

Supporting Information

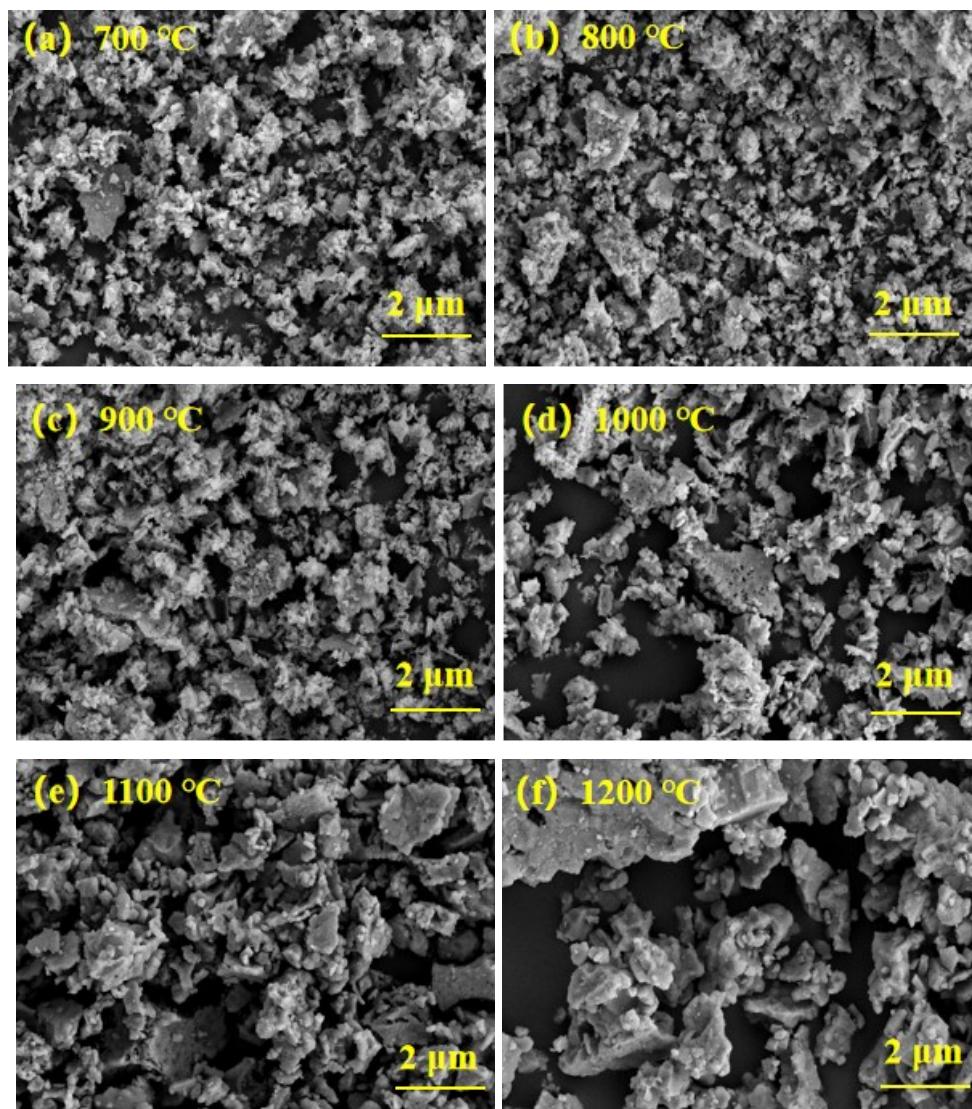


Fig S1 (a) - (f) SEM of the STFN samples at different calcination temperatures

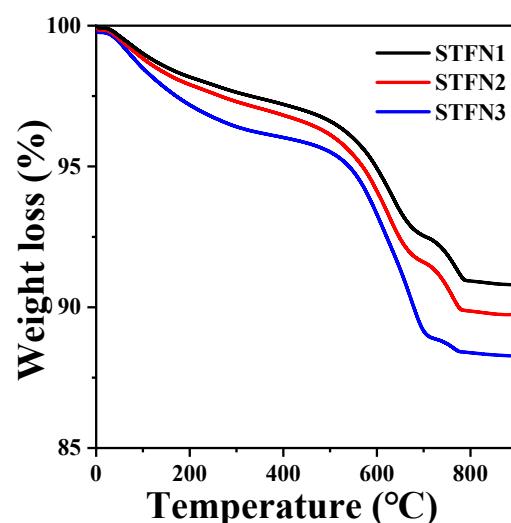


Fig S2 TGA of S_{1-x} TFN with an A-site vacancy**Table S1** Comparison of pore size and specific surface area of STFN at different calcination temperatures

Catalysts	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore width (nm)
STFN-700	32.839	0.104	3.828
STFN-800	33.933	0.050	3.939
STFN-900	25.549	0.047	3.806
STFN-1000	17.106	0.021	3.677
STFN-1100	8.404	0.012	3.539
STFN-1200	6.001	0.007	3.420

Table S2 ORR performance of sample STFN at different calcination temperatures

Catalysts	E _{onset} (V vs. RHE)	E _{1/2} (V vs. RHE)	J (mA cm ⁻²)	Tafel (mV dec ⁻¹)
STFN-700	0.8843	0.6151	-5.8040	106
STFN-800	0.8857	0.6411	-6.1971	103
STFN-900	0.8821	0.5961	-5.5891	123
STFN-1000	0.8812	0.5678	-5.3766	126
STFN-1100	0.8793	0.5318	-5.1958	129
STFN-1200	0.8762	0.5221	-4.0324	140

Table S3 OER performance and ΔE of STFN calcined at different temperatures

Catalysts	OER		ORR		ΔE (V)
	Tafel (mV dec ⁻¹)	η (mV)	@10 mA cm ⁻² (V)	@-3 mA cm ⁻² (V)	
STFN-700	127	450.6	1.6806	0.6001	1.0805
STFN-800	103	412.0	1.6420	0.6124	1.0296
STFN-900	136	463.3	1.6933	0.5972	1.0961
STFN-1000	153	526.3	1.7563	0.5815	1.1748
STFN-1100	159	553.3	1.7833	0.5279	1.2554

STFN-1200	211	568.3	1.7983	0.5128	1.2855
-----------	-----	-------	--------	--------	--------

Table S4 A-site-deficient STFN pore size and specific surface area data comparison

Catalysts	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore width (nm)
STFN1	32.839	0.104	3.828
STFN2	34.957	0.112	3.941
STFN3	36.828	0.153	4.154

Table S5 Oxygen species content of STFN1 and STFN3

Catalyst	H ₂ O (%)	-OH/O ₂ (%)	O ₂ ²⁻ /O [·] (%)	O _{latt} (%)
STFN1	11.28	32.34	35.37	21.01
STFN3	1.49	41.96	42.91	13.64

Table S6 Fe and Ni contents in STFN1 and STFN3

Catalyst	Fe ⁴⁺ (%)	Fe ³⁺ (%)	Ni ³⁺ (%)	Ni ²⁺ (%)
STFN1	30.37	69.63	60.96	39.04
STFN3	40.08	59.92	64.42	35.58

Table S7 ORR performance of A-site-deficient STFN samples

Catalysts	E _{onset} (V)	E _{1/2} (V)	J (mA cm ⁻²)	Tafel (mV dec ⁻¹)
STFN1	0.8857	0.6411	-6.1971	103
STFN2	0.8912	0.6679	-6.5671	98
STFN3	0.8934	0.6740	-6.9762	97

Table S8 OER performance and ΔE of A-site-deficient STFN samples

Catalysts	OER		ORR		ΔE (V)
	Tafel (mV dec ⁻¹)	η (mV)	@10 mA cm ⁻² (V)	@-3 mA cm ⁻² (V)	
STFN1	103	412.0	1.6420	0.6124	1.0296
STFN2	100	408	1.6380	0.6345	1.0335
STFN3	99	399.9	1.6299	0.7082	0.9217

Table S9 A comparison of ORR and OER activity for STFN3 and other reported perovskite catalysts. All the electrochemical measurements were carried out in 0.1 M KOH solution

Catalyst	ORR		OER			Ref.
	$E_{1/2}$ (V vs. RHE)	Tafel (mV dec ⁻¹)	Tafel (mV dec ⁻¹)	η (mV) @10 mA cm ⁻²	ΔE (V)	
(La _{0.8} Sr _{0.2}) _{0.95} Mn _{0.5} Fe _{0.5} O _{3-δ}	-0.124	132	230	-	-	[1]
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	-	-	-	380	-	[2]
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	-	-	94	510	-	[3]
La _{0.8} Sr _{0.2} Co _{0.4} Mn _{0.6} O _{3-δ}	0.888	90	113	506	1.032	[4]
La _{0.8} Sr _{0.2} Co _{0.6} Mn _{0.4} O _{3-δ}	0.881	104	113	515	1.104	[4]
Sr _{0.95} Nb _{0.1} Co _{0.7} Fe _{0.2} O _{3-δ}	-	-	70	420	-	[5]
La _{0.7} Sr _{0.15} Pd _{0.15} MnO _{3-δ}	0.973	87	-	-	-	[6]
La _{0.9} Y _{0.1} MnO _{3-δ}	0.909	101	-	-	-	[7]
La _{1.7} Sr _{0.3} Co _{0.5} Ni _{0.5} O _{4+δ}	0.696	-	125	592	1.126	[8]
La _{0.4} Sr _{0.6} Co _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	0.505	114	78	360	1.07	[9]
BaZr _{0.15} Fe _{0.85} O _{3-δ}	-	-	97	471	-	[10]
IrO ₂	-	-	115	413	-	This work
Pt/C	0.7054	99	-	-	-	This work
Sr _{0.9} Ti _{0.3} Fe _{0.6} Ni _{0.1} O _{3-δ}	0.7082	97	99	399.9	0.921	This work
					7	

References

- [1] R-H Yuan, Y He, W He, et al. Bifunctional electrocatalytic activity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ -based perovskite with the A-site deficiency for oxygen reduction and evolution reactions in alkaline media[J]. *Applied Energy*, 2019, 251:113406.
- [2] G Li, S Hou, L Gui, et al. Carbon quantum dots decorated $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ perovskite nanofibers for boosting oxygen evolution reaction[J]. *Applied Catalysis B: Environmental*, 2019, 257:117919.
- [3] Y Bu, O Gwon, G Nam, et al. A Highly Efficient and Robust Cation Ordered Perovskite Oxide as a Bifunctional Catalyst for Rechargeable Zinc-Air Batteries[J]. *ACS Nano*, 2017, 11(11): 11594-11601.
- [4] Q Wang, Y Xue, S Sun, et al. $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-x}\text{Mn}_x\text{O}_3$ perovskites as efficient bi-functional cathode catalysts for rechargeable zinc-air batteries[J]. *Electrochimica Acta*, 2017, 254: 14-24.
- [5] H Liu, X Ding, L Wang, et al. Cation deficiency design: A simple and efficient strategy for promoting oxygen evolution reaction activity of perovskite electrocatalyst[J]. *Electrochimica Acta*, 2018, 259: 1004-1010.
- [6] Y Xue, S Sun, Q Wang, et al. $\text{La}_{0.7}(\text{Sr}_{0.3-x}\text{Pd}_x)\text{MnO}_3$ as a highly efficient electrocatalyst for oxygen reduction reaction in aluminum air battery[J]. *Electrochimica Acta*, 2017, 230: 418-427.
- [7] H Miao, Z Wang, Q Wang, et al. A new family of Mn-based perovskite ($\text{La}_{1-x}\text{Y}_x\text{MnO}_3$) with improved oxygen electrocatalytic activity for metal-air batteries[J]. *Energy*, 2018, 154: 561-570.
- [8] P Li, B Wei, Z Lü, et al. $\text{La}_{1.7}\text{Sr}_{0.3}\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_{4+\delta}$ layered perovskite as an efficient bifunctional electrocatalyst for rechargeable zinc-air batteries[J]. *Applied Surface Science*, 2019, 464: 494-501.
- [9] L Yu, N Xu, T Zhu, et al. $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ perovskite prepared by the sol-gel method with superior performance as a bifunctional oxygen electrocatalyst[J]. *International Journal of Hydrogen Energy*, 2020, 45(55): 30583-30591.
- [10] K Zhu, H Liu, X Li, et al. Oxygen evolution reaction over Fe site of $\text{BaZr}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ perovskite oxides, *Electrochim. Acta*, 241 (2017) 433-439.