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Electrodeposited copper in an electrochemical ammonia reduction reaction

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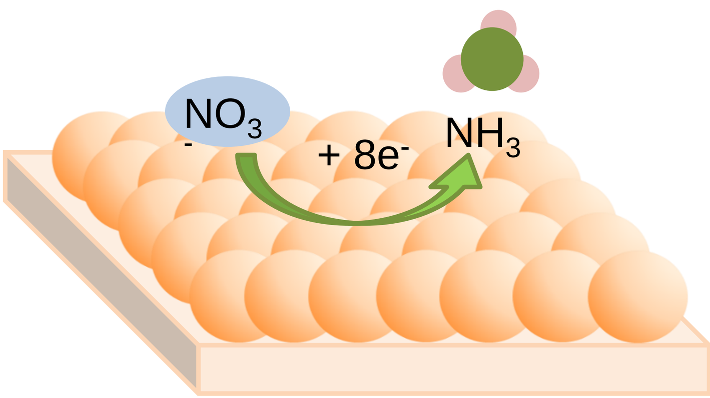
INTRODUCTION & AIM

Nitrate ions are widespread contaminants in agricultural and industrial wastewater. Nitrogen compounds accumulate in groundwater, soil and air, which at elevated concentrations cause health problems [1].

The electrochemical reduction of NO_3^- to NH_3 is used to reduce the concentration or completely remove nitrate ions. This process is quite complex and involves the transfer of eight electrons and the formation of numerous highly reactive and unstable intermediates [2].

Transition metal catalysts including bimetallic catalysts and oxide forms have high potential in the nitrate reduction reaction [3]. Copper-based catalysts show high catalytic activity for the selective reduction of nitrate to NH_3 [4].

The aim of the study was to synthesis an electrodeposited copper-based catalyst and to determine the conditions for the electrochemical reaction of ammonia production from a medium containing nitrate ions.



$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$, E°= 1.17 V vs. SHE [Ref 5]

$NO_3^- + 9H^+ + 8e^- \longrightarrow NH_3 + 3H_2O$, E°= – 0.12 V vs. SHE [Ref 5]

$NO_3^- + 6H_2O + 8e^- = NH_3 + 9OH^-$, E^0 = 0.88 B отн. RHE [Ref 6]

METHOD

Method of synthesis of catalysts
electrodeposition at direct current or potential

Characterization of synthesized catalysts
Scanning Electron Microscopy (SEM)

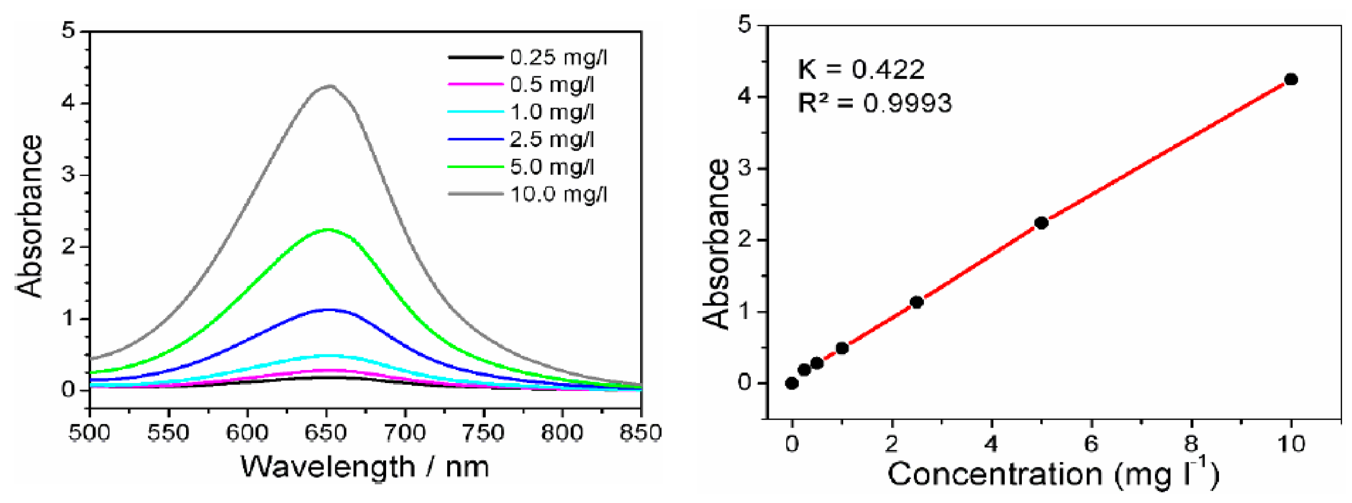
The electrolyte: 1.2 mM $NaNO_3$ in 0.05 M Na_2SO_4

Methods for determining optimal conditions (current density, potential) and conducting NO_3RR:

- Cyclic voltammetry (method of potentiodynamic curves)
- Linear voltammetry
- Electrochemical reduction at constant potential (Chronoamperometry Measurements)

Determination of ammonia

UV-vis spectroscopy



UV–vis spectra and calibration line for testing NH_3

Faradaic efficiency

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

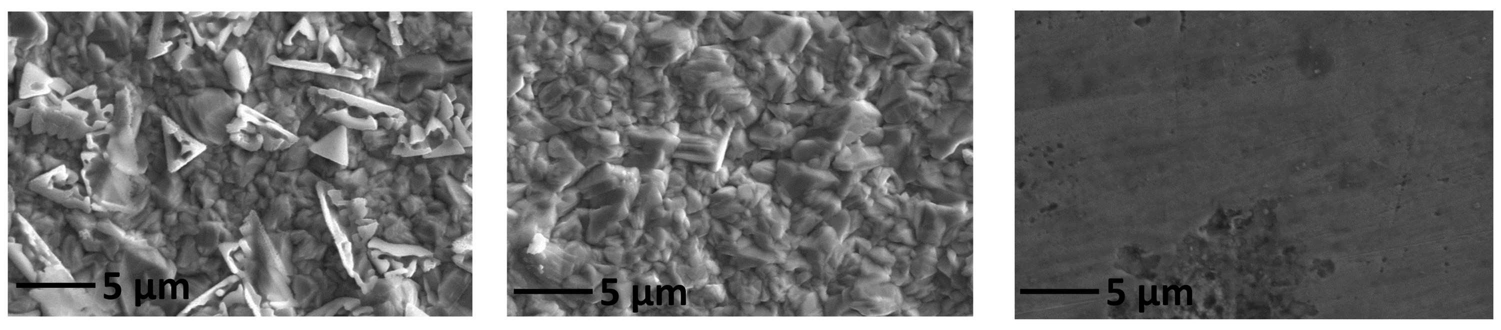
- ❑ $n(NH_3)$ denotes the amount (mol) of NH_3
- ❑ F is the Faradaic constant (96,485 C mol^{-1})
- ❑ Q is the total charge passed through the electrode
- ❑ 8 is the number of electron (n) transfers required to form 1 mol of ammonia

The ammonia yield (NH_3) rate (yield)

$$yield(NH_3) = \frac{C(NH_3) \times V}{17 \times t \times S}$$

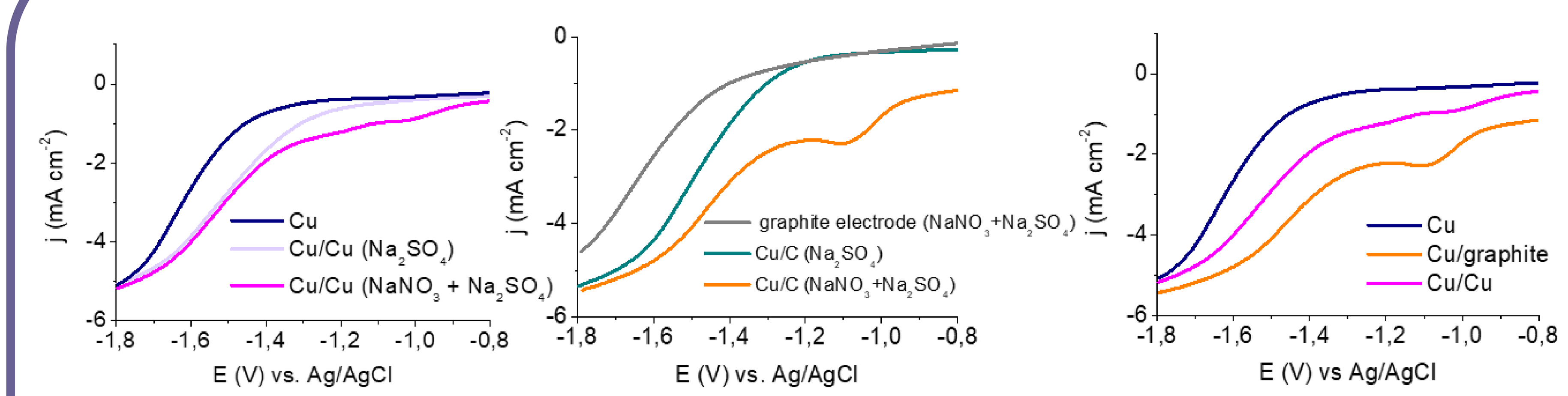
- ❑ $C(NH_3)$ denotes the mass concentration (μg mL^{-1}) of NH_3 calculated from the UV–vis spectra
- ❑ t is the electrolysis time
- ❑ S is the geometric area of the working electrode (1 cm^{-2})
- ❑ V is the volume of the electrolyte

RESULTS & DISCUSSION

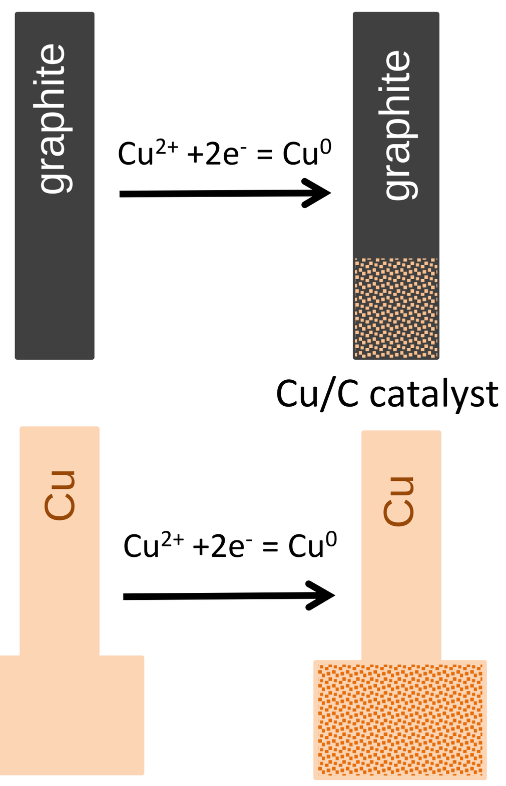


SEM image Cu/C   SEM image Cu/Cu   SEM image Cu

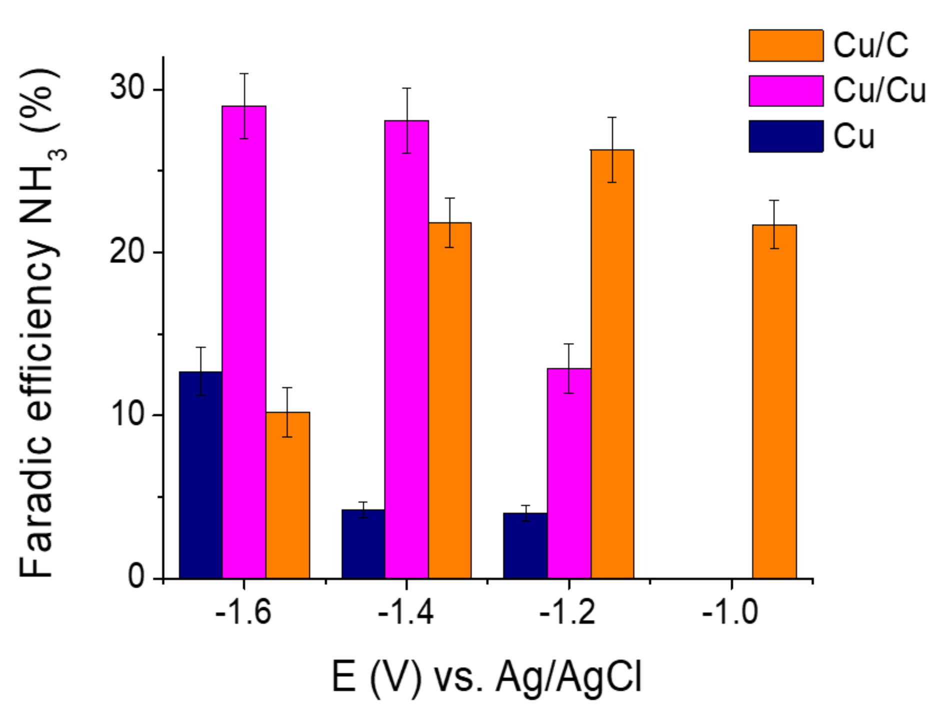
Linear Voltammetry Research



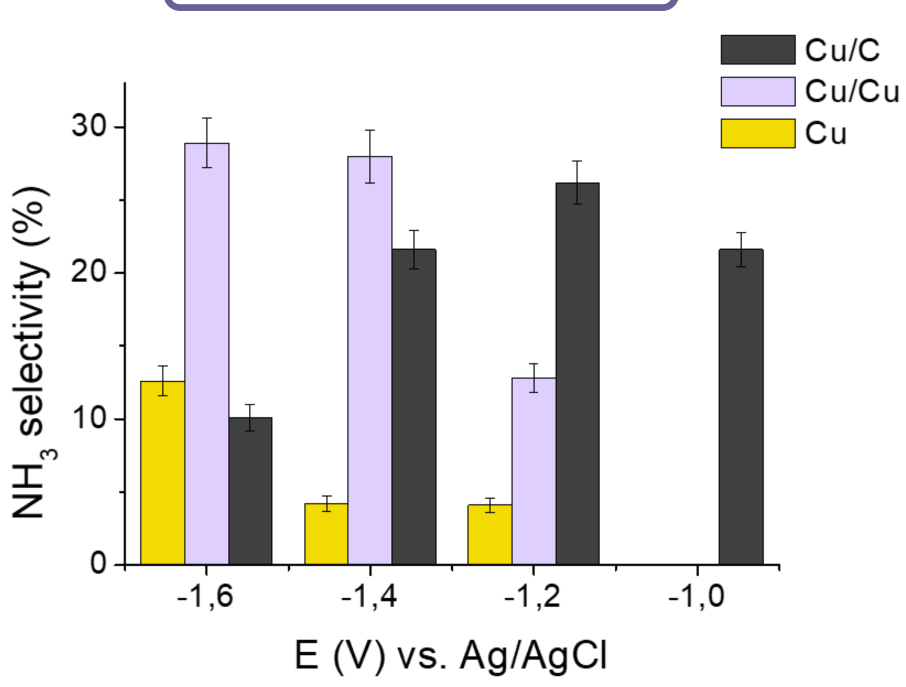
Linear voltammetric curves in Na2SO4 electrolyte containing and not containing nitrate ions at a potential scan rate of 50 mV s^{-1} for electrocatalyst samples: Cu/Cu; Cu/C;comparison of catalysts Cu/Cu and Cu/C



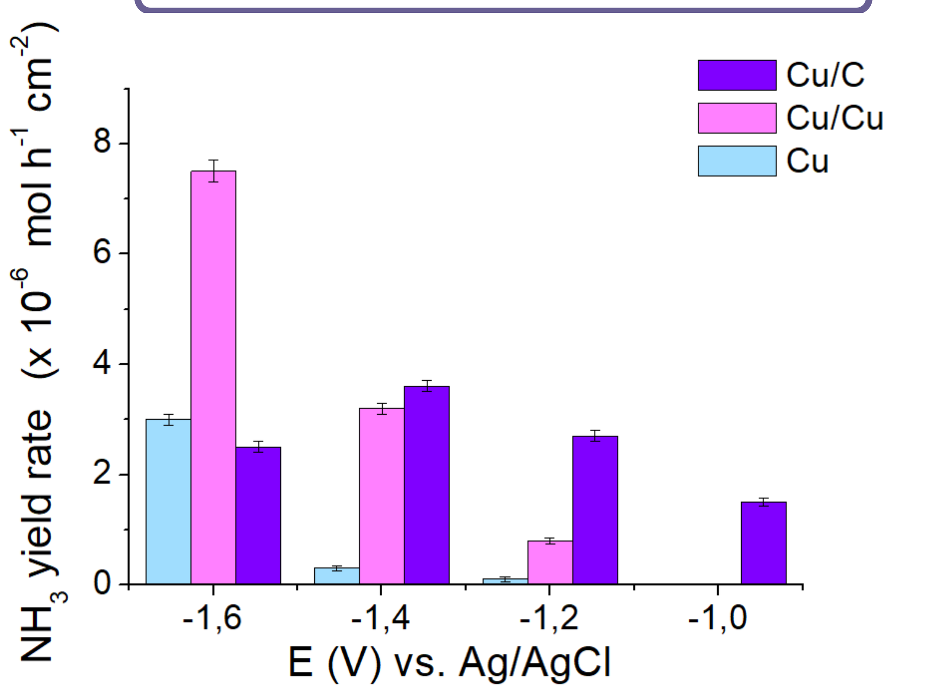
Faradaic efficiency (%) of catalysts



Selectivity (%) of catalysts



The rate of conversion (%) of catalysts



CONCLUSION

- Work continues on the development of a catalyst based on copper and its oxides to improve reaction efficiency and nitrate conversion rate.
- This work could be a starting point for investigation of the mechanism of the nitrate reduction reaction on copper-containing including bimetallic catalysts.

References:

[1] Hao D., Chen Z. G., Figiela M., Stepniak I., Wei W., Ni B. J. *J. Mater. Sci. Technol.* **2021**; 77, 163.
[2] Wei J., Li Y., Lin H., Lu X., Zhou C., Li Y. Y. *Environ. Sci. Ecotechnology.* **2023**; 100383.
[3] Kuznetsova I.; Lebedeva O.; Kultin D.; Mashkin M.; Kalmykov K.; Kustov L. *Int. J. Mol. Sci.* **2024**; 25, 7089.
[4] Yu Z., Gu M., Wang Y., Li H., Chen Y., Wei L. *Adv. Energy Sustainability Res.* **2024**; 5; 5, 2300284.
[5] Lu X., Song H., Cai J., Lu S. *Electrochem. commun.* **2021**; 129, 107094.
[6] Zhang K., Zhang K.,. Liu Y ., Pan Z., Xia Q., Huo X ., Esan O., Zhang X., An L. *EES Catalysis.* **2024**.

Acknowledgments

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