All-iron redox flow battery in flow-through and flow-over set-ups: the critical role of cell configuration

Josh J. Bailey,[a] Maedeh Pahlevaninezhad,[b] H. Q. Nimal Gunaratne,[a] Hugh O'Connor,[a] Kate Thompson,[a] Pranav Sharda,[a] Paul Kavanagh,[a] Oana M. Istrate,[c] Stephen Glover,[c] Peter A. A. Klusener,[d] Edward P. L. Roberts,[*b] Peter Nockemann.[*a]

Supplementary Information

Solubility

Ultraviolet-visible (UV-Vis) spectroscopy and inductively coupled plasma-optical emission spectroscopy (ICP-OES) were used to characterise the solubility of pure $Na_4Fe(CN)_6$ and $K_4Fe(CN)_6$ for comparison with literature values. A saturated solution of $Na_4Fe(CN)_6$ (prepared from a mixture of 0.1 mol of the salt in 100 mL of deionized water) demonstrated concentrations of 0.50 M by UV-Vis and 0.54 M by ICP-OES, which compare well with literature reports of 0.56 M.[68] When repeated for $K_4Fe(CN)_6$, values of 0.72 M and 0.67 M were observed by UV-Vis and ICP-OES, respectively, slightly below the value of 0.76 M reported previously.[68]

Density and viscosity

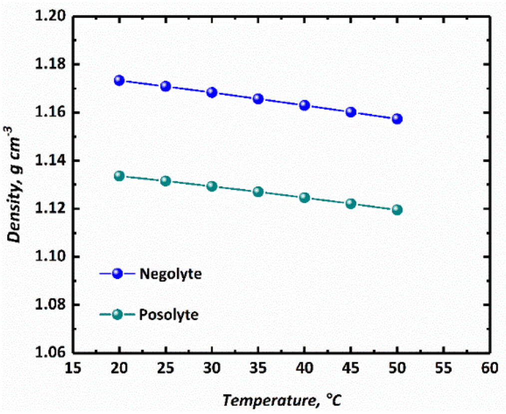

Figure S1: Densities of posolyte (0.25 M $Na_4[Fe(CN)_6]$, 0.25 M $K_4[Fe(CN)_6]$, 1.00 M NaCl) and negolyte (0.50 M $FeCl_3$, 1.00 M BIS-TRIS, 2.50 M NaOH) as a function of temperature.

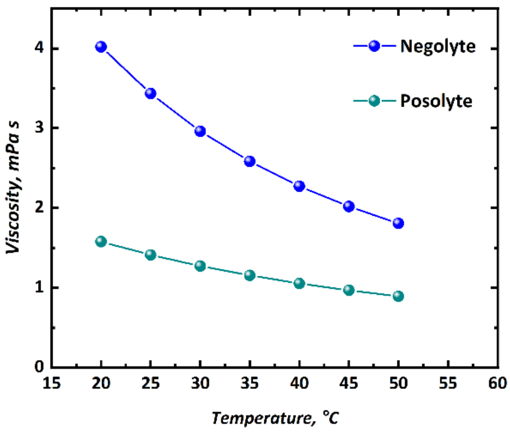

Figure S2: Viscosities of posolyte (0.25 M $Na_4[Fe(CN)_6]$, 0.25 M $K_4[Fe(CN)_6]$, 1.00 M NaCl) and negolyte (0.50 M $FeCl_3$, 1.00 M BIS-TRIS, 2.50 M NaOH as a function of temperature.

Table S1: Negolyte (0.50 M $FeCl_3$, 1.00 M BIS-TRIS, 2.50 M NaOH) density and viscosity as a function of temperature.

Temp. (°C)	Density (g cm^{-3})	Dyn. Viscosity (mPa·s)	Kin. Viscosity (mm^2 s^{-1})
20	1.17334	4.021	3.427
25	1.17090	3.433	2.932
30	1.16834	2.960	2.534
35	1.16570	2.583	2.216
40	1.16299	2.272	1.953
45	1.16020	2.018	1.740
50	1.15734	1.806	1.561

Table S2: Posolyte 0.25 M $Na_4[Fe(CN)_6]$, 0.25 M $K_4[Fe(CN)_6]$, 1.00 M NaCl) density and viscosity as a function of temperature.

Temp. (°C)	Density (g cm^{-3})	Dyn. Viscosity (mPa·s)	Kin. Viscosity (mm^2 s^{-1})
20	1.13360	1.577	1.391
25	1.13153	1.413	1.249
30	1.12933	1.272	1.126
35	1.12702	1.154	1.024
40	1.12462	1.053	0.936
45	1.12212	0.967	0.862
50	1.11951	0.893	0.798

Cross-over

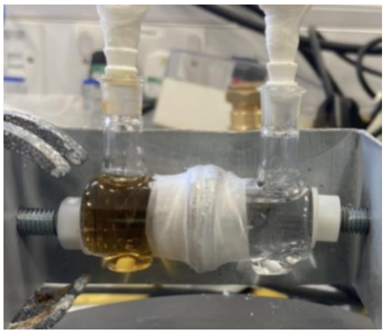

Figure S3: H-Cell set-up used to measure cross-over of negolyte.

Table S3: Iron concentrations by ICP-OES, as a function of time, of 110-times-diluted samples from the deficient side of the H-cell set-up.

Time (h)	Measured Fe concentration in diluted ICP-OES sample (ppm)	Calculated Fe concentration in electrolyte (M)
1	0.64	1.26E-4
2	0.43	8.47E-5
3	0.40	7.88E-5
4	0.36	7.09E-5
68	0.46	9.06E-5
69	0.41	8.08E-5
70	0.41	8.08E-5
71	0.41	8.08E-5

Table S4: Differences between studies carried out by Shin et al. (2022) and the studies carried out in this work.

	Shin *et al.* 2022	**Bailey *et al.* 2024**	**Comment**
Starting material	$Fe_2(SO_4)_3$	$FeCl_3$	May affect complex formed.
OCV	1.43 V	1.28 V	Consistent with a different complex.
Concentration	0.5 M	0.5 M	Unchanged.
M:L:B	1:2:8.6	1:2:5	Assuming x=7.4 for hydrate. This could also affect the complex formed.
Ppt removed	Yes	No	None formed *via* chloride.
$[Fe(CN)]^{3-}$ in posolyte	Yes	No	0.3 M ferricyanide highly likely to be contributing to stability.
Configuration	Flow-through	Flow-through	Unchanged.
Tank volumes	16 mL	25 mL	Longer cycles will adversely affect our stability.
Flow rate	23 mL min^{-1}	50 mL min^{-1}	Significantly higher in our case.
Active area	4 cm^2	5 cm^2	Similar.
Electrode Thickness	4.6 mm	6.5 mm	Multiple electrode pieces used in our cell due to design.
Compression ratio	N/A	*ca.* 53%	Not known how compressed their felt was.
Current density	80 mA cm^{-2}	60 mA cm^{-2}	Highest current density at which both configurations in this work could be cycled was 60 mA cm^{-2}.

M = metal; L = ligand; B = base