Supplementary Information

Target-customized carbon shell structure of carbon-encapsulated metal nanoparticles for fuel cell applications

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**Experimental**

We have obtained the electrochemically active surface areas (ECSAs) of the prepared catalysts from CO stripping curves using the well-known formula defined below.

\[
ECSA \left( m^2 g^{-1} \right) = \frac{\text{Total charge}(Q) \ for \ CO \ oxidation}{Q_{CO}(420 \ \mu C \ cm^{-2}) \times Pt \ loading(g_{Pt})}
\]

Furthermore, the exposed metal surface area (EMSA) of carbon shell-encapsulated metal nanoparticles was newly defined in this manuscript to quantitatively highlight the metal surface area exposed through the carbon shell regardless of metal composition. Therefore, the EMSA was simply calculated using “total metal loading (Pt + Fe)” instead of “Pt loading”.

\[
EMSA \left( m^2 g^{-1}_{metal} \right) = \frac{\text{Total charge}(Q) \ for \ CO \ oxidation}{Q_{CO}(420 \ \mu C \ cm^{-2}) \times Total \ metal \ loading(g_{metal})}
\]
Fig. S1 Structural change of PtFe@C/C with H\textsubscript{2} content in annealing gas at 900 °C. TEM images of (a) 0HCS\_900, (b) 5HCS\_900, (c) 10HCS\_900, and (d) 20HCS\_900. In each figure, the inset indicates a HR-TEM image of the corresponding nanoparticle to identify the thickness of the carbon shell.
Fig. S2 TEM images and particle size distribution for PtFe@C/C catalysts annealed at 700 °C. (a) 0HCS_700, (b) 5HCS_700, (c) 10HCS_700, and (d) 20HCS_700.
Fig. S3 TEM images and particle size distribution for PtFe@C/C catalysts annealed at 900 °C. (a) 0HCS_900, (b) 5HCS_900, (c) 10HCS_900, and (d) 20HCS_900.
Fig. S4 XRD patterns of PtFe@C/C catalysts annealed at 900 °C.
Fig. S5 CVs and CO stripping curves of PtFe@C/C catalysts annealed under different gas atmospheres at (a,b) 700 °C and (c,d) 900 °C.
Fig. S6 Changes in (a) mass activity (MA), (b) specific activity (SA), and (c) ECSA of Pt/C and PtFe@C/C catalysts during ASTs.
Fig. S7 TEM images and particle size distribution of Pt/C after ASTs. (a) 0k, (b) 10k, and (c) 20k cycles.
Fig. S8 TEM images and particle size distribution of 20HCS_700 after ASTs. (a) 0k, (b) 10k, and (c) 20k cycles.
Fig. S9 STEM image, EDX spectrum, and atomic ratio of Pt and Fe for 20HCS_700 after ASTs. (a) 0k, (b) 10k, and (c) 20k cycles.
Fig. S10 Radar chart showing changes in the current density at 0.9 V (i@0.9V), mass activity (MA), specific activity(SA), atomic ratio of metals (Fe/Pt), and ECSA of 20HCS_700 during the ASTs. The pentagonal line starts at the outermost 100 % (blue line, before AST) and decreases in steps of 20 %.
Fig. S11 TEM images and particle size distribution of 10HCS_700 after ASTs. (a) 0k, (b) 10k, and (c) 20k cycles.
**Fig. S12** STEM image, EDX spectrum, and atomic ratio of Pt and Fe for 10HCS_700 after ASTs. (a) 0k, (b) 10k, and (c) 20k cycles.
Fig. S13 STEM image, EDX spectrum, and atomic ratio of Pt and Fe for 5HCS_700 after ASTs.
(a) 0k, (b) 10k, and (c) 20k cycles.
**Fig. S14** TEM images and particle size distribution of 5HCS_700 after ASTs. (a) 0k, (b) 10k, and (c) 20k cycles.
Fig. S15 EIS spectra of the MEAs with (a) commercial Pt/C, (b) 20HCS_700, (c) 10HCS_700, and (d) 5HCS_700 before and after ASTs.
Fig. S16 CVs of the MEAs with (a) commercial Pt/C, (b) 20HCS_700, (c) 10HCS_700, and (d) 5HCS_700 before and after ASTs.
Table S1. Crystallite size (from XRD patterns) and particle size (from TEM analysis) of PtFe@C catalysts annealed under different gas atmospheres at 700 °C.

<table>
<thead>
<tr>
<th></th>
<th>20HCS_700</th>
<th>10HCS_700</th>
<th>5HCS_700</th>
<th>0HCS_700</th>
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<tbody>
<tr>
<td>Crystallite size</td>
<td>4.33 nm</td>
<td>2.31 nm</td>
<td>2.30 nm</td>
<td>2.03 nm</td>
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<tr>
<td>Particle size</td>
<td>4.53 nm</td>
<td>2.46 nm</td>
<td>2.24 nm</td>
<td>2.11 nm</td>
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Table S2. Crystallite size (from XRD patterns) and particle size (from TEM analysis) of PtFe@C catalysts annealed under different gas atmospheres at 900 °C.

<table>
<thead>
<tr>
<th></th>
<th>20HCS_900</th>
<th>10HCS_900</th>
<th>5HCS_900</th>
<th>0HCS_900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite size</td>
<td>5.15 nm</td>
<td>2.99 nm</td>
<td>2.83 nm</td>
<td>2.52 nm</td>
</tr>
<tr>
<td>Particle size</td>
<td>5.21 nm</td>
<td>2.97 nm</td>
<td>2.88 nm</td>
<td>2.57 nm</td>
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Table S3. ECSA values of PtFe@C catalysts annealed under different gas atmospheres at 700 °C and 900 °C.

<table>
<thead>
<tr>
<th>H₂ content in annealing gas</th>
<th>Annealing temperature</th>
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<tbody>
<tr>
<td></td>
<td>700 °C</td>
</tr>
<tr>
<td>0 %</td>
<td>14.6 m² gₚt⁻¹</td>
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<tr>
<td>5 %</td>
<td>62.3 m² gₚt⁻¹</td>
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<tr>
<td>10 %</td>
<td>97.3 m² gₚt⁻¹</td>
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<tr>
<td>20 %</td>
<td>87.7 m² gₚt⁻¹</td>
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