Surface micro-environment control by immobilizing ionic liquid-based molecules for tuning electrocatalytic reactions

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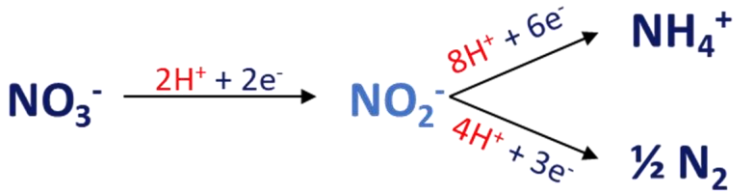
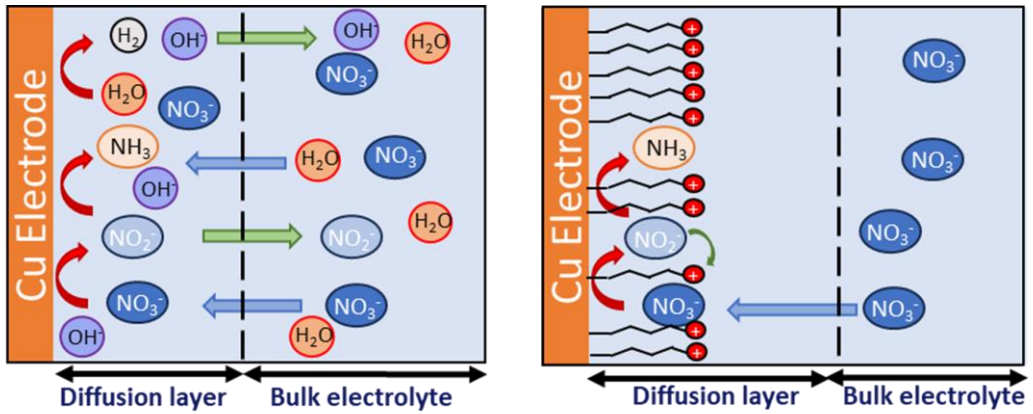
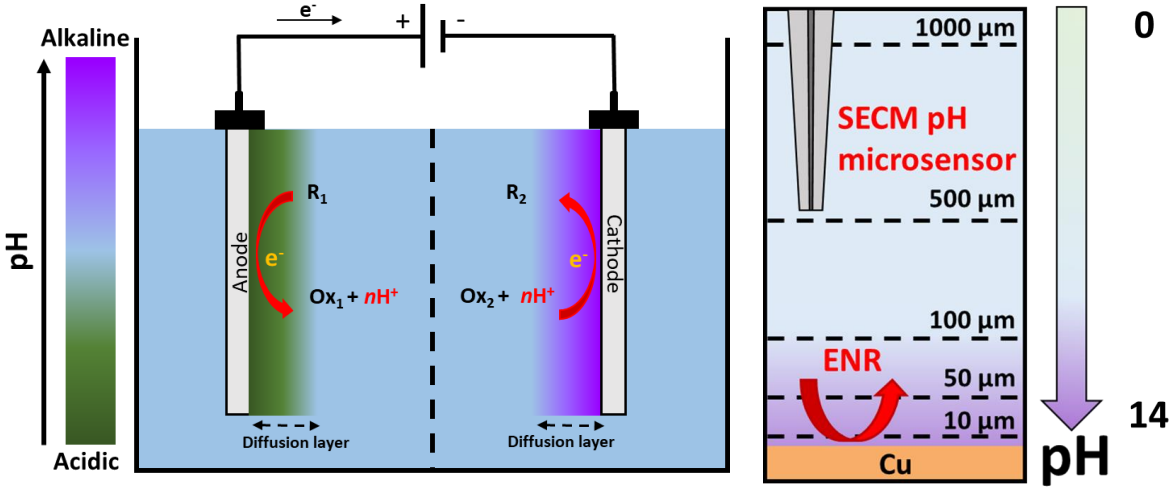
Electrocatalytic nitrate reduction (ENR)



- Electrode micro-environment is determinant for **efficiency** and **selectivity** in **electrocatalytic nitrate reduction (ENR)**.
- Controlling the micro-environment by immobilizing imidazolium based ionic liquids at the electrode surface



Local pH monitoring by SECM during ENR



Schematic representation of the electrolytic cell

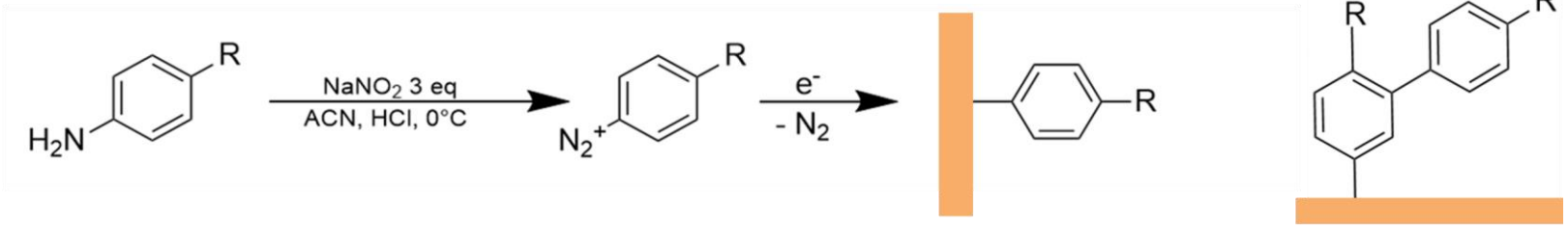
- Local pH generated near the electrode surface due to proton production/generation during the reaction

Local pH is correlated to selectivity of NO_3^- conversion to NH_3

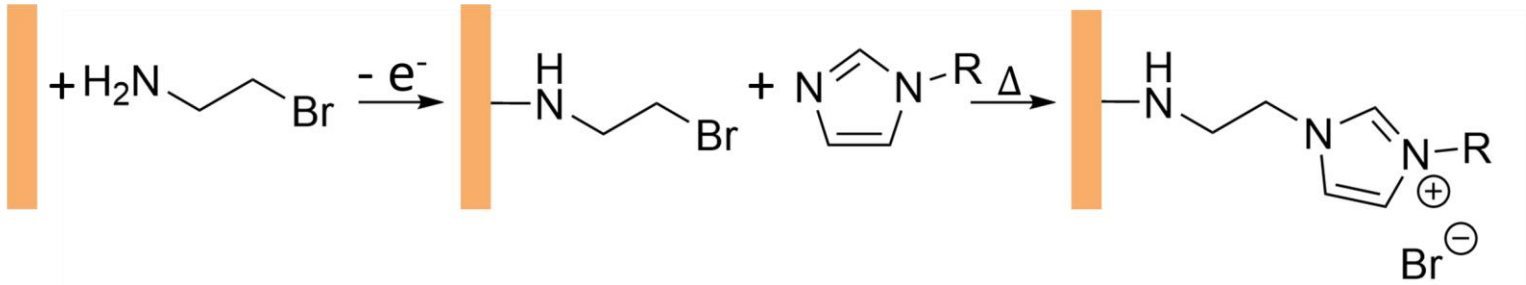
Surface modification

2 different strategies used:

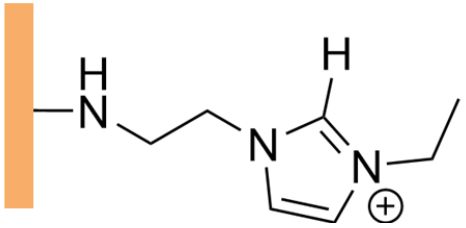
- **A:** Electro**reduction** of *in-situ* generated diazonium salt



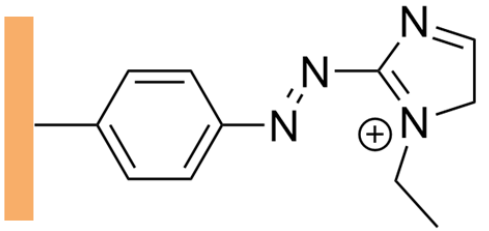
- **B:** Electro**oxidation**/chemical substitution of amine derivate



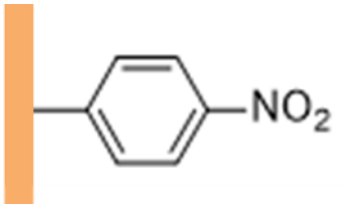
Hybrid cathodes obtained



Cu-IM$^+$

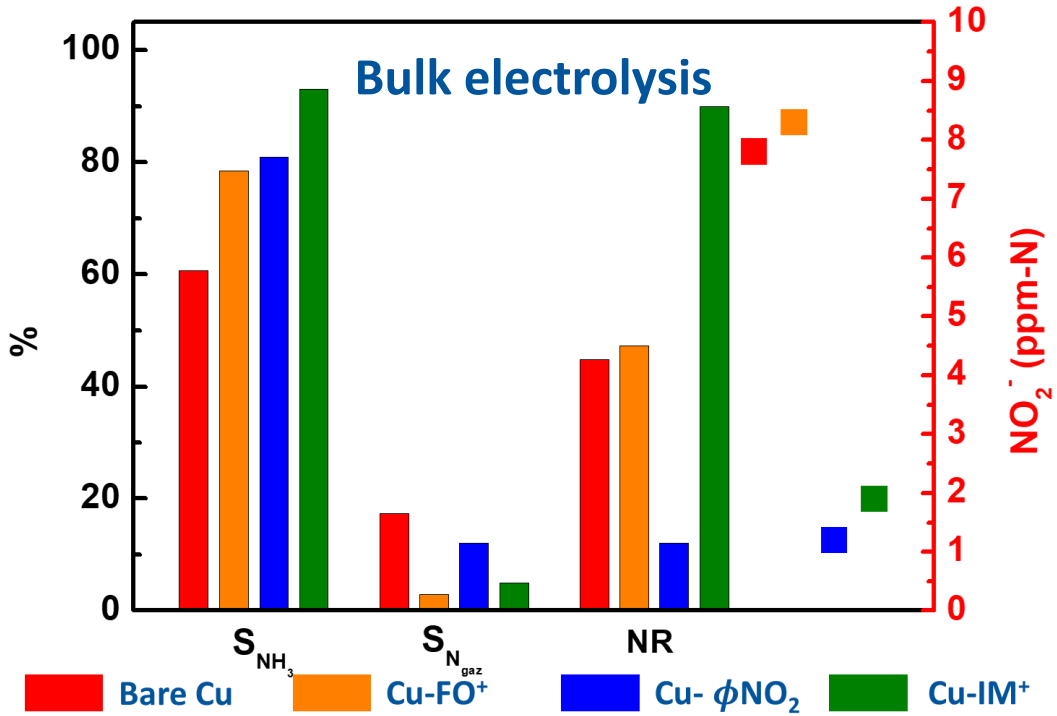


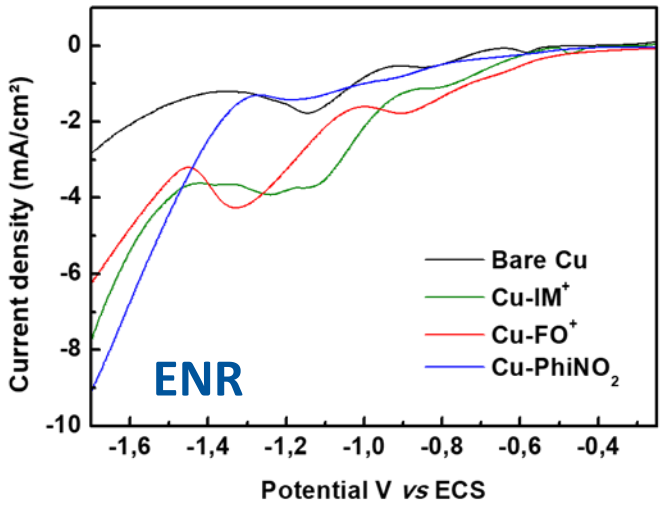
Cu-FO$^+$

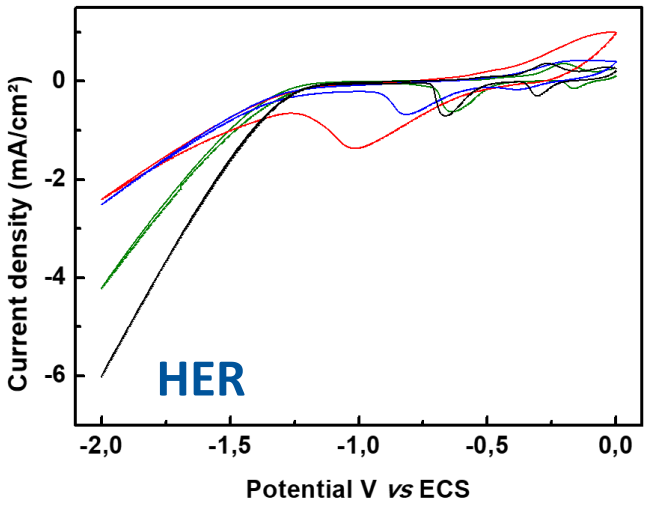


Cu- ϕNO_2

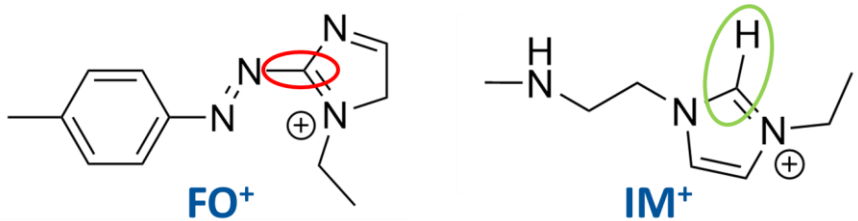
Correlating electrocatalytical properties with the different cathodes







Electrochemical characterization



Differences in chemical structure

Surface micro-environment control by immobilizing ionic liquid-based molecules for tuning electrocatalytic reactions

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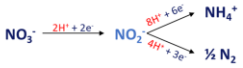
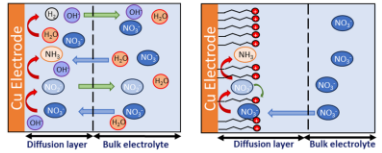
Context

- Electrode micro-environment (e.g. local pH, electrolyte nature, hydrophobicity or, local electric field) is determinant for **efficiency** and **selectivity**[1] in many electrocatalytic reactions such as **electrocatalytic nitrate reduction (ENR)**[2].
- Imidazolium-based ionic liquids are known to enhance catalytic activity in different reduction reactions and inhibit competitive hydrogen evolution reaction (HER)[3]



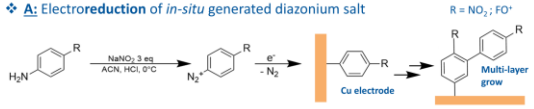


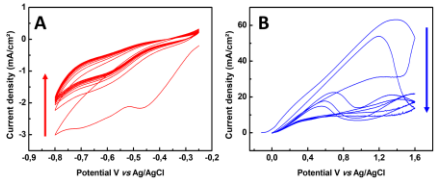
Micro-environment at Cu electrode during ENR

Surface modification

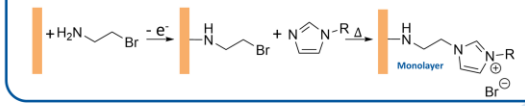
2 different strategies used:

❖ **A:** Electro**reduction** of *in-situ* generated diazonium salt





❖ **B:** Electro**oxidation**/chemical substitution of amine derivate

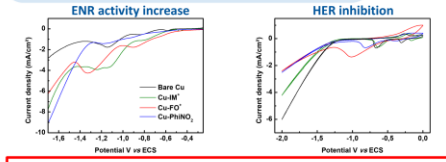


Electro-grafting of imidazolium-based molecules can be achieved by electro-oxidation or reduction leading to covalent attachment of a positively charged layer

Surface hydrophobicity

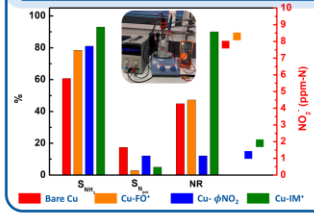
Immobilization of Imidazolium on Cu electrode increase the hydrophilicity of the electrode

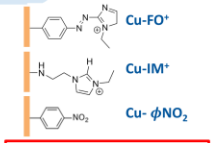
Electrochemical characterization



Electrografting of imidazolium on Cu electrode leads to an increase of ENR activity and HER inhibition

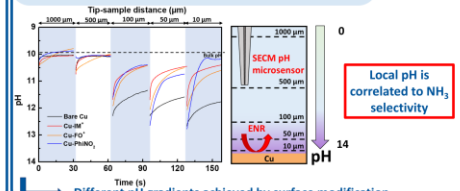
Galvanostatic bulk electrolysis





Higher selectivity toward NH_3 is reached with imidazolium charged layer

Local pH investigation by SECM

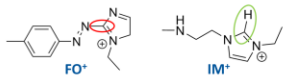


Local pH is correlated to NH_3 selectivity

Different pH gradients achieved by surface modification

Conclusion

- Immobilization of imidazolium-based molecule at the Cu electrode surface leads to a clear increase of efficiency and selectivity in NO_3^- conversion to NH_3 while inhibiting competitive HER.
- Less alkaline local pH is achieved with Cu-IM$^+$ and Cu-FO$^+$ cathodes, which might be a new descriptor for enhancing NH_3 production selectivity.
- Acidic proton on imidazolium ring might act as a proton reservoir to boost NH_3 production.



(1) *Decker et al., Current Opinion in Electrochemistry* **2025**, *53*, 101728. (2) *Guo et al., ACS Sustainable Chem. Eng.* **2023**, *11* (20), 7882–7893. (3) *Vichou et al., J. Am. Chem. Soc.* **2024**, *146* (4), 2824–2834.