

Understanding the role of imidazolium-based ionic liquids in the electrochemical CO₂ reduction reaction: an experimental and theoretical study

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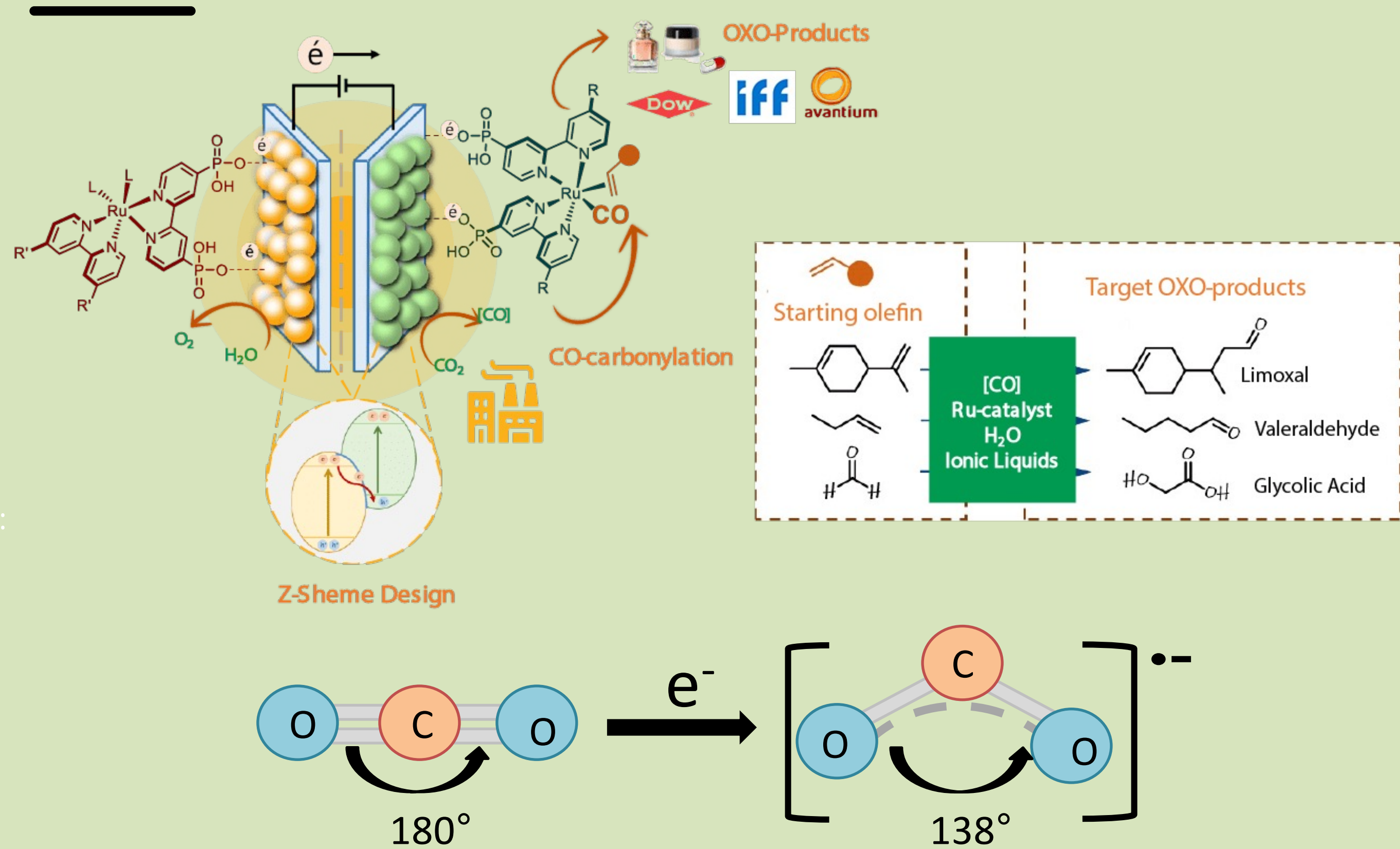
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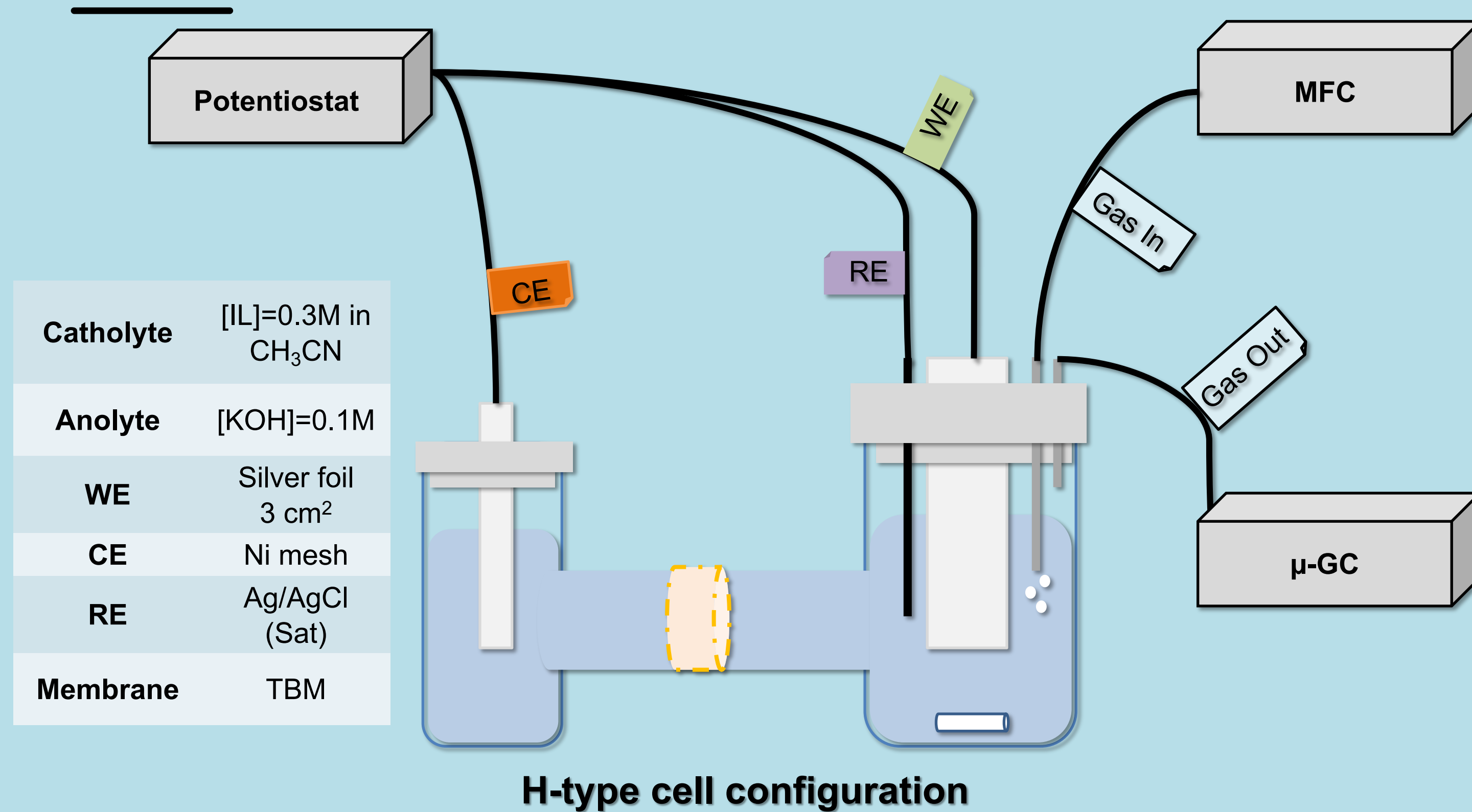


Introduction and aim of the work



The main objective of this work is to evaluate the performance of Ionic Liquids (IL) for CO₂ conversion and to understand the effects of different anion in the selectivity.

Materials and methods

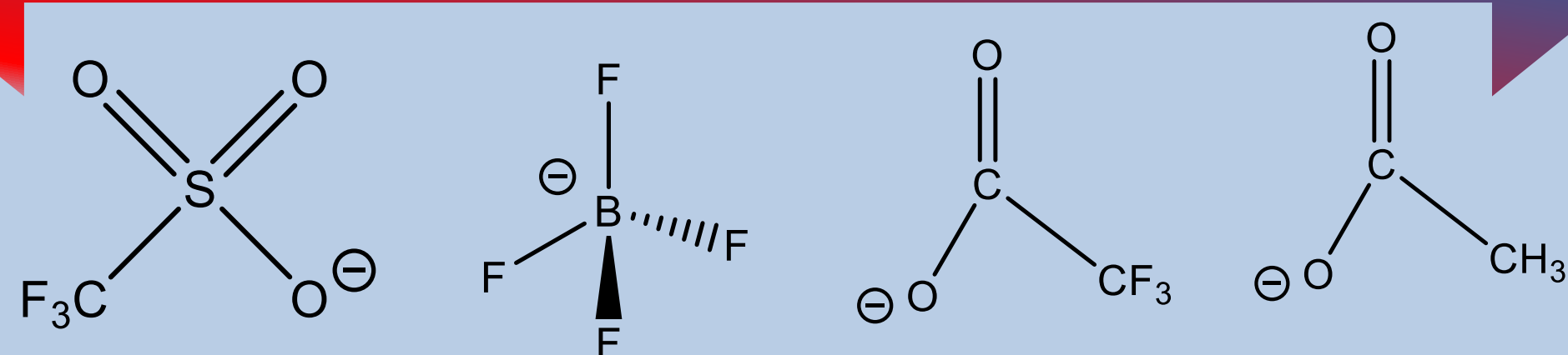
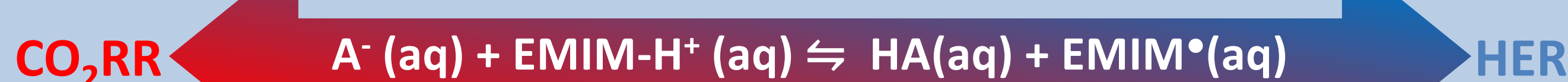
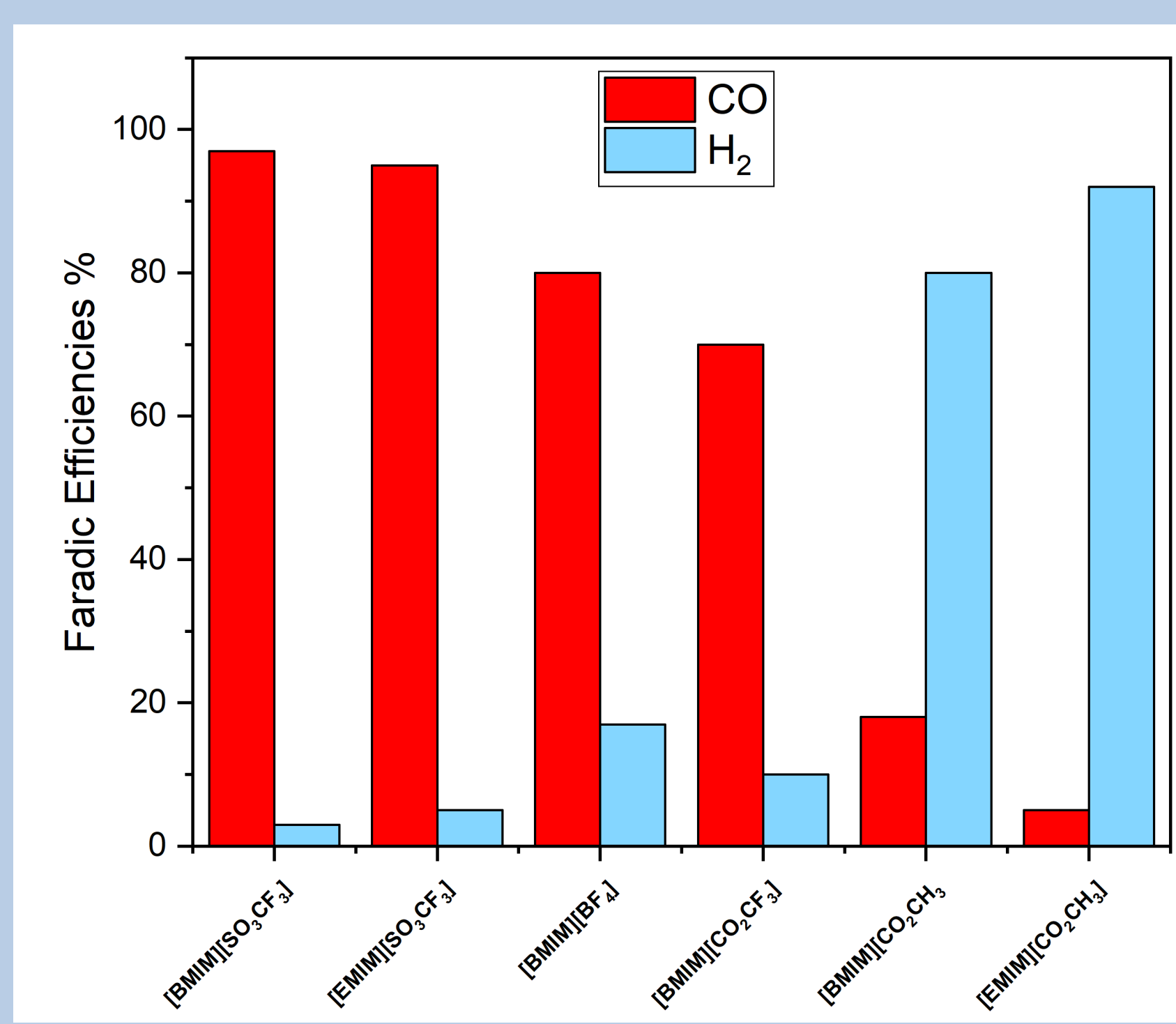


The electrochemical tests involved were cyclic voltammetry (CV), linear sweep voltammetry (LSV) and a chronopotentiometry (CP) in inert gas and pure CO₂.

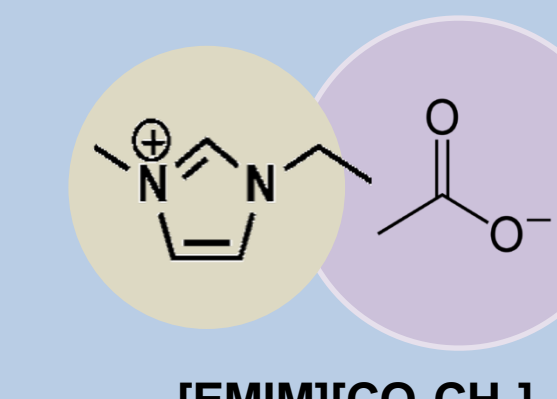
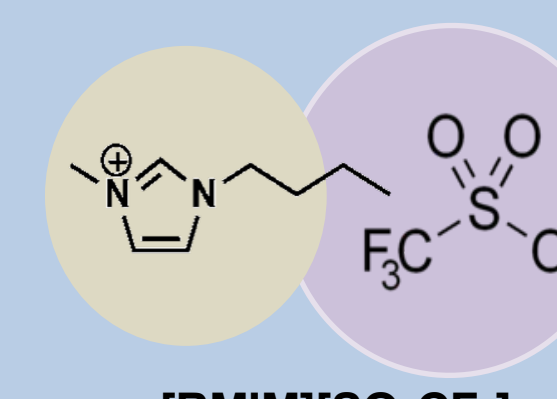
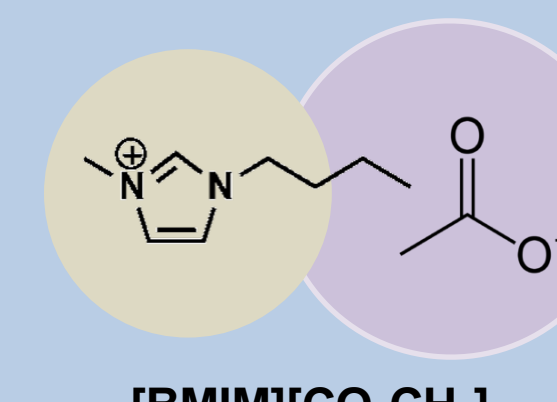
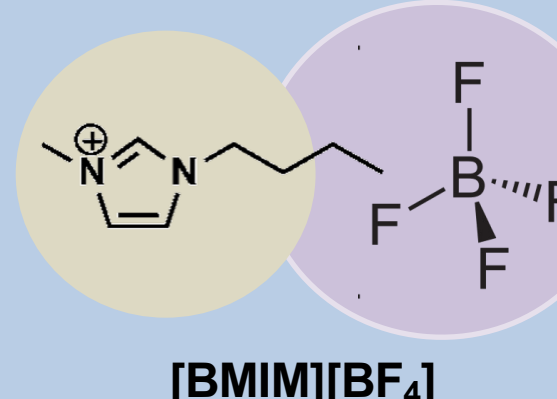
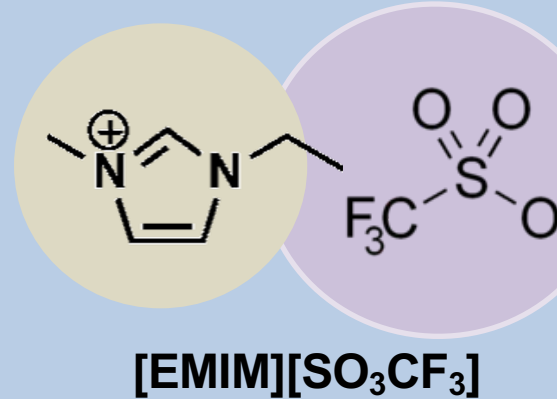
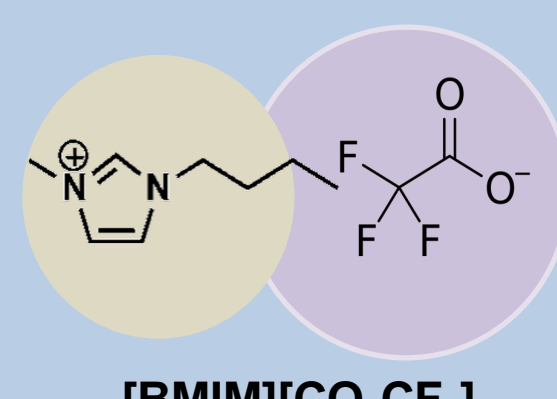
Calculations are based on ab-initio DFT employing a plane wave (cutoff 30Ry) and ultra-soft pseudopotentials. GGA-PBE was used for exchange and correlation functional. Brillouin Zone sampled in gamma.

Results and discussion

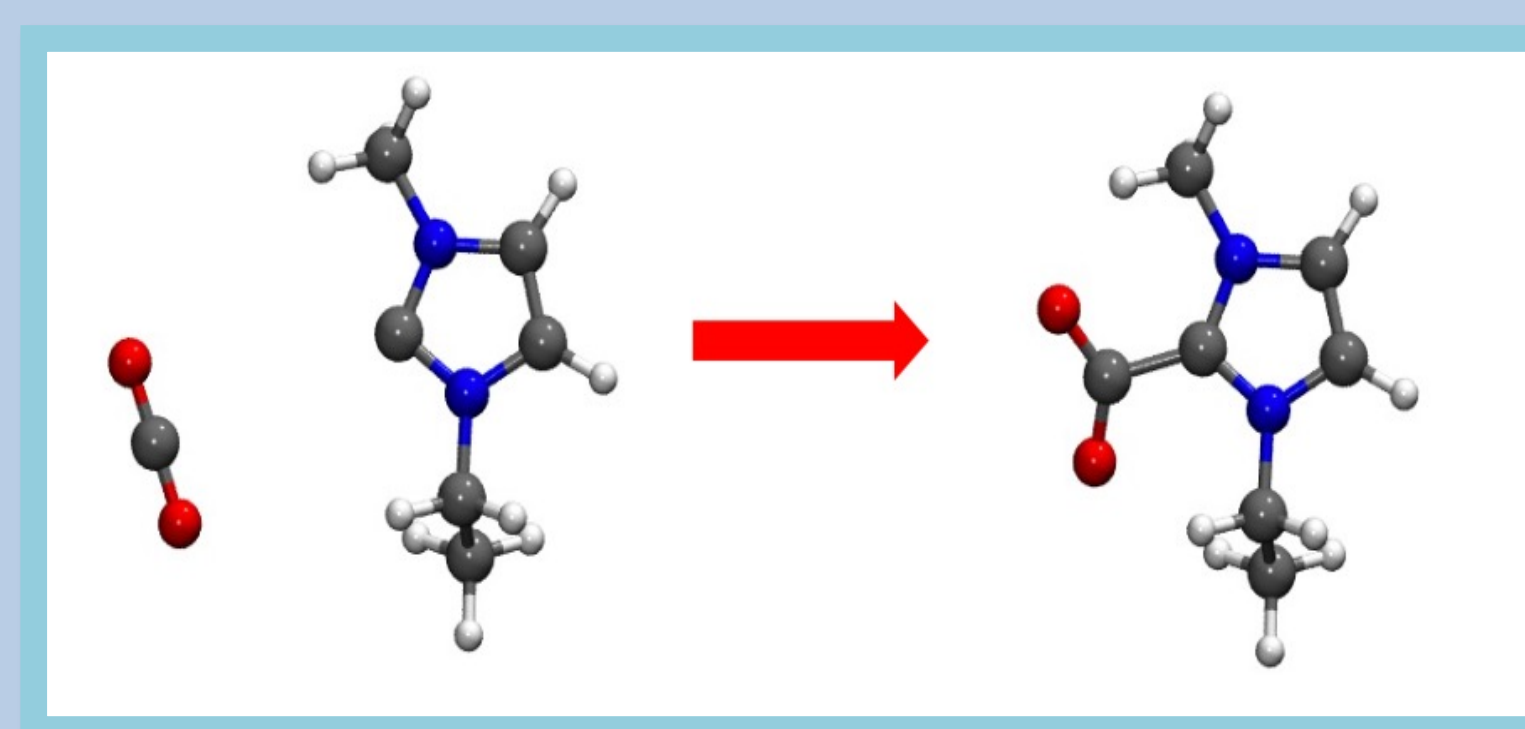
FE% of gaseous products collected during CP in CO₂, t= 2h, I= -20mA



- Ionic liquids with fluorinated anion are more selective toward the production of CO.
- The role of anions is to tune the ratio between protonated and deprotonated [EMIM-H⁺]:[EMIM⁺] or [BMIM-H⁺]:[BMIM⁺].

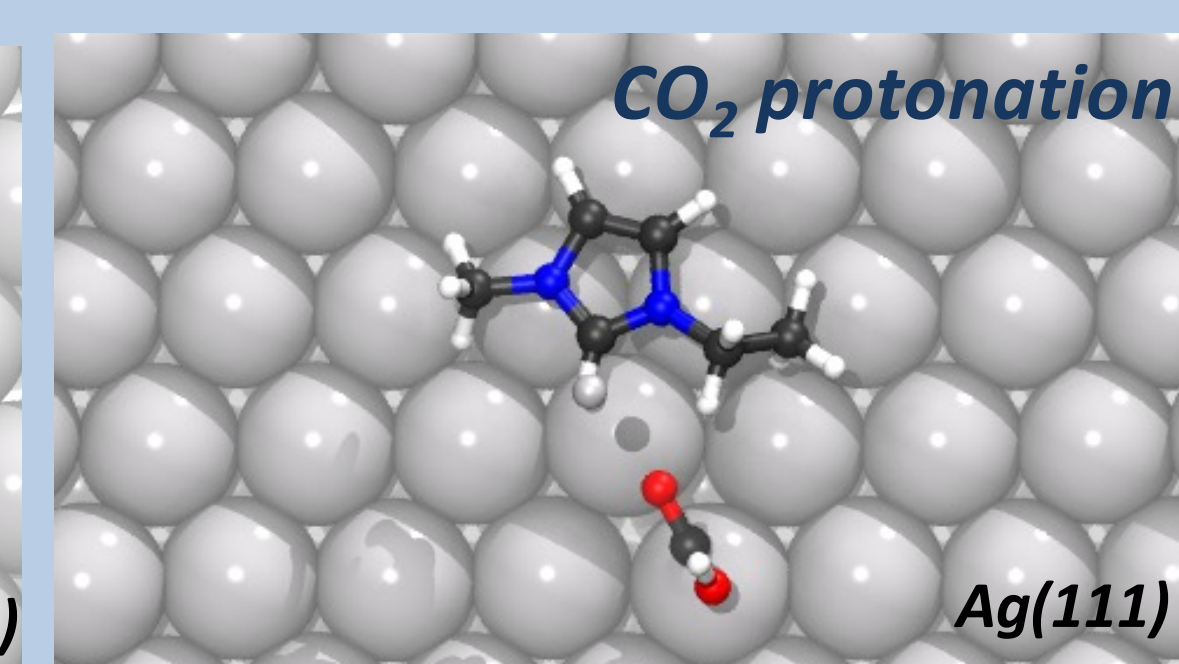
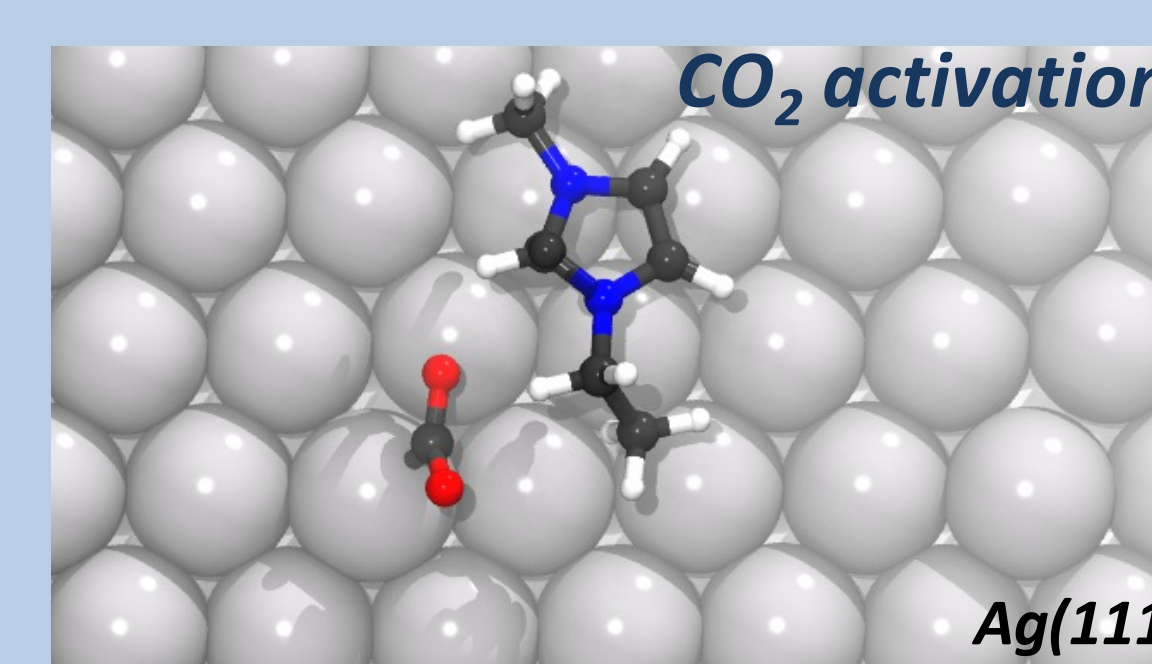
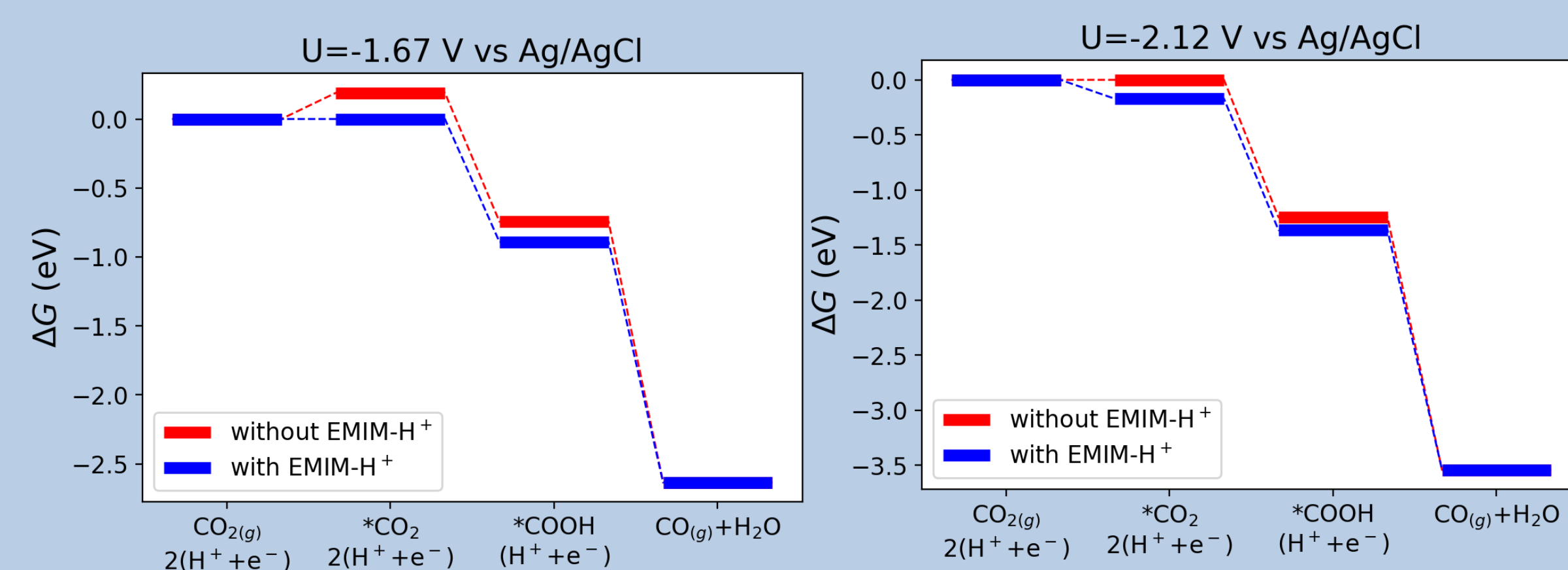


- Deprotonated IL cation can spontaneously bind CO₂ and the electrode surface, causing poisoning of active sites.



Cation	BE (eV)
BE _{CO₂} [EMIM ⁺]	-0.60
BE _{CO₂} [BMIM ⁺]	-0.67
BE _{Ag(111)} [EMIM ⁺]	-1.86

- CO₂RR intermediates are stabilized by the protonated form of the IL cation.



Conclusions

- ❖ Six imidazolium salts were tested for the electrocatalytic CO₂ conversion to CO. Acetonitrile was chosen as solvent to decrease the viscosity of pure IIs and increase the conductivity of the solution.
- ❖ Their electrocatalytic behavior in lowering the onset potential needed to overcome the first step of the CO₂RR was investigated.
- ❖ The type of anion regulates the ratio between of protonated or deprotonated cation
- ❖ It was theoretically demonstrated that the active species to work as co-catalyst in CO₂RR is the protonated cation.
- ❖ The cation deprotonated species spontaneously can bind both CO₂ and the electrode surface Ag(111), causing a decrease in terms of free active sites for CO₂.

Acknowledgements



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References

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