Supporting Information for

The thermoelectrochemistry of the aqueous iron(II) / iron(III) redox couple: Significance of the anion and pH in thermogalvanic thermal-to-electrical energy conversion

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Seebeck and Entropy values

Table S1 - Table of data showing the apparent Seebeck Coefficients, S_e, and corresponding difference in entropy between the redox couple, ΔS_{rc}. Values are reported in the absence ("As prepared") and presence ("Acidified") of 1 M of the systems' conjugate acid. All only apply for 0.2 M of the Fe(II) salt and 0.2 M of the Fe(III) and when measured at $\Delta T = 20°C$ ($T_{hot} = 35°C$; $T_{cold} = 15°C$) given the significant temperature and concentration sensitivities of these systems. Error values are the standard deviation of triplicate measurements.

Fe (II/III) system	Seebeck / mV K^{-1}		Entropy / J K^{-1} mol^{-1}	
	As prepared	Acidified	As prepared	Acidified
$[NH_4]FeSO_4$	0.13 ± 0.04	0.84 ± 0.02	13 ± 4	81 ± 2
$FeSO_4$	0.29 ± 0.03	0.90 ± 0.01	28 ± 2	87 ± 1
$FeCF_3SO_3$	1.35 ± 0.04	1.46 ± 0.02	130 ± 4	141 ± 2
$FeNO_3$	1.34 ± 0.02	1.38 ± 0.02	129± 2	133 ± 2

Power and Current Density values

Table S2 – Table of data showing the Short Circuit Current Density and maximum Power Density values for the four Fe(II)/Fe(III) systems (all for 0.2 M Fe(II) and 0.2 M Fe(III), recorded at Au electrodes with $T_{hot} = 35°C$ and $T_{cold} = 15°C$) . Error values are the standard deviation of triplicate measurements.

Fe (II/III) system	Current Density / Am^{-2}		Power Density / mWm^{-2}	
	As prepared	Acidified	As prepared	Acidified
$[NH_4]FeSO_4$	0.327 ± 0.001	0.795 ± 0.001	0.350 ± 0.003	3.45 ± 0.004
$FeSO_4$	0.223 ± 0.001	1.80 ± 0.02	0.340 ± 0.003	7.43 ± 0.003
$FeCF_3SO_3$	3.11 ± 0.02	4.93 ± 0.04	24.1 ± 0.2	39.5 ± 0.3
$FeNO_3$	5.34 ± 0.01	8.80 ± 0.02	38.1 ± 0.1	63.4 ± 0.2

Cyclic voltammetric key values

Table S3 - Table showing the potential of the oxidation peak (E_{ox}), reduction peak (E_{red}) and half-way point between the two peaks (E_{mid}) as well as the peak-to-peak separation for the voltammagrams of the four Fe salts (0.2 M Fe(II) and 0.2 M Fe(III)), in the absence of supporting electrolyte and either in the absence and presence of 1 M conjugate acid. The experimental setup comprised of a 1.6 mm diameter Au working electrode, Pt wire counter electrode *vs*. Ag|AgCl reference electrode at a scan rate of 50 mVs^{-1}.

Fe (II/III) system	E_{ox} / V	E_{red} / V	E_{mid} / V	Peak-to-peak separation / V
$[NH_4]FeSO_4$	0.640	0.185	0.412	0.455
$[NH_4]FeSO_4 + H^+$	0.543	0.355	0449	0.188
FeSO4	0.617	0.234	0.426	0.383
FeSO4 + H+	0.573	0.329	0.451	0.244
FeCF3SO3	0.607	0.400	0.504	0.207
FeCF3SO3 + H+	0.565	0.441	0.503	0.124
FeNO3	0.642	0.363	0.502	0.279
FeNO3 + H+	0.567	0.441	0.504	0.126

Impedance resistance values

Table S4 – Tabulated values of solution resistance (R_s) and electron transfer resistance (R_{ET}) obtained from the electrochemical impedance spectroscopy fitted with the model shown in Figure S4. The electrochemical impedance spectroscopy measurements were carried out for all four Fe salts (0.2 M Fe(II) and 0.2 M Fe(III)), in the isothermal thermoelectrochemical cell at *ca*. 20°C in the absence of supporting electrolyte, in the frequency range of 50,000 Hz to 1 Hz at an amplitude of 20 mV.

Fe (II/III) system	R_s / Ω		R_{ET} / Ω	
	As prepared	Acidified	As prepared	Acidified
$[NH_4]FeSO_4$	67.11 ± 0.21	3.890 ± 0.030	284.80 ± 1.40	482.80 ± 3.50
$FeSO_4$	29.54 ± 0.21	5.350 ± 0.034	323.50 ± 2.81	427.0 ± 2.03
$FeCF_3SO_3$	34.64 ± 0.17	10.440 ± 0.157	151.20 ± 1.13	58.38 ± 1.14
$FeNO_3$	30.29 ± 0.21	8.027 ± 0.095	40.19 ± 0.60	13.15 ± 0.33

Internal thermocell resistance values

Table S5 – Tabulated values of internal thermocell resistance calculated from the current *vs* potential plots (shown in Figure 6), in a non-isothermal thermoelectrochemical cell with ΔT = 20°C (T_{hot} = 35°C and T_{cold} = 15°C).

Fe (II/III) system	R_{cell} / Ω	
	As prepared	Acidified
$[NH_4]FeSO_4$	146.4	266.7
$FeSO_4$	364.6	135.9
$FeCF_3SO_3$	105.1	66.5
$FeNO_3$	62.2	38.0

List of chemicals used for cost analysis

The below table lists the compounds, their pack size and the cost used in the cost analysis. It should be noted that some of the chemicals listed here are not the ones purchased and used in this study, nor the prices paid; actual reagents were gathered from a diverse range of sources over different dates, and subject to internal discounts. Instead, these reagents are those found publically on the Sigma Aldrich website (sigmaaldrich.com; country set to United Kingdom) on 10th August 2018. Where ever possible, the reagents were (i) of ACS Reagent grade, (ii) solid pack sizes were 500 grams and (iii) liquid pack sizes were 2.5 litres. Where not available, the nearest reagent grade and pack size was selected.

There are significant variations in cost as a function of hydration, *e.g.* anhydrous Iron (II) Chloride (250 g, 98%, £441) *vs* Iron (II) Chloride tetrahydrate (250 g, ≥99.0%, £42). Since anhydrous reagents were not required, the (cheaper) hydrated forms were used here. Extremely high purity reagents were also significantly more expensive, but such reagents were neither required nor used in this study.

Notably, all of the trifluoromethanesulfonate materials (both iron salts and the acid) have significantly smaller pack sizes. While this must be detrimental to the overall cost comparison, larger pack sizes were not openly available. Therefore while this disadvantages

these systems, this also represents them suffering significantly at the earliest stages of economy-of-scale considerations, given their general lack of availability.

Table S6 – List of compounds, their pack sizes and the cost used in the cost analysis, as found on the Sigma Aldrich website (sigmaaldrich.com; country set to United Kingdom) on 10th August 2018.

Iron salt	**Grade (purity)[#]**	**Cost / £**	**Pack size / g**
Ammonium Iron (II) Sulfate hexahydrate	ACS (99%)	83.50	500
Ammonium Iron (III) Sulfate dodecahydrate	ACS (99%)	41.00	500
Iron (II) Sulfate heptahydrate	ACS (≥99.0%)	20.00	250*
Iron (III) Sulfate hydrate[¶]	n/a (97%)	100.00	500
Iron (II) Chloride tetrahydrate	puriss (≥99.0%)	43.50	250*
Silver (I) Nitrate	ACS (≥99.0%)	1,090.00	500
Iron (III) Nitrate nonahydrate	ACS (≥98%)	59.50	500
Iron (II) Trifluoromethanesulfonate	n/a (≥85%)	65.30	5*
Iron (III) Trifluoromethanesulfonate	n/a (90%)	30.80	1*
Acid	**Grade (purity)**	**Cost / £**	**Pack size / L**
Nitric Acid	ACS (70%)	204.10	2.5
Sulfuric Acid	ACS (95-98%)	108.80	2.5
Trifluoromethanesulfonic acid	n/a (98%)	117.00	0.059**

[#] The purity of the solid samples was not included when calculating the cost per cell; purity was simply used to ensure comparison of materials of similar grades

* Pack sizes of 500 g were not available; these represent the nearest pack size available on the Sigma Aldrich website.

** Only 100 g (or 59 mL) was available

[¶] Taken as nonahydrate

Example of potential *vs* temperature difference raw data

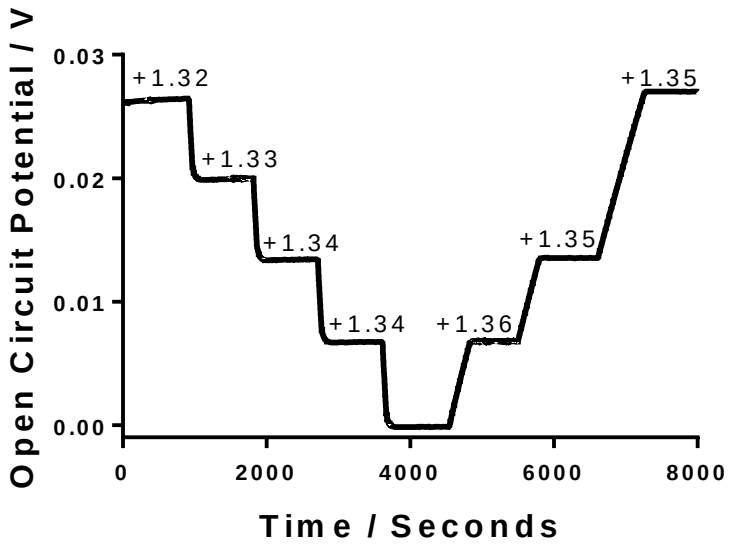

Figure S1 - Raw Data of the Seebeck coefficient measurement of $Fe(NO_3)_{2/3}$ with a changing ΔT of 20 K, 15 K, 10 K, 5 K, 0 K, 5 K, 10 K and 20 K, as clearly shown by steps in the data every *ca.* 1,000 s. The relevant apparent Seebeck Coefficient is indicated for each ΔT value.

Example of potential *vs* time and current *vs* time raw data when drawing power from the cells

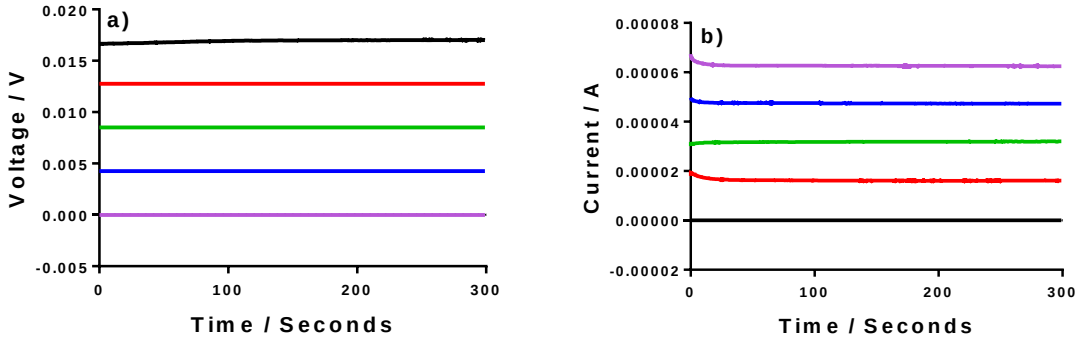

Figure S2 – Corresponding (a) potential and (b) current *vs.* time raw data for $[NH_4]FeSO_4$ (0.2 M Fe(II) and 0.2 M Fe(III)(in the presence of 1 M H_2SO_4 at a ΔT = 20°C (T_{hot} = 35°C and T_{cold} = 15°C); the colours are coded to correspond to the current at each potential over a period of 300 seconds.

Example UV-Vis data for Fe(II) vs Fe(III) features, and $[NO_3]^-$ features

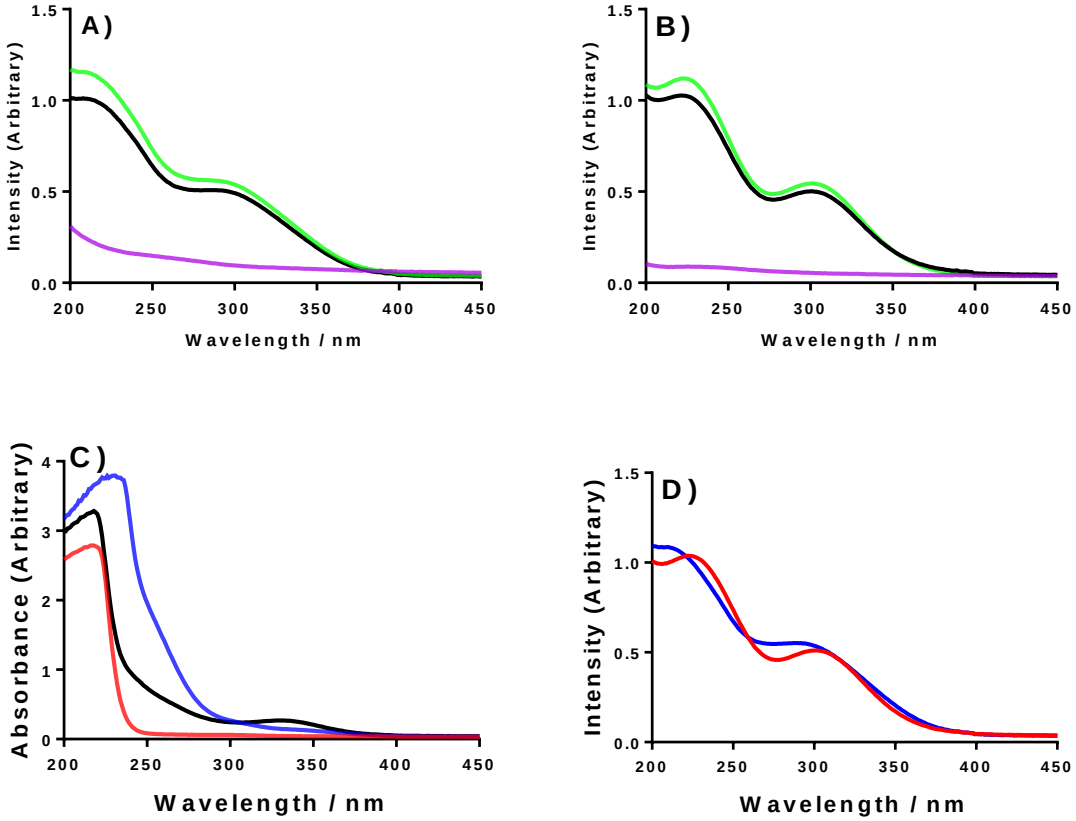

Figure S3 – A) and B) UV-Vis spectra of $FeSO_4$, for 20 mM concentration Fe(II) alone (purple) and 20 mM Fe(III) alone (green) and 20 mM of both Fe(II) and Fe(III) present (black). In the (A) absence and (B) presence of 0.1 M H_2SO_4; this clearly shows that the spectra is dominated by the Fe^{3+} ion. Also shown is (C) spectra of $FeNO_3$ (both Fe^{2+} and Fe^{3+} present at 20 mM concentration of both) and in the presence (blue) and absence (black) of 0.1 M HNO_3. Also shown in (C) is the absorbance of just $NaNO_3$ (red), which shows the peak at 220 nm dominating the spectra is that of the $[NO_3]^-$ anion. Finally, (D) shows the UV-Vis absorption spectra of the $[NH_4]FeSO_4$ system, containing both 20 mM Fe(II) and 20 mM Fe(III), in the absence (blue) and presence (red) of 0.1 M H_2SO_4, demonstrating how the $[NH_4]FeSO_4$ system is similar to that of the $FeSO_4$ system.

Basic EIS model used to fit impedance spectra

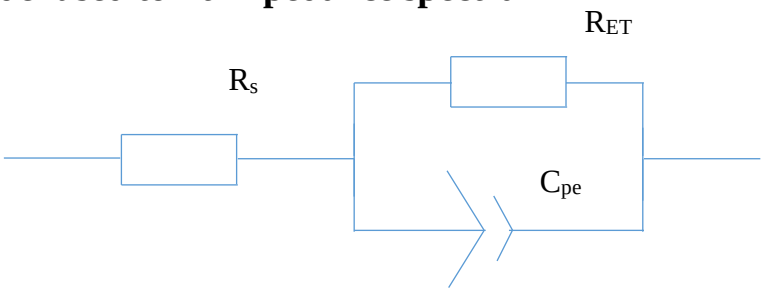

Figure S4 – The model cell used in to fit Impedance data in order to obtain values for R_s and R_{ET}.

Recorded and fit impedance spectra

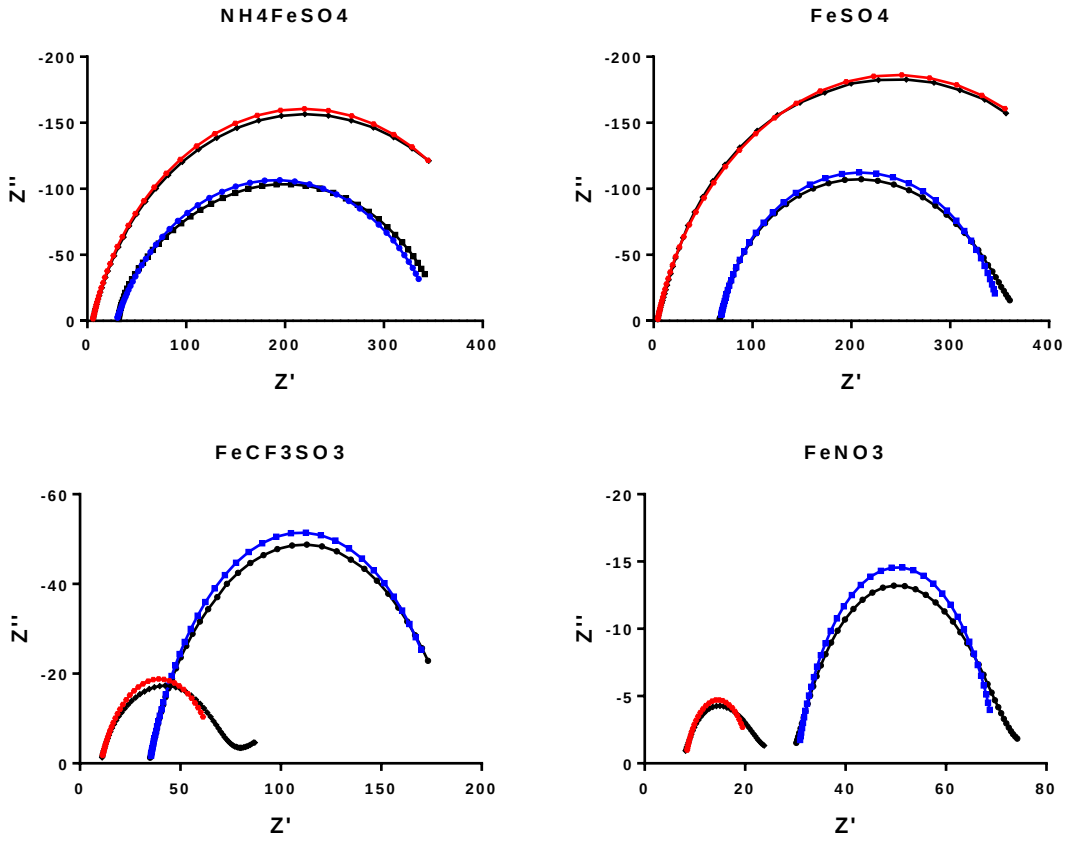

Figure S5 - Electrochemical Impedance Nyquist plots of the four Fe salts (0.2 M of the Fe(II) salt and 0.2 M of the Fe(III), in the isothermal thermoelectrochemical cell at *ca*. 20°C), showing experimental (black) and fitted (coloured) curves, in the absence (blue) and presence (red) of 1 M conjugate acid. The impedance spectra were obtained at the equilibrium potential with a frequency range from 50,000 Hz to 1 Hz and with an amplitude of 20 mV. Fitting was focussed on obtaining R_s and R_{ET} values from the Nyquist Semicircle, and therefore higher frequencies have been truncated. It is important to note the high concentration of redox active species and absence of supporting electrolyte, which is uncommon for Electrochemical Impedance Spectroscopy experiments.