Electronic Supplementary Information (ESI)

A Polymer-Coated Carbon Black-based Fuel Cell Electrocatalyst with High CO-Tolerance and Durability in Direct Methanol Oxidation

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**Fig. S1.** New test protocol of durability test for a half-cell proposed by the Fuel Cell Commercialization Conference of Japan (see K. Shinohara, A. Ohma, A. Iiyama, T. Yoshida and T. Daimaru, *ECS Transactions*, 2011, **41**, 775).

**Fig. S2.** The narrow scan of C$_{1s}$ region of CB/Pt (black line), CB/PyPBI/Pt (blue line) and CB/PyPBI/Pt/PVPA (red line).
Fig. S3. Histograms of the particle size distribution of CB/Pt, CB/PyPBI/Pt and CB/PyPBI/Pt/PVPA before (top column A) and after (bottom column B) the durability test. To present the histograms, 100 nanoparticles were taken from each TEM image.
Fig. S4. CV curves of CB/Pt (black line), CB/PyPBI/Pt (blue line), and CB/PyPBI/Pt/PVPA (red line) recorded in 0.1M HClO₄ solution at the scan rate of 50 mV/s at 25 °C.
Fig. S5. Rotating disc current density of CB/Pt (a), CB/PyPBI/Pt (b) and CB/PyPBI/Pt/PVPA (c) in O₂-saturated 0.1M HClO₄ solutions at 25 °C. (d) ORR polarization curves for CB/Pt (black line), CB/PyPBI/Pt (blue line), and CB/PyPBI/Pt/PVPA (red line) in O₂-saturated 0.1M HClO₄ at 25 °C and rotation rate of 1600 rpm, sweep rate of 10 mV/s. (e)Mass (red column) and specific activities (blue column) at 0.85 V vs. RHE (N=3). (f) Peroxide generation from the ORR detected at ring electrode in O₂-saturated 0.1M HClO₄ at sweep rate of 10 mV/s, and rotation rate of 1600 rpm. (g) Koutecky-Levich plots from ORR at 0.43 V vs. RHE for CB/Pt (black line), CB/PyPBI/Pt (blue line), and CB/PyPBI/Pt/PVPA (red line).
Fig. S6. Three ORR polarization curves for CB/Pt, CB/PyPBI/Pt, and CB/PyPBI/Pt/PVPA in O₂-saturated 0.1M HClO₄ at 25 °C and rotation rate of 1600 rpm, sweep rate of 10 mV/s.

Fig. S7. Ring \( (I_R) \) and disk currents \( (I_D) \) for the collection efficiency in N₂-saturated 0.1M KCl and 1mM K₃Fe(CN)₆ at the scan rate of 10 mV/s at 25°C.

Explanation of Fig. S5, 6 and 7: Before the durability test, the ORR was measured (Fig. S5†). Interestingly, after coating with PVPA, the CB/PyPBI/Pt PVPA showed a higher limiting disk current (-5.77mA/cm²) than the other two catalysts because of
the perfect oxygen accessibility, which contributed to a higher fuel cell performance of the PVPA coated catalyst. The mass and specific activities were calculated as a quantitative comparison to illustrate the performance of all catalysts using the Levich-Koutecky equation: \( \frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \). Three-times ORR measurements were carried out for each catalyst to calculate the average mass and specific activities (Fig. S6†). Compared to the CB/PyPBI/Pt (65.70 mA/mgPt and 0.14 mA/cm²Pt, respectively), the mass and specific activities of the CB/PyPBI/Pt/PVPA decreased due to coverage of the polymer layer on the Pt-NPs (44.72 mA/mgPt and 0.11 mA/cm²Pt, respectively). However, the value was almost the same as that of the commercial CB/Pt (49.33 mA/mgPt and 0.08 mA/cm²Pt, respectively) (Fig. S5e†). During the ORR, peroxide (H₂O₂) is generated as a by-product, which degrades the performance by deterioration of the Pt-based anode and carbon supporting materials. Thus, a lower H₂O₂ yield is very important for the catalyst durability. After being coated by PVPA, the H₂O₂ generation, which was calculated by the equation: \( \% \text{H}_2\text{O}_2 = \frac{200I_R}{(Nt_D + I_R)} \), where \( N \) is the collection efficiency, which corresponds to the \( I_R/I_D \) ratio (0.404, Fig. S7†), significantly decreased to 0.6 % (Fig. S5f†) attributed to the 4-electron transfer during the ORR (Fig. S5g†).
**Table S1.** Comparison of mass activity in methanol oxidation reaction (MOR).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Mass activity (mA/mg)</th>
<th>Methanol concentration (mol/L)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB/PyPBI/Pt/PVPA</td>
<td>817</td>
<td>1</td>
<td>this work</td>
</tr>
<tr>
<td>PtRu/MC</td>
<td>487.9</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>PtRu/graphene</td>
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<td>1</td>
<td>4</td>
</tr>
<tr>
<td>PtRu/graphene</td>
<td>33.5</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>PtRu/CNT/graphene</td>
<td>136.7</td>
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<td>6</td>
</tr>
<tr>
<td>PtRu/TiO$_2$/CNF</td>
<td>516</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>PtRu/PANI/CNT</td>
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<tr>
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<tr>
<td>PtRu/HPAs-CS/graphene</td>
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<td>PtRu/N-doped graphene</td>
<td>668</td>
<td>0.5</td>
<td>11</td>
</tr>
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</table>

**References**