

Durability of Pt and PtRu Electrocatalysts Supported in Carbons with a Hollow Core and a Mesoporous Shell of Varying Thickness

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A well-defined porous carbon structure with tunable parameters provides a platform for a systematic study of transport and confinement effects on electrochemical conversion. Synthesized via silica template techniques, the hierarchical structure has a hollow core within a mesoporous shell (HCMS) with uniform pore size, shell thickness, hollow core diameter, as shown in Fig. 1. Previously, electrochemical capacitance was studied with a series with meso-shell thickness stepwise increased from 0, 25, 50 to 100 nm while keeping an identical 330 nm hollow core and mesopore of 3.9 nm.[1, 2] Electrochemical impedance spectra (EIS) results reveal the need to match the AC frequency with the characteristic time constant of a structure for optimum active and reactive power.

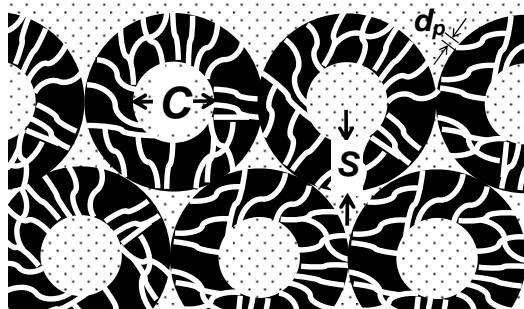


Fig. 1. A hollow core mesoporous shell (HCMS) carbon structure with three varying geometrical parameters: pore diameter (d_p), shell thickness (S), and diameter of core (C).

The present study focuses on durability of Pt and PtRu electrocatalysts supported on HCMS. The distribution of Pt and PtRu nanoparticles in a mesoporous carbon can vary according to the metallization procedure. Uniformly dispersed Pt and PtRu can be achieved using a CPDP (carbonization over protected and dispersed platinum) method [3]. 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. In Fig. 2, the methanol oxidation activity in terms of anodic peak for various Pt electrocatalysts is compared before and after accelerated stress tests (AST) of 2000 cycles between 0 and 1.1 V (NHE) at 20 mV/s in H_2SO_4 .

For PtRu nanoparticles, Pt:Ru can vary along with distribution of the metal nanoparticles in the porous carbon, depending on the method to prepare the PtRu/C electrocatalysts. The difference in Pt:Ru leads to difference in durability. There is a higher tendency of Ru particularly in Ru rich nanoparticles and the electrocatalysts that are surface located without protection by nano-confinement.

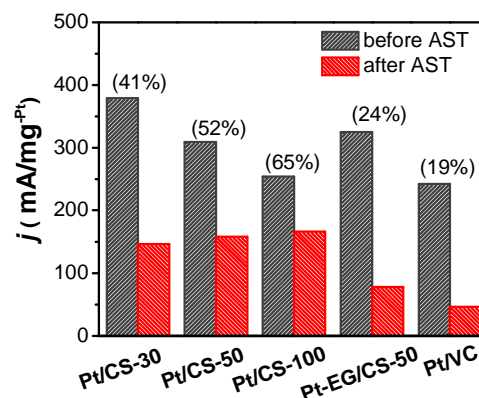


Fig. 2 Comparison of anodic peak current density of methanol oxidation anodic peak (MOR) before and after AST tests for each catalyst. The Pt/CS electrocatalysts are prepared via CPDP method with carbon shell thickness of 30, 50 and 100 nm. Compared also are Pt loaded via ethylene glycol method onto the same CS carbon of 50 nm thick shell and on Vulcan carbon. Methanol oxidation was carried in 1.0 M CH_3OH + 0.5 M H_2SO_4 solution at a scan rate of 20 mV s⁻¹. The current was normalized by the Pt mass loading on the glassy carbon electrode.

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References:

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