

Supporting Information

Investigation of non-precious metal cathode catalysts for direct borohydride fuel cells

*Yu Guo,^a Yingjian Cao,^a Qinggang Tan,^b Daijun Yang,^a Yong Che,^c Cunman Zhang,^a
Pingwen Ming,^a and Qiangfeng Xiao^{a*}*

^aSchool of Automotive Studies & Clean Energy Automotive Engineering Center,
Tongji University (Jiading Campus), 4800 Cao'an Road, Shanghai 201804, China

^bSchool of Materials Science & Engineering, Tongji University (Jiading Campus),
4800 Cao'an Road, Shanghai, 201804, China

^cEnpower Beijing Corp. 13 Area 2 Jinsheng Street, Daxing, Beijing, 06500

*Corresponding Authors. E-mail: xiaoqf@tongji.edu.cn (Q.X.).

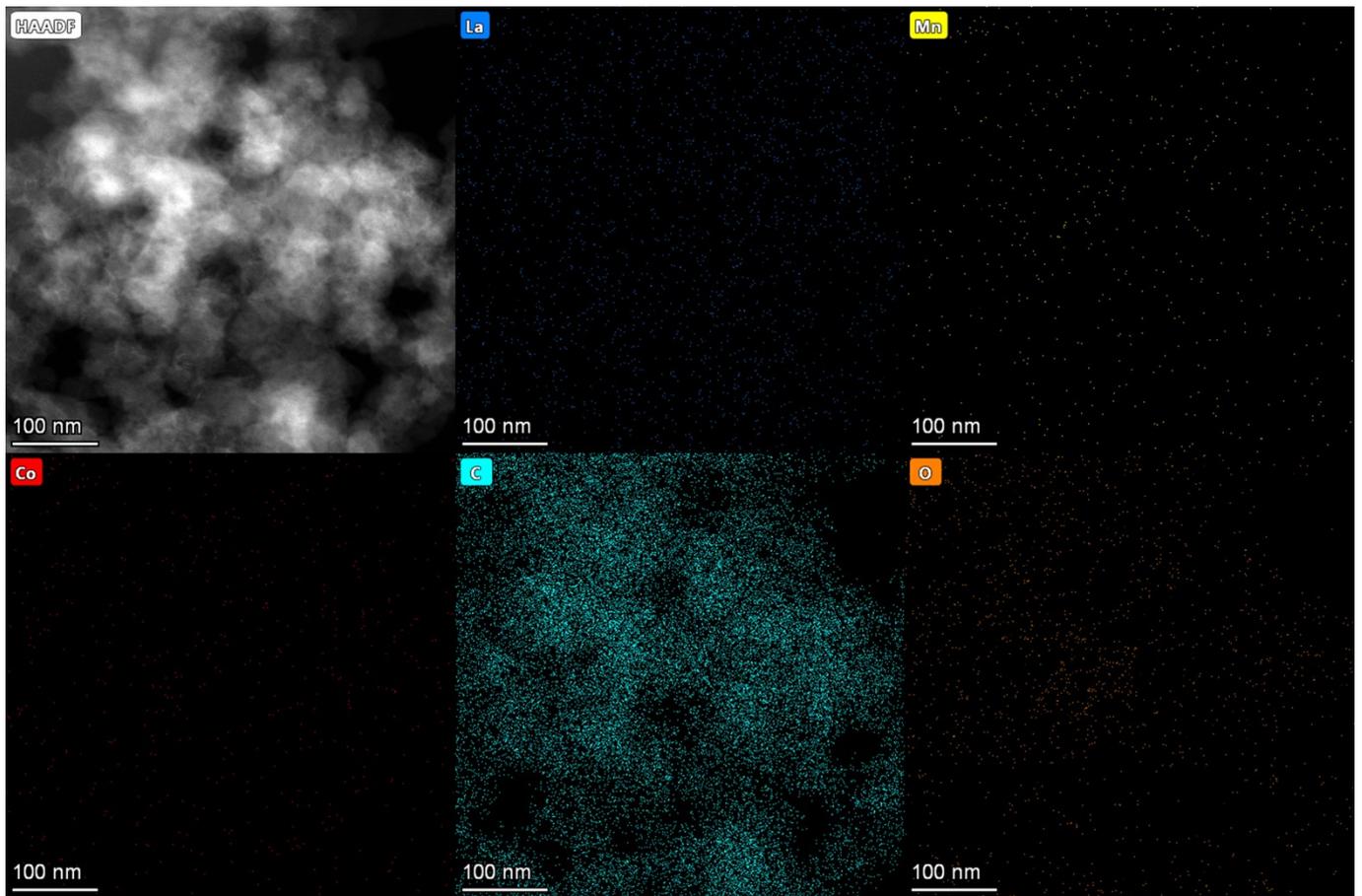


Figure S1. HAADF-TEM and EDS elemental mapping image of pristine LMCO electrode.

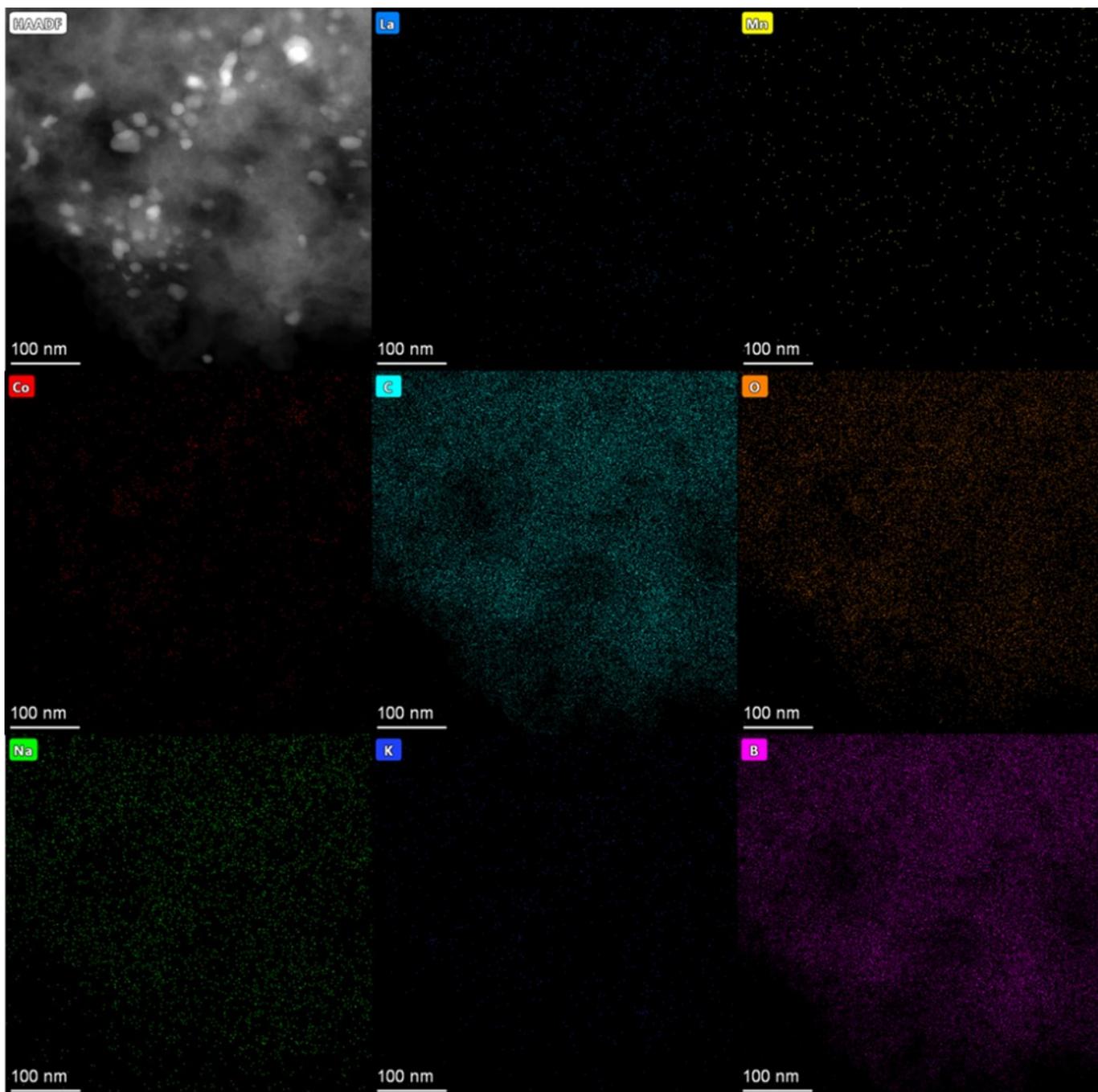


Figure S2. HAADF-TEM and EDS elemental mapping image of LMCO electrode after durability test.

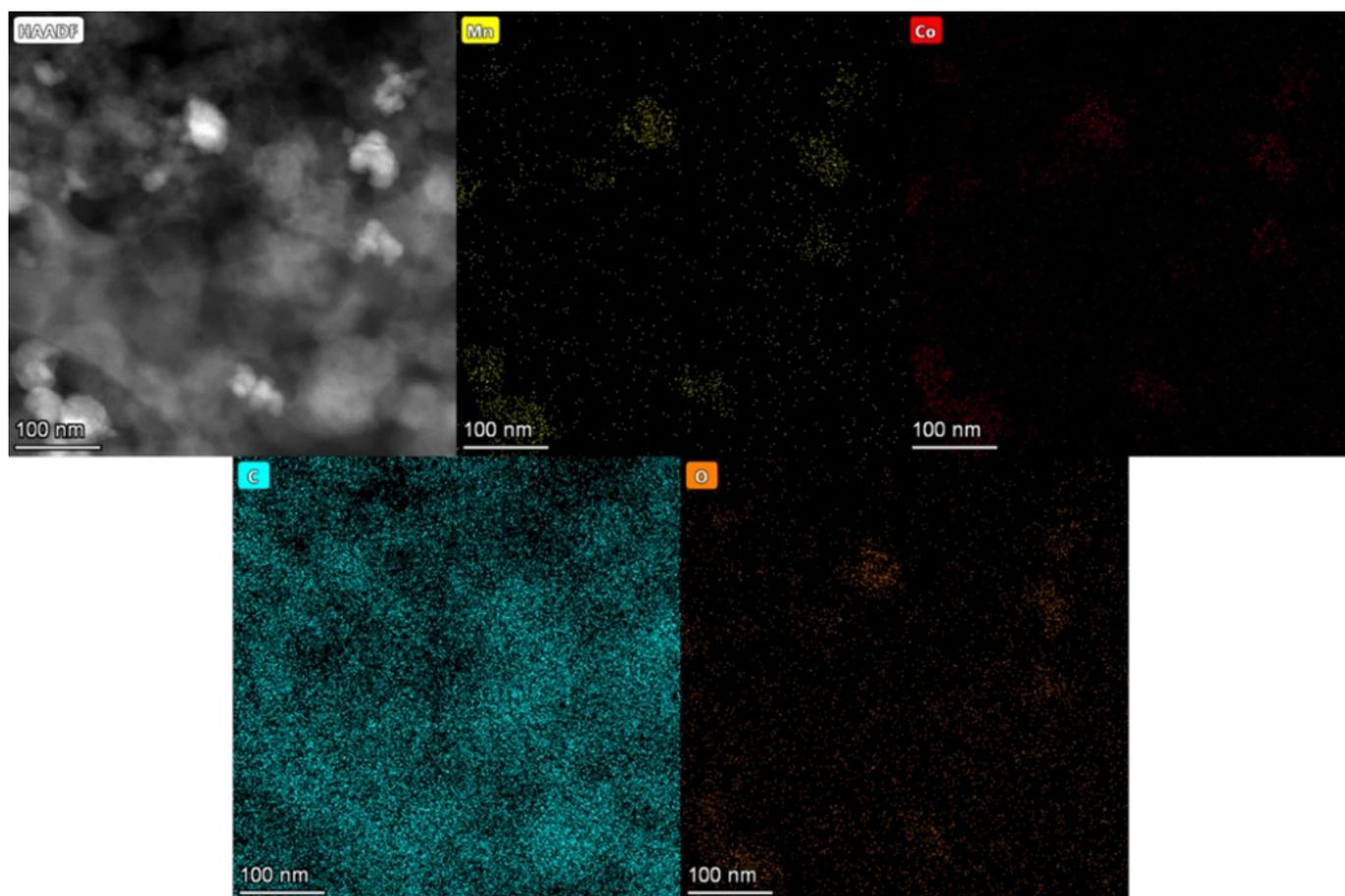


Figure S3. HAADF-TEM and EDS elemental mapping image of pristine MCS electrode.

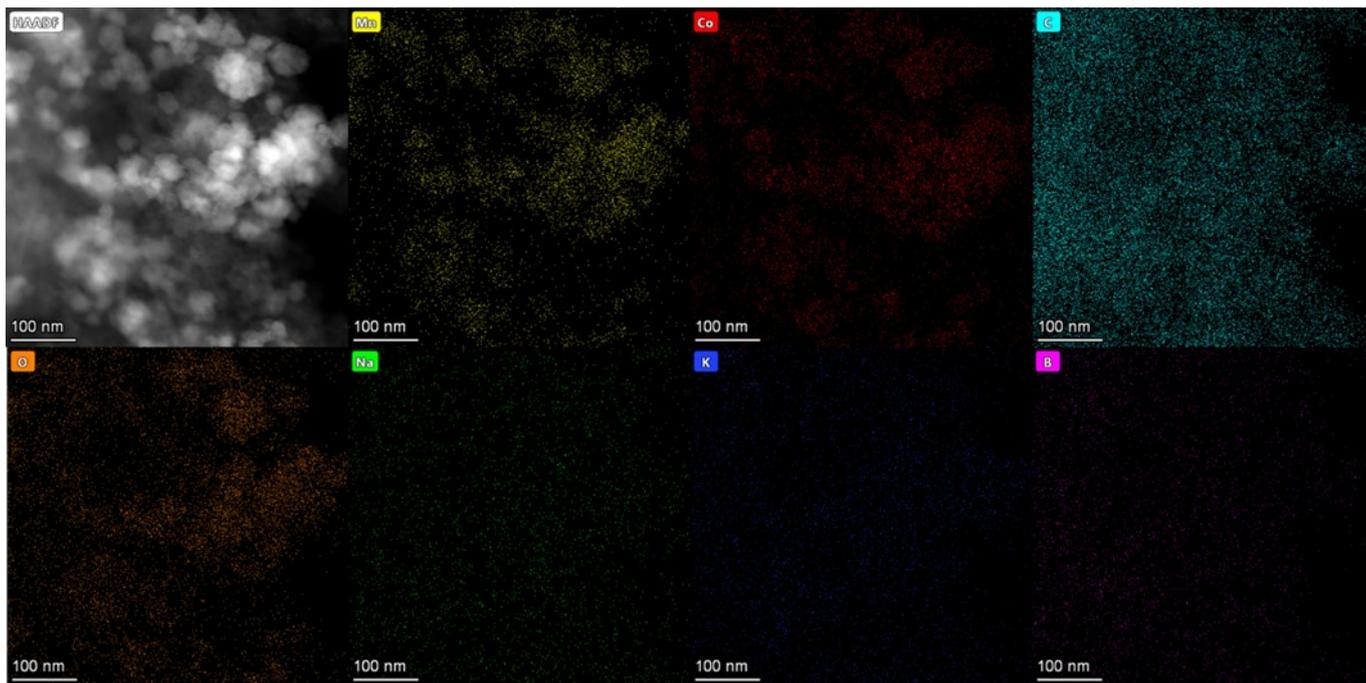


Figure S4. HAADF-TEM and EDS elemental mapping image of MCS electrode after durability test.

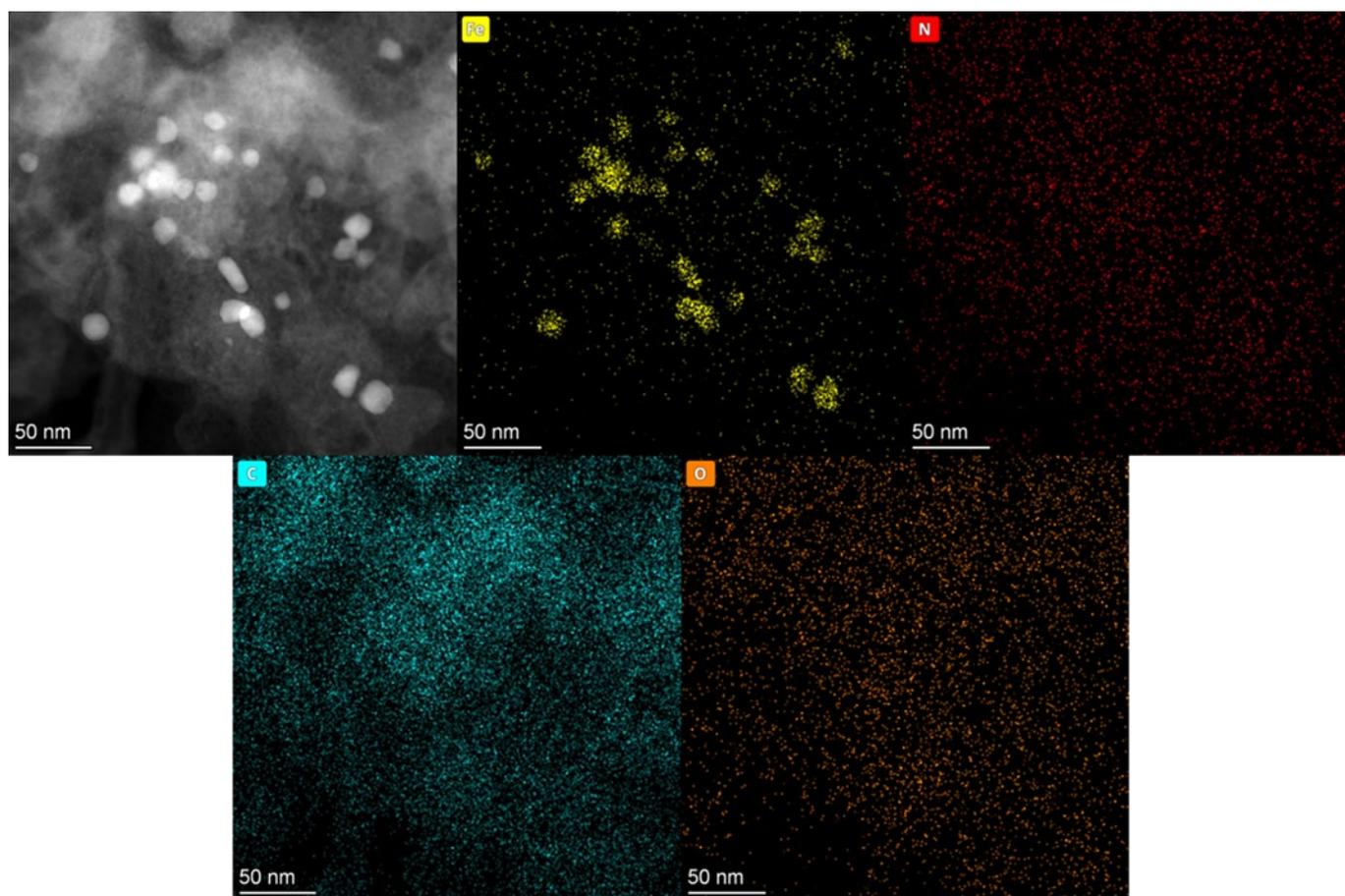


Figure S5. HAADF-TEM and EDS elemental mapping image of pristine Fe-N-C electrode.

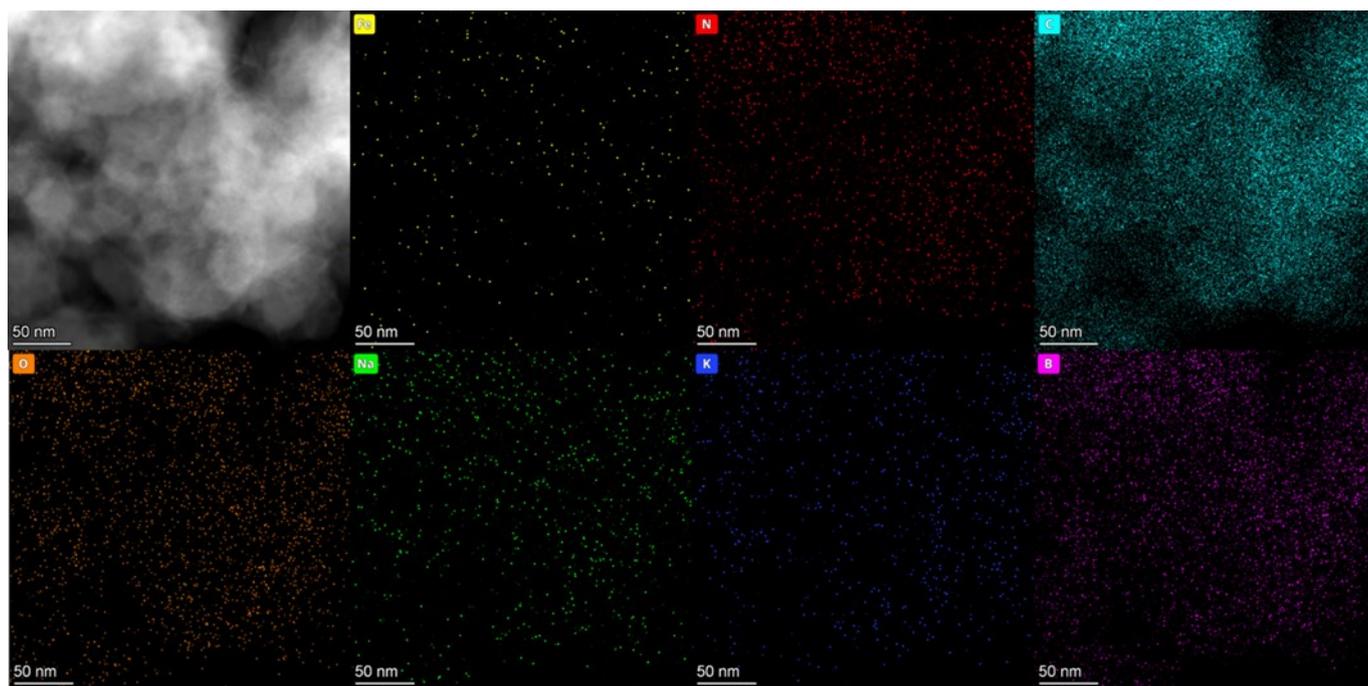


Figure S6. HAADF-TEM and EDS elemental mapping image of Fe-N-C electrode after durability test.

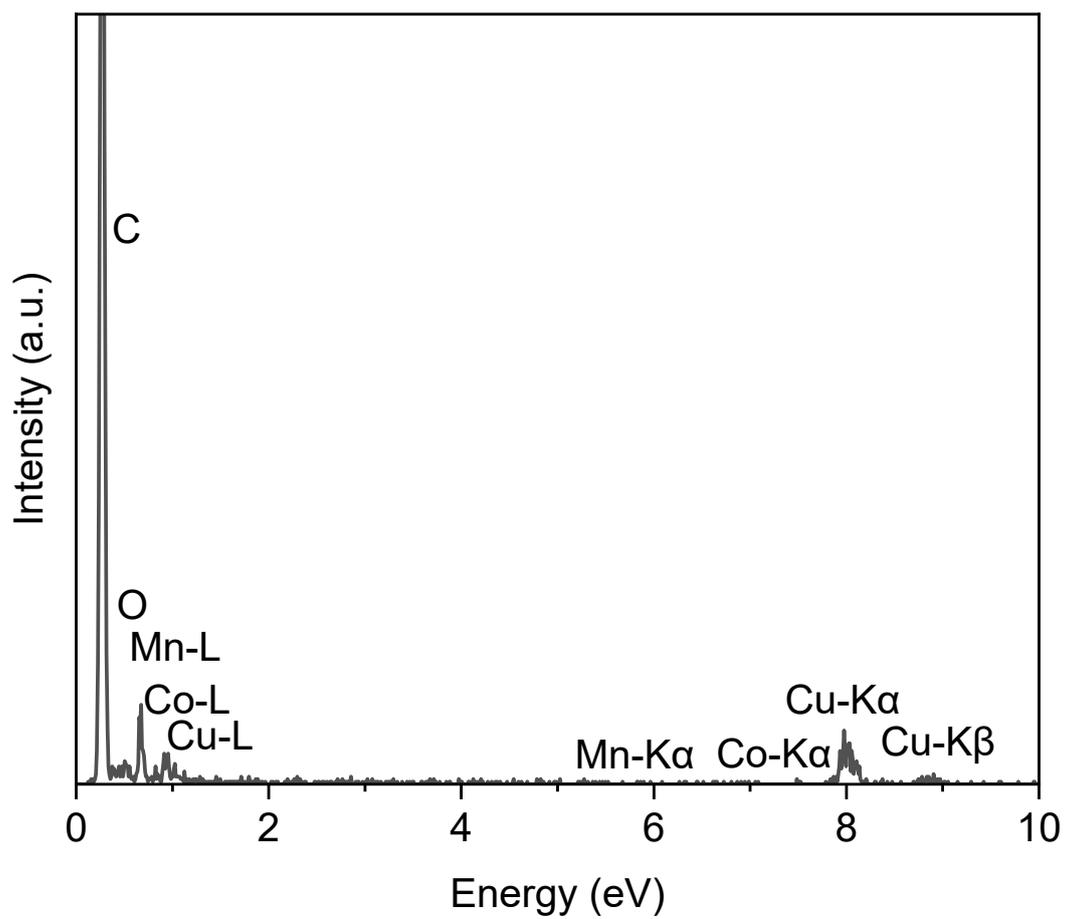


Figure S7. EDS elemental spectrum of pristine LMCO electrode.

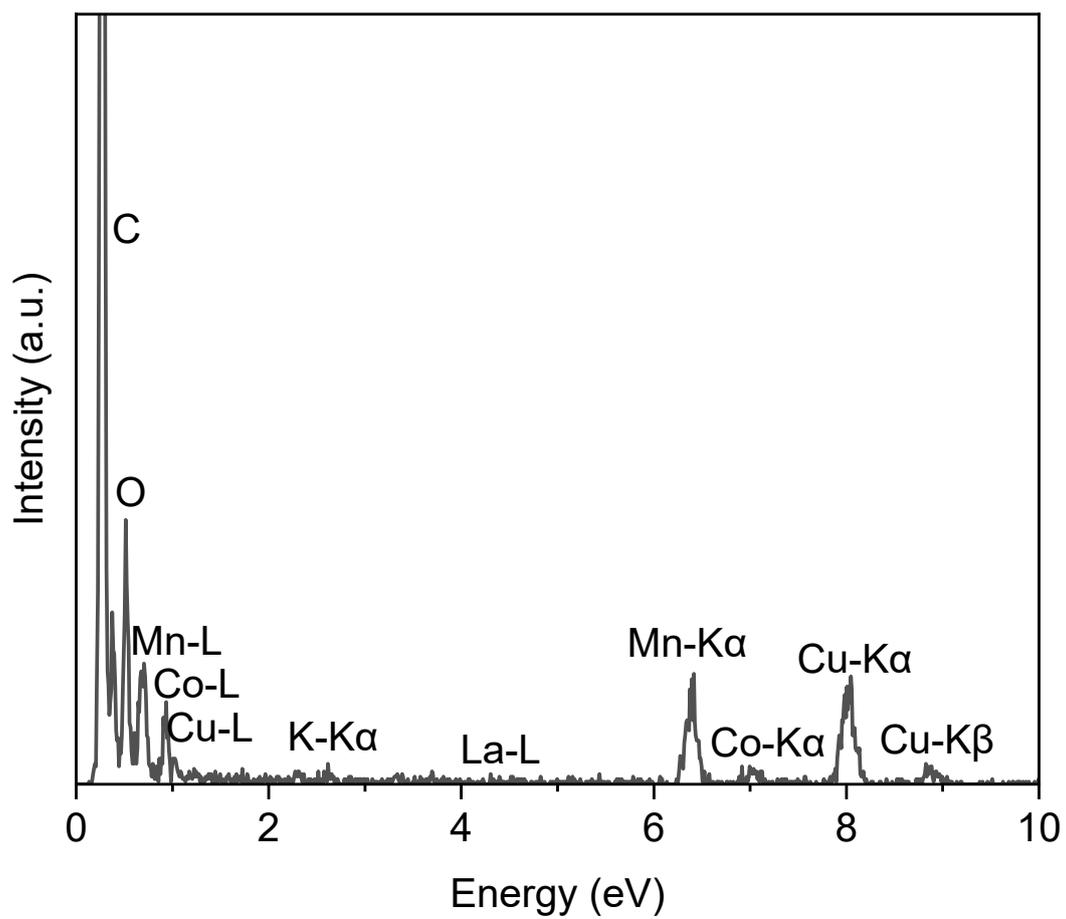


Figure S8. EDS elemental spectrum of LMCO electrode after durability test.

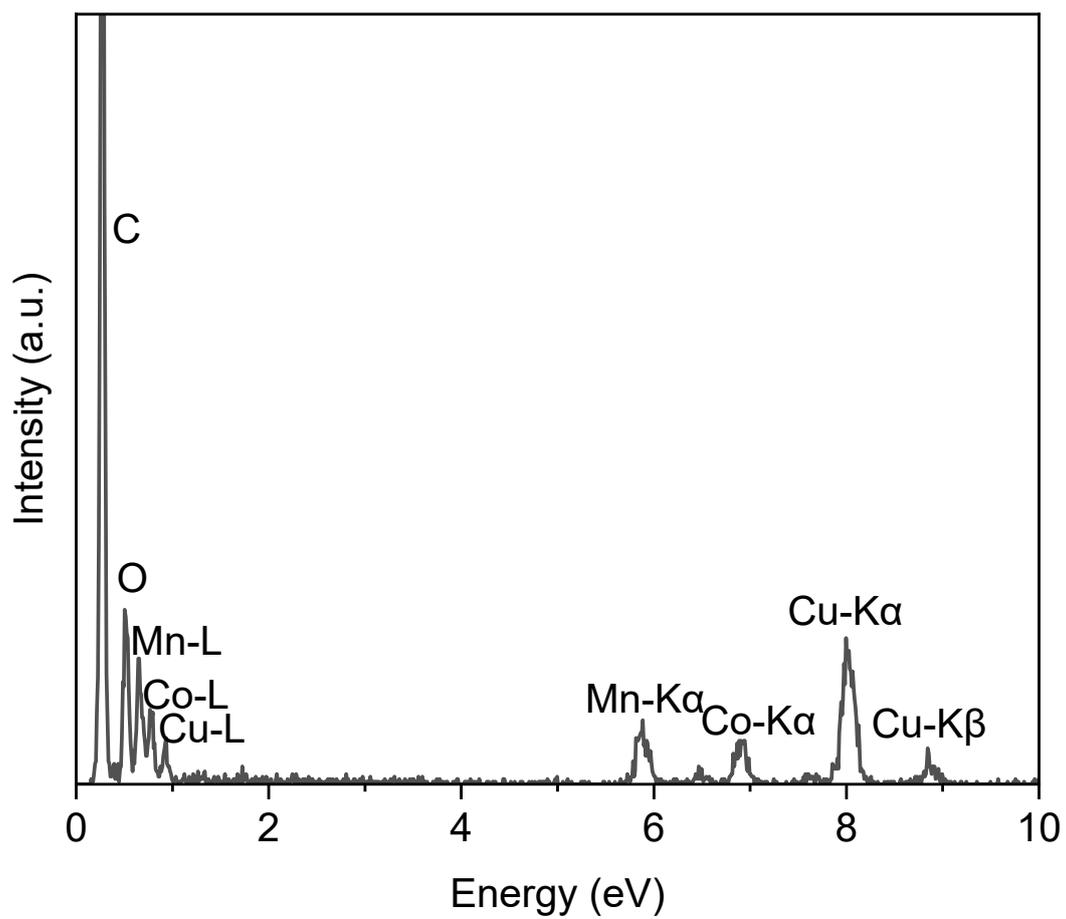


Figure S9. EDS elemental spectrum of pristine MCS electrode.

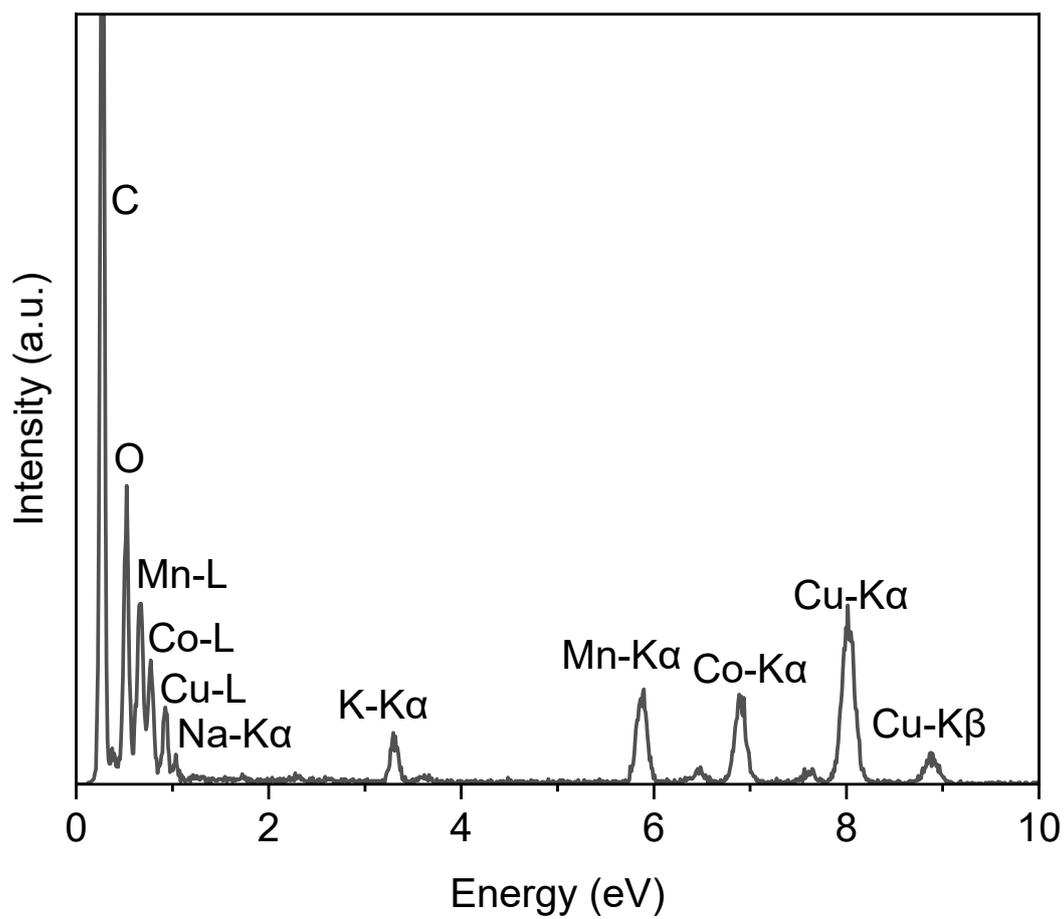


Figure S10. EDS elemental spectrum of MCS electrode after durability test.

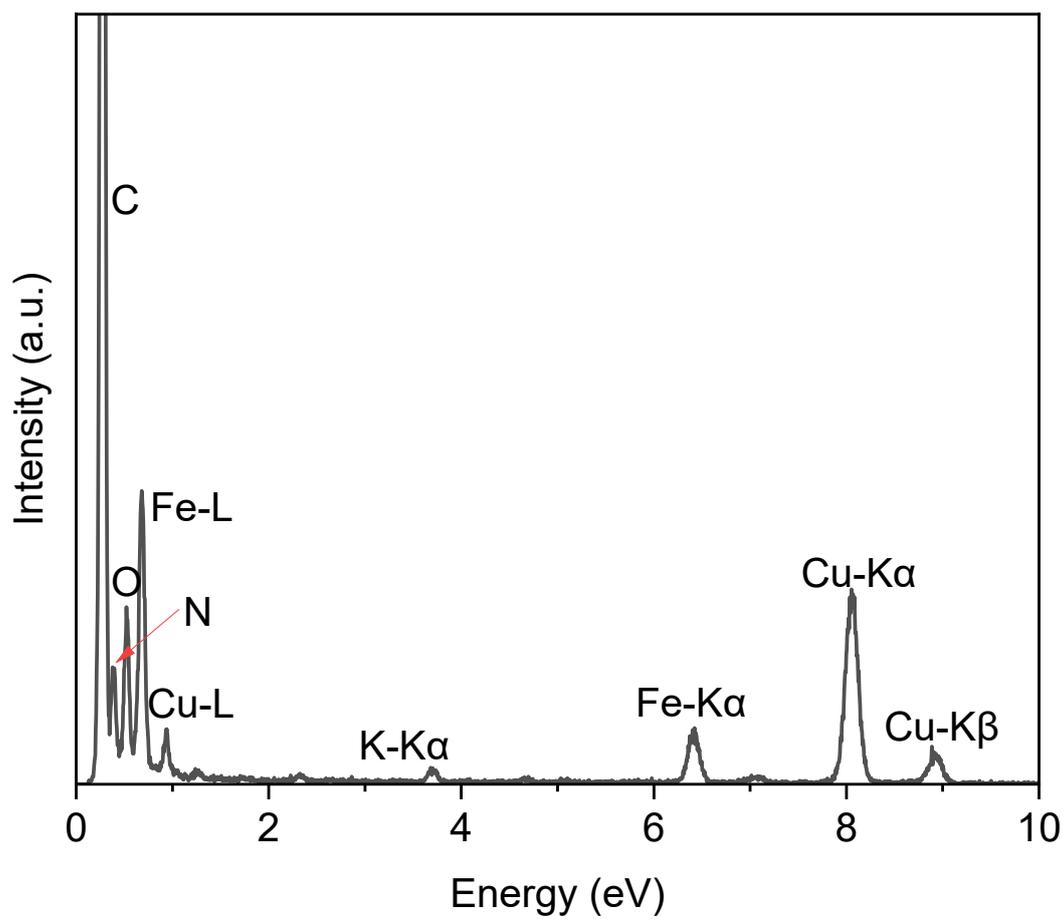


Figure S11. EDS elemental spectrum of pristine Fe-N-C electrode.

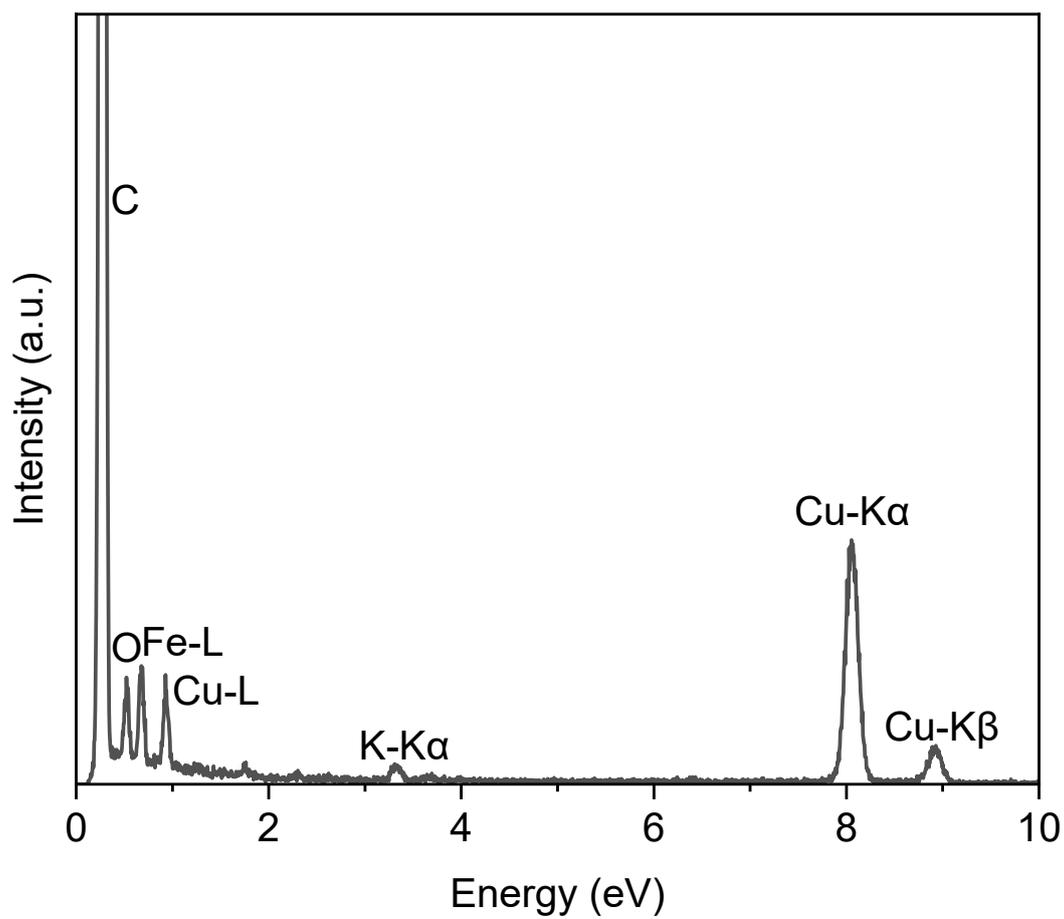


Figure S12. EDS elemental spectrum of Fe-N-C electrode after durability test.

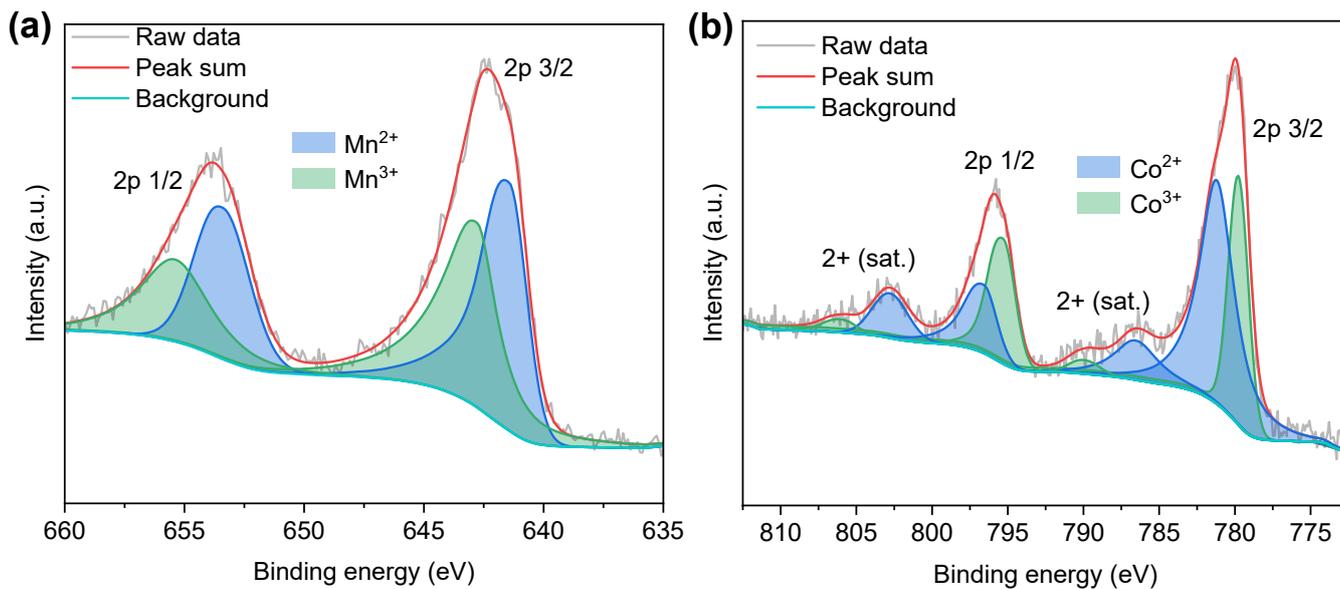


Figure S13. XPS high-resolution (a) Mn 2p, and (b) Co 2p spectra of pristine LMCO electrode.

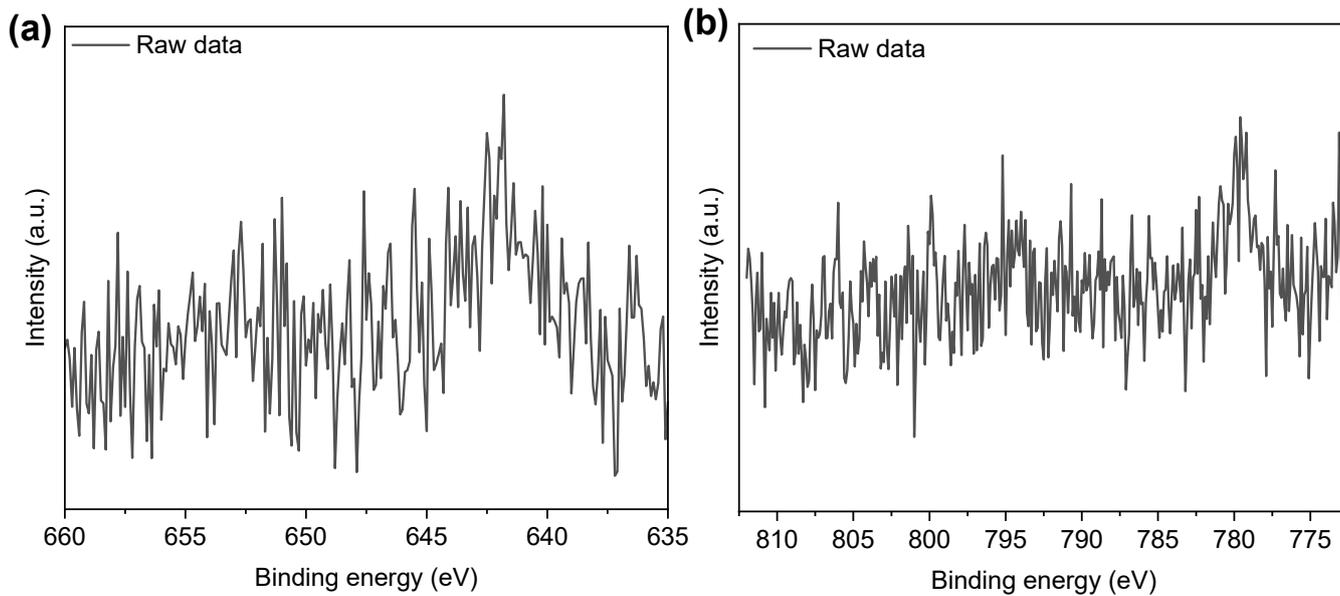


Figure S14. XPS high-resolution (a) Mn 2p, and (b) Co 2p spectra of LMCO electrode after durability test.

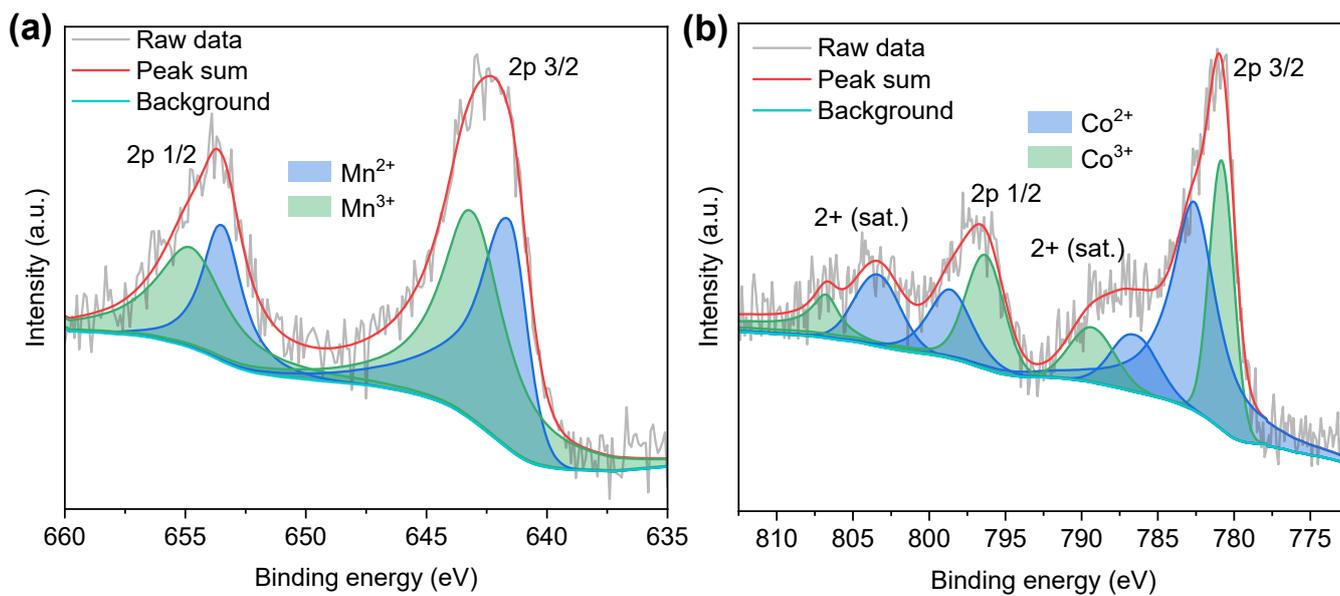


Figure S15. XPS high-resolution (a) Mn 2p, and (b) Co 2p spectra of pristine MCS electrode.

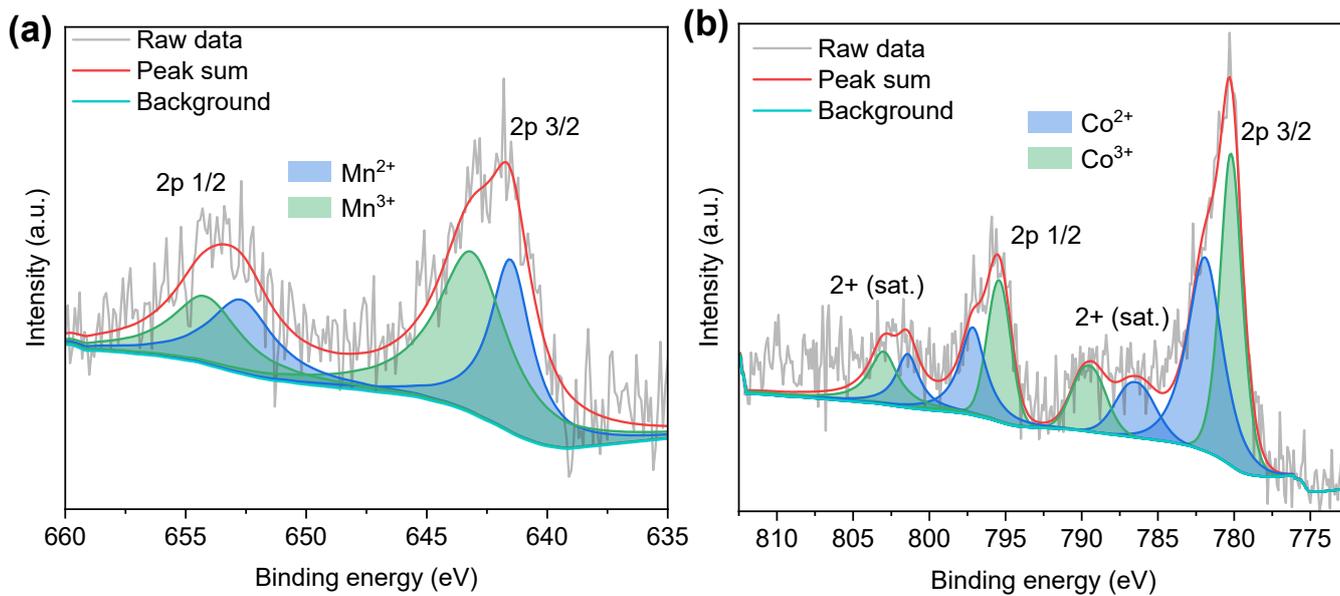


Figure S16. XPS high-resolution (a) Mn 2p, and (b) Co 2p spectra of MCS electrode after durability test.

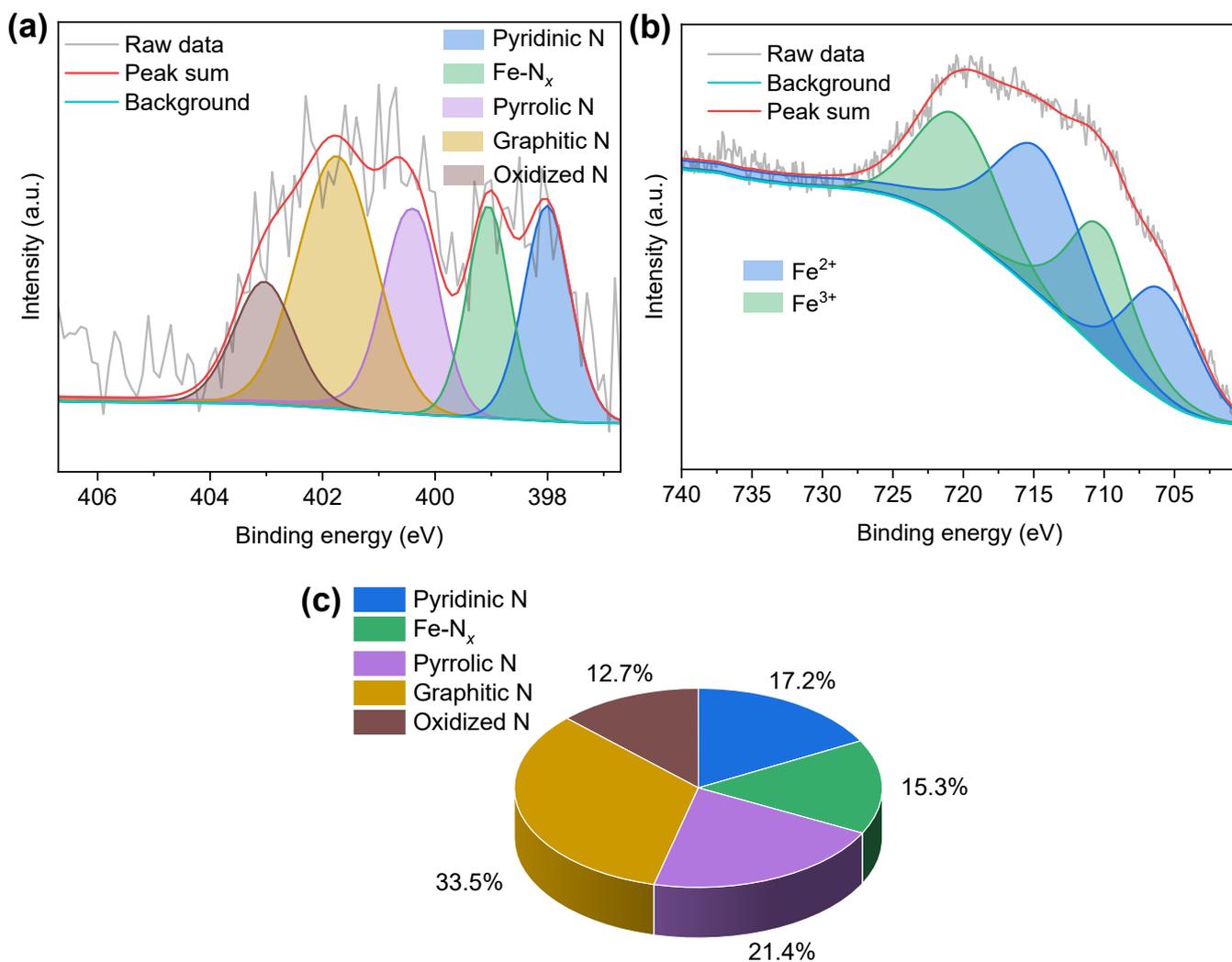


Figure S17. XPS high-resolution (a) N 1s, (b) Fe 2p spectra, and (c) comparison of different N species contents of pristine Fe-N-C electrode.

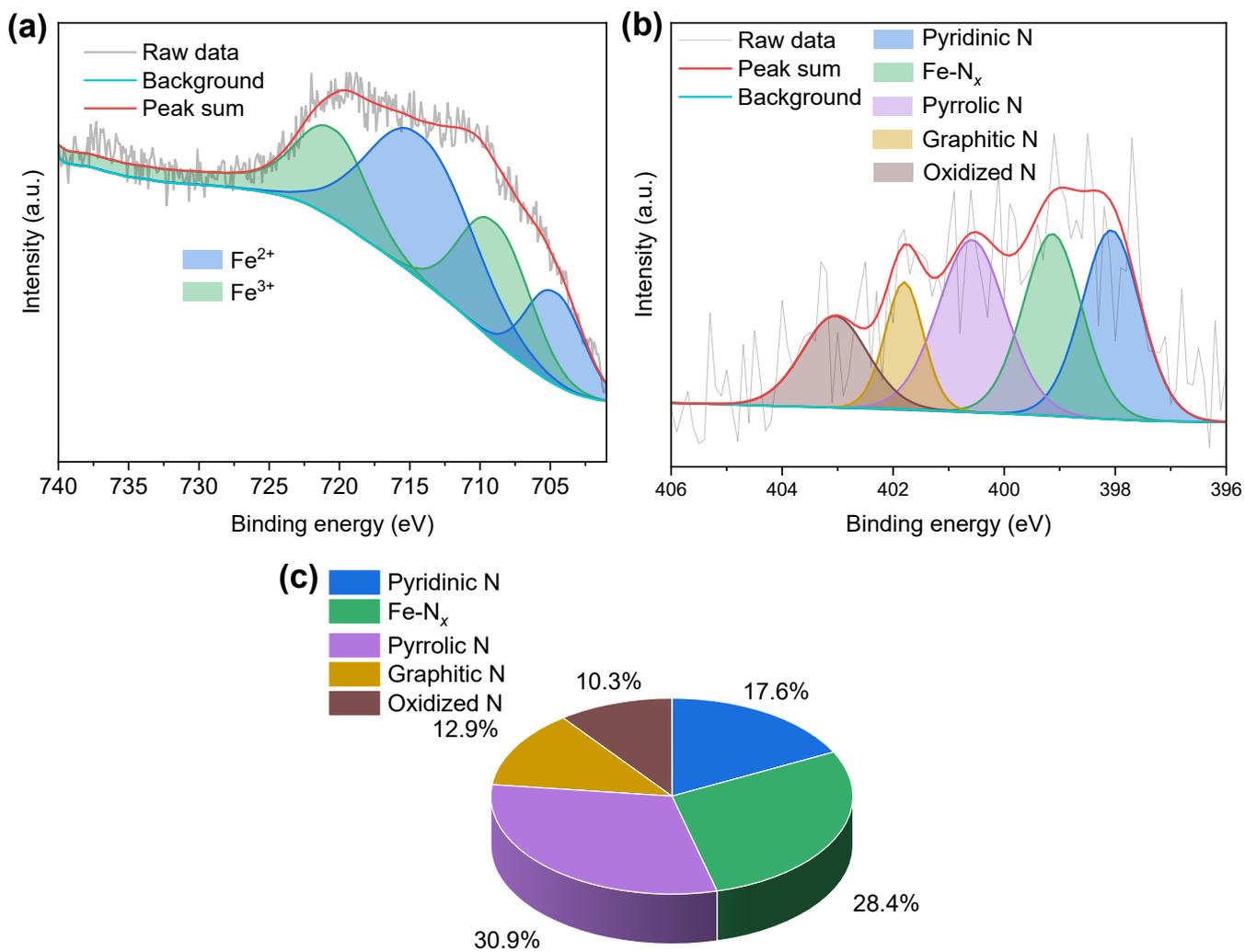


Figure S18. XPS high-resolution (a) N 1s, (b) Fe 2p spectra, and (c) comparison of different N species contents of Fe-N-C electrode after durability test.

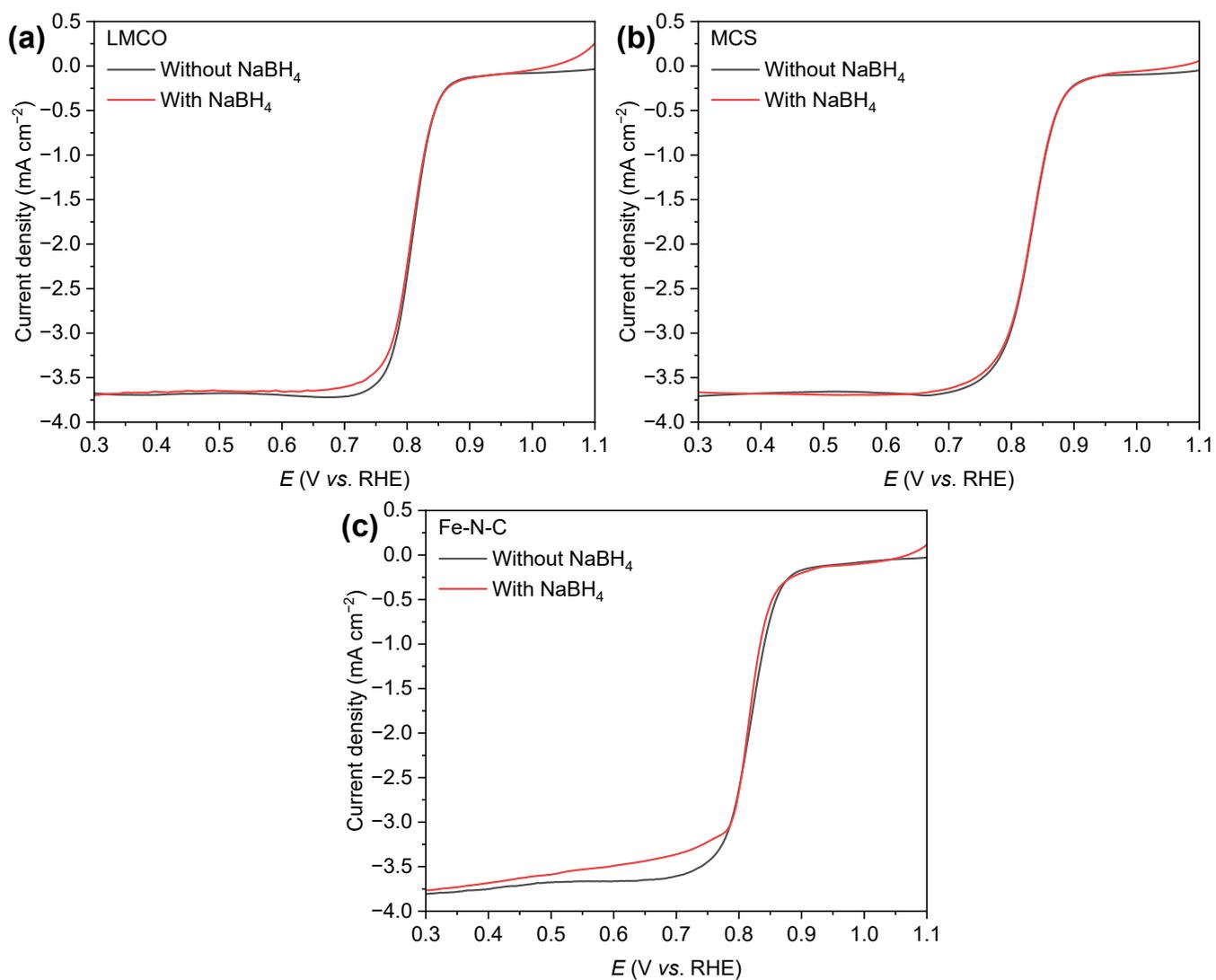


Figure S19. ORR polarization curves of (a) LMCO, (b) MCS, and (c) Fe-N-C at 25 °C, 20 mV s⁻¹, and 1600 rpm, in O₂-saturated 1 M KOH solution with or without 10 mM NaBH₄.

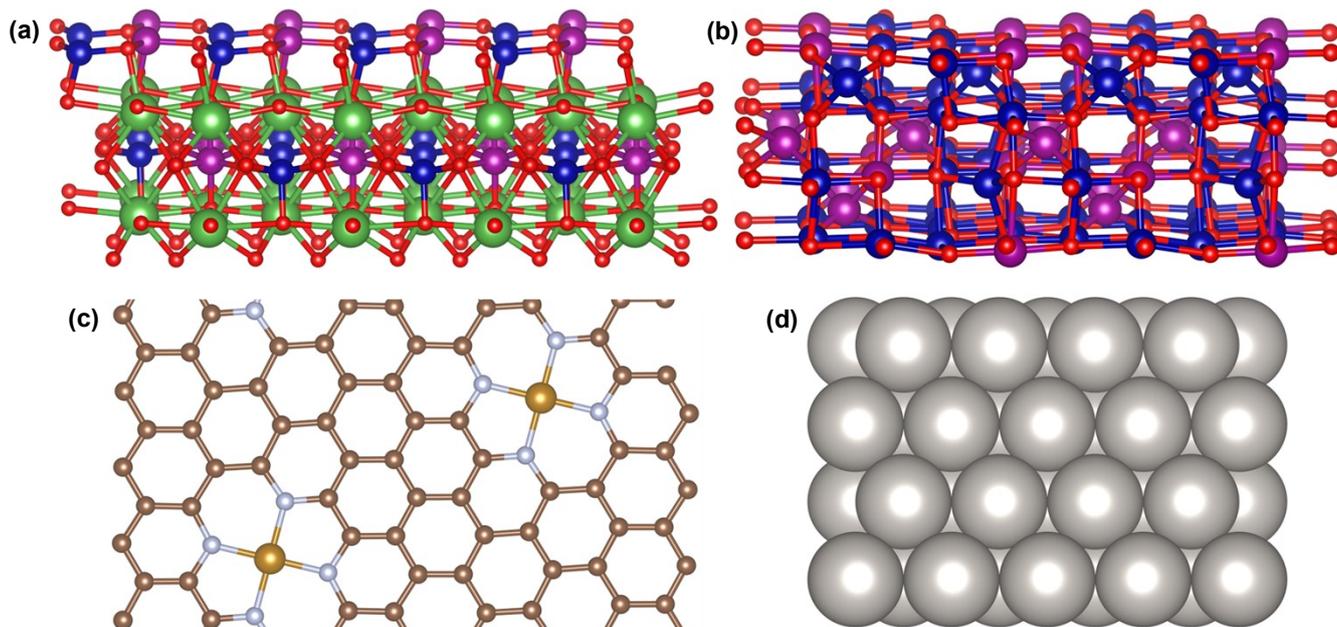


Figure S20. DFT optimized structure of (a) LMCO, (b) MCS, (c) Fe-N-C, and (d) Pt.

Table S1. Textural properties of the catalysts.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{m}^2 \text{g}^{-1}$)
LMCO	1451	910	541	2.24
MCS	1538	985	553	2.59
Fe-N-C	734	427	307	0.61

Table S2. The comparison of the single cell performance of representative studies.

Anode catalyst	Membrane	Cathode catalyst	Oxidant	Peak power density (mW cm ⁻²)	Ref.
Co-W-B	Membraneless	LaNi _{0.9} Ru _{0.1} O ₃ /CNT	Air	500	1
Pd/C + Ni	Nafion [®] 117	Pt/C	H ₂ O ₂	630	2
Pd/C + Ni	Nafion [®] 117	Pt/C	H ₂ O ₂	890	3
PdNi/C	Nafion [®] 117	Pt/C	H ₂ O ₂	630	4
CoO	Nafion [®] 211	RuO ₂	H ₂ O ₂	425	5
Pd/C + Ni	Nafion [®] 117	Pt/C	H ₂ O ₂	580	6
Pt/C	Nafion [®] 117	Pt/C	H ₂ O ₂	800	7
PteAu/C	Nafion [®] 117	Pt/C	H ₂ O ₂	345	8
Ni+Pd/C	Nafion [®]	Pt/C	H ₂ O ₂	590	9
AB ₅ alloy	Nafion [®] 117	Pt/C	H ₂ O ₂	352	10
AB ₅ alloy	Nafion [®] 117	Pd/C	H ₂ O ₂	589	11
Ni particle on Ni felt	Nafion [®] 117	Pt/C	H ₂ O ₂	446	12
Pd–Ni/N-rGO	Nafion [®] 117	Pt/C	H ₂ O ₂	353.84	13
Core (Ni)-Shell (Pd)/rGP1	Nafion [®]	Pt/C	H ₂ O ₂	339.1	14
Pt/[TaOPO ₄ /VC]	Nafion [®] 117	Pt/C	H ₂ O ₂	360	15
nanoporous Au	Nafion [®] 212	nanoporous Au	H ₂ O ₂	390	16
Au	Nafion [®]	Pd	H ₂ O ₂	680	17
Au	Nafion [®]	Pd	H ₂ O ₂	680	17
Au	Nafion [®]	Pd	H ₂ O ₂	1500	18
Zn foil	Nafion [®] 117	Pt	H ₂ O ₂	528	19
Ni + Pt/C	Nafion [®] 212	Pd	H ₂ O ₂	665	20
Ni + Pd/C	Polymer electrolyte membrane	Pt/C	H ₂ O ₂	810	21
Pt–Ru	Nafion [®] 115	Pd–Ir	H ₂ O ₂	345	22
Pd/C	A-006 (AEM)	Fe–Co	O ₂	890	23
Ni/C	Nafion [®] 212	Hypermec [™] K14	O ₂	460	24
Pd/C + Ni	triphosphate chitosan hydrogel	Pt/C	O ₂	685	25
Pd/C + Ni	cross-linked chitosan	Pt/C	O ₂	450	26
Ni-based thin film	chitosan hydrogel (AEM)	Pt/C	O ₂	429	27
Co–pyrrole/MPC	Nafion [®] 112	Pt/C	O ₂	325	28
Pd decorated Ni–Co/C	AEM	Fe–Co/C	O ₂	761	29

CoO	polymer fiber membrane	LaNiO ₃	O ₂	663	30
Co(OH) ₂ -PPy- BP	Nafion [®] 212	CoO Nanorods/C	O ₂	410	31
Co(OH) ₂ -PPy- BP	Co-PVA & PVA bilayer (AEM)	Co(OH) ₂ -PPy-BP	O ₂	327	32
Co(OH) ₂ -PPy- BP	AEM	Co(OH) ₂ -PPy-BP	O ₂	500	33
NiFe-2	Nafion [®] 117	Pt/C	H ₂ O ₂	540	34
Ni@NiP	Nafion [®] 117	Pt/C	H ₂ O ₂	474	35
Pt/C	Alkymer [®]	Mn-Co Spinel	O ₂	1518	This work

References

- 1 S. Li, X. Yang, H. Zhu, X. Wei and Y. Liu, *Int. J. Hydrog. Energy*, 2013, **38**, 2884–2888.
- 2 Z. Wang, J. Parrondo, C. He, S. Sankarasubramanian and V. Ramani, *Nat. Energy*, 2019, **4**, 281–289.
- 3 Z. Wang, S. Sankarasubramanian and V. Ramani, *Cell Rep. Phys. Sci.*, 2020, **1**, 100084.
- 4 S. Saha, P. Gayen, Z. Wang, R. J. Dixit, K. Sharma, S. Basu and V. K. Ramani, *ACS Catal.*, 2021, **11**, 8417–8430.
- 5 X. Yang, X. Wei, C. Liu and Y. Liu, *Mater. Chem. Phys.*, 2014, **145**, 269–273.
- 6 Z. Wang, M. Mandal, S. Sankarasubramanian, G. Huang, P. A. Kohl and V. K. Ramani, *ACS Appl. Energy Mater.*, 2020, **3**, 4449–4456.
- 7 N. Luo, G. H. Miley, J. Mather, R. Burton, G. Hawkins, R. Gimlin, J. Rusek, T. I. Valdez and S. R. Narayanan, *AIP Conf. Proc.*, 2006, **813**, 209–221.
- 8 O. Okur, E. Alper and A. Almansoori, *Energy*, 2014, **67**, 97–105.
- 9 Y. Ko, L. Lombardo, M. Li, T. H. M. Pham, H. Yang and A. Züttel, *Adv. Energy Mater.*, 2022, **12**, 2103539.
- 10 R. K. Raman, N. A. Choudhury and A. K. Shukla, *Electrochem. Solid-State Lett.*, 2004, **7**, A488.
- 11 N. A. Choudhury, J. Ma, Y. Sahai and R. G. Buchheit, *J. Power Sources*, 2011, **196**, 5817–5822.
- 12 G. Braesch, Z. Wang, S. Sankarasubramanian, A. G. Oshchepkov, A. Bonnefont, E. R. Savinova, V. Ramani and M. Chatenet, *J. Mater. Chem. A*, 2020, **8**, 20543–20552.
- 13 M. G. Hosseini, V. Daneshvari-Esfahlan, S. Wolf and V. Hacker, *ACS Appl. Energy Mater.*, 2021, **4**, 6025–6039.
- 14 R. Mahmoodi, M. G. Hosseini and H. Rasouli, *Appl. Catal., B*, 2019, **251**, 37–48.
- 15 R. M. E. Hjelm, Y. Garsany, C. Lafforgue, M. Chatenet and K. Swider-Lyons, *ECS Trans.*, 2018, **86**, 659.
- 16 W. Jin, J. Liu, Y. Wang, Y. Yao, J. Gu and Z. Zou, *Int. J. Hydrog. Energy*, 2013, **38**, 10992–10997.
- 17 L. Gu, N. Luo and G. H. Miley, *J. Power Sources*, 2007, **173**, 77–85.
- 18 N. Luo, G. H. Miley, K.-J. Kim, R. Burton and X. Huang, *J. Power Sources*, 2008, **185**, 685–690.
- 19 D. M. F. Santos and C. a. C. Sequeira, *J. Electrochem. Soc.*, 2009, **157**, B13.
- 20 J. Ma, Y. Sahai and R. G. Buchheit, *J. Power Sources*, 2010, **195**, 4709–4713.
- 21 N. A. Choudhury, J. Ma and Y. Sahai, *J. Power Sources*, 2012, **210**, 358–365.
- 22 D. Cao, D. Chen, J. Lan and G. Wang, *J. Power Sources*, 2009, **190**, 346–350.
- 23 M. Zhiani, I. Mohammadi and N. Salehi, *RSC Adv.*, 2015, **5**, 23635–23645.
- 24 G. Braesch, A. G. Oshchepkov, A. Bonnefont, F. Asonkeng, T. Maurer, G. Maranzana, E. R. Savinova and M. Chatenet, *ChemElectroChem*, 2020, **7**, 1789–1799.
- 25 J. Ma, Y. Sahai and R. G. Buchheit, *J. Power Sources*, 2012, **202**, 18–27.
- 26 J. Ma, N. A. Choudhury, Y. Sahai and R. G. Buchheit, *J. Power Sources*, 2011, **196**, 8257–8264.
- 27 J. Ma and Y. Sahai, *ECS Electrochem. Lett.*, 2012, **1**, F41.
- 28 Y. Chen, S. Wang and Z. Li, *RSC Adv.*, 2020, **10**, 29119–29127.
- 29 M. Zhiani and I. Mohammadi, *Fuel*, 2016, **166**, 517–525.
- 30 X. Yang, Y. Liu, S. Li, X. Wei, L. Wang and Y. Chen, *Sci. Rep.*, 2012, **2**, 567.
- 31 J. Jia, X. Li, H. Qin, Y. He, H. Ni and H. Chi, *J. Alloy. Compd.*, , DOI:10.1016/j.jallcom.2019.153065.
- 32 X. Li, H. Chen, W. Chu, H. Qin, W. Zhang, H. Ni, H. Chi, Y. He, Y. S. Chu, J. Hu and J. Liu, *ACS*

Appl. Mater. Inter., 2020, **12**, 27184–27189.

33 J. Wei, X. Han, X. Li, H. Qin, H. Yin, W. Zhang, H. Ni and X. Wang, *RSC Adv.*, 2022, **12**, 28707–28711.

34 Y. Yang, X. Zhu, C. Yi, H. Yang, X. Hou, X. Liao, C. Chen, D. Yu and X. Zhou, *Chem. Eng. J.*, 2023, **472**, 145097.

35 B. Hu, Y. Xie, Y. Yang, J. Meng, J. Cai, C. Chen, D. Yu and X. Zhou, *Appl. Catal., B*, 2023, **324**, 122257.