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Correlation of Double-Layer Capacitance with the Pore Structure of Sol-Gel Derived Carbon Xerogels

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Nine different sol-gel derived carbon xerogels were prepared with different pore structures by varying the carbonization temperature (in flowing N₂) and activation time (in 5% CO₂ in N₂). For each of these carbon xerogels, mesopore and micropore size distributions and cumulative surface areas were extracted from a density functional theory analysis. Increasing the carbonization temperature caused a decrease in the number of micropores in the 6 Å range but had little effect on the mesopore size distribution and thus mesopore cumulative surface area. Increasing the CO₂ activation time caused an increase in the number of both micro- and mesopores where pores in the 6 Å width range eventually became pores in the 12 Å width range. The electrochemical double-layer capacitance (DLC) of the carbon xerogels was found to correlate well with changes in the pore structure, and it was determined that pores less than about 8 Å in width did not contribute to the DLC.

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Research on carbon-based electrochemical double-layer capacitors (EDLCs) has focused on developing new and improved carbon materials with high surface areas and suitable pore structures.¹⁻⁵ Both of these characteristics have been shown to control the energy and power densities of EDLCs.⁶ However, the role of microporosity, *i.e.*, pores having diameters less than 20 Å, in the performance of an EDLC is still not very clear. In other words, what pore size is too small for the electrolyte to access, hence preventing it from forming a double layer?

Most of the studies in the literature have attempted to correlate the double-layer capacitance (DLC) simply in terms of the total Brunauer-Emmett-Teller (BET) surface area of a carbon material, with limited success.⁷⁻⁹ Some other studies have had better success by correlating the DLC in terms of the micropore and mesopore surface areas.¹⁰⁻¹² However, none of these studies has been able to identify the pore sizes that may not contribute to the DLC. Yet this information is crucial to understanding the performance of an EDLC from a molecular level and to designing better carbon-based EDLCs by tailoring the pore structure for optimum performance.

The main reason for this lack of quantification lies in the techniques that have been employed to determine the surface areas of carbon materials.⁷⁻⁹ The commonly used techniques are global in that they only provide information on the total surface area, which is sometimes divided into the total micropore and mesopore surface areas. These techniques are incapable of providing information on the pore size distributions (PSDs) and corresponding surface area distributions. However, a very promising technique, which has not been explored much in the characterization of EDLCs, is the use of density function theory (DFT) to determine the mesopore size distribution and the corresponding cumulative surface area of carbon materials.¹⁰

Therefore, the objectives here are to demonstrate the use of DFT in determining the PSD and cumulative surface area of carbon materials that are being evaluated as EDLCs, and to show how this information can be used to identify the pore sizes that are contributing to the DLC. The carbon material chosen for this purpose is a carbonized resorcinol-formaldehyde (R-F) resin derived from a sol-gel process. This material has been receiving considerable attention in the recent literature.^{1,6,11-17} In this study, the DLCs of a series of carbon xerogels fabricated from R-F resins, carbonized at different temperatures and CO₂-activated to different extents, are correlated with their corresponding PSDs and cumulative surface areas determined

from DFT. The contribution to the DLC of various pore sizes is revealed, including the pore size range that does not contribute to the DLC of these carbon materials. Qualitative explanations for the inactivity of these small pores are offered and contrasted with the correlation proposed by Shi.¹⁰

Experimental

The sol-gel synthesis procedure used to obtain the carbon xerogels is reported in detail elsewhere.^{13,17} It suffices to state that solutions containing 5 w/v % solids were prepared, in which the R-F mole ratio (R/F) was fixed at 1:2. Sodium carbonate was used as a catalyst and the resorcinol/sodium carbonate mole ratio (R/C) was fixed at 50. For the carbonization study, the carbon xerogels were formed by pyrolysis of the dried gels at the desired temperature for 3 h in a flowing N₂ atmosphere. For the CO₂ activation study, the carbon xerogels were formed by pyrolysis of the dried gels at 1050°C for 3 h in flowing N₂ and then at the same temperature for the desired time in flowing N₂ containing 5 vol % CO₂.

A typical three-electrode test cell was used to carry out the electrochemical measurements. The working electrode contained about 5 mg of the carbon xerogel together with 5 wt % Teflon binder. It was hand-pressed into a disk 8.5 mm in diam and 150 μm thick. The disk was sandwiched between two tantalum rods, with one rod used as a current collector and the other rod used as a support, which was physically separated from the disk using a porous glass fiber filter. This assembly was placed in a cell containing 30 wt % H₂SO₄ as the electrolyte. A saturated calomel electrode and platinum gauze were used as the reference and counter electrodes, respectively. Cyclic voltammetry (CV) was performed between 0 and 1 V (*vs.* saturated calomel electrode) with a sweep rate of 5 mV/s using a potentiostat (EG&G 273A). The experiments were conducted at room temperature.

The DLC of a single carbon xerogel electrode was calculated from the CV using

$$C = \frac{i}{sm} \quad [1]$$

where C is the specific DLC, i is the anodic current recorded at 0.5 V, s is the potential sweep rate, and m is the mass of the active electrode material. The PSD, $f(w)$, was calculated from the adsorption integral equation

$$n(P) = \int_{w_{\min}}^{w_{\max}} f(w)p(P, w)dw \quad [2]$$

where $n(P)$ is the experimentally measured adsorption isotherm in terms of the number of moles of N₂ adsorbed at 77 K as a function

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of pressure P , w_{\min} and w_{\max} are the widths of the smallest and largest pores in the material, and $\rho(P, w)$ is the local adsorption isotherm in terms of the molar density of N_2 at 77 K and pressure P in a pore of width w . By definition, $f(w) = dv/dw$, where v is the pore volume. The experimental adsorption isotherm for each of the carbon xerogels was measured using a Coulter Omnisorp 610,¹⁷ and the local adsorption isotherms were predicted from nonlocal DFT as described in detail elsewhere.¹⁸⁻²¹ With the above experimental and theoretical adsorption isotherms, the PSD for each carbon xerogel was obtained by solving Eq. 2 using a regularization technique.^{22,23} The cumulative surface area (S_c) was then estimated from Eq. 3 by assuming a slit pore model for the carbon xerogels

$$S_c = \int_{w_{\min}}^w \frac{2f(w)}{w} dw \quad [3]$$

Results and Discussion

The effects of the carbonization temperature and the CO_2 activation time on the PSDs of the carbon xerogels is shown in Fig. 1A and 1B, respectively. According to IUPAC nomenclature,²⁴ micropores are less than 20 Å in diam, mesopores are between 20 and 500 Å in diam, and macropores are greater than 500 Å in diam. Figure 1A shows that in the micropore region, all of the samples exhibited a peak with a mean pore width of about 6 Å. The height of this peak decreased with an increase in the carbonization temperature, clearly indicating the loss of microporosity. Three of the samples also exhibited a peak between pore widths of 10 and 20 Å. This peak was relatively small at 600°C, disappeared at 750 and 900°C, and reappeared at 1050 and 1200°C with a slight shift toward smaller pore

sizes, indicating the destruction and creation of microporosity with increasing carbonization temperature. In the mesopore region, a broad but small peak appeared with a mean pore width of around 200 Å; however, this peak did not change much with the carbonization temperature.

In contrast to the effect of the carbonization temperature, Fig. 1B shows that the effect of CO_2 activation time on the PSDs of the carbon xerogels was much more pronounced. All of the samples exhibited a peak with a mean pore width of about 6 Å, which increased with time up to 2.5 h, and then decreased slightly after 3 h. All of the samples also exhibited a peak with a mean pore width of about 13 Å, which increased consistently with time. Some peaks with pore widths between 20 and 100 Å also appeared and grew with time; however, the peak with a mean pore width of ~200 Å changed little with time. These trends show very clearly the creation and destruction of small micropores in the 6 Å range with increased CO_2 activation time, some of which became large micropores in the 12 Å range and small mesopores in the 30 Å range with the further burn-off of carbon. Moreover, these results, along with evidence in the literature,¹¹ which showed that these carbon xerogels are composed of carbon nanoparticles on the order of 10 to 20 nm in diam, also suggest that the larger mesopores (200 Å range) were derived from the voids between the carbon particles, the sizes of which were not affected by the carbonization temperature or CO_2 activation time, and that the smaller mesopores (30 Å range) and all of the micropores were derived from pores within the nanoparticles, the distributions of which were greatly affected by both the carbonization temperature and CO_2 activation time.

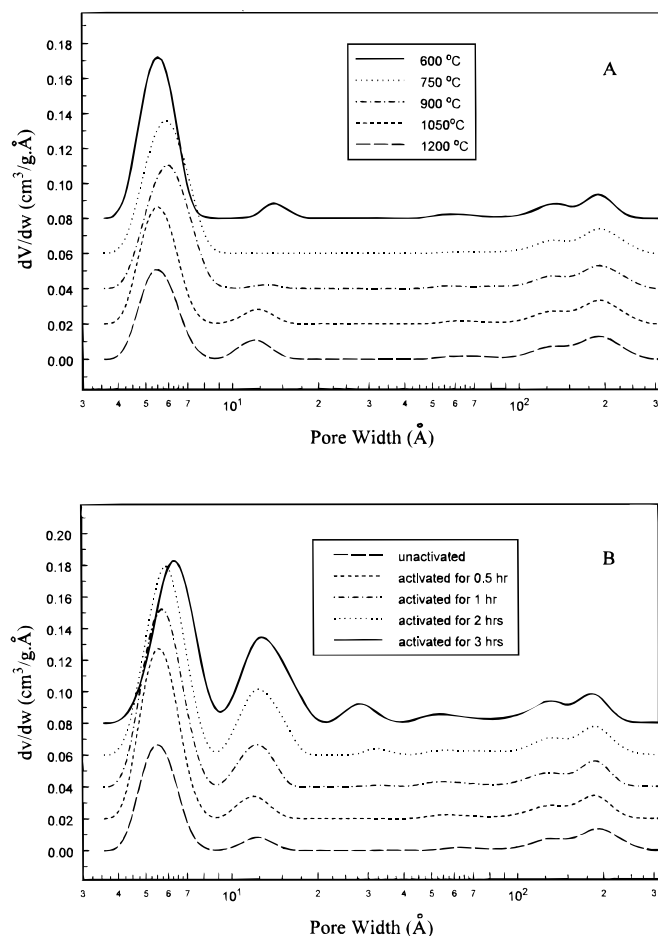


Figure 1. Effect of the carbonization temperature (A, top) and CO_2 activation time (B, bottom) on the PSDs of the carbon xerogels. The curves are offset from each other by $dv/dw = 0.02$.

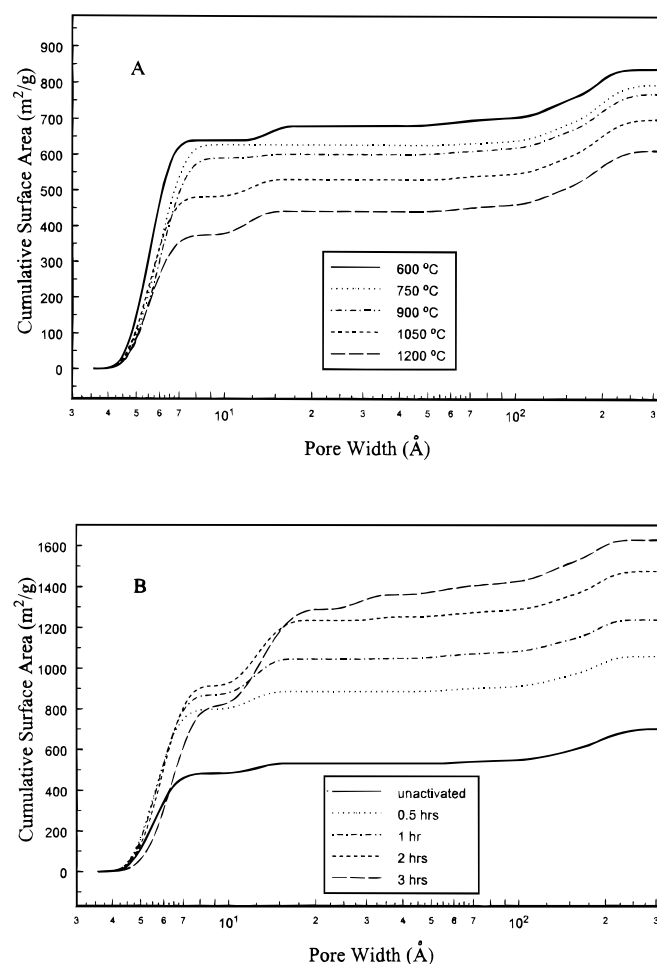


Figure 2. Effect of the carbonization temperature (A, top) and CO_2 activation time (B, bottom) on the cumulative surface areas of the carbon xerogels.

The PSDs shown in Fig. 1A and B were used to determine the total (S_{tot}), micropore (S_{mi}), and mesopore (S_{me}) surface areas, as described above and based on the cumulative surface areas shown in Fig. 2A and B, respectively, for the carbonization temperature and CO_2 activation time studies. For the carbonization temperature study, the DLC and S_{tot} , S_{mi} , and S_{me} are shown in Fig. 3A and B, all as a function of the carbonization temperature. S_{tot} was 840 m^2/g for the carbon xerogel carbonized at 600°C, then it decreased almost linearly with an increase in temperature and finally dropped to 610 m^2/g at 1200°C. However, the DLC of the carbon xerogel carbonized at 600°C was surprisingly almost zero. AC impedance tests indicated that this material had a very high ohmic resistance of $\sim 500 \text{ k}\Omega$, which indicates that it was not converted into an electrically conductive carbon material at such a low temperature. Excluding the sample at 600°C, the DLC exhibited a similar trend to S_{tot} . A maximum capacitance of 185 F/g was obtained at 750°C, then the capacitance decreased with an increase in temperature down to 98 F/g at 1200°C.

The origin of this decrease in the DLC with the carbonization temperature is revealed clearly in Fig. 3B and is related to a decrease in S_{mi} . S_{mi} decreased almost linearly with an increase in the carbonization temperature from 630 m^2/g at 750°C to 440 m^2/g at 1200°C; however, S_{me} remained nearly unchanged at about 170 m^2/g and was independent of the carbonization temperature. These results suggest that pores less than 20 Å in width contributed to the DLC, which is consistent with that reported elsewhere.^{10,25} However, the question that remains is what is the smallest pore size that can still contribute to the DLC? This question is addressed later.

For the CO_2 activation study, the DLC and S_{tot} , S_{mi} , and S_{me} are shown in Fig. 4A and B, all as a function of the CO_2 activation time. S_{tot} was around 700 m^2/g for the unactivated carbon xerogel, and it

increased with an increase in the CO_2 activation time up to about 1630 m^2/g after 3 h of activation; however, the rate of increase in S_{tot} decreased with time, as did S_{mi} . In contrast, the rate of increase in S_{me} increased with time. This result indicated that the activation process, which burns off carbon to create more pores and surface area, took place mainly within the carbon particles. In other words, the initial high rate of formation of micropores slowed at the expense of converting micropores into mesopores with increasing CO_2 activation time. These results certainly impacted the DLC of these materials, as shown in Fig. 4A.

The DLC was 112 F/g for the unactivated carbon xerogel, and it increased with an increase in the CO_2 activation time up to 170 F/g after 3 h of activation. The rate of increase in the DLC after 0.5 h also began to increase with time, *i.e.*, the slope was convex to the abscissa. The same trend was exhibited by S_{me} shown in Fig. 4B, whereas S_{mi} exhibited the opposite trend. This result indicates that the increase in S_{me} with time may have been controlling the increase in the DLC, a surprising result because the micropore surface areas were all significantly larger than the mesopore surface areas. For example, S_{mi} and S_{me} of the unactivated carbon xerogel were 530 and 170 m^2/g , respectively, and they became 1290 and 340 m^2/g after 3 h of CO_2 activation, respectively. These trends suggested that some of the micropores were not contributing to the DLC. An analysis to determine the sizes of these inactive pores follows.

The unactivated but carbonized sample at 750°C gave rise to a DLC of 23.1 $\mu\text{F}/\text{cm}^2$, based on the total surface area obtained from DFT. This value was slightly higher, however, than the ideal value that has been used to describe the DLC of clean graphite, which is about 20 $\mu\text{F}/\text{cm}^2$.²⁶ This slightly higher DLC was probably due to pseudocapacitance caused by the presence of surface functional groups. Kinoshita²⁶ has shown that a minimum pyrolysis tempera-

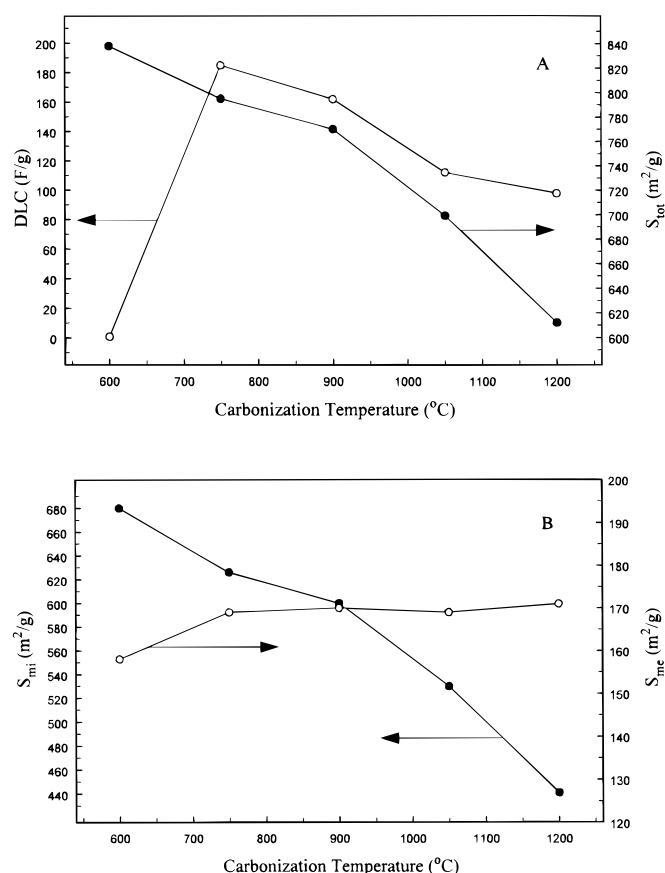


Figure 3. Effect of the carbonization temperature on the DLC and total surface area, S_{tot} , (A, top), and (B, bottom) micropore, S_{mi} , and mesopore, S_{me} , surface areas of the carbon xerogels.

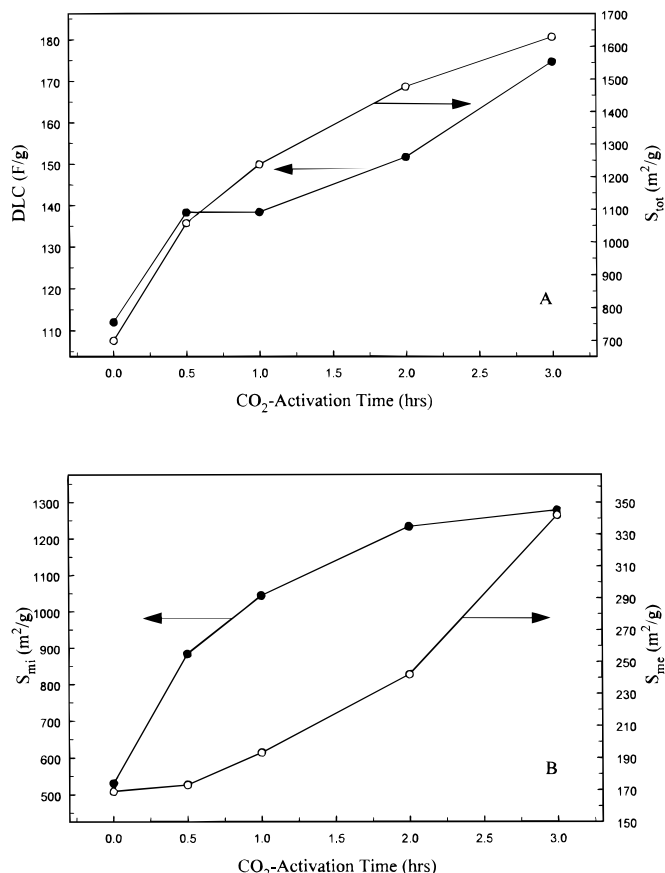


Figure 4. Effect of the CO_2 activation time on the DLC and total surface area, (A, top) S_{tot} , and (B, bottom) micropore, S_{mi} , and mesopore, S_{me} , surface areas of the carbon xerogels.

Table I. Minimum pore size that contributed to the DLC of the carbon xerogels.

Conditions	DLC (F/g)	Total surface area (m ² /g)	Active surface area (m ² /g)	Inactive surface area (m ² /g)	Minimum pore size Å
Carbonization temperature (°C)					
750	185.0	795.1	925.0	-129.9	— ^a
900	162.0	769.9	810.0	-40.1	— ^a
1050	112.0	698.8	560.0	138.8	5.1
1200	97.9	612.5	489.5	123.0	5.2
CO ₂ activation time (h)					
0	112.0	698.8	560.0	138.8	5.1
0.5	138.3	1056.9	691.5	365.4	5.5
1	138.4	1237.2	692.0	545.2	6.0
2	151.7	1476.0	758.5	717.5	6.6
3	174.7	1629.4	873.5	755.9	7.8

^a The minimum pore size was not discernible in this sample because of a pseudocapacitance contribution to the measured electrochemical capacitance.

ture of 1000°C is needed to destroy the residual surface functional groups (*e.g.*, OH and COOH) that are known to exist on these kinds of synthetic carbon materials. Therefore, the DLC of 20 $\mu\text{F}/\text{cm}^2$ was used as a benchmark to determine if a consistent trend could be found between the measured DLC of all of the samples and a characteristic pore size which indicated the minimum pore size that was contributing to these measured DLCs. For example, using this value of 20 $\mu\text{F}/\text{cm}^2$ for the sample carbonized at 1050°C resulted in an active surface area of 560 m²/g and an inactive surface area of 138.8 m² for a DLC of 112 F/g. According to the cumulative surface area for this sample shown in Fig. 2A, this cumulative inactive surface area corresponded to all of the pores less than 5.1 Å in width. Table I presents similar analyses for the eight electrochemically active samples from both the carbonization temperature and CO₂ activation time studies. Some very interesting trends were observed.

The two samples carbonized at 750 and 900°C resulted in higher active surface areas than their corresponding total surface areas, which correspondingly gave negative values for their inactive surface areas. As a result, no minimum pore size was reported for these two materials. Nevertheless, these results are consistent with the earlier statement about the effect of the presence of residual surface functional groups within the pores of carbon materials carbonized below 1000°C. These residual surface functional groups most likely produced a pseudocapacitance in these samples²⁶ that necessarily caused an overestimation in the active surface area, relative to the assumed ideal DLC of 20 $\mu\text{F}/\text{cm}^2$. For the sample carbonized at 750°C, this pseudocapacitance amounted to about 3 $\mu\text{F}/\text{cm}^2$ or about 15% of the measured capacitance. For the samples carbonized at temperatures higher than 1000°C, the pseudocapacitance contribution was considered to be negligible; and thus, the measured DLCs of these samples were considered to represent the actual DLCs of these materials, with no contribution from pseudocapacitance. For these six samples, this analysis consistently indicated that pore widths smaller than about 5 Å for the carbonized samples and between 5 and 8 Å for the CO₂ activated samples were not contributing to the DLC of these carbon xerogels. Within the error of this analysis, these results were considered to be consistent and show that the smaller micropores in these carbon materials, *e.g.*, those pores less than about 8 Å in diam, were not contributing significantly to the DLC.

It is interesting to compare the above analysis on synthetic carbon xerogels with a different analysis carried out by Shi¹⁰ on both activated carbon microbeads and activated carbon fibers; however, this comparison is restricted to the activated carbon fibers, since they

are typically made from carbonized resins, similarly to the carbon xerogels. Shi¹⁰ assumed that the DLC of a micropore surface is different than that of a mesopore surface, and from a simple linear correlation obtained capacitances of 14.5 and 7.5 $\mu\text{F}/\text{cm}^2$ for the micropore and mesopore surfaces of activated carbon fibers, respectively. When applied to the carbon xerogels, Shi's¹⁰ correlation did not produce a linear relationship. However, the DLC of the six carbon xerogels carbonized above 1000°C correlated fairly linearly with the total surface area, as shown in Fig. 5. The slope of this linear correlation corresponded to a DLC of 6.54 $\mu\text{F}/\text{cm}^2$, which was quite low compared to the ideal DLC of 20 $\mu\text{F}/\text{cm}^2$, because this value also included the inactive surface area. A plot of the DLC vs. only the active surface area (S_{act}) produced a straight line with a slope of 20 $\mu\text{F}/\text{cm}^2$, as also shown in Fig. 5. An intriguing feature of these results is the fact that the DLC of the activated carbon fibers studied by Shi¹⁰ also correlated fairly linearly with their total surface area, with a corresponding slope of 7.2 $\mu\text{F}/\text{cm}^2$.

The point to be made here is that these low and similar values for the DLC of the activated carbon fibers and carbon xerogels, compared to the ideal value of 20 $\mu\text{F}/\text{cm}^2$, can be accounted for in two ways. One way is to assume that the DLC of micropore and mesopore surfaces are different as done by Shi.¹⁰ The other way is to assume that they are the same (at 20 $\mu\text{F}/\text{cm}^2$) and then assume that some of the smaller micropores are inactive as done in this study. It is quite clear that the behavior observed by Shi¹⁰ by the activated carbon fibers can also be explained equally well by assuming that a minimum pore size exists, that below which does not contribute to the DLC. It is not clear at this time which assumption is correct, especially because both analyses produce physically realistic results. However, it suffices to state that the correlation of Shi¹⁰ does not seem to apply to all microporous carbon materials. In contrast, the current analysis, based on a minimum active pore size, does apply to all microporous carbon materials.

Conclusions

This work demonstrated very convincingly the ability of DFT to extract pore structure information from the physical adsorption isotherm. This information was used to follow the evolution of the micropore and mesopore structures in carbon xerogels during controlled, structure-altering experimentation with the carbonization temperature and CO₂ activation time. Careful analysis of the results from DFT coupled with the DLC of these materials revealed that pores less than about 8 Å in width were not contributing to the DLC in these carbon xerogels. Moreover, the carbonization temperature study showed very clearly that the main contribution to the DLC was from the larger micropores between 8 and 20 Å in width, and for these carbon xerogels a temperature of about 700°C appeared to be optimum. This work also showed that the CO₂ activation time can be

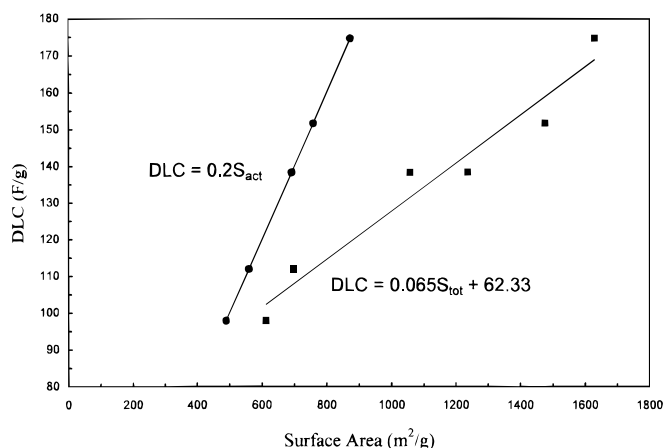


Figure 5. Linear correlations of the DLC with the total surface area, S_{tot} , and active surface area, S_{act} , of the carbon xerogels carbonized above 1000°C.

used to further optimize the performance of these carbon xerogels with respect to maximizing the number of micropores in the most active size range, *i.e.*, in the 8 to 20 Å range. Overall, the results from this work should provide valuable insight into the design of better microporous carbon materials for use in EDLCs and other applications.

Acknowledgments

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