

Supplementary Information

Redox Mediators as Charge Agent Changing Electrochemical Reactions

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Table S1. Potential redox mediators (RMs) applicable for various electrochemical systems

S. No.	Name redox mediator	Chemical formula	Electrolyte	Redox potential	Reference
1	1,5-naphthalenediamine (NDA)	C ₁₀ H ₁₀ N ₂	1 M LiTFSI/TEGDME	3.64 vs Li ⁺ /Li	¹
2	Tetrathiafulvalene (TTF)	C ₆ H ₄ S ₄	1 M LiTFSI/TEGDME	3.56 vs Li ⁺ /Li	²
3	Ferrocene (FC)	C ₁₀ H ₁₀ Fe	1 M LiTFSI/TEGDME	3.60 vs Li ⁺ /Li	²
4	Lithium iodide	LI	1 M LiTFSI/TEGDME	3.0 V vs Li ⁺ /Li	^{3, 4}
5	5,10-dimethylphenazine (DMPZ)	C ₁₄ H ₁₄ N ₂	1 M LiTFSI/TEGDME	3.0 V vs Li ⁺ /Li	³
6	(2,2,6,6-tetramethylpiperidinyloxy) (TEMPO)	C ₉ H ₁₈ NO	1 M LiTFSI/diglyme	3.74 V vs Li ⁺ /Li	⁵
7	4-Methoxy-2,2,6,6-tetramethylpiperidinyloxy (4-methoxy-TEMPO)	C ₁₀ H ₂₀ NO ₂	1 M LiTFSI in diglyme	3.76 V vs Li ⁺ /Li	⁶
8	Cobalt Bis(terpyridine) (Co(Terp) ₂)	C ₃₀ H ₂₂ CoN ₆	Co(Terp) ₂	3.12 - 3.38 vs Li ⁺ /Li	⁷
9	N, N, N', N'-tetramethyl-p-phenylenediamine (TMFD)	C ₁₀ H ₁₆ N ₂	1 M LiTFSI/TEGDME	3.33 vs Li ⁺ /Li	²
10	10-methyl-10H-phenothiazine (MPTA)	C ₁₃ H ₁₁ NS	1 M LiTFSI/TEGDME	3.67 V vs Li ⁺ /Li	²
11	2,5-di- <i>tert</i> -butyl-1,4-benzoquinone (DBBQ)	C ₁₄ H ₂₀ O ₂	1 M LiTFSI/TEGDME or DME	2.5 – 2.6 V vs Li ⁺ /Li	⁸
12	4, N, N-trimethylaniline (TMA)	C ₉ H ₁₃ N	1 M LiTFSI/TEGDME	3.81 vs vs Li ⁺ /Li	¹
13	1-phenylpyrrolidine (PPD)	C ₁₀ H ₁₃ N	1 M LiTFSI/TEGDME	3.89 vs Li ⁺ /Li	¹
14	Cobalt phthalocyanine (CoPC)	C ₃₂ H ₁₆ CoN ₈	1 M LiTFSI/TEGDME	3.82 V vs. vs Li ⁺ /Li	⁹
15	Butyl-hydroxytoluene (BHT)	C ₁₅ H ₂₄ O	1 M LiTFSI/TEGDME	3.0 V vs. vs Li ⁺ /Li	¹⁰
16	Naphthacene (NC)	C ₁₈ H ₁₂	1 M LiTFSI/TEGDME	3.83 vs Li ⁺ /Li	¹
17	1,4-dioxane	C ₄ H ₈ O ₂	1 M LiTFSI/TEGDME	6.87 vs Li ⁺ /Li	¹

18	N,N-dimethylformamide	C ₃ H ₇ NO	1 M LiTFSI/TEGDME	7.08 vs Li ⁺ /Li	¹
19	Tris[4-(diethylamino)phenyl] amine (TDPA)	[C ₂ H ₅) ₂ NC ₆ H ₄] ₃ N	0.1 M LiTFSI/TEGDME	3.1 V vs Li ⁺ /Li (1 e)	¹¹
20	Cobaltocene (CoCp ₂)	CoC ₁₀ H ₁₀	1 M LiTFSI in DME & DOL at a 1:1 vol. ratio	2.0 V vs Li ⁺ /Li	¹²
21	Poly(2,2,6,6-tetramethyl-1-piperinidyloxy-4-yl methacrylate) (PTMA)	C ₁₃ H ₂₃ NO ₃	1M LiPF ₆ in 1:1 by vol. mixture of EC/DEC	3.6 V vs Li ⁺ /Li	¹³
22	Iron Phthalocyanine (FePc)	C ₃₂ H ₁₆ FeN ₈	0.1 M LiTFSI/ TEGDME and 0.002 M FePc	Fe ^{III} / Fe ^{II} 3.65 V and Fe ^{II} /Fe ^I 2.5 V vs Li ⁺ /Li	¹⁴
23	Ethyl Viologen (EtV)	C ₁₄ H ₁₈ N ₂	0.3 M LiTFSI/ BMPTFSI added 2 mM EtV(OTf) ₂	2.4 V vs Li ⁺ /Li	¹⁵
24	N,N,-bis(salicylidene) ethylenediaminocobalt (Co-salen)	C ₁₆ H ₁₄ CoN ₂ O ₂	0.2 M LiClO ₄ in DMSO	-0.115 V vs Ag/AgNO ₃	¹⁶
25	Cobalt porphyrin (noted Co(II)-Po)	C ₂₀ H ₁₄ CoN ₄	0.2 M LiClO ₄ in DMSO	0.082 V vs Ag/AgNO ₃	¹⁶
26	Potassium ferricyanide/ potassium ferrocyanide	K ₃ Fe(CN) ₆ /K ₄ Fe(CN) ₆	1 M Na ₂ SO ₄ /1 M Na ₂ SO ₄	0.2 to 0.4 V vs Ag/AgCl	¹⁷
27	1,4-Benzoquinone (BQ)	C ₆ H ₄ O ₂	0.1 M Mg(TFSI) ₂ /DMSO	-0.07 vs NHE	¹⁸
28	Cobalt(II) 5,10,15,20-tetr phenyl-21H,23H-porphine (Co(II)TPP)	C ₄₄ H ₂₈ CoN ₄	0.1 M Mg(TFSI) ₂ /DMSO	0.75 vs NHE	¹⁸
39	Silicotungstic acid	H ₄ [SiW ₁₂ O ₄₀]	1 M H ₃ PO ₄ (PH=10)	+0.019 and -0.212 V vs NHE	^{19, 20}
30	Nickel hydroxide	Ni(OH) ₂ /NiOOH	1 M KOH	0.5 /0.45V vs Hg/HgO	²¹

References

1. H.-D. Lim, B. Lee, Y. Zheng, J. Hong, J. Kim, H. Gwon, Y. Ko, M. Lee, K. Cho and K. Kang, *Nature Energy*, 2016, **1**, 16066.
2. N. Feng, P. He and H. Zhou, *ChemSusChem*, 2015, **8**, 600-602.
3. Y. Ko, H. Park, B. Kim, J. S. Kim and K. Kang, *Trends in Chemistry*, 2019, **1**, 349-360.
4. C. M. Burke, R. Black, I. R. Kochetkov, V. Giordani, D. Addison, L. F. Nazar and B. D. McCloskey, *ACS Energy Letters*, 2016, **1**, 747-756.
5. B. J. Bergner, A. Schürmann, K. Peppler, A. Garsuch and J. Janek, *Journal of the American Chemical Society*, 2014, **136**, 15054-15064.
6. B. J. Bergner, C. Hofmann, A. Schürmann, D. Schröder, K. Peppler, P. R. Schreiner and J. Janek, *Physical Chemistry Chemical Physics*, 2015, **17**, 31769-31779.
7. K. P. C. Yao, J. T. Frith, S. Y. Sayed, F. Bardé, J. R. Owen, Y. Shao-Horn and N. Garcia-Araez, *The Journal of Physical Chemistry C*, 2016, **120**, 16290-16297.
8. X. Gao, Y. Chen, L. Johnson and P. G. Bruce, *Nature materials*, 2016, **15**, 882-888.
9. Z. Liu, Y. Zhang, C. Jia, H. Wan, Z. Peng, Y. Bi, Y. Liu, Z. Peng, Q. Wang, H. Li, D. Wang and J.-G. Zhang, *Nano Energy*, 2017, **36**, 390-397.
10. W. Yu, W. Yang, R. Liu, L. Qin, Y. Lei, L. Liu, D. Zhai, B. Li and F. Kang, *Electrochemistry Communications*, 2017, **79**, 68-72.
11. D. Kundu, R. Black, B. Adams and L. F. Nazar, *ACS Central Science*, 2015, **1**, 510-515.
12. K. R. Kim, K.-S. Lee, C.-Y. Ahn, S.-H. Yu and Y.-E. Sung, *Scientific Reports*, 2016, **6**, 32433.
13. A. Vlad, N. Singh, J. Rolland, S. Melinte, P. M. Ajayan and J. F. Gohy, *Scientific Reports*, 2014, **4**, 4315.
14. D. Sun, Y. Shen, W. Zhang, L. Yu, Z. Yi, W. Yin, D. Wang, Y. Huang, J. Wang, D. Wang and J. B. Goodenough, *Journal of the American Chemical Society*, 2014, **136**, 8941-8946.
15. M. J. Lacey, J. T. Frith and J. R. Owen, *Electrochemistry Communications*, 2013, **26**, 74-76.
16. R. Blanchard, V. Martin, A. Mantoux and M. Chatenet, *Electrochimica Acta*, 2018, **261**, 384-393.
17. J. Lee, S. Choudhury, D. Weingarth, D. Kim and V. Presser, *ACS Applied Materials & Interfaces*, 2016, **8**, 23676-23687.

18. Q. Dong, X. Yao, J. Luo, X. Zhang, H. Hwang and D. Wang, *Chemical Communications*, 2016, **52**, 13753-13756.
19. B. Rausch, M. D. Symes, G. Chisholm and L. Cronin, *Science*, 2014, **345**, 1326-1330.
20. J. Lei, J.-J. Yang, T. Liu, R.-M. Yuan, D.-R. Deng, M.-S. Zheng, J.-J. Chen, L. Cronin and Q.-F. Dong, *Chemistry – A European Journal*, 2019, **25**, 11432-11436.
21. L. Chen, X. Dong, Y. Wang and Y. Xia, *Nature Communications*, 2016, **7**, 11741.