SUPPORTING INFORMATION

Fe-N-doped Carbon Capsules with Outstanding Electrochemical Performance and Stability for the Oxygen Reduction Reaction in Both Acid and Alkaline Conditions

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Table S1. Summary of reported ORR performance for heteroatom-doped carbon catalysts in alkaline media (0.1 M KOH).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass loading (mg cm(^{-2}))</th>
<th>Onset Potential (V vs. RHE)</th>
<th>Kinetic current density (mA cm(^{-2}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-N-CC</td>
<td>0.10</td>
<td>0.94</td>
<td>18.3 (@ 0.58 V)</td>
<td>This work</td>
</tr>
<tr>
<td>NMCS-3</td>
<td>0.66</td>
<td>~ 0.86</td>
<td>-</td>
<td>1</td>
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<tr>
<td>NHPCM-1000</td>
<td>0.32</td>
<td>0.88</td>
<td>6.19 (@ 0.6 V)</td>
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<tr>
<td>NZ-13</td>
<td>0.21</td>
<td>~ 0.93</td>
<td>-</td>
<td>3</td>
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<tr>
<td>N-Fe-C@CNTs</td>
<td>0.09</td>
<td>0.88</td>
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<tr>
<td>N-OMCS-1.5-900</td>
<td>1.00</td>
<td>0.77</td>
<td>-</td>
<td>5</td>
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<tr>
<td>Meso/micro-PoPD</td>
<td>0.50</td>
<td>~ 0.90</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Meso-EmG</td>
<td>0.81</td>
<td>1 V</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>m-NC-600</td>
<td>1.14</td>
<td>0.92</td>
<td>10.54 (@ 0.57)</td>
<td>8</td>
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<tr>
<td>NC-A</td>
<td>0.128</td>
<td>0.90</td>
<td>33.24 (@ 0.34 V)</td>
<td>9</td>
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<tr>
<td>N-MCN</td>
<td>0.40</td>
<td>~ 0.83</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>SNGL-20</td>
<td>0.306</td>
<td>~ 0.88</td>
<td>10 (@ 0.73 V)</td>
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<tr>
<td>N-doped mesoporous nanosheets</td>
<td>0.60</td>
<td>0.97</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>N-doped carbon spheres</td>
<td>0.25</td>
<td>0.88</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>N-doped graphene</td>
<td>0.05</td>
<td>~ 0.95</td>
<td>~ 6.7 (@ 0.58 V)</td>
<td>14</td>
</tr>
<tr>
<td>R/Fe (~0.05 %)</td>
<td>0.21</td>
<td>~ 0.90</td>
<td>-</td>
<td>15</td>
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<tr>
<td>BP-NFe</td>
<td>0.40</td>
<td>1.06</td>
<td>-</td>
<td>16</td>
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<tr>
<td>PANI-4.5Fe-T2(SBA-15)</td>
<td>0.95</td>
<td>7.4 (@ 0.82 V)</td>
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<tr>
<td>N-Fe-co-doped CNTs</td>
<td>0.485</td>
<td>0.93</td>
<td>-</td>
<td>18</td>
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<tr>
<td>Fe-N-CNFs</td>
<td>0.60</td>
<td>0.93</td>
<td>48.15 (@ 0.53 V)</td>
<td>19</td>
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<tr>
<td>Fe-N/C</td>
<td>0.10</td>
<td>0.92</td>
<td>-</td>
<td>20</td>
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<tr>
<td>Fe–N–C–700</td>
<td>0.03</td>
<td>0.93</td>
<td>19.4 (@ 0.58 V)</td>
<td>21</td>
</tr>
<tr>
<td>Fe–N–C–900</td>
<td>0.03</td>
<td>~ 0.90</td>
<td>10.3 (@ 0.58 V)</td>
<td>21</td>
</tr>
<tr>
<td>Fe3C@NCNF-900</td>
<td>0.15</td>
<td>~ 0.98</td>
<td>~ 15 (@ 0.4 V)</td>
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</table>
Table S2. Summary of reported ORR performance for heteroatom-doped carbon catalysts in acidic media.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>Mass loading (mg cm$^{-2}$)</th>
<th>Onset Potential (V vs. RHE)</th>
<th>Kinetic current density (mA cm$^{-2}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-N-CC</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.10</td>
<td>0.80</td>
<td>4.85 (@ 0.46 V)</td>
<td>This work</td>
</tr>
<tr>
<td>NZ-13</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>0.21</td>
<td>~ 0.81</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Meso/micro-PoPD</td>
<td>Unknown</td>
<td>0.50</td>
<td>0.84</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>N-doped mesoporous nanosheets</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.60</td>
<td>0.75</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>N-doped Carbon Spheres</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.25</td>
<td>0.65</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>N-doped graphene</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.05</td>
<td>~ 0.76</td>
<td>0.5 (@ 0.47 V)</td>
<td>14</td>
</tr>
<tr>
<td>N-Fe-co-doped CNTs</td>
<td>0.1 M HClO$_4$</td>
<td>0.49</td>
<td>0.89</td>
<td>-</td>
<td>18</td>
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<tr>
<td>Fe-N-CNFs</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.60</td>
<td>0.79</td>
<td>-</td>
<td>19</td>
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<tr>
<td>Fe-N/C</td>
<td>0.1 M HClO$_4$</td>
<td>0.10</td>
<td>~ 0.78</td>
<td>-</td>
<td>20</td>
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<tr>
<td>Fe–N–C–700</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.03</td>
<td>0.89</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>Fe–N–C–900</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.03</td>
<td>0.85</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>Fe-N-HCMS</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>0.25</td>
<td>0.80</td>
<td>4.6 (@ 0.6 V)</td>
<td>23</td>
</tr>
<tr>
<td>Fe3C@NCNF-900</td>
<td>0.1 M HClO$_4$</td>
<td>0.15</td>
<td>0.78</td>
<td>-</td>
<td>22</td>
</tr>
</tbody>
</table>
Figure S1. Nitrogen sorption isotherm of the Fe-N-doped carbon capsules (Fe-N-CC).
Figure S2. XRD pattern of the Fe-N-CC (a) after and (b) before washing, (c) Raman spectra of amorphous (blue line) and graphitic carbon regions (red line), and (d) TGA analysis of Fe-N-CC in air.
Figure S3. (a) XPS general spectrum of Fe-N-CC and (b) high-resolution Fe 2p$_{3/2}$ XPS spectrum.

As can be seen in Figure S3b, the Fe 2p$_{3/2}$ XPS spectra shows multiple peaks, which indicates that metal species in the catalysts are complicated in terms of their chemical state. According to previous reports, the Fe 2p$_{3/2}$ peak located at around 712 eV is due to N-coordinated iron.\textsuperscript{19, 24} This metal species and Fe$_3$C have been demonstrated to be the main responsible active centers on iron and nitrogen co-doped carbon materials.\textsuperscript{25, 26} However, no peak corresponding to Fe$_3$C (located at 706.7-706.9 eV)\textsuperscript{27, 28} can be identified, which agrees with the TEM/HRTEM studies that show its encapsulation in a relatively thick graphitic carbon layer. The other peaks may be attributed to Fe$^{2+}$ (709.05 eV) and Fe$^{3+}$ (710.8 eV), and the corresponding satellite peaks (714.3 and 716.1 eV respectively).\textsuperscript{29, 30} As shown by previous studies, these peaks may as well correspond to N-coordinated iron.\textsuperscript{20, 31}
Figure S4. (a) TEM image and its corresponding EDX mappings for (b) carbon, (c) nitrogen, (d) iron and (e) oxygen for the corresponding Fe-N-CC.
Figure S5. (a) HRTEM image of a Fe$_3$C nanoparticle, (b) an enlarged HRTEM image of the graphitic layer, (c) an enlarged HRTEM image of the Fe$_3$C nanoparticle and (d) its SAED pattern.
Figure S6. Cyclic voltammograms of Fe-N-CC in N\textsubscript{2} and O\textsubscript{2} saturated (a) 0.1 M KOH and (b) 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolytes.
Figure S7. LSVs at 10 mV s\(^{-1}\) in the presence of oxygen with rotation speed from 400 to 2400 rpm in (a) 0.1 M KOH and (b) 0.5 M H\(_2\)SO\(_4\), and the corresponding Koutecky-Levich plots in (c) 0.1 M KOH and (d) 0.1 M H\(_2\)SO\(_4\), compared with those of an ideal 2-electron process (red line) and an ideal 4-electron process (black line).
Figure S8. Comparison of the chronoamperometric response of Fe-N-CC and Pt/C over 10,000 s at 0.68 V and a constant rotation speed of 800 rpm in O\textsubscript{2}-saturated solution 0.1 M KOH.

Figure S9. Nyquist plots of the whole cell, including the half-cell measurements of the cathode, at current densities in the 10 – 100 mA cm\textsuperscript{-2} range. Anode half-cell measurements are not shown for clarity.
References


