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Supporting Information

Redox-Flow Batteries: From Metals to Organic Redox-Active Materials

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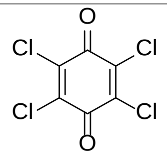
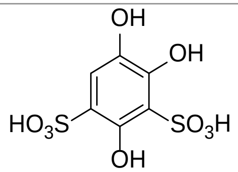
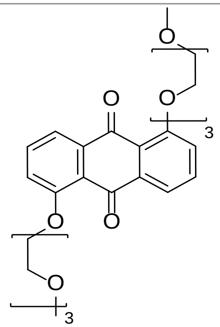
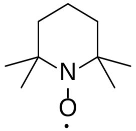
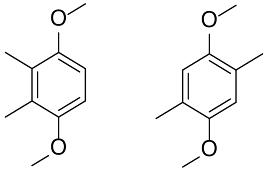
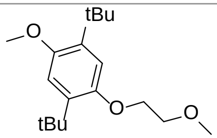
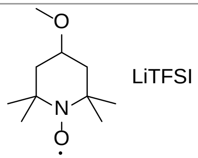
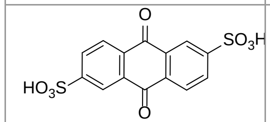
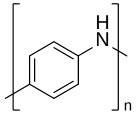
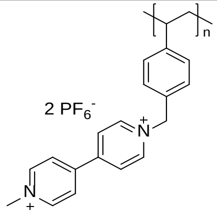
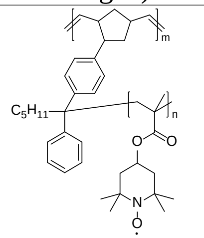
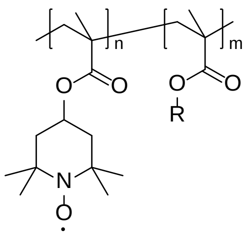
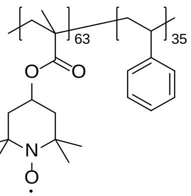
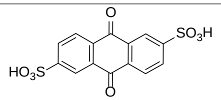
anie_201604925_sm_miscellaneous_information.pdf

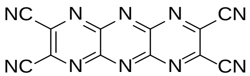
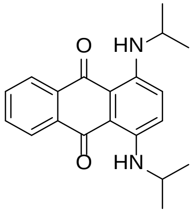
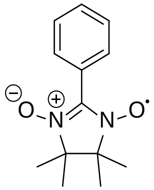
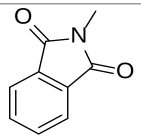
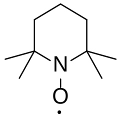
Extended Data Table: Utilized redox-active materials.

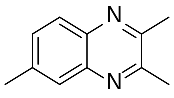
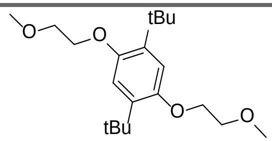
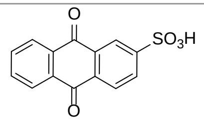
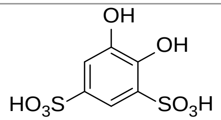
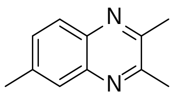
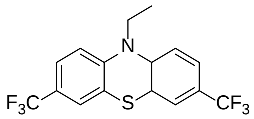
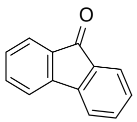
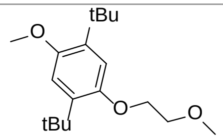
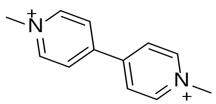
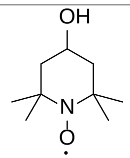
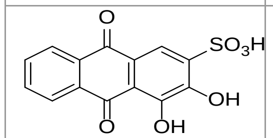
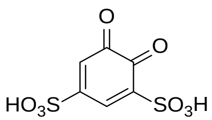
Anode	Cathode	Electrolyte	Theoretical cell voltage / V	Current density / mA cm^{-2}	Theoretic energy density / Wh L^{-1}	Maximal observed energy density / Wh L^{-1}	Cycles reported	Membrane	Ref.
1. Flow batteries utilizing organic/inorganic redox-active materials									
Cd/$CdSO_4$ (single flow)	 Chloranil	H_2SO_4/ $(NH_4)_2SO_4$/ $CdSO_4$	1.14	10	-	-	100	None	[131]
Pb/$PbSO_4$	 Tiron	H_2SO_4	1.1	10	-	2.8	10	Nafion 115	[133]
Li	 15D3GAQ	$LiPF_6$/PC	2.3	0.1 to 10	25	25[a]	9 to 40	PP separator	[138]

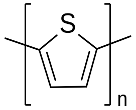
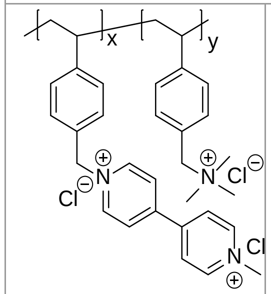
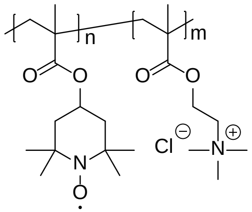
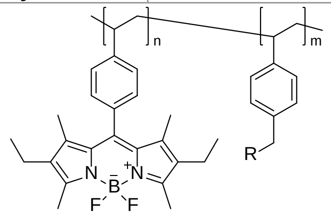
Anode	Cathode	Electrolyte	Theoretical cell voltage / V	Current density / mA cm^{-2}	Theoretic energy density / Wh L^{-1}	Maximal observed energy density / Wh L^{-1}	Cycles reported	Membrane	Ref.
Li, solid	 TEMPO	$LiPF_6$/ (EC)/(PC)/ (EMC)	3.5	1 to 10	64 to 126	64 to 126[a]	30 to 100	PE separator	[126]
(bulky electrolysis cell)	 23DDB and 25DDB	LiTFSI/PC	3.97 (225DDB) 4.05 (23DDB)	0.4 mA (charging current)	-	0.05[a]	100	Not specified	[162]
Li metal strips (bulk electrolysis cell)	 ANL-8	$LiBF_4$/PC	~4	0.4 mA (charging current)	-	0.05[a]	30	Porous glass or ceramic frits	[134]
Li, solid	 MTLT (IL)	LiTFSI/PC	3.65	0.1 to 1.0	200	200[a]	20	Lithium ion-conducting glass ceramics	[41]
 2,6-DHAQ	$K_4Fe(CN)_6$	KOH	1.2	100	6.8	6.8	100	Nafion 212	[147]
2. Flow batteries utilizing polymer-based organic/inorganic redox-active materials									

Anode	Cathode	Electrolyte	Theoretical cell voltage / V	Current density / mA cm^{-2}	Theoretic energy density / Wh L^{-1}	Maximal observed energy density / Wh L^{-1}	Cycles reported	Membrane	Ref.
Zn	 PANI	$ZnCl_2/NH_4Cl$	1.1	10 to 30	66.5	9.5	32	PP micro porous membrane	[35]
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	 Poly(vinylbenzyl ethyl viologen)	$LiBF_4/CH_3CN$	1.11	0.2 mA (current)	15.5[a] (14 Ah L^{-1} volumetric energy density)	15.5[a]	11	PP/PE separator	[36]
Half-cell only	 Poly(norbornene)-*g*-poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl) (PNB-g-PTMA)	$(C_4H_9)_4NClO_4$/EC/DEC	Half-cell-only	-	-	0.94 [a]	2	PP/PE separator	[166]

Anode	**Cathode**	**Electrolyte**	**Theoretical cell voltage / V**	**Current density / mA cm^{-2}**	**Theoretic energy density / Wh L^{-1}**	**Maximal observed energy density / Wh L^{-1}**	**Cycles reported**	**Membrane**	**Ref.**
Hybrid Zn(II)/Zn(0)	 TEMPO containing polymers	$Zn(ClO_4)_2 \times 6H_2O$/ EC/DMC/ DEC or $ZnCl_2$, NH_4Cl/water or NaCl, $ZnCl_2$, NH_4Cl/water	1.69	0.5 to 20	8.1	4.1	1,000	Dialysis membrane (regenerated cellulose, MWCO of 1.000 g mol^{-1})	[32]
Hybrid Zn(II)/Zn(0)	 TEMPO containing polymers	$Zn(ClO_4)_2 \times 6H_2O$/ EC/DMC/ DEC or $ZnCl_2$, NH_4Cl/water or NaCl, $ZnCl_2$, NH_4Cl/water	1.69	0.5 to 20	1.6	0.8	1,000	Dialysis membrane (regenerated cellulose, MWCO of 1.000 g mol^{-1})	[33]
3. RFBs based on organic/halogen redox-active materials									
 AQDS ($ADQSH_2$)	Br_2	HBr/H_2SO_4 (aq)	0.81	200 to 500	-	9.4	15	Nafion 212	[78]
AQDS ($ADQSH_2$)	Br_2	HBr/H_2SO_4 (aq)	0.85	250 to 750	-	9.4	106 to 750	Nafion 115	[168]

Anode	Cathode	Electrolyte	Theoretical cell voltage / V	Current density / mA cm^{-2}	Theoretic energy density / Wh L^{-1}	Maximal observed energy density / Wh L^{-1}	Cycles reported	Membrane	Ref.
AQDS ($ADQSH_2$)	Br_2	HBr/H_2SO_4 (aq)	0.85	>4000	-	-	-	Nafion 212	[127]
AQDS ($ADQSH_2$)	Br_2	HBr/H_2SO_4 (aq)	0.75	100 to 1000	-	5.2	5 to 40	Nafion 115	[170]
4. RFBs utilizing low molar mass organic redox-active materials for catholyte and anolyte									
 TCAA		$CH_3CN/TEABF_4$ or EC/PC/ $TEABF_4$	~2.8		-	-	-	PP separator	[173]
 DB-134		CH_3CN/ toluene	1.76; 2.72 (for the 1st and 2nd respective oxidations and reductions)	0.67 (2 mA charging current)	-	1.00	6	Medium porosity glass frit	[28]
 PTIO		CH_3CN	1.73	20	9 (during charging) 5 (during discharging)	8.00	15, 35, 100	Daramic porous separator	[174]
 *N*-methylphthalimide	 TEMPO	$NaClO_4$/ CH_3CN	1.6	0.35	-	1.7	20	Nepem 117	[129]

Anode	**Cathode**	**Electrolyte**	**Theoretical cell voltage / V**	**Current density / mA cm^{-2}**	**Theoretic energy density / Wh L^{-1}**	**Maximal observed energy density / Wh L^{-1}**	**Cycles reported**	**Membrane**	**Ref.**
 TMeQ	 DBBB	$LiBF_4$/PC	1.12; 1.44 (TMeQ shows two reversible redox events)	0.0625	-	1.1	30	Nafion 117	[159]
 AQS	 BQDS	$H_2SO_{4(aq)}$	0.97	2 to 10	-	1.25	12	Nafion 117	[128]
 TMeQ	 BCF3EPT	$LiBF_4$/PC	1.1; 1.4 (TMeQ shows two reversible redox events)	0.14 (0.1 mA charging current)	-	0.84 to 5.91	50 to 100	Nafion 117	[184]
 FL	 ANL-8	TEA-TFSI/CH_3CN	2.37	10 to 15	15 (for charging) 11 (for discharging)	13.63	100	Micro porous PE/silica separator	[136]
 Methyl viologen	 4-HO-TEMPO	NaCl/H_2O	1.25	20 to 100	8.4	6.9	100	"Selemin" AEM	[199]
 ARS	 BQDS	$H_2SO_{4(aq)}$	0.83	20 to 60	-	0.38	3	Nafion 212	[161]

Anode	Cathode	Electrolyte	Theoretical cell voltage / V	Current density / mA cm^{-2}	Theoretic energy density / Wh L^{-1}	Maximal observed energy density / Wh L^{-1}	Cycles reported	Membrane	Ref.
5. RFBs utilizing polymer-based organic redox-active materials for catholyte and anolyte									
 Poly(thiophene) microparticles		$TEABF_4$/PC	2.5	0.5 to 5 (static cell); 0.2 to 1 (pumped cell)	-	3.2 (static cell); 2.7 (pumped cell)	30 (static cell); 20 (pumped cell)	FAP-PP-375 AEM	[132]
 Viologen copolymer	 TEMPO copolymer	NaCl/H_2O	1.1	20 (static cell) 20 to 100 (pumped cell)	10.8	5.5	10,000 (static cell) ~95 (pumped cell)	Cellulose-based dialyses membrane	[34, 186]
 R = solubility promoting substituent Poly(BODIPY)		PC	2.2 V	0.25 mA (current)	0.3	0.07	100	Cellulose-based dialyses membrane	[187]

a) The energy density was calculated excluding the anolyte, due to a hybdrid flow setup. In case no further information like the capacity [Ah L^{-1}] are available, the maximal observed energy density [Wh L^{-1}] was calculated by the following equation: energy density = (concentration of the electrolyte solution × 26.8 Ah L^{-1} for one-electron redox-reaction × average cell voltage [V])/2.