

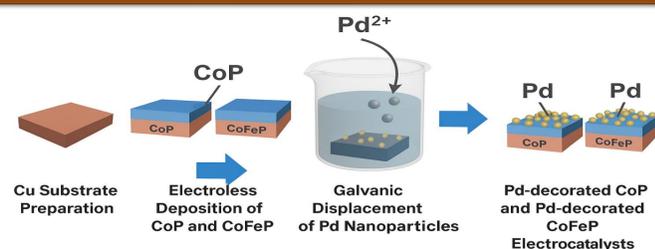
Cobalt-Based Electrocatalysts: A Pathway Toward Cost-Effective and High-Performance Energy Conversion

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INTRODUCTION & AIM

- The Hydrogen Evolution Reaction (HER) is pivotal for electrochemical water splitting and sustainable hydrogen production.
- Platinum-based catalysts exhibit excellent HER activity, but their high cost and scarcity limit their widespread use.
- Cobalt–phosphide (CoP) and Cobalt–iron–phosphide (CoFeP) electrocatalysts offer a promising alternative due to their low cost, abundance, favourable electronic properties, and tunable catalytic performance. Co and Fe exhibit synergistic effects in enhancing the electronic conductivity and catalytic sites. P incorporation can modulate the electronic structure and improve the kinetics of hydrogen adsorption, while Pd modification further enhances the catalytic activity by improving electron transfer and surface reactivity. Sodium hypophosphite (NaH_2PO_2) was used as the reducing agent.
- Research Objective:** This research aims to develop Pd-decorated CoP and CoFeP coatings on copper (Cu) substrate via electroless deposition and galvanic displacement method, and to evaluate their hydrogen evolution performance in alkaline media using Linear Sweep Voltammetry (LSV), Chronoamperometry (CA), and Chronopotentiometry (CP) techniques.

FABRICATION OF CATALYSTS



SEM & EDX ANALYSIS

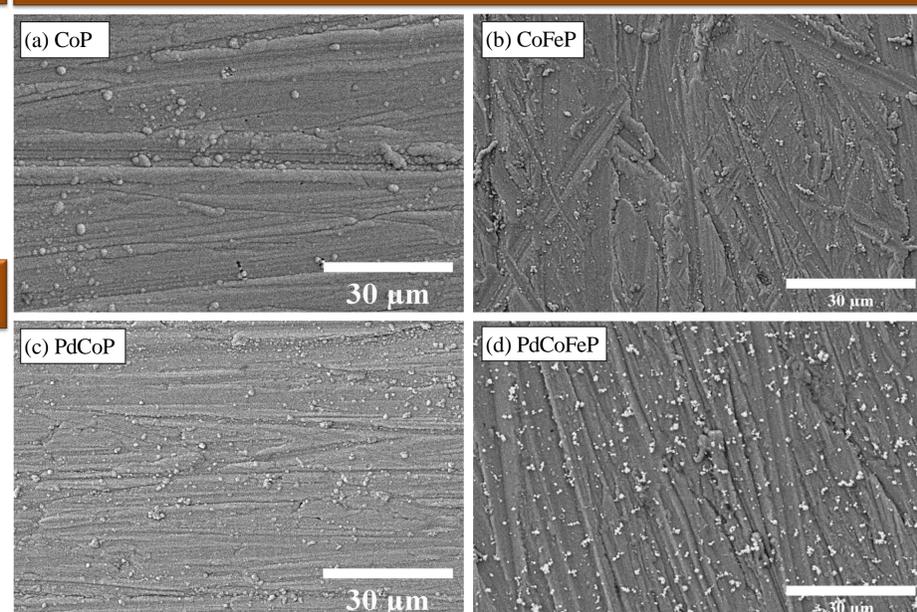


Fig. 1. The SEM views of CoP (a), CoFeP (b), PdCoP (c) and PdCoFeP (d) catalysts. **Table 1.** Elemental composition of Co-based and Pd-decorated coatings deposited on copper substrates, as determined by EDX analysis.

Catalyst	Wt. %			
	Pd	Co	Fe	P
CoP/Cu	-	95.31	-	4.69
CoFeP/Cu	-	85.19	11.42	3.39
PdCoP/Cu	8.27	91.60	-	0.14
PdCoFeP/Cu	12.23	67.18	16.57	4.02

RESULTS & DISCUSSION

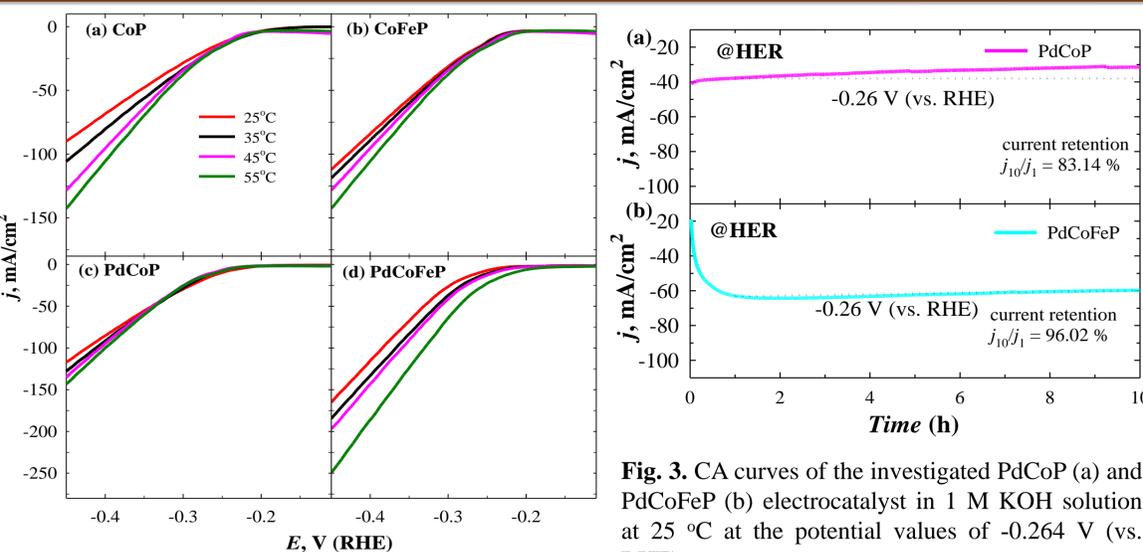


Fig. 3. CA curves of the investigated PdCoP (a) and PdCoFeP (b) electrocatalyst in 1 M KOH solution at 25 °C at the potential values of -0.264 V (vs. RHE).
current retention $j_{10}/j_1 = 83.14\%$
current retention $j_{10}/j_1 = 96.02\%$

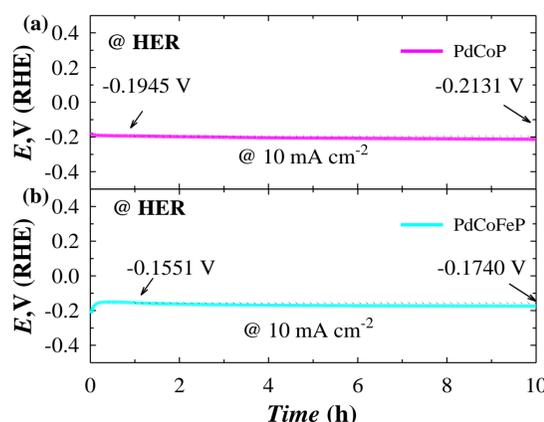
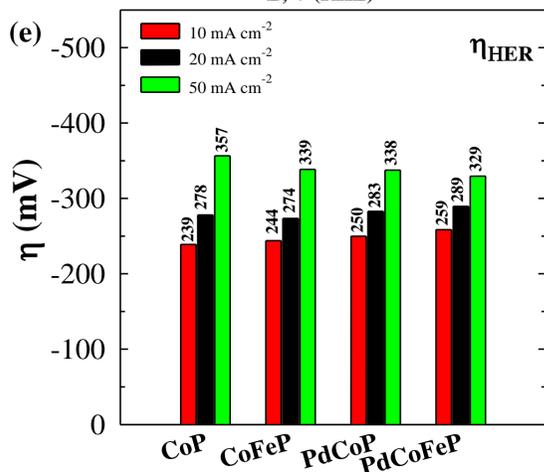


Fig. 4. CP curves in 1 M KOH solution at a constant current density of 10 mA cm⁻² at 25 °C of the investigated catalyst PdCoP (a) and PdCoFeP (b).

Fig. 2. The HER polarization curves recorded on CoP (a), CoFeP (b), PdCoP (c), and PdCoFeP (d) catalysts in 1 M KOH at 5 mV s⁻¹ and a temperature range (25–55°C). (e) HER overpotential column bar to reach a current density of 10 mA cm⁻².

Table 2. Electrochemical parameters of the investigated catalysts for HER in alkaline media.

Catalysts	j (mA cm ⁻²) in Different Temperatures at -0.464 V (vs. RHE)				η ₁₀ (mV) at 25°C	η ₁₀ (mV) at 55°C	Tafel slope, mV dec ⁻¹
	25	35	45	55			
	CoP/Cu	-94.28	-110.78	-127.27			
CoFeP/Cu	-117.55	-124.60	-133.48	-149.23	243.90	228.95	90.19
PdCoP/Cu	-122.65	-128.68	-141.98	-151.05	249.71	258.86	76.14
PdCoFeP/Cu	-180.37	-192.14	-214.71	-259.71	258.55	215.86	84.79

CONCLUSION

In summary, Pd-decorated CoP and CoFeP coatings were successfully fabricated on Cu substrate via a two-step process involving electroless deposition followed by galvanic displacement. Structural and morphological characterization using techniques such as scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) confirmed the successful formation of uniform surface coverage. Electrochemical evaluations in alkaline media, including LSV, CA, and CP, demonstrated that all the synthesized catalysts exhibited good catalytic activity toward the HER. In particular, the PdCoFeP catalyst exhibited a slightly higher overpotential value of 258.55 mV compared to PdCoP, which showed 249.71 mV at a current density of 10 mA cm⁻² at 25 °C. However, it delivered a higher current density, indicating more efficient hydrogen generation at higher load conditions. Similarly, the undecorated CoFeP showed a slightly higher overpotential 243.90 mV than CoP with 239.02 mV at a current density of 10 mA cm⁻² at 25 °C, but outperformed it in terms of current density. These improvements are attributed to the synergistic interactions between Co, Fe, P, and Pd, which enhance electron transfer and facilitate HER kinetics. Furthermore, CP curves of the PdCoP and PdCoFeP electrocatalysts also showed excellent long-term electrocatalytic stability in an alkaline environment, as the recorded potentials did not change significantly after 10 h of continuous HER electrolysis at a constant current density of 10 mA cm⁻² while, the CA measurements confirmed the catalysts ability to maintain steady current densities after 10 h at fixed potential of -0.26 V (vs. RHE) thus both indicating excellent electrochemical robustness (Fig. 4. & 3). This study demonstrates that all synthesized catalysts CoP, CoFeP, PdCoP, and PdCoFeP are effective and stable electrocatalysts for hydrogen evolution in alkaline media. Among these catalysts, PdCoFeP exhibits particular promise for applications requiring high current densities. Overall, these materials have significant potential for use in large-scale hydrogen production, renewable energy storage, and clean fuel cell technologies to support the transition to a sustainable energy future.

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