

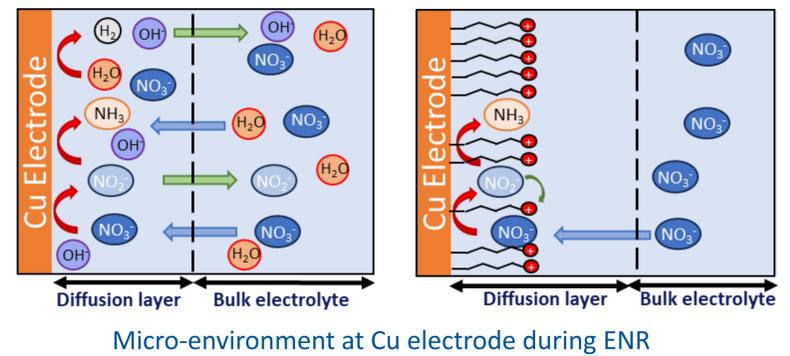
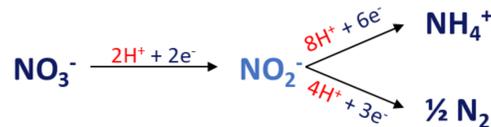
Surface micro-environment control by immobilizing ionic liquid-based molecules for tuning electrocatalytic reactions

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Context

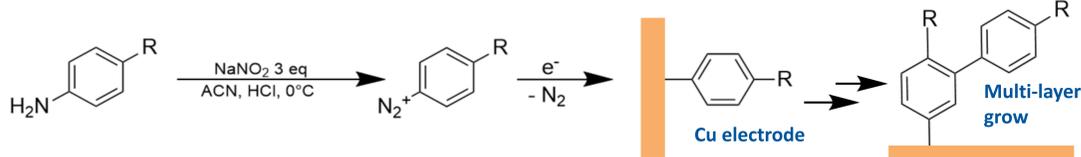
- Electrode micro-environment (e.g. local pH, electrolyte nature, hydrophobicity or, local electric field) is determinant for **efficiency** and **selectivity**⁽¹⁾ in many electrocatalytic reactions such as **electrocatalytic nitrate reduction (ENR)**⁽²⁾.
- Imidazolium-based ionic liquids are known to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



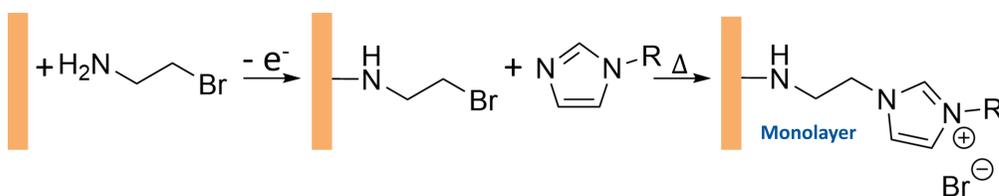
Surface modification

2 different strategies used:

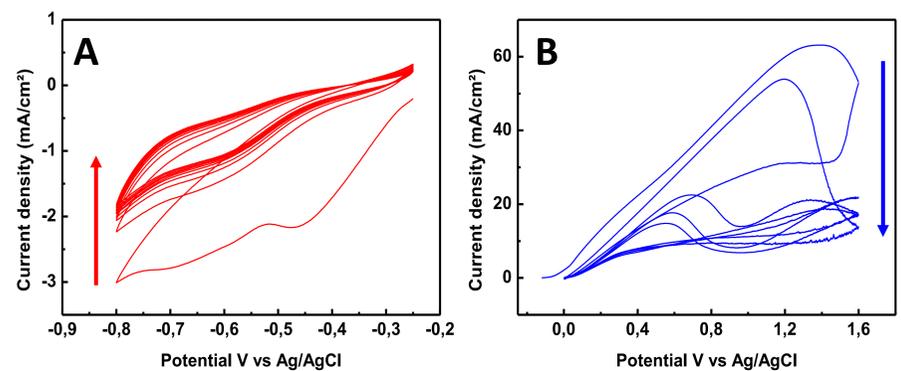
❖ **A:** Electroreduction of *in-situ* generated diazonium salt



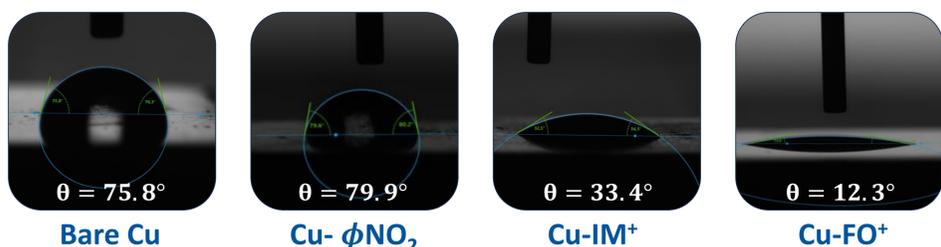
❖ **B:** Electrooxidation/chemical substitution of amine derivate



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

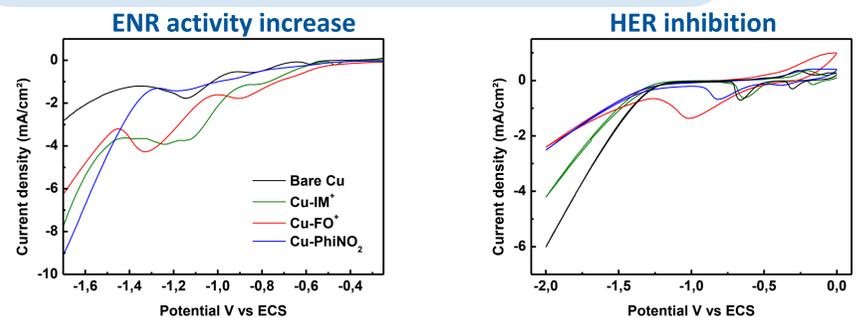


Surface hydrophobicity



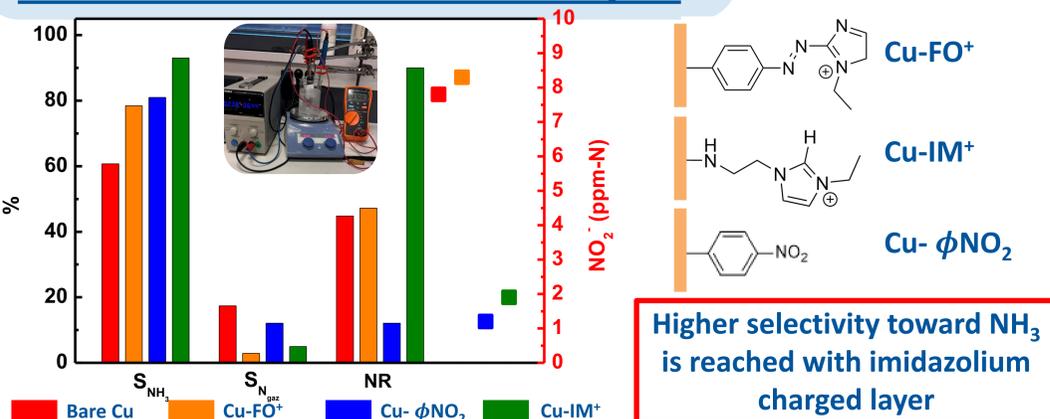
Immobilization of Imidazolium on Cu electrode increase the hydrophilicity of the electrode

Electrochemical characterization

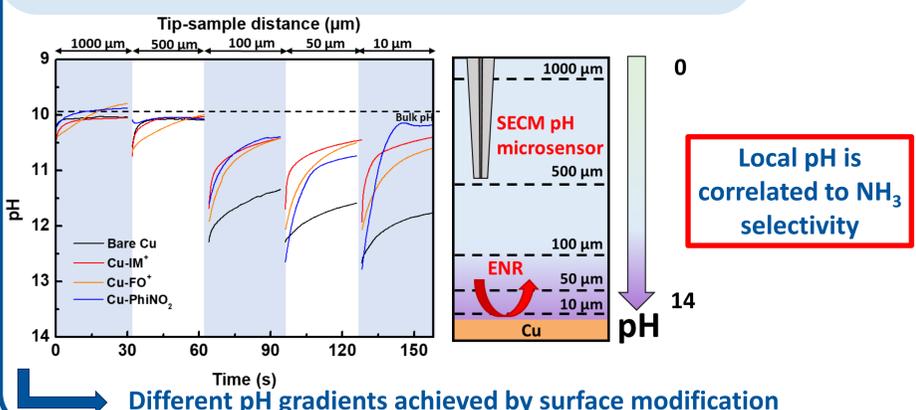


Electrografting of imidazolium on Cu electrode leads to an increase of ENR activity and HER inhibition

Galvanostatic bulk electrolysis



Local pH investigation by SECM



Conclusion

- Immobilization of imidazolium-based molecule at the Cu electrode surface leads to a clear increase of efficiency and selectivity in NO₃⁻ conversion to NH₃ 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 NH₃ production selectivity.
- Acidic proton on imidazolium ring might act as a proton reservoir to boost NH₃ production.

