

Electronic Supplementary Information (ESI †)

Viologen-based aqueous organic redox flow battery: material synthesis, property, and cell performance

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Table S1. The performance of different AORFBs based on viologens

Anode	Cathode	Electrode	Concentration (M) (Supporting electrolyte)	Flow rates	Membrane	Voltage(V)	Power Density (mW/cm ²)	Energy Density (Wh/L)	CE(%) (Current Density /mA cm ⁻²)	EE(%) (Current Density /mA cm ⁻²)	Ref.
MV	4OH-TEMPO	Graphite felt electrodes (SGL Carbon Group, Germany)	0.5 (1.5M NaCl)	20 mL min ⁻¹	Selemion AEM	1.25	-	8.4	99.8% (60)	62.5% (60)	1
MV	TEMPTMA	Graphite felt electrodes(SG L GFA6, 6mm dry thickness	2.0 (-)	20 mL min ⁻¹	Fumasep FAA-3-PE-30	1.4	-	38	~100% (80)	~70% (60)	2
MV	FcNCl	Graphite felt electrodes (SGL Carbon Group, Germany)	0.5 (2.0M NaCl)	60 mL min ⁻¹	Selemion AMV	1.06	125	7	~100% (60)	~60% (60)	3
EV+ α -CD	FcNEBr	-	1.0 (-)	60 mL min ⁻¹	Selemion AMV	1.06	-	-	>99.5% (20- 40)	59.8% (40)	4
(NPr) ₂ V	N ^{Me} -TEMPO	Graphite felt electrodes (SGL Carbon Group, Germany)	0.5 (0.5M NaCl)	60 mL min ⁻¹	Selemion AMV	1.38	134.0	-	~100% (60)	61.3% (60)	5
BTMAP-Vi	TMAP-TEMPO	Sigracet SGL 39AA carbon paper	0.1 (1.0M NaCl) 0.5 (1.0M NaCl) 1.5 (1.0M NaCl)	60 rpm	Selemion AMV	1.19	99.03	-	> 99.73% (40)	~65% (40)	6
BTMAP-Vi	TMAP-TEMPO			60 rpm	Selemion AMV	1.19	134	-	> 99.9% (100)	~60% (100)	6
BTMAP-Vi	TMAP-TEMPO			60 rpm	Selemion AMV	1.19	~100	-	~100% (100)	~50%(100)	6

BTMAP-Vi	BTMAP-Fc	Sigracet SGL 39AA porous carbon paper	0.75 (-)	60 mL min ⁻¹	Selemion DSV	0.748	60	13	>99.9% (50)	66.3% (50)	7
BPP-Vi	Ferrocyanide	Sigracet SGL 39AA porous carbon paper	1.0 (14.0M NH ₄ OH)	60 mL min ⁻¹	Nafion 117	0.9	143	11.8	>99.0% (10-150)	70% (100)	8
(SPr) ₂ V	KI	Graphite felt electrodes (SGL Carbon)	0.5 (2.0 M KCl)	60 mL min ⁻¹	Nafion	0.86	67.5	-	~100% (60)	58% (60)	9
(SPr) ₂ V	KI	Group, Germany)	0.5 (2.0 M KCl)	60 mL min ⁻¹	Selemion CSO	1.0	92.5	-	~100% (60)	67% (60)	9
Diquat 5	FcNCl	GFD3 electrodes	0.5 (1.5 M NaCl)	50 mL min ⁻¹	Selemion AMV	1.12	-	-	98.4% (5)	84.1% (5)	10
Vi-OEG3	FcNEBr	Graphite felt (GFD 4.6 EA, SGL, Germany)	0.5 (1.0 M NaBr)	50 mL min ⁻¹	AMV	0.9	-	-	>99.6% (20 -50)	56.64% (50)	11
BHOP-Vi	FcNCl	Sigracet SGL 39AA carbon paper	2.0 (1.0M NaCl)	-	Selemion DSV	1.021	110.87	-	~100% (80-140)	~70% (80)	12
Dex-Vi	BTMAP-Fc	Graphite felt electrodes (GFD 3 EA, SIGRACELL®)	1.5 (1.0M NaCl)	20 mL min ⁻¹	Selemion DSV	1.021	-	-	~100% (25)	75% (50)	13
BSP-Vi	DS-Fc	Carbon felts(Sigracet SGL39AA) 4.6 mm thick	1×10 ⁻² (0.5 M NaNO ₃)	100 mL min ⁻¹	Nafion N212	1.3	-	14	98% (5.33)	97% (5.33)	14
[(DMAE-Pr) ₂ -Vi]Cl ₄	4-OH-TEMPO	Sigracell GDF 4,6 EA carbon felt (SGL)	0.1 (1.0 M KCl)	50 rpm	Fumasep FAS-30	1.15	-	-	~100% (40)	78% (60)	15

R-Vi	K ₄ [Fe(CN) ₆]	Carbon) Commercial carbon felt electrode	0.5 (1.0M KCl) 90 mL min ⁻¹	Nafion	1.05	117	-	~100%(60-140)	76% (80)	16		
(CBu) ₂ V	(CBu) ₂ V	- 0.5 (0.5M (NH ₄) ₄ [Fe(CN) ₆ -])		Selemion CSO	0.89	85	9.5	>99.9% (20- 100)	70% (60)	17		
3,4-S ₂ V	(NH ₄) ₄ [Fe(CN) ₆]	Graphite felt electrodes (SGL Carbon Group, Germany)	1.1 (1.0M NH ₄ Cl)	60 mL min ⁻¹	Selemion CSO	0.88	99.5	13.0	>99.9% (40)	66% (40)	18	
₂	₂	[(bpy(CH ₂) ₃ NMe ₃)]I [(bpy(CH ₂) ₃ NMe ₃)]I	Graphite-plate electrodes	0.8 (-)	23 mL min ⁻¹	Microporous membrane	1.38	-	0.79	90% (10)	70% (20)	19
Viologen polymer	TEMPO-polymer	Graphite felt electrodes (GFA6, SGL)	0.37 (2.0M NaCl)	20 mL min ⁻¹	Dialysis membrane	1.1	-	9.0	~97.5% (40)	75-80% (40)	20	

Table S2. The lifetime of different AORFBs based on viologens

Anode	Cathode	Electrode	Concentration (M) (Supporting)	Flow rates	Applied current density	Capacity Decay rate	Duration	Ref
MV	4OH-TEMPO	Graphite felt electrodes (SGL 0.5 (1.5M NaCl) Carbon Group, Germany)		20 mL min ⁻¹	60	19.60%	~13h	1
MV	TEMPTMA	Graphite felt electrodes(SGL 2.0 (-) GFA6, 6mm dry thickness		20 mL min ⁻¹	80	1.11%	~237 h	2
MV	FcNCl	Graphite felt electrodes (SGL 0.5 (2.0M NaCl) Carbon Group, Germany)		60 mL min ⁻¹	60	0.53%	~406h	3
EV+ α -CD	FcNEBr	-	0.5 (-)	60 mL min ⁻¹	10	0.32%	216h	4
EV+ α -CD	FcNEBr	-	1.0 (-)	60 mL min ⁻¹	10	0.54%	288h	4
(NPr) ₂ V	N ^{Me} -TEMPO	Graphite felt electrodes (SGL 0.5 (0.5M NaCl) Carbon Group, Germany)		60 mL min ⁻¹	60	0.09%	~269h	5
BTMAP-Vi	TMAP-TEMPO	Sigracet SGL 39AA carbon	0.5 (1.0M NaCl)	60 rpm	100	1.47%	80.6h	6
BTMAP-Vi	TMAP-TEMPO	paper	1.5 (1.0M NaCl)	60 rpm	100	0.51%	171.7h	6
BTMAP-Vi	BTMAP-Fc	Sigracet SGL 39AA carbon paper	0.75 (1.0M NaCl)	60 mL min ⁻¹	50	0.033%	~398h	7
BPP-Vi	Ferrocyanide	Sigracet SGL 39AA carbon paper	1.0 (14.0M NH ₄ OH)	60 mL min ⁻¹	40	0.016%	312h	8
(SPr) ₂ V	KI	Graphite felt electrodes (SGL 0.5 (2.0 M KCl) Carbon Group, Germany)		60 mL min ⁻¹	60	7.34%	~112h	9
(SPr) ₂ V	KI		0.5 (2.0 M KCl)	60 mL min ⁻¹	60	6.44%	~48h	9
Diquat 5	FcNCl	GFD3 electrodes	0.5 (1.5 M NaCl)	50 mL min ⁻¹	5	0.80%	597h	10

Vi-OEG3	FcNEBr	Graphite felt (GFD 4.6 EA, SGL, Germany)	0.5 (1.0 M NaBr)	50 mL min ⁻¹	30	0.00253%	144h	11
BHOP-Vi	FcNCl	Sigracet SGL 39AA carbon paper	2.0 (1.0M NaCl)	-	100	1.128%	~115h	12
Dex-Vi	BTMAP-Fc	Graphite felt electrodes (GFD 3 EA, SIGRACELL®)	1.5 (1.0M NaCl)	20 mL min ⁻¹	25	0%	720h	13
BSP-Vi	DS-Fc	Carbon felts(Sigracet SGL39AA)	1×10 ⁻² (0.5 M NaNO ₃)	100 mL min ⁻¹	2.67	5.52%	~73h	14
(CBu) ₂ V	(NH ₄) ₄ Fe(CN) ₆	-	0.9 (0.5M (NH ₄) ₄ [Fe(CN) ₆])	-	40	0%	1200h	17
3,4-S ₂ V	(NH ₄) ₄ [Fe (CN) ₆]	Graphite felt electrodes (SGL Carbon Group, Germany)	1.1 (1.0M NH ₄ Cl)	60 mL min ⁻¹	40	0.045%	1200h	18
[(bpy(CH ₂) ₃ NMe ₃)]I ₂ [(bpy(CH ₂) ₃ NMe ₃)]I ₂		Graphite-plate electrodes	0.8 (-)	23 mL min ⁻¹	10	3.53%	~3.4h	19
Viologen polymer	TEMPO-polymer	Graphite felt electrodes (GFA6, SGL)	0.37 (2.0M NaCl)	20 mL min ⁻¹	40	0.4%	~13h	20

Table S3. Comparison of viologen-based AORFBs with other state-of-the-art AORFBs

Anode	Cathode	Electrolyte	Solubility Concentration		AORFBs Performance					Ref.
			(M)	(M)	Voltage (V)	Energy Density (Wh L ⁻¹)	Peak Power Density (mW cm ⁻²)	EE (%) (Current Density /mA cm ⁻²)	Capacity Decay Rate	
V(II)	MB	3.5M H ₂ SO ₄	~1.7	1.0	-	-	-	73 (100)	0% per day in 24 days	21
2,3-O-DBAP	K ₄ [Fe(CN) ₆]	2M KOH	0.6	0.5	1.12	18.5	110	52.4 (100)	0.066% per day in 62 days	22
1,8-PFP	K ₄ [Fe(CN) ₆]	1M KOH	2.05	1.0	1.15	-	94	~60 (50)	0% per day in 53 days	23
Zn	PSPR	1M KCl	1.4	0.5	1.0/1.8	-	53	76.5 (20)	0% per day in 15 days	24
BHPC	K ₃ [Fe(CN) ₆]	1M KOH	1.55	1.0	1.27	9.5	430	~80 (100)	0.08% per day	25
1,6-DPAP	K ₄ [Fe(CN) ₆]	1M KCl	1.005	1.0	~1.06	-	103	~96.5 (100)	0.0015% per day	26
2,6-DBEAQ	K ₃ [Fe(CN) ₆]	1M KOH	1.1	0.5	1.05	17	240	80 (100)	0.0075% per day in 28 days	27
2,3-HCNQ	K ₄ [Fe(CN) ₆]	1M NaOH	1.2	1.0	1.02	-	255	68.8 (100)	3.4% per day in 1.5 days	28
DPIvOHAQ	K ₄ [Fe(CN) ₆]	1M KCl	0.74	0.5	0.98	-	340	91.5 (50)	0.0018% per day in additional 16 days (pH=14)	29
1,3,5,7-THAQ	K ₄ [Fe(CN) ₆]/K ₃ [Fe(CN) ₆]	2M KOH	1.88	1.0	~1.18	20	360	75 (100)	0.35% per day	30
2,6-DHAQ	K ₄ [Fe(CN) ₆]	1M KOH	>0.6	0.5	1.20	8.04	400	84 (100)	10% after 100 cycles	31
AADA	K ₄ [Fe(CN) ₆]	2M NaOH	2.0	0.8	1.06	-	-	87.6 (10)	0.05% per cycle in 500 cycles	32
4C7SFL	K ₄ [Fe(CN) ₆]	1M NaOH	1.5	1.36	3.04	-	-	77.6 (60)	0.0209% per day in 120 days	33
MV	TEMPTMA	2M NaCl	3.0	0.5	1.06	7	125	~60 (60)	0.53% per day	3
BPP-Vi	K ₄ [Fe(CN) ₆]	1M KCl	1.23	1.0	0.90	11.8	143	70 (100)	0.016% per day	8
(CBu) ₂ V	K ₄ [Fe(CN) ₆]	2M NH ₄ Br	2.1	0.9	0.89	9.5	85	70 (60)	0% per day in 50 days	17
Dex-Vi	BTMAP-Fc	1M NaCl	2.0	1.5	~0.712	-	-	75 (50)	0% per day in 30 days	13

(PPBPy)Br ₂	PSS-TEMPO	2M NaCl	1.1	0.45	1.606	-	509	76 (100)	0% per day in 11 days	34
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