Supporting Information

Electrochemical Capacitance and Ionic Transport in the Mesoporous Shell of a Hierarchical Porous Core-Shell Carbon Structure

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Symbols used in the calculations:
C: Diameter of hollow core;
S: Shell thickness;
VC: Volume of hollow core region;
VS: Volume of shell region;
VI: Volume of interstitial region.
VS+C: Volume of shell and hollow core regions,
VS+C = VS + VC.
Total volume of an fcc pattern: Vt = VI + VS+C.

According to an fcc pattern, the volumetric fractions of different regions can be estimated as following:

VS+C/Vt = 0.74, VS/VI = 0.26
VC/VI = [C/(C+S)]³ × 0.74
VS/VI = 0.74 – VC/VI
Using the above equations, the fractions can be obtained as shown in the table.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$0.5C$ / nm</th>
<th>$(0.5C+S)$ / nm</th>
<th>$V_C/V_I$</th>
<th>$V_S/V_I$</th>
<th>$V_I/V_I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-CS0</td>
<td>165</td>
<td>165</td>
<td>0.74</td>
<td>0</td>
<td>0.26</td>
</tr>
<tr>
<td>C-CS50</td>
<td>165</td>
<td>190</td>
<td>0.48</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>C-CS80</td>
<td>165</td>
<td>215</td>
<td>0.33</td>
<td>0.41</td>
<td>0.26</td>
</tr>
<tr>
<td>C-CS150</td>
<td>165</td>
<td>265</td>
<td>0.18</td>
<td>0.56</td>
<td>0.26</td>
</tr>
</tbody>
</table>

**Sample calculation: Take 350C-50S as an example:**

The density of carbon was considered as 1.79 g/cm$^3$, then, 1 g of carbon has a volume of 0.56 cm$^3$. Pore volume from N$_2$ sorption was integrated from the PSD based on BJH method, 1.10 cm$^3$/g.

**Total volume of 1.0 g porous carbon including solid carbon, mesopores and hollow macro-cores:**

\[
\text{(Pore volume + Volume of solid carbon) / (1 - Fraction of hollow core region)}
\]

\[
= (1.10 \text{ cm}^3 + 0.56 \text{ cm}^3) / (1 - 0.48) = 3.19 \text{ cm}^3
\]

**Volume of hollow cores:**

\[
\text{Total volume of 1.0 g porous carbon} \times \text{Fraction of hollow core region}
\]

\[
= 3.19 \times 0.48 = 1.53 \text{ cm}^3
\]

**Total Void of Pore volume from N$_2$ sorption and calculated macro-core volume:**

\[
\text{Pore volume from N$_2$ sorption + Volume of hollow cores}
\]

\[
= 1.10 \text{ cm}^3/\text{g} + 1.53 \text{ cm}^3 = 2.63 \text{ cm}^3
\]

Reference: