Supporting Information

An organic-based aqueous hybrid flow battery with high power and long cycle life: tetrapyridophenazine/ferrocyanide system

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Electrochemical analyses for kinetic parameters

Transfer electron number \((n)\) for ET1

According to the Laviron theory, \(^{[S1]}\) the peak current \((i_p)\) has the following relationship with the transfer electron number \((n)\) \(^{[S2]}\):

\[
i_p = \frac{n^2 F^2 A \tau v}{4RT} = \frac{n F Q v}{4RT} \]  

(Eq. S1)

where \(i_p\) is the oxidation or reduction peak current (the contribution of non-Faraday currents has been substracted), \(A\) is the electrode surface area (0.0707 cm\(^2\)), \(\tau\) is the amount of the electro-active species, \(Q\) is the amount of electricity consumed in the process and calculated from the peak area, and \(F, R,\) and \(T\) are the Faraday constant, the universal gas constant, and the Kelvin temperature, respectively.
**Fig. S1** Dependence of the reduction peak current \((i_p,\text{red})\) of ET1 of TPPHZ on the scan rate. The dependence of the reduction peak current \((i_p,\text{red})\) of ET1 of TPPHZ on the scan rate is extracted from the CV curves shown in **Fig. 1a**. The \(n\) value is calculated to be about 0.932 from the slope of the \(i_p-\nu\) dependence, indicating that the ET1 reaction of TPPHZ is one-electron reaction in alkaline electrolyte.

**Electron transfer coefficient (\(\alpha\)) and charge transfer rate constant (\(k_{ET}\)) for ET1**

The \(k_{ET}\) of ET1 has been determined using Laviron’s method \([53]\) from the following equation:

\[
\Delta E_p = \frac{2.3RT}{\alpha(1-\alpha)nF}\left[\alpha \log(1 - \alpha) + (1 - \alpha)\log\alpha - \log\left(\frac{RTk_{ET}}{nF}\right)\right] + \frac{2.3RT}{\alpha(1-\alpha)nF}\log\nu \quad \text{(Eq. S2)}
\]

where \(\Delta E_p\) is the potential difference between the oxidation and reduction peak, \(\nu\) is the scan rate, \(n\) is the transfer electron number \((n=1)\) and \(\alpha\) is electron transfer coefficient, respectively.
Fig. S2 (a) CVs of TPPHZ electrode in 1 M KOH solution at different scan rates (the scan rates (ν) from 0.4 to 4 V s⁻¹). (b) Plot of ΔE_p versus log (ν) for ET1 of TPPHZ electrode. The plot of ΔE_p versus log(ν) produces a straight line along with an intercept. The k_{ET} can be obtained from the intercept value. The α value is calculated to be about 0.57 from the slope of the ΔE_p-log (ν) dependence (2.3RT/α(1-α)nF). Then, the k_{ET} value is calculated to be ca. 17.3 s⁻¹.

Transfer electron number (n) for ET2

The plot of E_{20} vs log[OH⁻] shown in Fig. S8 can be fitted well by a linear relation E_{20} = -944-63.3log[OH⁻]. The slope is -63.3 mV pH⁻¹, corresponding to a 2-proton/2-electron reaction. Therefore, the n value for ET2 is evaluated to be 2.

Diffusion coefficient for ET2

To estimate the diffusion coefficient (D) for ET2 reaction, the chronoamperometry results was analyzed by the following Cottrell equation assuming semi-infinite diffusion [S4]:

\[ j = nFC_E \left( \frac{D}{\pi t} \right)^{1/2} \]  
(Eq. S3)
where $j$ is the current density, $n$ is the transfer electron number, $C_E$ is the concentration of redox sites and $t$ is time, respectively.

The concentration of TPPHZ in the electrode layer ($C_E$) can be obtained by using the following equation:

$$C_E = \frac{m/M_W}{S L}$$

(Eq. S4)

where $m$ is the mass of TPPHZ in the electrode layer (5.58 μg), $M_W$ is the molecular weight (384.4 g mol$^{-1}$), $S$ is the electrode area (0.0707 cm$^2$) and $L$ is the average thickness of the electrode layer.

The thickness of the TPPHZ electrode layer was measured by using confocal laser scanning microscopy (CLSM, LEXT OLS4000, Olympus). Table S1 presents the thickness values of the TPPHZ electrode layer obtained from CLSM. The average thickness is calculated to be 3.08 μm. Therefore, the $C_E$ value can be calculated to be about 0.665 mol L$^{-1}$.

Cottrell equation with finite diffusion [S5] undoubtedly would give more precise results since the thickness of the electrode layer is ~3 μm. However, calculation results given recently by Sato and Oyaizu [S6] indicated that the finite effect only appeared after the longtime electrolysis (e.g. $t > 100$ s). Therefore, the semi-infinite Eq. S3 can be utilized to analyse the experimental data at $t < 100$ s. The chronoamperometry curve of TPPHZ electrode in 1 M KOH solution was recorded (Fig. S3a). Corresponding Cottrell plots shows good linear dependence of $j$ versus $t^{-1/2}$. The $D$ of the reduction process is calculated to be about $2.18 \times 10^{-10}$ cm$^2$ s$^{-1}$ from the slope of the $j$-$t^{-1/2}$ plot.
(Fig. S3b) while that of the oxidation process is about $2.45 \times 10^{-10}$ cm$^2$ s$^{-1}$ (Fig. S3c).

Therefore, the average $D$ value is determined to be ca. $2.32 \times 10^{-10}$ cm$^2$ s$^{-1}$.

**Table S1** Thickness data of the TPPHZ electrode layer obtained from CLSM measurements.

<table>
<thead>
<tr>
<th>No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (μm)</td>
<td>3.03</td>
<td>3.03</td>
<td>2.67</td>
<td>2.84</td>
<td>3.32</td>
<td>3.47</td>
<td>3.20</td>
<td>3.21</td>
</tr>
<tr>
<td>No.</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>Average value</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>3.07</td>
<td>3.21</td>
<td>2.98</td>
<td>3.01</td>
<td>3.10</td>
<td>3.03</td>
<td>2.98</td>
<td>3.08</td>
</tr>
</tbody>
</table>

**Fig. S3** (a) The chronoamperometry curve of TPPHZ electrode in 1 M KOH solution.
(b) Cottrell plot for the reduction. (c) Cottrell plot for the oxidation. The results of the linear regression are also shown.
**Charge transfer rate constant \((k_{ET})\) for ET2**

The charge transfer rate constant \((k_{ET})\) for ET2 is estimated by Nicholson’s method. \[^{[S7]}\]

The CV curves of the TPPHZ electrode in a 1 M KOH electrolyte were recorded at different scan rate (**Fig. 1a**). The potential gap between the oxidation and reduction peak \((\Delta E_p)\) was utilized to calculate the kinetic parameter, \(\Psi\), from **Eq. S5**. Then, \(k_{ET}\) can be calculated using the slope of the plot of \(\Psi\) versus \(v^{-1/2}\) based on the relationship between \(\Psi\) and \(v^{-1/2}\) (**Eq. S6**).

\[
\Psi = \frac{(0.0021\Delta E_p - 0.6288)}{(1 - 0.017\Delta E_p)} \tag{Eq. S5}
\]

\[
\Psi = k_{ET}(\frac{nDnF}{RT})^{-1/2}v^{-1/2} \tag{Eq. S6}
\]

where \(F\), \(D\), and \(n\) are defined previously, and \(v\) represents the scan rate. The average \(D\) value \((2.32 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1})\) was used for \(k_{ET}\) calculation.

![Plot of \(\Psi\) versus \(v^{-1/2}\)](image)

**Fig. S4** Plot of \(\Psi\) versus \(v^{-1/2}\) (The linear relationship was shown with scan rates of 10~200 mV s\(^{-1}\)). The \(k_{ET}\) value is calculated to be about \(3.81 \times 10^{-4} \text{ cm s}^{-1}\) from the slope of the \(\Psi\sim v^{-1/2}\) dependence.
Table S2  Electrochemical kinetic parameters of TPPHZ electrode in alkaline aqueous electrolyte (1 M KOH). NA, not applicable.

<table>
<thead>
<tr>
<th>Redox reaction</th>
<th>Types of control</th>
<th>Transfer electron number ((n))</th>
<th>Diffusion coefficient ((D))</th>
<th>Charge transfer rate constant ((k_{ET}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPPHZ + e(^-) = TPPHZ(^-)</td>
<td>absorption</td>
<td>1</td>
<td>NA</td>
<td>17.3 s(^-1) (at (\alpha=0.57))</td>
</tr>
<tr>
<td>TPPHZ + 2e(^-) = TPPHZ(^2-)</td>
<td>diffusion</td>
<td>2</td>
<td>(2.32 \times 10^{-10}) cm(^2) s(^-1)</td>
<td>(3.81 \times 10^{-4}) cm s(^-1)</td>
</tr>
</tbody>
</table>

Fig. S5 CVs of TPPHZ and TPPHZ/G composite electrode in 1 M KOH solution at a scan rate of 25 mV s\(^{-1}\).

Fig. S6 PXRD patterns of TPPHZ and TPPHZ/G composite.
Fig. S7 (a) CVs of TPPHZ electrode at 25 mV s\(^{-1}\) in a 0.1 M KOH (pH=13) solution containing different concentrations of potassium ions. (b) Plot of redox potentials \((E_1^0\) and \(E_2^0\)) versus the logarithm of potassium concentration \((\log[K^+])\). The \(E_1^0\) and \(E_2^0\) is the standard redox potentials of ET1 and ET2, respectively. The standard redox potential is defined as the average value of anodic peak potential \((E_{pa})\) and cathodic peak potential \((E_{pc})\).

Fig. S8 (a) CVs of TPPHZ electrode at 25 mV s\(^{-1}\) in KOH electrolyte of different concentrations. (b) Plot of redox potentials \((E_1^0\) and \(E_2^0\)) versus the logarithm of potassium ion or hydroxide concentration \((\log[K^+]\) or \((\log[\text{OH}^-]))\).
**Fig. S9** (a) CVs of TPHHZ electrode at 25 mV s⁻¹ in 1 M strongly alkaline electrolytes containing different cations. (b) CVs of TPHHZ electrode in 1 M NaOH solution at a scan rate of 100 mV s⁻¹ during the 2nd, 10th, 30th, 50th and 100th cycles. (c) CVs of TPHHZ electrode in 1 M LiOH solution at a scan rate of 100 mV s⁻¹ during the 2nd, 10th, 30th, 50th and 100th cycles.

**Table S3** Effect of the type of alkaline electrolytes on the equilibrium potential and reversibility of TPHHZ.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E_1^0$ (mV), ET1</th>
<th>$\Delta E_1$ (mV), ET1</th>
<th>$E_2^0$ (mV), ET2</th>
<th>$\Delta E_2$ (mV), ET2</th>
<th>$j_{pa}/j_{pc}$, ET1</th>
<th>$j_{pa}/j_{pc}$, ET2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M KOH</td>
<td>-633</td>
<td>5</td>
<td>-944</td>
<td>134</td>
<td>1.10</td>
<td>0.80</td>
</tr>
<tr>
<td>1 M NaOH</td>
<td>-588</td>
<td>12</td>
<td>-932</td>
<td>129</td>
<td>1.02</td>
<td>1.01</td>
</tr>
<tr>
<td>1 M LiOH</td>
<td>-606</td>
<td>21</td>
<td>-913</td>
<td>131</td>
<td>1.06</td>
<td>1.26</td>
</tr>
</tbody>
</table>
Fig. S10 Chemical stability of TPPHZ. $^1$H NMR (500 MHz, CDCl$_3$) spectra. (A) TPPHZ δ: 7.82 (4H), 9.35 (4H), 9.55 (4H). (B) TPPHZ, after 3 days treating in 1 M KOH at 25 °C. (C) TPPHZ, after 1,200 charge-discharge cycles at 10 A g$^{-1}$ in 1 M KOH + 0.2 M KCl solution at 25 °C.

Fig. S11 (a) UV-vis absorption spectra of the TPPHZ solutions in chloroform with different concentration. (b) The linear plot between the concentration of TPPHZ and the maximum absorbance recorded at λ=276 nm. The solubility of TPPHZ in 1 M KOH was calculated to be ~0.047 mg L$^{-1}$ at 25±1 °C.
**Table S4** Performance comparisons of the TPPHZ//K₄[Fe(CN)₆] AHFB at different current densities. CD, current density; CE, coulombic efficiency; EE, energy efficiency; SDC, specific discharge capacity; TC, theoretical capacity.

<table>
<thead>
<tr>
<th>CD(A g⁻¹)</th>
<th>CE(%)</th>
<th>EE(%)</th>
<th>SDC(mAh g⁻¹)</th>
<th>TC(mAh g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>72.1</td>
<td>68.3</td>
<td>79.6</td>
<td>128.8</td>
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<tr>
<td>2</td>
<td>83.9</td>
<td>77.0</td>
<td>78.0</td>
<td>128.8</td>
</tr>
<tr>
<td>3</td>
<td>89.9</td>
<td>82.8</td>
<td>75.0</td>
<td>128.8</td>
</tr>
<tr>
<td>4</td>
<td>92.8</td>
<td>84.3</td>
<td>71.5</td>
<td>128.8</td>
</tr>
<tr>
<td>5</td>
<td>93.8</td>
<td>84.7</td>
<td>68.3</td>
<td>128.8</td>
</tr>
</tbody>
</table>
Fig. S12 Possible resonance structures. (a)TPPHZ, (b)TPPHZ\(^{\cdot}\) and (c)TPPHZ-H\(_2\).

References


