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Intermetallic compounds from the non-noble metals as the catalysts in the electrochemical reactions of ammonia synthesis

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INTRODUCTION & AIM

Intermetallic compounds (IMCs), which have a homogeneous structure of active centers with controlled electronic structure and atomic ensemble size and, can be used to create catalysts with unsurpassed practical characteristics, including for demanded and stable electrochemical reactions: nitrogen reduction (NRR) nitrate reduction (NO_3RR) and nitrite reduction (NO_2RR), which can serve as a replacement for the industrial Haber-Bosch process. An urgent task is to creation of efficient electrocatalysts for using cheap base metals, with partial or complete replacement of noble metals. For this purpose, it is proposed to use IMCs based on cobalt, iron, silicon, as well as some rare earth elements.

Cobalt-iron silicide catalysts exhibit outstanding electrocatalytic characteristics. The use of silicon as an additive to intermetallic compounds with a hcp phase structure leads to stabilization of the hcp phase and ensures good wear resistance of the material during operation [1].

The aim of the work was to synthesize an intermetallic compound based on cobalt, study its polarization characteristics and compare it with bare cobalt and an alloy containing iron, as well as to test a catalyst containing IMC in the reaction of electrocatalytic production of ammonia from nitrate.

METHOD

Method of synthesis of catalysts
using an arc melting system

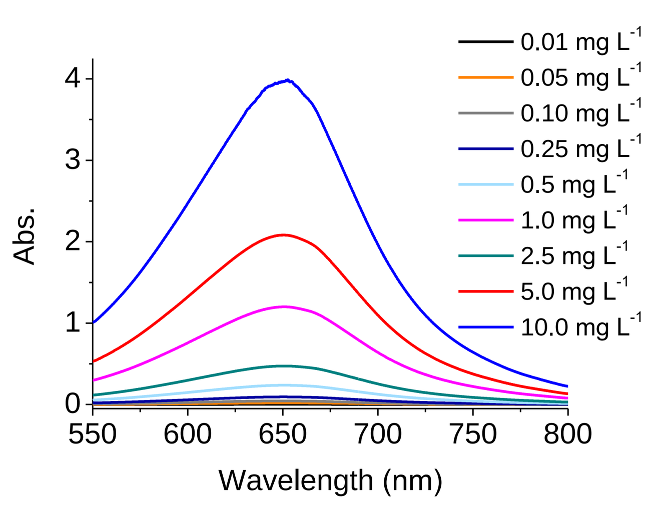
Characterization of synthesized catalysts
- Scanning Electron Microscopy (SEM)
- Measurement of polarization curves

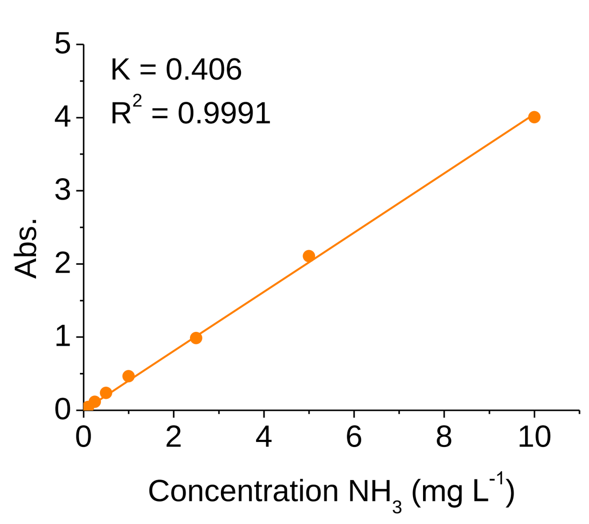
The electrolyte for polarization: Ringer's solution (NaCl - 0,147 M; KCl – 0,3 M; $CaCl_2$ – 0,33 M)

Catalysts (Co-content > 70 at.%)
- Co-Si (two-phase alloy containing IMC)
- Co-Fe (one-phase alloy that does not contain IMS)

Electrodes
- IMC and alloy – work electrode
- Pt plate – counter electrode
- Ag/AgCl – reference electrode

Sample	The content of elements in the alloy, at. % (EDX)			Composition of samples
	Co	Si	Fe	
Co-Si	67,5±0,1	32,6±0,1	-	IMC - Co_2Si
	74,5±0,2	25,5±0,2	-	The solid solution based on hcp Co
Co-Fe	69,4±0,1	-	30,6±0,1	The solid solution - Co0.70Fe0.30





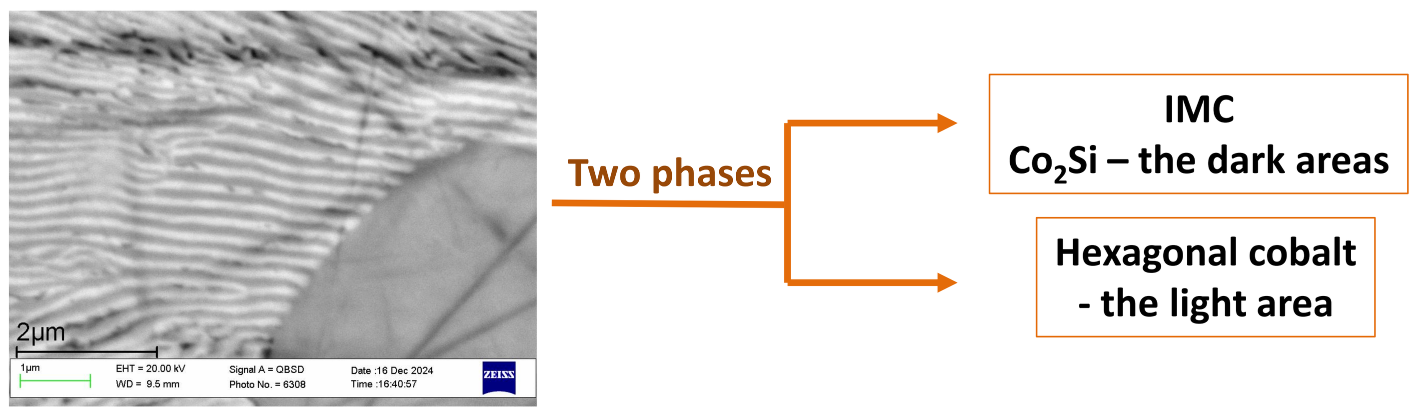
Calibration curves of UV-vis spectroscopy for determining the concentration of ammonia and the calibration equation of a straight line for calculating the concentration of ammonia [2]

Faradaic efficiency

$$FE(NH_3) = \frac{8 \times F \times n(NH_3)}{Q}$$

- n(NH_3) denotes the amount (mol) of NH_3
- F is the Faradaic constant (96,485 C mol^{-1})
- Q is the total charge passed through the electrode
- 8 is the number of electron (n) transfers required to form 1 mol of ammonia

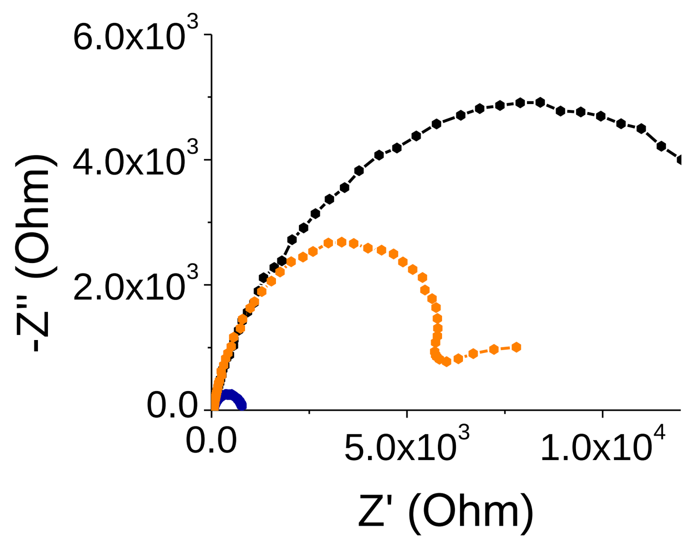
RESULTS & DISCUSSION

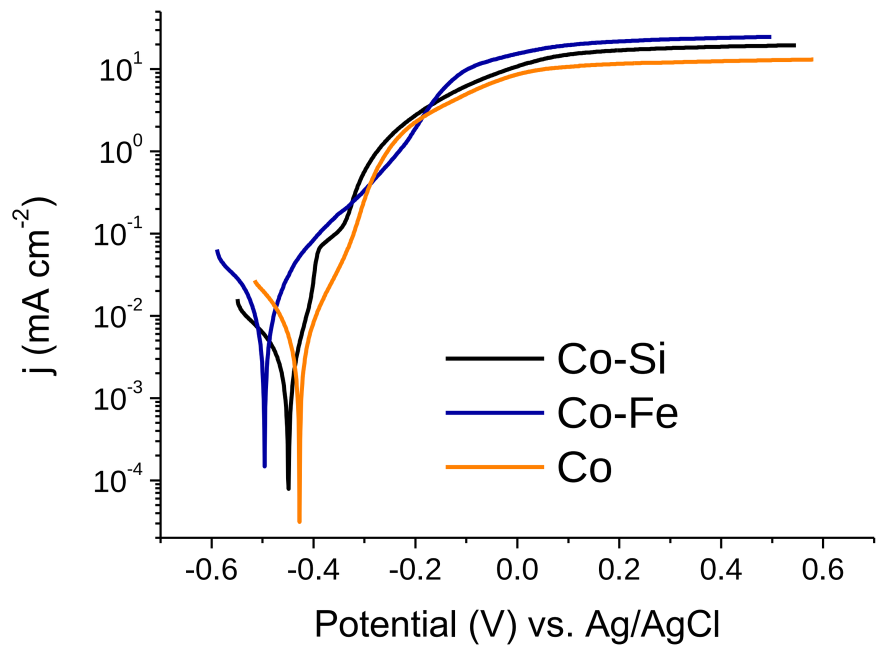


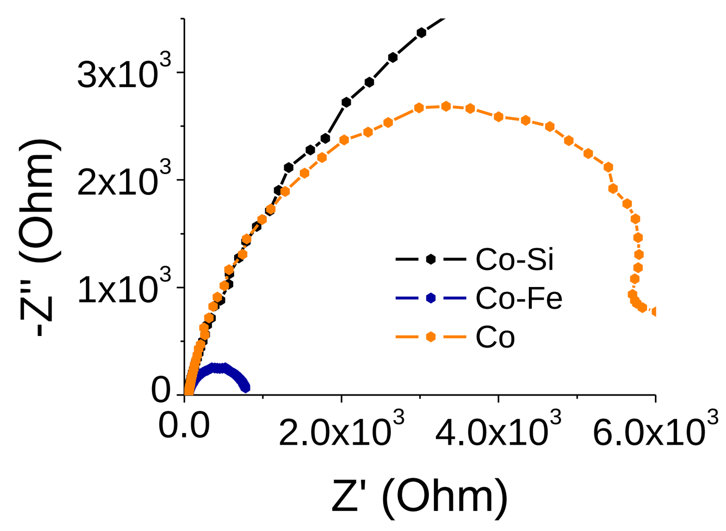
SEM image Co-Si alloy

Potentiodynamic polarization results and electrochemical impedance spectroscopy

Sample	$E_{cor\ exp}$ (mV)	Rp×10^5 (Ohm)	j_{cor} (A cm^{-2})
Co-Si	–450	0,3	9,7×10^{-7}
Co-Fe	–506	0,1	8,1×10^{-6}
Co	–429	0,1	2,0×10^{-6}



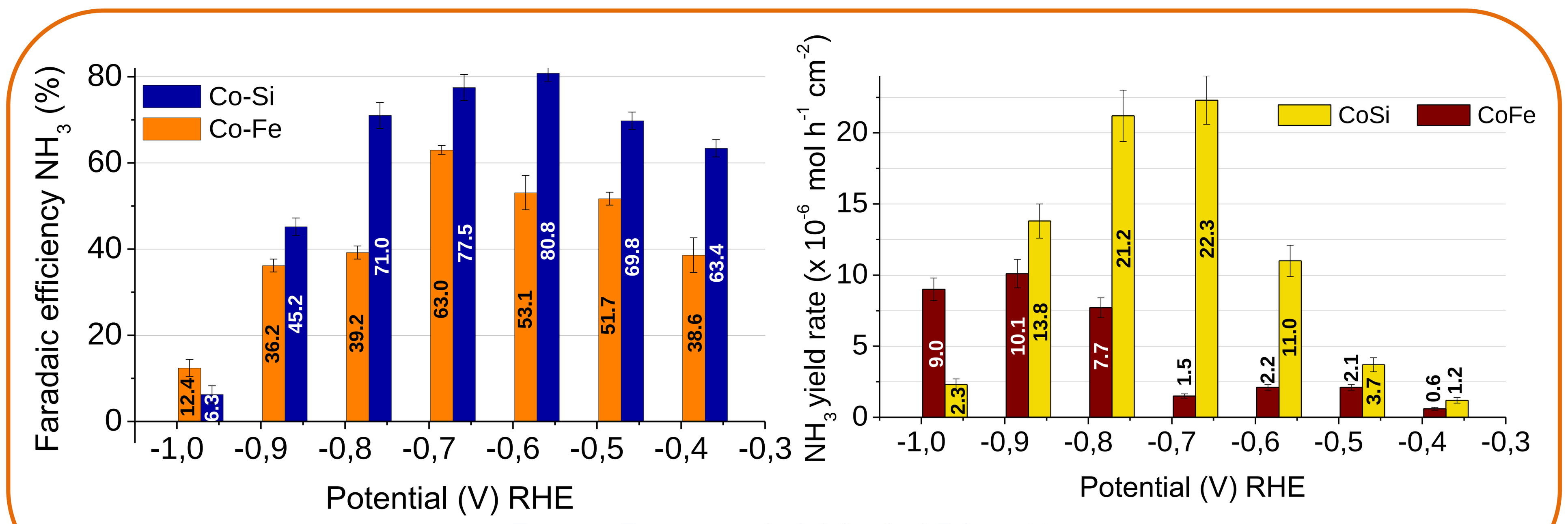




Polarization curves for IMC alloy, Co and Co-Fe alloy in Ringer solution and representative Nyquist spectra for IMC alloy, Co and Co-Fe alloy in Ringer solution measured at double layer potential (E=-0.45 V).

Polarization resistance: Co-Si > Co > Co-Fe

Faradaic efficiency results [2]



$E_{RHE} = E_{Ag/AgCl} + 0.202 + 0.059 \times pH$

CONCLUSION

The addition of silicon increases the polarization stability of a cobalt (Co-Si) catalyst compared to cobalt without additives and an alloy containing iron.
The results show the advantages of using electrocatalysts in the form of IMCs, which demonstrated increased value of Faraday efficiency and ammonia yield rates.
The chosen strategy, as well as method, make it possible to confidently predict the advantages in the NO_3RR reaction.

FUTURE WORK / REFERENCES

[1] Han Z., Zhang Y., Lv T., Tan X., Wang Q., Wang Y., Meng C. *J. Colloid Interface Sci.* **2025**; 682, 1-10.
[2] Kuznetsova I., Kultin D., Lebedeva O., Nesterenko S., Murashova E., Kustov L. *Int. J. Mol. Sci.* **2025**; 26 (13), 1650.

Acknowledgments

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