CuNi Sulphidation Maximizes MOR Activity by Expanding the Accessibility of Active Sites!

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Electrochemical Measurements: All electrochemical measurements were conducted in 1.0 M KOH solution, with methanol concentrations ranging from 0.25 M to 1.25 M depending on the study. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were extensively employed to preliminarily assess activity, using a scan rate of 10 mV s⁻¹ against a Hg/HgO reference electrode. These results were presented without correction for iR drop and double layer charging. Stability was investigated through 12-hour chronoamperometry (CA) at 1.574 V vs RHE. Electrochemical impedance spectroscopy (EIS) studies were conducted in a frequency range of 1 MHz to 0.1 Hz with an AC amplitude of 10 mV. Temperature-dependent LSVs were obtained by gradually heating the electrolyte using a temperature-controlled hot-plate stirrer, with temperature monitored by a calibrated thermometer immersed in the electrolyte.

Determination of Faradaic Efficiency: NMR results revealed the formation of methyl formate. However, direct electrooxidation of methanol into methyl formate is deemed impossible. A plausible explanation is the post-oxidation esterification of formic acid resulting from the 4e⁻ MOR pathway. This is supported by a 24 h gap between electrolysis and NMR analysis. Nonetheless, this does not alter the fact that CuNi-S-catalyzed MOR displayed high selectivity for the 4e⁻ pathway. To quantify formate ions in the electrolyte, volumetric analysis was conducted using standardized HCl (0.21 M) and methyl orange indicator after neutralizing excess KOH with required HCl amounts. The concentration of formate in the electrolyte was experimentally determined to be 0.00054 M. Using Faraday's law of electrolysis, the expected formate concentration from the charge amount was calculated as 0.00098 M. The Faradaic efficiency (FE) was then calculated using these values.

FE (%) = ([HCOOH_{exp}] / [HCOOH_{theory}]) × 100 = (0.00054/0.00061) × 100 = **88.5%**

The remainder of the charge passed is attributed to be used for catalyst's self-oxidation and competing OER.



Figure S1: (a) XRD patterns of CuNi and CuNi-S in comparison with the standard patterns of $Cu_{0.81}Ni_{0.19}$ and $Cu_{1.9}S$. (b) Raman spectra of CuNi and CuNi-S. (c) stacked version of the same XRD patterns given in (a) for a better clarity.



Figure S2: (a-c) SEM Images of CuNi before sulphidation with increasing magnifications.



Figure S3: Energy dispersive X-ray spectroscopic (EDS) elemental mapping of Cu, Ni, and S of CuNi after sulphidation.



Figure S4: SAED pattern of CuNi-S showing clear dot patterns belonging to several phases of Ni and Cu sulphides.



Figure S5: XPS narrow scans of S 2p (a) and C 1s (b) levels of CuNi-S.



Figure S6: NMR spectrum of the electrolyte containing KOH, MeOH, and methyl formate drawn after 6 h of electrolysis at 0.7 V vs Hg/HgO, respectively. The gap between electrolysis and NMR analysis was 24 h which facilitated the condensation of formate with methanol as the pH was high enough.



Figure S7: (a) CVs of CuNi and CuNi-S showing distinct redox peaks magnified in (b) where (c) shows only the reduction peak used for integration. (d) Bar diagram comparing $ECAS_{Ni+Cu}$ of both CuNi and CuNi-S.



Figure S8: The free energy change associated with the adsorption of intermediates (CH_3O^- , HCHO, CO, and HCOO⁻) of 4e⁻ MOR on Cu_{13} (a), $Cu_{12}Ni$ (b), and $Cu_{12}NiS$ (c) clusters, respectively.



Figure S9: (a) MOR LSVs of CuNi-S before and after 12 h CA in MeOH replenished medium. Raman spectra (b), FESEM image (d), and TEM images (d and e) of the same after 12 h of CA. (f and g) XPS narrow scans of Cu 2p3/2 ad Ni 2p3/2 states of CuNi-S after 12 h of CA.

Table S1: Benchmarking Cu and Ni-based MOR electrocatalysts by their apparent activity at1.524 V vs RHE

Catalyst	Method of Preparation	Activity @ 1.524
		V vs RHE
Cu(OH) ₂ ¹	Chemical oxidation	0.1
Cu ²	Activated by potential cycling	0.6
Ni-Cu Alloy ³	Potential cycling in 1 M NaOH	1.6
CuS microflower ⁴	Hydrothemal sulphidation	3
Cu ₂ O ⁵	RF magnetron sputtering	6
Ni _{0.5} Cu _{0.5} Co ₂ O ₄ /ZSM-5 ⁶	Ion-exchange process	6
CuO ⁵	RF magnetron sputtering	10
	Chemical oxidation followed by	
CuO ¹	annealing	10
Ni/GC ⁷	Electrodeposition	40
	Potentiostatic anodization	
Cu(OH) ₂ -CuO/Cu ⁸	for 60 s	42
NiO-Cu 1200 ⁹	Co-sputtering	46
	Hydrothermal method followed by	
Cu-Co@N-C ¹⁰	pyrolysis	68
$Cu(OH)_2@CoCO_3(OH)_2 \cdot nH_2O^{11}$	Hydrothermal	78
	Hydrothermal sulfidation of CuNi	
CuNi-S (This work)	alloy	102

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