Insight into Ni active sites coordination in nickelmanganese spinels for methanol oxidation catalysis

Supplementary Information

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Experimental

Materials

All the reagents in the experiment were of analytical grade and were utilized without further purification. Nickel acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O), manganese acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O), and potassium hydroxide (KOH) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. A 5 wt% Nafion ionomer was purchased from Sigma-Aldrich. All solutions were prepared with ultrapure water with a resistance of 18.2 M Ω (Thermo Fisher Scientific Co., LTD, USA). Tafel slope analysis

The Tafel slope was calculated from the following equation (1): $\eta = a + b \log (j)$, where η is the overpotential (mV), b is the Tafel slope, and j is the current density.

Mass activity and Specific activity

The values of mass activity (mA mg_{Ni}^{-1}) were calculated from formula (2): Mass activity = j / m

The specific activity was obtained by normalizing the apparent current to ECSA, where m is the catalyst loading, and j is the measured current density (mA cm^{-2}).

Turnover frequency (TOF)

The turnover frequency (TOF) was calculated from the following formula (3): TOF = $\frac{j * 0.07 cm^2 * 0.001}{0.05 * 0.9mg * 0.001 * \frac{M_{Ni}}{M_{total}}}$ $j * A/_{6 * F * n=} \frac{6 * 96485 * \frac{M_{Ni}}{M_{Ni}}}{M_{Ni}}$

where j is the current density corresponding to different potentials (1.45, 1.50, and 1.55 V vs. RHE, respectively). A represents the surface area of the electrode. F is the Faraday constant (96485 C mol⁻¹), the number 6 means 6-mole electrons per mole CO₂, and n is the number of moles of active materials that are deposited onto the electrode. The active sites are not easy to obtain. A simple method, generally employed by assuming all metal cations to be an "active site," was also used here, and it was estimated by the number of moles of active materials that are deposited onto the electrode.

Theoretical calculations

Quantum chemistry calculations were performed using the CASTEP module within the Materials Studio software (Accelrys Inc.).¹ The Perdew-Burke-Ernzerhof (PBE) approximation was selected for the exchange-correlation energy with the generalized gradient approximation (GGA). During the computations, Hubbard U-corrections were applied to the d electrons of V (LDA+U, effective U(V) = 2.5 eV) and spin-polarized.² The energy cutoff was 380 eV, and the self-consistent field (SCF) tolerance was 1.0×10^{-6} eV/ atom. The optimization was considered complete when the energy, maximum force, maximum stress, and maximum displacement were less than 5.0×10^{-6} eV/ atom, 0.01 eV/Å, 0.02 GPa, and 5.0×10^{-4} Å, respectively. A vacuum slab with a thickness greater than 15 Å was introduced along the z-direction to prevent contact between periodic units. The adsorption energy (E_{ads}) was calculated using the following formula (4): $E_{ads} = E_{molecule+surface} - E_{molecule} - E_{surface}$

where $E_{molecule+surface}$ is the total energy of the system after adsorbing the molecule, $E_{molecule}$ is the energy of adsorption molecules, and $E_{surface}$ is the total energy of the system before adsorbing the molecule.³

The Gibbs free energy of the reaction can be obtained from formula (5). $\Delta G_{ads^*} = \Delta E_{ads} + \Delta ZEP$ - T ΔS

where T is the standard temperature (298 K), ZPE is the zero-point energy for the species as calculated, and S is the entropy of the species. The values of ZPE and S were from the literature.



Fig S1. Schematic illustration of the synthesis of $MnNi_2O_4$.



Fig S2. The optimized model for the adsorption of reaction intermediates on $MnNi_2O_4$ -Ni site surfaces.



*OCH



CO*



*COOH



CO₂

Fig S3. The optimized model for the adsorption of reaction intermediates on MnNi₂O₄-Mn site surfaces.



CH₃OH



*OCH₃



*OCH₂



*OCH



CO*

*СООН



Fig S4. The optimized model for the adsorption of reaction intermediates on NiMn₂O₄-Ni site surfaces.



Fig S5. The Gibbs free energy diagram for MOR of MnNi₂O₄ and NiMn₂O₄.



Fig S6. Adsorption energy of CO* intermediate on the surface of catalysts.



Fig S7. EDS spectrum of $NiMn_2O_4$ and $MnNi_2O_4$.



Fig S8. The elemental mapping of MnNi₂O₄.



Fig S9. XPS survey spectra of $NiMn_2O_4$ and $MnNi_2O_4$.



Fig S10. XPS spectra of C 1s (a), O 1s (b) of $NiMn_2O_4$ and $MnNi_2O_4.$



Fig S11. Cyclic voltammetry curves measured in 1M KOH with and without 1 M CH_3OH at 50 mV s⁻¹ for NiMn₂O4 (a), MnNi₂O4 (b), NiO (c), and Mn₂O₃ (d).



Fig S12. CA experiment of these catalysts at 1.56 V vs. RHE for 25 hours.



Fig S13. TEM image (a) and XRD pattern (b) of $MnNi_2O_4$ after MOR test.



Fig S14. Mass activity (a), Specific activity (b) polarization curves of NiMn₂O₄ and MnNi₂O₄.



Fig S15. TOF curves of $NiMn_2O_4$ and $MnNi_2O_4.$

Name	Ni(CH ₃ COO) ₂ ·4H ₂ O/ g	Mn(CH ₃ COO) ₂ ·4H ₂ O/ g
Mn ₂ O ₃	0	2.94
NiMn ₂ O ₄	0.99	1.96
MnNi ₂ O ₄	1.49	1.47
NiO	2.99	0

Table S1. Metal precursor amount added for catalyst fabrication.

Catalysta	Ni 2p _{3/2}		Ni 2p _{1/2}			Ni 2p
Catalysis	Peak	Binding Energy/ eV	Peak	Binding Energy/ eV	Content	Ni ³⁺ /Ni ²⁺
	Ni ²⁺	854.83	Ni ²⁺	872.43	53%	
NIMIn ₂ O ₄	Ni ³⁺	856.38	Ni ³⁺	873.98	47%	0.89
MANO	Ni ²⁺	854.52	Ni ²⁺	872.12	42%	
MnNı ₂ O ₄	Ni ³⁺	856.07	Ni ³⁺	873.67	58%	1.38

Table S2. The binding energy of Ni 2p for $NiMn_2O_4$ and $MnNi_2O_4.$

]	Mn 2p _{3/2}	Mn 2p _{1/2}		
Catalysts	Peak	Binding Energy / eV	Peak	Binding Energy/ eV	
NiMn ₂ O ₄	Mn ³⁺	642.69	Mn ³⁺	654.29	
MnNi ₂ O ₄	Mn^{4+}	644.82	Mn ⁴⁺	656.42	

Table S3.	The binding	energy of M	n 2p for Nil	Mn_2O_4 and	MnNi ₂ O ₄ .

Catalysts	Electrolyte	Potential/ V	Current density/ mA cm ⁻²	Ref.
MnNi ₂ O ₄	1 mol/L KOH+	1 50 V vg DHE	40.7	This work
	1 mol/L CH ₃ OH	1.50 V VS. KHE	40.7	
NiSnPH@OOH/C	1 mol/L KOH+	1.70 Mars. DHE	115	
	1 mol/L CH ₃ OH	1.70 V VS. KHE	115	4
NiCo ₂ O ₄ /rGO	1 mol/L KOH+		70	
	0.5 mol/L CH ₃ OH	1.62 V VS. KHE	/8	5
N'C. DO A	0.5 mol/L KOH+	1.86 V vs. RHE	39	6
NICOPO-2	1 mol/L CH ₃ OH			0
N' E. G.	1 mol/L KOH+	1.5 V vs. RHE	50	7
N1 _{0.75} Fe _{0.25} Se	1 mol/L CH ₃ OH			
	1 mol/L KOH+	0.55 V vs. SCE	40	8
NIFe LDH	2 mol/L CH ₃ OH			6
	0.1 mol/L KOH+	1.72 V vs. RHE	28	9
NI-NICu-3	1 mol/L CH ₃ OH			
	1 mol/L NaOH+	1.53 V vs. RHE	17.1	10
$N_{60}Cr_{10}Ia_{10}P_{16}B_4$	1 mol/L CH ₃ OH			10
	1 mol/L KOH+	0.4 V vs. Ag/AgCl 2	22.5	11
C0 ₁ -N1 ₄ /G	1 mol/L CH ₃ OH		22.5	11
	1 mol/L KOH+		50	12
NI(OH) ₂ /MnCO ₃	1 mol/L CH ₃ OH	1.49 V vs. KHE	50	12

Table S4. Comparison of catalytic performance of non-noble metal catalysts for methanol

oxidation reaction

Sample	R_s/Ω	R_{ct}/Ω	CPE/ S S ⁻ⁿ	Chi-squared
NiO	8.4	518	1.882E-005	1.401E-02
NiMn ₂ O ₄	9.8	253	2.203E-004	3.596E-03
MnNi ₂ O ₄	8.6	128	4.527E-004	5.690E-04
Mn ₂ O ₃	9.2	989	1.485E-004	1.769E-03

Table S5. EIS fitting parameters from equivalent circuits for different catalyst samples.

Catalysts	ECSA/ cm ²	R _f
NiMn ₂ O ₄	0.37	37.2
MnNi ₂ O ₄	0.39	70

Table S6. The ECSA and $R_{\rm f}$ values for $NiMn_2O_4$ and $MnNi_2O_4.$

Catalysts	Mass activity/ mA mg _{Ni} ⁻¹	Specific activity/ mA cm ⁻²	TOF/ s ⁻¹	Potential/ V vs. RHE
NiMn2O4	61.08 121.24	0.99 2.07	0.0035 0.0069	1.45 1.50
	192.57	3.29	0.0110	1.55
MnNi ₂ O ₄	136.55	4.43	0.0078	1.45
	225.05	7.30	0.0129	1.50
	288.88	9.37	0.0165	1.55

Table S7. The mass activity, specific activity, and TOF of $NiMn_2O_4$ and $MnNi_2O_4$ at 1.45, 1.50,

References

- X. Wang, S. Xi, W. S. V. Lee, P. Huang, P. Cui, L. Zhao, W. Hao, X. Zhao, Z. Wang, H. Wu, H. Wang, C. Diao, A. Borgna, Y. Du, Z. G. Yu, S. Pennycook and J. Xue, *Nat. Commun.*, 2020, 11, 4647.
- 2 Y. Kuang, M. Li, L. Fu and L. Feng, J. Colloid Interface Sci., 2025, 679, 921-929.
- 3 S. Periyasamy, P. Subramanian, E. Levi, D. Aurbach, A. Gedanken and A. Schechter, *ACS Appl. Mater. Interfaces*, 2016, **8**, 12176-12185.
- J. Shao, Y. Fang, X. Wu, M. I. Abdullah and Y. Tao, *Nano Research*, 2024, 17, 2388-2399.
- 5 N. Narayanan and N. Bernaurdshaw, *ChemCatChem*, 2020, **12**, 771-780.
- 6 Y. Y. Tong, C. D. Gu, J. L. Zhang, H. Tang, Y. Li, X. L. Wang and J. P. Tu, *Electrochimica Acta*, 2016, **187**, 11-19.
- J. Li, C. Xing, Y. Zhang, T. Zhang, M. C. Spadaro, Q. Wu, Y. Yi, S. He, J. Llorca, J. Arbiol,A. Cabot and C. Cui, *Small*, 2021, 17, 2006623.
- 8 Y. Vlamidis, S. Fiorilli, M. Giorgetti, I. Gualandi, E. Scavetta and D. Tonelli, *RSC Advances*, 2016, **6**, 110976-110985.
- 9 S. Liu, Y.-Y. Sun, Y.-P. Wu, Y.-J. Wang, Q. Pi, S. Li, Y.-S. Li and D.-S. Li, ACS Appl. Mater. Interfaces, 2021, 13, 26472-26481.
- N. Boostani, S. Vardak, R. Amini and Z. Mohammadifard, *Int. J. Hydrogen Energy*, 2023, 48, 10002-10015.
- E. Sarwar, T. Noor, N. Iqbal, Y. Mehmood, S. Ahmed and R. Mehek, *Fuel Cells*, 2018, 18, 189-194.
- 12 C. Liu, F. Yang, Y. Yang, S. Wang and L. Feng, ChemComm, 2024, 60, 1591-1594.