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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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The sol-gel synthesis procedure used to obtain the carbon xerogels is reported in detail elsewhere. 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

\[ C = \frac{i}{sm} \]  

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

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

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 of...
of pressure \( P \), \( w_{\text{min}} \) and \( w_{\text{max}} \) are the widths of the smallest and largest pores in the material, and \( \mu(P, w) \) is the local adsorption isotherm in terms of the molar density of \( \text{N}_2 \) 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 \( (S_f) \) was then estimated from Eq. 3 by assuming a slit pore model for the carbon xerogels

\[
S_f = \int_{w_{\text{min}}}^{w_{\text{max}}} \frac{2f(w)}{w} dw
\]  

**Results and Discussion**

The effects of the carbonization temperature and the \( \text{CO}_2 \) 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 diameter, mesopores are between 20 and 500 Å in diameter, and macropores are greater than 500 Å in diameter. 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 diameter, 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) activation time.

![Figure 1](https://example.com/figure1.png)  
**Figure 1.** Effect of the carbonization temperature (A, top) and \( \text{CO}_2 \) 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](https://example.com/figure2.png)  
**Figure 2.** Effect of the carbonization temperature (A, top) and \( \text{CO}_2 \) 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 ($S_{\text{tot}}$), micropore ($S_{\text{mi}}$), and mesopore ($S_{\text{me}}$) 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 $S_{\text{tot}}$, $S_{\text{mi}}$, and $S_{\text{me}}$ are shown in Fig. 3A and B, all as a function of the carbonization temperature. $S_{\text{tot}}$ was $840 \text{ m}^2/\text{g}$ for the carbon xerogel carbonized at 600°C, then it decreased almost linearly with an increase in temperature and finally dropped to $610 \text{ m}^2/\text{g}$ 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 $S_{\text{tot}}$. 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 $S_{\text{mi}}$. $S_{\text{mi}}$ 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, $S_{\text{me}}$ 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. 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 $S_{\text{tot}}$, $S_{\text{mi}}$ and $S_{\text{me}}$ are shown in Fig. 4A and B, all as a function of the CO$_2$ activation time. $S_{\text{tot}}$ was around 700 m$^2$/g for the unactivated carbon xerogel, and it increased with the 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 $S_{\text{tot}}$ decreased with time, as did $S_{\text{mi}}$. In contrast, the rate of increase in $S_{\text{me}}$ 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 $S_{\text{me}}$ shown in Fig. 4B, whereas $S_{\text{mi}}$ exhibited the opposite trend. This result indicates that the increase in $S_{\text{me}}$ 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, $S_{\text{mi}}$ and $S_{\text{me}}$ 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 µF/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 µF/cm$^2$. This slightly higher DLC was probably due to pseudocapacitance caused by the presence of surface functional groups. Kinoshita has shown that a minimum pyrolysis tempera-

![Figure 3](image-url)  
**Figure 3.** Effect of the carbonization temperature on the DLC and total surface area, $S_{\text{tot}}$ (A, top), and (B, bottom) micropore, $S_{\text{mi}}$, and mesopore, $S_{\text{me}}$, surface areas of the carbon xerogels.

![Figure 4](image-url)  
**Figure 4.** Effect of the CO$_2$ activation time on the DLC and total surface area, (A, top) $S_{\text{tot}}$ and (B, bottom) micropore, $S_{\text{mi}}$, and mesopore, $S_{\text{me}}$, surface areas of the carbon xerogels.
duced a pseudocapacitance in these samples that necessaril
ly caused this comparison to be restricted to the activated carbon fibers, since they are typically made from carbonized resins, similarly to the carbon xerogels. Shi\textsuperscript{10} 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 \(\mu F/cm^2\) for the micropore and mesopore surfaces of activated carbon fibers, respectively. When applied to the carbon xerogels, Shi’s\textsuperscript{10} correlation did not produce a linear relationship. However, the DLC of the six carbon xerogels carbonized above 1000\(^\circ\)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 \(\mu F/cm^2\), which was quite low compared to the ideal DLC of 20 \(\mu F/cm^2\), because this value also included the inactive surface area. A plot of the DLC vs. only the active surface area (\(S_{\text{act}}\)) produced a straight line with a slope of 20 \(\mu F/cm^2\), as also shown in Fig. 5. An intriguing feature of these results is that the DLC of the activated carbon fibers studied by Shi\textsuperscript{10} also correlated fairly linearly with their total surface area, with a corresponding slope of 7.2 \(\mu F/cm^2\).

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 \(\mu F/cm^2\), 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.\textsuperscript{10} The other way is to assume that they are the same (at 20 \(\mu F/cm^2\)) 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 Shi\textsuperscript{10} 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 Shi\textsuperscript{10} 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 \(CO_2\) activation time. Careful analysis of the results from DFT coupled with the DLC of these materials revealed that pores less than about 8 \(\AA\) 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 \(\AA\) in width, and for these carbon xerogels a temperature of about 700\(^\circ\)C appeared to be optimum. This work also showed that the \(CO_2\) activation time can be

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

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Total surface area (m²/g)</th>
<th>Active surface area (m²/g)</th>
<th>Inactive surface area (m²/g)</th>
<th>Minimum pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonization temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>185.0</td>
<td>795.1</td>
<td>925.0</td>
<td>~129.9</td>
</tr>
<tr>
<td>900</td>
<td>162.0</td>
<td>769.9</td>
<td>810.0</td>
<td>~40.1</td>
</tr>
<tr>
<td>1050</td>
<td>112.0</td>
<td>698.8</td>
<td>560.0</td>
<td>138.8</td>
</tr>
<tr>
<td>1200</td>
<td>97.9</td>
<td>612.5</td>
<td>489.5</td>
<td>123.0</td>
</tr>
<tr>
<td>(CO_2) activation time (h)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>112.0</td>
<td>698.8</td>
<td>560.0</td>
<td>138.8</td>
</tr>
<tr>
<td>0.5</td>
<td>138.3</td>
<td>1056.9</td>
<td>691.5</td>
<td>365.4</td>
</tr>
<tr>
<td>1</td>
<td>138.4</td>
<td>1237.2</td>
<td>692.0</td>
<td>545.2</td>
</tr>
<tr>
<td>2</td>
<td>151.7</td>
<td>1476.0</td>
<td>758.5</td>
<td>717.5</td>
</tr>
<tr>
<td>3</td>
<td>174.7</td>
<td>1629.4</td>
<td>873.5</td>
<td>755.9</td>
</tr>
</tbody>
</table>

\(\text{#}^a\) The minimum pore size was not discernible in this sample because of a pseudocapacitance contribution to the measured electrochemical capacitance.

\[\text{DLC} = 0.2S_{\text{act}}\]

\[\text{DLC} = 0.065S_{\text{act}} + 62.33\]

**Figure 5.** Linear correlations of the DLC with the total surface area, \(S_{\text{act}}\), and active surface area, \(S_{\text{act}}\), of the carbon xerogels carbonized above 1000\(^\circ\)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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