

One pot synthesis and characterization of binary and ternary metal organic frameworks (MOFs) as tri-modal catalysts for thiophene electrooxidation, water splitting and 4-nitrophenol reduction

Mahendran Manivannan,^{a,b} Venkatachalam Rajagopal,^{a,b,d} Lalithambigai Krishnamoorthy,^c Dhanasurya Selvam^e, Vembu Suryanarayanan,^{a,b*} Murugavel Kathiresan ^{a,b}, Thasan Raju,^{a,b} Lathe A. Jones,^d

^aElectro Organic & Materials Electrochemistry Division, CSIR-Central Electrochemical Research Institute, Karaikudi-630003, Tamil Nadu, India E-mail: vidhyasur@yahoo.co.in

^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

^cDepartment of Electronics and Communication Engineering PSG College of Technology Coimbatore – 641 004, Tamil Nadu, India.

^dCentre for Advanced Materials and Industrial Chemistry (CAMIC), School of Science, STEM College, RMIT University, GPO Box 2476, Melbourne, Victoria 3001, Australia.

^eCentre for Education (CFE), CSIR—Central Electrochemical Research Institute (CECRI), Karaikudi 630003, Tamil Nadu, India.

Corresponding author e-mail id : vidhyasur@yahoo.co.in, surya@cecri.res.in

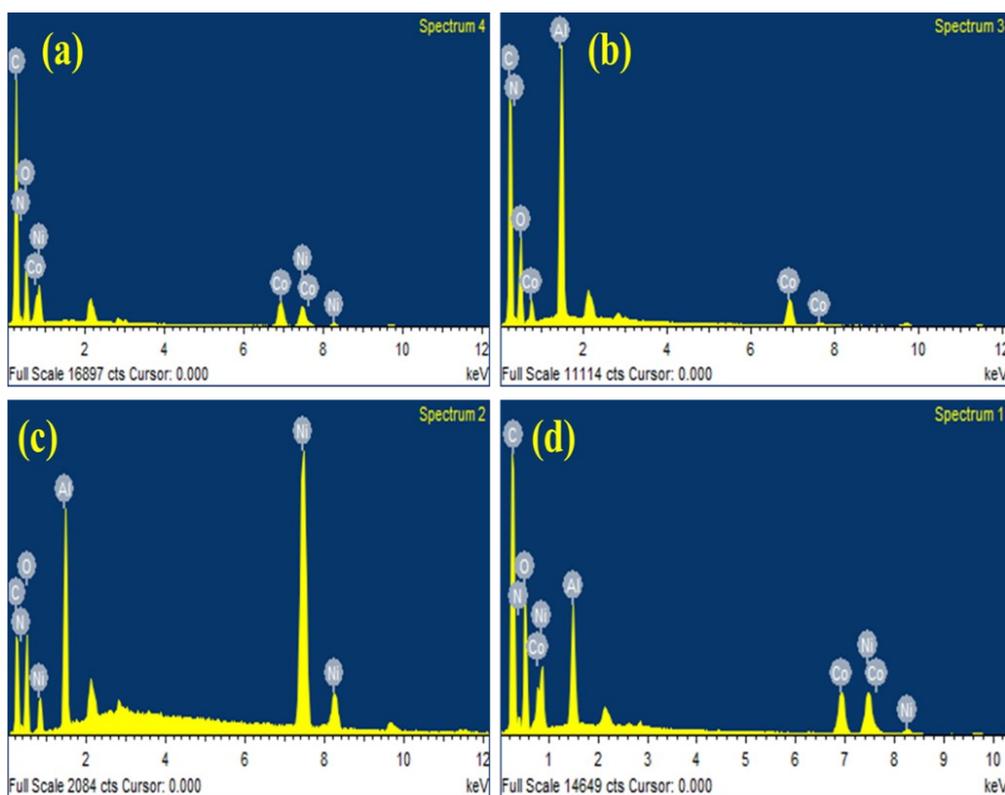


Figure S1. EDAX images of a) Co-Ni-MOF, b) Co-Al-MOF c) Ni-Al-MOF, and d)Co-Al-Ni-MOF.

Table S1. EDAX analysis of the synthesized composite weight percentage

S.No.	Catalyst	Element weight (%)					
		Al	Co	Ni	C	N	O
1	Co-Ni-MOF	-	7.71	7.22	53.59	9.20	22.29
2	Co-Al-MOF	10.49	6.22	-	51.85	7.15	24.30
3	Ni-Al-MOF	8.70	-	49.57	25.92	3.72	12.09
4	Co-Al-Ni-MOF	3.94	7.41	8.61	44.66	8.83	26.54

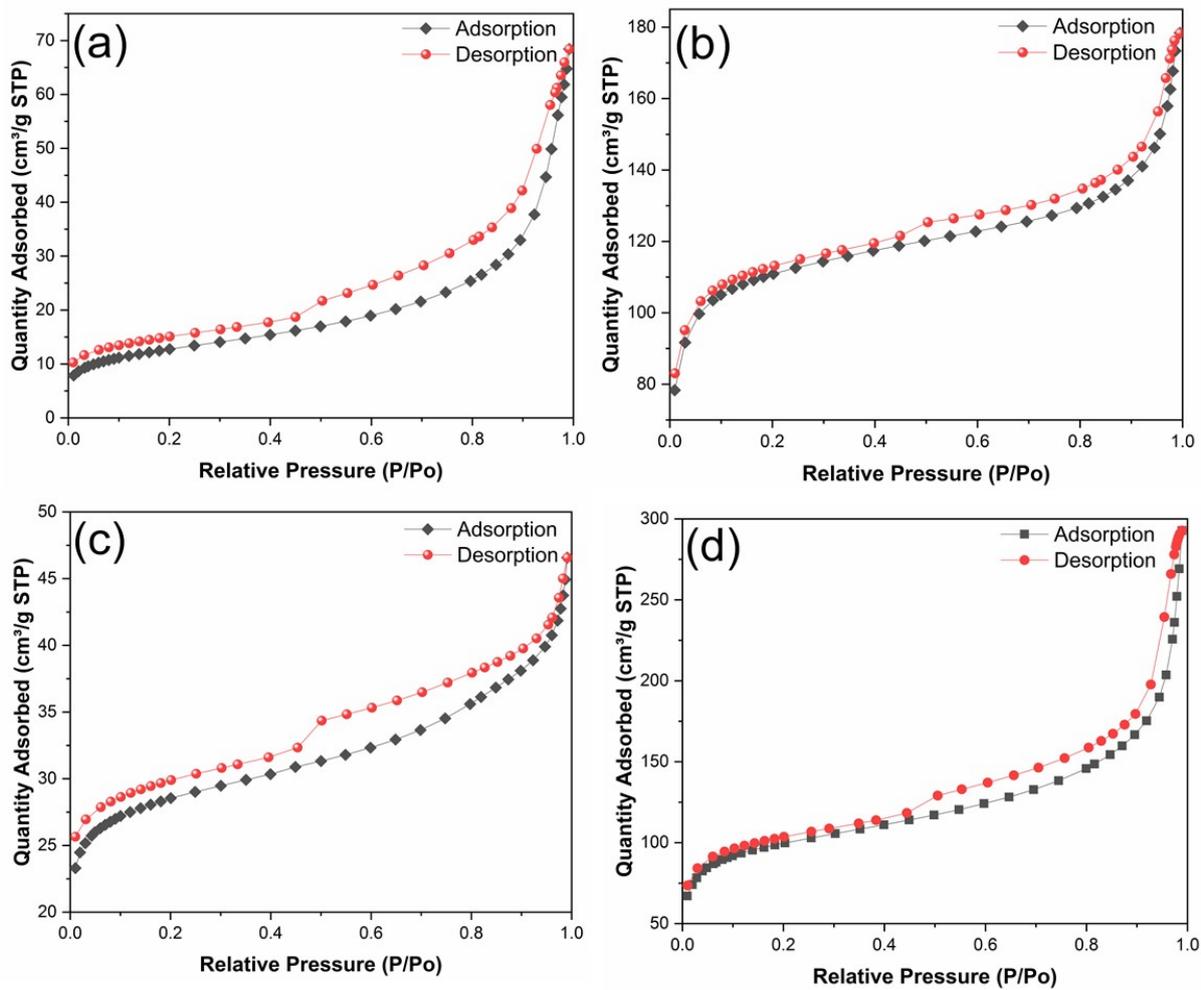


Figure S2. BET results of a) Ni-Al-MOF, b) Co-Al-MOF, c) Co-Ni-MOF and d) Co-Al-Ni-MOF.

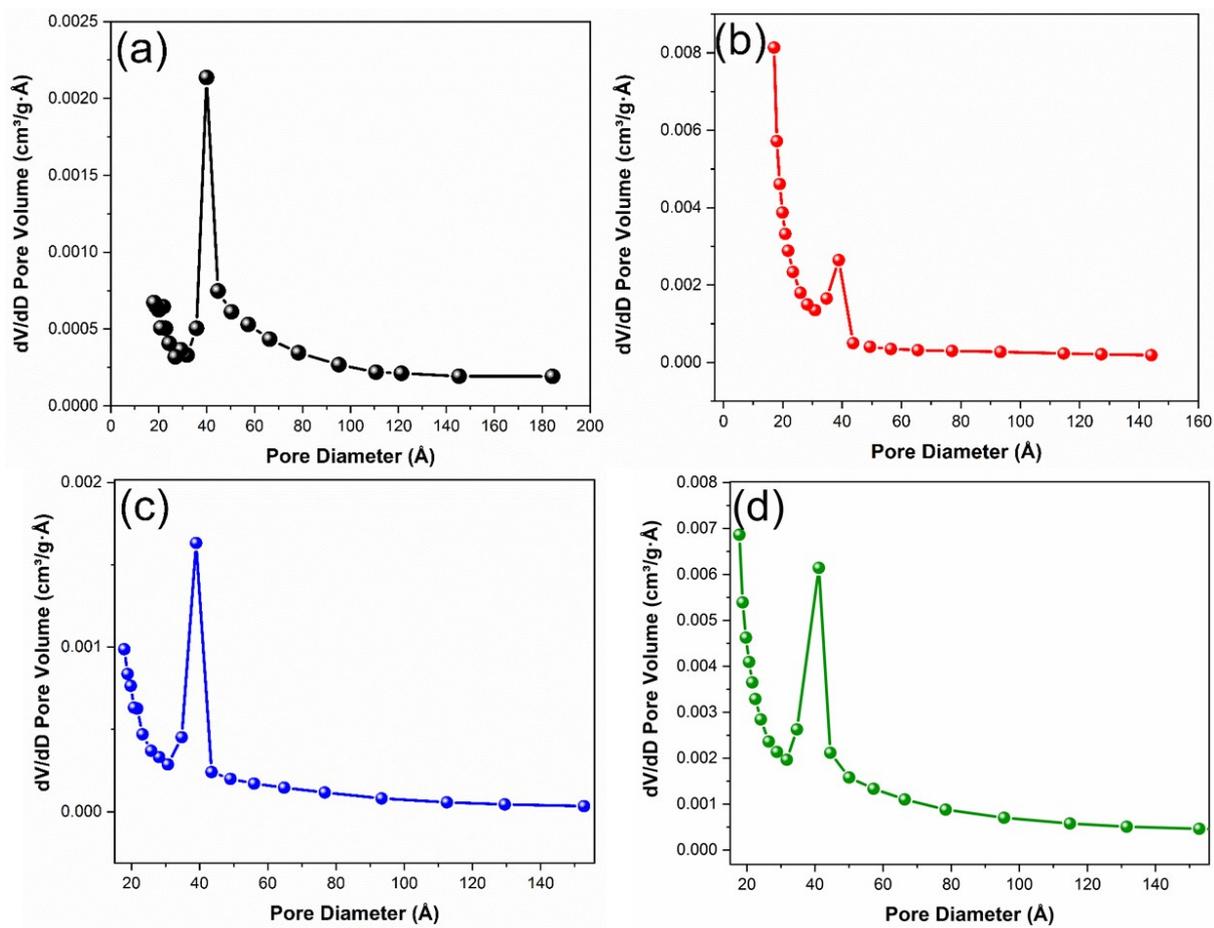


Figure S3. BET pore size distribution plot of a) Ni-Al-MOF, b) Co-Al-MOF, c) Co-Ni-MOF and d) Co-Al-Ni-MOF.

Table S2. BET surface area ($\text{m}^2 \text{g}^{-1}$), pore volume ($\text{cm}^3 \text{g}^{-1}$) and mean pore diameter (\AA) of Ni-Al-MOF, Co-Al-MOF, Co-Ni-MOF and Co-Al-Ni-MOF obtained using the N_2 absorption-desorption isotherms.

S.No.	Catalyst	BET surface area ($\text{m}^2 \text{g}^{-1}$)	pore volume ($\text{cm}^3 \text{g}^{-1}$)	mean pore diameter (\AA)
1	Ni-Al-MOF	7.8144	0.1058	40
2	Co-Al-MOF	19.8026	0.2758	38.77
3	Co-Ni-MOF	6.0303	0.0720	39.26
4	Co-Al-Ni-MOF	38.777	0.4528	41.58

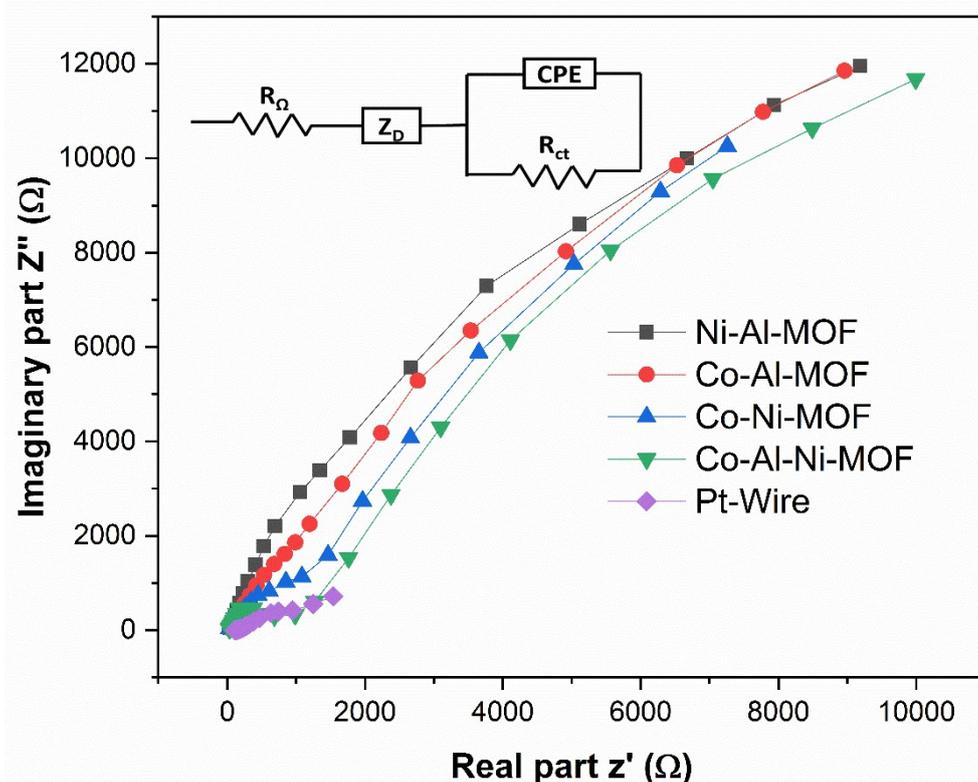


Figure S4. Impedance curves for synthesized MOFs for electrooxidation of thiophene

Table S3 Summary of comparative performance of Ni and Co based MOF catalysts recently reported for water splitting along with the present one.

No.	Catalyst	Electrolyte	Overpotential [mV]	Tafel slope [mV dec ⁻¹]	References
1	Ni-MOF	0.1 M KOH	296	45	1
2	Ni-BTC	0.1 M KOH	330	63	2
3	Ni-MOF-74	1.0 M KOH	313	134.1	3
4	Ni-MOF	1.0 M KOH	268	132.5	4
5	3D NibpyfcdHp	0.5 M H ₂ SO ₄	350	60	5
6	3D CobpyfcdHp	0.5 M H ₂ SO ₄	400	65	5
7	Co ₂ (Hpycz) ₄ ·4H ₂ O	0.5 M H ₂ SO ₄	223	121	6
8	THTA–Co H ₃ [Co ₃ (tht)(tha)]	0.5 M H ₂ SO ₄	283	71	7
9	H ₃ [Ni ₃ (tht)(tha)]	0.5 M H ₂ SO ₄	315	76	7
10	CoNi-MOF	1.0 M KOH	265	56	8
11	Ni/Co(10:1)-MOFs	1.0 M KOH	248	40.92	9
12	Co, 0.3Ni	1.0 M KOH	330	66	10
13	CoNi-MOF/rGO	1.0 M KOH	318	48	11
14	NiCo-UMOFNs	1.0 M KOH	250	42	12
15	CoNi-MOF	1.0 M KOH	304	89.7	13
16	3D Co/Ni-MOFs	0.5 M H ₂ SO ₄	357	107	14
17	Ni/Co(II) MOFs/PPPT	0.5 M H ₂ SO ₄	369	127.1	15
18	Ni-Co-Al -MOF	1.0 M KOH (OER)	220	97	This work
		1.0 M KOH (HER)	174	108	This work

References

1. J. Duan, S. Chen, C. Zhao, *Nat. Commun.* 2017, **8**, 15341.
2. L. Wang, Y. Wu, R. Cao, L. Ren, M. Chen, X. Feng, J. Zhou, B. Wang, *ACS Appl. Mater. Interfaces* 2016, **8**, 16736.
3. J. Xing, K. Guo, Z. Zou, M. Cai, J. Du, C. Xu, *Chem. Commun.* 2018, **54**, 7046.
4. X. Ling, F. Du, Y. Zhang, Y. Shen, T. Li, A. Alsaedi, T. Hayat, Y. Zhou, Z. Zou, *RSC Adv.* 2019, **9**, 3558.
5. V. Khrizanforova, R. Shekurov, V. Miluykov, M. Khrizanforov, V. Bon, S. Kaskel, A. Gubaidullin, O. Sinyashin and Y. Budnikova, *Dalton Trans.*, 2020, **49**, 2794–2802.
6. R. Shekurov, V. Khrizanforova, L. Gilmanova, M. Khrizanforov, V. Miluykov, O. Kataeva, Z. Yamaleeva, T. Burganov, T. Gerasimova and A. Khamatgalimov, *Dalton Trans.*, 2019, **48**, 3601–3609.
7. R. Dong, Z. Zheng, D. C. Tranca, J. Zhang, N. Chandrasekhar, S. Liu, X. Zhuang, G. Seifert and X. Feng, *Chem. Eur. J.*, 2017, **23**, 2255–2260.
8. M. Liu, W. Zheng, S. Ran, S. T. Boles, L. Y. S. Lee, *Adv. Mater. Interfaces* 2018, **5**, 1800849.
9. X. Wang, H. Xiao, A. Li, Z. Li, S. Liu, Q. Zhang, Y. Gong, L. Zheng, Y. Zhu, C. Chen, D. Wang, Q. Peng, L. Gu, X. Han, J. Li, Y. Li, *J. Am. Chem. Soc.* 2018, **140**, 15336.
10. Y. Li, Z. Gao, H. Bao, B. Zhang, C. Wu, C. Huang, Z. Zhang, Y. Xie, H. Wang, *J. Energy Chem.* 2020, **53**, 251.
11. X. R. Zheng, Y. H. Cao, D. Y. Liu, M. Cai, J. Ding, X. R. Liu, J. H. Wang, W. B. Hu, C. Zhong, *ACS Appl. Mater. Interfaces* 2019, **11**, 15662.
12. S. L. Zhao, Y. Wang, J. C. Dong, C. T. He, H. J. Yin, P. F. An, K. Zhao, X. F. Zhang, C. Gao, L. J. Zhang, J. W. Lv, J. X. Wang, J. Q. Zhang,

- A. M. Khattak, N. A. Khan, Z. X. Wei, J. Zhang, S. Q. Liu, H. J. Zhao, Z. Y. Tang,
Nat. Energy 2016, **1**, 16184.
13. J. Wu, Z. Yu, Y. Zhang, S. Niu, J. Zhao, S. Li, P. Xu, *Small* 2021, **17**, 2105150.
14. X. Wang, J.-Y. Luo, J.-W. Tian, D.-D. Huang, Y.-P. Wu, S. Li and D.-S. Li, *Inorg. Chem. Commun.*, 2018, **98**, 141–144.
15. J.L. Liu, X.Y. Zhou, L. Qin, Y.Q. Wang, H.J. Zhu, G. Ni, M.L. Ma, Zhang, M.D. *J. Mol. Struct.* 1252, 132184.