# **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, <sup>[S1]</sup> the peak current ( $i_p$ ) has the following relationship with the transfer electron number (n) <sup>[S2]</sup>:

$$i_p = \frac{n^2 F^2 A \tau v}{4RT} = \frac{n F Q v}{4RT}$$
(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<sup>2</sup>),  $\tau$  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  $(i_{p,red})$  of ET1 of TPPHZ on the scan rate. The dependence of the reduction peak current  $(i_{p,red})$  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  $i_p$ -v dependence, indicating that the ET1 reaction of TPPHZ is one-electron reaction in alkaline electrolyte.

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

The  $k_{\text{ET}}$  of ET1 has been determined using Laviron's method <sup>[S3]</sup> from the following equation:

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

where  $\Delta E_p$  is the potential difference between the oxidation and reduction peak, v 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 (v) from 0.4 to 4 V s<sup>-1</sup>). (b) Plot of  $\Delta E_p$  versus log (v) for ET1 of TPPHZ electrode. The plot of  $\Delta E_p$  versus log(v) produces a straight line along with an intercept. The *k*<sub>ET</sub> can be obtained from the intercept value. The  $\alpha$  value is calculated to be about 0.57 from the slope of the  $\Delta E_p$ -log (v) dependence (2.3*RT*/ $\alpha$ (1- $\alpha$ )*nF*). Then, the *k*<sub>ET</sub> value is calculated to be ca. 17.3 s<sup>-1</sup>.

## Transfer electron number (n) for ET2

The plot of  $E_2^0$  vs log[OH<sup>-</sup>] shown in **Fig. S8** can be fitted well by a linear relation  $E_2^0$ = -944-63.3log[OH<sup>-</sup>]. The slope is -63.3 mV pH<sup>-1</sup>, corresponding to a 2-proton/2electron 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 <sup>[S4]</sup>:

$$j = nFC_E(\frac{D}{\pi t})^{1/2}$$
(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:

$$C_E = \frac{m/M_W}{SL}$$
(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<sup>-1</sup>), *S* is the electrode area (0.0707 cm<sup>2</sup>) 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  $3.08 \ \mu\text{m}$ . Therefore, the C<sub>E</sub> value can be calculated to be about 0.665 mol L<sup>-1</sup>.

Cottrell equation with finite diffusion <sup>[S5]</sup> 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 <sup>[S6]</sup> 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<sup>2</sup> s<sup>-1</sup> 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<sup>2</sup> s<sup>-1</sup> (Fig. S3c). Therefore, the average *D* value is determined to be ca.  $2.32 \times 10^{-10}$  cm<sup>2</sup> s<sup>-1</sup>.

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



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 $(k_{\text{ET}})$ for ET2

The charge transfer rate constant ( $k_{\text{ET}}$ ) for ET2 is estimated by Nicholson's method. <sup>[S7]</sup> 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,  $k_{\text{ET}}$ 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**).

$$\Psi = (0.0021\Delta E_p - 0.6288) / (1 - 0.017\Delta E_p)$$
 (Eq. S5)

$$\Psi = k_{ET} \left(\frac{\pi D n F}{RT}\right)^{-1/2} \nu^{-1/2}$$
(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*<sub>ET</sub> calculation.



**Fig. S4** Plot of  $\Psi$  versus  $v^{-1/2}$  (The linear relationship was shown with scan rates of 10~200 mV s<sup>-1</sup>). The *k*<sub>ET</sub> value is calculated to be about  $3.81 \times 10^{-4}$  cm s<sup>-1</sup> from the slope of the  $\Psi \sim v^{-1/2}$  dependence.

**Table S2** Electrochemical kinetic parameters of TPPHZ electrode in alkaline aqueouselectrolyte (1 M KOH). NA, not applicable.

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



Fig. S5 CVs of TPPHZ and TPPHZ/G composite electrode in 1 M KOH solution at a

scan rate of 25 mV s<sup>-1</sup>.



Fig. S6 PXRD patterns of TPPHZ and TPPHZ/G composite.



**Fig. S7** (a) CVs of TPPHZ electrode at 25 mV s<sup>-1</sup> in a 0.1 M KOH (pH=13) solution containing different concentrations of potassium ions. (b) Plot of redox potentials  $(E_1^0 \text{ and } E_2^0)$  versus the logarithm of potassium concentration (log[K<sup>+</sup>]). 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<sup>-1</sup> 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<sup>+</sup>] or (log[OH<sup>-</sup>]).



**Fig. S9** (a) CVs of TPPHZ electrode at 25 mV s<sup>-1</sup> in 1 M strongly alkaline electrolytes containing different cations. (b) CVs of TPPHZ electrode in 1 M NaOH solution at a scan rate of 100 mV s<sup>-1</sup> during the 2<sup>nd</sup>, 10<sup>th</sup>, 30<sup>th</sup>, 50<sup>th</sup> and 100<sup>th</sup> cycles. (c) CVs of TPPHZ electrode in 1 M LiOH solution at a scan rate of 100 mV s<sup>-1</sup> during the 2<sup>nd</sup>, 10<sup>th</sup>, 30<sup>th</sup>, 50<sup>th</sup> and 100<sup>th</sup> cycles.

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

Electrolyte	$E_1^0 (mV),$ ET1	$\Delta E_1 (\mathrm{mV}),$ ET1	$E_2^0 $ (mV), ET2	$\begin{array}{c} \Delta E_2 \ (\mathrm{mV}), \\ \mathrm{ET2} \end{array}$	jpa∕jpc, ET1	j <sub>pa</sub> /j <sub>pc</sub> , ET2
1 M KOH	-633	5	-944	134	1.10	0.80
1 M NaOH	-588	12	-932	129	1.02	1.01
1 M LiOH	-606	21	-913	131	1.06	1.26



Fig. S10 Chemical stability of TPPHZ. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup> 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  $\lambda$ =276 nm. The solubility of TPPHZ in 1 M KOH was calculated to be ~0.047 mg L<sup>-1</sup> at 25±1 °C.

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$CD(A g^{-1})$	CE(%)	EE(%)	SDC(mAh g <sup>-1</sup> )	TC(mAh g <sup>-1</sup> )
1	72.1	68.3	79.6	128.8
2	83.9	77.0	78.0	128.8
3	89.9	82.8	75.0	128.8
4	92.8	84.3	71.5	128.8
5	93.8	84.7	68.3	128.8

**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.







Fig. S12 Possible resonance structures. (a)TPPHZ, (b)TPPHZ<sup>-+</sup> and (c)TPPHZ-H<sub>2</sub>.

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