Politecnico di Torino

CREST Catalytic Reaction Engineering for Sustainable Technologies

io·li·tec Ionic Liquids Technologies

Horizon2020 European Union Funding for Research & Innovation

SunCO2Chem

Electrochemical CO_2 conversion in Ionic Liquid-based electrolytes

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Società Chimica Italiana

SCI2021

Talk ID: **ELEOR21**

Session: **ELE03**

1. Introduction and aim of the work

2. State of the Art

3. Materials and Methods

4. Results and Discussion

5. Conclusions and Next Steps

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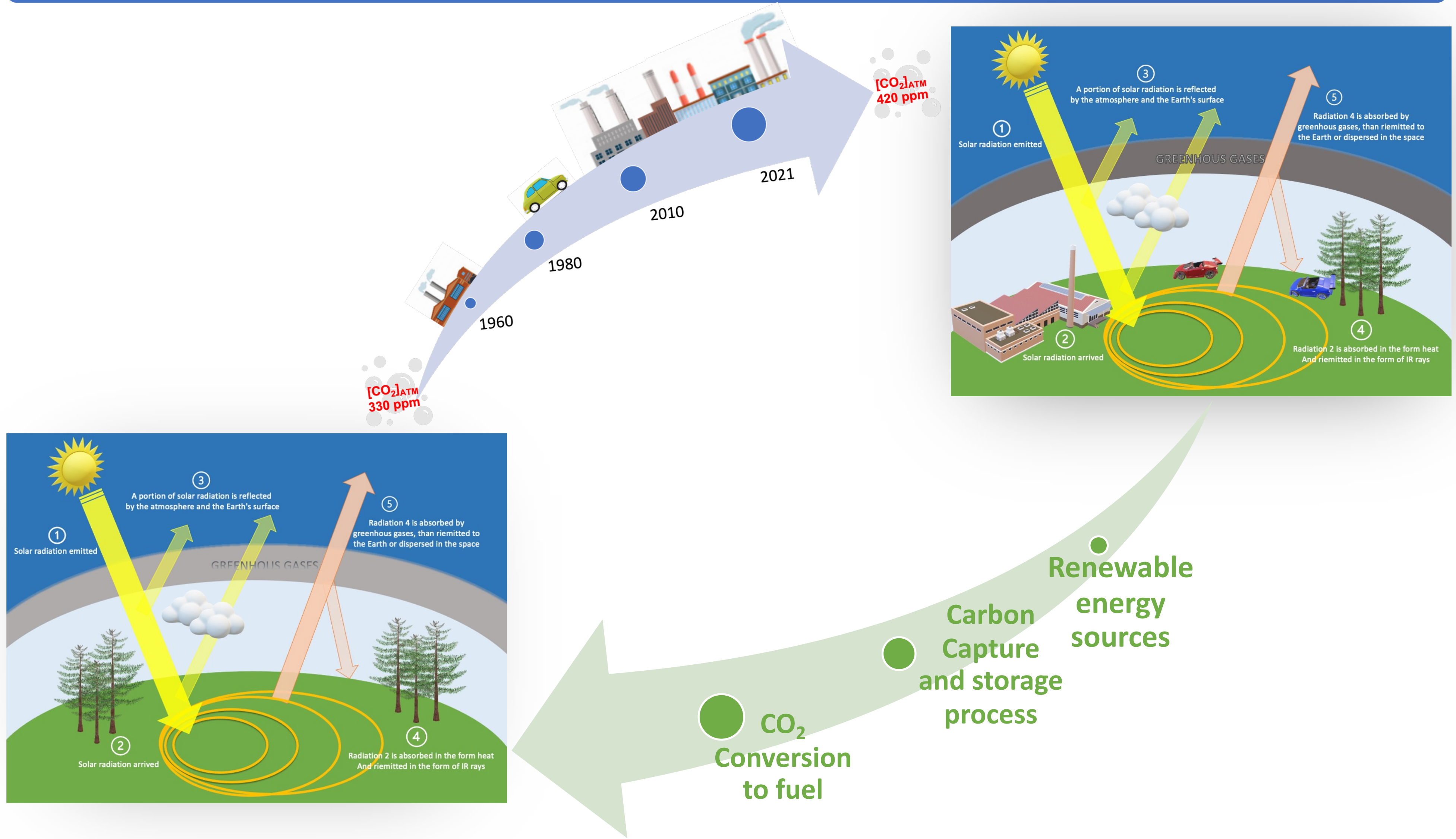
Introduction and aim of the work

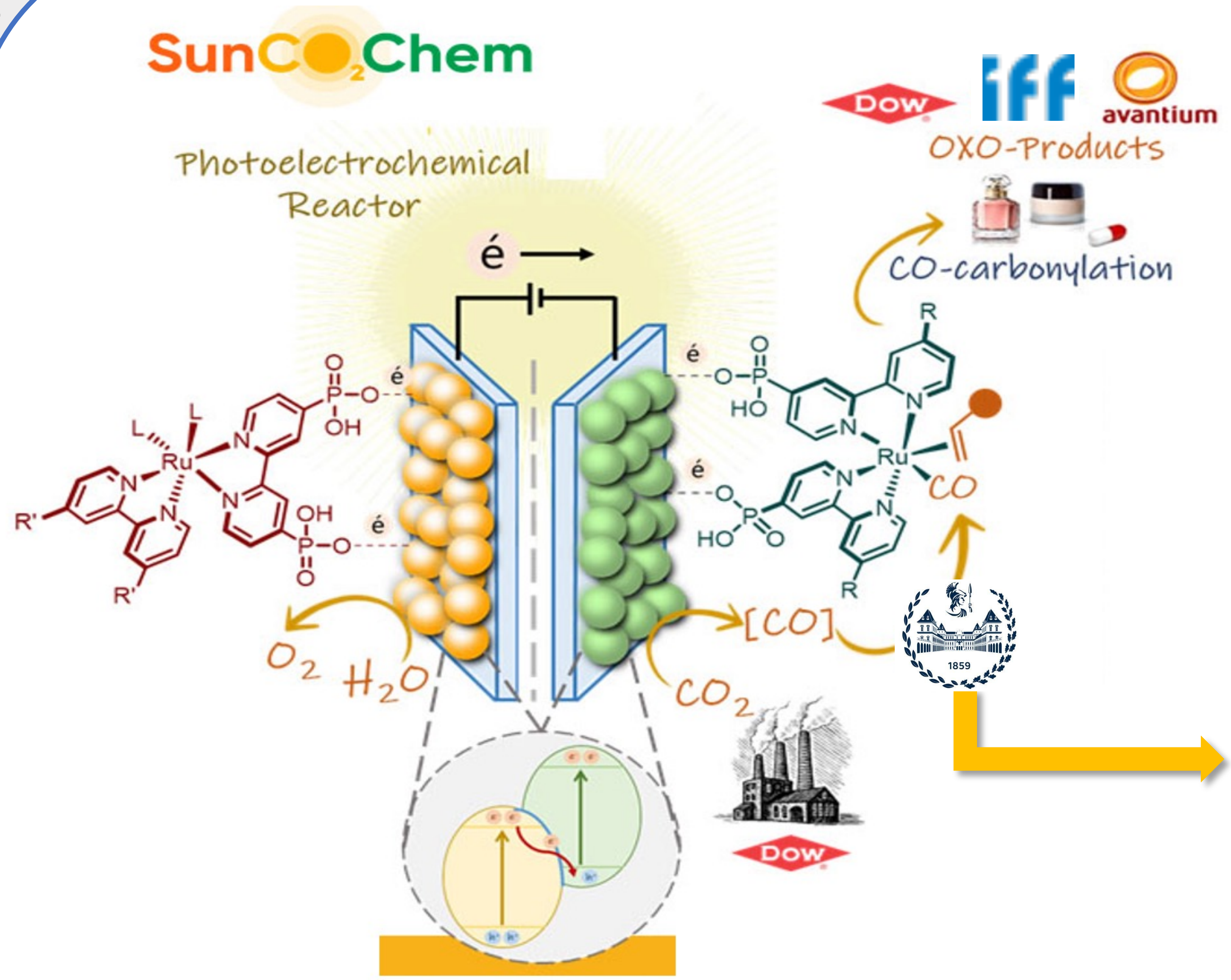


Anthropogenic greenhouse effect

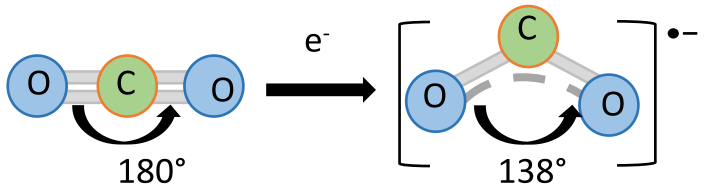
Alternatives to address this problem

Anderson, T. R., Hawkins, E., & Jones, P. D. (2016). CO2, the greenhouse effect and global warming: from the pioneering work of Arrhenius and Callendar to today's Earth System Models. Endeavour, 40(3), 178–187.

Introduction and aim of the work



At high current densities, the RDS involved in the CO_2 reduction to CO is the formation of the reactive $CO_2^{\bullet-}$ anion radical.



E^0 = -1,9V *vs* NHE[1] (~ -2,1 *vs* Ag/AgCl)

The main objective of this work is to study the influence of different **Ionic Liquids (ILs)** in the performance and selectivity of the electrocatalytic CO_2 reduction to CO.

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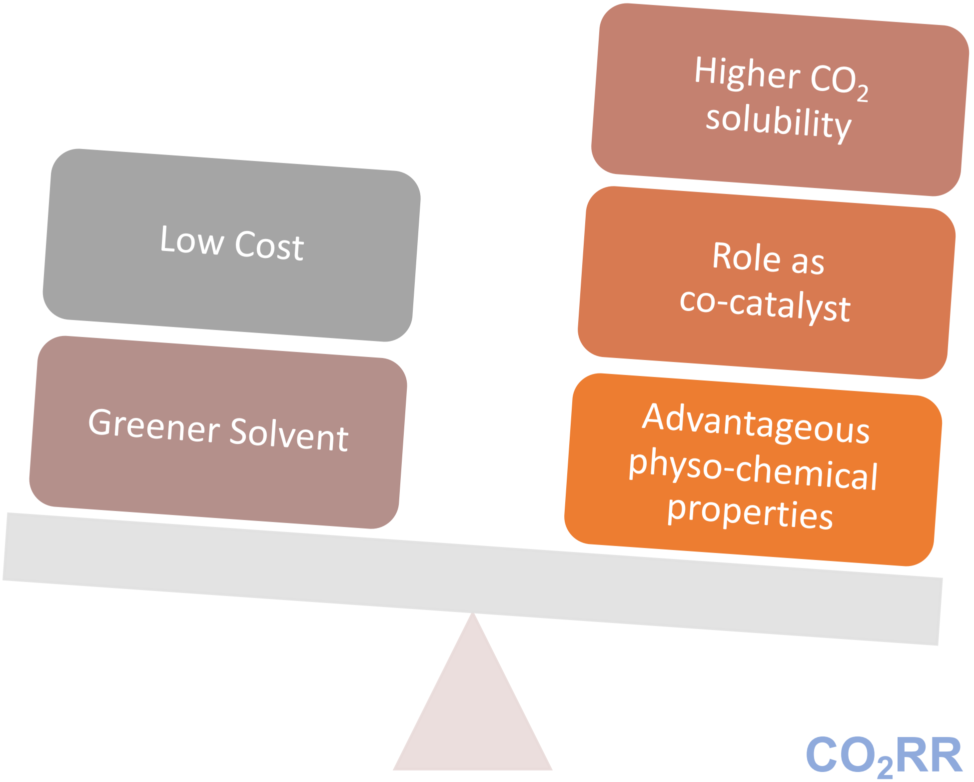
Aqueous Media

Ioni Liquid Media



Other ILs advantages

- ✓ Good conductivity
- ✓ Thermal stability
- ✓ Wide electrochemical stability window
- ✓ Good solvation ability
- ✓ Low melting temperature
- ✓ Large variety of physical and chemical properties thanks to several combination of anion and cation

CO_2RR in liquid phase

Advantages of using Ionic Liquid

Lau, G. P. S., Schreier, M., Vasilyev, D., Scopelliti, R., Grätzel, M., & Dyson, P. J. (2016). New Insights into the Role of Imidazolium-Based Promoters for the Electroreduction of CO2 on a Silver Electrode. Journal of the American Chemical Society, 138(25), 7820–7823.

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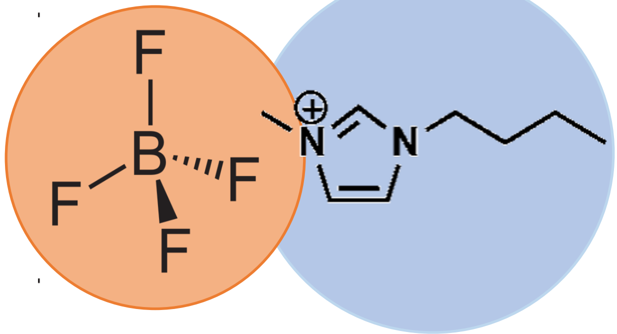
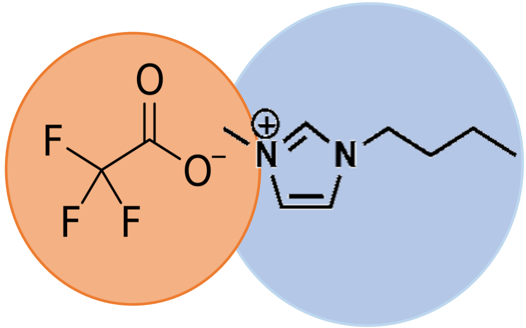
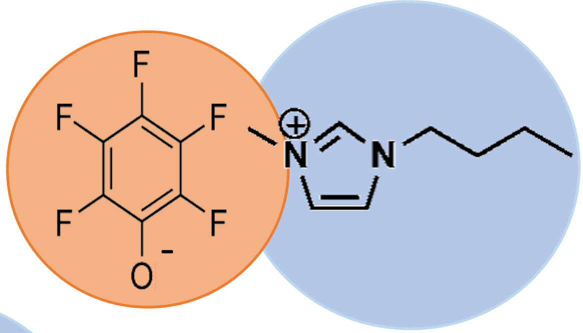
Materials and methods



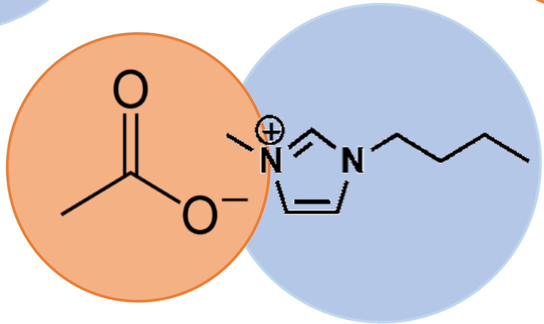
[BMIM][BF_4]



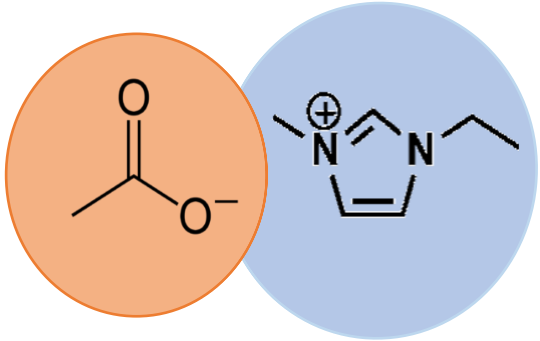
[BMIM][CO_2CF_3]



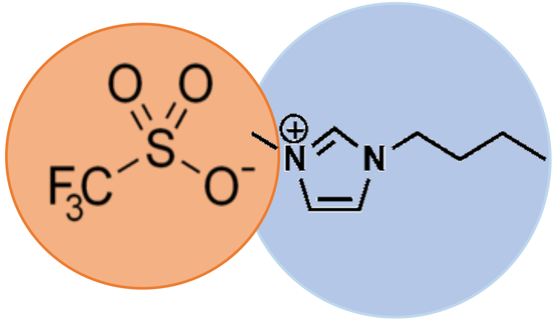
[BMIM][5FF]



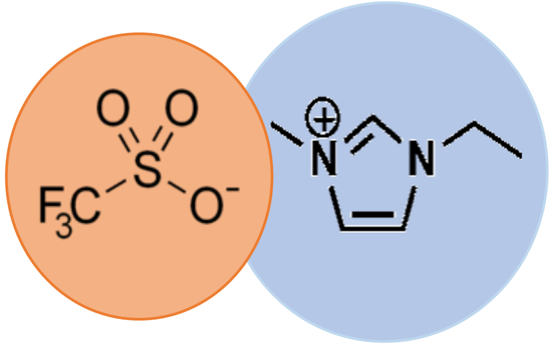
[BMIM][CO_2CH_3]



[EMIM][CO_2CH_3]



[BMIM][SO_3CF_3]

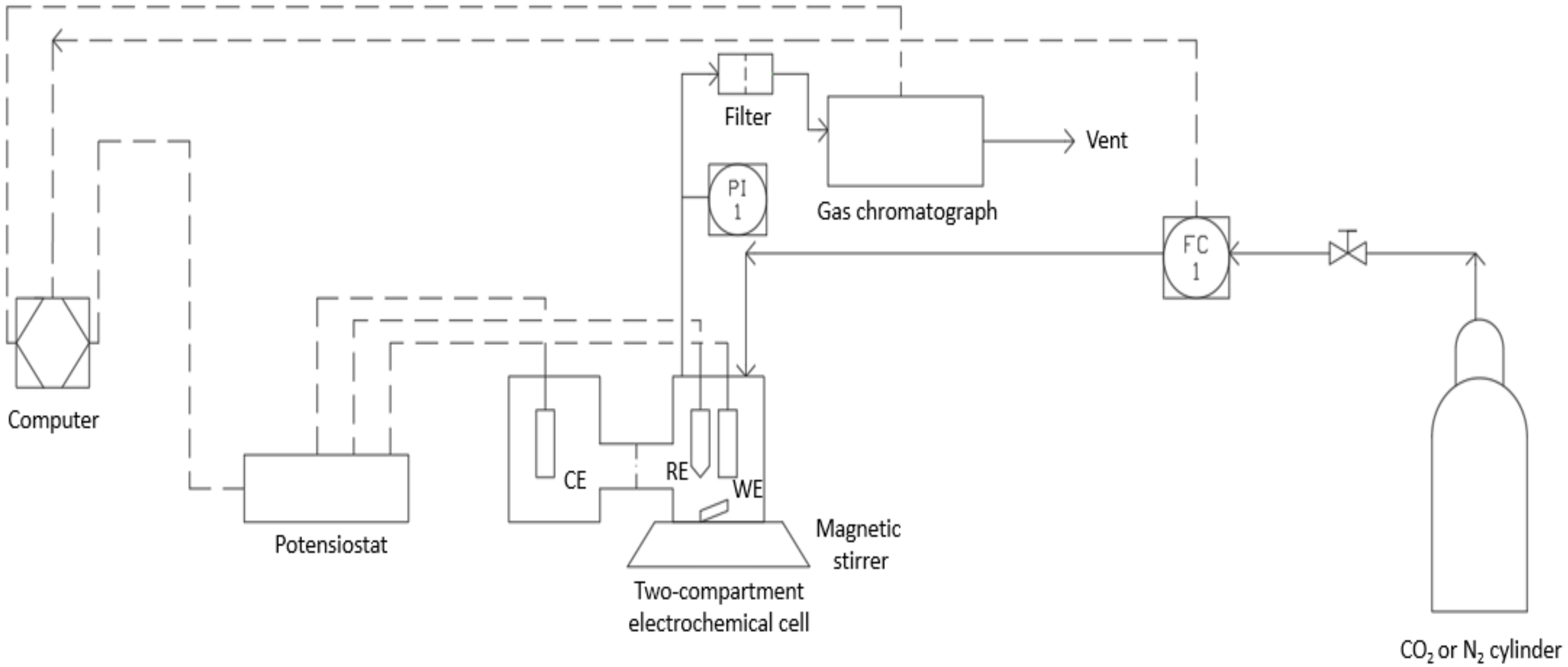


[EMIM][SO_3CF_3]

io·li·tec
Ionic Liquids Technologies

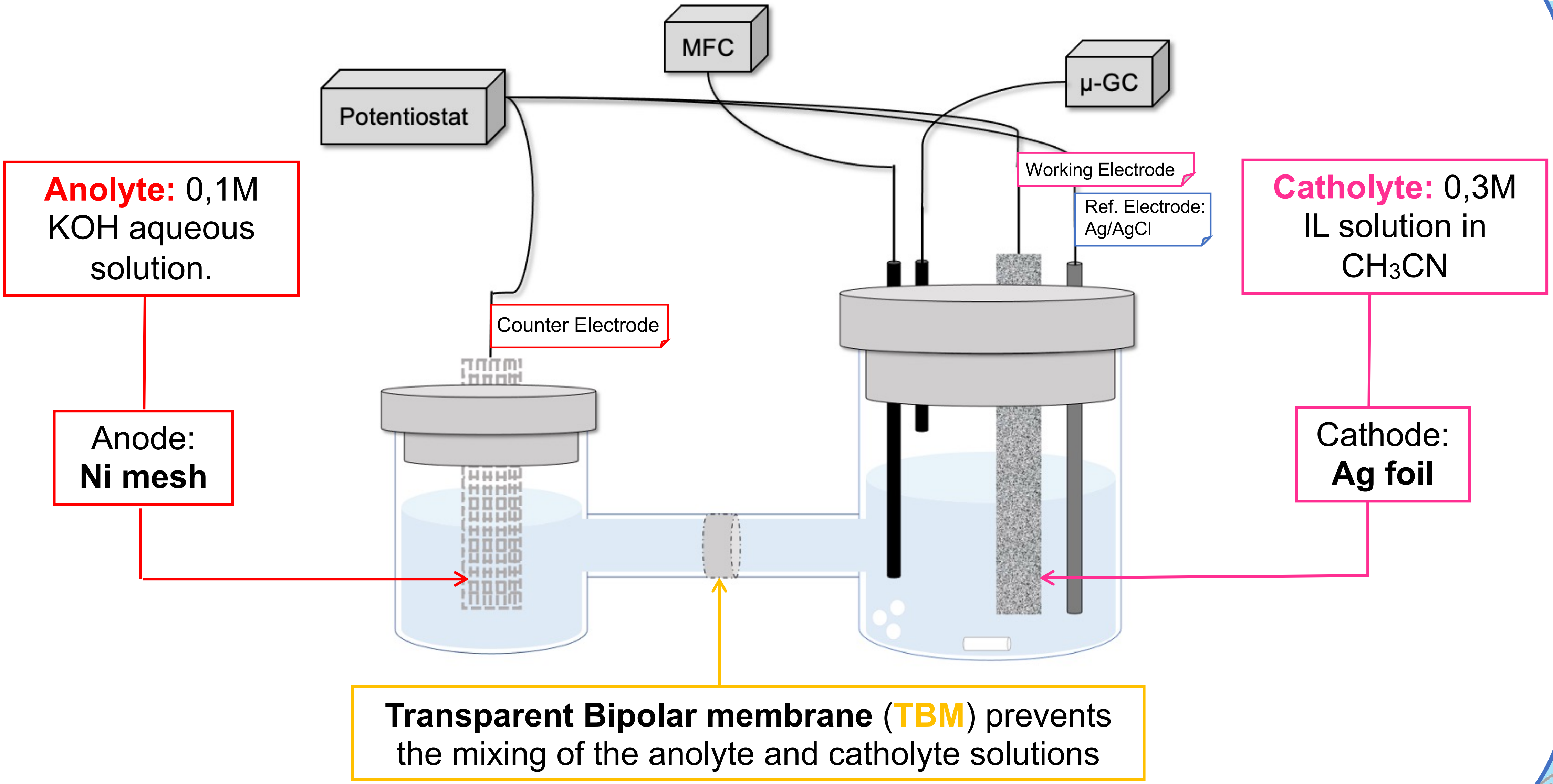
List of ILs studied in this work. They are composed by:
Cationic Part: [$BMIM^+$] or [$EMIM^+$]
Anionic Part: [BF_4^-], [CO_2CF_3], [CO_2CH_3], [5FF] or [SO_3CF_3]

Materials and methods



✓ **Set-up:** The experimental setup to perform the CO_2 ECR was defined. Typical CO_2 reduction cells in IL-based electrolytes include a two-compartment cell (H-type) or continuous flow electrochemical reactors. Concerning our electrochemical application, a two compartments cell (H-type) was chosen.

Materials and methods



H-type cell configuration

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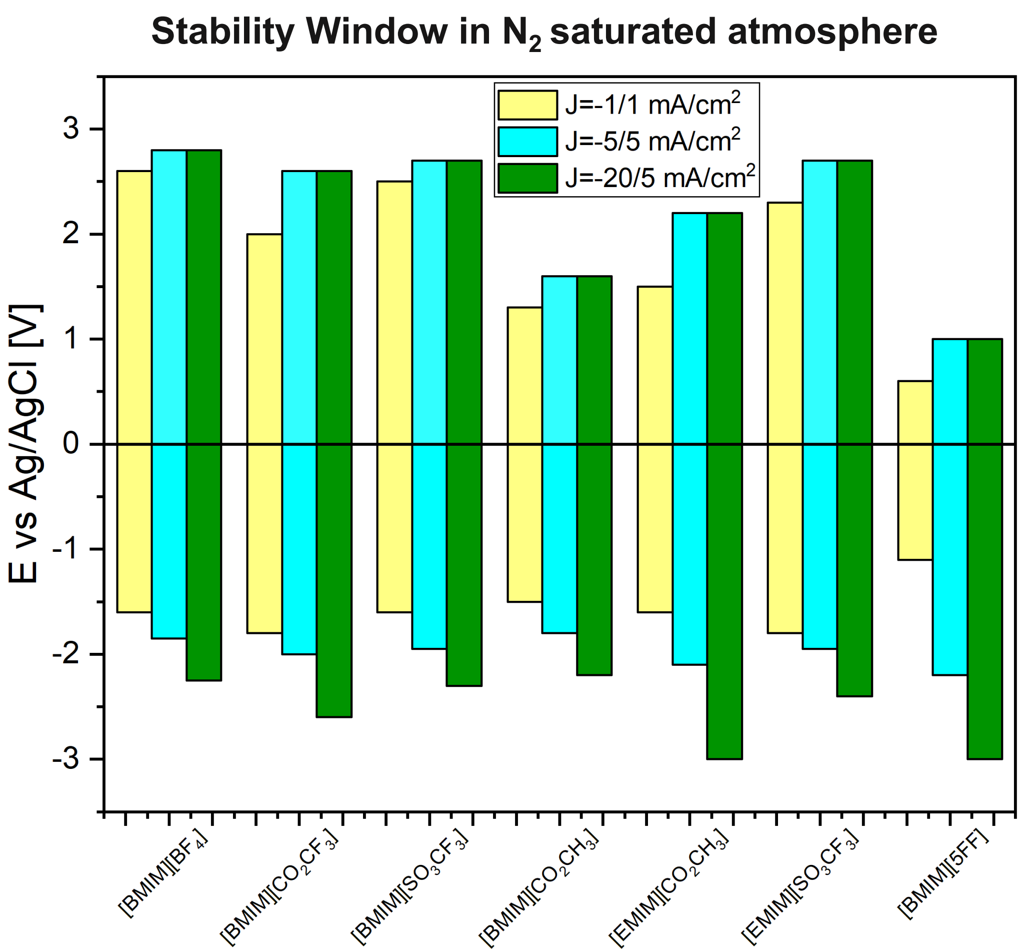
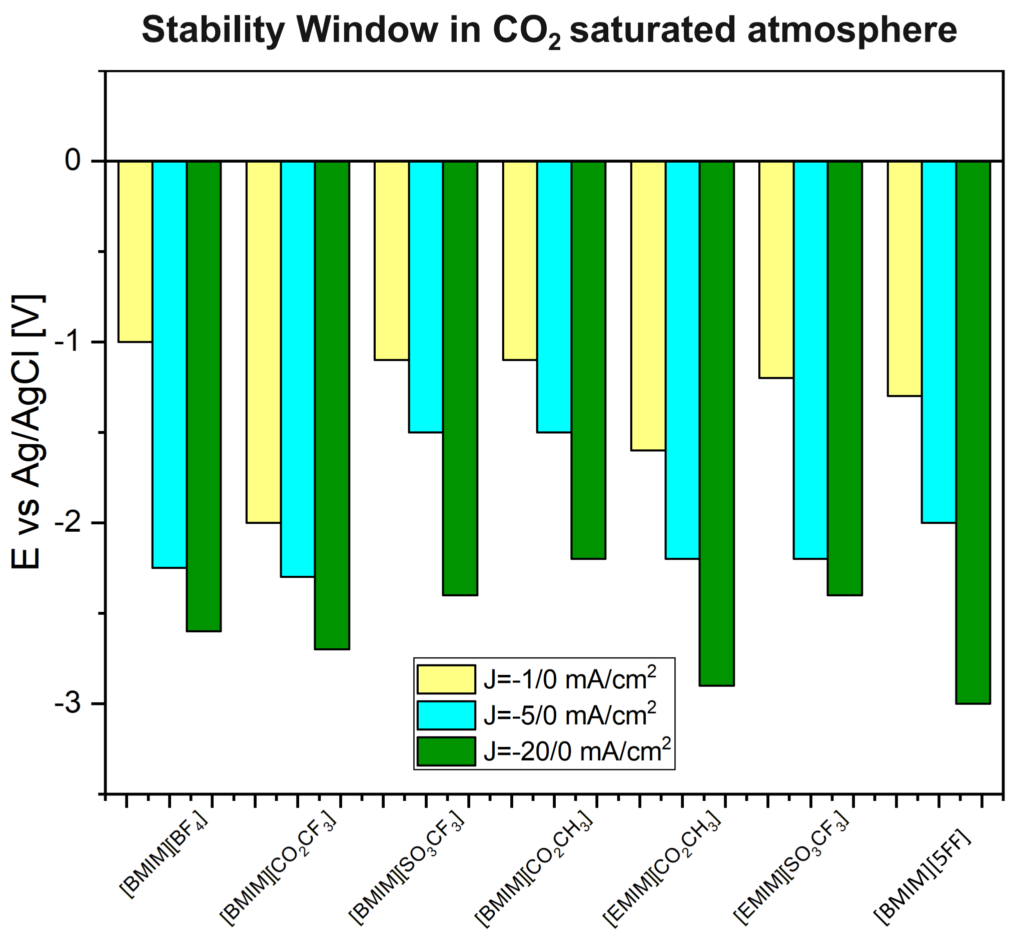
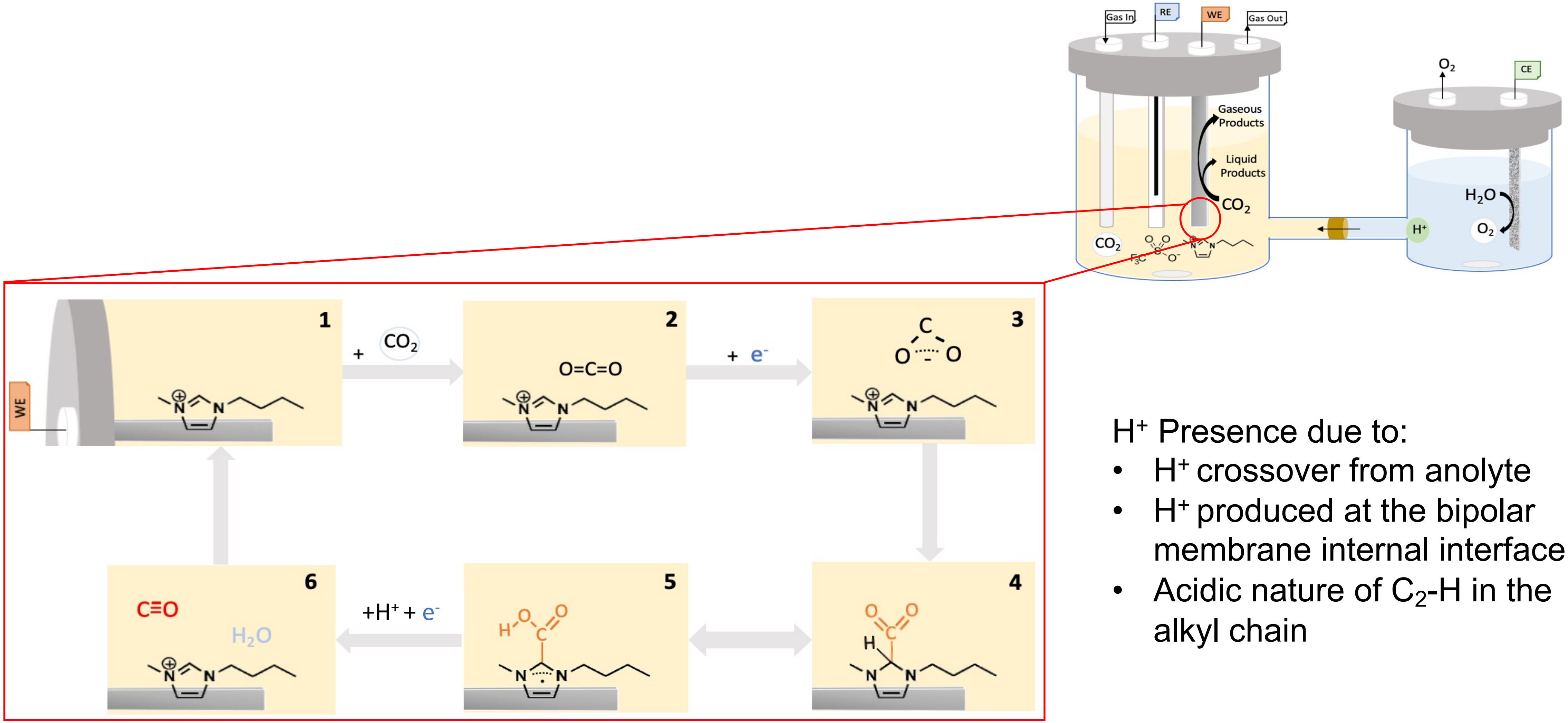




Electrochemical Stability Window

Single compartment cell, WE=Pt, CE=Pt, REF=Ag/AgCl



H⁺ Presence due to:

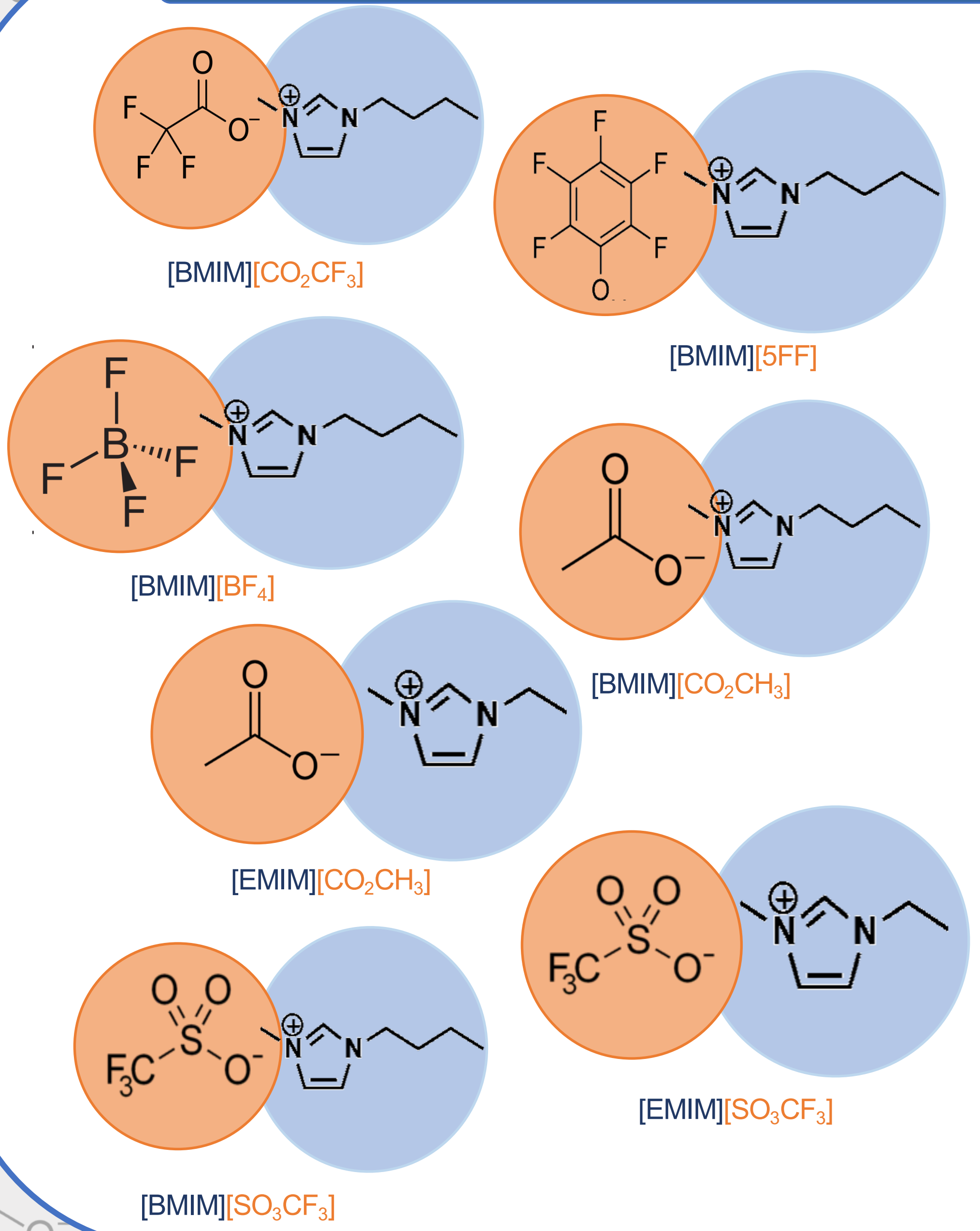
- H⁺ crossover from anolyte
- H⁺ produced at the bipolar membrane internal interface
- Acidic nature of C_2-H in the alkyl chain

Hypothesis of reaction mechanisms

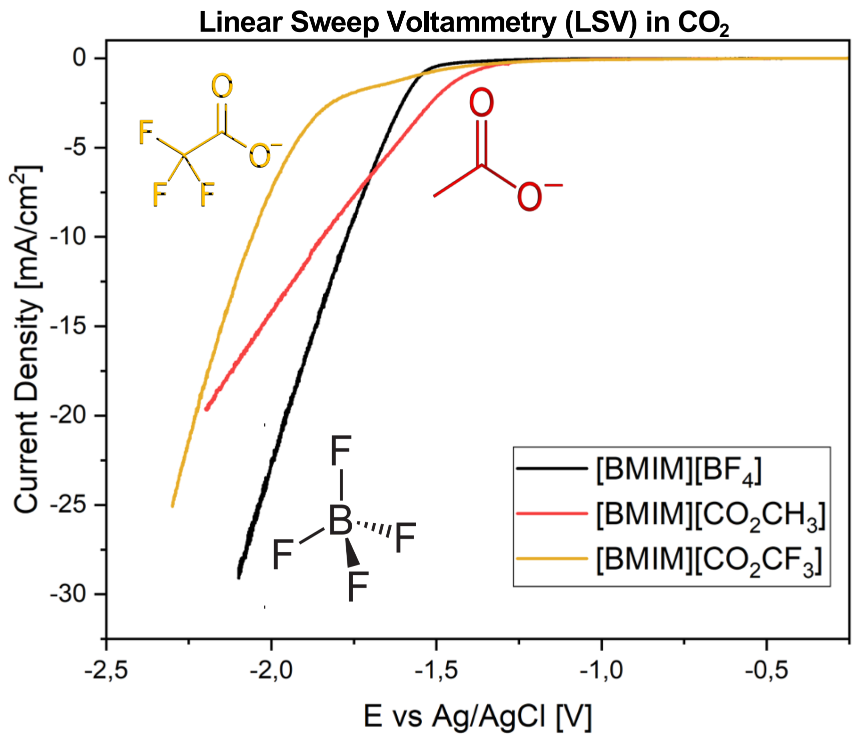
Cation role

Phys.Chem.Chem.Phys., 2015, 17, 23521

Results and discussion



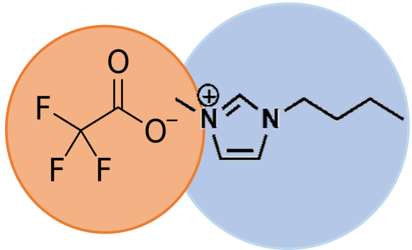
ANION ROLE of IL



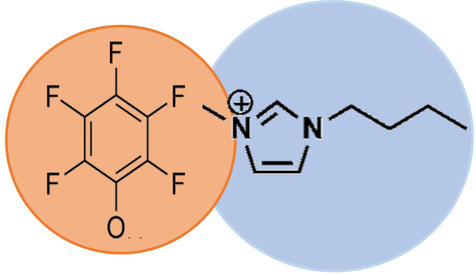
- **CO_2 solubility** strongly depends on the anion influence.
- A higher fluorination degree in the IL leads to a higher CO_2 solubility and current density.
- It might be related to the anion electronegativity.

Dębski, B. et al (2019), Journal of Molecular Liquids, 29

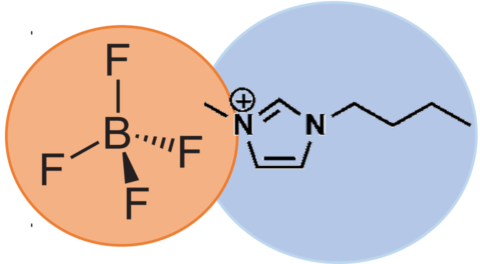
Results and discussion



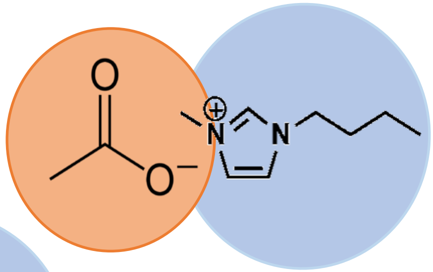
[BMIM][CO_2CF_3]



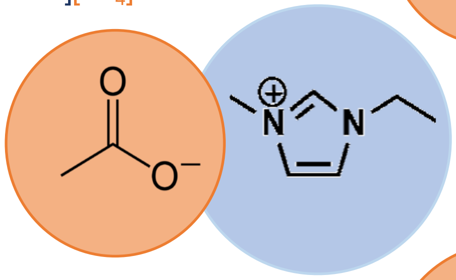
[BMIM][5FF]



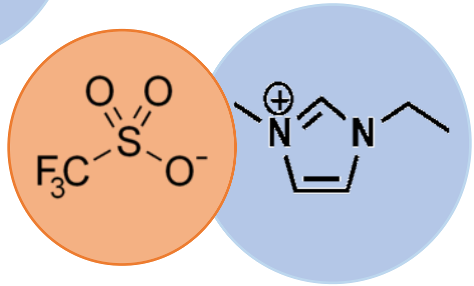
[BMIM][BF_4]



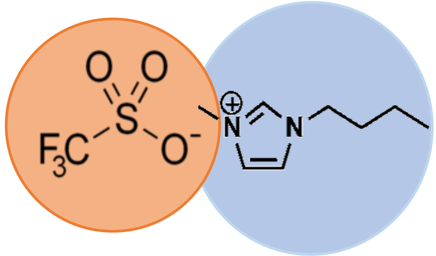
[BMIM][CO_2CH_3]



[EMIM][CO_2CH_3]



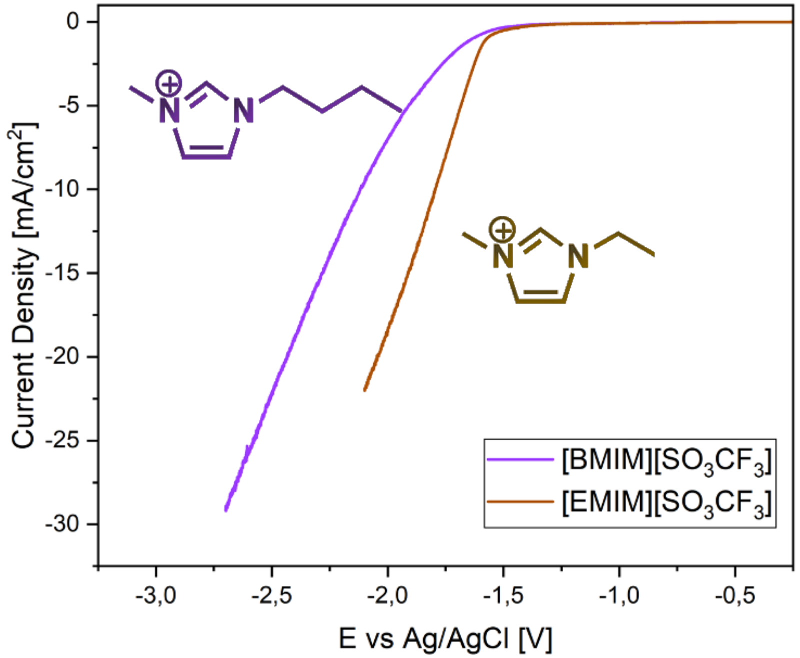
[EMIM][SO_3CF_3]



[BMIM][SO_3CF_3]

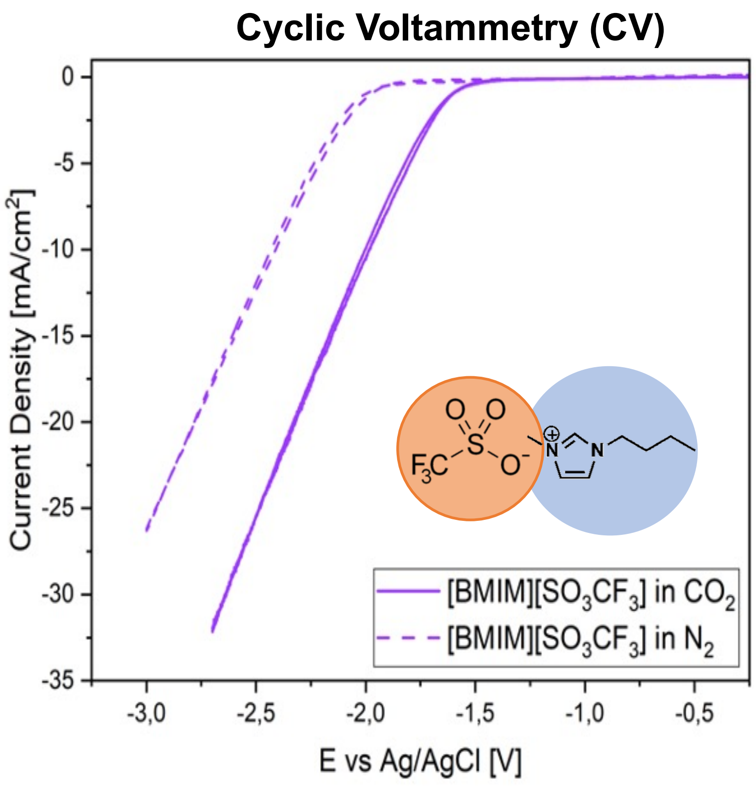
CATION ROLE of IL

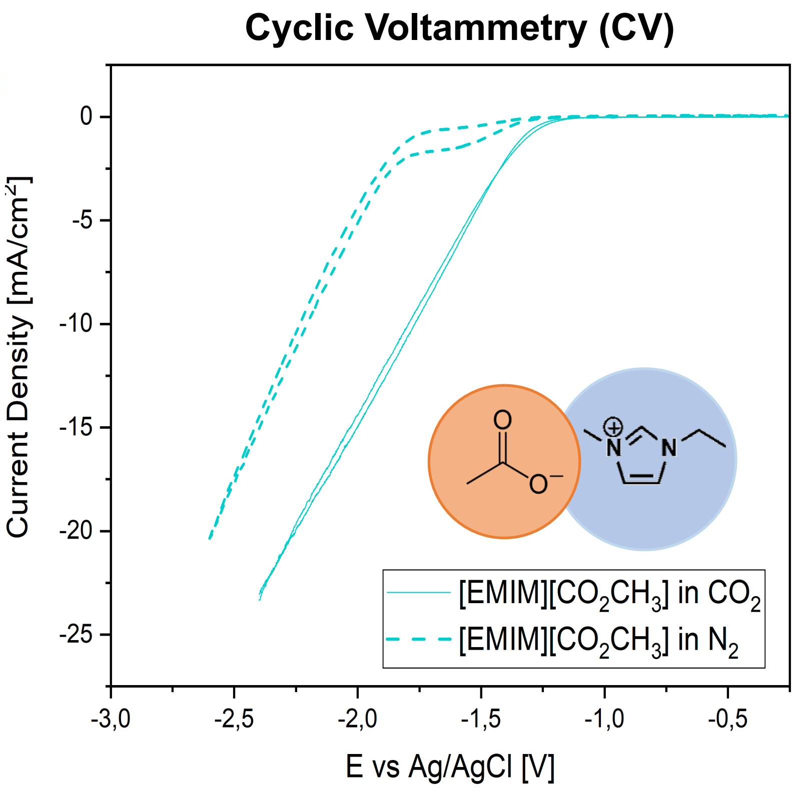
Linear Sweep Voltammetry (LSV) in CO_2

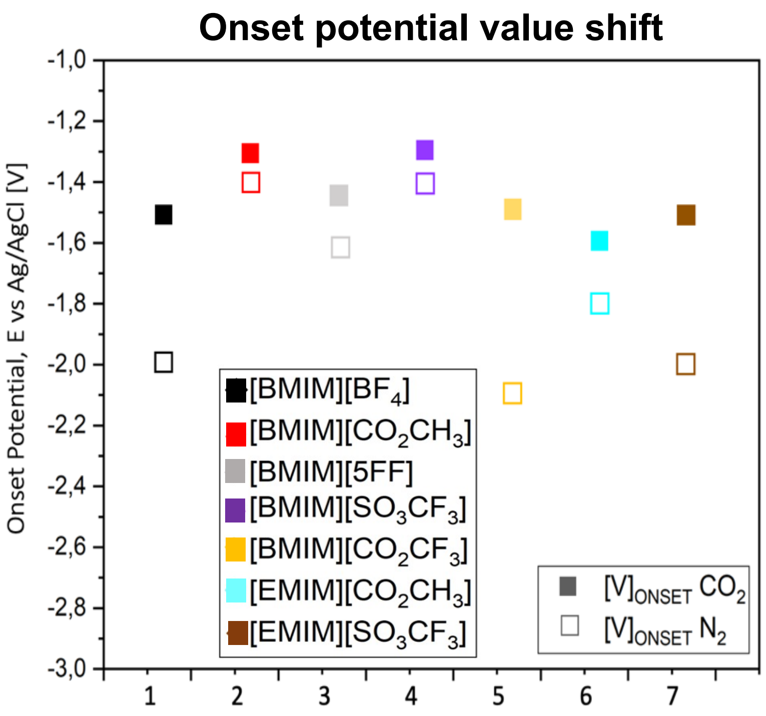


- The alkyl chain of the cation plays an **orientation role**.
- When the **alkyl chain decreases**, the imidazolium ring finds a **more convenient position** in the cathode to reduce and form the complex with the carbon dioxide molecule, which might be translated into a less negative onset potentials.

Lockett, V. et al, (2008), Journal of Physical Chemistry C, 112(19), 7486–7495



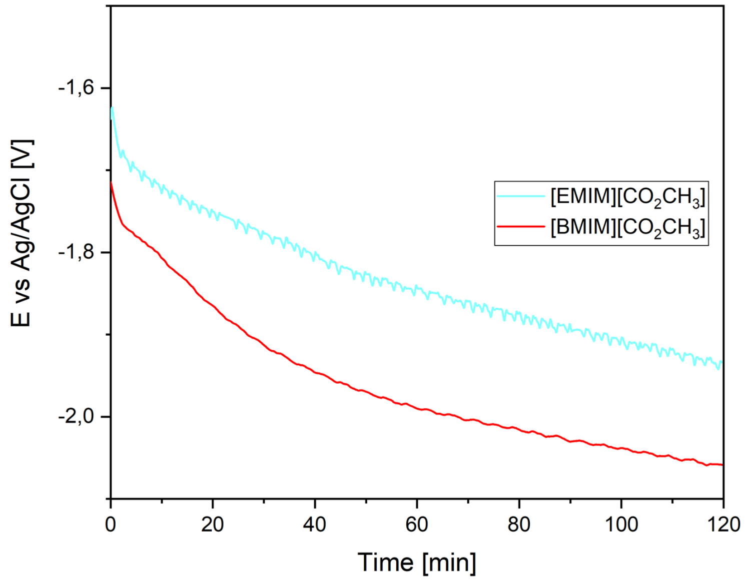


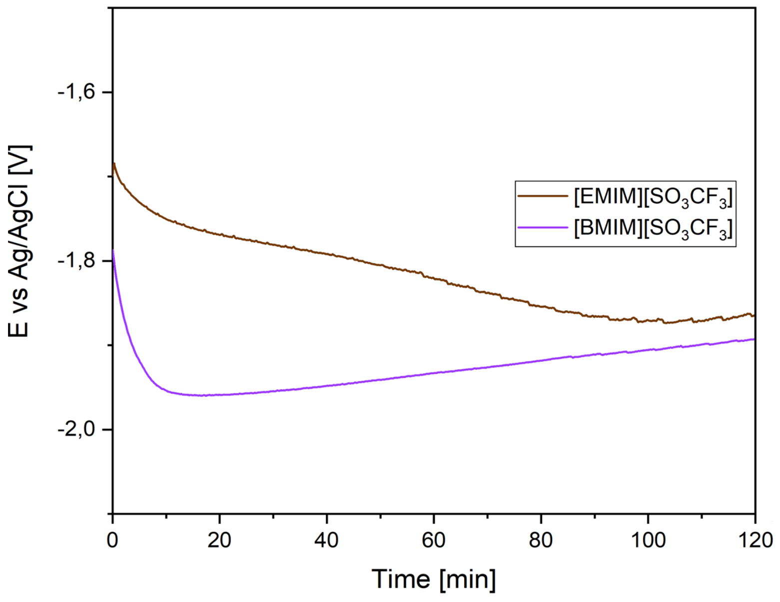


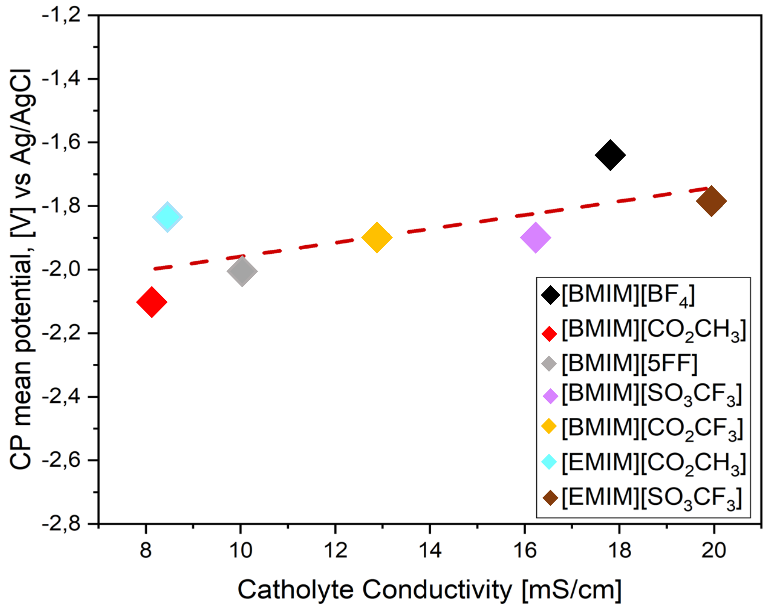
✓ ***CVs' highlights:*** Onset potential of all the ILs is shifted to less negative potentials when atmosphere is saturated with CO_2.

Results and discussion

Chronopotentiometry (CP) in CO_2, t=120 min, -20 mA





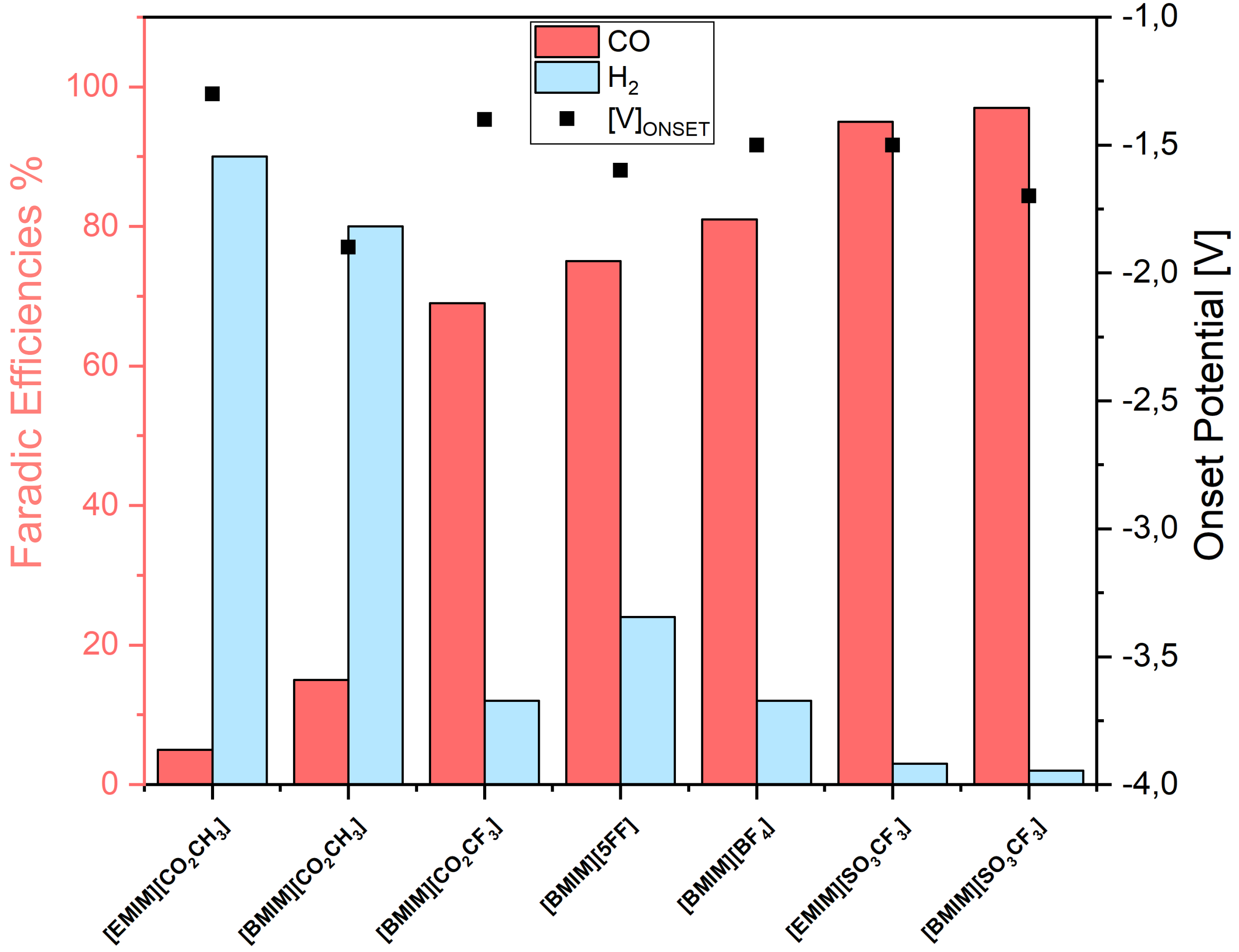


✓ ***CP's highlights:*** comparing the CP's curves, for the same anion with EMIM cation there are fewer potentials than with BMIM. Probably this trend is due to two aspects:

1- A more convenient orientation reached by a shorter cation alkyl chain on the electrode surface

2- It can be linked to the conductivity of the catholyte. Catholyte conductivities of **[EMIM][CO_2CH_3]** and **[EMIM][SO_3CF_3]** solutions are higher than **[BMIM][CO_2CH_3]** and **[BMIM][SO_3CF_3]** respectively.

Chronopotentiometry (CP) in CO_2, t=120 min, -20 mA



✓ $[V]_{Onset}$'s highlights

- Imidazolium salts of $[SO_3CF_3]$, [BMIM][5FF] and $[BMIM][CO_2CH_3]$ are able to decrease the overpotential for the CO_2RR to CO with respect to the most used $[BMIM][BF_4]$.

✓ Selectivity highlights

- The maximum FE% to CO is reached by $[BMIM][SO_3CF_3]$.
- Ionic Liquids with acetate anion are more selective towards the production of H_2 than CO.

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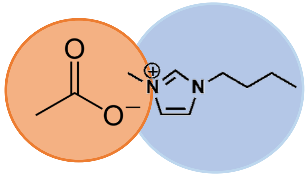
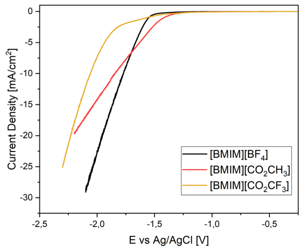
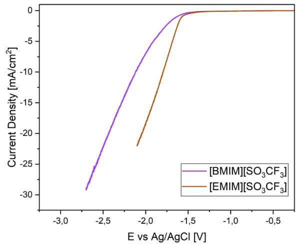
Conclusions



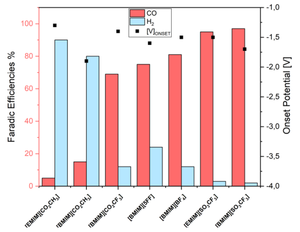
❖ Seven imidazolium salts were tested for the electrocatalytic CO_2 conversion to CO.



❖ CO_2 solubility depends on the anion of the imidazolium salt, which tends to be higher for fluorinated anions.



❖ The cation has a steric effect and an orientation role. When the alkyl chain decreases, the imidazolium ring finds a more convenient position in the cathode surface.



❖ Imidazolium salts of acetate are more selective towards the production of H_2. [BMIM][SO_3CF_3] promotes the reduction of CO_2 to CO better than the commonly used [BMIM][BF_4].

Next Steps

i. Test **other Ionic Liquids** with different anionic and cationic part, and consequently different properties. We are also evaluating a mixture of different ionic liquids.

ii. Test **other solvents** (for example: Propylene carbonate).

iii. Optimize analytical methods for other liquid and gaseous products of CO_2RR in Ionic Liquid-based media.

iv. We plan to **deepen the reaction mechanisms** of ionic liquids on the surface of the catalyst, to investigate the reactions that regulate the CO_2 reduction thanks to the intermediation of the ionic liquid on the surface of the catalyst.

Acknowledgements

The research leading to these results has received funding from the European Union's Horizon 2020 Research and Innovation Action programme under the SunCoChem project. (Grant Agreement No 862192)

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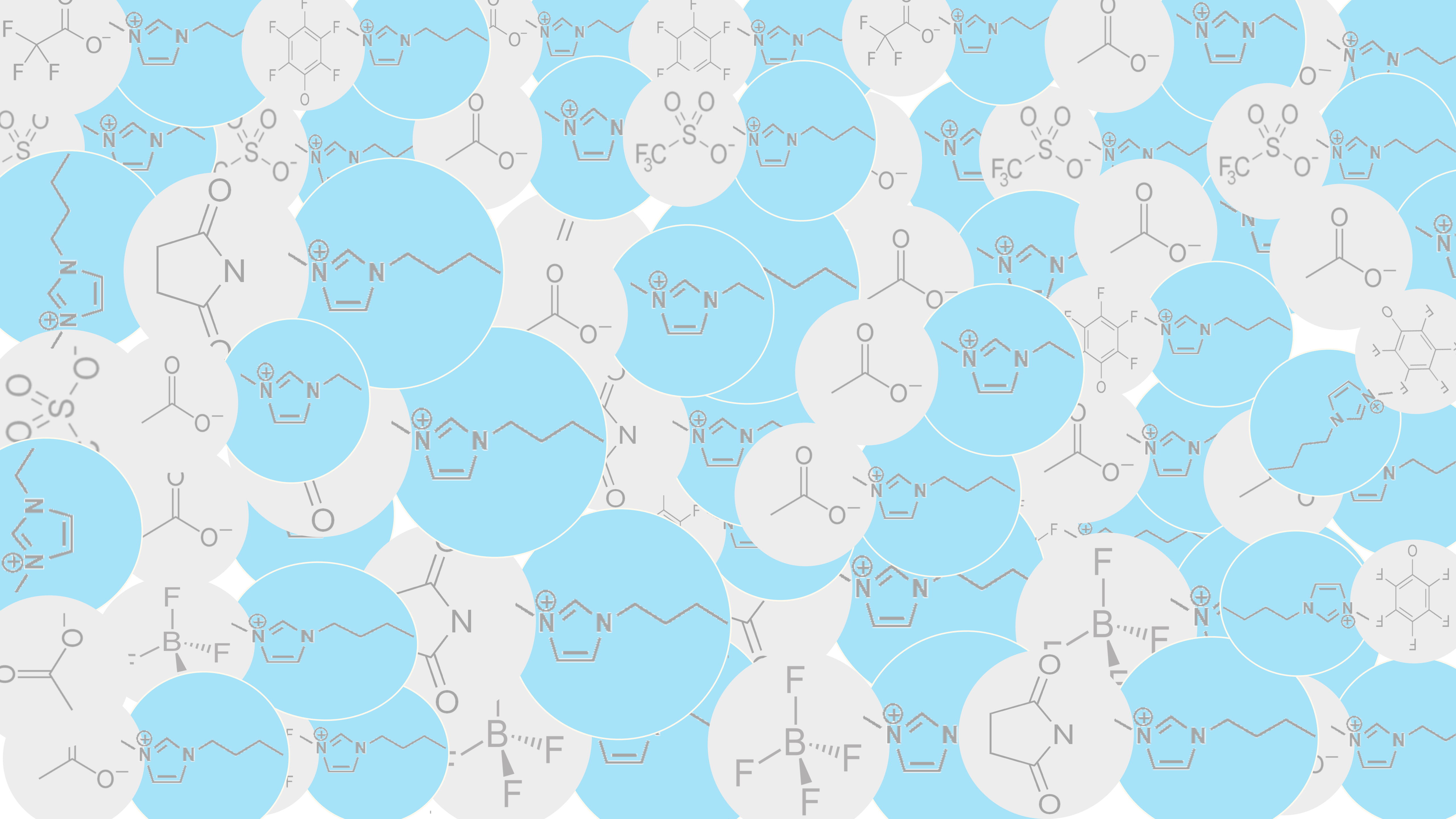


Anolyte: 0,1M KOH aqueous solution.

Anode: **Ni mesh**

Anolyte: 0,1 M KOH

- Very conductive aqueous solution
- Helps an effective passage of current
- The use of a **1M KOH** , a high concentration of potassium ions incentivizes the transfer of them into the cathodic compartment, and an increase in **precipitate formation** was observed.

MFC

Catholyte: 0,3M IL solution in CH_3CN

Cathode: **Ag foil**

Transparent Bipolar membrane (**TBM**) prevents the mixing of the anolyte and catholyte solutions

H-type cell configuration

MFC

Anolyte: 0,1M KOH aqueous solution.

Anode: **Ni mesh**

Catholyte: 0,3 M IL in CH_3CN

- ILs cannot be used pure for high viscosity
- MeCN is able to solve all ILs studied in this work
- MeCN has a lower molecular weight than most organic solvents
- Guarantees high conductivity
- Low viscosity of the final solution

Catholyte: 0,3M IL solution in CH_3CN

Cathode: **Ag foil**

Transparent Bipolar membrane (**TBM**) prevents the mixing of the anolyte and catholyte solutions

H-type cell configuration

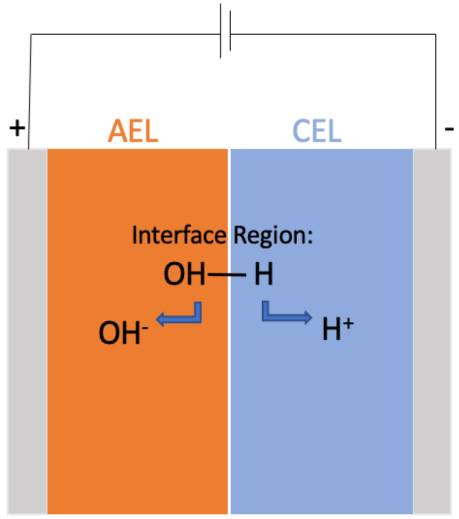
Materials and methods

AEL: Anion exchange layer
CEL: Cation exchange layer

Anolyte: 0,1M KOH aqueous solution.

Anode: **Ni mesh**

ANODE: OER
$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$



CATHODE: CO_2RR/HER
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$
$2H^+ + 2e^- \rightarrow H_2$

Catholyte: 0,3M IL solution in CH_3CN

Cathode: **Ag foil**

MFC

Transparent Bipolar membrane (TBM) prevents the mixing of the anolyte and catholyte solutions

H-type cell configuration

Pärnamäe, R., Mareev, S., Nikonenko, V., Melnikov, S., Sheldeshov, N., Zabolotskii, V., Hamelers, H. V. M., & Tedesco, M. (2020). Bipolar membranes: A review on principles, latest developments, and applications. Journal of Membrane Science, 617, 118538.