Supplementary Information

Dysprosium based new Coordination Polymer and its Application towards Oxygen Reduction Reaction

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Crystal structure details-

Single crystals of Dy³⁺ suitable for X-ray diffraction were grown in DMF/H₂O via solvothermal method. Diffraction studies were performed on Agilent Technologies SUPERNOVA diffractometer with a CCD detector, using a Mo-Kα radiation (λ=0.71073Å). Crystal data was collected and reduced using the standard “CrysAlisPro” Software. The crystal structure was solved by direct method using SHELXS-97 and refining of structure was done by full matrix least squares using SHELXL-97. The positions of non-hydrogen atoms were located and refined anisotropically. After that hydrogen atoms were obtained from residual density map and refined with isotropic thermal parameters. The PLATON program was used to refine the disordered solvent molecules.

Fig. 1 FTIR Data of Dysprosium coordination polymer (Dy-CP)
Fig. 2 (a) shows SEM image of Dysprosium coordination polymer (Dy-CP) 2 (b) shows EDS data of Dy-CP.

SEM image shows that particles are elongated, plate like in structure.
Fig. 3  Raman data of Dy-CP annealed at 800°C.

Fig. 4  XPS spectrum (Wider scan of Dy-CP annealed at 800°C.)
The O1s spectrum is deconvoluted into three peaks at 531.3, 533.2 and 534.7 eV which correspond to Oxygen bonded to Dysprosium, oxygen bonded to carbon and adsorbed hydroxides or carbonates.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>7.66</td>
<td>22.43</td>
</tr>
<tr>
<td>N K</td>
<td>6.46</td>
<td>18.23</td>
</tr>
<tr>
<td>O K</td>
<td>21.57</td>
<td>47.42</td>
</tr>
<tr>
<td>Dy L</td>
<td>64.31</td>
<td>13.92</td>
</tr>
</tbody>
</table>

Fig. 6 EDAX spectrum of Dy-CP annealed at 800°C.
CV data shows that Dy-CP is ORR active material. There is a small reduction peak of material in N₂ saturated solution and there is a well defined reduction peak in O₂ saturated solution (0.1M KOH) at 0.73V.

Fig. 7 Shows the CV data of Dy-CP

Fig. 8 Shows overall comparison of ORR activity of Dy-CP at 1600rpm.

The comparison of ORR activity at 1600rpm indicates that ORR activity increases after adding Vulcan carbon to Dy-CP as a support material, but on annealing Dy-CP at 800°C, ORR activity further increases without Vulcan carbon. So, the increasing order of ORR activity is Dy-CP< Dy-CP with Vulcan carbon< annealed Dy-CP.
Fig. 9 Shows K-L plot for (a) Dy-CP (b) Dy-CP with Vulcan carbon.

The linearity of K-L plots indicates the first order kinetics.

Fig. 10 Shows Ring current for (a) Dy-CP (b) Dy-CP with Vulcan carbon as a support.

For non-annealed Dy-CP, we got a 4e⁻ mechanism:

<table>
<thead>
<tr>
<th>Dy-CP</th>
<th>Potential</th>
<th>n=No. of electrons involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy-CP</td>
<td>0.78</td>
<td>3.2</td>
</tr>
<tr>
<td>Dy-CP</td>
<td>0.76</td>
<td>3.6</td>
</tr>
<tr>
<td>Dy-CP</td>
<td>0.72</td>
<td>3.7</td>
</tr>
<tr>
<td>Dy-CP</td>
<td>0.70</td>
<td>3.7</td>
</tr>
<tr>
<td>Dy-CP</td>
<td>0.66</td>
<td>3.9</td>
</tr>
</tbody>
</table>

For annealed Dy-CP, we got a mixed mechanism (2e⁻ and 4e⁻)
For non annealed sample with Vulcan carbon as a support, (n) electron transfer no. came out to be four. So, it follows four electron mechanism -

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potential</th>
<th>n=No. of electrons involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy -800</td>
<td>0.78</td>
<td>2.8</td>
</tr>
<tr>
<td>Dy - 800</td>
<td>0.76</td>
<td>2.9</td>
</tr>
<tr>
<td>Dy - 800</td>
<td>0.72</td>
<td>3.3</td>
</tr>
<tr>
<td>Dy -800</td>
<td>0.70</td>
<td>3.2</td>
</tr>
<tr>
<td>Dy 800</td>
<td>0.66</td>
<td>3.4</td>
</tr>
<tr>
<td>Dy 800</td>
<td>0.64</td>
<td>3.6</td>
</tr>
<tr>
<td>Dy 800</td>
<td>0.62</td>
<td>3.8</td>
</tr>
<tr>
<td>Dy 800</td>
<td>0.60</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Fig. 11 shows the detailed mechanism of Dy-CP, Dy annealed at 800°C and Dy-CP with Vulcan carbon.

The detailed mechanism shows that in Dy-CP annealed at 800 °C , n value changes from 2.8 to 3.9 and the overall value is about 3.6 which is close to 4. It means that here some amount of HOO⁻ is generated as an intermediate which is then further reduced to OH⁻.