

Electronic Supplementary Information

Temperature switch of electrochemical Seebeck coefficient of $\text{Fe}^{2+}/\text{Fe}^{3+}$ via formation of $[\text{FeCl}_4]^{2-}/[\text{FeCl}_4]^-$ complex

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T [°C]	$n_{\text{Fe}^{3+}}$ (reference)	$n_{\text{Fe}^{3+}}$ (sample)	V [mV]										
			1	2	3	4	5	6	7	8	9	m	σ
25	0.1	0.2	11.3	10.8	10.2	9.8	9.9	10.0	10.6	11.2	10.9	10.5	0.5
		0.3	25.6	25.1	24.8	24.4	24.1	23.9	24.0	24.0	23.9	24.4	0.6
		0.4	41.4	41.3	40.9	41.2	41.3	41.3	41.5	41.2	41.4	41.3	0.2
		0.5	48.6	47.7	46.8	45.6	45.6	45.7	45.6	45.6	45.8	46.3	1.1
		0.6	60.0	60.0	59.9	60.0	60.1	60.3	60.3	60.2	60.4	60.1	0.2
		0.7	80.3	79.7	79.6	79.8	79.9	80.0	80.0	79.9	79.8	79.9	0.2
		0.8	96.1	96.5	96.8	96.7	96.6	97.3	97.1	97.5	97.7	96.9	0.5
		0.9	118.4	118.1	118	118.3	118.7	119.1	119.4	119.6	119.9	118.8	0.6
		50	0.1	0.2	23.6	24.8	24.6	23.7	23.3	23.4	23.6	22.8	23.0
0.3	31.6			33.5	33.0	31.6	31.1	30.5	30.5	30.3	30.1	31.4	1.1
0.4	47.1			45.7	45.7	45.9	46.3	47.6	47.7	47.2	47.5	46.7	0.8
0.5	60.4			60.4	59.1	59.5	59.5	59.3	59.7	59.3	60.3	59.7	0.5
0.6	59.8			61.1	61.9	62.2	61.9	62.8	64.0	63.3	63.4	62.3	1.2
0.7	76.8			77.4	78.2	78.3	78.6	79.9	79.5	80.3	80.9	78.9	1.3
0.8	93.3			94.4	94.7	95.4	95.4	95.3	96.1	98.3	101.2	96.0	2.2
0.9	115.7			115.2	115	116.3	117.2	116.8	116.2	116.6	116.3	116.2	0.7

Table S1. Relative potential (V) between the reference and sample DSMO solution containing 0.3vol% 19 M LiCl aqueous solution at T °C. The solutions contain 0.5 (1 – $n_{\text{Fe}^{3+}}$) mM FeCl₂ and 0.5 $n_{\text{Fe}^{3+}}$ mM FeCl₃, where $n_{\text{Fe}^{3+}} [= [\text{Fe}^{3+}]/([\text{Fe}^{2+}]+[\text{Fe}^{3+}])]$ is the molar ratio of Fe³⁺. The V values were measured every five minutes. m and σ represent the mean value and standard deviation, respectively.

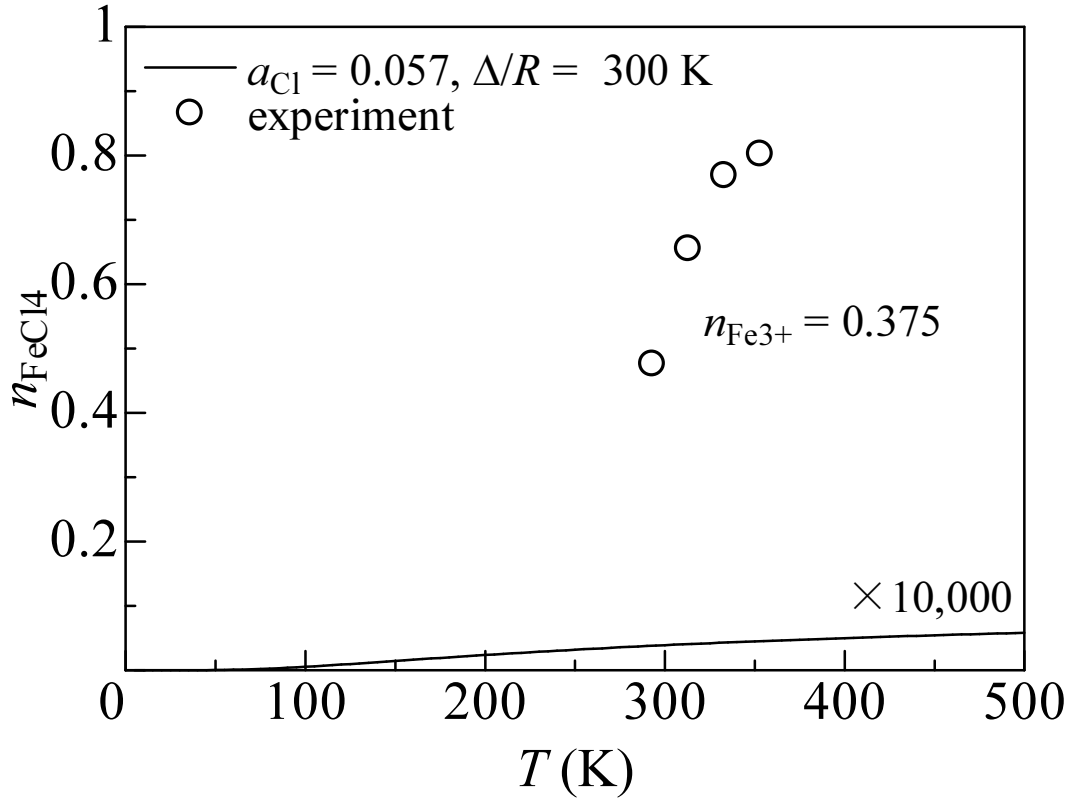


Fig. S1: Calculation of n_{FeCl_4} against temperature (T) based on the equilibrium equation, $[\text{FeL}_6]^{3+} + 4\text{Cl}^- \leftrightarrow [\text{FeCl}_4]^- + 6\text{L}$. Open circles are the experimental data at $n_{\text{Fe}^{3+}} = 0.375$. $n_{\text{Fe}^{3+}}$ is the molar ratio of Fe^{3+} among Fe ions.

We calculated n_{FeCl_4} against T based on the equilibrium equation, $[\text{FeL}_6]^{3+} + 4\text{Cl}^- \leftrightarrow [\text{FeCl}_4]^- + 6\text{L}$. The equilibrium constant K is represented as $K = \exp(-\Delta G/RT) = a_{\text{FeCl}_4} a_{\text{L}}^6 / a_{\text{FeL}_6} a_{\text{Cl}}^4$, where ΔG , R , and a_i is, the standard reaction Gibbs energy, the gas constant, and activity of i , respectively. a_{FeCl_4} , a_{L} , and a_{FeL_6} are $0.0005n_{\text{Fe}^{3+}} + n_{\text{FeCl}_4}$, 1, and $0.0005n_{\text{Fe}^{3+}}(1 - n_{\text{FeCl}_4})$, respectively. After simple calculation, we obtain $n_{\text{FeCl}_4} = a_{\text{Cl}}^4 \exp(-\Delta G/RT) / [1 + a_{\text{Cl}}^4 \exp(-\Delta G/RT)]$. We set a_{Cl} to 0.057 since the average Cl^- concentration ($[\text{Cl}^-]$) in solution is 57 mM. As exemplified by broken curve, the calculation fails to reproduce the experimental data. This is because $a_{\text{Cl}}^4 \exp(-\Delta G/RT) \ll 1$ at any $\Delta G (> 0)$.