Supplementary Information

Highly Durable Fuel Cell Catalysts Using Crosslinkable Block Copolymer-Based Carbon Supports with Ultralow Pt Loadings

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† Equally contributed
Figure S1. Schemes for (a) photo-crosslinking of P(S-r-N$_3$) under ultraviolet light (254 nm) and (b) crosslinking using Friedel-Crafts reaction (FDA: formaldehyde dimethyl acetal).
Figure S2. Small angle X-ray scattering (SAXS) data of bulk film of PS-\(b\)-PDMS containing P(S-\(r\)-N\(_3\)), oBCP, and cBCP-900 °C.
Figure S3. (a) SEM and (b) TEM images of mesoporous hyper-crosslinked BCP particles.
Figure S4. SEM and TEM images of (a-b) PS-\(b\)-PDMS particles prepared without P(S-\(r\)-N\(_3\)) after Friedel-Crafts reaction and (c-d) PS-\(b\)-PDMS/P(S-\(r\)-N\(_3\)) particles carbonized at 900 °C under N\(_2\) gas flow without Friedel-Crafts reaction.
Figure S5. TEM images of cBCPs carbonized at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C.
Figure S6. Cross-sectional TEM images of cBCP carbonized at 900 °C.
Figure S7. Formation of carbon shell. HR-TEM images of cBCP-PtFe catalyst after the reduction at 500 °C of (a) 10 min, (b) 30 min, (c) 60 min, (d) HR-TEM image of PtFe catalyst deposited on Vulcan carbon; the same synthesis procedure was used as the cBCP-PtFe carbonized at 900 °C except that Vulcan carbon was used instead of cBCP. (e) TEM and (f) HR-TEM images of cBCP-Fe catalyst prepared without Pt precursor using otherwise the same synthesis procedure.
Table S1. Elemental analysis results of hBCP, bare cBCP and cBCP-PtFe carbonized at 900 °C containing 1 wt% Pt.

<table>
<thead>
<tr>
<th></th>
<th>hBCP (atomic %)</th>
<th>cBCP (atomic %)</th>
<th>cBCP-PtFe (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>83.5</td>
<td>98.0</td>
<td>98.0</td>
</tr>
<tr>
<td>H</td>
<td>8.6</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>N</td>
<td>7.9</td>
<td>0.2</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure S8. N 1s XPS results for (a) hBCP, and (b) bare cBCP carbonized at 900 °C. (c) N 1s HR-PES result for cBCP-PtFe carbonized at 900 °C containing 1 wt% Pt. XPS spectra were obtained at a fixed photon energy of 1486.7 eV using a monochromated Al K-alpha source. HR-PES spectrum was obtained at a photon energy of 650 eV using a synchrotron radiation source.
Figure S9. (a) BET N$_2$ adsorption-desorption isotherms, and (b) pore size distribution.
**Table S2.** Textural property of cBCP-PtFe carbonized at various temperatures.

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m² g⁻¹)</th>
<th>Pore Volume (cm³ g⁻¹)</th>
<th>Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cBCP-PtFe-700°C</td>
<td>488.5</td>
<td>0.33</td>
<td>20.1</td>
</tr>
<tr>
<td>cBCP-PtFe-800°C</td>
<td>508.9</td>
<td>0.35</td>
<td>22.4</td>
</tr>
<tr>
<td>cBCP-PtFe-900°C</td>
<td>567.7</td>
<td>0.38</td>
<td>24.1</td>
</tr>
<tr>
<td>cBCP-PtFe-1000°C</td>
<td>575.8</td>
<td>0.42</td>
<td>26.6</td>
</tr>
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</table>
Figure S10. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) results of cBCP-PtFe with 1 wt% Pt carbonized at (a-b) 700 °C, (c-d) 800 °C, (e-f) 900 °C, (g-h) 1,000 °C, and (i-j) 20 wt% commercial Pt/C. CV and LSV results were obtained in Ar- and O₂-saturated 0.1 M HClO₄ solution, respectively.
Figure S11. (a) ORR mass activities at 0.9 V<sub>RHE</sub> for cBCP-PtFe electrocatalysts with 1 wt% Pt and 20 wt% commercial Pt/C, and (b) H<sub>2</sub>O<sub>2</sub> selectivity and electron transfer number of the cBCP-PtFe carbonized at 900 °C. The ring currents for H<sub>2</sub>O<sub>2</sub> oxidation were measured by holding the Pt ring potential at 1.2 V during the ORR. The electron transfer number (n) and H<sub>2</sub>O<sub>2</sub> selectivity were calculated from the equations of

\[
 n = \frac{4I_d}{I_r + \frac{N}{I_d}}
\]

\[
 H_2O_2 selectivity \% = \frac{2I_r}{N \times \frac{I_r}{I_d} + \frac{N}{I_d}} \times 100\%
\]

where \( I_d \) is the disk current, \( I_r \) is the ring disk, and \( N \) is the collection efficiency (0.37) of the working electrode.
**Table S3.** The concentrations of Fe ions leached after 10,000 cycles of ORR ADT in a half-cell for cBCP-PtFe carbonized at various temperatures.

<table>
<thead>
<tr>
<th></th>
<th>700 °C</th>
<th>800 °C</th>
<th>900 °C</th>
<th>1000 °C</th>
</tr>
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<tbody>
<tr>
<td><strong>Leached Fe ion</strong> (ppb)</td>
<td>2.35</td>
<td>2.54</td>
<td>2.12</td>
<td>3.24</td>
</tr>
<tr>
<td><strong>Fe retention</strong> (%)</td>
<td>84.3</td>
<td>83.1</td>
<td>85.9</td>
<td>78.4</td>
</tr>
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</table>
Figure S12. (a) CV and (b) LSV results of bare cBCP, cBCP-Pt, cBCP-Fe, and cBCP-PtFe, which were obtained with neither Pt nor Fe, with Pt only, with Fe only, and with both Pt and Fe, respectively. CV and LSV results were obtained in Ar- and O$_2$-saturated 0.1 M HClO$_4$ solution, respectively.
Figure S13. ORR polarization curves of cBCP-PtFe (900 °C) catalysts with various Fe contents. The durability test was performed by repeating CVs in 0.6-1.0 V<sub>RHE</sub>.
Table S4. Mass activity of the cBCP-PtFe (900 °C) catalysts with various Fe contents

<table>
<thead>
<tr>
<th>Fe Content</th>
<th>Initial</th>
<th>After 5K</th>
<th>After 10K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 wt% Fe</td>
<td>2.1</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>5 wt% Fe</td>
<td>9.0</td>
<td>7.6</td>
<td>6.2</td>
</tr>
<tr>
<td>10 wt% Fe</td>
<td>2.9</td>
<td>1.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Figure S14. Cross-sectional SEM images of MEAs for (a) commercial Pt/C containing 20 wt% and (b) eBCP-PtFe containing 1 wt% Pt (carbonized at 900 °C).
### Table S5. Pt loading required for the production of a kilowatt electricity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$g_{Pt}$ kW$^{-1}$</th>
<th>Cathode Pt loading (mg$_{Pt}$ cm$^{-2}$)</th>
<th>Gas flow</th>
<th>Back pressure (bar)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>cBCP-PtFe (900 °C) (This work)</td>
<td>0.011</td>
<td>0.01</td>
<td>H$_2$O$_2$</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>LP@PF-1</td>
<td>0.031</td>
<td>0.03</td>
<td>H$_2$O$_2$</td>
<td>0.5</td>
<td>Science 362, 1276-1281 (2018)</td>
</tr>
<tr>
<td>LP@PF-2</td>
<td>0.025</td>
<td>0.04</td>
<td>H$_2$O$_2$</td>
<td>0.5</td>
<td>Science 362, 1276-1281 (2018)</td>
</tr>
<tr>
<td>Au-doped PtCo/C</td>
<td>0.168</td>
<td>0.20</td>
<td>H$_2$O$_2$</td>
<td>1.6</td>
<td>Appl. Catal. B:Environ, 247, 142-149 (2019)</td>
</tr>
<tr>
<td>NSTF-Pt$_3$Ni$_7$</td>
<td>0.143</td>
<td>0.10</td>
<td>H$_2$-Air</td>
<td>0.5</td>
<td>J. Electrochem. Soc. 158, B910-B918 (2011)</td>
</tr>
<tr>
<td>P2-NA</td>
<td>0.111</td>
<td>0.10</td>
<td>H$_2$-Air</td>
<td>0.7</td>
<td>Energy Environ. Sci. 8, 258-266 (2015)</td>
</tr>
</tbody>
</table>
Figure S15. TEM images observed after the durability test (a) in a half-cell setup and (b) in a single-cell setup. The durability in a half-cell setup was tested by repeating the CV between 0.6 \text{ V}_{\text{RHE}} and 1.0 \text{ V}_{\text{RHE}} in O_2-saturated 0.1 M HClO_4 solution for 10,000 cycles. The durability in a single cell setup was tested by repeating the CV between 0.6 V and 1.0 V with humidified H_2 (200 sccm) to the anode and N_2 (75 sccm) to the cathode for 30,000 cycles.
Figure S16. TEM-EDS mapping images of the eBCP-PtFe (900 °C) catalyst obtained after 30,000 cycles of the single cell durability tests.
Figure S17. (a) i-V curves (inset: TEM image of a nonporous cPS-PtFe particle and HR-TEM image of carbon shell-capsulated PtFe particles located on the cPS-PtFe). (b) Power density curves in a single cell setup for cBCP-PtFe (porous particles) and cPS-PtFe (nonporous particles). Both samples contain 1 wt% Pt and were carbonized at 900 °C.
Figure S18. Textural property of the porous and nonporous particles. (a) BET N₂ adsorption-desorption isotherms, and (b) pores size distributions of the cBCP-PtFe and cPS-PtFe containing 1 wt% Pt. The carbonization was performed at 900 °C for both samples.
Table S6. Textural property of cBCP-PtFe and cPS-PtFe carbonized at 900 °C.

<table>
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<tr>
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<tr>
<td>cBCP-PtFe</td>
<td>567.7</td>
<td>0.38</td>
<td>24.1</td>
</tr>
<tr>
<td>cPS-PtFe</td>
<td>109.8</td>
<td>0.11</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Figure S19. Single cell performance of cBCP-PtFe (900 °C) in H₂-air flow condition; (a) i-V curve, (b) power density curve, and (c) high frequency resistance.
Figure S20. TEM image of cBCP-PtFe (900 °C) with 41 nm-sized pores, and its single cell performance in H₂-air flow condition; (b) i-V curve, and (c) power density curve.
Figure S21. *In situ* XANES results of cBCP-PtFe with 1 wt% Pt carbonized at (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C, and (e) commercial Pt/C with 20 wt% Pt. The XANES were measured by fluorescence mode using a home-made electrochemical cell when the potentials of 0.4, 0.6, 1.0, 1.1, 1.2 V\textsubscript{RHE} were applied. The working electrode was catalyst-coated carbon papers (39BC, SGL Carbon). Pt wire and Ag/AgCl electrode was used as counter electrode and reference electrode, respectively. Before acquiring the XAFS spectra, chronoamperometry was performed to obtain the stable current in each potential.
Figure S22. EXAFS results of cBCP-PtFe carbonized at various temperatures. (a) Pt L$_3$-edge and (b) Fe-K edge $k^3$-weighted R-space FT-EXAFS spectra of the cBCP-PtFe electrocatalysts.
Figure S23. TEM images of cBCP-PtFe carbonized at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C, in which all the samples contain 1 wt% Pt, after leaching. (e) TEM image of commercial Pt/C (20 wt% Pt) after leaching. The leaching treatment was performed with 0.1 M of aqua-regia solution under stirring (800 rpm) at 80 °C for 8 h.
Figure S24. UV-Vis spectra for potassium hydrogen phthalate (KHP) decomposition test. The catalysts ((a) cBCP-PtFe (900 °C), (b) Pt$_3$Fe/C, and (c) commercial Pt/C), H$_2$O$_2$, and KHP were stirred at 100 rpm and 80 °C for 1 h, 2 h, 4 h, and 6 h. When Fenton reaction occurs, the KHP peak at 350 nm would decrease because the leached Fe ions would have reactions with H$_2$O$_2$, generating OH$^-$ or OOH$^-$ radicals, which subsequently decompose KHP (Appl. Sci. 2019, 9, 23). The Pt$_3$Fe/C were synthesized by depositing 108 mg of Pt(acac)$_2$ and 32 mg of Fe(acac)$_3$ on 200 mg of Vulcan carbon (XC 72R) using incipient impregnation method and reducing under H$_2$/N$_2$ flow (20:180 sccm) at 500 °C for 2 h.
Figure S25. Selective poisoning on the PtFe nanoparticles without carbon shell. Oxygen reduction reaction (ORR) was performed in a half-cell setup for Pt$_1$Fe$_1$/C containing 20 wt% Pt. ORR curves for ‘SCN poisoning’ were obtained in 0.1 M HClO$_4$ including 30 mM KSCN. ORR curves for ‘after washing’ were obtained in pure 0.1 M HClO$_4$ after washing the SCN$^-$-poisoned electrode in deionized water with 400 rpm for 1 h. The Pt$_1$Fe$_1$/C were synthesized by depositing 108 mg of Pt(acac)$_2$ and 98 mg of Fe(acac)$_3$ on 200 mg of Vulcan carbon (XC 72R) using incipient impregnation method and reducing under H$_2$/N$_2$ flow (20:180 sccm) at 500 °C for 2 h.
Figure S26. Schemes of ORR in the presence of SCN⁻. The SCN⁻ remained on the commercial Pt/C after washing, hindering ORR. The SCN⁻ was easily removed on the cBCP-PtFe catalyst after washing, recovering the ORR activity.
Figure S27. Work-function of graphene-layered or bare metal surface with various molar ratios of Pt, estimated by density functional theory calculations.