allow them to complement or replace batteries and fuel cells in applications where high power and low weight are essential, such as mobile electronic and communication devices, back-up power storage, power-quality devices, and peak power sources for hybrid electric vehicles. Power systems with battery-supercapacitor,³⁻⁵ engine-supercapacitor,⁶ and fuel cell-supercapacitor⁷ combinations are attractive due to their unprecedented efficiency, power, and energy characteristics.

State-of-the-art activated carbons (ACs) used in commercial EDLCs offer 80–120 F/g when used in organic electrolytes. The intrinsic properties of the ACs and the challenges associated with precise and consistent control over porosity, surface chemistry, and microstructure during activation limit the performance characteristics of EDLCs.⁸ Carbon synthesis methods provide better control over the structure and properties most vital for EDLC performance improvements. For example, the use of metal carbides as inorganic precursors for porous carbon synthesis allows a tight control over pore-size distribution in the 0.6–1 nm range.⁹⁻¹¹ The microporosity developed in those carbons resulted in high capacitance values in organic electrolytes¹²⁻¹⁵ but rather limited frequency response. Another attractive route to control pore size and structure during syn-

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thesis is to use inorganic templates for carbon deposition, followed by the subsequent template removal.¹⁶⁻²¹ This approach allows keeping the pore-size constant and understanding effects of other structural parameters, such as nitrogen doping, available surface area, or carbon ordering, on the electrochemical performance of po-rous carbons. Pioneering work by Kyotani et al.²² suggested the use of zeolites with strictly defined pores as templates for the formation of carbons with uniform structure, high surface area, and pores in the 1–3 nm range. Subsequent work by Paredes and Kyotani et al., $^{23,24}_{23,24}$ Pacula and Yang et al., $^{25-28}$ Gaslain et al., 29 and Garsuch et al.,^{23,24} Pacula and Yang et al.,²³⁻²⁶ Gaslain et al.,^{\sim} and Garsuch et al.,³⁰⁻³² reproduced and confirmed the preservation of the structural regularity of zeolites in carbons. In addition, zeolite-templated carbons demonstrated excellent gas-sorption properties.^{25,26} Recent work by Ania et al.³³ demonstrated that zeolite-templated carbons doped with nitrogen have excellent capacitance characteristics when used in aqueous electrolytes due to the pseudocapacitance effects of nitrogen-containing functional groups. However, most commercial EDLCs use organic electrolytes capable of withstanding higher operating voltages and thus offering a higher energy density. In addition, organic electrolytes offer increased cycling life, which is limited in the case of aqueous electrolytes by redox reactions. It is therefore important to investigate zeolite-templated carbons in organic electrolytes, which are of practical interest for EDLC applications. In this work we explore the potential of zeolite-templated carbons for EDLC in organic electrolytes and discuss the correlation between their performances and the carbon structure and properties, such as specific surface area, (SSA), pore volume, and nitrogen doping.

Experimental

Carbon synthesis.— The zeolite Y powder purchased from Fluka (Buchs, Switzerland) was used as the template for carbon deposition. The detailed preparation procedure is described elsewhere.²⁷ Briefly, zeolite samples were heated to the deposition temperature under a nitrogen flow. Once the desired temperature was reached, pure ethylene (series E samples) or nitrogen saturated with acetonitrile vapors (series Y samples) were introduced into the system at 100 cm³/min for 3 h to deposit carbon onto the zeolite. Synthesis temperatures were selected within the range of pyrolysis of precursors used and were chosen to be 550, 650, and 750°C for E samples (C_2H_4), and 700, 800, 850, and 900°C for Y samples (acetonitile). Deposition temperatures above 750°C for E samples and below 700°C for Y samples resulted in substantially smaller SSA, and these samples were not considered in the present study. After carbon

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Figure 1. Electron microscopy of the templated carbon samples: (A) low- and (B) high-magnification SEM micrographs demonstrating conservation of zeolite shape during carbon synthesis and (C) low- and (D) high-resolution TEM micrographs demonstrating formation of coatings on the surface of the porous carbon particles.

deposition, the samples were cooled down to room temperature under a nitrogen flow. Zeolite templates were dissolved using 10% HF solution in order to produce zeolite-free porous carbon with less than 5% oxide residues, according to the thermogravimetric analysis.²⁷

Material characterization.— Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies were undertaken in order to analyze the structure and morphology of the synthesized samples. SEM analysis was done at a working distance of 2-4 mm and an accelerating voltage of 2-5 kV (Supra 50VP field-emission scanning electron microscope, Carl Zeiss. Oberkochen, Germany). TEM samples were prepared by sonicating powders dispersed in ethanol. A droplet was deposited on a laceycarbon-coated copper grid (200 mesh). Observations were performed using an accelerating voltage of 200 kV (JEOL 2010F, Tokyo, Japan). Nitrogen sorption measurements were performed at 77 K using an ASAP 2020 (Micromeritics, Norcross, GA, USA) or Quadrasorb (Quantachrome Instruments, Boynton Beach, FL, USA) pore size and surface area analyzer. The SSA was calculated using the Brunauer-Emmett-Teller (BET) method from N2 adsorption isotherms in the range of relative pressures from 0.05 to 0.2. The poresize distribution was obtained from the adsorption isotherms using the nonlocal density functional theory (DFT). The pore-size distributions were determined assuming a cylindrical pore shape.³⁴ The range of relative pressures from 0.05 to 0.2 was used for BET SSA calculations. X-ray photoelectron spectroscopy (XPS) analysis was conducted using a model 1600 system (Physical Electronics-PHI, Chanhassen, MN, USA) to determine the elemental composition of the synthesized samples. Al foil was used as a sample holder. Charging was reduced by covering the sample with a conductive mesh and using a discharging gun.

Electrochemical characterization.— Electrochemical tests were performed in a symmetrical two-electrode configuration with 2 \times 2 cm electrodes. Aluminum foil 300 µm in thickness was roughened using SiC 600 grit sandpaper and coated with a conductive polyurethane paint containing acetylene black particles to serve as a current collector. The employed procedure was found to provide low interface resistance between the Al current collectors and the electrodes.^{35,36} The active material consisted of 95 wt % carbon and 5 wt % poly(tetrafluoroethylene) (PTFE) (60 wt % suspension in water, Sigma-Aldrich, St. Louis, MO, USA). The mass of the active material was kept constant at 40 mg for all the tested samples. A 50 μ m thick polymeric separator (W. L. Gore & Associates, Inc., Newark, DE, USA) was used. PTFE plates and stainless steel clamps were used to maintain current collector/electrode/separator/ electrode/current collector assembly under a pressure of approximately 0.2 MPa. An acetonitrile (Acros Organic, Geel, Belgium) solution of a vacuum-dried NEt₄BF₄ salt (Alfa Aesar, Ward Hill, MA, USA) was used as the electrolyte. The electrochemical capacitor was assembled in a glove box, and the moisture and oxygen content were kept below 10 ppm.

Galvanostatic cycling measurements were performed using an SI 1286 galvanostat/potentiostat (Solartron Analytical, Farnborough, Hampshire, UK) between 0 and 2.3 V at various currents ranging from 10 to 200 mA. The gravimetric capacitance, C (F/g), was calculated according to Eq. 1

$$C = \frac{2I}{(dV/dt) \times m_{\rm AM}}$$
[1]

where *I* is the current (A), dV/dt is the slope of the discharge curve (V/s), and m_{AM} is the mass of the active material in a single electrode (g).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a PCI4/300 potentiostat (Gamry Instruments, Warminster, PA, USA). Cyclic voltammograms were recorded between -2 and 2 V at a scan rate of 10 mV/s. The capacitance was calculated from the voltammograms according to Eq. 2

$$C = \frac{Ia - Ic}{SR \times m_{\rm AM}}$$
[2]

where *Ia* and *Ic* are the anodic and cathodic currents (A), respectively, and *SR* is the scan rate (0.01 V/s). EIS was performed on a fully discharged cell (0 V) in a frequency range between 7 mHz and 50 kHz with a signal amplitude of 5 mV.

Results and Discussion

All samples retained the size and shape of the zeolite template particles (Fig. 1A and B), as previously observed.²⁵⁻²⁸ Because the particle size is known to affect the electrochemical performance of porous carbons,³⁷ conservation of size and shape was an important parameter for the performed parametric studies. The microstructure of the synthesized carbons slightly varied within the produced samples. Each particle consisted of two regions, an internal highly

Table I. Composition of the templated carbons derived from XPS analysis.^a

Sample	C (atom %)	N (atom %)	F (atom %)
Y 700	89.9	6.5	3.6
Y 800	92.8	4.6	2.6
Y 850	90.7	7.2	2.1
Y 900	95.2	4.4	0.4
E 550	96.7	0	3.3
E 650	98.4	0	1.6
E 750	99	0	1

^a Oxygen detected during the analysis is not considered in the present table.

porous and disordered carbon core and a graphitic surface coating (Fig. 1C and D). The thickness of the coatings varied from particle to particle (2–20 nm) but, in general, was larger for samples produced at higher temperatures and for E series of samples (not shown). It may result from carbon deposition on the surface of the particles during the precursor pyrolysis after all zeolite pores have been filled with carbon. The coating is porous and, as is discussed in the following sections, allows diffusion of gas molecules and ions into the high-surface-area core of the particles. Existence of such a coating may contribute to lowering the pore volume and surface area but, at the same time, is expected to improve the electrical conductivity of the carbon electrodes.

A prior XPS study indicated that the chemical composition of the nitrogen-doped (i.e., acetonitrile-derived) zeolite-templated carbons is the same on the surface and in the bulk of the samples.²⁵ As such, we expect that nitrogen is homogeneously distributed in the carbon structure. Our XPS studies identified four distinguished peaks corresponding to C_{1S} , O_{1S} , N_{1S} , and F_{1S} core-level transitions (not shown). Chemical composition of the samples presented in Table I was obtained from analyzing the XPS spectra. In these calculations we assumed that oxygen content (commonly in the range of 3–5 atom % for our samples) mostly comes from the moisture adsorbed

Table II	Table II. Porosity of the synthesized carbons.				
Sample	BET SSA (m^2/g)	DFT SSA (m^2/g)	Pore volume (cm^3/g)		
Y 700	1122	1179	0.81		
Y 800	1941	2196	0.97		
Y 850	1987	2205	1.08		
Y 900	1403	1606	0.81		
E 550	853	1120	0.46		
E 650	1370	1625	0.74		
E 750	1032	1075	0.60		

in the micropores after exposure of the samples to the ambient atmosphere. The presence of oxygen-containing functional groups was neglected. As expected, Y samples synthesized by decomposition of acetonitrile contained a substantial amount of nitrogen (up to ~7 atom %), which was not present in the E series prepared using ethylene precursor. Detected fluorine is believed to come from the HF treatment. Samples in each series synthesized at higher temperatures trapped less fluorine because of a higher level of graphitization²⁷ and fewer dangling bonds.

The shape of the N₂ sorption isotherms of the synthesized carbons (not shown) indicates the presence of both micropores and mesopores. Pore-size distribution determined from the isotherms of all the samples (Fig. 2) is similar. The most pronounced peaks are at around 1.5 and 2 nm, similar to previous reports.^{24,33} The 0.7–1.5 nm pores are likely to be directly templated by the zeolite framework, while the larger pores arise from incomplete filling of the zeolite pores during the templating process.³³ The pore volume and SSA showed substantial variations, depending on the synthesis conditions (Fig. 3 and Table II). The peak of the pore volume and SSA corresponded to 650 and 850°C for E and Y samples, respectively. Y samples demonstrated a noticeably better developed porosity with nearly double the pore volume (Fig. 3 and Table II), as expected from the prior studies.²³ Differences in the micropore volume were slightly less pronounced (Fig. 3B). Figure 3B shows that the micropore volume does not follow the same trend as the SSA



Figure 2. (Color online) Pore-size distribution calculated from N_2 isotherms collected at 77 K. The shape of the pores was assumed to be cylindrical.

Figure 3. (Color online) Porosity variation with the precursor and the synthesis temperature: (A) total pore volume and (B) volume of pores <2 nm (micropores).



Figure 4. (Color online) Specific capacitance dependence on (A) BET SSA and (B) pore volume.

and the total pore volume for the Y samples; it continuously decreases with the synthesis temperature. On average, a slightly higher pore volume is obtained for the Y compared to the E sample series.

Figure 4 represents the specific capacitance of the E and Y series measured by galvanostatic cycling measurements at low current (10 mA). A linear charge-discharge was observed during cycling with the same charge and discharge time, suggesting that no faradaic reactions occurred between the carbon and the electrolyte. Both the pore size¹² and the particle size³⁷ of porous carbons are among the parameters affecting the specific capacitance. However, those are similar in all our samples. As a result, we observed a linear relation between the gravimetric capacitance with the BET SSA and total pore volume (Fig. 4). The average value for specific capacitance per BET SSA was ~8 μ F/cm². The maximal capacitance of 146 F/g was obtained for the carbon sample having the largest SSA and pore volume (Fig. 3 and 4). In contrast to capacitance saturation observed in activated carbons at $\sim 1500 \text{ m}^2/\text{g}$ by Barbieri et al.,³⁸ capacitance of the zeolite-templated carbon samples with increased order and uniformity in the pore structure continues to grow with more developed porosity. This result shows the significant potential advantage of the periodic structure obtained in the zeolite-templated carbon. The micropore volume contribution generally observed in high-capacitive carbons^{12,39} does not significantly affect the variation in capacitance of our samples, presumably due to the small relative volume of micropores. As a result, we did not observe any clear correlation between the capacitance and the micropore volume. While the specific capacitance per unit of SSA may be lower for mesopores compared to subnanometer pores,¹² high capacitance values can be achieved for mesoporous carbons, if the available SSA and pore volume are large enough. Small mesopores or meso- and micropores together can provide SSA in excess of 2000 m^2/g and pore volume above 1 cm³/g, which have not been achieved in subnanometer pores so far.

Several authors have suggested that nitrogen enrichment of carbon may increase the capacitance in organic electrolytes due to the pseudocapacitance effect.⁴⁰ While in our case the highest capacitance is achieved in the sample containing nitrogen, we attribute the high capacitance solely to the highest SSA. Experimental data for the Y series do not show any signs of pseudocapacitance; cyclic voltammograms obtained for the Y series presented no additional peaks (not shown). Capacitance measurements obtained from both the discharge curves and the cyclic voltammograms show a good consistency with the capacitance variation of about 5%, which is traditionally observed in such measurements.

As compared to carbon nanotubes and onions,⁴¹ commercial ac-tivated carbons,⁴² and carbide-derived carbons,³⁷ a larger capacitance decrease was observed in our samples at high discharge rates (Fig. 5). It is generally assumed that the capacitance loss under large currents is due to the presence of micropores. In our case, the volume of micropores is rather small, and no clear correlation between the micropore volume and capacitance fading was observed. For example, Y 800 possesses the worst overall micropore volume (Fig. 3B), while Y 850 demonstrates the highest capacitance fading. We hypothesize that two main factors contributed to the impeded transport of ions at high current density: (i) dangling bonds and surface functionalities, particularly the nitrogen-containing ones (Table I), and (*ii*) graphitic coating of the particles, which is likely to serve as a bottleneck and restrict the ion transport toward the internal volume of the particles (Fig. 1D). The first factor clearly has the largest impact (Fig. 5). The Y series demonstrated worse retention of the capacity than the E series. Y 850 with the highest nitrogen content showed the largest capacitance fading. If our hypothesis is correct, future work directed toward synthesis of high-surface-area templated carbons with the smallest content of impurities (fluorine, nitrogen, and oxygen) may produce excellent materials for EDLCs operating in organic electrolytes. This is in contrast to the use of



Figure 5. (Color online) Variation of capacitance with current density. C_0 represents the maximum capacitance at 10 mA.



Figure 6. (Color online) Frequency response of the synthesized carbons: (A) Nyquist plots and (B) variation of ESR with synthesis temperature.

templated carbons in aqueous solutions,³³ where surface functional groups substantially contribute to the overall capacitance and do not impede the transport of smaller hydrated ions to any significant degree.

EIS provides complementary information about the frequency response of carbons in EDLCs. The Nyquist plots of cells assembled with templated carbon electrodes (Fig. 6A) demonstrate no highfrequency loop, indicating a good contact between the current collector and the active material. The frequency behavior varies from one cell to another. The higher Z' and Z" at low frequency observed in the E sample series indicates their lower capacitance values, in agreement with CV and discharge experiments (Fig. 4 and 5). From these plots, the equivalent internal series resistance (ESR) of the cells measured at 1 kHz and corresponding to Z'' = 0 was plotted as a function of the synthesis temperature (Fig. 6B). There are several contributions to ESR, including the electrical resistance of the carbon electrodes and the current collector/electrode interfaces and ionic resistance of the electrolyte, among others. The resistance decrease with increasing synthesis temperature could be due to an increase in the electrical conductivity of the carbon. However, sample E 750 breaks the observed trend. Some inconsistency in the material or the electrode preparation might be responsible for the observed deviation.

The variation of the real and imaginary capacitance with frequency (Fig. 7) was calculated according to Eq. 3^{40}

$$C' = -\frac{1}{2\pi f Z''}; \quad C'' = \frac{1}{2\pi f Z'}$$
[3]

where f is the frequency. The plots of the real part of the complex capacitance C' as a function of the frequency (Fig. 7A and B) demonstrated variations of the frequency response among the samples. Furthermore, even at the lowest frequency (7 mHz) the graphs do not show saturation, and the full capacitance is not reached. Among



Figure 7. (Color online) Variation of the (A and B) real part C' and (C and D) imaginary part C'' of the capacitance for the (A and C) E and (B and D) Y sample series.



Figure 8. (Color online) Variation of the time constant with synthesis temperature.

the Y sample series, sample Y 900 showed the best frequency response (shortest response time which allows reaching half of the maximum capacitance $C_{LF}/2$), possibly due to higher conductivity (Fig. 6B), fewer structural defects, and functional groups (Table I) resulting from the higher synthesis temperature. Within the E series, E 650 demonstrated the fastest response (Fig. 7A), possibly resulting from its lower ESR (Fig. 6B) and low impurity content (Table I). A more pronounced difference is observed when considering the dissipative part of the capacitance (Fig. 7C and D). The maximum of each curve corresponds to the frequency of the transition from the capacitive (low frequency) to the purely resistive (high frequency) behavior of the cell. Y 900 clearly has the highest transition frequency.

The reciprocal of the characteristic (transition) frequency is a time constant τ_0 (Fig. 8), which varies with the synthesis temperature for both the E and Y sample series. This time constant, derived from the C'(f) and C''(f) plots (Fig. 7), characterizes how fast the device can be efficiently charged and discharged. This time depends on both the real resistance and capacitance of the device. The resistance, in turn, has two contributions: the frequency-dependent part related to the ion diffusion within the porous carbon electrodes and the frequency-independent ESR. The slight increase in τ_0 for the Y 850 sample as compared to the Y 800 sample in spite of its higher synthesis temperature and lower ESR could be related to both the presence of the functional groups and the higher capacitance of Y 850. E 750 also does not follow the trend of decreasing the time constant at higher temperatures, and its high τ_0 could be related to the unexpectedly high resistance (Fig. 6). The time constant of E550, not plotted in Fig. 8, is \sim 30 s. The relatively high τ_0 values for the Y samples in spite of their higher synthesis temperatures and lower ESR are related to the higher capacitance of these samples. The overall τ_0 values for the zeolite-templated carbon samples are lower than those observed in high-capacitance microporous carbons ² but higher than those of carbon nanotubes and carbon onions⁴¹ that have an open pore structure and limited capacitance.

Conclusion

We have synthesized porous carbons with well-developed porosity by chemical vapor deposition of carbon onto zeolite templates using acetonitrile and ethylene precursors. Electron microscopy studies showed shape conservation during the carbon template synthesis and the formation of a graphitic carbon coating of up to 20 nm in thickness on the particle surface. CV and charge-discharge tests showed high-energy-storage characteristics of the produced materials. The capacitance of the synthesized carbons in the NEt₄BF₄-acetonitile electrolyte reached 146 F/g and was among the highest reported so far. The capacitance values scaled well with the SSA of the samples and, in contrast to activated carbons, did not show saturation at high surface areas, opening avenues for further capacitance enhancement. XPS studies revealed up to ~ 7 atom % of nitrogen in samples synthesized using an acetonitrile precursor. In contrast to expectations, nitrogen doping was not found to increase the total capacitance values but negatively affected the capacitance retention at high current densities. This suggests that pure carbon electrodes might be better for EDLCs using organic electrolytes. The frequency response of the synthesized materials was better than that of the high-capacitance microporous carbons. The combination of high capacitance with a short time constant makes zeolitetemplated carbon a promising material for high-energy, high-power EDLCs using organic electrolytes.

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References

- 1. B. E. Conway, *Electrochemical Supercapacitors*, p. 698, Kluwer Academic/Plenum Publishers, New York (1999).
- 2. J. R. Miller and P. Simon, Science, 321, 651 (2008).
- 3. G. Sikha, R. E. White, and B. N. Popov, J. Electrochem. Soc., 153, L9 (2006).
- L. T. Lam and R. Louey, J. Power Sources, 158, 1140 (2006).
- H. A. Catherino, J. F. Burgel, P. L. Shi, A. Rusek, and X. L. Zou, J. Power Sources, 162, 965 (2006).
- 6. H. Yoo, S. K. Sul, Y. Park, and J. Jeong, IEEE Trans. Ind. Appl., 44, 108 (2008).
- L. P. Jarvis, T. B. Atwater, and P. J. Cygan, J. Power Sources, **79**, 60 (1999) A. G. Pandolfo and A. F. Hollenkamp, J. Power Sources, **157**, 11 (2006). 8
- Y. Gogotsi, A. Nikitin, H. Ye, W. Zhou, J. E. Fischer, B. Yi, H. C. Foley, and M. W. 9.
- Barsoum, *Nature Mater.*, **2**, 591 (2003). 10. G. Yushin, A. Nikitin, and Y. Gogotsi, in Nanomaterials Handbook, Y. Gogotsi,
- Editor, pp. 239-282, CRC Press, Boca Raton, FL (2006). G. Yushin, R. K. Dash, Y. Gogotsi, J. Jagiello, and J. E. Fischer, Adv. Funct. Mater., 11.
- 16, 2288 (2006) 12. J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, and P. Simon, Science, 313, 1760
- (2006).13. L. Permann, M. Latt, J. Leis, and M. Arulepp, Electrochim. Acta, 51, 1274 (2006).
- 14. M. Arulepp, J. Leis, M. Latt, F. Miller, K. Rumma, E. Lust, and A. F. Burke, J. Power Sources, 162, 1460 (2006).
- 15. J. S. Huang, B. G. Sumpter, and V. Meunier, Angew. Chem., Int. Ed., 47, 520 (2008).
- 16. R. Ryoo, S. H. Joo, and S. Jun, J. Phys. Chem. B, 103, 7743 (1999).
- 17. T. Kyotani, L. F. Tsai, and A. Tomita, Chem. Mater., 8, 2109 (1996).
- T. Kyotani, Carbon, 38, 269 (2000).
- 19. J. Lee, J. Kim, and T. Hyeon, Adv. Mater. (Weinheim, Ger.), 18, 2073 (2006).
- Y. D. Xia and R. Mokaya, Adv. Mater. (Weinheim, Ger.), 16, 886 (2004). 20.
- 21. Y. D. Xia and R. Mokaya, Adv. Mater. (Weinheim, Ger.), 16, 1553 (2004).
- 22. T. Kyotani, T. Nagai, S. Inoue, and A. Tomita, Chem. Mater., 9, 609 (1997).
- 23. J. I. Paredes, A. Martinez-Alonso, T. Yamazaki, K. Matsuoka, J. M. D. Tascon, and T. Kyotani, Langmuir, 21, 8817 (2005).
- 24. T. Kyotani, Z. X. Ma, and A. Tomita, Carbon, 41, 1451 (2003).
- 25. A. Pacula and R. Mokaya, J. Phys. Chem. C, 112, 2764 (2008).
- 26. Z. X. Yang, Y. D. Xia, and R. Mokaya, J. Am. Chem. Soc., 129, 1673 (2007).
- 27. Z. X. Yang, Y. D. Xia, X. Z. Sun, and R. Mokaya, J. Phys. Chem. B, 110, 18424 (2006).
- 28. Z. X. Yang, Y. D. Xia, and R. Mokaya, Adv. Mater. (Weinheim, Ger.), 16, 727 (2004).
- 29. F. O. M. Gaslain, J. Parmentier, V. P. Valtchev, and J. Patarin, Chem. Commun. (Cambridge), 2006, 991.
- 30. O. Klepel, H. Strauss, A. Garsuch, and K. Bohme, Mater. Lett., 61, 2037 (2007). 31. A. Garsuch, O. Klepel, R. R. Sattler, C. Berger, R. Glaser, and J. Weitkamp,
- Carbon, 44, 593 (2006).
- 32. A. Garsuch and O. Klepel, Carbon, 43, 2330 (2005).
- 33. C. O. Ania, V. Khomenko, E. Raymundo-Pinero, J. B. Parra, and F. Beguin, Adv. Funct. Mater., 17, 1828 (2007).
- 34. P. I. Ravikovitch and A. V. Neimark, Colloids Surf., A, 187-188, 11 (2001).
- 35. C. Portet, P. L. Taberna, P. Simon, and E. Flahaut, J. Electrochem. Soc., 153, A649 (2006).
- 36. C. Portet, P. L. Taberna, P. Simon, and C. Laberty-Robert, Electrochim. Acta, 49, 905 (2004).
- 37. C. Portet, G. Yushin, and Y. Gogotsi, J. Electrochem. Soc., 155, A531 (2008).
- O. Barbieri, M. Hahn, A. Herzog, and R. Kotz, *Carbon*, **43**, 1303 (2005).
 E. Raymundo-Pinero, K. Kierzek, J. Machnikowski, and F. Beguin, *Carbon*, **44**, 2498 (2006).
- 40. D. Hulicova, M. Kodama, and H. Hatori, Chem. Mater., 18, 2318 (2006).
- 41. C. Portet, G. Yushin, and Y. Gogotsi, Carbon, 45, 2511 (2007).
- 42. P. L. Taberna, G. Chevallier, P. Simon, D. Plee, and T. Aubert, Mater. Res. Bull., 41, 478 (2006)