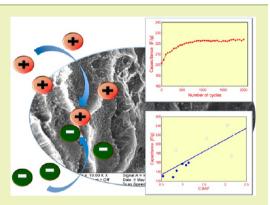# Charge Storage Accessibility Factor as a Parameter Determining the Capacitive Performance of Nanoporous Carbon-Based Supercapacitors

Mykola Seredych,[†] Mikolaj Koscinski,[†,‡] Malgorzata Sliwinska-Bartkowiak,[‡] and Teresa J. Bandosz*[†,§]

[†]The City College of New York, Department of Chemistry, [§]CUNY Energy Institute, 160 Convent Avenue, New York, New York 10031, United States

[‡]The NanoBioMedical Centre, Faculty of Physics, Adam Mickiewicz University, Umultowska 85, Poznan 61-614, Poland

ABSTRACT: Composites of commercial graphene and polymer-derived nanoporous carbons were activated with KOH and CO_2 to increase the porosity. The materials are characterized using the adsorption of nitrogen, SEM/EDX, and potentiometric titration. Their electrochemical performance was measured in two and three electrode cells in H_2SO_4 as an electrolyte. Activation results in a significant increase in the capacitance owing to the development of porosity and an increase in the surface oxygen content. To account for the beneficial effect of the volume of pores smaller than 0.7 nm on the double layer capacitance and of surface wettability on ion transfer to these pores, a charge storage accessibility factor, CSAF, was proposed as a product of the volume of pores smaller than 0.7 nm and surface oxygen content. The results indicate that there is a dependence between CSAF and the energy storage in carbon-based supercapacitors provided that the electrical double layer capacitance in small pores is the predominant mechanism of charge storage.

KEYWORDS: Capacitance, Nanoporous carbon, Graphene/carbon composite, Conductivity, Porosity

INTRODUCTION

It is generally accepted that the porosity of activated carbons in combination with their surface chemistry governs their capacitive performance.[1−17] That performance is based on the formation of an electrical double layer in the small pores and on the Faradaic reactions on the surface.[1−16] The latter determine pseudocapacitance, and they are especially important in aqueous electrolytes.[6,8−16] Surface functional groups, which contribute to pseudocapacitance are quinones/hydroquinones and pyridinic and pyrrolic-like nitrogen moieties.[8−10,13,15,16]

Since the capacitance in aqueous electrolytes is based on the deposition of hydrated ions, the wettability of a carbon surface and not restricted charge transfer are also important features to consider.[18,19] While the former can be enhanced by the presence of polar heteroatoms, for the latter high electronic conductivity is beneficial. Generally the electrical conductivity of the electrodes is enhanced by an addition of conductive graphite or carbon black for electrochemically active carbon materials. They certainly help in a charge transfer within the electrode but the internal conductivity in the pore space where ions are stored is rather not affected. To improve the properties of active material carbon nanofibers,[20,21] carbon nanotubes,[17,22−24] and graphene[25,26] are added to the porous carbons. Graphene[25] and electrochemically modified graphite,[27] owing to their conductivity and a theoretically high surface area, have been recently explored as additives to nanoporous carbons. Even though some studies report a significant improvement in the capacitance owing to the graphene addition,[26,28] there are some results published with contradictory findings. For instance, Totir and co-workers indicated the negative effects of commercial graphene addition to activated carbons,[29] and Buglione and Pumera demonstrated that the capacitance of the composites of graphene and carbon nanotubes was an arithmetic average of the capacitance of the individual components.[30]

Recently, we have addressed the complexity of the factors affecting the capacitive behavior of the composites built from graphite oxide (GO) or graphene and nanoporous carbons.[31,32] The results suggested that for a good performance the right combination of the volume of small pores and conductivity are important. The polar functional groups also play a role since they affect the wettability of carbons and thus the charge transfer to very small pores. To account for all these factors the parameter describing the utilization of the pore space for double layer capacitance was derived by dividing the capacitance by the volume in pores smaller than 0.7 nm. These pores were indicated as crucial for accumulating the charge owing to the similarity of their size to the size of the electrolyte ions.[1,2] The linear trend of the dependence of this parameter on conductivity of the specific composite tested was
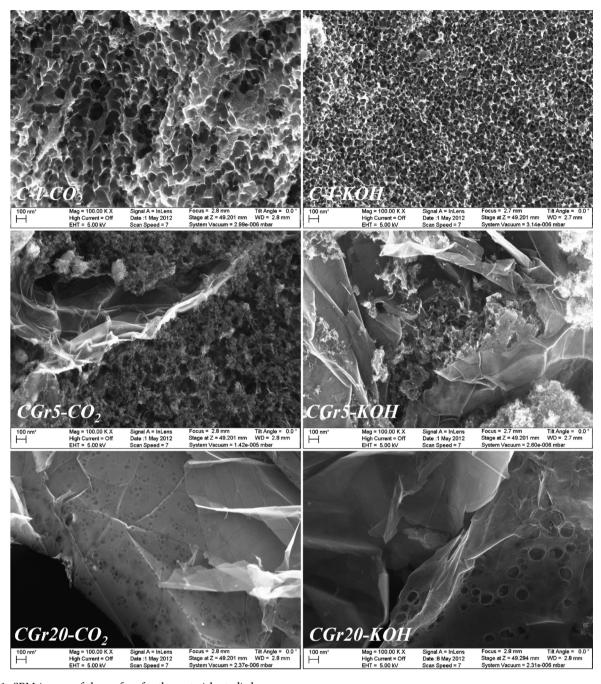
Figure 1. SEM images of the surface for the materials studied.

found. In recent papers, Gogotsi and co-workers addressed in detail the effect the pore size and pore size distributions on the energy density.[33,34] Analyzing the performance of various carbons of specific pore sizes in various electrolytes, they stressed the effects of ion desolvation and their accessibility to the small pores similar to the size of the ions.[4] Since the maximum energy density can be reached with the "optimal" pore size and it depends on the ion size and the operating voltage, the carbons with narrow pore size distribution and very small pores were indicated as the most suitable energy storage media.[34]

Since the performance of supercapacitors is based on the presence of the proper porosity and this includes the size of the pores and their volume, the aim of this work is to further explore the concept of the active pore space utilization and its

importance for the capacitive behavior. The composites of graphene and nanoporous carbons derived from the commodity polymer addressed previously[32] were activated with CO_2 and KOH to increase/change the volumes of pores active in energy storage and to broader the range of surface properties. Even though quite high capacitances were measured, we focus rather on determining the factors, which contribute to these values and not on achieving the record performances. These factors include the specific porosity, conductivity, and wettability of the resulting composites.

■ EXPERIMENTAL SECTION

Materials. Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (PS) was used as a nanoporous carbon precursor. The details of this carbon preparation are published elsewhere.[35] This sample is referred

1025

dx.doi.org/10.1021/sc400092g | ACS Sustainable Chem. Eng. 2013, 1, 1024−1032

Table 1. Parameters of Porous Structure Calculated from Nitrogen Adsorption Measurements and the Samples' Conductivities, σ

sample	S_{BET} (m²/g)	V_t (cm³/g)	V_{meso} (cm³/g)	$V_{<0.7\ nm}$ (cm³/g)	$V_{<1\ nm}$ (cm³/g)	V_{mic}(DFT) (cm³/g)	σ (S/m)
C−I	1386	0.904	0.463	0.140	0.232	0.441	14.4
C−I−CO₂	1615	1.237	0.692	0.190	0.251	0.545	20.1
C−I−KOH	1766	1.527	0.990	0.163	0.264	0.537	38.9
CGr5	775	0.540	0.269	0.134	0.172	0.271	123.1
CGr5−CO2	1231	1.437	1.168	0.091	0.116	0.269	32.5
CGr5−KOH	1315	0.886	0.451	0.180	0.264	0.435	54.8
CGr20	783	0.608	0.364	0.101	0.145	0.244	209.2
CGr20−CO2	1083	0.870	0.553	0.140	0.187	0.317	93.2
CGr20−KOH	1162	0.868	0.499	0.139	0.219	0.369	120.8

to as C−I. The polymer was used as a source of nanoporous carbon in graphene−carbon composites. The content of graphene recalculated per carbon yield of the C−I material was 5 and 20%. The dissolved in distilled water polymer was mixed with graphene, and the formed dense suspensions were dried before the carbonization. Commercial graphene was obtained from the METSS Corporation. The composites were referred to be CGr5 and CGr20. Then, the samples were activated with CO_2 (flow rate 50 mL/min) at 850 °C for 2 h and with KOH. In the case of the latter, carbon was impregnated with an aqueous solution of 6 M KOH (KOH/carbon weight ratios of 1/1), as described elsewhere.[36] Then the sample was dried and heated at 300 °C for 3 h in nitrogen atmosphere. As a next step, it was heated at 800 °C for 2 h in N_2. The heating rate was 10 °C/min. To remove potassium, the carbons were extensively washed in 0.1 M HCl in a Soxhlet apparatus and then with water to constant pH. The activated materials have CO_2 or KOH added to their names.

Methods. *Electrochemical Measurements.* The capacitive performance of all carbon samples was investigated in 1 M H_2SO_4 using two- and three-electrode cells. The working electrode was prepared by mixing the active material with polyvinylidene fluoride (PVDF) and commercial carbon black (carbon black, acetylene, 50% compressed, Alfa Aesar) (8:1:1) in N-methyl-2-pyrrolidone (NMP) until homogeneous slurry. The slurry was coated on a Ti foil (current collector) with the total surface area of 1 cm² of an active material. The electrodes were dried at 120 °C for 24 h and then weighted. The total mass was between 3 and 5 mg and two electrodes with identical weight were selected for the measurements.

Cyclic voltammetry and galvanostatic charge−discharge were used in evaluation of the capacitive performance. The measurements were carried out using VersaSTAT MC (AMETEK, Princeton Applied Research) within the potential window of 0−1 V with the scanning rate of 5 and 100 mV/s (cyclic voltammetry) and the current loads of 50 and 100 mA/g and 1 A/g (galvanostatic charge/discharge).

Cyclic voltammetry at the scan rate of 5 mV/s was also recorded in a three-electrode cell using the Ag/AgCl (3 M KCl) reference electrode and an active material as a working and platinum rod as counter electrode, respectively.

Potentiometric Titration. Potentiometric titration measurements were performed with a DMS Titrino 716 automatic titrator (Metrohm). The details on the experiments are presented in Ref 18. The experimental data was transformed into proton binding curves, Q, representing the total amount of protonated sites. From them, the pK_a distributions and the numbers of groups represented by certain pK_a values were calculated.[37,38]

Evaluation of porosity. Sorption of nitrogen at its boiling point was carried out using ASAP 2020 (micromeritics, surface area, and porosity analyzer). Before the experiments, samples were outgassed at 120 °C to constant vacuum (10^{-4} Torr). The surface areas (BET method), total pore volumes, V_t (from the last point of isotherm at relative pressure equal to 0.99), volumes of micropores, V_{mic}, volume in pores less than 0.7 and 1 nm, $V_{<0.7\ nm}$ and $V_{<1\ nm}$, mesopore volumes, V_{meso}, along with pore size distributions were calculated from the isotherms. The last four quantities were calculated using density functional theory, DFT.[39]

SEM/EDX. Scanning electron microscopy (SEM) images were performed at Zeiss Supra 55 VP. The accelerating voltage was 5.00 kV. Scanning was performed in situ on a sample powder without coating. Electron-dispersive X-ray spectroscopy (EDX) analysis was done at magnification 5000× and the content of elements on the surface was calculated.

DC Conductivity Measurements. The DC conductivity was measured using a 4-probe method on the polymer-based carbon and composites graphene/carbon pellets with the same composition as that used to make the electrodes (see description in Electrochemical Measurements). The prepared powder was pressed by a Carver Press machine applying 2 tons pressure and a disk-shaped well-packed pellets with diameter 8 mm were formed. The pellets were dried in oven for 12 h. The pellets' thickness was measured by a spring micrometer. The measurement of conductivity was carried out using the Keithley 2400 multimeter.

■ RESULTS AND DISCUSSION

The activation of nanoporous carbon and its composites with graphene addressed in ref 32 was done to increase the porosity. Since the small pores, similar to the sizes of the electrolyte ions are expected to be the main contributor for charge storage,[4,33,34] and sulfuric acid is our electrolyte with the sizes of hydrated sulfate ions $[SO_4^{2-}(H_2O)_{12}]$ of 0.533 nm,[40] the pores smaller than 0.7 nm should be the features of paramount importance in our composites provided that the formation of EDL is the main charge storage mechanism. The SEM images presented in Figure 1 show that activation visibly increased the porosity. Interestingly, after activation with KOH very uniform transport mesopores or macropores are present in the nanoporous carbon. On the other hand, activation with CO_2 results in more heterogeneous morphology with much larger pores. While compared to the nontreated samples,[32] the significant activation of the carbon phase is found. The changes in the graphene phase seem to be much less visible indicating its resistance to activation.

The details on the porous structure obtained from the analysis of the nitrogen adsorption isotherms are collected in Table 1 and Figure 2. Apparently activation with KOH is much more aggressive on the composites than on the nanoporous carbons. It significantly increases the volume of micropores and the volume of small mesopores. While the former governs the capacitance, the latter is important for the ion transport. The mesopores in the broad range of their sizes are especially developed in the composite with 5% Gr activated with CO_2. This is consistent with the morphology of the nanoporous carbon phase visible in Figure 1. Activation of CGr20 either with CO_2 or KOH results in a similar porosity in the range of pores with sizes less than 2 nm. Pores with sizes bet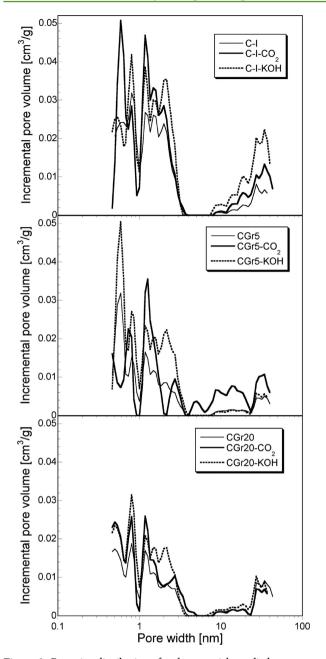ween 3 and 5 nm are formed only after activation with KOH. That high porosity of the materials activated with KOH is expected to be

Figure 2. Pore size distributions for the materials studied.

the composites oxidized with CO_2. One reduction hump at the potential 0.5 V vs Ag/AgCl is seen on the CV curve for CGr5−CO_2 and two humps—at about 0.55 and 0.25 V vs Ag/AgCl for CCr20−CO_2. That latter hump is also seen for both composites oxidized with KOH. Both activated nanoporous carbons do not exhibit the hump at 0.25 V, which is an indication of the differences in surface chemistry between the carbon and the composites. We link the reversible humps to the presence of quinone/hydroquinone groups.[8,9,16] The semi-quinone radical anions ($Q^{\bullet-}$) might contribute to oxygen reduction reactions[41] as proposed by Kruusenberg and co-workers.[42] The irreversible humps at 0.25 V vs Ag/AgCl might be related to oxygen reduction reaction (ORR). They are especially visible for the samples activated with KOH which is in agreement with the results presented in Figure 4. Moreover, in the case of carbons activated with CO_2 where sulfur is present, the humps in the CV curves can be also linked to the Faradaic reactions of sulfoxides and sulfones.[43]

The capacitance was calculated from charge discharge profiles collected in Figure 5. At low current, the triangular shapes are exhibited. The shape changes with an increase in a current load and at 1 A/g the Ohmic drop is clearly visible for C−I−CO_2 and CGr5−KOH. This drop was taken into account in calculating the specific capacitance. Comparison of the capacitance at different current loads for the initial and activated samples is presented in Figure 6. Apparently a significant increase in the capacitance is found on the modified composites and the best performing samples are those activated with KOH. That superiority of the KOH activation method over CO_2 is especially seen for the sample with 5% graphene. On the other hand, when the capacitance retention ratio (ratio the gravimetric capacitance at 50 mA/g and 1 A/g) is compared (Figure 7), CGr5−CO_2 is much more stable than its counterpart activated with KOH. For the sample with 20% Gr, the opposite trend is found.

The dependence of the capacitance on the volume of pores smaller than 0.7 nm is plotted in Figure 8. Although a weak trend of an increase in the capacitance with an increase in $V_{< 0.7\ nm}$ is found, the dependence is far from linear and it becomes even worse with an increase in the size of the pores whose volume is considered. This is consistent with the results reported by Kondrat and co-workers[34] and the detailed analysis of the pore accessibility related to the size of the electrolyte ions presented by Gogotsi and co-workers.[4,33] The contribution of pseudocapacitance, which should play a more dominant role in larger pores where functional groups can exist, can contribute to this poor correlation. Its effect is visible and is especially important for the KOH activated materials. The observed trend follows the trends in the redox reactions visible on CV curves measured in three electrode cells (Figure 4).

To address the effects of functional groups on the overall performance, the surface chemistry has to be analyzed. Although not all oxygen-containing groups can contribute to the pseudocapacitance, all of them should affect the wettability of the carbon surface owing to the polarity of oxygen. Table 2 collects the surface contents of elements and the numbers of strong acids ($pK_a < 7$), weak acids ($pK_a > 7$), and the total number of groups. The latter three quantities were determined from potentiometric titration experiments. As seen, two activation methods used have quite opposite effects on the distribution of surface acidic groups. While the KOH treatment results in an increase in the number of strong acids, after CO_2 treatment the number of weak acids visibly increased with the
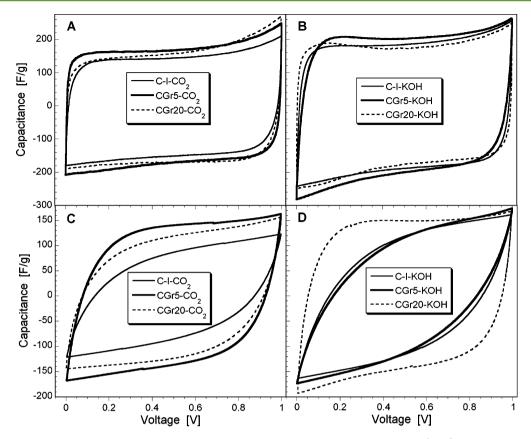
an important factor affecting their electrochemical performance. If we consider the ratio of the volume of micropores to the total pore volume as a parameter describing the degree of microporosity, the materials studied certainly have a high volume of large transport pores and activation with CO_2 results in the mesoporous materials especially in the case of CGr5−CO_2 for which the degree of microporosity is only 20%.

The examples of the CV curves measured in two electrode cell are presented in Figure 3. The curves for the activated composites have rectangular shapes, and the shape is only slightly disturbed with the high scan rate. On the other hand, the unactivated samples show the limitations in charge transfer with an increase in the scan rate.[32]

The CV curves measured in three electrode cell also show the rectangular shape with the humps representing Faradaic reactions (Figure 4). While the reduction processes are visible for all samples, oxidation reactions are very weakly marked for

1027

dx.doi.org/10.1021/sc400092g | ACS Sustainable Chem. Eng. 2013, 1, 1024−1032

Figure 3. CV curves in two electrode cell at different scan rates in 1 M H_2SO_4 as an electrolyte: 5 mV/s (A, B) and 100 mV/s (C, D).
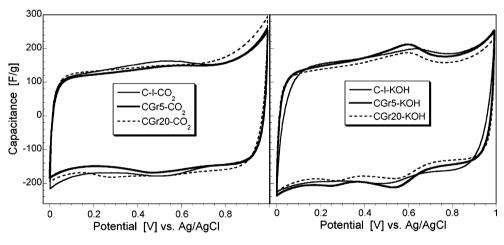

Figure 4. CV curves in three electrode cell vs Ag/AgCl at scan rate 5 mV/s in H_2SO_4 as an electrolyte.

small fraction of the strongly acidic groups. Even though strong acids are not expected to contribute to the pseudocapacitance, their presence should positively affect the wettability of carbons and thus should result in a more efficient ion transfer to small pores, provided that those pores are not blocked by the functional groups and the material has a sufficient DC conductivity. Some of the surface functional groups contribute to pseudocapacitance as seen in the reversible redox humps in H_2SO_4.

Potentiometric titration results are in a general agreement with those of EDX surface analysis. Apparently activation with KOH results in more oxygen on the surface than after the CO_2 treatment and an increase is especially visible for the composite with 5% graphene. Less sulfur is detected on the surface of the

CGr20 sample than on that of CGr5. Interestingly on the surface of CGr5−CO_2, a marked amount of sodium is present. Since that amount is higher than that of sulfur, we linked it to sodium carbonates existing in the small pores of this composite formed during activation. The removal of carbonates by water washing from such pores can be restricted. More oxygen on the surface of CGr20 than on that of CGr5 detected by EDX can have a positive effect on wettability of this sample and its capacitive behavior. In fact, at the high scan rate, the CV curves for CGr20 measured in two electrode cells show the least limitation in the charge transfer (Figure 3). On the surface of the composites activated with KOH a noticeable amount of potassium is present. As in the case of sodium, its effective
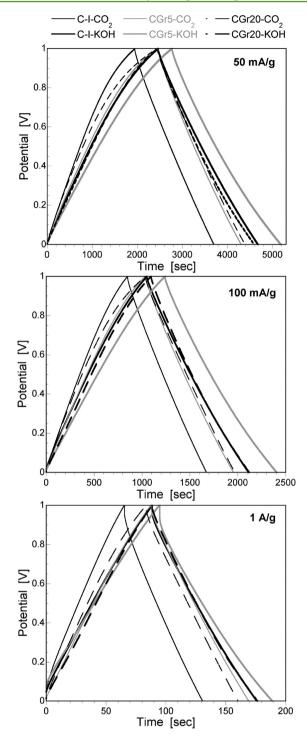
Figure 5. Charge/discharge profiles at different current loads in H_2SO_4.

Figure 6. Comparison of the capacitance at different current loads in H_2SO_4 as an electrolyte for the initial samples[32] and those activated with CO_2 and KOH.

Figure 7. Comparison of the capacitance retention ratio in H_2SO_4 for the initial samples[32] and those activated with CO_2 and KOH.

removal from small pores is difficult to achieve and its presence can enhance the conductive properties.

While the volume of pores smaller than 0.7 nm is very well-defined and measured, as a main quantity affecting the wettability, we have chosen to use the content of oxygen atoms on the surface determined from EDX analysis. Since the volume of small pores, and wettability, should increase the active pore space utilization for EDLC,[32] we define the product of the volume of pores smaller than 0.7 nm and the content of oxygen atoms as a new empirical quantity, a charge storage
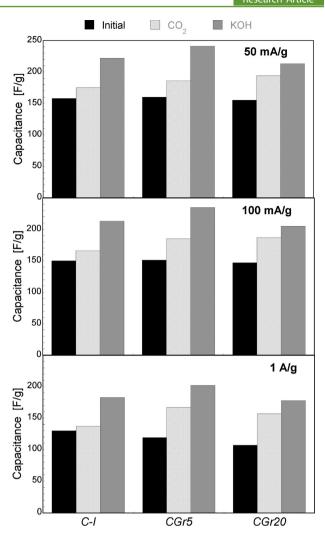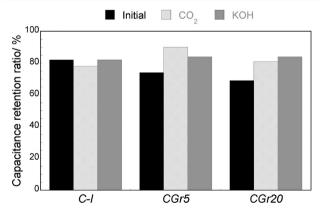
accessibility factor, CSAF. In Figure 9 the dependence of the capacitance on the CSAF is presented. To better visualize the broader applicability of this new parameter to assess the capability of carbons to store energy, the data on the unactivated samples, presented in ref 32 is also included. In the case of these samples the effect of pseudocapacitance on the overall performance was very small and therefore we found
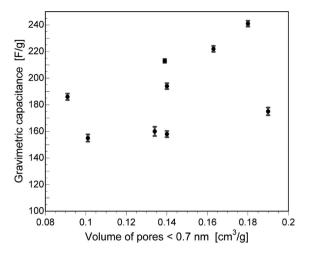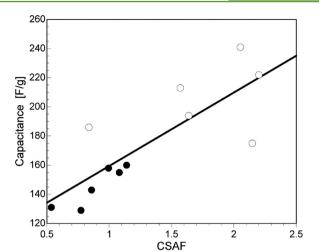
Figure 8. Dependence of the capacitance in H_2SO_4 on the volume of pores smaller than 0.7 nm.

Figure 9. Dependence of the capacitance measured in H_2SO_4 on the CSAF. The data from ref 32 is marked as dark symbols.

them as suitable to support the dependence proposed in this paper. Although not perfect, there is an indication of a linear trend between the electrochemical capacitance and the CSAF. Even though other factors such as electronic conductivity must affect the performance,[31,32] we hypothesize that the deviations from linearity are caused by Faradaic reactions and for the carbon systems with an exclusive EDL charge storage mechanism more ideal behavior is expected. Since CSAF links the pore volume, where the actual energy storage takes place, and the hydrophilicity determining feature that enhances the ions transport to these pores, assessment of its value can lead to the information on an expected specific capacitance of carbon. It is important to understand that the limits must exist in the values of CSAF for nanoporous carbons. The content of oxygen on their surface is limited to preserve the integrity of graphene layers. Usually the carbons with a high content of oxygen have a small volume of pores smaller than 0.7 nm owing to the high extent of the activation/oxidation process that results in a pore broadening effect. Moreover, a high number of oxygen functional groups can also block the small pores for adsorbate molecules and even nitrogen or carbon dioxide used to determine the pore volume might not be able to enter them.

The DC conductivity of the samples studied is collected in Table 1. Interestingly, the activation of nanoporous carbon slightly increases its conductivity in spite of the increase in the pore volume in the surface oxygen content. A plausible explanation for this is an increase in the degree of carbon matrix aromatization by prolonged exposure to a high temperature

treatment. Activation of the composites, especially with CO_2 decreases the conductivity significantly. We link this effect to the formation of pores and defects in the composites. The larger pores in the samples activated with CO_2 lead to lower conductive properties. Taking into account that in the composite with 5% graphene sodium and potassium cations are present and they increase the apparent conductivity, the conductivity of the pure carbon phase in these materials is expected to be even lower. This low conductive properties must be compensated by other factors as surface wettability since the active pore space utilization defined as the capacitance per unit volume of pores smaller than 0.7 nm[32] is rather high, especially for CGr5−CO_2 (over 2000 F/cm^3). This composite has a high surface area in pores larger than 1 nm, and the effect of functional groups on the small pores accessibility should be minimal. Owing to the contribution of cations to the measured conductivity and the importance of surface wettability in the case of highly porous materials with the marked volume of transport pores no direct linear dependence of the active pore space utilization on conductivity was found. Although some trend of an increase in this parameter with an increase in the conductivity can be noticed, there are some "outliers". For these samples obviously other factors as wettability and pore accessibility play an important role. The lack of the dependence of the pore space utilization[32] on the conductivity does not necessary cross out the significance of conductivity for charge storage utilization. The latter is apparently very important but

Table 2. Contents of Surface Elements from EDX Analysis and the Numbers of Strongly Acidic (pK_a < 7), Weakly Acidic (pK_a > 7), and Total Acidic Groups

	EDX (in atomic %)					(mmol/g)		
sample	C	O	S	Na	K	pK_a < 7	pK_a > 7	total
C−I	91.9	7.1	1.0			0.377	0.311	0.688
C−I−CO_2	88.4	11.3	0.3			0.171	0.529	0.700
C−I−KOH	86.5	13.5				0.247	0.426	0.673
CGr5	89.2	8.5	1.7	0.6		0.273	0.441	0.714
CGr5−CO_2	87.5	9.2	1.7	1.7		0.117	0.534	0.651
CGr5−KOH	87.1	11.4			1.5	0.256	0.550	0.806
CGr20	88.4	10.7	0.9			0.127	0.294	0.421
CGr20−CO_2	87.5	11.7	0.8			0.122	0.301	0.423
CGr20−KOH	88.4	11.3			0.3	0.218	0.419	0.637

its direct effects can be only seen if other crucial factors such as pore size distributions and wettability of the sample surfaces are more or less comparable and not other factors as, for instance, the presence of metals affect the conductivity.

For the performance of carbonaceous materials as supercapacitors, the stability after multiple cycles of charge/discharge is an important factor. As seen from Figure 10 both nanoporous
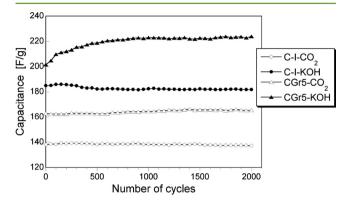

Figure 10. Specific discharge capacitance during galvanostatic cycling at 1 A/g in 1 M H_2SO_4.

carbon and the composite with 5% the graphene phase are very stable. Interestingly, for the composite activated with KOH, CGr5−KOH, an increase in the performance is found. This increase in sulfuric acid is about 10%. One reason for this behavior can be the decomposition/reduction of surface functional groups blocking the entrances to the small pores[44] and carbon aging.[45] Even though the pseudocapacitive effect is expected to decrease in its extent, its contribution to the overall capacitance could be compensated by the electrical double layer storage mechanism. Another plausible explanation is in the nanoscale expansion of porous carbon electrodes as recently discussed by Arruda and co-workers.[46] They found that a charging/discharging process can lead to the swelling of carbon pore networks, especially when the subnanometers pores are present. The occurrence of 1.5 at % potassium in the small pores of CGr5-KOH and the chemical reactions in the pore system can also contribute to this hypothesized swelling effect.

■ CONCLUSIONS

The results presented in this paper support the importance of pores smaller than 0.7 nm, and their accessibility for electrolyte ions for the double layer capacitance. Activation of the nanoporous carbon−graphene composites increased not only the volume of small pores but also the amount of oxygen groups on the surface. Even though the effects of these groups on the capacitance via Faradaic reactions are not very significant, they increased the wettability of the surface and thus the pore space could be more efficiently used by the electrolyte ions. The product of the volume of pores smaller than 0.7 nm and the atomic % of oxygen on the surface was defined as the charge storage accessibility factor, CSAF. The indication of the dependence of the gravimetric capacitance on this factor was demonstrated, especially for the system when the pseudocapacitance was marginal and a double layer capacitance was the main charge storage mechanism.

■ AUTHOR INFORMATION

Corresponding Author
*Tel.: (212) 650-6017. Fax (212) 650-6107. E-mail: tbandosz@ccny.cuny.edu.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Salitra, G.; Soffer, A.; Eliad, L.; Cohen, Y.; Aurbach, D. Carbon electrodes for double-layer capacitors. I. Relations between ion and pore dimensions. *J. Electrochem. Soc.* **2000**, *147*, 2486−2493.

(2) Eliad, L.; Salitra, G.; Soffer, A.; Aurbach, D. On the mechanism of selective electroadsorption of protons in the pores of carbon molecular sieves. *J. Phys. Chem. B* **2001**, *105*, 6880−6887.

(3) Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. Anomalous increase in carbon capacitance at pore sizes less than 1 nm. *Science* **2006**, *313*, 1760−1763.

(4) Largeot, C.; Portet, C.; Chmiola, J.; Taberna, P. L.; Gogotsi, Y.; Simon, P. Relation between the ion size and pore size for an electric double-layer capacitor. *J. Am. Chem. Soc.* **2008**, *130*, 2730−2731.

(5) Wang, D.; Li, F.; Liu, M.; Lu, G. Q.; Cheng, H. M. 3D Aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage. *Angew. Chem., Int. Ed.* **2008**, *47*, 373−376.

(6) Janes, A.; Permann, L.; Arulepp, M.; Lust, E. Electrochemical characteristics of nanoporous carbide-derived carbon materials in non-aqueous electrolyte solutions. *Electrochem. Commun.* **2004**, *6*, 313−318.

(7) Pandolfo, A. G.; Hollenkamp, A. F. Carbon properties and their role in supercapacitors. *J. Power Sour.* **2006**, *157*, 11−27.

(8) Hulicova-Jurcakova, D.; Seredych, M.; Lu, G. Q.; Bandosz, T. J. Combined effect of nitrogen- and oxygen-containing functional groups of microporous activated carbon on its electrochemical performance in supercapacitors. *Adv. Funct. Mat.* **2009**, *19*, 438−447.

(9) Seredych, M.; Hulicova-Jurcakova, D.; Lu, G. Q.; Bandosz, T. J. Surface functional groups of carbons and the effects of their chemical character density and accessibility to ions on electrochemical performance. *Carbon* **2008**, *46*, 1475−1488.

(10) Byon, H. R.; Lee, S. W.; Chen, S.; Hammond, P. T.; Shao-Horn, Y. Thin films of carbon nanotubes and chemically reduced graphenes for electrochemical micro-capacitors. *Carbon* **2011**, *49*, 457−467.

(11) Conway, B. E. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*; Kluwer Academic/Plenum: New York, 1999.

(12) Kawaguchi, M.; Itoh, A.; Yagi, S.; Oda, H. Preparation and characterization of carbonaceous materials containing nitrogen as electrochemical capacitor. *J. Power Sour.* **2007**, *172*, 481−486.

(13) Hulicova, D.; Kodama, M.; Hatori, H. Electrochemical performance of nitrogen-enriched carbons in aqueous and non-aqueous supercapcitors. *Chem. Mater.* **2006**, *18*, 2318−2326.

(14) Xu, B.; Hou, S.; Cao, G.; Wu, F.; Yang, Y. Sustainable nitrogen-doped porous carbon with high surface areas prepared from gelatin for supercapacitors. *J. Mater. Chem.* **2012**, *22*, 19088−19093.

(15) Wang, D.-W.; Li, F.; Yin, L.-C.; Lu, X.; Chen, Z.-G.; Gentle, I. R.; Lu, G. Q.; Cheng, H.-M. Nitrogen-doped carbon monolith for alkaline supercapacitors and understanding nitrogen-induced redox transitions. *Chem.—Eur. J.* **2012**, *18*, 5345−5351.

(16) Andreas, H. A.; Conway, B. E. Examination of the double-layer capacitance of an high specific-area C-cloth electrode as titrated from acidic to alkaline pHs. *Electrochim. Acta* **2006**, *51*, 6510−6520.

(17) Kim, J.-I.; Rhee, K.-Y.; Park, S.-J. Interactive effects of pore size control and carbonization temperatures on supercapacitive behaviors

of porous carbon/carbon nanotube composites. *J. Colloid Interface Sci.* **2012**, *377*, 307−312.

(18) Hulicova-Jurcakova, D.; Seredych, M.; Lu, G. Q.; Bandosz, T. J. Specific anion and cation capacitance in porous carbon blacks. *Carbon* **2010**, *48*, 1767−1778.

(19) Gomez, H.; Ram, M. K.; Alvi, F.; Villalba, P.; Stafanakos, E.; Kumar, A. Graphene-conducting polymer nanocomposite as novel electrode for supercapacitors. *J. Power Sources* **2011**, *196*, 4102−4108.

(20) Huang, C. W.; Hsu, C. H.; Kuo, P. L.; Hsieh, C. T.; Teng, H. Mesoporous carbon spheres grafted with carbon nanofibers for high-rate electric double layer capacitors. *Carbon* **2011**, *49*, 895−903.

(21) Kim, B.-H.; Yang, K. S.; Kim, Y. A.; Kim, Y. J.; An, B.; Oshida, K. Solvent-induced porosity control of carbon nanofiber webs for supercapacitor. *J. Power Sources* **2011**, *196*, 10496−10501.

(22) Lu, X.; Dou, H.; Gao, B.; Yuan, C.; Yang, S.; Hao, L.; Shen, L.; Zhang, X. A flexible graphene/multiwalled carbon nanotube film as a high performance electrode material for supercapacitors. *Electrochim. Acta* **2011**, *56*, 5115−5121.

(23) Huang, C. W.; Chuang, C. M.; Ting, J. M.; Teng, H. Significantly enhanced charge conduction in electric double layer capacitors using carbon nanotube-grafted activated carbon electrodes. *J. Power Sources* **2008**, *183*, 406−410.

(24) Kim, K.-S.; Park, S.-J. Synthesis and high electrochemical capacitance of N-doped microporous carbon/carbon nanotubes for supercapacitor. *J. Electroanal. Chem.* **2012**, *673*, 58−64.

(25) Zhu, Y.; Murali, S.; Stoller, M. D.; Ganesh, K. J.; Cai, W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychosz, K. A.; Thommes, M.; Su, D.; Stach, E. A.; Ruoff, R. S. Carbon-based supercapacitors produced by activation of graphene. *Science* **2011**, *332*, 1537−1541.

(26) Tai, Z.; Yan, X.; Lang, J.; Xue, Q. Enhancement of capacitance performance of flexible carbon nanofiber paper by adding graphene nanosheets. *J. Power Sources* **2012**, *199*, 373−378.

(27) Fan, X.; Lu, Y.; Xu, H.; Kong, X.; Wang, J. Reversible redox reaction on the oxygen-containing functional groups of an electro-chemically modified graphite electrode for the pseudo-capacitance. *J. Mater. Chem.* **2011**, *21*, 18753−18760.

(28) Zhang, K.; Ang, B. T.; Zhang, L. L.; Zhao, X. S.; Wu, J. Pyrolyzed graphene oxide/resorcinol-formaldehyde resin composites as high-performance supercapacitor electrodes. *J. Mater. Chem.* **2011**, *21*, 2663−2670.

(29) Carruthers, J. D.; Chung, J.; Do, I.; Letaj, S.; Petruska, M. A.; Sturm, E. A.; Totir, D. A. Performance evaluation of graphene/activated carbon composite electrodes in EDLCs with non-aqueous electrolyte. Presented at *CESEP'11*, Vichy, France, Sep 25−29, 2011.

(30) Buglione, L.; Pumera, M. Graphene/carbon nanotube composites not exhibiting synergic effect for supercapacitors: The resulting capacitance being average of capacitance of individual components. *Electrochem. Commun.* **2012**, *17*, 45−47.

(31) Seredych, M.; Chen, R.; Bandosz, T. J. Effects of the addition of graphite oxide to the precursor of a nanoporous carbon on the electrochemical performance of the resulting carbonaceous composites. *Carbon* **2012**, *50*, 4144−4154.

(32) Seredych, M.; Koscinski, M.; Sliwinska-Bartkowiak, M.; Bandosz, T. J. Active pore space utilization in nanoporous carbon-based supercapacitors: Effects of conductivity and pore accessibility. *J. Power Sour.* **2012**, *220*, 243−252.

(33) Simon, P.; Gogotsi, Y. Capacitive energy storage in nano-structured carbon-electrolyte systems. *Acc. Chem. Res.* **2013**, *46*, 1094−1103.

(34) Kondrat, S.; Perez, C. R.; Presser, Y.; Gogotsi, Y.; Kornyshev, A. A. Effect of pore size and its dispersity on the energy storage in nanoporous supercapacitors. *Energy Environ. Sci.* **2012**, *5*, 6474−6479.

(35) Hines, D.; Bagreev, A.; Bandosz, T. J. Surface properties of porous carbon obtained from polystyrene sulfonic acid-based organic salts. *Langmuir* **2004**, *20*, 3388−3397.

(36) Ubago-Perez, R.; Carrasco-Marın, F.; Fairen-Jimenez, D.; Moreno-Castilla, C. Granular and monolithic activated carbons from KOH-activation of olive stones. *Microporous Mesoporous Mater.* **2006**, *92*, 64−70.

(37) Jagiello, J. Stable numerical solution of the adsorption integral equation using splines. *Langmuir* **1994**, *10*, 2778−2785.

(38) Jagiello, J.; Bandosz, T. J.; Schwarz, J. A. Carbon surface characterization in terms of its acidity constant distribution. *Carbon* **1994**, *32*, 1026−1028.

(39) Jagiello, J.; Olivier, J. P. A simple two-dimensional NLDFT model of gas adsorption in finite carbon pores. Application to pore structure analysis. *J. Phys. Chem. C* **2009**, *113*, 19382−19385.

(40) Endo, M.; Maeda, T.; Takeda, T.; Kim, Y. J.; Koshiba, K.; Hara, H.; Dresselhaus, M. S. Capacitance and pore-size distribution in aqueous and nonaqueous electrolytes using various activated carbon electrodes. *J. Electrochem. Soc.* **2001**, *148*, A910−A914.

(41) Tammeveski, K.; Kontturi, K.; Nichols, R. J.; Potter, R. J.; Schiffrin, D. Surface redox catalysis for O_2 reduction on quinone-modified glassy carbon electrodes. *J. Electroanal. Chem.* **2001**, *515*, 101−112.

(42) Kruusenberg, I.; Matisen, L.; Jiang, H.; Huuppola, M.; Kontturi, K.; Tammeveski, K. Eletrochemical reduction of oxygen on double-walled carbon nanotube modified glassy carbon electrodes in acid and alkaline solutions. *Electrochem. Commun.* **2010**, *12*, 920−923.

(43) Zhao, X.; Zhang, Q.; Chen, C.-M.; Zhang, B.; Reiche, S.; Wang, A.; Zhang, T.; Schlogl, R.; Su, D. S. Aromatic sulfide, sulfoxide, and sulfone mediated mesoporous carbon monolith for use in super-capacitor. *Nano Energy* **2012**, *1*, 624−630.

(44) Berenguer, R.; Marco-Lozar, J. P.; Quijada, C.; Cazorla-Amoros, D.; Morallon, E. Effect of electrochemical treatments on the surface chemistry of activated carbon. *Carbon* **2009**, *47*, 1018−1027.

(45) Zhu, M.; Weber, C. J.; Yang, Y.; Konuma, M.; Starke, U.; Kern, K.; Bittner, A. M. Chemical and electrochemical ageing of carbon materials used in supercapacitor electrodes. *Carbon* **2008**, *46*, 1829−1840.

(46) Arruda, T. M.; Heon, M.; Presser, V.; Hillesheim, P. C.; Dai, S.; Gogotsi, Y.; Kalinin, S. V.; Balke, N. In situ tracking of the nanoscale expansion of porous carbon electrodes. *Energy Environ. Sci.* **2013**, *6*, 225−231.