

Supporting Information

Advancements towards optimization of metal-organic frameworks-based polymer electrolyte membranes for aqueous redox flow batteries

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Table S1 Cell performance of Inorganic-based ARFBs

Type	Positive	Negative	Electrolyte	E_{Cell} (V)	EE (%)	Ref
Vanadium-Based	$VO_2^+ + e^- \leftrightarrow VO^{2+}$	$V^{2+} \leftrightarrow V^{3+} + e^-$	1.7-2M V in 1.5-5M H ₂ SO ₄ , HCl, H ₃ PO ₄ , and CH ₃ SO ₃ H	1.26	82-87	1-3
Zn-Br	$Br_2 + 2e^- \leftrightarrow 2Br^-$	$Zn \leftrightarrow Zn^{2+} + 2e^-$	2M ZnBr ₂ -3M KCl-0.8M MEP and 2.25M ZnBr ₂ -0.5M ZnCl ₂ -0.8M MEP+Br ₂	1.85	69.4-82.1	4-6
Zn-I ₂ (Zn-I ₂ Br)	$I_3^- + 2e^- \leftrightarrow 3I^-$	$Zn \leftrightarrow Zn^{2+} + 2e^-$	0.5-5.0M ZnI ₂	0.9-1.27	67.8-91	7
	$I_3^- + 2e^- \leftrightarrow 3I^-$	-	7.5M KI-3.75M ZnBr ₂	1.35	81	8
	-	-	2-6M KI+1-3 M ZnBr ₂	1.33	80	9
	$2I^- + Br^- \leftrightarrow I_2Br^- + Zn^{2+} + 2e^- \leftrightarrow Zn$	$Zn \leftrightarrow Zn^{2+} + 2e^-$	5M ZnI ₂ -2.5M ZnBr ₂	1.35	NA	10
Zn-Ce	$Zn \leftrightarrow Zn^{2+} + 2e^-$	$2Ce^{4+} + 2e^- \leftrightarrow 2Ce^{3+}$	1.5M Zn(CH ₃ SO ₃) ₂ /0.2M Ce(CH ₃ SO ₃) ₃ in 0.5M CH ₃ SO ₃ H	2.43	75	11
Alkaline Zn-I ₂	$I_3^- + 2e^- \leftrightarrow 3I^-$	$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn$	Zn plate in 6M KOH 6M KI-6M I ₂	1.79	80	12
	$Fe(CN)_6^{4-} \leftrightarrow Fe(CN)_3^3$	$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn$	1.0M Na ₄ Fe(CN) ₆ -3M KOH 0.5M Zn(OH) ₄ ²⁻ -4M NaOH	1.74	89	13
Alkaline Zn-Fe						

	$Fe(CN)_6^{4-} \leftrightarrow Fe(CN)_6^{3-}$, $Zn(OH)_4^{2-} + 2e^- \rightarrow Zn$	0.4M Zn(OH) ₄ ²⁻ + 3M NaOH 0.8M Na ₄ Fe(CN) ₆ +3M KOH	1.81	87.72	14
Zn-Fe	$2Fe^{3+} + 2e^- \leftrightarrow 2Fe^{2+}$ $Zn(OH)_4^{2-} + 2e^- \rightarrow Zn$	0.3M Na ₂ [Zn(OH) ₄] ⁻ 0.5 M NaCl-2.4M NaOH 0.6M FeCl ₂ -0.5M NaCl-1M HCl	≈1.7	75.9	15
Neutral Zn-Fe	$Fe^{3+}(Gly)_2 + e^- \leftrightarrow Fe^{2+}$ $Zn^{2+} + 2e^- \leftrightarrow Zn$	0.8M ZnBr ₂ -2.0M KCl 1.6M FeCl ₂ - 3.2M glycine-2.0 M KCl	1.4	84	16
Acidic Zn-Fe	$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ $Zn^{2+} + 2e^- \leftrightarrow Zn$	1M ZnSO ₄ -1.5M HAc/NaAc 1M FeCl ₂ -1.5M H ₂ SO ₄ 1.6M ZnCl ₂ -0.8M FeCl ₂ -2M NH ₄ Cl- 2gL ⁻¹ PEG8000	1.53	71.1	17
Fe-Cr	$Fe^{2+} + e^- \leftrightarrow Fe^{3+}$ $Cr^{2+} \leftrightarrow Cr^{3+} + e^-$	Iron-based 1M FeCl ₂ /1M CrCl ₃ in 2-3M HCl	1.18	73	19
Fe-V	$Fe^{2+} + e^- \leftrightarrow Fe^{3+}$ $V^{2+} \leftrightarrow V^{3+} + e^-$	1M FeCl ₂ in 2M HCl/2M V in 4M H ₂ SO ₄	1.02	80	20
All-Iron	$Fe^{2+} + e^- \leftrightarrow Fe^{3+}$ $Fe^{2+} + 2e^- \leftrightarrow Fe$	FeCl ₂ (Negative) FeCl ₂ & FeCl ₃ (Positive)	1.21	>45	21
	$Fe(CN)_6^{3-} + e^- \leftrightarrow Fe([Fe(TEOA)OH]^- + e^-)$	Fe-TEOA in 0.8M alkaline (Negative)	1.22	73	21
	$Fe(CN)_6^{3-} + e^- \leftrightarrow Fe([Cr(PDTA)]^- + e^-)$	chrome alum with PDTA in the presence of KOH and buffered at pH 9.5 with 0.2 M KB _i (Negative) K ₃ Fe(CN) ₆ and K ₄ Fe(CN) ₆ (0.75 M total Fe conc.) and buffered with 25 mM KB _i (Positive)	2.13	76-80	22
Fe-organic complex	$[Co(mTEA)(H_2O)] + [Fe(TEOA)OH]^- + e^-$	cobalt with 1- [Bis(2- hydroxyethyl)amin o]-2-propanol in 5M NaOH (Positive) iron with triethanolamine in	0.93	71	23

				5 M NaOH (Negative)	M	NaOH			
Polysulphide-based									
Polysulphide-Bromine (PSB)	$Br_2 + 2e^- \leftrightarrow 2Br^-$	$S_4^{2-} + 2e^- \leftrightarrow 2S_2^{2-}$		5M NaBr/ Na ₂ S ₅ and NaOH	1.3M	1.36	72		24
Polysulphide-Iodine(PSIB)	$I_3^- + 2e^- \leftrightarrow 3I^-$	$2S^{2-} \leftrightarrow S_2^{2-} + 2e^-$		2-6M KI+2-3.3M K ₂ S ₂		1.05	63-73		25
Polysulphide-Iron	$Fe(CN)_6^{3-} + e^- \leftrightarrow Fe(\frac{1}{2}S_4^{2-} + e^- \leftrightarrow S_2^{2-})$			1M K ₃ Fe(CN) ₆ -1M Na ₂ S ₂		0.91	74		26
Air-breathing S-O ₂	Acidic catholyte: $2H_2O \leftrightarrow O_2 + 4H^+ + e^-$	$xS_y^{2-} + 2(y-x)e^- \leftrightarrow$ Alkaline catholyte: $4OH^- \leftrightarrow O_2 + 2H_2O + xS_y^{2-} + 2(y-x)e^- \leftrightarrow$		1M Li ₂ S ₄ -1M LiOH or NaOH (Negative) 1M Li ₂ SO ₄ or Na ₂ SO ₄ -0.1 or 0.5M		1.26	-		27
Polysulphide-polybromine	$Br_3^- + 2e^- \leftrightarrow 3Br^-$	$2S^{2-} \leftrightarrow S_4^{2-} + 2e^-$		Solid state electrolyte (NASICON)		1.55	≈50		
Polysulphide-polyiodide	$3I^- \leftrightarrow I_3^- + 2e^-$	$S_2^{2-} + 2e^- \leftrightarrow 2S^{2-}$		(Na ₃ Zr ₂ Si ₂ PO ₁₂) and LATP (Li _{1+x+y} Al _x Ti _{2-x} P _{3-y} Si _y O ₁₂)		1.05	80		28
Br-V	$Br_2 + 2e^- \leftrightarrow 2Br^-$	$V^{2+} \leftrightarrow V^{3+} + e^-$		3.5M V in 7M HBr + 2M HCl/ 2M V in 4M H ₂ SO ₄		1.30	-		29
Mn-V	$Mn^{2+} + e^- \leftrightarrow Mn^{3+}$	$V^{2+} \leftrightarrow V^{3+} + e^-$		0.3M V ³⁺ in 5M H ₂ SO ₄ /0.3M Mn ²⁺ in 5M H ₂ SO ₄		1.77	63		30
Lead-based									
Pb-Ce	$2Ce^{3+} \leftrightarrow 2Ce^{4+} + 2e^-$	$Pb^{2+} + 2e^- \leftrightarrow Pb$		1.5MPb ^{II} methanesulfonate in 1.0 M MSA (Negative); 1.0MCe ^{III} methanesulfonate in 1.0M MSA (Positive)		1.7	83		31
Soluble-Pb	$Pb^{2+} + 2H_2O + 2e^- \cdot$	$Pb^{2+} + 2e^- \leftrightarrow Pb$		Lead(II) in methanesulfonic acid		1.78	65		32
Polyoxometalate (POM)-based									
All-POM (Symmetric POM-based)	SiV ₃ W ^{VI} ₉ O ₄₀ ⁷⁻ / SiV ^{IV} ₃ W ^{VI} ₉ O ₄₀ ¹⁰⁻	SiV ^{IV} ₃ W ^{VI} ₉ O ₄₀ ¹⁰⁻ /SiV ^{IV} ₃ W ^{VI} ₃ W ^{VI} ₆ O ₄₀ ¹³⁻)		Tungsten based Keggin POM K ₆ H[A- α-SiV ₃ W ₉ O ₄₀] (ASi)		1.0	50		33
Vanadium, tungsten,	$PV_3W_9O_{40}^9 \leftrightarrow PV_3W_9$	$PV_3W_9O_{40}^9 + 3e^- \leftrightarrow I$		A-α-PV ₃ W ₉ O ₄₀ ⁶⁻ , B- α-PV ₃ W ₉ O ₄₀ ⁶⁻ , and		>2	-		34

phosphorus-based POM		$P_2V_3W_{15}O_{62}^{9-}$					
All Tungsto-cobalt-POM	$Co^{II}W_{12}O_{40}^{6-} \leftrightarrow Co^{III}W$	$CoW_{12}O_{40}^{6-} + 2e^- + \text{; tungsten-cobalt heteropoly acid (H6[CoW12O40])}$	-	86	35		
Asymmetric POM-based	$2Br^- \leftrightarrow Br_2 + 2e^-$	$[P_2W_{18}O_{62}]^{6-} + 2e^- \text{ Li}_6[P_2W_{18}O_{62}]$ (Negative)	-	76	36		
PTA-POM based	$3I^- - 2e^- \leftrightarrow I_3^-$	$[PW_{12}O_{40}]^{5-} + 2e^- \text{ 1.6 M HI 0.25 M PTA (Positive) , 12-1.1 M HI 0.25 M PTA (Negative)}$	0.84	80.1	37		
Polyoxovanadate –POM based	$[PV_{14}O_{42}]^{9-} \leftrightarrow [H_xPV [SiW_{12}O_{40}] + 4e^- \leftrightarrow [SiW_{12}O_{40}]^{4-}$	$(SiW_{12})^{(Negative)} PV_{14}^{(Positive)}$	-		38		

Table S2 Cell performance of organic-based ARFBs

Type	Positive	Negative	Electrolyte	E_{Cell} (V)	EE (%)	Ref
Viologen-based						
Methyl viologen-based	$4-OH-TEMPO \leftrightarrow [MV_i^{2+} + e^- \leftrightarrow MV_i^+$	3M in 1.5M NaCl methyl viologen (anolyte) 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (Catholyte)	1.25	62.5	39	
Ferrocene-based	$[FcN]^{+} \leftrightarrow [FcN]^{2+} - [(Me)(NPr)V]^{3+} + e^-$	1.3M in 2M NaCl 1,10-bis[3-(trimethylammonio)propyl]4,40-bipyridinium tetrabromide (Anolyte) BTMAP-Fc (Catholyte)	0.75	≈65	40	
Viologen/Br ₂	$Br_2 + 2e^- \leftrightarrow 2Br^-$	(2HO-V) ^{2+/1+} and (2HO-V) ^{1+/0}	2M in H ₂ O (2HO-V)Br ₂ (anolyte) and KBr-MEP (Catholyte)	1.49 1.89	80 1.89	41
Viologen-Thiazolo	$[N^{Me}TEMPO]^{+} \leftrightarrow [N[(NPr)_2TTz]^{4+} + e^-$	1.1 M in 2M NaCl [(NPr) ₂ TTz]Cl ₄ (anolyte) N ^{Me} -TEMPO (catholyte)	1.44	70	42	
Viologen-Ferrocene	-	$4MV^{+} + O_2 + 2H_2O$ ((3-trimethylammonio)propyl)-ferrocene dichloride (catholyte) bis(3-trimethylammonio)propyl viologen tetrachloride (Anolyte)	0.748	-	43	

Sulphonate viologen-KI	$I_3^- + 2e^- \leftrightarrow 3I^-$	$(SPr_2)V + e^- \leftrightarrow [(SPr)_2V\text{ (anolyte)}]$ KI (Catholyte)	1.0	67	44	
Sulphonate viologen-Br	$Br_2 + 2e^- \leftrightarrow 2Br^-$	$(SPr_2)V + e^- \leftrightarrow [(SPr)_2V\text{ (anolyte)}]$ NH ₄ Br (catholyte)	1.51	80	45	
Poly viologen	$TEMPO \leftrightarrow TEMPO^+$	$Viol^{++} + e^- \leftrightarrow Viol^{\cdot -}$	PolyVi (anolyte) PolyTEMPO (Catholyte)	1.19	75	46
TEMPO-Viologen	TEMPO-based		3M in 1.5M NaCl methyl viologen (anolyte)	1.25	62.5	39
N ^{Me} -TEMPO based	$TEMPO^+ \leftrightarrow TEMPO$	$Viol^{++} + e^- \leftrightarrow Viol^{\cdot -}$	N,N,N-2,2,6,6-heptamethyl piperi-dinyloxy-4-ammoniumchloride (TEMPTMA) (Catholyte)	1.4	70	47
GTMA ⁺ grafted 4-OH-TEMPO	$g^+ - TEMPO^+ + e^- \leftrightarrow Zn^{2+} + 2e^- \leftrightarrow Zn$	0.3M ZnCl ₂ +0.3MNH ₄ Cl (anolyte) 0.2M 4-hydroxy-TEMPO in 1M NaCl (catholyte)	1.55	72.7	48	
TEMPO-4-sulphate based	$R - TEMPO^+ + e^- \leftrightarrow Zn^{2+} + 2e^- \leftrightarrow Zn$ R=solubility promoting substituent	ZnCl ₂ +NH ₄ Cl (anolyte) Aqueous 2,2,6,6-Tetramethyl piperidine-N-oxyl (catholyte)	1.5	-	49	
TMAP-TEMPO	$TMAP - TEMPO^+ + BTMAP^{++} + e^- \leftrightarrow B'$	TMAP-TEMPO (catholyte) BTMAP-Vi (anolyte)	1.5	60-	50	
80						
TEMPO-phenazine	$p(TEMPO - co - zw) MV^{++} + e^- \leftrightarrow MV^{\cdot +}$	N,N'-dimethyl-4,4'-bipyridinium dichloride (MV) (anolyte) p(TEMPO-co-zwitterion)(catholyte)	1.3	93	51	
VIOTEMP	$TEMPO^+ + e^- \leftrightarrow TE$	$Viol^{++} + e^- \leftrightarrow Viol^{\cdot -}$	TEMPO (catholyte) Viologen (anolyte)	1.16	-	52
TEMPO-polymer	$P1^+ + e^- \leftrightarrow P1$ P1=TEMPO containing copolymer	$MV^{++} + e^- \leftrightarrow MV^{\cdot +}$	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl-containing polymer(catholyte) dimethyl viologen (anolyte)	1.3	85	53
Poly(TEMPO)-Zinc	$TEMPO^+ + e^- \leftrightarrow TE$	$Zn^{2+} + 2e^- \leftrightarrow Zn$	ZnCl ₂ (anolyte)TEMPO-polymer(catholyte)	1.69	80	54
Quinone-Br	$Br_2 + 2e^- + 2H^+ \leftrightarrow AQDSH_2 \leftrightarrow AQDS + 2.$	HBr/Br ₂ (catholyte) 9,10-anthraquinone-2,7-	0.81	NA	55	

			disulphonic acid (AQDS)(anolyte)			
Alkaline-Quinone	$Fe(III)(CN)_6^{3-} + 2e^{-} \rightleftharpoons reDHAQ \leftrightarrow 2,6 - Fe(CN)_6^{4-}(Catholyte)2,6 - dihydroxyanthraquinone (2,6-DHAQ)(anolyte)$			1.2	84	56
Naphtha-Quinone	$K_3Fe(III)(CN)_6 + e^{-} \rightleftharpoons 2,3 - reHCNQ \leftrightarrow 2,3 - 2\text{-hydroxy-3-carboxy-1,4-naphthoquinone(2,3-HCNQ)(anolyte)}K_4Fe(CN)_6(catholyte)$			1.02	68.8	57
Alkaline Benzoquinone	$K_3Fe(III)(CN)_6 + e^{-} \rightleftharpoons 2,5 - reDHBQ \leftrightarrow 2,5 - 2,5\text{-dihydroxy-1,4-benzoquinone (anolyte)}K_4Fe(CN)_6(catholyte)$			1.21	65	58
Ammonium anthraquinone	$I_3^- + 2e^{-} \leftrightarrow 3I^- \quad reAQDS(NH_4)_4 \leftrightarrow AQ \cdot 0.75M \text{ 9,10-antraquinone-2,7-disulfonic diammoniumsalt AQDS-(NH}_4)_2 \text{ in } 0.75 \text{ M NH}_4I \text{ (anolyte) } 2.25M \text{ NH}_4I \text{ aqueous solution (catholyte)}$			0.865	70	59
Alkaline-Quinone	$Fe(III)(CN)_6^{3-} + 2e^{-} \rightleftharpoons reDBEAQ \leftrightarrow 2,6 - Fe(CN)_6^{4-}(Catholyte)4,40\text{-(9,10-antraquinone-2,6-diyl)dioxydibutyrate (2,6-DBEAQ) (anolyte)}$			1.05	88	60
Phosphonate-Functionalized Quinone	$e(III)(CN)_6^{3-} + 2e^{-} \rightleftharpoons reDPPEAQ \leftrightarrow 2,((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)bis(oxy))bis(propane-3,1-diyl))bis(phosphonic acid)(anolyte)K_4Fe(CN)_6K_3Fe(CN)_6(catholyte)$			1.0	65	61
Water-Miscible Quinone	$e(III)(CN)_6^{3-} + 2e^{-} \rightleftharpoons rePEGAQ \leftrightarrow PEGAQ + K_4Fe(CN)_6K_3Fe(CN)_6(catholyte) \quad 1.5 \text{ M AQ-1,8-3E-OH (anolyte)}$			1.0	NA	62
phenazine-based	Nitrogen-centered heteroatomic molecule based					
	$Fe(III)(CN)_6^{3-} + 2e^{-} \rightleftharpoons [Phenazine - R]^n + 2(7,8-dihydroxyphenazine-2-sulfonic acid)(anolyte)Fe(CN)_6^{4-3-}(Catholyte)$			1.4	82	63
Fused-Ring Phenazine	$K_3Fe(III)(CN)_6 + e^{-} \rightleftharpoons - \quad benzo[a]hydroxyphenazine-7/8-carboxylicacid (anolyte)K_4Fe(CN)_6(catholyte)$			1.27	80	64
flavin mononucleotide	$Fe(CN)_6^{3-} + e^{-} \leftrightarrow F\epsilon FMN^{5-} + 2e^{-} \leftrightarrow FM\epsilon I \quad K_4Fe(CN)_6(catholyte) \quad sodium \text{ salt of flavin mononucleotide (anolyte)}$			1.03	80	65
Phenothiazine-Based	$VO^{2+} \leftrightarrow VO_2^+ + e^{-} \quad MB + 2e^{-} + 2H^+ \leftrightarrow methylene \text{ blue (MB)} \quad (anolyte) V(II) \text{ (catholyte)}$			0.83	76	66

Table S3 Synthesis strategies of pristine MOFs

MOFs	Synthesis method	Metal/Ligand/Solvent	Ref
MIL-53(Cr)	Hydrothermal method	Cr(NO ₃) ₃ .xH ₂ O/1,4-BDC/HF:H ₂ O	67
Fe-MIL-88A	Ultrasound synthesis	FeCl ₃ .6H ₂ O/ fumaric acid	68
ZIF-8	Colloidal chemistry	Zn(NO ₃) ₂ .6H ₂ O/2-methylimidazole/Methanol	69
MOF-5	Solvothermal	Zn(NO ₃) ₂ .4H ₂ O/H ₂ BDC/DMF/chlorobenzene	70
Cr-MIL-101	Solvothermal	Cr(NO ₃) ₃ .9H ₂ O/H ₂ BDC/H ₂ O (add 1M HF aq.)	71
Al-MIL-53-NH ₂	Solvothermal	Al(NO ₃) ₃ .9H ₂ O/ H ₂ BDC-NH ₂ / DMF	72
UiO-66	Solvothermal	ZrCl ₄ /H ₂ BDC/DMF	73
Co-MOF-74	Microwave-assisted	Co(NO ₃) ₂ .6H ₂ O/H ₂ DHBDC/DMF:EtOH:H ₂ O	74
HKUST-1	Microwave-assisted	Cu(NO ₃) ₂ .3H ₂ O/ H ₃ BTC/ EtOH	75
Mg-MOF-74	Sonochemical	Mg(NO ₃) ₂ .6H ₂ O/ H ₄ DHBDC/ DMF: EtOH:H ₂ O	76
Al-MIL-100	electrochemical	Al(NO ₃) ₃ .9H ₂ O/ H ₃ BTC/ H ₂ O:EtOH	77
ZIF-4	mechanochemical	ZnO/ Him/DMF	78

Table S4 Compilation of some conducting MOFs and derivatives

MOFs	Condition	Conductivity/ S cm ⁻¹	Ref
{[Co(bpy)(H ₂ O) ₄](btec) _{0.5} .H ₂ O}	80°C and 98% RH	4.85 ×10 ⁻³	79
Ni ₃ (HITP) ₂	25°C	4×10 ⁻³	80
[(CH ₃) ₂ NH ₂][In(<i>m</i> -TTFTB)]	70°C and 98% RH	4.05×10 ⁻³	81
Ni-CAT-1	25°C	3.2×10 ⁻²	82
(NH ₄) ₂ (adp)[Zn ₂ (ox) ₃]·3H ₂ O	25°C and 98% RH	8 ×10 ⁻³	83
BUT-8(Cr)A	80°C and 100% RH	1.27 × 10 ⁻¹	84
NNU-66a	180°C and anhydrous	1.94×10 ⁻³	85
MOF-74(Mg)-urea	25°C and 95% RH	2.64×10 ⁻²	86
MIP-202(Zr)	90°C and 95% RH	1.1×10 ⁻²	87
TMOF-2	90°C and 98% RH	1.23×10 ⁻⁴	88
Ni-HAB	65°C	45× 10 ⁻¹	89
β-PCM OF2	85°C and 90% RH	10 ⁻¹	90
FeTHQ	27°C	3.3±0.55	91
[Co(DCDPP)]·5H ₂ O	80°C and 97% RH	3.9 × 10 ⁻²	92
Cu ₃ (HITP) ₂	25°C	0.2	93
{H[(N(CH ₃) ₄) ₂][Gd ₃ (NIPA) ₆]}3H ₂ O	75°C and 98% RH	7.17×10 ⁻²	94
MFM-300(Cr)·SO ₄ (H ₃ O) ₂	25°C and 99% RH	1.26×10 ⁻²	95
[Sr(DMPH ₂ IDC) ₂] _n	100°C and 98% RH	0.92×10 ⁻³	96
{[Cd(p-TIPH ₂ IDC) ₂]·H ₂ O} _n	100°C and 98% RH	1.24×10 ⁻⁴	96
Ni-PTC ([Ni ₃ (C ₂₄ S ₁₂)] _n)	127°C	~10	97

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