

Supporting Information

For

Core-shell FTO@Co₃O₄ Nanoparticles as Active and Stable Anode

Catalysts for Acidic Oxygen Evolution Reaction and Proton

Exchange Membrane Water Electrolysis

**Yong-Xian Yeh, Chih-Chieh Cheng, Pei-Syuan Jhu, Shin-Hong Lin, Po-Wei
Chen, Shih-Yuan Lu***

Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013,
Taiwan.

***Email: sylu@mx.nthu.edu.tw (Shih-Yuan Lu)**

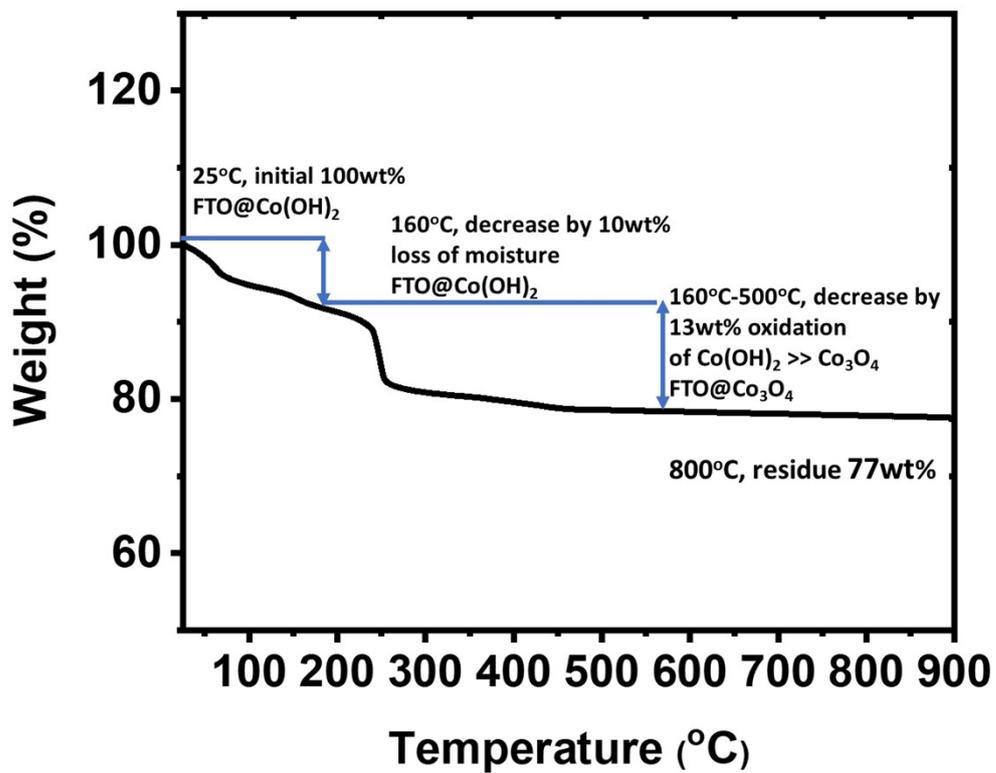


Figure S1. Thermogravimetric curve of FTO@Co(OH)₂ in air. Heating rate: 5 °C min⁻¹.

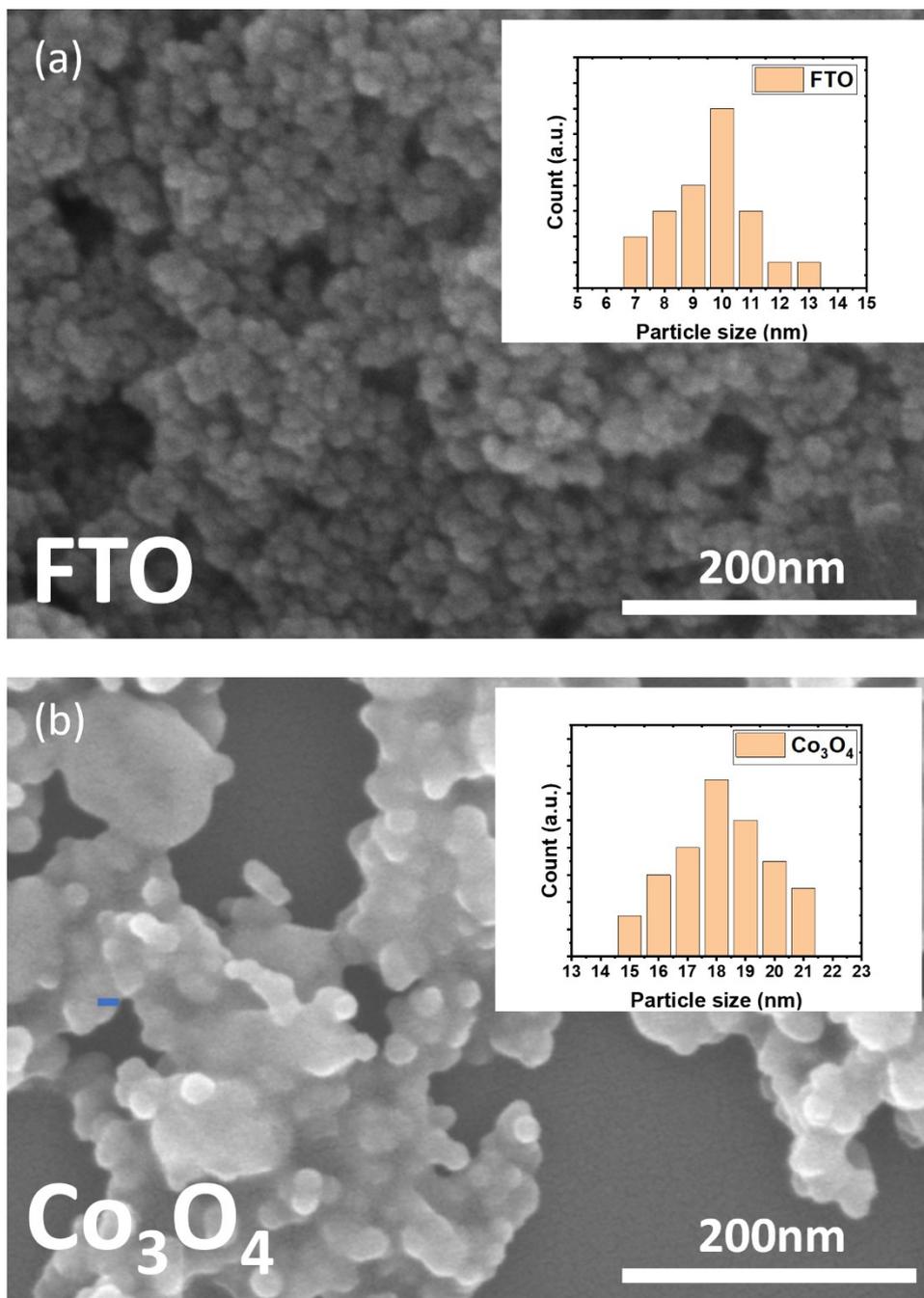


Figure S2. SEM images of (a) FTO and (b) Co_3O_4 nanoparticles. Insets show size distributions of nanoparticles.

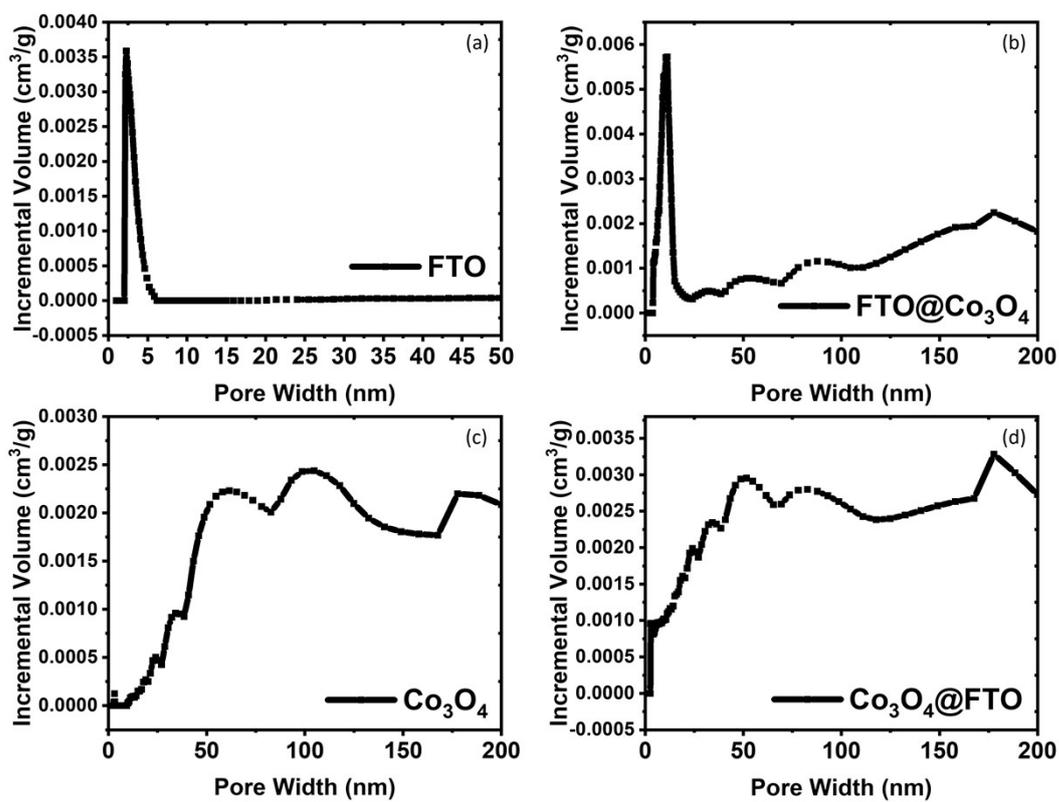


Figure S3. Pore size distribution of (a)FTO (b)FTO@Co₃O₄ (c) Co₃O₄ (d) Co₃O₄@FTO nanoparticles.

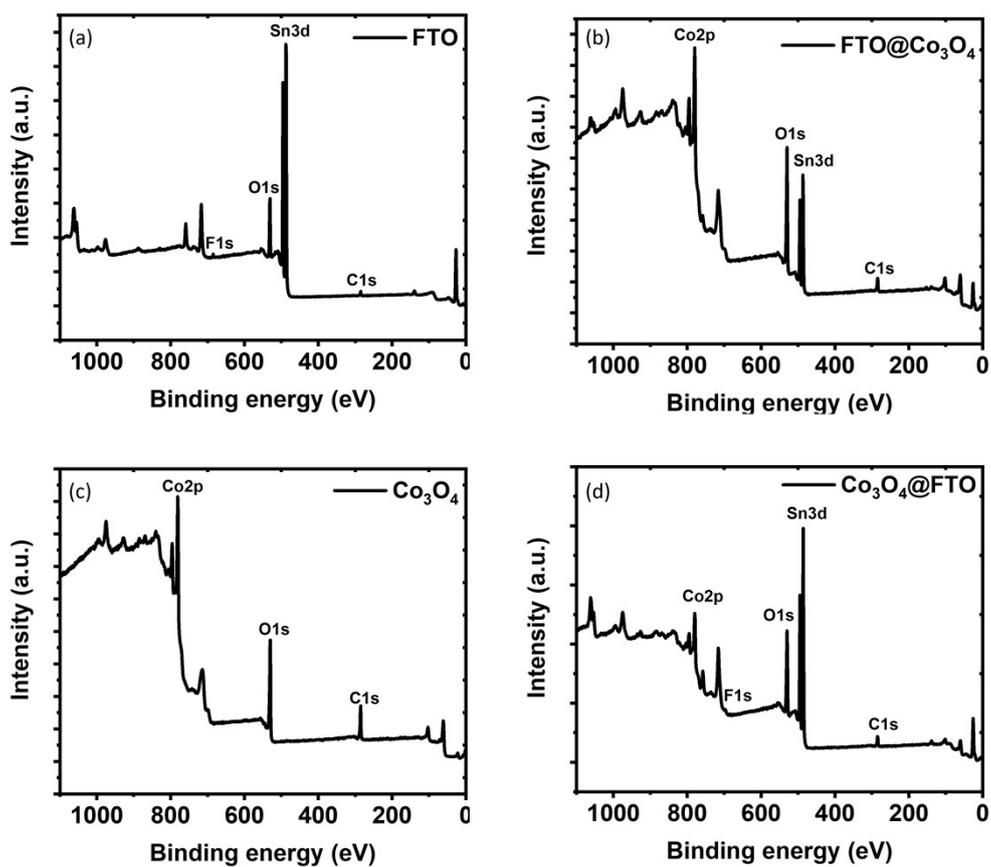


Figure S4. XPS survey spectra of (a) FTO, (b) FTO@Co₃O₄, (c) Co₃O₄, and (d)Co₃O₄@FTO.

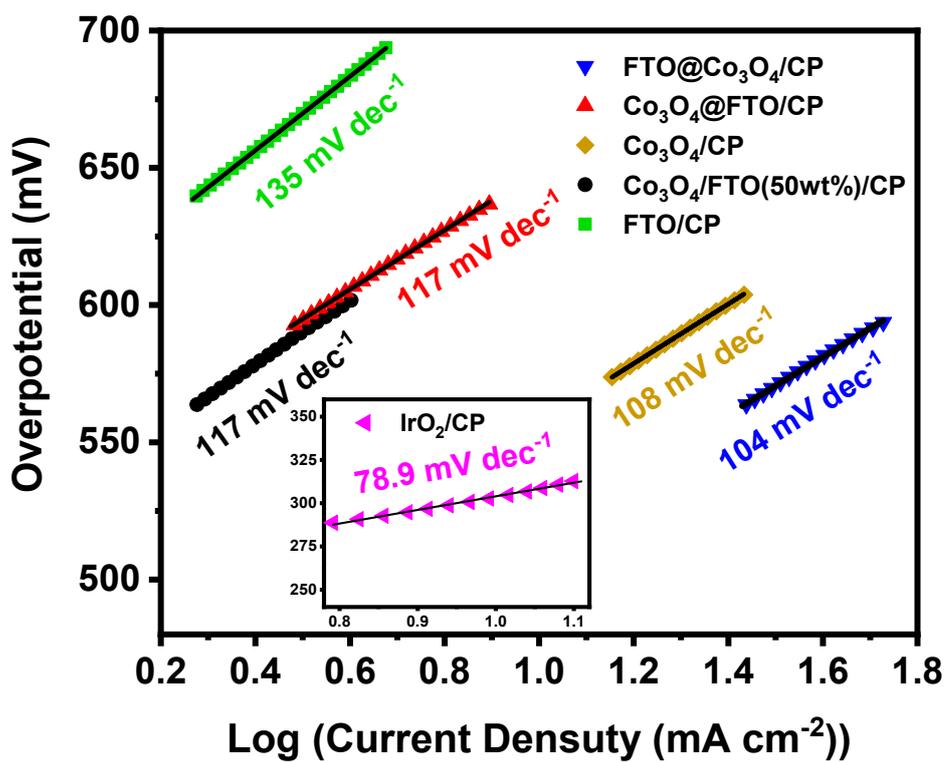


Figure S5. Tafel plots of FTO/CP, FTO@Co₃O₄/CP, Co₃O₄/CP, Co₃O₄@FTO/CP, and Co₃O₄/FTO(50wt%)/CP.

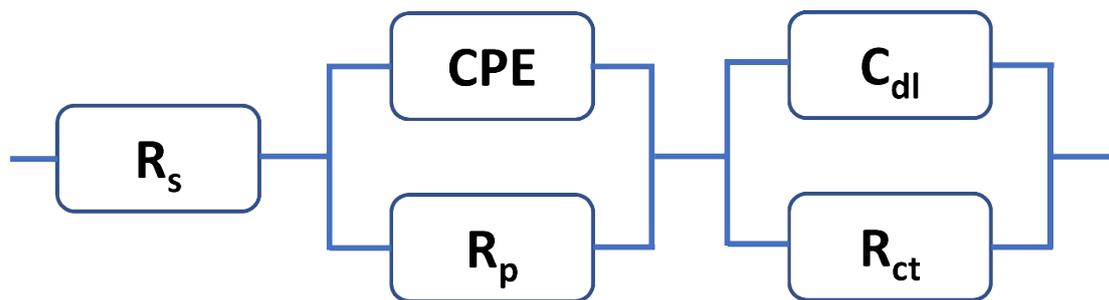


Figure S6. Equivalent circuit model: R_s for solution resistance, CPE for constant phase element accounting for electrode porosity, R_p for electrode porosity resistance, C_{dl} for double layer capacitance, and R_{ct} for charge transfer resistance.

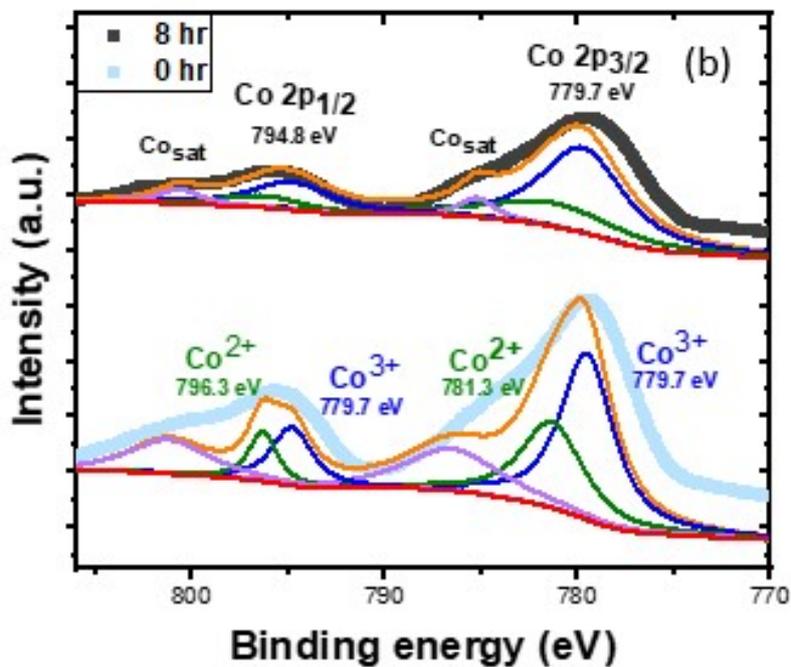
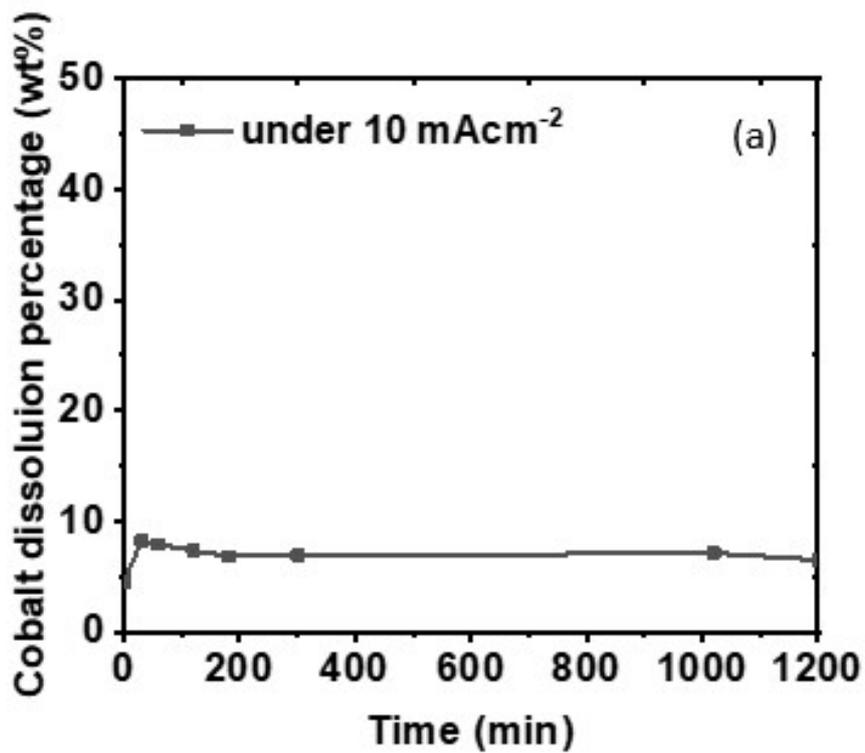


Figure S7. (a) Percentages of Co leaching from FTO@Co₃O₄/CP operated at 10 mA cm⁻² during course of 20 hours. (b) HRXPS spectra of Co 2p of FTO@Co₃O₄/CP after operations at 10 mA cm⁻² for 0 and 8 hours.

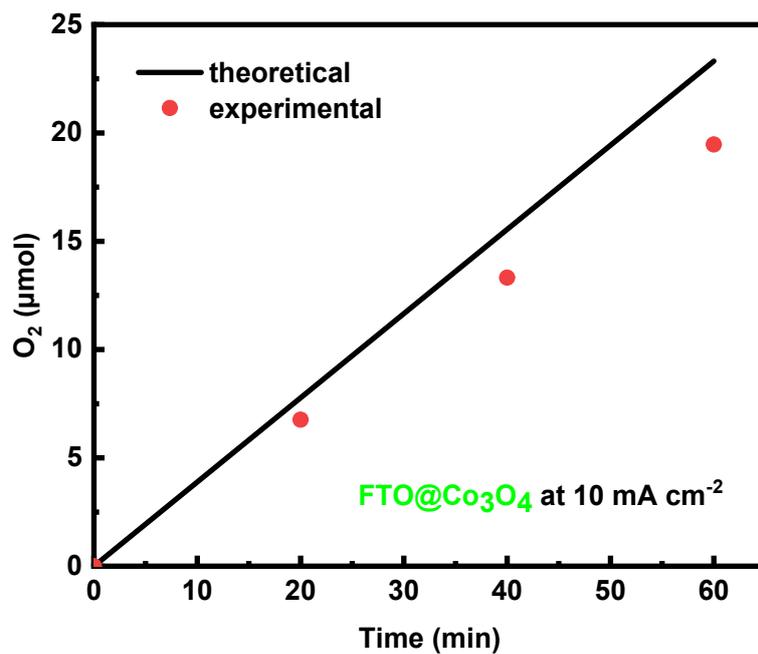


Figure S8. Theoretical and experimental O₂ generation for determination of Faradaic efficiency of FTO@Co₃O₄/CP operated at 10 mA cm⁻² for 60 min. Experimental test conditions: 0.25 cm² for electrode surface area and 298 K for temperature.

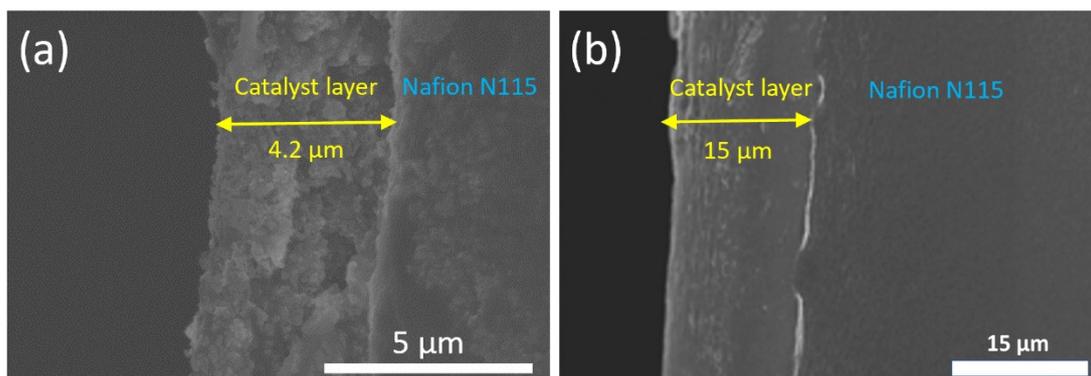


Figure S9. SEM images of (a) anode (FTO@Co₃O₄) and (b) cathode (Pt/C).

Table S1. PEMWE performances of non-noble metal based anode catalysts.

Membrane (temperature)	Cathode catalyst (loading in mg cm ⁻²)	Anode catalyst (loading in mg cm ⁻²)	Current density @2 V (in A cm ⁻²)	Reference
N115 (25°C)	Pt/C (0.2)	FTO@Co ₃ O ₄ (3.0)	0.205	This work
N115 (80 °C)	Pt/C (0.5)	CoHFe/ATO (2.0)	0.05-0.1	[S1]
N117 (25°C)	Pt/C (0.5)	Co/29BC (N/A)	0.12	[S2]
N117 (25°C)	Pt/C (0.1)	γ-MnO ₂ (3.5)	0.13	[S3]

Reference:

[S1] B. Rodríguez-García, Á. Reyes-Carmona, I. Jiménez-Morales, M. Blasco-Ahicart, S. Cavaliere, M. Dupont, D. Jones, J. Rozière, J.R. Galán-Mascarós, F. Jaouen, Cobalt hexacyanoferrate supported on Sb-doped SnO₂ as a non-noble catalyst for oxygen evolution in acidic medium, *Sustainable Energy & Fuels* 2(3) (2018) 589-597. <https://doi.org/10.1039/C7SE00512A>.

[S2] Q. Lai, V. Vedyappan, K.-F. Aguey-Zinsou, H. Matsumoto, One-Step Synthesis of Carbon-Protected Co₃O₄ Nanoparticles toward Long-Term Water Oxidation in Acidic Media, *Advanced Energy and Sustainability Research* 2(11) (2021) 2100086. <https://doi.org/https://doi.org/10.1002/aesr.202100086>.

[S3] A. Li, H. Ooka, N. Bonnet, T. Hayashi, Y. Sun, Q. Jiang, C. Li, H. Han, R. Nakamura, Stable Potential Windows for Long-Term Electrocatalysis by Manganese Oxides Under Acidic Conditions, *Angew Chem Int Ed Engl* 58(15) (2019) 5054-5058. <https://doi.org/10.1002/anie.201813361>.