Supplementary Information (SI) for Journal of Materials Chemistry A.

Metal-Organic Frameworks: Classifications, Synthesis, Structure-Property-Performance Relationship, and Techno-Economic Analysis of Redox Flow Batteries

Soumen Giri,[1],* Manasi Roy[2[a]], Sujoy Bandyopadhyay,[2[a,b]],* Sourav Das, [3],* Sutanu Mangal,[4] Subhankar Samanta [5]

[1]Department of Chemistry, School of Applied Sciences, Kalinga Institute of Industrial Technology (KIIT) Deemed to be University, Bhubaneswar-751024, Odisha, India

[2] [a] Department of Chemistry, Indrashil University, Rajpur, Kadi, Mehsana, Gujarat, 382740, India;

[b] Department of Chemistry, Research Institute for Convergence of Basic Science,and Research Institute for Natural Sciences, Hanyang University, Seoul 04763, Republic of Korea

[3 3] Department of Basic Sciences, Chemistry Discipline, Institute of Infrastructure Technology Research and Management, Near Khokhra Circle, Maninagar East, Ahmedabad-380026, Gujarat, India.

[4]Department of Physics, School of Applied Sciences, Kalinga Institute of Industrial Technology (KIIT) Deemed to be University, Bhubaneswar-751024, Odisha, India

[5] Bidhannagar College, Kolkata, West Bengal, India 700064

*Corresponding Author: giri.soumen02@gmail.com, sujoyb9@gmail.com, d.sourav245@gmail.com

Table S1: 2nd generation MOF which may be useful for RFBs development

MOF Name	Pore Size (nm) volume (cc/g)	Surface Area (m^2/g)	Chemical Stability	Key Applications	Special Features	Ref.
MIL-53(Al)	0.85-1.0	~ 1410	water stability at higher relative humidity	applications in gas adsorption, chemical sensing	Flexible framework with “breathing” behaviour Micro-crystalline materials	[1]
NH_2-MIL-53(Al)	1.3	340.92	Stable in water (pH 1-11) and mildly acidic environments	Hg^{2+} removal from water	Enhanced functionality due to -NH_2 groups	[2]
ZIF-8	~ 0.549 (cc/g)	~ 2000	Stable in water and high temperature 170°C to 535°C	CO_2 uptake capacity	Thermal stability	[3]

Table S2: Structure-property-relationship performance

Sr No	MOF	Surface Area (m²/g)	Chemical Stability	Electronic Conductivity (S/cm)	Energy Efficiency (EE)	Applications in RFBs	Ref
1.	MIL-125-NH_2 / UiO-66-CH_3 modified graphite felts (GFs)	1198	excellent chemical stability in the weakly acidic electrolyte	MIL-125-NH_2 has poor conductivity but distribution on the GF surfaces increases conductivity.	70% and 66 % EE MIL-125-NH_2 and UiO-66-CH_3 modified graphite felts (GFs) respectively at a current density of 30 mA/cm² with is 6.4% better than pristine GF	MOF act as an electrocatalyst that accelerate the I_3^-/I^- redox reaction can significantly improve energy efficiency in applications like redox flow batteries	[4]
2.	ZnO from the metal organic framework (Zn-MOF/ZnO),	10.82	-	electrode materials derived from carbonaceous materials that promote good electrical conductivity	voltage efficiency of 92% at 5 mA/cm²	The reusable glucose kit as a flow cell minimizes costs and balances pump losses, showcasing innovative applications in RFBs	[5]
3.	The electrolyte containing 0.1 M Fc1N112-TFSI	Not explicitly mentioned in the contexts, but inferred from the importance of separator properties.	The separator demonstrates high chemical stability in organic solvents, which is essential for maintaining performance over time in non-aqueous environments.	The specific values for electronic conductivity are not provided, the design of the separator aims to facilitate ionic conductivity, which is critical for the efficient operation of NARFBs. The use of MOF nanoparticles enhances this property	The electrochemical efficiency (EE) of the Li-based hybrid NARFB using the MOF-5 separator is indicated by a high Coulombic efficiency of 99.7%. This suggests that the separator effectively minimizes losses during charge and discharge cycles.	The MOF-5 based separator is specifically designed for use in non-aqueous redox flow batteries (NARFBs), addressing challenges such as electrolyte crossover and low ionic conductivity. Its unique properties make it suitable for grid-scale energy storage applications.	[6]
4.	The carbon felt electrode modified with ZIF-8 derivative	200	High chemical stability	specific numerical values are not provided in the contexts	ZnCF-6 achieves an average EE of 80.0% over 14 cycles; CoCF achieves 86.07% in the first cycle.	The advancements in electrode materials can lead to more efficient and stable RFB systems	[6]
5.	MOF-derived WZ-decorated GF Electrode; named as WZ-22-650	122.86	The formation of new W−O−Zr bonds indicates strong anchoring of WOx to ZrO_2, contributing to the chemical stability of the catalyst.	The presence of oligomeric tungsten clusters improves electronic conductivity, although specific values are not mentioned.	Energy Efficiency (EE): 83.94% at 80 mA cm^{-2}, 74.86% at 160 mA cm^{-2}. Voltage Efficiency (VE): 87.76% at 80 mA cm−2, 76.76% at 160 mA cm^{-2}.	The WZ-22-650 catalyst is specifically designed for vanadium redox flow batteries (VRFBs), enhancing their electrochemical performance due to increased surface electroactive sites	[7]

6.	sPBI−MGE-2 composite	The introduction of MGE enhances the surface area due to the porous structure of MOF-808. But has not mentioned any specific value	The sPBI−MGE-2 membrane shows great chemical stability, with mass loss rates comparable to Nafion117	The sPBI−MGE-2 membrane exhibits high proton conductivity of 30.8 mS cm −1, significantly higher than pristine sPBI (12.5 mS cm $^{-1}$).	The sPBI−MGE-2 membrane achieves an EE of 83.81% at 60 mA cm −2, outperforming Nafion117	The sPBI−MGE-2 membrane demonstrates superior performance in RFBs due to its high conductivity and stability.	[8]
7.	Zr-metal organic framework (MOF-801 and MOF-808)	The surface area of MOF-801 and MOF-808 is optimized for high-quality composite membranes, aiding in ion transport and interaction. But has not mentioned any specific value	Both MOF-801 and MOF-808 exhibit acid stability, ensuring durability under operational conditions.	The incorporation of Zr-MOFs significantly enhances the proton conductivity of the membranes, with S/808-3 showing the highest conductivity of 0.0766 S cm^{-1}.	The coulombic efficiency (CE) of the membrane with MOF-801 ranges from 98.5% to 99.2%, while the voltage efficiency (VE) for MOF-808 is between 93.7% and 84.1%.	The Zr-MOFs are used to create membranes that improve ion sieving and proton conductivity, leading to enhanced performance in vanadium redox flow batteries.	[9]
8.	porous ZrO_2@C nanocomposite derived from MOF UiO- 66	79.81	Good chemical stability	Value not found in the articles	ZrO_2@C electrodes show improved VE (77.5) and EE (75.2) at 200 mA cm-2 compared to pristine cells.	Graphite felt modified with ZrO2@C is used to enhance performance in VRFBs.	[10]

Table S3: Various MOF structures used in RFBs with their metal nodes and linker/functional groups, also the properties therein and corresponding results.

Sl.	MOF	Metal or SBUs and Substituent/ Linker	Properties	Results/Advantage	Ref.
1.	NiO-ZnO composite derived from related MOFs	Ni and Zn/-	Synergistic combination between	Higher redox activity, better efficiency	[11]
2.	MIL-125-NH_2	Ti/2-amino benzene dicarboxylic acid	Crystal structure (pore size 0.6 nm)	No Zr leached after 1-7 days	[4]
3.	UiO-66-CH_3	Zr/ 2,5-dimethyl terephthalic acid	Crystal structure (pore size 1.2 nm)	Ti was detected leaching out	[4]

4.	MOF-801	Zr or $Zr_6O_4(OH)_4$ SBUs/fumaric acid (-COOH),	- More Hydrogen Bonding - fumarate linker (5.2 Å) - cavities 0.58 Å - triangular window 3.5 Å	- Ion selectivity is less - Take part synergistic combination with MOF-808.	[9]
5.	MOF-808	Zr or $Zr_6O_4(OH)_4$ /trimesic acid (-COOH),	- More Hydrogen Bonding - linker (7.2 Å) longer and bulkier - cavities 1.92 Å. - faster proton transfer rate than MOF-801 - hexagonal window≈10.1 Å	- Abundant hydrogen bond network for proton hopping - Higher ion selectivity	[9]
6.	MOF-808	Zr/H_3BTC amino groups and carboxyl groups present	Acid−base pair effect (amino groups and sulfonic acid groups).	Amino groups and carboxyl groups can offer more pathways for the passage of protons	[8]
7.	MOF-derived ZrO_2	Zr/-	Collapse of the benzene ring structure in the Zr-MOF	Calcination tetragonal ZrO_2	[12]
8.	Ultrathin Ni-MOF nanosheets	Ni/H_2BDC	2D MOF	- the nanosheet more effective in impeding the ion crossover. - coexistence of micropore and mesopore in the MOF layer.	[13]
9.	MOF derived WO_x/ZrO_2, tungstated zirconia	Zr/BDC (benzene-1,4-dicarboxylate)	Surface area: 122.86 $m^2 g^{-1}$ Pore volume: 0.1839 ore volume ($cm^3 g^{-1}$) Pore diameter: 10.125 nm	- New W−O−Zr bondscreated confirms that WO_x the strong anchoring of ZrO_2	[7]
10.	Bimetallic metal–organic framework (NiCo-MOF)	NiCo/BTC	BTC and 4,40 -bipyridine were coordinated to the Ni, Co metal ions	- hydrogen bonding with the free carbonyl group stabilized 2D layer - unsaturated metal coordination sites enable a robust active site for the	[14]

				$2Br^{-}/Br_2$ redox couple.	
11.	Metal–organic frame work derivative ZIF-8 and ZIF-67 derivative	Zn/2-methylimidazole Co/2-methylimidazole	• ZIF-8-hydrophilic surface(carbonized derivatives) • Zn deposition and reduce dendrite generation.	• rhombic dodecahedral morphology of ZIF-8	[6]
12.	MOF-5	Zn/H_2BDC	Size of the pores of MOF-5 is 0.8 nm	• block the active species, but also provide an efficient Li^+ ion pathway through the structural nanopores	[15]
13.	CAU-10-H	Al/1,3-H_2BDC	• Pore size of 0.7 nm • Under acidic, it is chemically stable	• Prevent the passage of vanadium ions by ion screening.	[16]
14.	CAU-10-X (X = –OH, –CH_3, –OS1, –OS2)	Al/5-hydroxy isophthalic acid or 5- methyl isophthalic acid	• Smaller channel size than that of CAU-10-H (0.7 nm) • Functionalized	• Combination of hydroxyl and sulfonic acid groups were more effective in suppressing the crossover phenomenon	[17]

References:

1. W. P. Mounfield and K. S. Walton, *Journal of Colloid and Interface Science*, 2015, **447**, 33-39.
2. M. Jian, X. Yang, C. Huang, C. Tang, X. Zhang, R. Liu and H. Li, *Chemical Engineering Journal*, 2024, **483**, 149022.
3. A. Chakraborty, S. Laha, K. Kamali, C. Narayana, M. Eswaramoorthy and T. K. Maji, *Inorganic Chemistry*, 2017, **56**, 9426-9435.
4. B. Li, J. Liu, Z. Nie, W. Wang, D. Reed, J. Liu, P. McGrail and V. Sprenkle, *Nano Letters*, 2016, **16**, 4335-4340.
5. P. Lakshmanan, S. Rengapillai, S. Marimuthu and S. Vembu, *Energies* 2022, **15**, 7635.
6. Y. Xie, L. Zhou, J. Li, X. Zhang, K. Liu, H. Zhang and T. Qi, *Journal of Electroanalytical Chemistry*, 2024, **952**, 117863.
7. A. M. Demeku, D. M. Kabtamu, G.-C. Chen, Y.-T. Ou, Z.-J. Huang, T.-C. Chiang, H.-C. Huang and C.-H. Wang, *ACS Applied Materials & Interfaces*, 2024, **16**, 7047-7056.
8. T. Gao, C. Li, W. Bai, Y. Luo, D. Yu and S. Wang, *ACS Applied Polymer Materials*, 2024, **6**, 6552-6560.
9. L. Xin, D. Zhang, K. Qu, Y. Lu, Y. Wang, K. Huang, Z. Wang, W. Jin and Z. Xu, *Advanced Functional Materials*, 2021, **31**, 2104629.

10. Y. Jiang, G. Cheng, Y. Li, Z. He, J. Zhu, W. Meng, L. Dai and L. Wang, *Chemical Engineering Journal*, 2021, **415**, 129014.
11. P. Lakshmanan, P. J. Janshirani, S. Rengapillai and M. Sivakumar, *ChemPhysChem*, 2023, **24**, e202300283.
12. Y.-T. Ou, D. M. Kabtamu, A. W. Bayeh, H.-H. Ku, Y.-L. Kuo, Y.-M. Wang, N.-Y. Hsu, T.-C. Chiang, H.-C. Huang and C.-H. Wang, *Catalysts,* 2021, **11**, 1188.
13. J. Yuan, C. Zhang, T. Liu, Y. Zhen, Z.-Z. Pan and Y. Li, *Journal of Membrane Science*, 2020, **612**, 118463.
14. R. Naresh, K. Satchidhanandam, K. R. Ilancheran, B. Ambrose, M. Kathiresan and P. Ragupathy, *Journal of Materials Chemistry A*, 2024, **12**, 14669-14678.
15. J. Yuan, C. Zhang, Q. Qiu, Z.-Z. Pan, L. Fan, Y. Zhao and Y. Li, *Chemical Engineering Journal*, 2022, **433**, 133564.
16. C. Li, T. Gao, W. Wu, X. Zhou, S. Zhang, G. Ma, X. Guan and S. Wang, *ACS Applied Energy Materials*, 2024, **7**, 7534-7544.
17. H. J. Choi, C. Youn, S. C. Kim, D. Jeong, S. N. Lim, D. R. Chang, J. W. Bae and J. Park, *Microporous and Mesoporous Materials*, 2022, **341**, 112054.