Electronic Supplementary Information (ESI) for:

A fundamental study of the thermoelectrochemistry of ferricyanide/ferrocyanide: Cation, concentration, ratio, and heterogeneous and homogeneous electrocatlaysis effects in thermogalvanic cells

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Tabulated values for concentration dependence on $[Fe(CN)_6]^{3-/4-}$ thermogalvanic output

Table S1 – Table of data showing the Seebeck coefficient, Current density and power density of the $K_{3/4}[Fe(CN)_6]$ thermocell of varying concentration. Values correspond to Fig. 1.

Concentration /M	S_e / mV K^{-1}	S_e Error / (1 SD)	j_{SC} / A m^{-2}	j_{SC} Error (1 SD)	P_{max} / mW m^{-2}	P_{max} Error (1 SD)
0.00	-	-	0.00	0.00	0.00	0.00
0.05	-1.54	0.01	-3.98	0.43	27.56	2.94
0.1	-1.49	0.01	-7.49	0.62	50.30	3.81
0.15	-1.46	0.02	-11.71	0.49	77.12	2.94
0.2	-1.42	0.03	-17.25	1.06	110.19	6.98
0.25	-1.42	0.01	-20.75	2.51	132.96	16.37

Tabulated values for ratio dependence on $[Fe(CN)_6]^{3-/4-}$ thermogalvanic output

Table S2 – Table of data showing the Seebeck coefficient, current density and power density of the $K_{3/4}[Fe(CN)_6]$ thermocell where the ratio of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ has been altered, maintaining a total concentration of 0.4 M $[Fe(CN)_6]$. Corresponding to Fig. 2.

$[Fe(CN)_6]^{3-}$ Concentration	S_e / mV K^{-1}	S_e Error / (1 SD)	j_{SC} / A m^{-2}	j_{SC} Error (1 SD)	P_{max} / mW m^{-2}	P_{max} Error (1 SD)
0.00	-	-	0.0	0.0	0.0	0.0
0.025	-1.62	0.03	-6.7	0.9	48.7	5.4
0.050	-1.58	0.01	-11.4	0.9	81.2	6.7
0.100	-1.49	0.03	-16.4	0.8	110.3	7.4
0.150	-1.46	0.01	-17.2	0.6	112.5	4.4
0.200	-1.42	0.03	-16.9	1.0	108.6	7.6
0.250	-1.34	0.02	-16.4	0.5	98.6	4.2
0.300	-1.30	0.03	-13.3	0.8	78.1	5.7
0.350	-1.27	0.01	-9.5	0.2	54.0	1.4
0.375	-1.22	0.00	-5.2	0.3	28.4	1.6
0.400	-	-	0.0	0.0	0.0	0.0

Tabulated values for Butler-Volmer kinetic model of the $[Fe(CN)_6]^{3-/4-}$ thermocell

Table S3 – Table of values for the experimentally determined current density and power density of the ratio study of the $K_{3/4}[Fe(CN)_6]$ thermocell. Compared to Bulter-Volmer calculated values of the same ratio. Corresponding to Fig. 4.

$[Fe(CN)_6]^{3-}$ Concentration	Current Density / A m^{-2}	Butler-Volmer Calculated Current Density / A m^{-2}	Power Density / mW m^{-2}	Butler-Volmer Calculated Power Density / mW m^{-2}
0.00	0.00	0.00	0.0	0.00
0.025	6.68	9.26	48.7	67.62
0.050	11.40	12.33	81.2	87.74
0.100	16.35	15.19	110.3	101.82
0.150	17.16	16.59	112.5	108.72
0.200	16.91	16.69	108.6	106.62
0.250	16.37	15.22	98.6	91.69
0.300	13.29	13.26	78.1	77.88
0.350	9.46	9.84	54.0	56.12
0.375	5.18	6.92	28.4	37.92
0.400	0.00	0.00	0.00	0.00

Tabulated values for cation effect on Se of $[Fe(CN)_6]^{3-/4-}$ thermocell

Table S4 – Table of values for the Seebeck coefficient for the $[Fe(CN)_6]^{3-/4-}$ thermocell with varying metal cations. Corresponding to Fig. 7.

Cation (M)	MCl Se / mV K^{-1}	Error	M_2SO_4 Se / mV K^{-1}	Error
Li	-1.299	0.032	-1.237	0.016

Na	-1.419	0.024	-1.354	0.034
K	-1.323	0.032	-1.306	0.032
Rb	-1.437	0.036	-1.412	0.032
Cs	-1.575	0.026	-1.502	0.024

Table S5 - Table of values for the Calculated entropy (based on the Seebeck coefficient) for the $[Fe(CN)_6]^{3-/4-}$ thermocell with varying metal cations. Corresponding to Fig. 7.

Cation (M)	MCl Entropy / J K^{-1} mol^{-1}	Error	M_2SO_4 Entropy / J K^{-1} mol^{-1}	Error
Li	-125.3	3.0	-119.4	1.6
Na	-137.0	2.4	-130.6	6.6
K	-127.7	3.0	-126.0	3.2
Rb	-138.7	3.4	-136.3	3.2
Cs	-152.0	2.4	-145.0	2.2

Tabulated values for cation effect on power density of $[Fe(CN)_6]^{3-/4-}$ thermocell

Table S6 – Table of values for the power density of the $[Fe(CN)_6]^{3-/4-}$ thermocell with varying cations at both carbon and platinum electrodes. Corresponding to Fig. 7 and Fig. S1.

Cation	P_{max} (Amorphous Carbon) / mW m^{-2}	P_{max} (Amorphous Carbon) Error (1 SD)	P_{max} (Platinum) / mW m^{-2}	P_{max} (Platinum) Error (1 SD)
Li	11.68	1.14	14.97	0.41

K	19.48	1.04	20.50	0.39
Cs	25.26	1.32	30.07	0.21

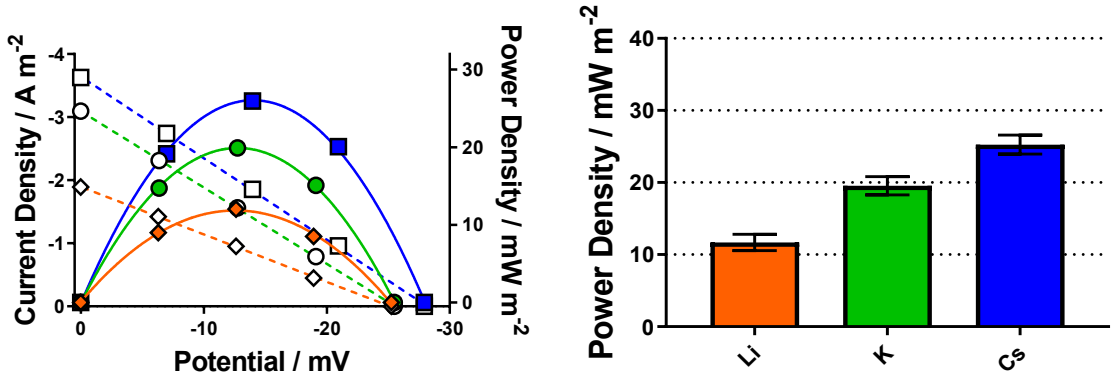

Figure S1 – Showing **(a)** representative power curves for Cs^+ (blue square), K^+ (green circle) and Li^+ (orange diamond), and **(b)** bar chart summarising the effect of the dominant alkali metal cation on the maximum power density. All recorded for 25 mM $K_4[Fe(CN)_6]$, 25 mM $K_4[Fe(CN)_6]$ and 1.5 M of MCl in a non-isothermal thermogalvanic cell, with ΔT = 20 K (T_{cold} = 15°C) at carbon electrodes.

Tabulated values for heterogeneous *vs* homogeneous electrocatalysis of the $[Fe(CN)_6]^{3-/4-}$ thermocell

Table S7 – Table of values for the obtained power density and normalised power density of the $K_{3/4}[Fe(CN)_6]$ thermocell at various electrode surfaces.

Electrode Material	Added CsCl?	V_{OCP} / mV	j_{SC} / A m^{-2}	P_{max} / mW m^{-2}	k_{agg} / cm s^{-1}
Crystalline Graphite	No CsCl	-25.15	-5.68	36 ± 1	5.80 x10^{-5}
	+ 0.7 M CsCl	-28.17	-9.24	65 ±1	8.00 x10^{-5}
Amorphous Graphite	No CsCl	-25.97	-16.18	108 ± 7	1.70 x10^{-4}
	+ 0.7 M CsCl	-24.89	-23.81	153 ± 1	2.31 x10^{-4}

Platinum	No CsCl	-24.73	-20.05	124 ± 5	1.93 x10^{-4}
	+ 0.7 M CsCl	-25.49	-23.98	155 ± 5	2.41 x10^{-4}

List of materials used for Techno-economic evaluation

Table S8 – List of compounds, grade, pack size and costing utilised in the techno-economic evaluation. All costs are as found on the Sigma Aldrich website (sigmaaldrich.com; country set to UK) on the 16th of December 2019.

Salt	Grade	Cost in GBP / £	Mass / g	Cost / £ g^{-1}	Mw / g mol^{-1}	Cost / £ mol^{-1}
$K_3[Fe(CN)_6]$	ReagentPlus	107.00	500	0.21	329.24	70.46
	ACS	65.5	500	0.13		43.20
$K_4[Fe(CN)_6]$ $\bullet 3H_2O$	ReagentPlus	64.60	500	0.13	422.39	54.57
	ACS	107.00	500	0.21		90.39
CsCl	ReagentPlus	240.00	100	2.40	168.36	404.06

Table S9 – Table denoting the ratio of $K_3[Fe(CN)_6]$ to $K_4[Fe(CN)_6]$ with or without added CsCl. The power density comes from a graphite cell, and the cost based upon using *ReagentPlus* grade chemicals, for each ratio. Values correspond to Fig. 10.

$K_3[Fe(CN)_6]$ / M	$K_4[Fe(CN)_6]$ / M	CsCl / M	P_{max} / mW m^{-2}	Cost / £ L^{-1}	Cost / £ L^{-1} per mW m^{-2}	Relative Cost to 0.2 M
0.05	0.35	0	81.2	22.6	0.28	1.21
0.10	0.30	0	110.3	23.4	0.21	0.92
0.15	0.25	0	112.5	24.2	0.22	0.93
0.20	0.20	0	108.6	25.0	0.23	1.00
0.25	0.15	0	98.7	25.8	0.26	1.14
0.30	0.10	0	78.1	26.6	0.34	1.48
0.2	0.2	0.7	141.5	223.0	1.58	6.85