

## Electronic Supplementary Information

### Evaluation of redox pairs for low-grade heat energy harvesting with thermally regenerative cycle

José Tomás Bórquez Maldifassi,<sup>a</sup> Joseph B. Russell,<sup>b</sup> Jungmyung Kim,<sup>b</sup> Edward Brightman,<sup>c</sup> Xiangjie Chen,<sup>b</sup> Downon Bae<sup>a,b</sup>

<sup>a</sup>Institute of Mechanical, Process and Energy Engineering (IMPEE), School of Engineering and Physical Sciences, Heriot-Watt University

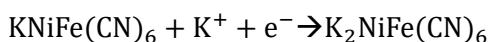
<sup>b</sup>Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University

<sup>c</sup>Department of Chemical and Process Engineering, University of Strathclyde

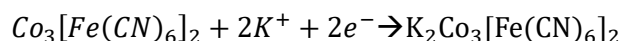
#### 1. Redox reactions of NiHCF, CoHCF, and CuHCF

Solubilities for NiHCF, CoHCF, and CuHCF depend on the ion absorbed and released during the cyclic redox reactions within the TRFB, as they are present in the reaction as a solid electrode.

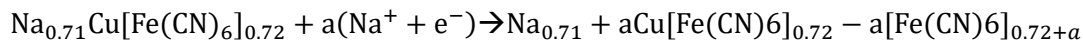
For NiHCF, the reaction is the following:



For CoHCF, the reaction is the following:



For CuHCF, the reaction is the following:



#### 2. State of charge to volumetric charge capacity conversion

First, find Coulombs of Charge per litre for the current state of charge using the following equation:

$$\frac{C}{\text{litre}} = n \cdot F \left( \frac{\text{Coulombs}}{\text{mol}} \right) \cdot \text{Conc} \left( \frac{\text{mol}}{\text{litre}} \right) \cdot \text{SoC}(\%) \quad (\text{Eq. S1})$$

Where  $n$  is the number of transferred charges per reaction,  $F$  is Faraday's constant (96485.3321),  $\text{Conc}$  is the max concentration of the redox pair, and  $\text{SoC}$  is the current state of charge.

Then, convert Coulombs per litre to Ampere hours per litre by using the relationship that one Ah is equivalent to one Coulomb applied for one hour.

$$\frac{\text{Ah}}{\text{litre}} = \frac{n \cdot F \cdot \text{Conc} \cdot \text{SoC}}{60\text{sec} \cdot 60\text{min}} = \frac{n \cdot F \cdot \text{Conc} \cdot \text{SoC}}{3600} \quad (\text{Eq. S2})$$

This conversion was performed for all four pairs in Fig. 4 in the main manuscript so that we could perform the net work and conversion efficiency calculation. The charge was estimated by estimating the number of charges that could be stored using the  $n$  number and the concentration of the limiting factor in the combined redox equations. For example, in the  $[\text{Fe(CN)}_6]^{3-/4-} || \text{I}_3^- / 3\text{I}^-$  pair 0.2M of  $\text{I}_3^- / 3\text{I}^-$  will react with 0.4M of  $[\text{Fe(CN)}_6]^{3-/4-}$  which is saturated. Therefore, the limiting factor in charge capacity is  $[\text{Fe(CN)}_6]^{3-/4-}$ , which has an  $n$  number of 1 and a concentration of 0.4M, giving 0.4M of electrons per litre. This is converted to Ah/ litre as per equations 1 and 2. The relevant values for each pair are shown in the table below.

**Table S1** Chemical Properties of Redox Pairs

Pair	Limiting factor concentration (M)	Molar charges	99 % Charge capacity (Ah/l)
$[\text{Fe}(\text{CN})_6]^{3-/4-}    \text{I}_3^- / 3\text{I}^-$	0.4	1	10.6
$\text{Fe}^{2+/3+}    \text{Cu}^{0/2+}$	1.3	2	34.49
$\text{Fe}^{2+/3+}    \text{CuHCF}$	1.3	1	37.15
$[\text{Zn}(\text{NH}_3)_4]^{2+} / \text{Zn}    \text{NiHCF}$	3.33	2	176.71

Note that the volumetric charge capacity is referred to as the half-cell; therefore, there will be a complimentary litre associated with the other half-cell, i.e., it is referred to as two litres of liquid.

### 3. Note on heat capacity

The heat capacity estimation is achieved by assuming the electrolyte is KCl, assumed to be 2M per litre. Dissolved ions tend to disrupt the hydrogen bonding within pure water, and this causes a reduction in heat capacity with increased salt concentration. Toner et al. have studied the relationship between salt concentrations and heat capacities [1]. We use their data on the heat capacity of KCl to estimate the electrolyte heat capacity at 3.5 J/g for a 2M KCl concentration.

Based on these previously measured values, the heat capacity value for the example cases is taken as 3.5 J/g. As both halves of the cell are saturated the charge capacity is referenced to a half cell; therefore, the heat capacity for the whole cell concerns two litres of KCl solution. Clearly, this has limited accuracy as it does not account for all ionic interactions and electrodes in the system. Heat capacity is normally measured experimentally once a TREC cell system is realised so an accurate heat-to-chemical efficiency can be calculated. This somewhat arbitrary estimation will have to suffice, although it will be the major cause of error in estimated efficiency values. Therefore, each per litre heat capacity is identical, and the corresponding absorbed heat  $Q$  is calculated using equation 3.

$$Q = mC_p\Delta T$$

$$Q = 2000 * 3.5 * 55 = 385 \text{ KJ} = 106.95 \text{ Wh} \quad (\text{Eq. S3})$$

This heat capacity value, along with the charge capacities in the previous table, was used to estimate conversion efficiencies using Equation 1 in the main manuscript.

### 4. Tables of Estimated Performance Values

Each pair was analysed at four levels of heat recovery (0.5, 0.7, 0.9 and 0.99) and three charge depths (0.5, 0.8, 0.99). Note that the charge depth has no absolute defined range, i.e., in the 50% case, this could start and finish at any state of charge.

**Table S2**  $[\text{Fe}(\text{CN})_6]^{3-/4-} || \text{I}_3^- / 3\text{I}^-$ 

Depth of Discharge / %	Net work / Wh L <sup>-1</sup>	Qc / Ah L <sup>-1</sup>	Qh / Wh L <sup>-1</sup>	Qhr / Wh L <sup>-1</sup>	$\eta_{\text{HR}}$	$\eta_{\text{HTC}} / \%$	$\eta_{\text{Carnot}} / \%$
50	0.71	5.36	4.66	2940.97	0.50	0.02	0.15
50	0.71	5.36	4.66	1764.58	0.70	0.04	0.26
50	0.71	5.36	4.66	588.19	0.90	0.12	0.77
50	0.71	5.36	4.66	58.82	0.99	1.12	7.19
80	1.14	8.58	7.45	2940.97	0.50	0.04	0.25
80	1.14	8.58	7.45	1764.58	0.70	0.06	0.41
80	1.14	8.58	7.45	588.19	0.90	0.19	1.23
80	1.14	8.58	7.45	58.82	0.99	1.72	11.02

99	1.41	10.61	9.22	2940.97	0.50	0.05	0.31
99	1.41	10.61	9.22	1764.58	0.70	0.08	0.51
99	1.41	10.61	9.22	588.19	0.90	0.24	1.51
99	1.41	10.61	9.22	58.82	0.99	2.07	13.28

**Table S3**  $\text{Fe}^{2+/3+} \parallel \text{CuHCF}$

Depth of Discharge / %	Net work / Wh L <sup>-1</sup>	Qc / Ah L <sup>-1</sup>	Qh / Wh L <sup>-1</sup>	Qhr / Wh L <sup>-1</sup>	$\eta_{\text{HR}}$	$\eta_{\text{HTC}} / \%$	$\eta_{\text{Carnot}} / \%$
50	1.99	17.42	13.04	2940.97	0.50	0.07	0.43
50	1.99	17.42	13.04	1764.58	0.70	0.11	0.72
50	1.99	17.42	13.04	588.19	0.90	0.33	2.13
50	1.99	17.42	13.04	58.82	0.99	2.77	17.79
80	3.19	27.87	20.87	2940.97	0.50	0.11	0.69
80	3.19	27.87	20.87	1764.58	0.70	0.18	1.15
80	3.19	27.87	20.87	588.19	0.90	0.52	3.36
80	3.19	27.87	20.87	58.82	0.99	4.00	25.66
99	3.94	34.49	25.82	2940.97	0.50	0.13	0.85
99	3.94	34.49	25.82	1764.58	0.70	0.22	1.41
99	3.94	34.49	25.82	588.19	0.90	0.64	4.12
99	3.94	34.49	25.82	58.82	0.99	4.66	29.90

**Table S4**  $[\text{Zn}(\text{NH}_3)_4]^{2+} / \text{Zn}^0 \parallel \text{NiHCF}$

Depth of Discharge / %	Net work / Wh L <sup>-1</sup>	Qc / Ah L <sup>-1</sup>	Qh / Wh L <sup>-1</sup>	Qhr / Wh L <sup>-1</sup>	$\eta_{\text{HR}}$	$\eta_{\text{HTC}} / \%$	$\eta_{\text{Carnot}} / \%$
50	10.97	89.25	71.55	2940.97	0.50	0.36	2.34
50	10.97	89.25	71.55	1764.58	0.70	0.60	3.84
50	10.97	89.25	71.55	588.19	0.90	1.66	10.67
50	10.97	89.25	71.55	58.82	0.99	8.41	54.02
80	17.55	142.80	114.47	2940.97	0.50	0.57	3.69
80	17.55	142.80	114.47	1764.58	0.70	0.93	6.00
80	17.55	142.80	114.47	588.19	0.90	2.50	16.04
80	17.55	142.80	114.47	58.82	0.99	10.13	65.02
99	21.72	176.71	141.66	2940.97	0.50	0.70	4.52
99	21.72	176.71	141.66	1764.58	0.70	1.14	7.31
99	21.72	176.71	141.66	588.19	0.90	2.98	19.11
99	21.72	176.71	141.66	58.82	0.99	10.83	69.55

**Table S5**  $\text{Fe}^{2+/3+} \parallel \text{Cu}^{0/2+}$

Depth of Discharge / %	Net work / Wh L <sup>-1</sup>	Qc / Ah L <sup>-1</sup>	Qh / Wh L <sup>-1</sup>	Qhr / Wh L <sup>-1</sup>	$\eta_{\text{HR}}$	$\eta_{\text{HTC}} / \%$	$\eta_{\text{Carnot}} / \%$
50	1.96	17.42	12.67	2940.97	0.50	0.07	0.43
50	1.96	17.42	12.67	1764.58	0.70	0.11	0.71
50	1.96	17.42	12.67	588.19	0.90	0.33	2.10
50	1.96	17.42	12.67	58.82	0.99	2.75	17.66
80	3.14	27.87	20.28	2940.97	0.50	0.11	0.68
80	3.14	27.87	20.28	1764.58	0.70	0.18	1.13
80	3.14	27.87	20.28	588.19	0.90	0.52	3.32
80	3.14	27.87	20.28	58.82	0.99	3.97	25.55
99	3.89	34.49	25.09	2940.97	0.50	0.13	0.84

99	3.89	34.49	25.09	1764.58	0.70	0.22	1.40
99	3.89	34.49	25.09	588.19	0.90	0.63	4.08
99	3.89	34.49	25.09	58.82	0.99	4.63	29.80