Electrochemical Conversion in Carbon Structures with a Hollow Core and a Mesoporous Shell

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Electrochemical capacitance and methanol oxidation are investigated with a set of well-defined carbon structures having a hollow core and mesoporous shell (HCMS) as shown in Fig. 1. The 3-D hierarchical HCMS carbon structure has an assembly of spherical carbon particles each with a hollow core surrounded by a shell which contains mesopores of 3.9 nm [1]. The series of mesoporous shell structures has thickness stepwise increased from 0, 25, 50 to 100 nm while keeping an identical 330 nm hollow core. A systematic investigation of electrochemical capacitance and ionic transport is enabled. A thicker shell has a higher surface area with a proportional increase of electrochemical capacitance which however, can only be fully realized at low scan rates/currents. At high currents, ionic transport limits the electrochemical capacitance of a thick mesoporous shell. Electrochemical impedance spectroscopy (EIS) performed on the family of shell HCMS carbon structures reveals the need to match penetrating and frequency for optimum power with a characteristic time constant for a given structure.

In fuel cells, effective utilization and stability of precious metal is necessary for commercial considerations. The distribution of Pt and PtRu nanoparticles in a mesoporous carbon can impact on electrode performance. We synthesis HCMS with Pt particles uniformly dispersed into the mesoporous shell using a previously developed CPDP method [2]. Fig. 2 shows three such HCMS carbon structures loaded with nanoparticles of a narrow size distribution.

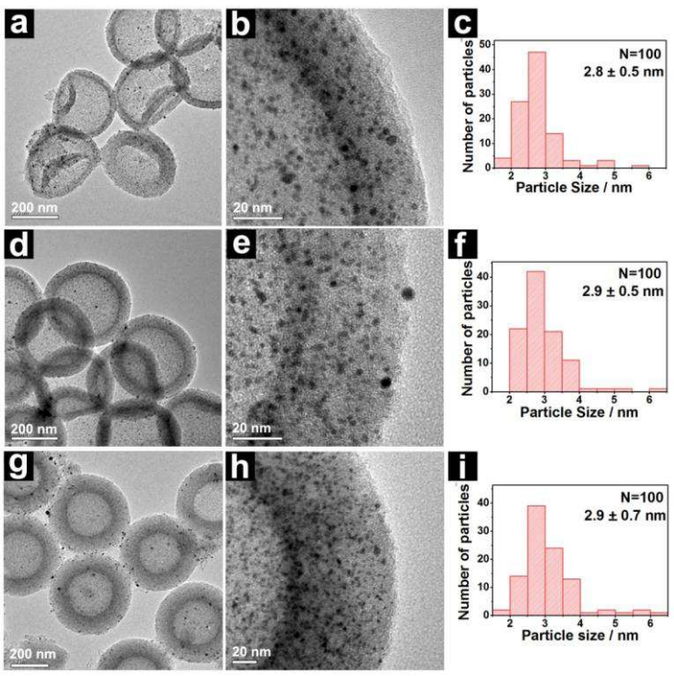

Fig. 2 TEM images of Pt nanoparticles loaded in mesoporous carbons of same hollow core diameter, C = 330 nm but different Shell thickness (a)-(c) Pt@CS-30, S=30 nm ; (d)-(f) Pt@CS-50, S=50 nm ; (g)-(i) Pt@CS-100, S=100 nm.

Distributing Pt nanoparticles into a thicker shell does not give better Pt utilization for methanol oxidation. However, the particles dispersed into a thicker shell are more stable and give better performance over time, as shown in voltage cycling and extended methanol oxidation.

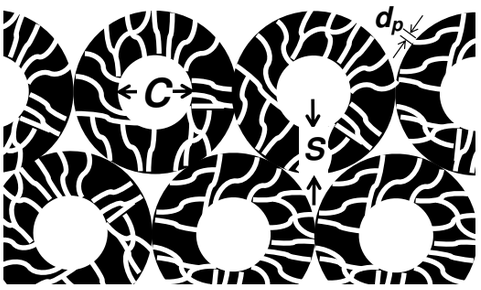

Fig. 1. A hollow core mesoporous shell (HCMS) carbon structure with three varying geometrical parameters: pore diameter (dp), shell thickness (S), and diameter of core (C).

References:

[1]. F. Li, M. Morris and K.Y. Chan*, “Electrochemical Capacitance and Ionic Transport in the Mesoporous Shell of a Hierarchical Porous Core-Shell Carbon Structure”, J. Mater. Chem. 21 (2011) 8880-8886.
[2] F. Li, K.Y. Chan*, and H. Yung, “Carbonization over PFA-Protected Dispersed Platinum: An Effective Route to Synthesize High Performance Mesoporous-Carbon Supported Platinum”, J. Mater. Chem. 21 (2011) 12139-12144.