

Figure S1. Schematic diagram of the synthesis of N-C, Mn-N-C, and Mn-N-C/XO₂ catalysts.



Figure S2. Schematic diagram of experimental apparatus for fabricating Mn-N-C/XO₂ (X=S, Se and Te) catalysts.



Figure S3. XRD spectrum of Mn-N-C/SO₂ and Mn-N-C/TeO₂ catalyst.



Figure S4. SEM image of (a) Mn-N-C, (b) Mn-N-C/SO₂ and (c) Mn-N-C/TeO₂ catalysts, size distribution of (d) Mn-N-C, (e) Mn-N-C/SO₂ and (f) Mn-N-C/TeO₂ catalysts.



Figure S5. HADDF-STEM images of (a)Mn-N-C, (b) Mn-N-C/SO₂, and (c) Mn-N-C/TeO₂.



Figure S6. HADDF-STEM images of Mn-N-C/SO₂ and the corresponding EDS mappings of Mn, N, S, O and C elements.



Figure S7. HADDF-STEM images of Mn-N-C/TeO₂ and the corresponding EDS mappings of Mn, N, Te, O and C elements.



Figure S8. N 1s XPS spectra of (a) Mn-N-C/SO₂ and (b) Mn-N-C/TeO₂ catalysts.



Figure S9. (a) S 2p XPS spectrum of Mn-N-C/SO₂. (b) Te 3d XPS spectrum of Mn-N-C/TeO₂.



Figure S10. FT-EXAFS of the experimental and fitted Mn K-edge spectra of (a) Mn-N-C, (b) Mn-N-C/SO₂ and (c) Mn-N-C/TeO₂ catalysts in R space, respectively.



Figure S11. WT-EXAFS signals of (a) Mn-N-C, (b) Mn-N-C/SO₂, (c) Mn-N-C/TeO₂, (d) MnO, (e) Mn₂O₃ and (f) Mn foil.



Figure S12. Raman spectra of (a) N-C, (b) Mn-N-C, (c) Mn-N-C/SO₂, (d) Mn-N-C/SeO₂ and (e) Mn-N-C/TeO₂.



Figure S13. EIS spectra of Mn-N-C and Mn-N-C/XO₂ at 0.8 V_{RHE} collected from 100 kHz to 0.1



Figure S14. LSV curves of (a) Mn-N-C, (b) Mn-N-C/SO₂ and (c) Mn-N-C/TeO₂ catalyst at the initial cycle and after 10,000 cycles.



Figure S15. Electrocatalytic stability testing of (a) Mn-N-C/SO₂ and (b) Mn-N-C/TeO₂ by chronoamperometry from 0.6 V_{RHE} to 1.0 V_{RHE} .



Figure S16. SEM image of (a) Mn-N-C, (b) Mn-N-C/SO₂, (c) Mn-N-C/SeO₂ and (d) Mn-N-C/TeO₂ catalysts under long-term post-ORR conditions.



Figure S17. XRD patterns of (a) N-C, Mn-N-C, Mn-N-C/SeO₂ catalysts and (b) Mn-N-C/SO₂, Mn-N-C/TeO₂ catalysts under long-term post-ORR conditions.

Hz.



Figure S18. High-resolution (a) Mn 2*p* spectra of Mn-N-C and Mn-N-C/XO₂ catalysts under long-term post-ORR conditions.



Figure S19. Projected density of states on Mn *d*-orbitals in (a) Mn-N-C, (b) Mn-N-C/SO₂, Mn-N-C/SeO₂ and (d) Mn-N-C/TeO₂ catalyst.



Figure S20. The calculated atomic structures of the Mn-N-C and Mn-N-C/XO₂ catalyst models after the relaxation. (a) Mn-N-C, (b) Mn-N-C/SO₂, (c) Mn-N-C/SeO₂ and (d) Mn-N-C/TeO₂.