

Supporting Information

Electrochemical performance of permanganate considered as active material for catholyte in aqueous alkaline flow batteries

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Author Contributions

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Table of Contents

Experimental Procedure	3
Materials.....	3
Preparation of active materials.....	3
Electrochemical and spectroscopical methods.....	3
Result and Discussion	4
Supplementary Figures (Includes Figure S1 to S6).....	4-9
Supplementary Tables (Includes Table S1 to S3).....	10-12
References	13

Experimental Procedures

Materials.

Sodium permanganate monohydrate (95%), potassium hexacyanoferrate(II) trihydrate (Ferricyanide, 98.5%) and sodium ferrocyanide decahydrate (98.0%) were purchased from Sigma-Aldrich. Bis(hydroxymethyl)-2,2',2''-nitrilotriethanol (BIS-TRIS, 98%) was purchased from Alfa Aesar. Sodium hydroxide (NaOH, 98.0%) and potassium hydroxide (KOH, 93.0%) were purchased from Samchun Chemical (Republic of Korea). All chemicals were used without further purification. Deionized water (DIW) was purified by a Pure Power 1+ (Human corporation, Republic of Korea).

Preparation of active materials.

Fe(BIS-TRIS) as active material for anolyte was synthesized by the recipe of previous literature ¹. First, Fe₂(SO₄)₃ or FeSO₄ was dissolved in DIW, and then, BIS-TRIS ligand was further included to the solution and stirred until the ligand was completely dissolved into the solution. Subsequently, NaOH solution was slowly added to the mixture of Fe and BIS-TRIS to initiate the reaction, and then sufficient stirring was conducted for 24 h to complete the reaction. The precipitated Na₂SO₄ was then separated using centrifugation. The amount of each reagent used for preparing electrolytes of different concentrations was the same as their molar concentrations mentioned in reference ¹.

For preparing active materials for catholyte such as [Fe(CN)₆]⁴⁻ and MnO₄, no special synthetic process was required. Instead, a specific amount of the active materials was dissolved in DIW. For 0.5 M [Fe(CN)₆]⁴⁻ solution, 0.25 M potassium hexacyanoferrate(II) trihydrate and 0.25 M potassium hexacyanoferrate(II) trihydrate were dissolved in a mixed solution of 0.5M NaOH and 0.5M KOH. MnO₄ solution was prepared by dissolving the desired concentration of sodium permanganate monohydrate in 5 M NaOH solution.

Electrochemical and spectroscopical methods.

The electrochemical properties of active materials were evaluated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). These measurements were conducted with a Bio-Logic VSP potentiostat. The experimental setup included a three-electrode cell. The working electrode was a glassy carbon electrode (GCE, 0.1963 cm²), the reference electrode was a Mercury/Mercury oxide (Hg/HgO) electrode, and the counter electrode was a platinum wire. Linear sweep voltammetry (LSV) experiments were conducted under the same condition to cyclic voltammetry (CV) except for the use of rotating disk electrode (RDE, 0.1963 cm²) as working electrode.

The spectroscopical properties of electrolytes containing MnO₄⁻/MnO₄²⁻ ions were measured using UV-VIS spectrophotometer (UV-2600i, Shimadzu). The scanned wavelength range of UV-VIS spectrophotometer was 200 to 800 nm. All samples were diluted with 5 M NaOH solution. The path length of each sample was 1 cm.

The performance of FB single cells was measured using electrolyte storage tanks, unit cells, pumps, and a WBC3000S battery charge/discharge unit. The carbon felt used for these tests was GFD 4.6 whose active area was 6 cm² (purchased from Sigracell). The ion-exchange membrane used was Nafion 212 (purchased from Chemours, USA). This membrane was soaked in DIW for 24 h before use. Electrolyte including Fe(BIS-TRIS) was filled with the anolyte storage tank, while either [Fe(CN)₆]⁴⁻ or MnO₄ was filled with the catholyte storage tank. These electrolytes were then circulated between the electrolyte storage tanks and FB single cells at a flow rate of 23 mL min⁻¹ using Masteflex tubing (purchased from Cole-Parmer Instrument Co). The procedures for evaluating performance of the FB single cells were the same with those used in previous studies ^{1,2}.

Results and Discussion

Supplementary Figures.

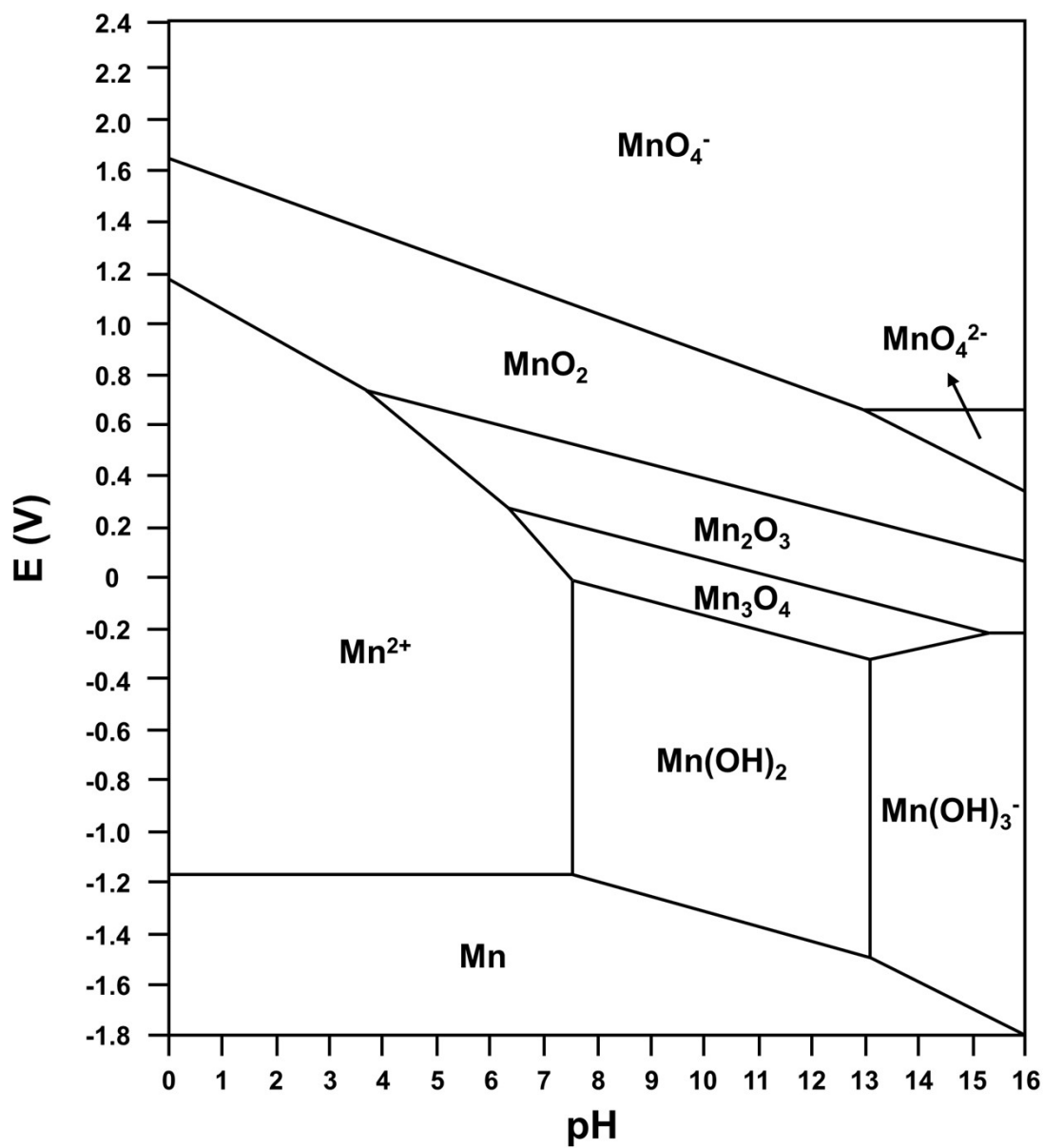


Figure S1. Pourbaix's diagram depicting manganese compounds dissolved in aqueous solution at 25°C.³

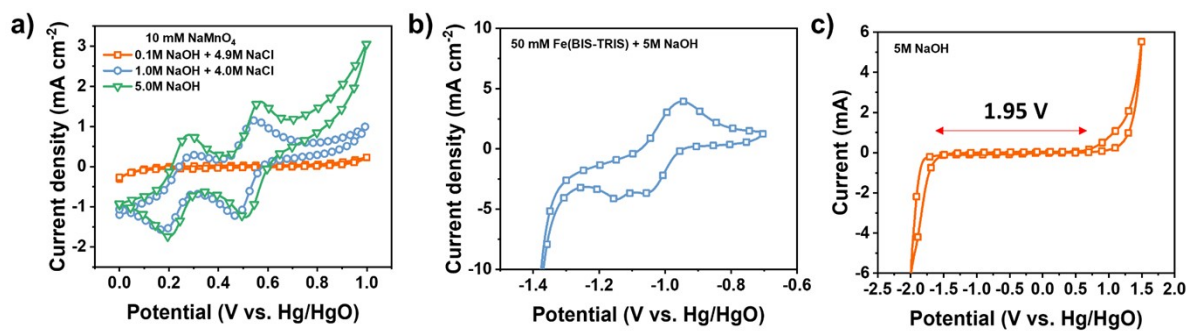


Figure S2. (a) Cyclic voltammogram curves of electrolytes consisting of 10 mM NaMnO₄, 0.1 M NaOH + 4.9M NaCl, 1.0M NaOH + 4.0M NaCl, and 5.0M NaOH solutions. (b) Cyclic voltammogram curve of electrolyte consisting of 50mM Fe(BIS-TRIS) and 5 M NaOH. (c) Electrochemical potential window of 5M NaOH aqueous electrolyte

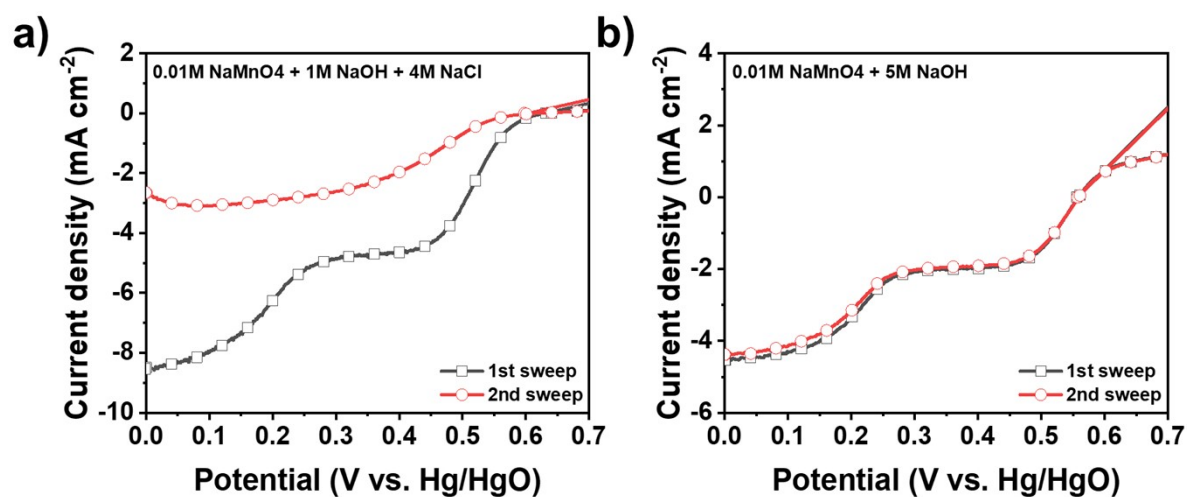


Figure S3. Linear sweep voltammogram curves of electrolytes consisting of 10mM NaMnO₄ and a) 1.0M NaOH + 4.0M NaCl and, b) 5.0M NaOH solutions measured with the use of rotating disk electrode.

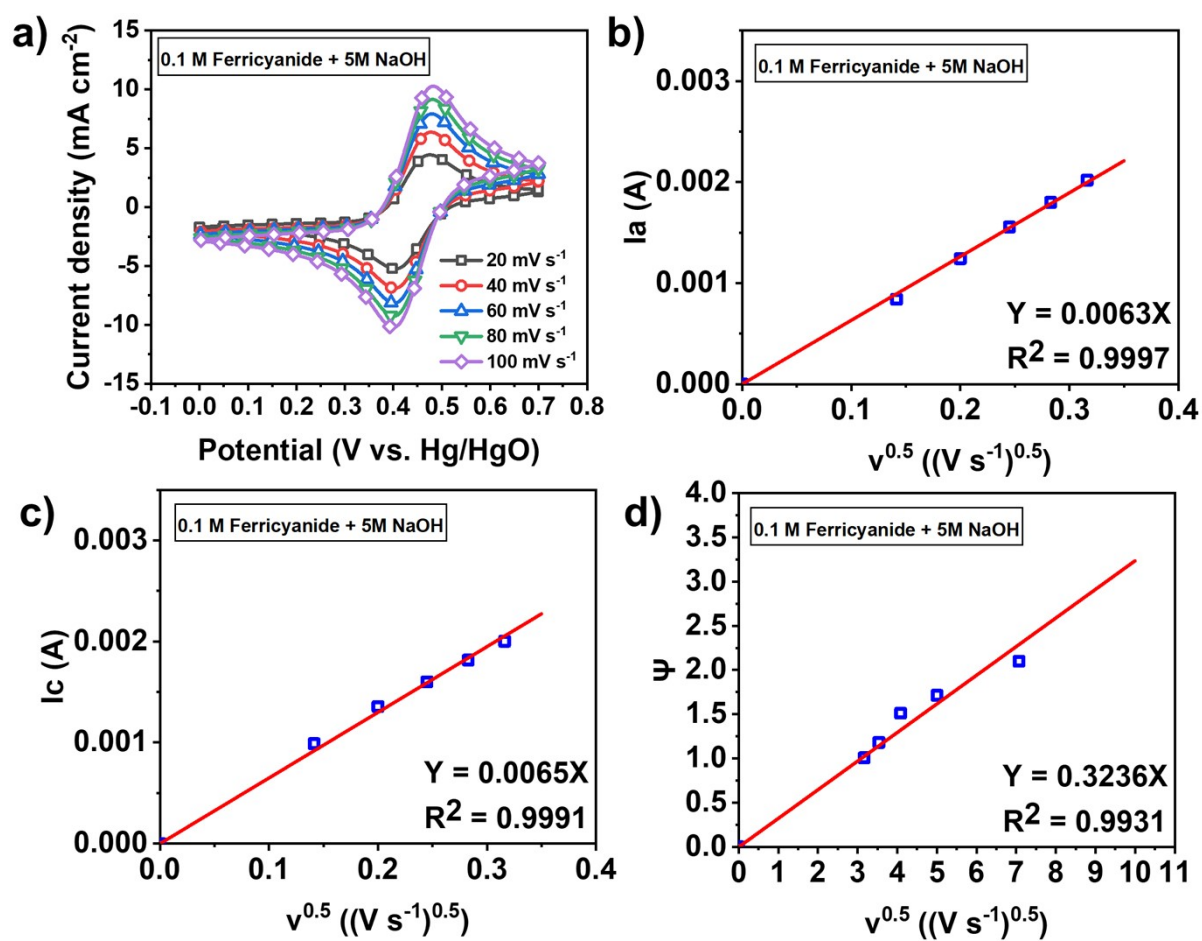


Figure S4. a) Cyclic voltammogram curves of electrolytes consisting of 0.1M Na₃Fe(CN)₆ and 5M NaOH. Here, potential scan rate used was 20, 40, 60, 80, 100 mV s⁻¹. Relationships between square root of scan rate and b) anodic peak current, c) cathodic peak current, d) Ψ value for experiments of electrolyte consisting of 0.1M Na₃Fe(CN)₆ and 5M NaOH.

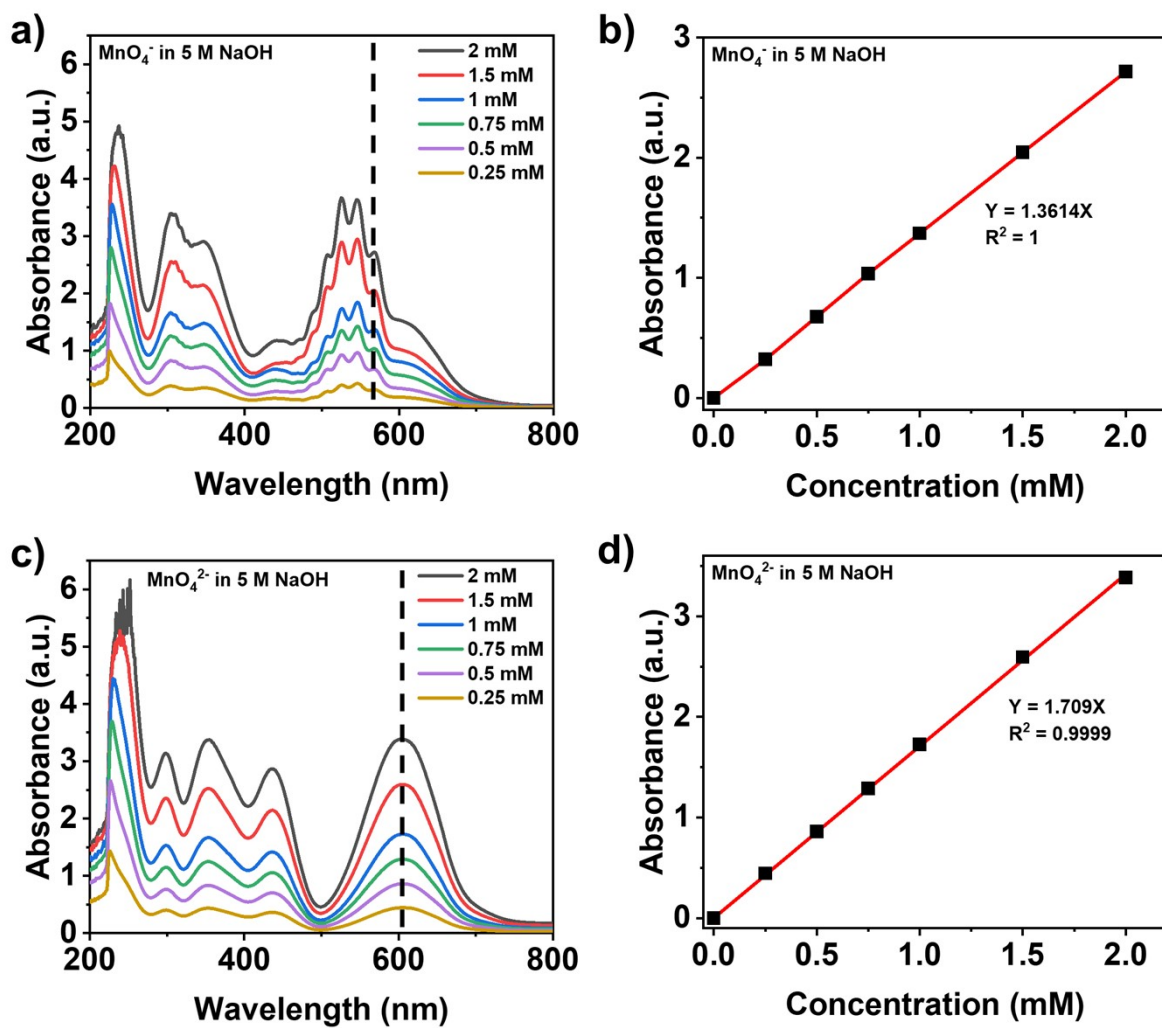


Figure S5. UV-VIS spectra of (a) NaMnO_4 and (c) Na_2MnO_4 dissolved in 5M NaOH aqueous electrolytes. Graphs of absorbance peaks versus concentration measured at (b) 569 nm (NaMnO_4) and (d) 606 nm (Na_2MnO_4).

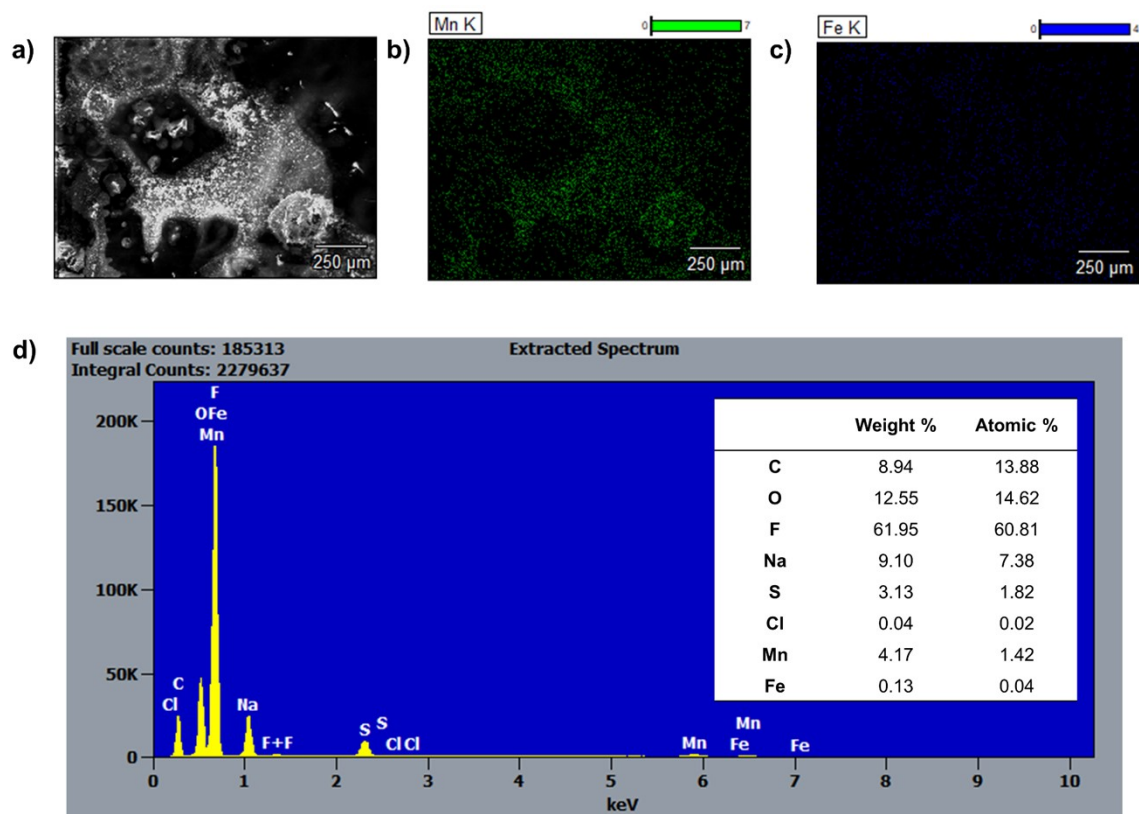


Figure S6. a) SEM image of Nafion 212 membrane, images taken by energy-dispersive X-ray spectrometer of b) Mn and c) Fe elements, and d) analysis of elements of Nafion 212 membrane collected after cycling test of Fe-Mn FBs.

Supplementary Tables.

Table S1. D and k_0 calculated using Randle-Sevcik's equation and Nicholson's Method of electrolytes consisting of (i) 0.1M $\text{Na}_3\text{Fe}(\text{CN})_6$ and 1M NaOH, (ii) 0.1M $\text{Na}_3\text{Fe}(\text{CN})_6$ and 5M NaOH, and (iii) 0.1M NaMnO_4 and 5M NaOH.

Electrolytes	D_O ($\text{cm}^2 \text{s}^{-1}$)	D_R ($\text{cm}^2 \text{s}^{-1}$)	D_{Avg} ($\text{cm}^2 \text{s}^{-1}$)	k^0 (cm s^{-1})
0.1M $\text{Na}_3\text{Fe}(\text{CN})_6$ + 1M NaOH	$1.92 \cdot 10^{-6}$	$3.24 \cdot 10^{-6}$	$2.58 \cdot 10^{-6}$	$1.06 \cdot 10^{-3}$
0.1M $\text{Na}_3\text{Fe}(\text{CN})_6$ + 5M NaOH	$1.44 \cdot 10^{-6}$	$1.52 \cdot 10^{-6}$	$1.48 \cdot 10^{-6}$	$4.35 \cdot 10^{-3}$
0.1M NaMnO_4 + 5M NaOH	$2.08 \cdot 10^{-6}$	$3.32 \cdot 10^{-6}$	$2.70 \cdot 10^{-6}$	$5.03 \cdot 10^{-3}$

Table S2. Resistances measured from Nyquist plots of electrolytes consisting of (i) 0.01M $\text{Na}_3\text{Fe}(\text{CN})_6$ and 1M NaOH, (ii) 0.01M $\text{Na}_3\text{Fe}(\text{CN})_6$ and 5M NaOH, and (iii) 0.01M NaMnO_4 and 5M NaOH.

Electrolytes	R_s (Ohm cm^2)	R_{ct} (Ohm cm^2)
0.01M $\text{Na}_3\text{Fe}(\text{CN})_6$ + 1M NaOH	1.576	39.32
0.01M $\text{Na}_3\text{Fe}(\text{CN})_6$ + 5M NaOH	0.713	19.48
0.01M NaMnO_4 + 5M NaOH	0.971	9.501

Table S3. Comparison table of performances of various iron and manganese-based flow batteries

Reference	Anolyte	Catholyte	OCV (V)	Membrane	Current density (mA cm ⁻²)	N/P ratio	Energy efficiency (%)	Capacity (Ah L ⁻¹)	MPD (mWh cm ⁻²)
4	Fe(DIPSO)	Co(TiPA)	0.9	Nafion 117	60	0.75	64.2	15.5	-
2	Fe(BIS-TRIS)	Ferrocyanide	1.43	Nafion 212	80	0.63	70.9	11.6	223
	Fe(DIPSO)	Ferrocyanide	1.36	Nafion 212	80	0.63	73.2	12	211
5	Fe(DIPSO)	Ferrocyanide	1.36	Nafion 212	80	0.59	82	9.9	310
1	Fe(BIS-TRIS)	Ferrocyanide	1.43	Nafion 212	80	4	76.9	40.4	-
6	Fe(TEA)	Co(TEA)	0.95	Nafion 117	40	1	60	11.1	61.31
7	Fe(TiPA)	Co(TiPA)	0.96	Nafion 117	40	1.25	77	14.5	81.3
8	Fe(TEA)MM	Ferrocyanide	1.37	SPEEK membrane	80	0.5	80.5	10.7	427
9	Fe-glutamate	Ferrocyanide	1.19	SPEEK membrane	40	1	90.3	23.2	459.4
10	Cr(PDTA)	Ferrocyanide	1.54	Nafion 212	100	0.53	78.1	8.58	515
11	Fe-DMSO	Fe-DMSO	1.21	KMVF 2125	30	1	75	21.5	134
12	Fe-racEDDHA	Ferrocyanide	0.83	Nafion324	20	0.76	68	4.56	44.5
13	Zinc	EDTA-Mn	1.66	perfluorinated sulfonic acid membrane	20	- (zinc plate used)	75	4.67	90
14	K ₂ S ₂	Mn(Ac) ₂	1.74	CRIS membrane	10	1.5	-	38	-
15	Zinc	Mn(Ac) ₂	1.78	Nafion 115	40	- (zinc plate used)	78	9	-
16	(Spr) ₂ V	Mn ^{III} W ₁₂ O ₄₀	1.14	Nafion 212	20	1.7	71.29	10.2	68.0

17	FeCl ₂	MnCl ₂	1.57	Nafion 117	7	1	67.2	0.132	-
18	FeCl ₃	MnSO ₄	0.7	SPEEK membrane	30	1	55	1.62	70
19	Mn(CN) ₆	Ferrocyanide	1.56/0.73	Nafion 212	30	2.5	70.1	4.5	-
This work	Fe(BIS-TRIS)	Permanganate	1.58	Nafion 212	40	1	91.9	13.4	590.13
					80		84.7	12.7	
					40		71.5	38.1	-

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