Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Redox Flow Batteries: a new frontier on energy storage

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Supplemental material

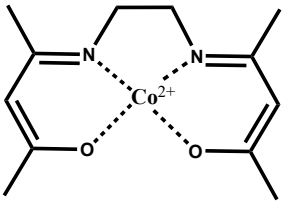
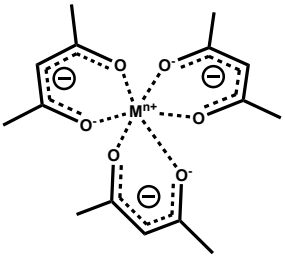
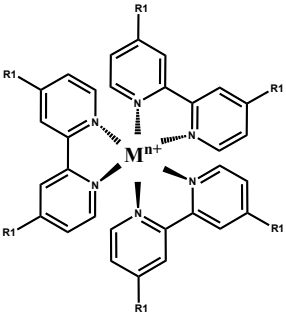
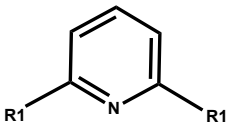
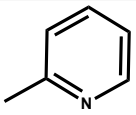
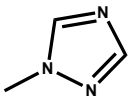
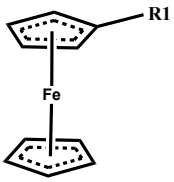
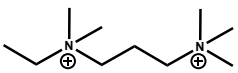
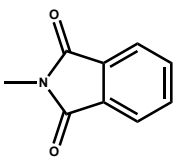
Table S1 – Summary of metal complexes used as RFBs active species.

Complex	*E* (V) (Charge)	Reference electrode	Electrolyte	Ref.
Acetylacetonate derivative				
Co(acacen)	-0.2 (+/0) -2.2 (0/-)	Ag^+/Ag	0.01 M Co(acacen) and 0.1 M $TEAPF_6$ in ACN	(1)
$Cr(acac)_3$	0.5 (+/0) -2.3 (0/-)	Ag^+/Ag	0.05 M $Cr(acac)_3$ and 0.5 M $TEABF_4$ in ACN	(2)
$Mn(acac)_3$	0.7 (+/0) -0.4 (0/-)	Ag^+/Ag	0.05 M Mn(acac)3 and 0.5 M $TEABF_4$ in ACN	(3)
$Ru(acac)_3$	1.0 (+/0) -0.7 (0/-)	SCE	0.02 M [$Ru(acac)_3$] and 0.1 M Et4NBF4 in ACN	(4)
$V(acac)_3$	0.5 (+/0) -1.7 (0/-)	Ag^+/Ag	0.01 M $V(acac)_3$ and 0.5 M $TEABF_4$ in ACN	(5)
$V(acac)_3$	0.8 (+/0) -1.25 (0/-)	Ag^+/Ag	0.01 M $V(acac)_3$ and 0.5 M TEABF4 in Choline chloride: Ethylene glycol 1:2 (DES)	(6)
$V(acac)_3$	0.8 (+/0) -1.4 (0/-)	Ag^+/Ag	0.005 M $V(acac)_3$ and 0.05 M $TBAPF_6$ in ACN-DMSO-1,3-DO mixture	(7)
$V(acac)_3$	0.8 (+/0) -1.4 (0/-)	Ag^+/Ag	0.01 M $V(acac)_3$ and 0.05 M $TEABF_4$ in ACN	(8)
$V(acac)_3$	0.90 (2+/+) 0.63 (+/0) -1.37 (0/-)	Ag^+/Ag	0.01 M $V(acac)_3$ in [C2C1Im][N(Tf2)] (IL)	(9)
$UO_2(acac)_2$	-1.46 (0/-)	Fc/Fc^+	0.1 M TBAP in DMSO. (Concentration of UO_2 non specified)	(10)
Pyridine derivatives				
$[Co(bpy)_3]^{2+}$	-1.02 (2+/+)	SCE	0.1 M [$Co(bpy)_3$]Tf_2 and 0.4 M LiTf in EC:PC 1:1	(11)
$[Fe(bpy)_3]^{2+}$	0.98 (3+/2+)	SCE	0.1 M [$Fe(bpy)_3$]Tf_2 and 0.4 M LiTf in EC:PC 1:1	(11)
$[Fe(bpy)_3]^{2+}$	1.1 (3+/2+) -1.3 (2+/+) -1.5 (+/0) -1.75 (0/-)	SCE	0.002 M [$Fe(bpy)_3$]BF_4 and 0.1 M Et_4NBF_4 in ACN.	(12)
$[Fe(bpy)_3]^{2+}$	0.59 (3+/2+) -1.76 (2+/+) -2.00 (+/0) -2.29 (0/-)	SCE	0.02 M $Fe(Bpy)_3(BF_4)_2$ with 0.05 M $TEABF_4$ in PC	(13)
$[Ni(bpy)_3]^{2+}$	1.0 (3+/2+) -2.1 (2+/0)	Ag^+/Ag	0.04 M $[Ni(bpy)_3]^{2+}$ in BMPTFSA (IL)	(14)
$[Ni(bpy)_3]^{2+}$	-1.70 (2+/0)	Ag^+/Ag	0.02 M $Ni(Bpy)_3(BF_4)_2$ with 0.05 M $TEABF_4$ in PC	(13)
$[Ru(bpy)_3]^{2+}$	1.0 (3+/2+) -1.6 (2+/+)	Ag^+/Ag	0.02 M [$Ru(bpy)_3$]$(BF_4)_2$ and 0.1 M Et_4NBF_4 in ACN	(4)

Complex	*E* (V) (Charge)	Reference electrode	Electrolyte	Ref.
$[Ru(bpy)_3]^{2+}$	1.3 (3+/2+) -1.35 (2+/+) -1.55 (+/0) -1.8 (0/-)	SCE	0.002 M $[Ru(bpy)_3]BF_4$ and 0.1 M Et_4NBF_4 in ACN.	(12)
$[bis(DIP)_2Fe]^{2+}$	0.8 (3+/2+) -1.3 (2+/+) -1.6 (+/0)	Fc/Fc+	0.6 mM $[bis(DIP)_2Fe][PF_6]_2$ and 0.1 M nBu_4PF_6 in ACN	(15)
$[Cr(EstBpy)_3]^{3+}$	-0.18 (3+/2+) -0.58 (2+/+) -1.14 (+/0) -1.66 (0/-) -1.86 (-/2-) -2.01(2-/3-)	Ag^+/Ag	0.001 M $[Cr(EstBpy)_3]^{3+}$ and 0.1 M $(TBA)BF_4$ in ACN	(16)
$[Co(AzPy2)_2]_{2+}$	0.16 (3+/2+) -1.22 (2+/+) -2.01 (+/0)	Fc/Fc^+	$[Co(AzPy2)_2](PF_6)_2$ and 0.1 M $(TBA)PF_6$ in ACN	(17)
Metallocenes				
FcN^{2+}	0.27 (2+/+)	Fc/Fc^+	0.001 M FcN-TFSI and 1.0 M LiTFSI in ACN	(18)
FcN^{2+}	0.55 (2+/+)	Ag^+/Ag	0.01 M of FcNCl in 1 M NaCl	(19)
FcN^{2+}	0.61(2+/+)	NHE	0.5 M for FcNCl in 2.0 M NaCl	(20)
FcN_2^{3+}	0.61 (3+/2+)	NHE	0.5 M for FcN_2Br_2 in 2.0 M NaCl	(20)
FcPI	0.07 (+/0) -1.87 (0/·)	Fc/Fc^+	0.01 M FcPI and 1.0 M $(TBA)BF_4$ in 1,3-dioxolane	(21)
BTMAP-Fc^{2+}	0.39 (3+/2+)	NHE	0.005 M BTMAP-$FcCl_2$ in 1.0 M NaCl	(22)
BTMAP-Fc^{2+}	0.390 (3+/2+)	SHE	0.001 M BTMAP-$FcCl_2$ in 0.5 M NaCl	(23)
Fc-Vi	0.15 (4+/3+) -0.54(3+/2·+)	Ag^+/Ag	0.5 M Fc-$ViCl_3$ in 1 M NaCl	(24)
Fc	3.6 (+/0)	Li^+/Li	0.05 M $FeCp_2$, 0.05 M $FeCp_2PF_6$, 0.5 M $LiPF_6$ in DMF	(25)
$CoCp_2$	1.9 (0/-)	Li^+/Li	0.05 M $CoCp_2$, 0.5 M LiTFSI in 1,3-DO	(25)
$CoCp_2$	-1.23 (0/-)	Ag^+/Ag	0.14 of $[Co(Cp)_2]PF_6$ and 0.05 M $TBAPF_6$ in ACN	(26)
Other used complexes				
$[V(mnt)3]^{2-}$	0,856 (4-/3-) -0.227 (3-/2-) -1.41 (2-/-)	SHE	0.02 M $[V(mnt)3]TBA_2$ and 0.1 M [TBA][PF_6] in ACN	(27)
$[CrPDTA]^-$	-1.31 (-/2-)	Ag^+/Ag	0.005 M KCrPDTA in 0.125 M potassium tetraborate buffer (pH 9)	(28)
$[Fe(AEDT)]^-$	−0.104 (-/2-)	SCE	0.1 M Fe(III)-EDTA and 1 M sodium acetate in water	(29)
$Fe(Ox)_3$	−0.190 (0/-)	SCE	0.1 M Fe(III)-oxalate and 1 M sodium acetate in water	(29)

Complex	*E* (V) (Charge)	Reference electrode	Electrolyte	Ref.
Fe(Cit)	−0.213 (0/-)	SCE	0.1 M Fe(III)-citrate and 1 M sodium acetate in water	(29)
Fe-TEA	-1.25	Ag^{+}/Ag	0.001 M Fe-TEA in 1 M KOH	(30)
$Ni(Cyclam)^{3+}$	-1.7 (3+/2+) 0.7 (2+/+)	Fc/Fc^{+}	0.01 M Ni(cyclam)[TFSI]2 and 1.0 M TEABF4 in EC:PC 1:1	(31)
$Ni([14]aneS4)^{3+}$	1.11 (3+/2+) -0.80 (2+/+)	Fc/Fc^{+}	0.3 M Ni([14]aneS4)$[TFSI]_2$ and 1.0 M $LiPF_6$ in EC:PC=1:1	(32)
$[Fe(CN)_6]^{4-}$	0.49 (4-/3-)	NHE	0.001 M $K_4[Fe(CN)_6]$ 1.0 M NaOH	(33)
$[Fe(CN)_6]^{4-}$	0.3 (4-/3-)	Ag^{+}/Ag	0.005 M $K_4Fe(CN)_6$ in 0.125 M potassium tetraborate buffer (pH 9)	(28)
$[Fe(CN)_6]^{4-}$	0.496 (4-/3-)	SHE	0.01 M $K_4Fe(CN)_6$ in 1 M KOH	(34)
$[Fe(CN)_6]^{4-}$	0.29 (4-/3-)	Ag^{+}/Ag	0.002 M $K_4Fe(CN)_6$ in 1.0 M KOH.	(35)
$[Fe(CN)_6]^{4-}$	0.53 (4-/3-)	SHE	0.002 M $K_4Fe(CN)_6$ in 1.0 M KOH.	(36)
$[Fe(CN)_6]^{4-}$	0.50 (4-/3-)	SHE	0.001 M $K_4Fe(CN)_6$ in 1.0 M KOH.	(37)

Table S2 – Summary of most common organic/organometallic structures used as RFBs active species.

General name	*Structure*	Modifications	Abbreviature	Ref.
Acetylacetonate complexes				
Co(acacen)		-	-	(1)
$M(acac)_3$		-	-	[2-10]
Pyridine complexes				
$[M(bpy)_3]^{n+}$		R1 = H	Bpy	[4, 11-14]
		R1= -COOR	EstBpy	[16]
$[M(AzBpy)_2]^{n+}$		R1 =  or 	AzBpy	[17]
Metallocenes				
Fc		R1 = CH_2-$N(CH_3)_3$	FcN^+	[18-20]
		R1 = 	FcN_2^+	[20]
		R1 = 	FcPI	[21]
		R1 = $(CH_2)_3$-$N(CH_3)_3$	BTMAP-Fc	[22, 23]
		R1 = H	Fc	[25]

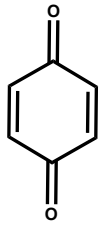
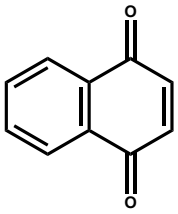
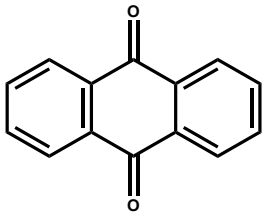
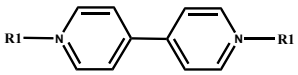
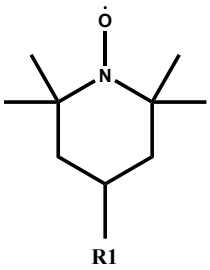
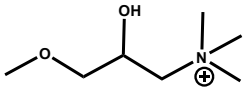
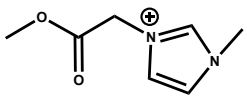
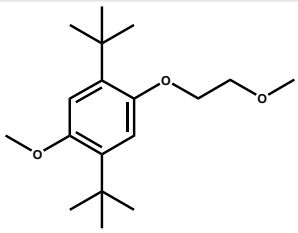
General name	*Structure*	Modifications	Abbreviature	Ref.
Quinones				
Benzoquinone		-	BQ	(38–41)
Naphtoquinone		-	NQ	(38,41)
Anthraquinone		2 x $-SO_3^-$	AQDS	(38,39,41,42)
		2 x -OH	AQDH	(38,41)
		Other	AQ	(38,41)
Nitrogen-containing aromatics				
Viologen		$R1 = CH_3$	MV	(18,20,43,44)
		$R1 = (CH_2)_3\text{-}N(CH_3)_3$	BTMAP-Fc	(22,23,45)
Nitroxides		R1 = H	TEMPO	(46–48)
		R1 = OH	TEMPOL	(43,49)
		$R1 = O\text{-}(CH_2)_3\text{-}N(CH_3)_3$	TMAP-TEMPO	(45)
		R1 = 	g+-TEMPO	(50)
		R1 = 	ImTEMPO	(51)
Other organic molecules				
		-	DBMMB	(52–54)

Table S3 – Summary of the properties or the referred membranes.

Membrane	**Thickness (µm)**	***Electrolyte uptake (%)***	***IEC (mmol·g^{-1})***	**Ion Conductivity (mS·cm^{-1})**	**Area Resistance (Ω·cm^{-2})**	**Battery**	**Ref.**
Cation-exchange membranes (CEM)							
Nafion212	50	30.8	0.88	72.4	-	VRFB	(55)
Nafion117	215	26.0	0.97	-	1.14	VRFB	(56)
Nafion115	127	25.8	0.91	-	0.95	VRFB	(57)
Nafion212-cover PTFE	45	24.9	0.69	68.1	-	VRFB	(55)
Nafion117-SiO_2-TiO_2	217	22.5	0.95	-	1.26	VRFB	(56)
Nafion117-SiO_2	204	21.5	0.96	56.2	-	VRFB	(58)
Nafion117-TiO_2	90	19.13	0.85	-	1.05	VRFB	(59)
SPEEK (DS = 40)	90	26.7	1.45	-	1.22	VRFB	(57)
SPEEK-SBA15 20%	61	31.8	1.72	6.4	-	VRFB	(60)
SPEEK-Graphene	90	50.9	1.98	14.1	1.28	VRFB	(61)
NafionR1000-SPEEK	100	-	1.67	-	1.6	VRFB	(62)
Sulfonated-PFAE	55-64	48	1.8	61	-	VRFB	(63)
Anion-exchange membranes (AEM)							
QPEK	45-55	87	2.3	15.2	-	V-Ce	(64)
Q-adamantane-PAEK	40-45	18.8	1.75	-	0.49	VRFB	(65)
Phthalazinone-PAEK	47	23.8	1.53	-	0.58	VRFB	(66)
Q-Radel®	55-60	73	2.5	49	-	VRFB	(67)
Imidazolium-Udel®	60	20	-	24	-	VRFB	(68)
Benzophenone-Q- Udel®	70	60.3	1.74	-	-	VRFB	(69)
QPS-PVDF	130	22	2.1	2.2	-	VRFB	(70)
P(QVBC-St-HEA)	70	37.5	1	2.2	3	VRFB	(71)
TEA-VBC	37	43.8	1.09	29.6	-	NAVRFB	(72)
VI-co-TFEMA-co-DVB	150	-	1	-	2.8	VRFB	(73)

Membrane	Thickness (μm)	*Electrolyte uptake (%)*	*IEC (mmol·g^{-1})*	Ion Conductivity (mS·cm^{-1})	Area Resistance (Ω·cm^{-2})	Battery	Ref.
P(TPP-TFAP)	50	35	2.13	9.4	0.53	VRFB	(74)
Urushi-chitosan	29	75	0.59	6.4	-	NAVRFB	(75)
Urushi-PDDA	45	-	-	130	-	NAVRFB	(76)
Amphoteric ion-exchange membranes (AIEM)							
PSSS-Selemion®	-	-	1.74	-	1.25	VRFB	(77)
SPEEK-QPEI	60	39.97	1.553	47.37	0.158	VRFB	(78)
PTFE-QAPSF-SPEEK	-	73	0.9 (+)/4.5 (-)	10.27	-	VRFB	(79)
ImSPEEK	80	45	1.78	70	-	VRFB	(80)
ImPSf-SPEEK	65	56	2.04	135	0.48	VRFB	(81)
N-morpholine-SPSt	150	21	0.62 (+)/1.11 (-)	31.2	-	VRFB	(82)
Acid-doped membranes (ADM)							
H_2SO_4-PBI	15	6-12	-	4.9	1.62	VRFB	(83)
PBI-SPAEK	64	-	1.56	-	11.9	VRFB	(84)
PAES-PBI	50	23.8-26.6	1.75	-	0.1-0.25	VRFB	(85)
PBI-SPEEK	-	43.63	-	-	0.4	VRFB	(86)
PBI-Nafion	4	-	-	-	0.56	VRFB	(87)
SPBI-DCDPE-APTA	-	47.4	3.15	32	-	VRFB	(88)
P(SSS-DMAEMA-VDF)	50	14	0.65	-	65	VRFB	(89)
SPEEK-Graphene-NH_2	60	29.59	2.07	-	0.154	VRFB	(90)
SPI/PEI-rGO	50	44.2	1.16	6.2	-	VRFB	(91)
SPEEK-poly(etheimide)		32.9	1.38	72	-	VRFB	(92)
SPFEKA	140-180	36.5	1.47	10.8	-	VRFB	(93)
Size-exclusion porous membranes (SEPM)							
PAN	-	-	-	-	-	VRFB	(94)
PVDF	155	-	-	-	1.50	VRFB	(95)
Silicalite	5-8	-	-	-	10.8	VRFB	(96)
ZSM-35 zeolite	8	-	-	-	0.61	VRFB	(97)

Membrane	Thickness (μm)	*Electrolyte uptake (%)*	*IEC (mmol·g^{-1})*	Ion Conductivity (mS·cm^{-1})	Area Resistance (Ω·cm^{-2})	Battery	Ref.
TiO_2	2	-	-	-	1.29	VRFB	(98)

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