Electrochemical CO2 conversion in Ionic Liquid-based electrolytes

Electrochemical CO_2 co
Ionic Liquid-based el

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Società Chimica Italiana | SCI2021 Talk ID:
Session

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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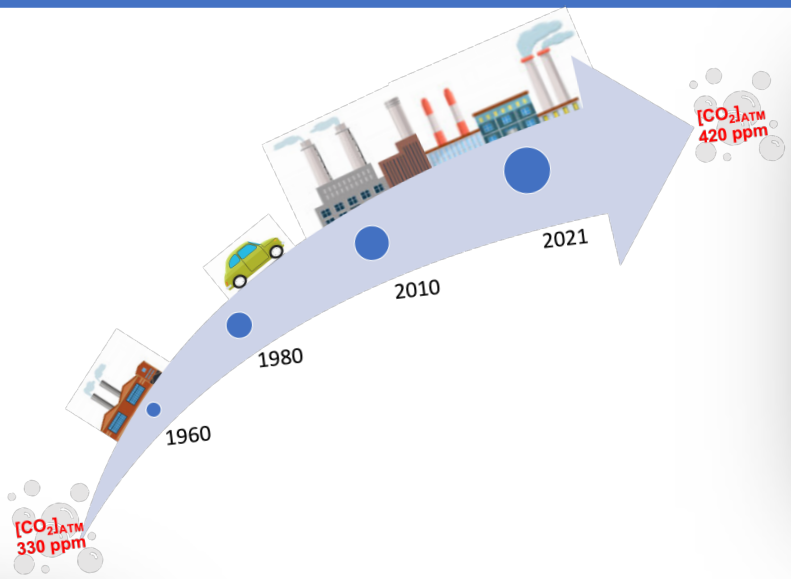
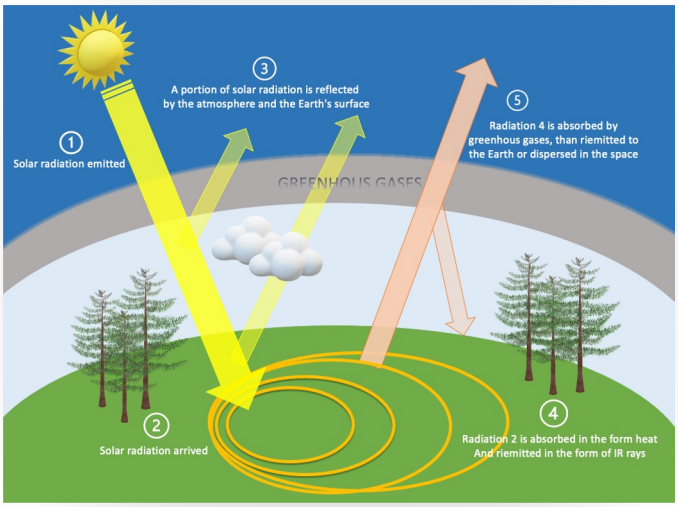
Introduction and aim of the work





Carb
Capt
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proc

CO_2
Conversion
to fuel

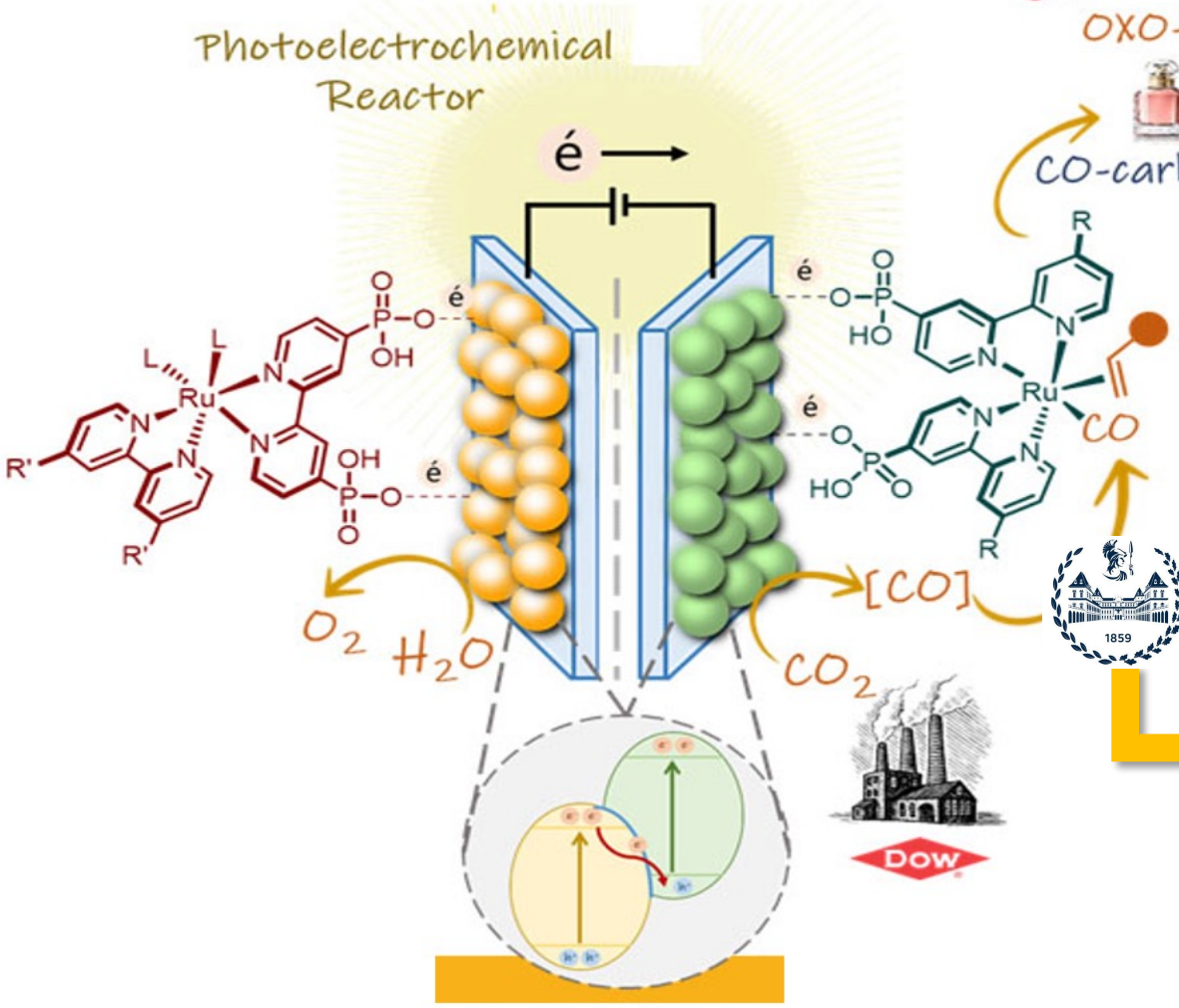
Anthropogenic greenhouse effect

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 Ear

Introduction and aim of the work

SunCO$_2$Chem



DOW iff avantium

OXO-Products

CO-carbonylation

DOW

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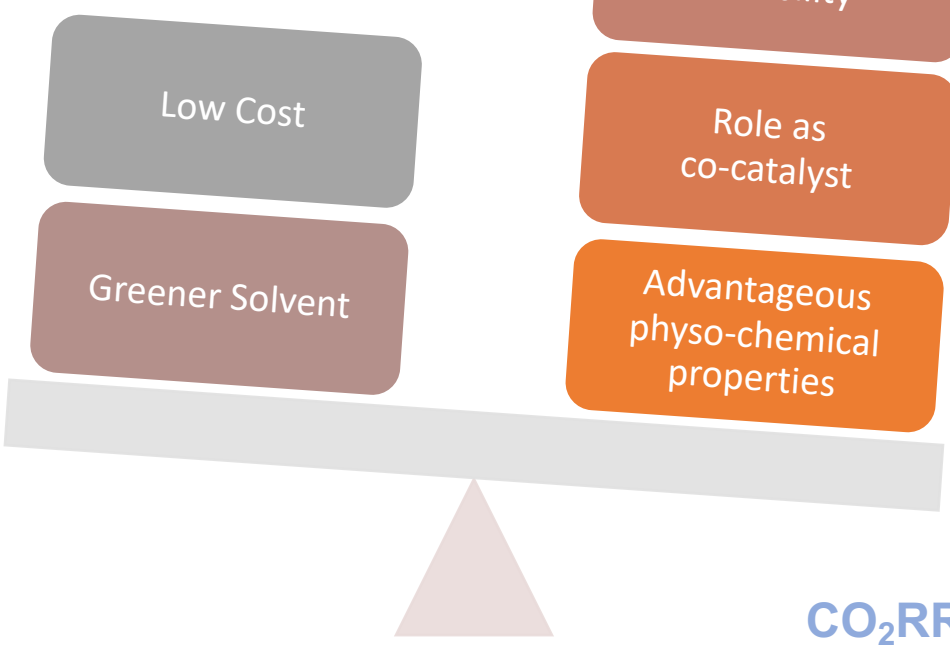
State of the art

Aqueous Media

Ioni Liquid Media

- Low Cost
- Greener Solvent
- Higher CO_2 solubility
- Role as co-catalyst
- Advantageous physo-chemical properties



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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 Electrored
7820–7823.

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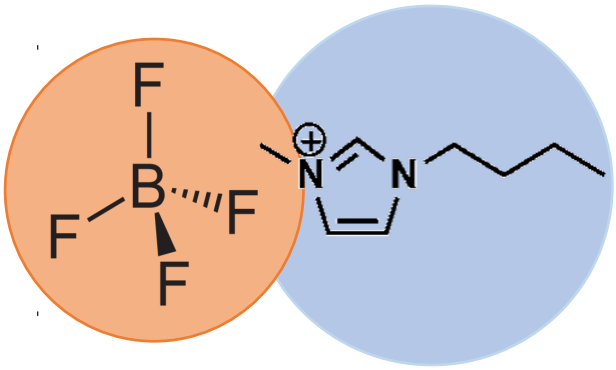
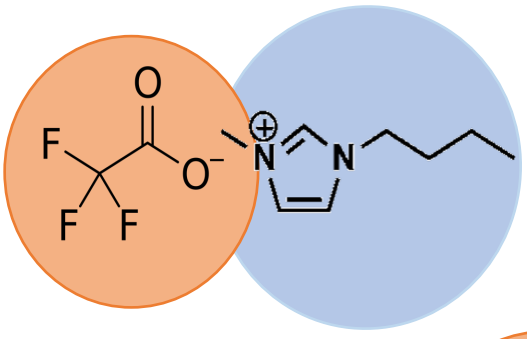
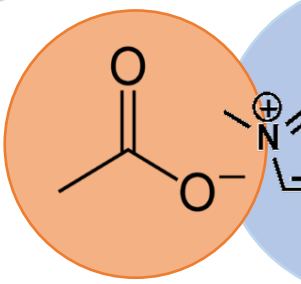
Materials and methods



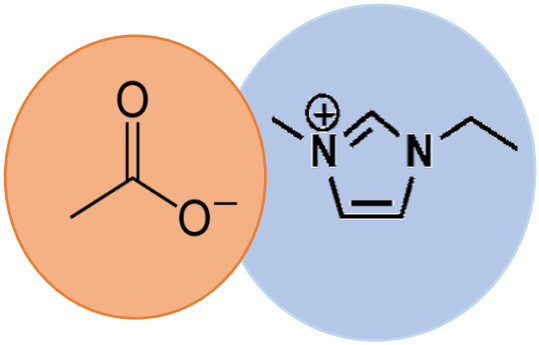
[BMIM][BF_4]



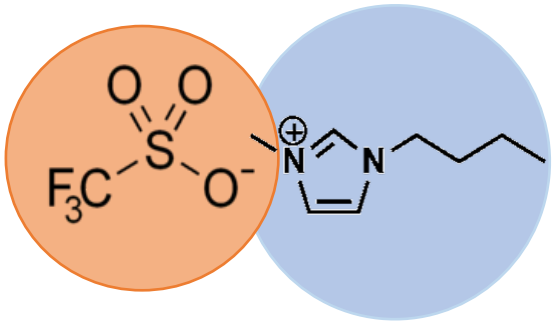
[BMIM][CO_2CF_3]



[BMIM][CO_2



[EMIM][CO_2CH_3]



[BMIM][SO_3CF_3]

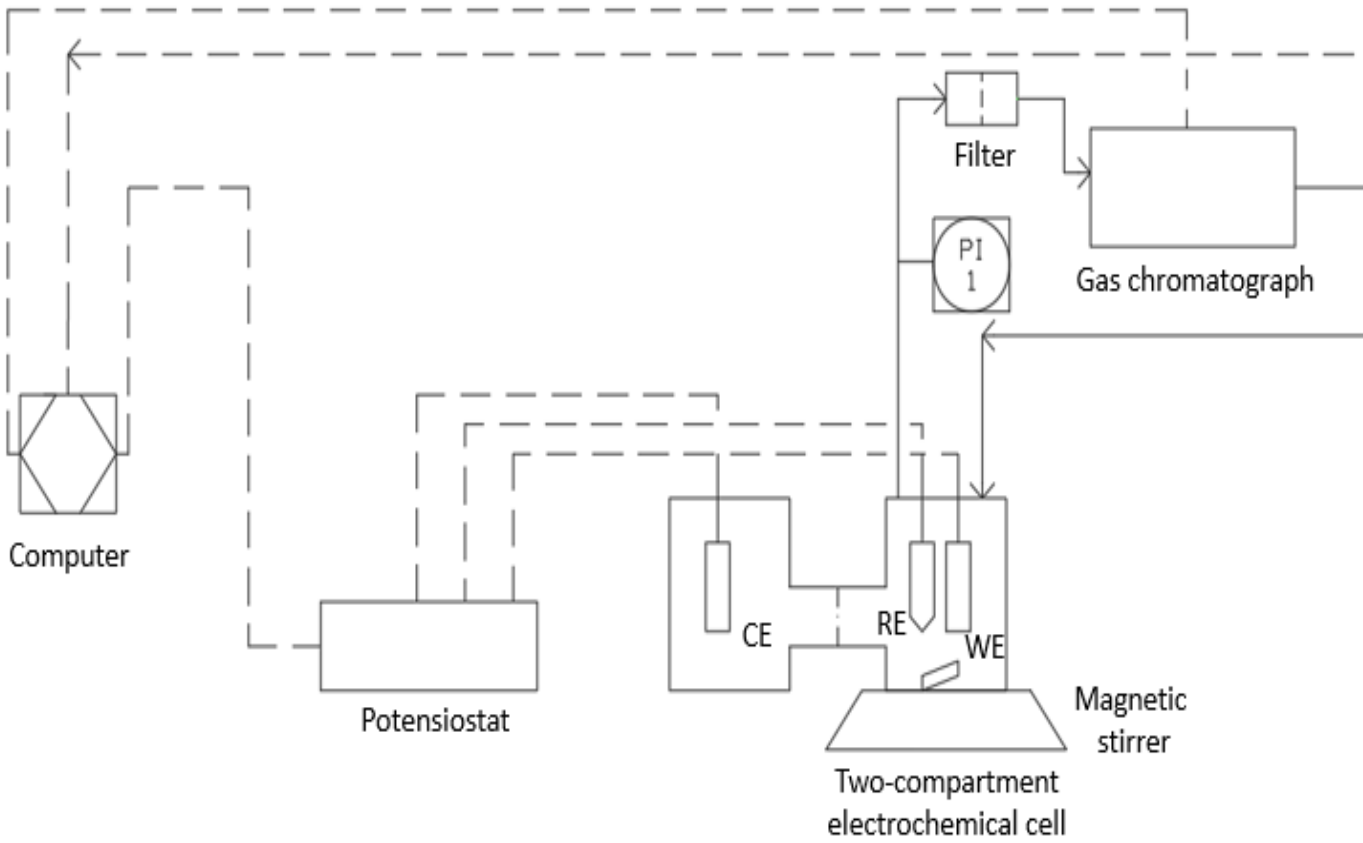
io·li·tec
Ionic Liquids Technologies

List of ILs studied in this work. They are compo

Cationic Part: [$BMIM^+$] or [$EMIM^+$]

Anionic Part: [BF_4^-], [CO_2CF_3], [CO_2CH_3], [5FF] or

Materials and methods

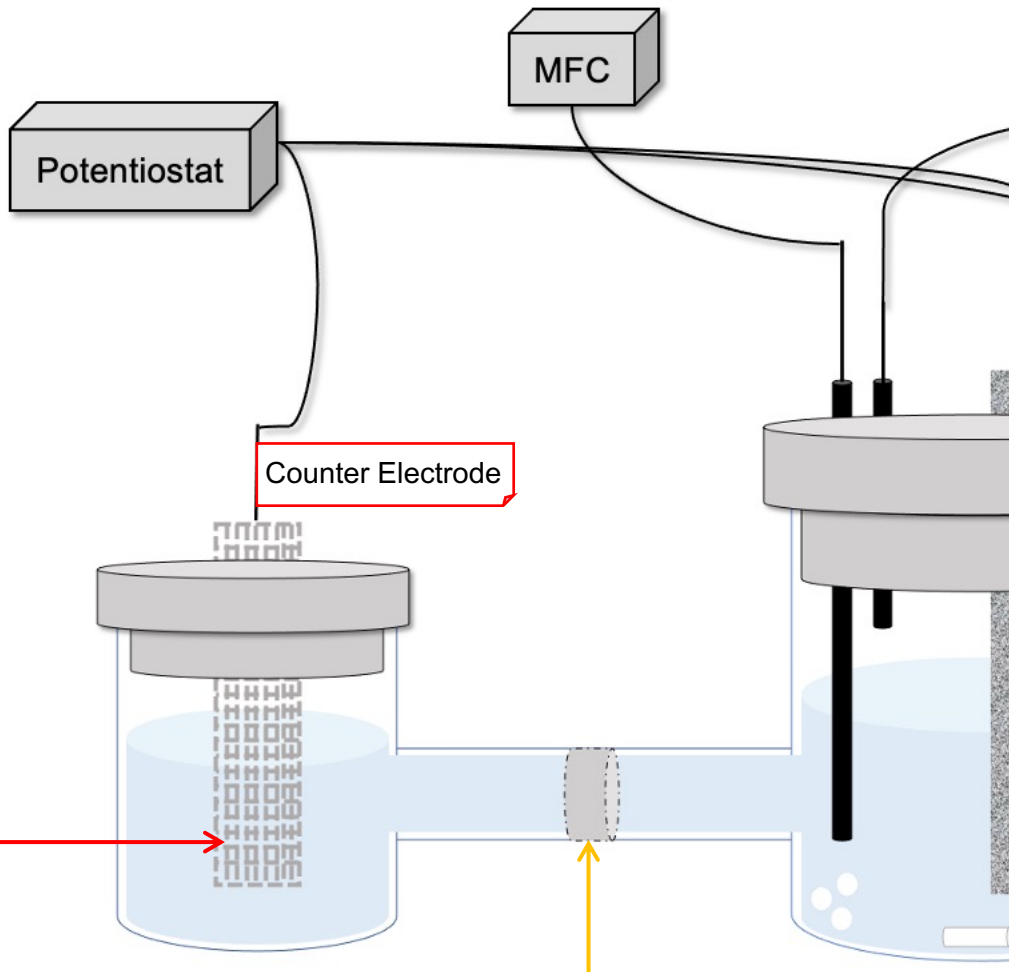


✓ **Set-up:** The experimental setup to perform the CO_2 ECR was defined. T
electrolytes include a two-compartment cell (H-type) or continuous flow ele
electrochemical application, a two compartments cell (H-type) was chosen.

Materials and methods

Anolyte: 0,1M KOH aqueous solution.

Anode: **Ni mesh**



Transparent Bipolar membrane (**TBM**) pr
the mixing of the anolyte and catholyte sol

H-type cell configuration

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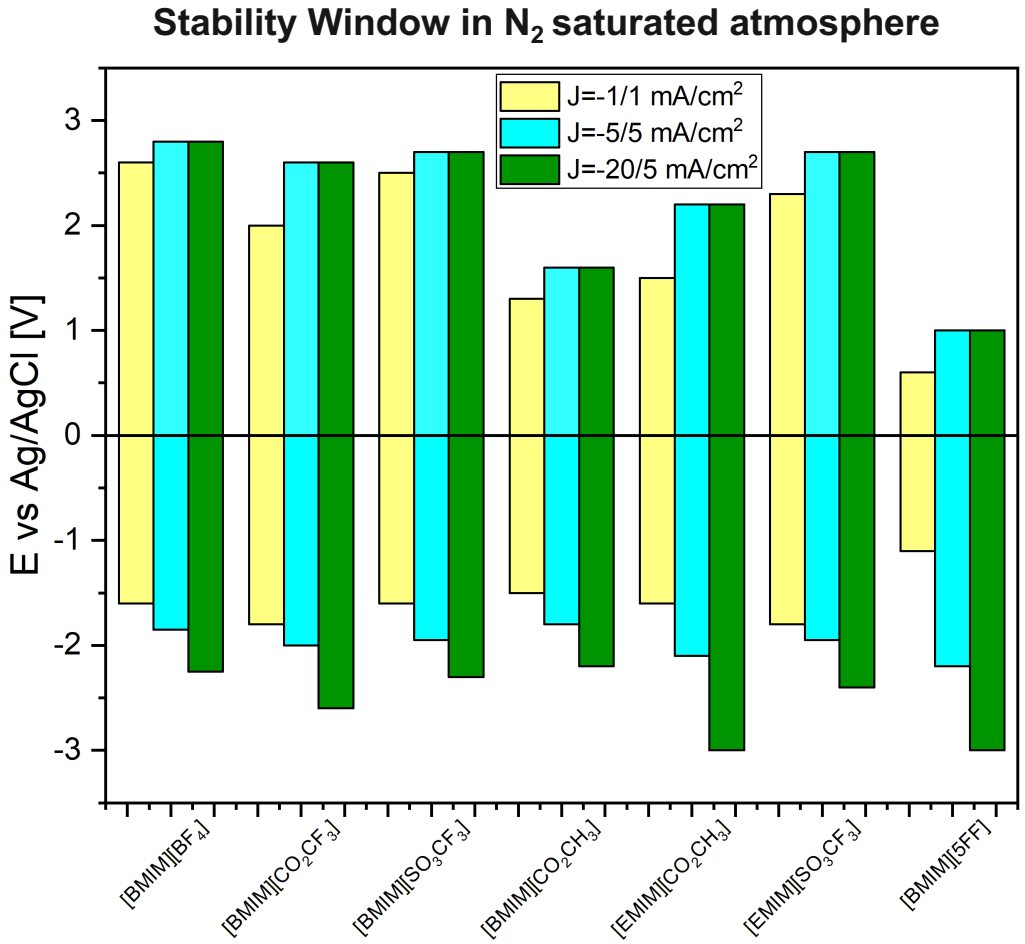
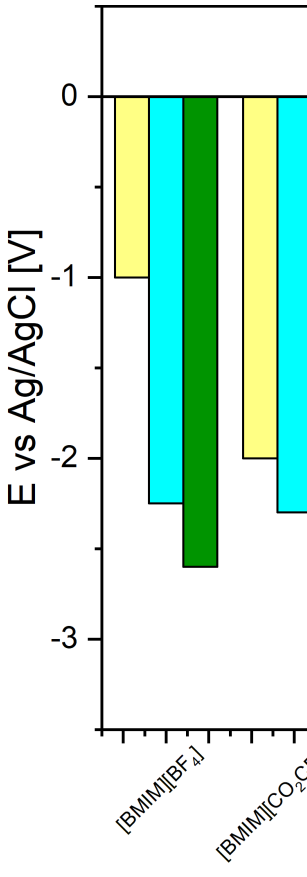
Results and discussion

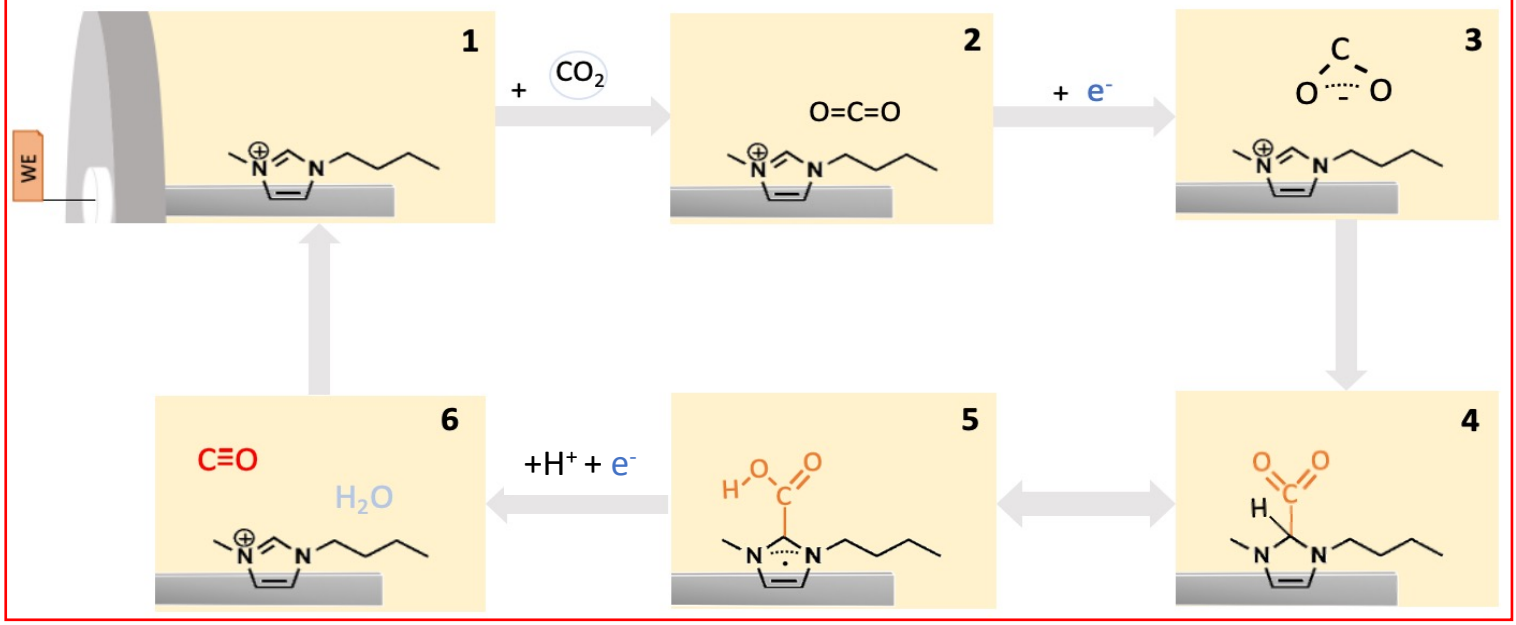




Electrochemical Stability Window

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

Results and discussion

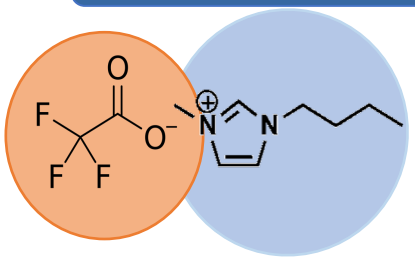


Hypothesis of reaction mechanism

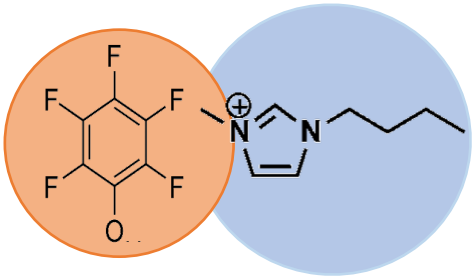
Cation role

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

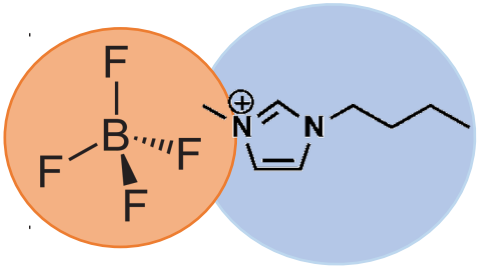
Results and discussion



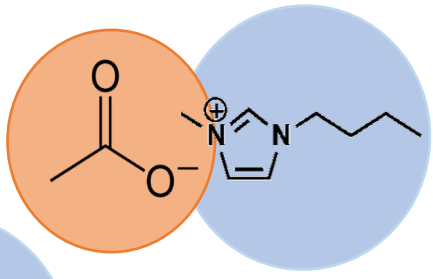
[BMIM][CO_2CF_3]



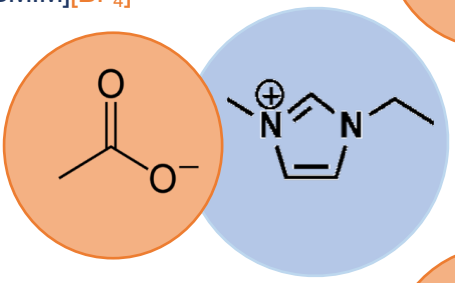
[BMIM][5FF]



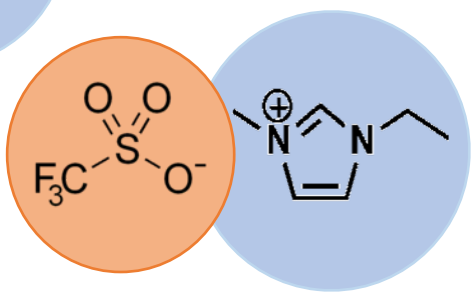
[BMIM][BF_4]



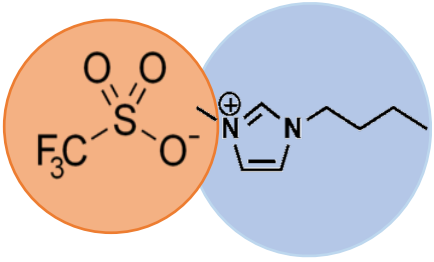
[BMIM][CO_2CH_3]



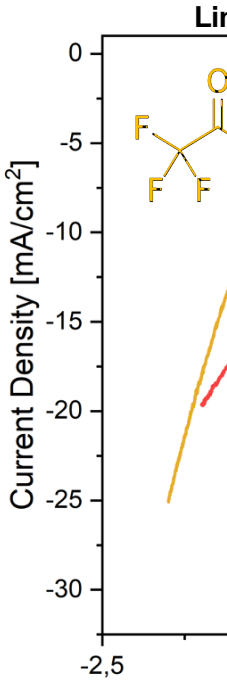
[EMIM][CO_2CH_3]



[EMIM][SO_3CF_3]



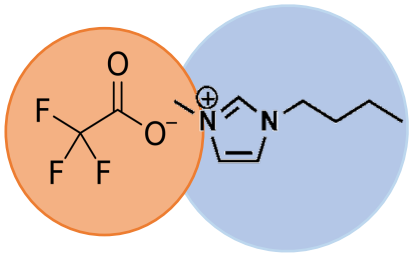
[BMIM][SO_3CF_3]



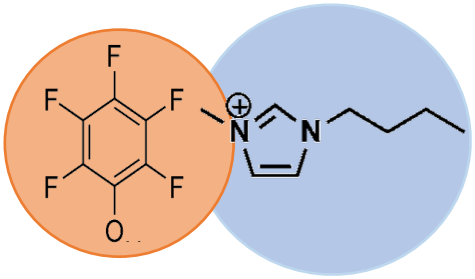
- **CO_2 solubility** s
- A higher fluorinat
  CO_2 solubility an
- It might be relate

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

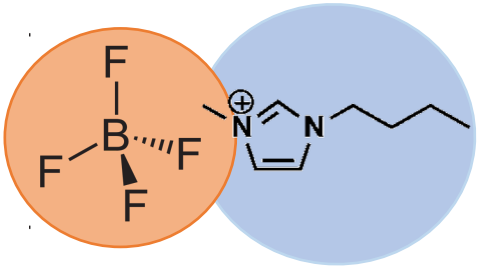
Results and discussion



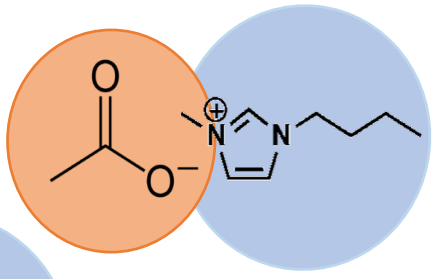
[BMIM][CO_2CF_3]



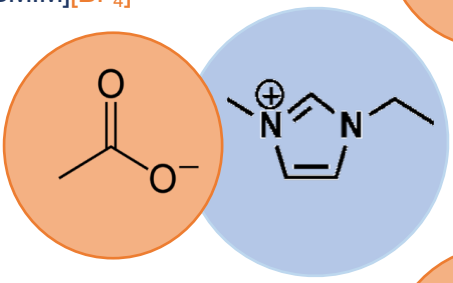
[BMIM][5FF]



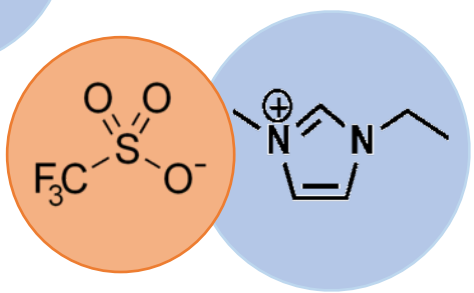
[BMIM][BF_4]



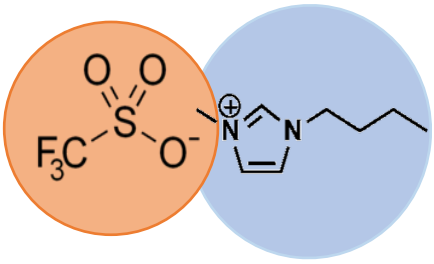
[BMIM][CO_2CH_3]



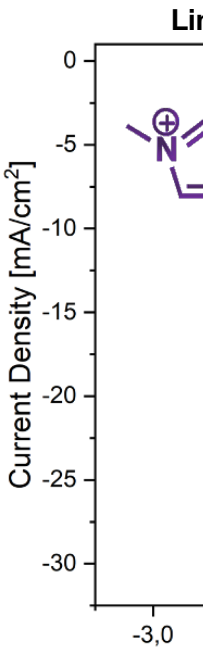
[EMIM][CO_2CH_3]



[EMIM][SO_3CF_3]



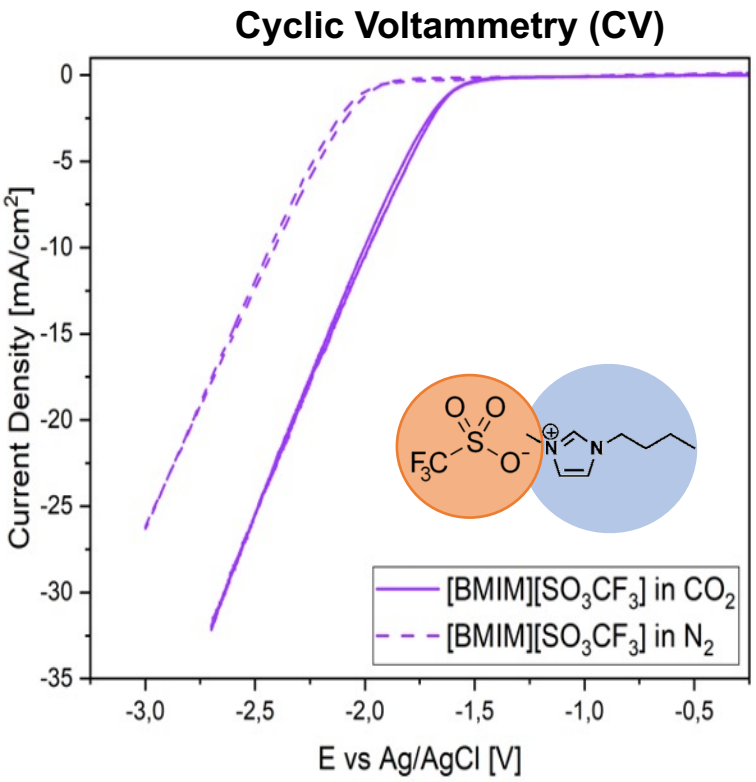
[BMIM][SO_3CF_3]

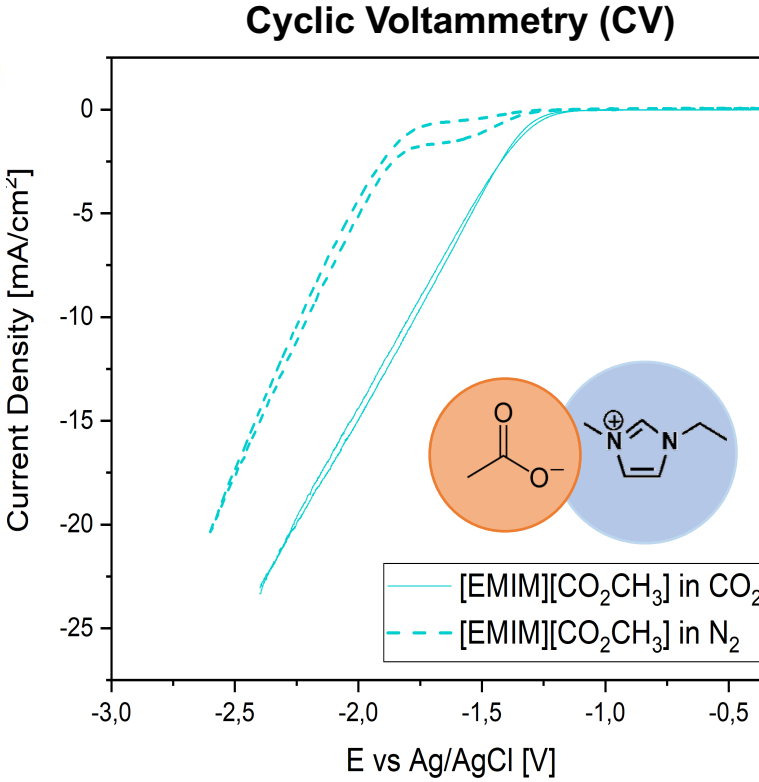


- The alkyl chain c
- When the **alky** ring finds a **mor** to reduce and dioxide molecule negative onset p

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

Results and discussion

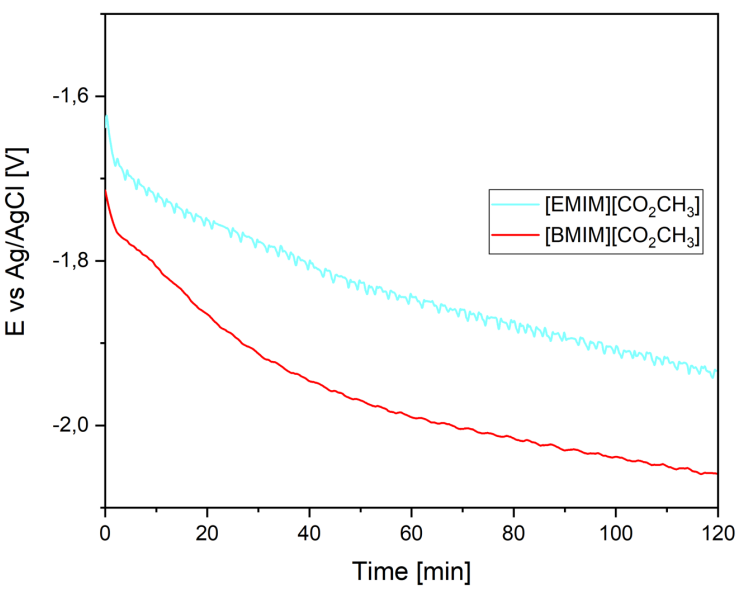


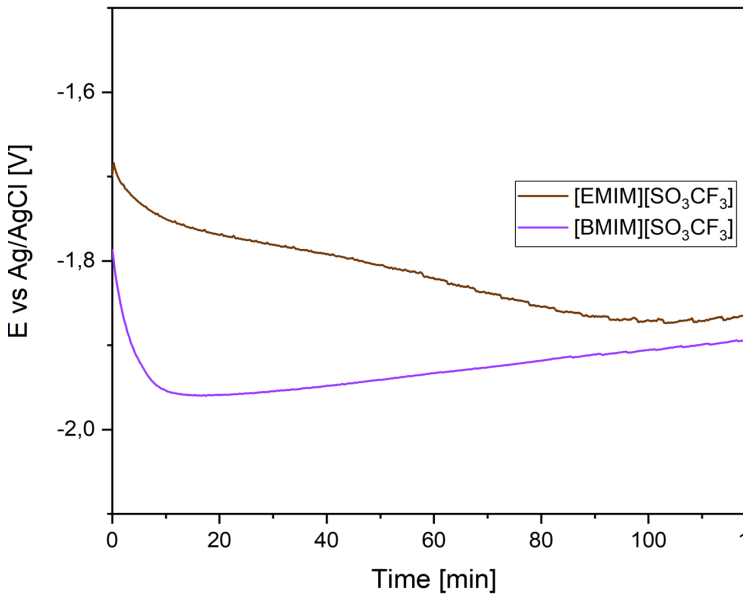


✓ ***CVs' highlights:*** Onset potential of all the ILs is shifted to less negative p
with CO_2.

Results and discussion

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

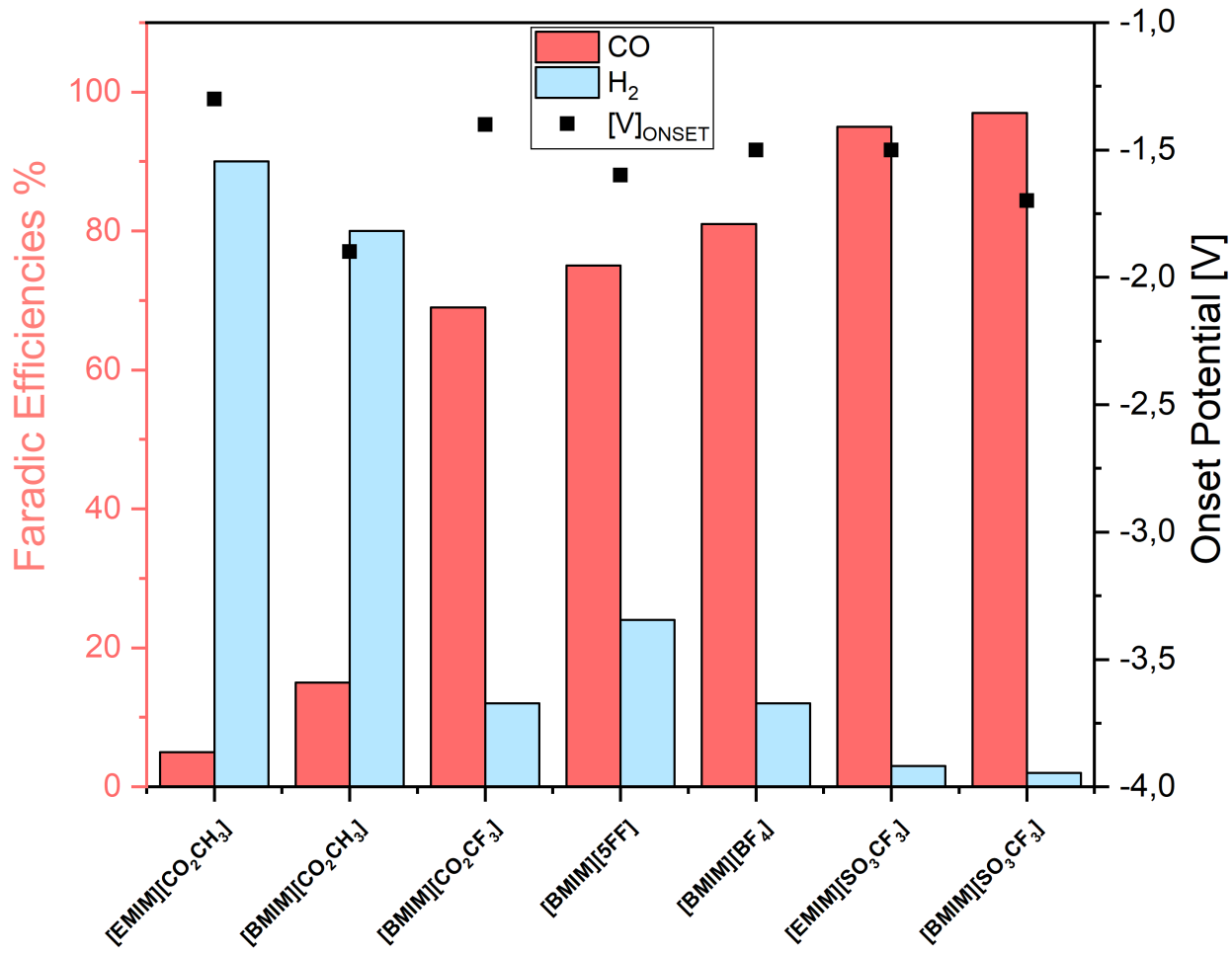




✓ ***CP's highlights:*** comparing the CP's curves, for the same anion with EM
with BMIM. Probably this trend is due to two aspects:
1- A more convenient orientation reached by a shorter cation alkyl chain on t
2- It can be linked to the conductivity of the catholyte. Catholyte conductivitie
[EMIM][SO_3CF_3] solutions are higher than **[BMIM][CO_2CH_3]** and **[BMIM]**

Results and discussion

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



✓ ***[V]o***

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✓ ***Selec***

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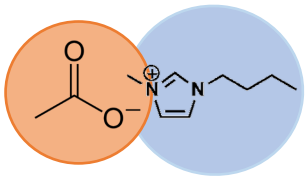
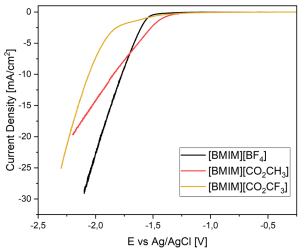
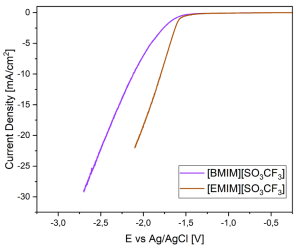
Conclusions



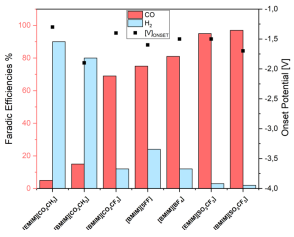
- Seven imidazolium salts were tested for the el CO.



- CO_2 solubility depends on the anion of the imid higher for fluorinated anions.



- The cation has a steric effect and an orienta decreases, the imidazolium ring finds a more co surface.



- Imidazolium salts of acetate are more selectiv [BMIM][SO_3CF_3] promotes the reduction of CO_2 used [BMIM][BF_4].

Next Steps

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

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

iii. Optimize analytical methods for other liquid and gaseous product
media.

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

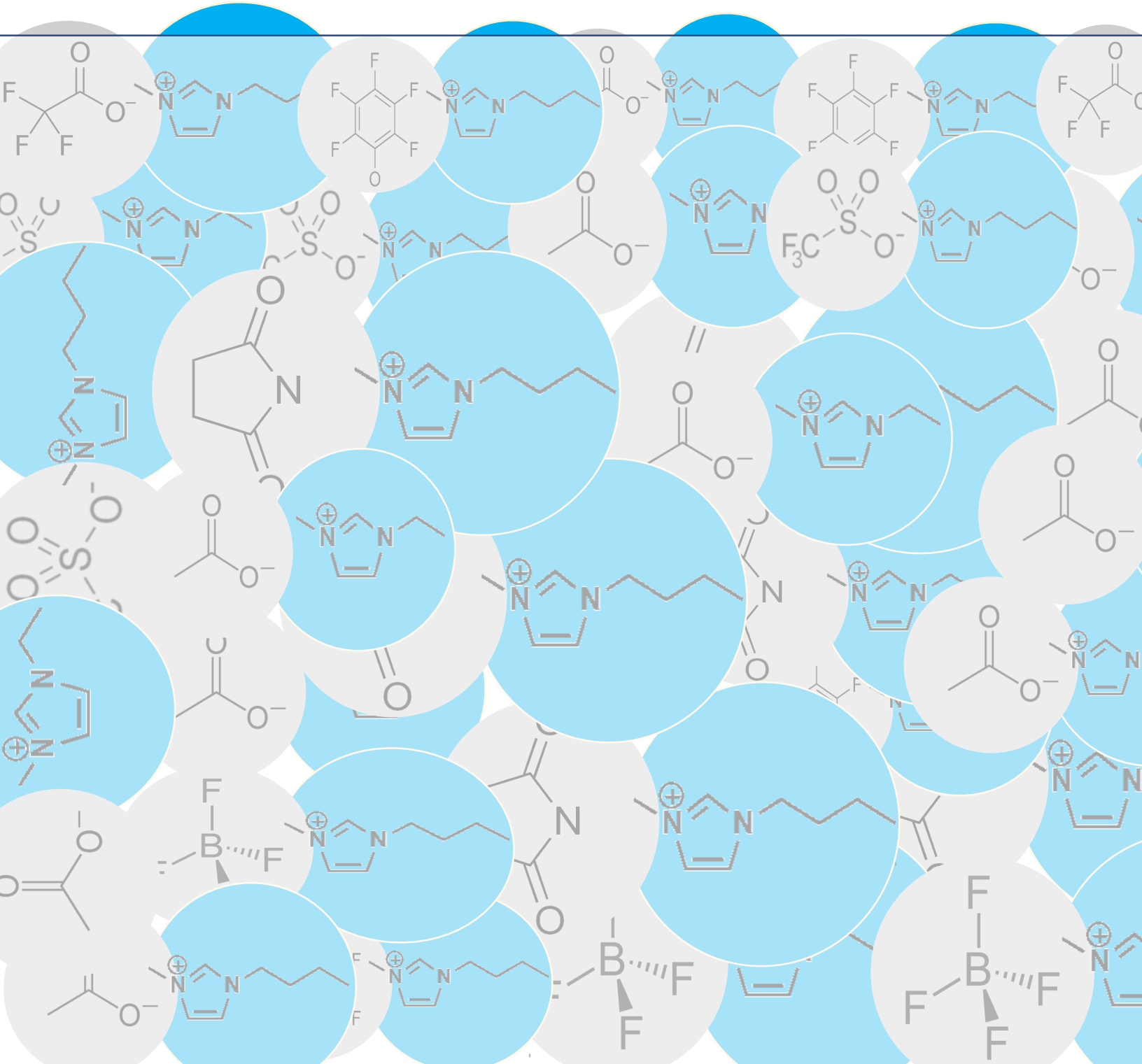
Acknowledgements

The research leading to these results has re
the European Union's Horizon 2020 Resea
Action programme under the SunCoC
(Grant Agreement No 8621

Politecnico di Torino

io·li·tec
Ionic Liquids Technologies

CREST
Catalytic Reaction Engineering for Sustainable Technologies



Materials and methods

Anolyte: 0,1M KOH aqueous solution.

Anode: **Ni mesh**

MFC

Anolyte: 0,1 M KOH

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

Transparent Bipolar membrane (TBM) pr the mixing of the anolyte and catholyte sol

H-type cell configuration

Materials and methods

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
- MeCN has a lower molecular weight than m solvents
- Guarantees high conductivity
- Low viscosity of the final solution

Transparent Bipolar membrane (TBM) pr
the mixing of the anolyte and catholyte sol

H-type cell configuration

Materials and methods

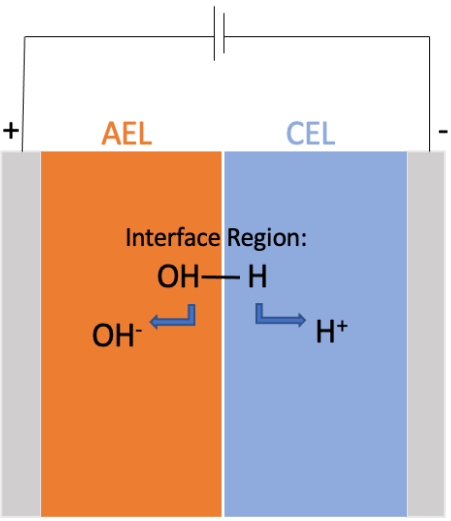
MFC

AEL: Anion exchange layer
CEL: Cation exchange layer

fumatech
functional membranes for fuel cells
BWT GROUP

Anolyte: 0,1M KOH aqueous solution.

Anode:
Ni mesh



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

CATHO
$CO_2 + 2H^+$
$2H^+ + 2e^-$

Transparent Bipolar membrane (TBM) pr
the mixing of the anolyte and catholyte sol

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 princi