

Electrodeposition of Nickel-Based Catalysts for Electrochemical CO₂ Reduction

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Introduction

Recent studies suggest that **nickel-based catalysts** may promote electrochemical Fischer-Tropsch, potentially forming **longer-chain hydrocarbons**.

Because nickel compounds can pose health risks, especially when inhaled as fine particles during spray coating, safer fabrication methods such as **electrodeposition** provide a more controlled alternative.

Challenges for nickel electrodeposition

At lower pH, nickel deposition from free Ni²⁺ ions competes with the **hydrogen evolution reaction**. At higher pH, **passivation** (hydroxide precipitation) can suppress metal deposition. **Pourbaix (E–pH) diagrams** are a map of electrochemical experiments (e.g. **electrodeposition**, **electrocatalysis**) and they identify the main stability regions associated with metals i.e. **immunity**, **passivation**, and **corrosion**

Additives as solution

Increasing **[NH₃]/[Ni]** and **[Cit]/[Ni]** shifts the passivation boundary to higher pH and introduces ammine-complex and citrate-complex stability regions.

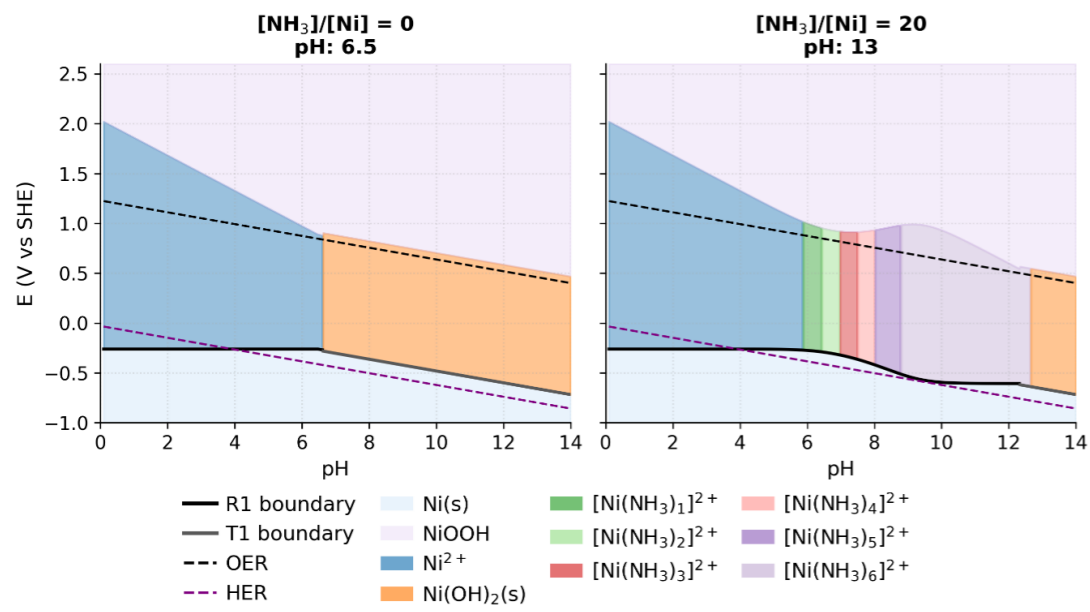


Figure 1: Addition of ammonia as complexing agent

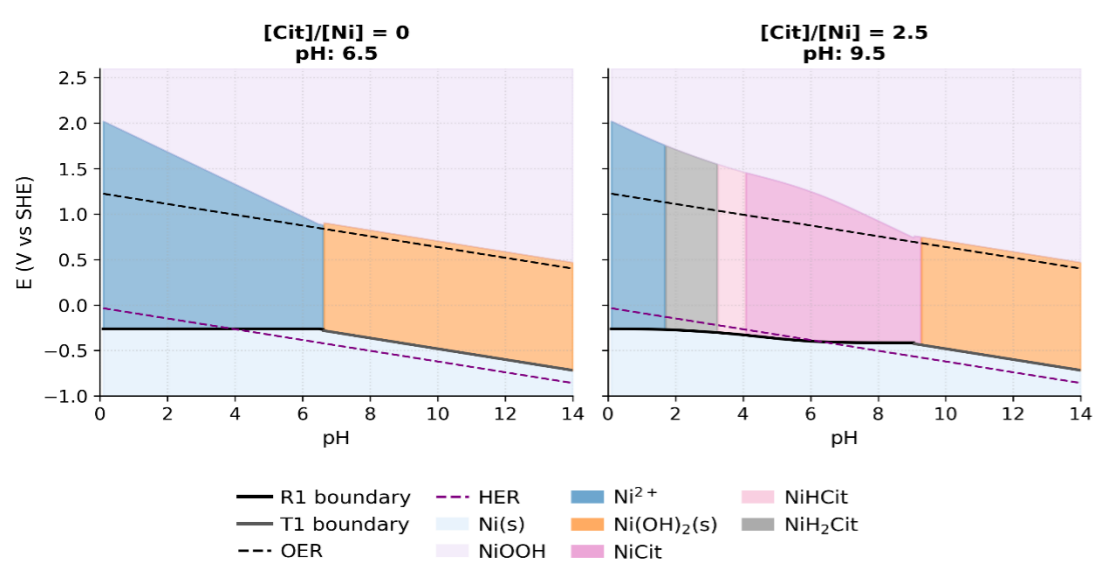


Figure 2: Addition of citric acid as complexing agent.

Thermodynamic Model : Variability problem

At each pH, the Ni–ammonia–citrate system is solved with coupled equilibrium equations and mass-balance constraints. Equilibrium constants in the literature vary enormously.

Table 1: Core reactions included in the speciation model.

Reaction Class	Representative Species
Free Ni reduction	Ni ²⁺ / Ni ⁰
Ammine complexes	[Ni(NH ₃) _n] ²⁺ , n = 1...6
Hydroxide precipitation	Ni(OH) ₂ , Ni(OH) ₃
Citrate complexes	NiCit ⁻ , NiHCit, NiH ₂ Cit ⁺
Water equilibria	H ⁺ , OH ⁻

Table 2: Mean and standard deviation used for Monte Carlo sampling.

Parameter	Mean(μ)	S.D(σ)
K _{sp} of Ni(OH) ₂	-15.74	2.03
NH ₄ ⁺	9.24	0.15
[Ni(NH ₃) ₁] ²⁺	2.78	0.07
[Ni(NH ₃) ₂] ²⁺	5.02	0.13
[Ni(NH ₃) ₃] ²⁺	6.75	0.19
[Ni(NH ₃) ₄] ²⁺	7.97	0.27
[Ni(NH ₃) ₅] ²⁺	8.73	0.34
[Ni(NH ₃) ₆] ²⁺	8.84	0.46

Literature values for key constants can vary significantly, making deterministic boundaries potentially misleading.

Probabilistic Pourbaix Diagram

Monte Carlo propagation yields a probability distribution over E–pH space. Instead of a single boundary, the model reports confidence bands and low-confidence regions where predictions are less certain.

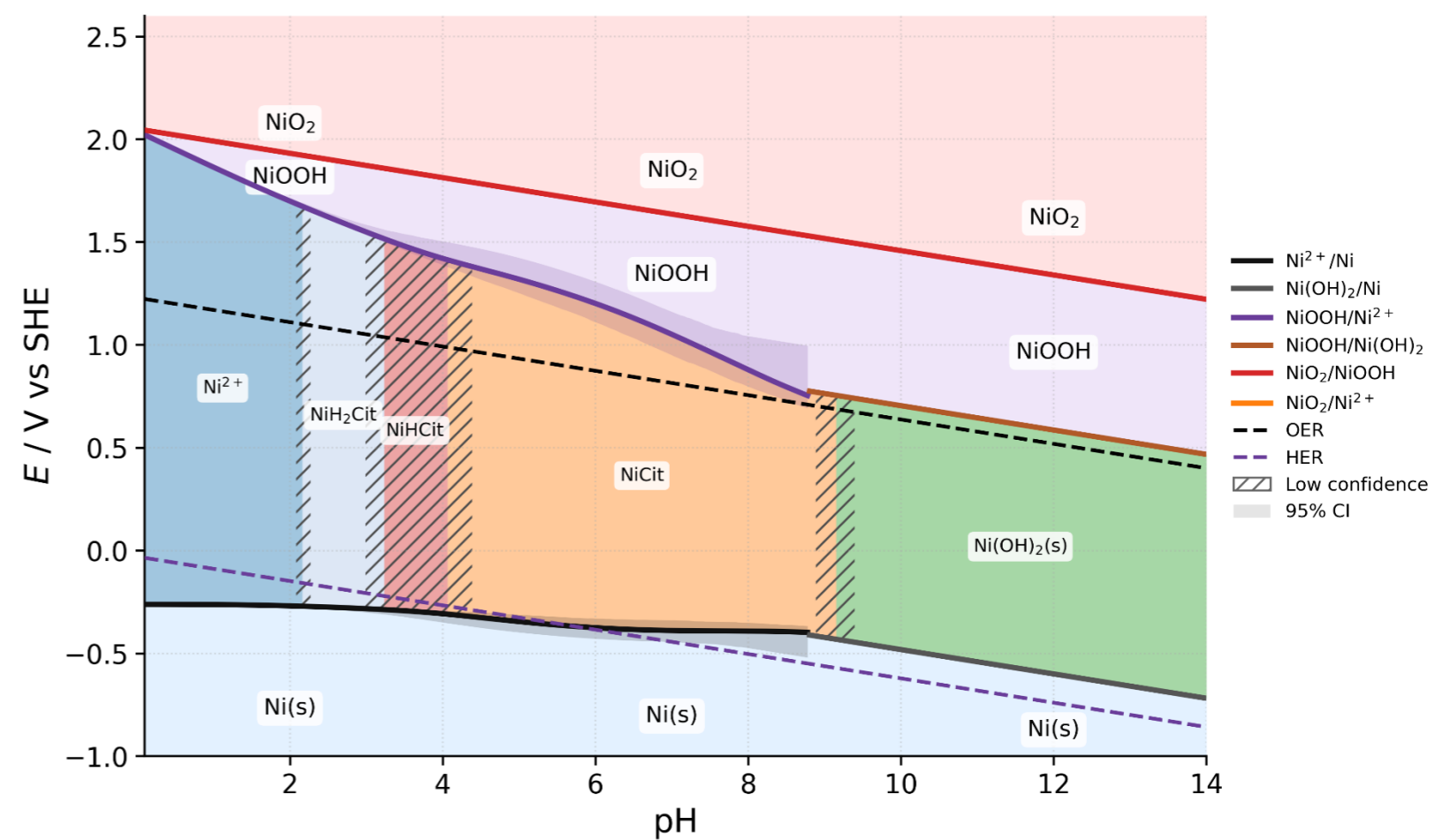


Figure 3: Probabilistic Pourbaix diagram for nickel: ammonia: citrate (0.2 : 0.33 : 0.25)

Conclusions

- Ammonia and citrate both shift the nickel deposition window to higher pH
- Citrate has the stronger effect on the passivation boundary
- Literature constants vary substantially across sources
- Monte Carlo Pourbaix diagrams convert binary predictions into probability distributions

View the model online



Acknowledgments

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