

Supporting Information

A novel monoclinic metal oxide catalyst for oxygen evolution reaction in alkaline media

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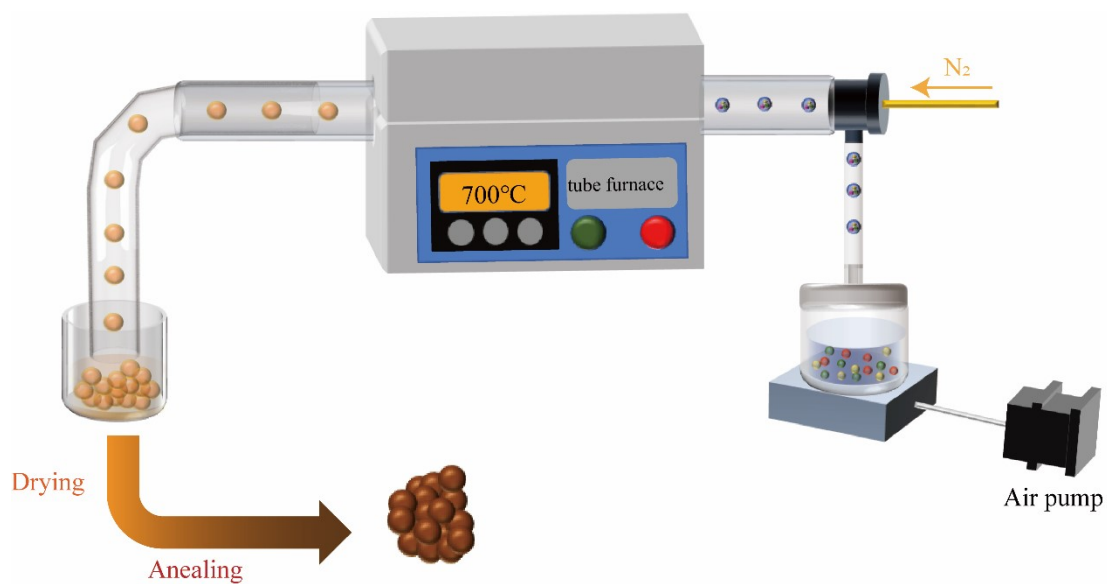


Figure S1. Synthesis strategy of $\text{Co}_x\text{-Fe}_2(\text{MoO}_4)_3$.

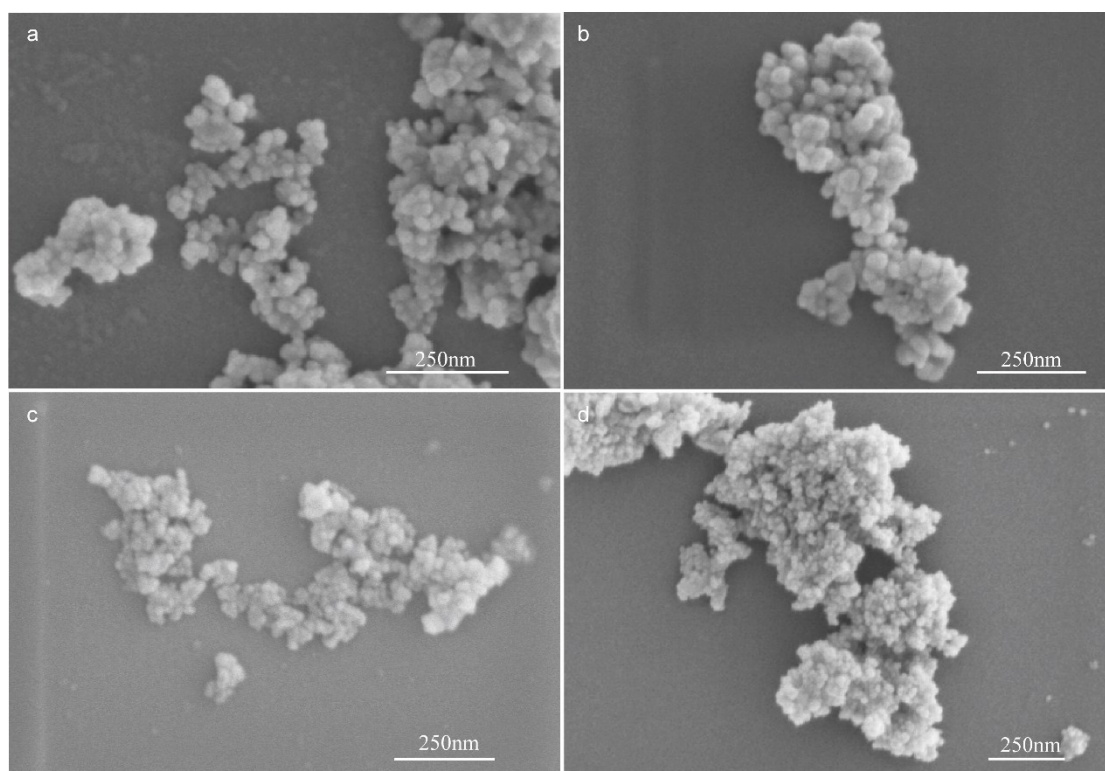


Figure S2. SEM images of (a) pure $\text{Fe}_2(\text{MoO}_4)_3$, (b) $\text{Co}_{0.05}\text{-Fe}_2(\text{MoO}_4)_3$, (c) $\text{Co}_{0.1}\text{-Fe}_2(\text{MoO}_4)_3$, (d) $\text{Co}_{0.2}\text{-Fe}_2(\text{MoO}_4)_3$.

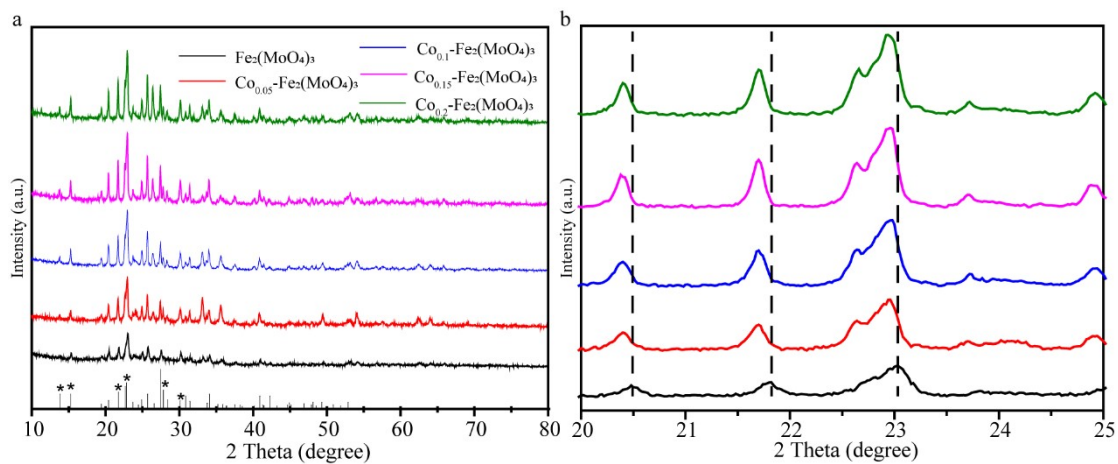


Figure S3. XRD patterns for with $\text{Fe}_2(\text{MoO}_4)_3$ different cobalt doping ratio.

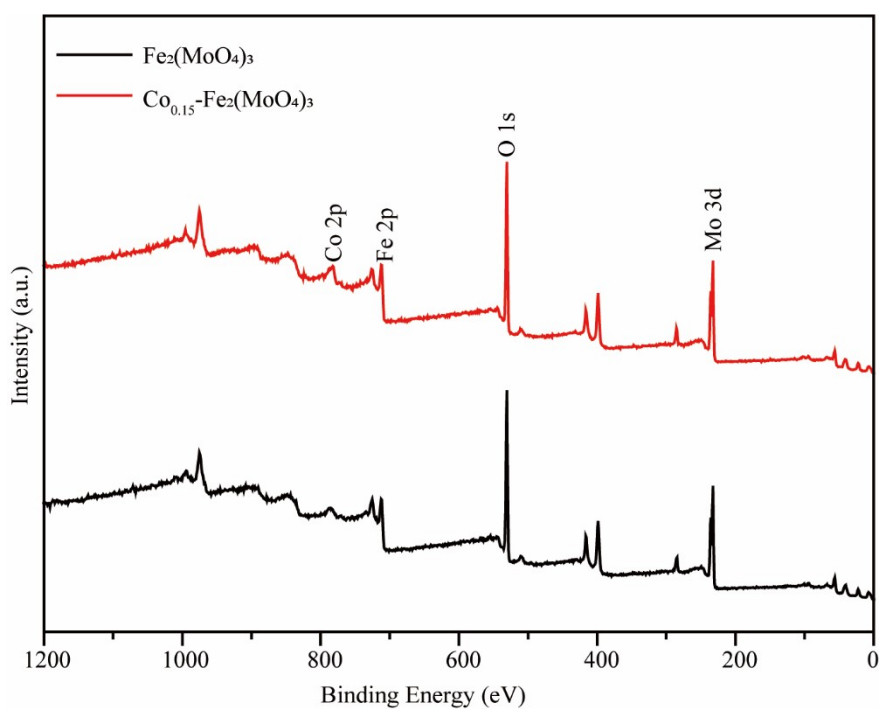


Figure S4. Full XPS survey scan for $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Co}_{0.15}\text{-Fe}_2(\text{MoO}_4)_3$.

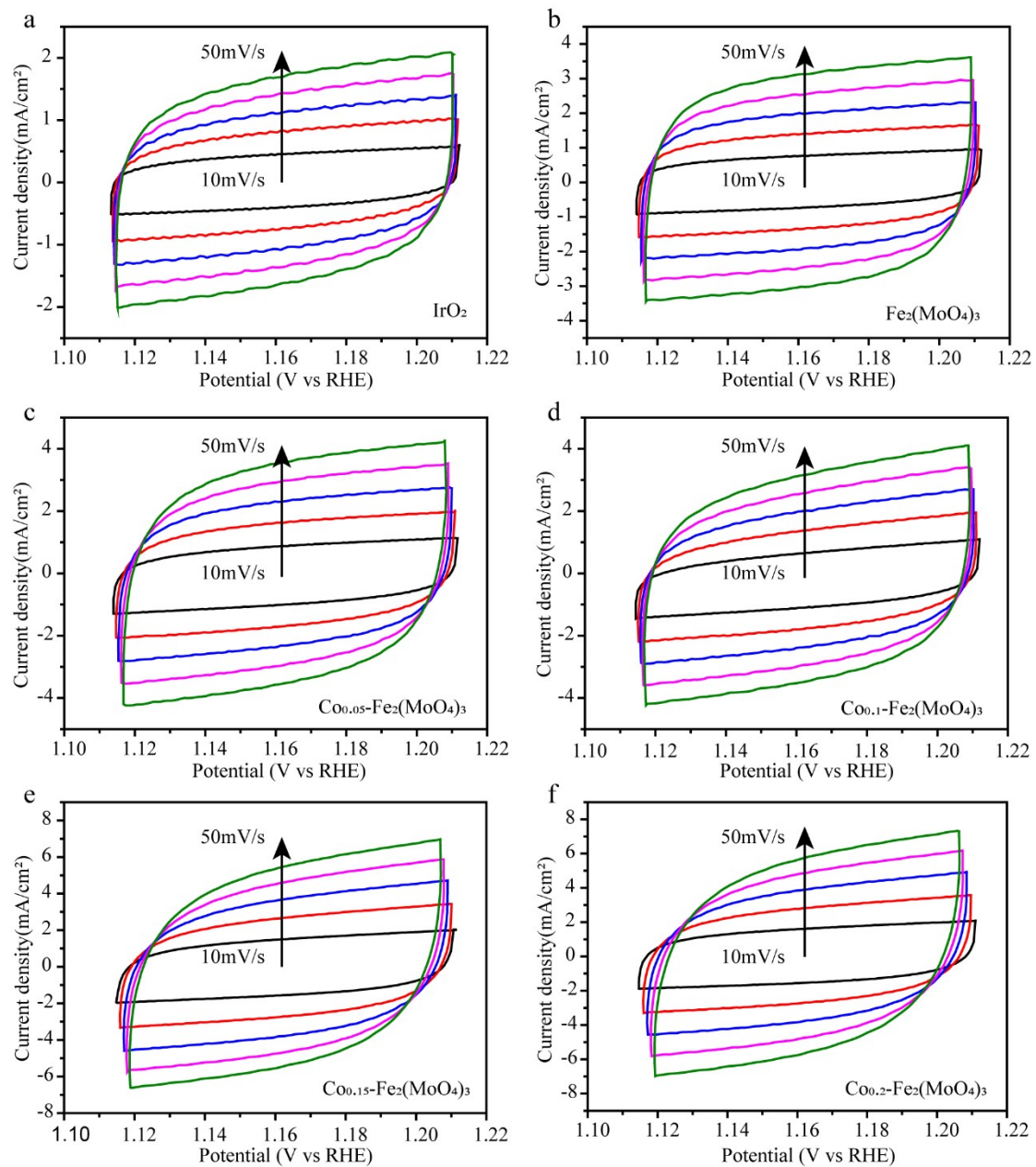


Figure S5. CV diagrams of (a) IrO₂, (b) Fe₂(MoO₄)₃, (c) Co_{0.05}-Fe₂(MoO₄)₃, (d) Co_{0.1}-Fe₂(MoO₄)₃, (e) Co_{0.15}-Fe₂(MoO₄)₃, (f) Co_{0.2}-Fe₂(MoO₄)₃.

Table S1 Comparison between $\text{Co}_{0.15}\text{-Fe}_2(\text{MoO}_4)_3$ of this work and different reported transition metal oxide catalysts for OER in alkaline media

Catalyst	Overpotential (mV) at 10mA cm^{-2}	Stability	Reference
$\text{Co}_3\text{O}_{3.87}\text{F}_{0.13}$	430	1500 cycles	1
$\text{CoVO}_x\text{-300}$	330	10h	2
$\text{NiCo}_{1.7}\text{Ru}_{0.3}\text{O}_4$	280	15h	3
Co/CoO@NC@CC	284	25h	4
$\text{NiMn/ NiCo}_2\text{O}_4$	310	8h	5
$\text{Co@Co}_3\text{O}_4\text{/NC-2}$	410	45h	6
$\text{CoMoO}_x\text{/CoMoS}_x\text{/CoS}_x$	281	40h	7
CoV_2O_6	324	24h	8
$\text{Geobacter-Mn}_2\text{O}_3$	290	22.5h	9
$\text{Co}_{0.708}\text{Fe}_{0.292}\text{WO}_4$	327	7h	10
CoMoO_4 nanorod	350	10h	11
$\text{LaSr}_3\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_{10-\delta}$	388	5h	12
$\text{Co}_{0.15}\text{-Fe}_2(\text{MoO}_4)_3$	273	80h	This work

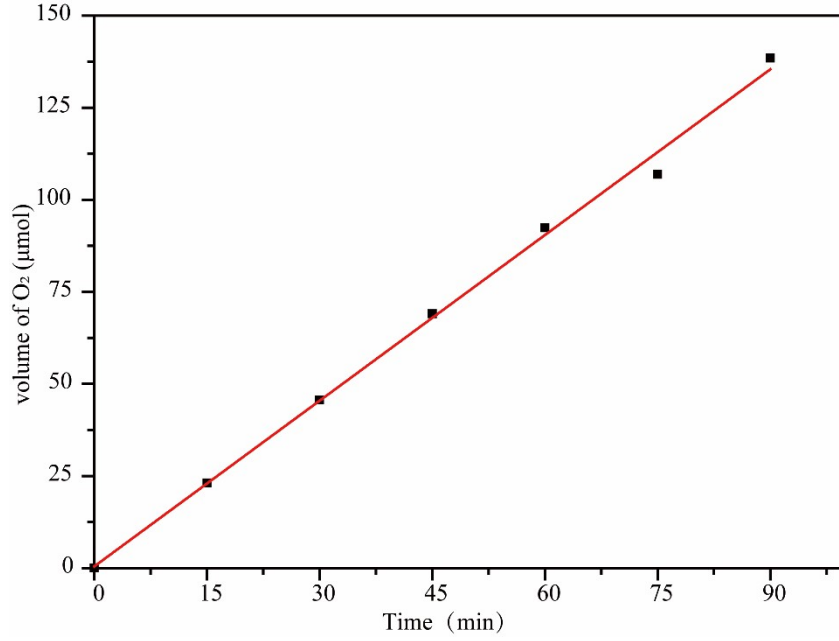


Figure S6. Content of O₂ generated of OER for Co_{0.15}-Fe₂(MoO₄)₃.

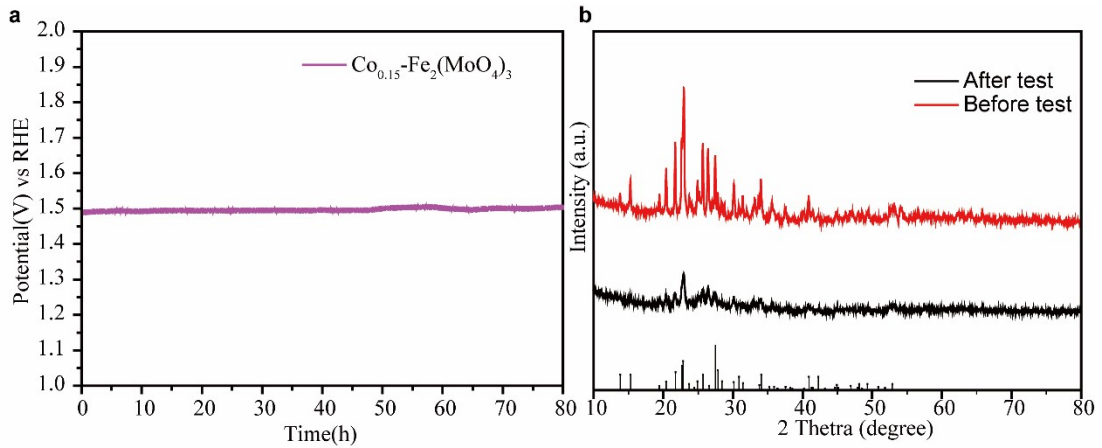
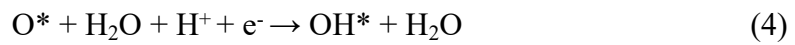
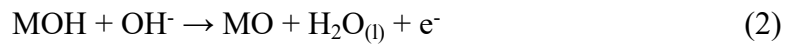


Figure S7. (a) Chronopotentiometry durability test under 10 mA cm⁻² for Co_{0.15}-Fe₂(MoO₄)₃, (b) The comparison diagram for XRD patterns of Co_{0.15}-Fe₂(MoO₄)₃ before and after stability test.

The chemical equations of OER mechanism in alkaline media^{13, 14}:



The active site is written as “M”. In most cases, the reaction process follows the steps of (1) → (2) → (3.1) → (4) instead of (1) → (2) → (3.2)

Table S2. ICP analysis for as-prepared $\text{Co}_{0.15}\text{-Fe}_2(\text{MoO}_4)_3$

Catalysts	Element	Sample amount	Element Content	wt%
$\text{Co}_{0.15}\text{-Fe}_2(\text{MoO}_4)_3$	Co	108.7 mg	16276.45 mg/kg	1.628
	Fe	108.7 mg	171320.15 mg/kg	17.132
	Mo	108.7 mg	461591.54 mg/kg	46.159

Reference

1. H. Zeng, M. h. Oubla, X. Zhong, N. Alonso-Vante, F. Du, Y. Xie, Y. Huang and J. Ma, Rational defect and anion chemistries in Co₃O₄ for enhanced oxygen evolution reaction, *Appl. Catal., B*, 2021, **281**, 119535.
2. C. Jiang, J. Yang, T. Zhao, L. Xiong, Z.-X. Guo, Y. Ren, H. Qi, A. Wang and J. Tang, Co³⁺-O-V⁴⁺ cluster in CoVO_x nanorods for efficient and stable electrochemical oxygen evolution, *Appl. Catal., B*, 2021, **282**, 119571.
3. C. Peng, H. Liu, J. Chen, Y. Zhang, L. Zhu, Q. Wu, W. Zou, J. Wang, Z. Fu and Y. Lu, Modulating the potential-determining step in oxygen evolution reaction by regulating the cobalt valence in NiCo₂O₄ via Ru substitution, *Appl. Surf. Sci.*, 2021, **544**, 148897.
4. K. Dai, N. Zhang, L. Zhang, L. Yin, Y. Zhao and B. Zhang, Self-supported Co/CoO anchored on N-doped carbon composite as bifunctional electrocatalyst for efficient overall water splitting, *Chem. Eng. J.*, 2021, **414**, 128804.
5. L. Yang, L. Chen, D. Yang, X. Yu, H. Xue and L. Feng, NiMn layered double hydroxide nanosheets/NiCo₂O₄ nanowires with surface rich high valence state metal oxide as an efficient electrocatalyst for oxygen evolution reaction, *J. Power Sources*, 2018, **392**, 23-32.
6. A. Aijaz, J. Masa, C. Rosler, W. Xia, P. Weide, A. J. Botz, R. A. Fischer, W. Schuhmann and M. Muhler, Co@Co₃O₄ Encapsulated in Carbon Nanotube-Grafted Nitrogen-Doped Carbon Polyhedra as an Advanced Bifunctional Oxygen Electrode, *Angew. Chem., Int. Ed.*, 2016, **55**, 4087-4091.
7. H. Xu, H. Shang, C. Wang, L. Jin, C. Chen, C. Wang and Y. Du, Three-dimensional open CoMoO_x/CoMoS_x/CoS_x nanobox electrocatalysts for efficient oxygen evolution reaction, *Appl. Catal., B*, 2020, **265**, 118605.
8. G. M. Thorat, H. S. Jadhav, A. Roy, W.-J. Chung and J. G. Seo, Dual Role of Deep Eutectic Solvent as a Solvent and Template for the Synthesis of Octahedral Cobalt Vanadate for an Oxygen Evolution Reaction, *ACS Sustain. Chem. Eng.*, 2018, **6**, 16255-16266.
9. S. Kalathil, K. P. Katuri and P. E. Saikaly, Synthesis of an amorphous Geobacter-manganese oxide biohybrid as an efficient water oxidation catalyst, *Green Chem.*, 2020, **22**, 5610-5618.
10. W. Shao, Y. Xia, X. Luo, L. Bai, J. Zhang, G. Sun, C. Xie, X. Zhang, W. Yan and Y. Xie, Structurally distorted wolframite-type Co_xFe_{1-x}WO₄ solid solution for enhanced oxygen evolution reaction, *Nano Energy*, 2018, **50**, 717-722.
11. X. Liu, Y. Yang and S. Guan, An efficient electrode based on one-dimensional CoMoO₄ nanorods for oxygen evolution reaction, *Chem. Phys. Lett.*, 2017, **675**, 11-14.
12. S. Liu, H. Luo, Y. Li, Q. Liu and J.-L. Luo, Structure-engineered electrocatalyst enables highly active and stable oxygen evolution reaction over layered perovskite LaSr₃Co_{1.5}Fe_{1.5}O_{10-δ}, *Nano Energy*, 2017, **40**, 115-121.
13. Z. Y. Yu, Y. Duan, X. Y. Feng, X. Yu, M. R. Gao and S. H. Yu, Clean and

Affordable Hydrogen Fuel from Alkaline Water Splitting: Past, Recent Progress, and Future Prospects, *Adv Mater*, 2021, **33**, e2007100.

14. F. Song, L. Bai, A. Moysiadou, S. Lee, C. Hu, L. Liardet and X. Hu, Transition Metal Oxides as Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Solutions: An Application-Inspired Renaissance, *J. Am. Chem. Soc.*, 2018, **140**, 7748-7759.