Vitalizing Fuel Cells with Vitamin: Pyrolyzed Vitamin B12 as Non-precious Catalyst for Enhanced Oxygen Reduction Reaction of Polymer Electrolyte Fuel Cell

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Supporting Text

Nominal Co wt.% calculation
The nominal Co wt.% in py-B12/C and Co/C were calculated by assuming no Co loss after pyrolysis.

As py-B12/C for example:
Before pyrolysis, B12: 0.1 g and carbon black: 0.4 g
Co loading: 0.1×99%×(59/1355.37) = 0.00431 g
After pyrolysis, total loading of B12/C: 0.455 g
Co wt.%: 0.00431/0.455×100% = 0.947%

As py-CoTMPP/C for example:
Before pyrolysis, CoTMPP: 0.1 g and carbon black: 0.4 g.
Co loading: 0.1×99%×(59/791.76) = 0.00738 g
After pyrolysis, total loading of py-CoTMPP/C: 0.425 g
Co wt.%: 0.00738/0.425×100% = 1.736% ≒ 1.74%

Total electron-transfer number (n) and hydrogen peroxide yield (%H2O2) determined by RRDE approach
The total electron-transfer number (n) and the hydrogen peroxide yield (%H2O2) in the catalyzed ORR were calculated as:

\[
\frac{I_r}{I_c} = 1 + \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{Z_{\text{H}_2\text{O}_2}} \left(k_3 + (k_4 + 1 + \frac{k_1}{k_2})/\omega^{0.5}\right)
\]

\[
Z_{\text{H}_2\text{O}_2} = 0.62D_{\text{H}_2\text{O}_2}^{0.7} \omega^{-0.75}
\]

where D and \(\omega\) were the diffusion coefficient in the solution and the solution viscosity, respectively. The rate constants \(k_1\) and \(k_4\) are those of Reaction 3 in the forward and backward directions, respectively. Using \(I_r/I_c\) vs. \(\omega^{0.5}\) as y vs. x coordinates, respectively, the curve was a straight line with an intercept value, A,

\[
A = 1 + \frac{k_1}{k_2}
\]

where the \(k_1/k_2\) ratio was obtained from each potential.

Definition of \(\alpha\) and \(\beta\) sites of B12
For the cyanocobalamin, the axial position below the corrin (\(\alpha\) site) is occupied by an intermolecularly bound 5,6-dimetylbenzimidazole group (DMB) and that above the corrin (\(\beta\) site) is occupied by a ligand of -CN.

Determination of ohmically corrected cell voltage (iR compensation)
According to Gasteiger et al. report,2 the ohmically corrected cell voltage, \(E_{\text{iR-free}}\), can be corrected by the iR compensation, as shown:

\[
E_{\text{iR-free}} = E_{\text{cell}} + i \cdot R_{\Omega}
\]

where \(E_{\text{cell}}\), i and \(R_{\Omega}\) are cell voltage, cell current and cell resistances, respectively.

The \(R_{\Omega}\) of py-B12/C cell was 0.25 Ω cm², determined by AC impedance at the frequency of 20 kHz.

For example:
\(E_{\text{cell}} = 0.4\ V, i = 955.8\ mA\ cm², R_{\Omega} = 0.25\ Ω\ cm²\)
\(E_{\text{iR-free}} = 0.4+955.8/1000×0.25 = 0.641\ V, R_{\text{iR-free}}\)
Supporting figures

Figure S1. ORR curves of py-B12/C pyrolyzed at various temperatures in oxygen-saturated 0.1 M HClO₄ by RRDE tests. Scan rate: 10 mV s⁻¹; rotation rate: 1600 rpm.

Figure S2. CV curves for py-B12/C, py-B12 and pyrolyzed carbon blacks in nitrogen-purged 0.1 M HClO₄ solution. Scan rate: 50 mV s⁻¹.

Figure S3. XRD spectra of py-B12 and pristine B12. The reference patterns are shown below the figure.

Figure S4. The potential energy profiles of oxygen decomposition reaction. The red, black, green, blue, and light blue atoms express the oxygen, cobalt, nitrogen, carbon, and hydrogen atoms, respectively. (Unit: kcal/mol)

Supporting Tables
**Table S1** The fitting results of XANES spectra corresponding to Figure 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Energy value, (E_0) (eV)</th>
<th>Cobalt oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine CoTMPP</td>
<td>7720.1</td>
<td>2+</td>
</tr>
<tr>
<td>Pristine B12</td>
<td>7724.5</td>
<td>3+</td>
</tr>
<tr>
<td>Py-B12</td>
<td>7718.5</td>
<td>2+</td>
</tr>
<tr>
<td>CoO powder</td>
<td>7720.8</td>
<td>2+</td>
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</tbody>
</table>

**Table S2** Curve-fitting results of the EXAFS data at Co K-edge.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>(\Delta \sigma_j^2) (Å)</th>
<th>(\Delta E_0) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine B12</td>
<td>Co-N(eq)(^1)</td>
<td>3.9</td>
<td>1.89</td>
<td>0.001</td>
<td>0.2</td>
</tr>
<tr>
<td>(R factor: 0.005)</td>
<td></td>
<td></td>
<td></td>
<td>(+0.1)</td>
<td>(+0.03)</td>
</tr>
<tr>
<td></td>
<td>Co-C(CN)(^2)</td>
<td>1.2</td>
<td>1.93</td>
<td>0.003</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(+0.2)</td>
<td>(+0.02)</td>
</tr>
<tr>
<td>Py-B12</td>
<td>Co-N</td>
<td>4.1</td>
<td>1.96</td>
<td>0.007</td>
<td>-6.0</td>
</tr>
<tr>
<td>(R factor: 0.002)</td>
<td></td>
<td></td>
<td></td>
<td>(+0.2)</td>
<td>(+0.04)</td>
</tr>
</tbody>
</table>

Notation: N, coordination number; R, distance between absorber and back-scatter atoms; \(\Delta \sigma_j^2\), Debye–Waller factor; \(\Delta E_0\), inner potential corrections. The error bounds stated here were obtained from the statistical analysis of the data by FEFFIT software.

\(^1\) Co-N(eq): Co-N\(_4\) moiety in the corrin ring.
\(^2\) Co-C(CN): Co binding –CN.
\(^3\) Co-N(DMB): Co binding 5,6-dimetrylbenzimidazole group

**Table S3** The geometries of the potential energy profiles in Figure S1.
The bond length differences between corrin and \(O_2\)-adsorbed corrin more than 0.1 Å are marked.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Top view</th>
<th>Side view</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrin</td>
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<td><img src="image" alt="Corrin" /></td>
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<tr>
<td>Corrin(^+)</td>
<td><img src="image" alt="Corrin(^+)" /></td>
<td><img src="image" alt="Corrin(^+)" /></td>
</tr>
<tr>
<td>OO-Co</td>
<td><img src="image" alt="OO-Co" /></td>
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</tbody>
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References
