

## Supporting Information

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

Fujun Li, Madeleine Morris, Kwong-Yu Chan\*

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#### *Symbols used in the calculations:*

$C$ : Diameter of hollow core;

$S$ : Shell thickness;

$V_C$ : Volume of hollow core region;

$V_S$ : Volume of shell region;

$V_I$ : Volume of interstitial region.

$V_{S+C}$ : Volume of shell and hollow core regions,  $V_{S+C} = V_S + V_C$ .

Total volume of an fcc pattern:  $V_t = V_I + V_{S+C}$ .

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

$$V_{S+C}/V_t = 0.74, V_I/V_t = 0.26$$

$$V_C/V_t = [C/(C+S)]^3 \times 0.74$$

$$V_S/V_t = 0.74 - V_C/V_t$$

Using the above equations, the fractions can be obtained as shown in the table.

Samples	$0.5C / \text{nm}$	$(0.5C+S) / \text{nm}$	$V_C/V_t$	$V_S/V_t$	$V_I/V_t$
C-CS0	165	165	0.74	0	0.26
C-CS50	165	190	0.48	0.26	0.26
C-CS80	165	215	0.33	0.41	0.26
C-CS150	165	265	0.18	0.56	0.26

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

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

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

$$\begin{aligned} & (\text{Pore volume} + \text{Volume of solid carbon}) / (1 - \text{Fraction of hollow core region}) \\ & = (1.10 \text{ cm}^3 + 0.56 \text{ cm}^3) / (1 - 0.48) = 3.19 \text{ cm}^3 \end{aligned}$$

*Volume of hollow cores:*

$$\begin{aligned} & \text{Total volume of 1.0 g porous carbon} \times \text{Fraction of hollow core region} \\ & = 3.19 \times 0.48 = 1.53 \text{ cm}^3 \end{aligned}$$

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

$$\begin{aligned} & \text{Pore volume from } \text{N}_2 \text{ sorption} + \text{Volume of hollow cores} \\ & = 1.10 \text{ cm}^3/\text{g} + 1.53 \text{ cm}^3 = 2.63 \text{ cm}^3 \end{aligned}$$

Reference:

1. M. A. Capano, N. T. McDevitt, R. K. Singh and F. Qian, *J. Vac. Sci. Technol. A*, 1996, **14**, 431-435.