Ionic Liquid Based Sorbents for Acidic Gas Capture.

AFS: FILTCON 2018 Conference

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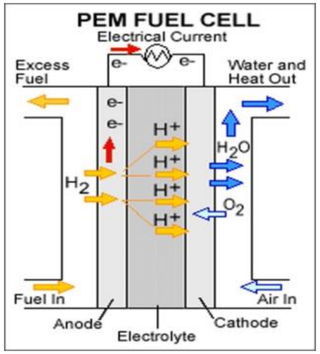
Outline

- Motivation of Research
- Background
  - Fuel Cell Air Contaminants Filtration
  - Ionic Liquids in Gas Contaminant Capture
- Experimental
  - Preparation of Supported Ionic Liquid Sorbents
  - Gas contaminant Sorption Testing
- Results and Discussion:
  - 1-ethyl-3-methylimidazolium acetate supported on activated carbon.
  - Single Gas contaminant Sorption: SO_2
  - Mixed Gas Contaminant Sorption: SO_2 and NO_2
- Conclusion
- Acknowledgements

Motivation

Development of advanced air filtration materials for fuel cell operations in harsh environments.

- Gaseous air contaminants (SO_x, NO_x, H_2S and VOCs) are detrimental to fuel cells.
- Potential of supported ionic liquids materials in reversible acidic gas capture.



Stringent fuel cell air requirements
High air flow rates
Low pressure drop
Low air pollutant tolerant levels

Goal: Development of high performance, reversible air contaminant sorbents.

Background: Fuel Cell Air Filtration

Classic PEM Fuel Cell Air Contaminant Filters.

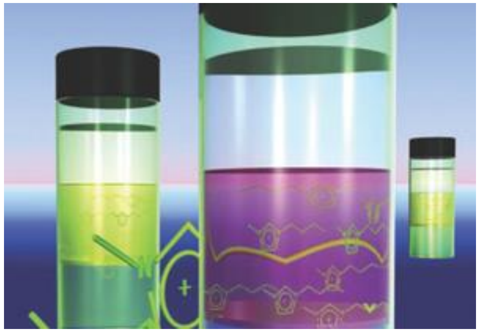
- Combine both dust and gas contaminant filtration
- Contains activated carbon impregnated with chemicals
  - Activated carbon effective for VOCs
  - Chemicals for effective removal of acidic gases, especially SO_2
- Low breakthrough capacity under harsh conditions
- Non reversible

Xuan Cheng et. al, Journal of Power Sources 165 (2007) 739–756; Xiaowei Ma et. al, Journal of Power Sources 175 (2008) 383–389

Background: Ionic Liquid Based Sorbents for Air Purification

Characteristics of ionic liquids

- Negligible volatility
- Large liquidus range: 25-400 °C
- High viscosity
- Non flammable
- Tunable chemical properties



Advantages of IL in gas absorption

- Potential for reversible gas absorption
- Non volatile
- High gas pollutant sorption kinetics

Challenges of Bulky IL in gas sorption

- Poor gas contaminant permeation into the bulky
- Poor gas pollutant selectivity

Ionic liquid supported onto high surface area porous materials.

✓ Increase sorption kinetics, capacities and reduce sorbent waste.

B. Kirchner, Topics in current chemistry, in: B. Kirchner (Ed.) Ionic liquids, Springer-Verlag new york, 2009, pp. 40.
P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH Verlag, Weinheim, 2003.
http://www.chem.uniroma1.it,

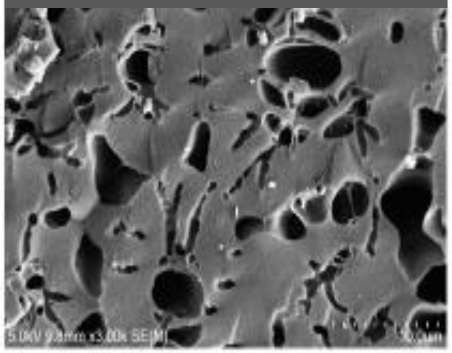
Background: Ionic Liquid Syntheses Methods

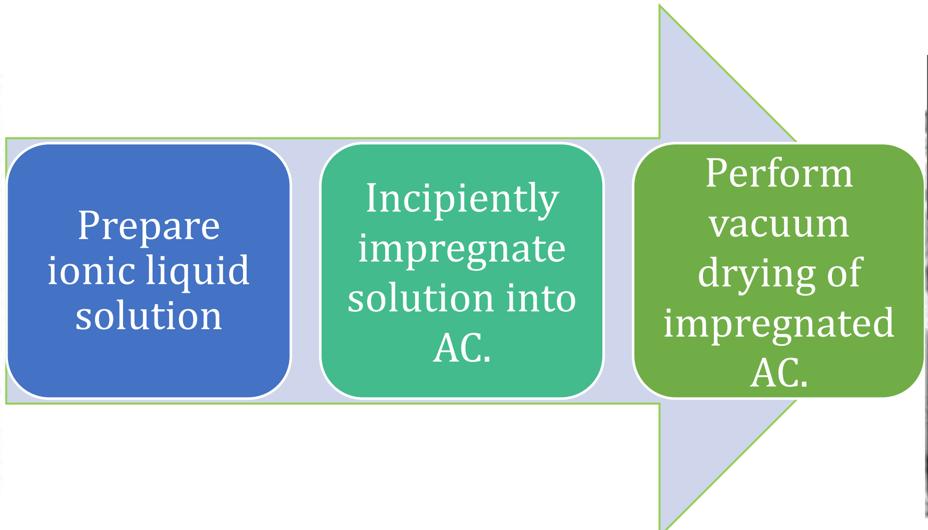
- Metathesis reactions:
  - [Cat][X] + MA ⟶ [Cat][A] + MX, M=H^+, $[metal]^+$, $NR4^+$; X = Halide ion
  - Cation halide salts where reacted with either free acid of anion, organic salt or ammonium salt .
  - Room temperature, 24 hour reaction.
- Neutralization reactions:
  - [R][OH] + MA ⟶ [R][A] + H_2O
  - Cation hydroxide reacted with free acid of anion
  - Room temperature, 24 hours.
- Characterizations: Performed using NMR, FTIR, TGA-DSC

B. Kirchner, Topics in current chemistry, in: B. Kirchner (Ed.) Ionic liquids, Springer-Verlag new york, 2009, pp. 40.
P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH Verlag, Weinheim, 2003.

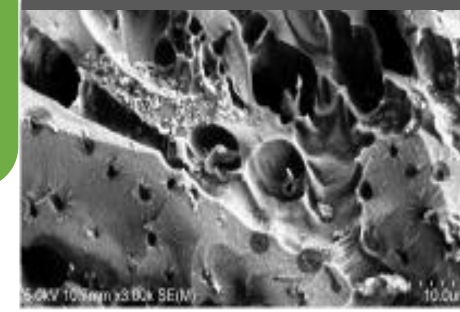
Experimental: Process of Supporting Ionic Liquid onto Porous Materials

Pure activated carbon

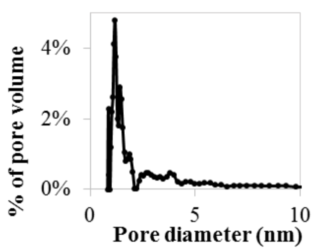


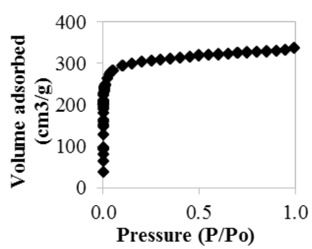


Ionic liquid impregnated activated carbon (EMA)



- SEM images of pure and ionic liquid impregnated activated carbon (AC)





- Microporous and mesoporous activated carbon
  - Pore volume> 0.48 cm^3/g
  - Surface area >1000 cm^2/g

Impregnated AC maintains porosity after ionic liquid impregnation process.

Severa, G., et al., SO_2 sorption by activated carbon supported ionic liquids under simulated atmospheric conditions. Chemical Engineering Journal, 2015. **265**: p. 249-258.

Experimental: Gas Contaminant Sorption Testing

Experimental conditions.

- 5-30 LPM purified air
- 2-15 ppm acidic gas contaminants (SO_2 and NO_2)
- 20-80 % RH @ 25 ^oC.
- 3 g samples.

Measurements

- Break through times
- Inlet and outlet gas pollutant concentrations (C_o and C_t)

Custom made air filtration material gas sorption testing stand.

Sulfur dioxide and nitrogen dioxide sorption testing of supported ionic liquids

Experimental: Impregnation of Ionic Liquids on Activated Carbon

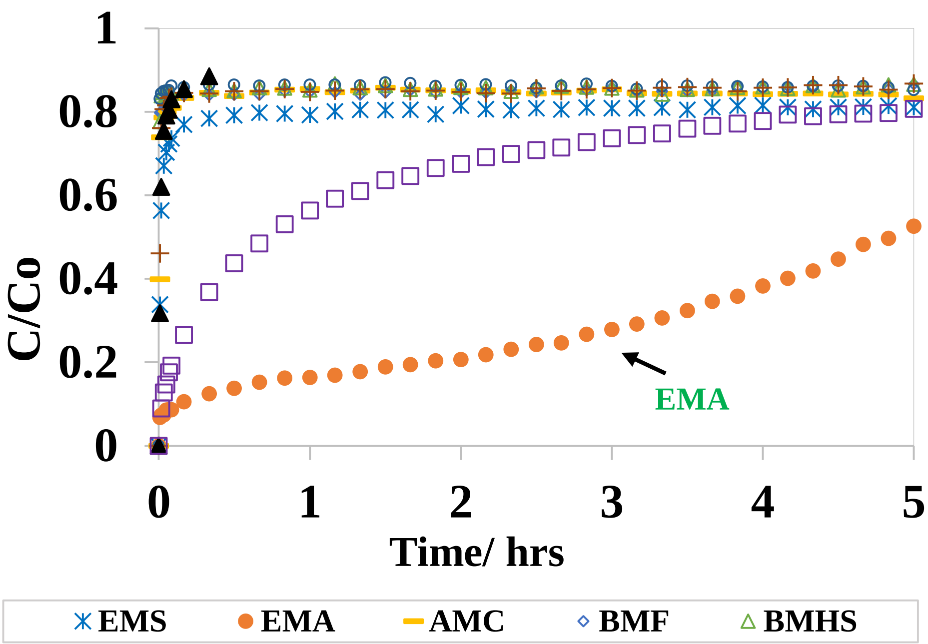
Ionic liquid	Ionic Liquid Impregnated AC sorbent ID
1-ethyl-3-methylimidazolium acetate	EMA
1-ethyl-3-methylimidazolium lactate	EML
1-ethyl-3-methylimidazolium methyl sulfate	EMS
1-ethyl-3-methylimidazolium hydrogen sulfate	EMHS
1-butyl-3-methylimidazolium hydrogen sulfate	BMHS
1-butyl-3-methylimidazolium tetra fluoroborate	BMF
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	HMN
1-hexyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate	HMS
1-allyl-3-methylimidazolium chloride	AMC

AC impregnated with 36-38 wt% ionic liquid

- Most of selected IL were previously reported to have high gas pollutant absorption capability in pure or ideal gas pollutant mixtures.

Z. Lei, C. Dai, B. Chen, Chemical Reviews 114 (2013) 1289-1326.

Results: Screening of Select IL Impregnated Sorbents



- Highest sorption capacity and break through time from 1-ethyl-3-methylimidazolium acetate impregnated activated carbon (**EMA**).

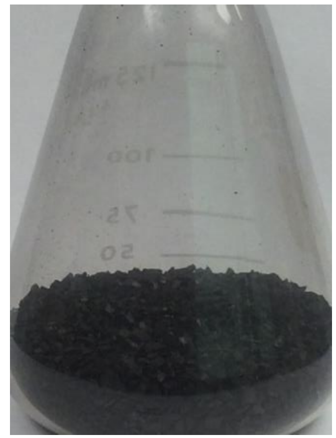
❑ EMA chosen as model impregnated ionic liquid sorbent for detailed study.

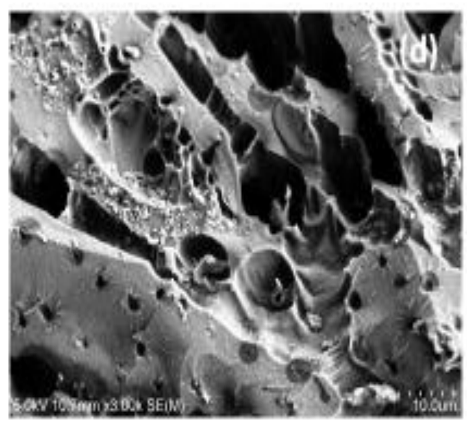
Experimental conditions:

- ❖15 LPM purified air
- ❖15 ppm SO_2 contaminants
- ❖50 % RH @ 25 ^{o}C.
- ❖3 g samples.

- **Break through times:**
  - EMA>EML>HMN, EMS>AMC, HMS, BMHS >EMHS >BMF.

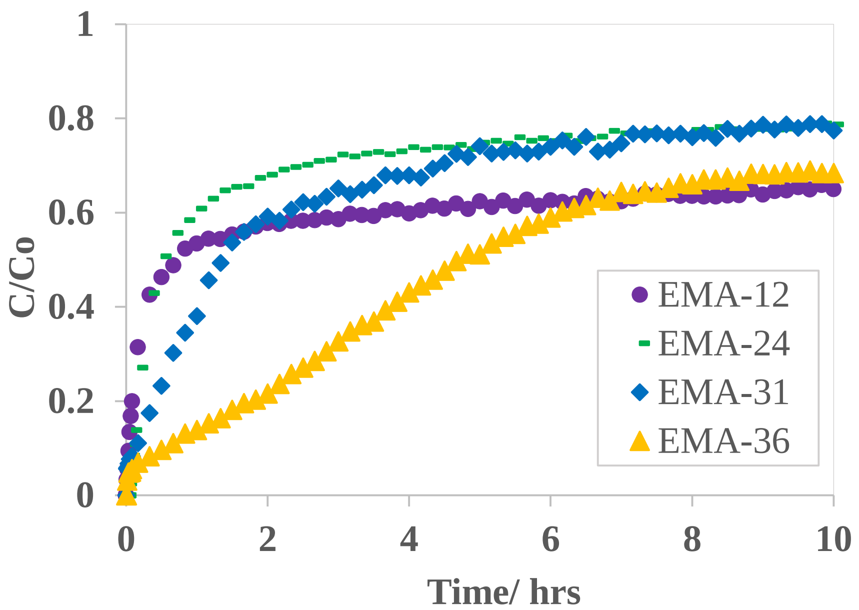
Results: Study of 1-ethyl-3-methylimidazolium Acetate Impregnated Activated Carbon sorbent





[C_2mim][Ac]-Activated carbon sorbents (EMA) chosen as model impregnated ionic liquid sorbent for detailed study.

Results: Effect of Ionic Liquid Loading on SO_2 Sorption



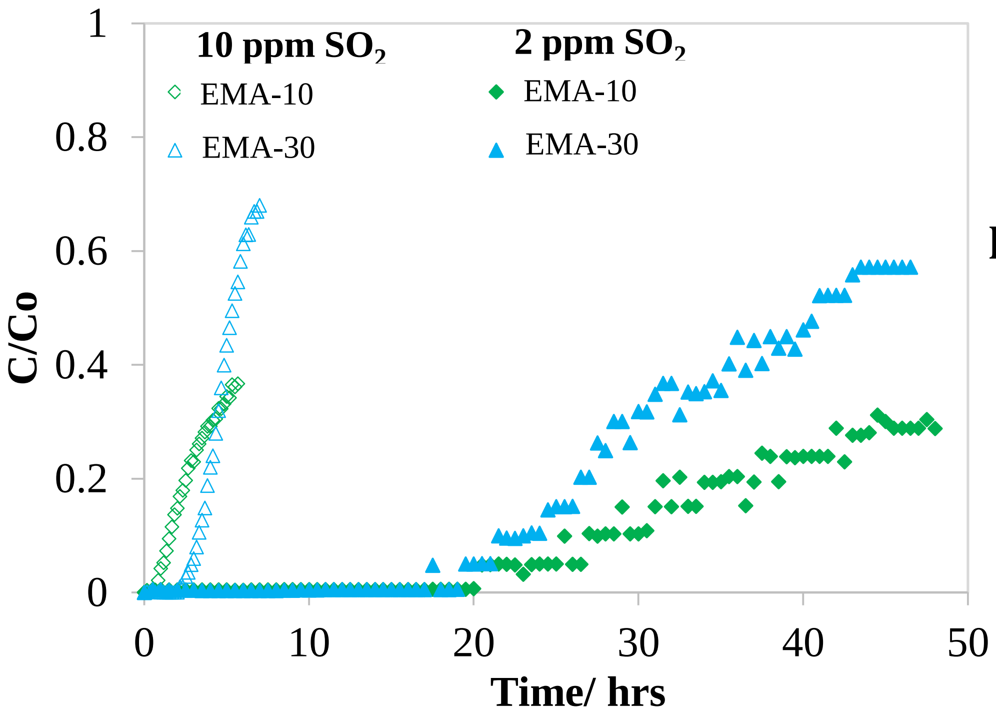
Wt % IL Loading	Break through time (min)
12	3
24	5
31	13.5
36	53.5

Experimental conditions:

- ❖ 15 LPM purified air
- ❖ 15 ppm SO_2
- ❖ 50 % RH @ 25 ^oC.

- **Higher IL loaded sorbents show better sorption capacity and breakthrough time.**

Results: Effect of SO_2 Concentration on Sorption

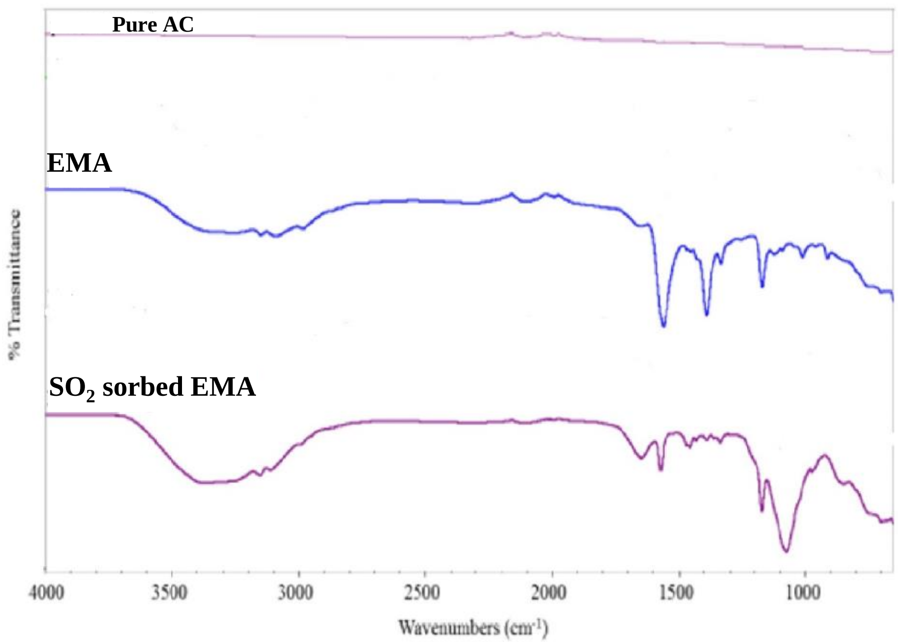


Experimental conditions:

- ❖ 30 LPM purified air
- ❖ 50 % RH @ 25 °C.

Shorter sorbent breakthrough times at higher SO_2 concentration.

Results: Characterization of SO_2 Gas Absorption by FTATR

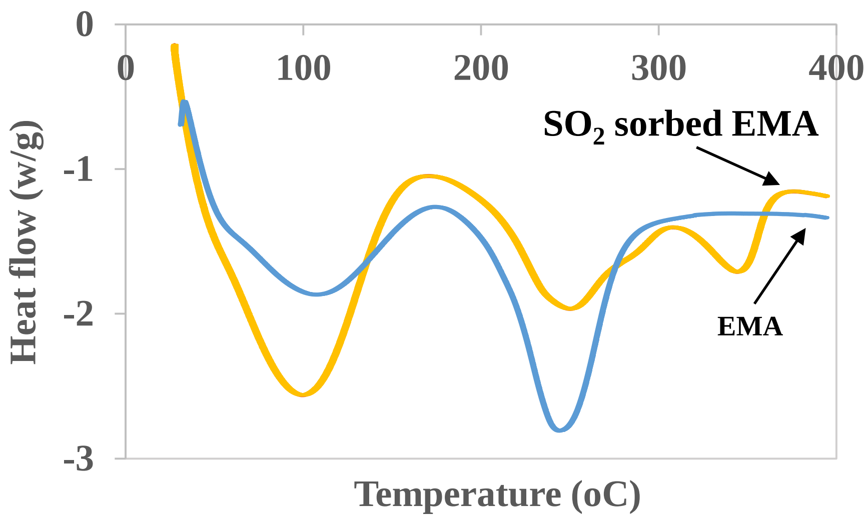


- New peaks observed after SO_2 sorption.
  - $\upsilon_{S=O}$: 1430 cm^{-1} – 1470 cm^{-1}.
  - $\upsilon_{S\text{-}O}$: 973, 1070, 1170, 1220 cm^{-1}.

S-O vibrational frequencies indicate presence of chemically bound sulfur oxide species.

Severa, G., et al., SO_2 sorption by activated carbon supported ionic liquids under simulated atmospheric conditions. Chemical Engineering Journal, 2015. **265**: p. 249-258.

Results: Characterization of EMA SO_2 Gas Absorption by DSC

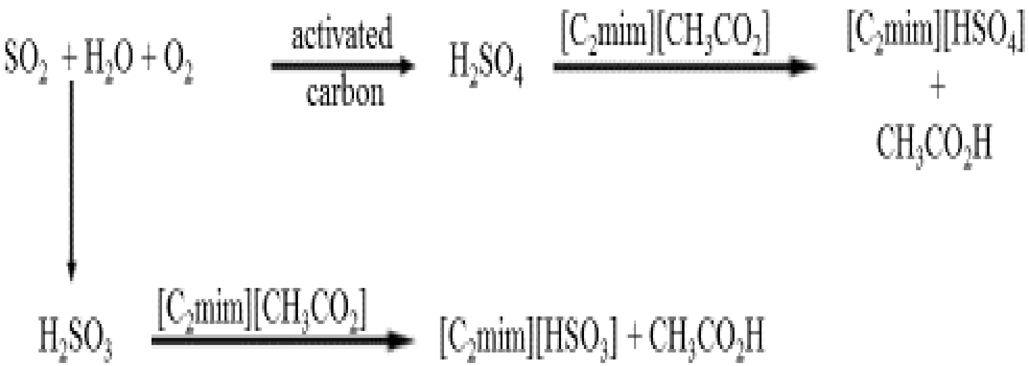


Peak temp region (°C)	Assignment
100	Loss of moisture
240	Ionic liquid decomposition
270	Loss of chemically bound SO_x
350	Loss of sulfuric acid

Some products of EMA SO_2 sorption very stable.

Severa, G., et al., SO_2 sorption by activated carbon supported ionic liquids under simulated atmospheric conditions. Chemical Engineering Journal, 2015. **265**: p. 249-258.

Results: Mechanism of SO_2 Capture by EMA: Chemisorption



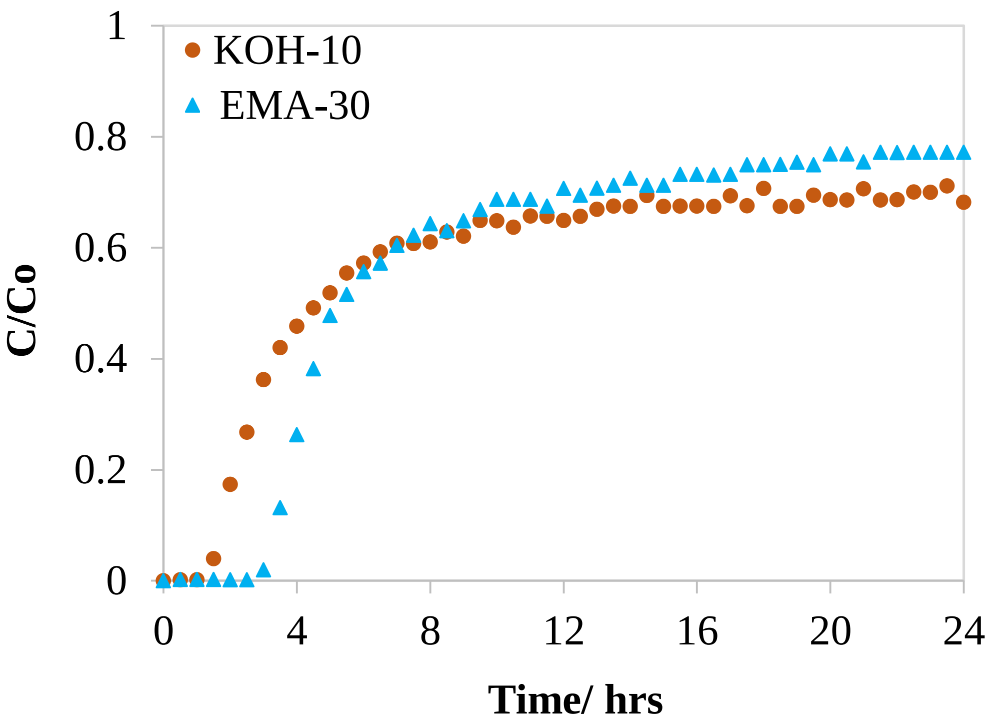
I. Absorption/Adsorption of SO_2 into IL and onto AC surface of EMA.
II. Conversion of sorbed SO_2 to sulfate and sulfites (acids).
III. Protonation of acetate by the strong acids.
IV. Displacement of protonated acetate by the weak bases, HSO_3^- and HSO_4^-

Mechanism derived from FTIR, thermal analysis and NMR data.

Severa, G., et al., SO_2 sorption by activated carbon supported ionic liquids under simulated atmospheric conditions. Chemical Engineering Journal, 2015. **265**: p. 249-258.

Results: Comparison of EMA and 10 wt% KOH-AC in SO_2 Removal

Promising Supported Ionic Liquid Material for SO_2 capture



Experimental conditions:

- 30 LPM purified air
- 5 ppm SO_2
- 50 % RH @ 25 °C.

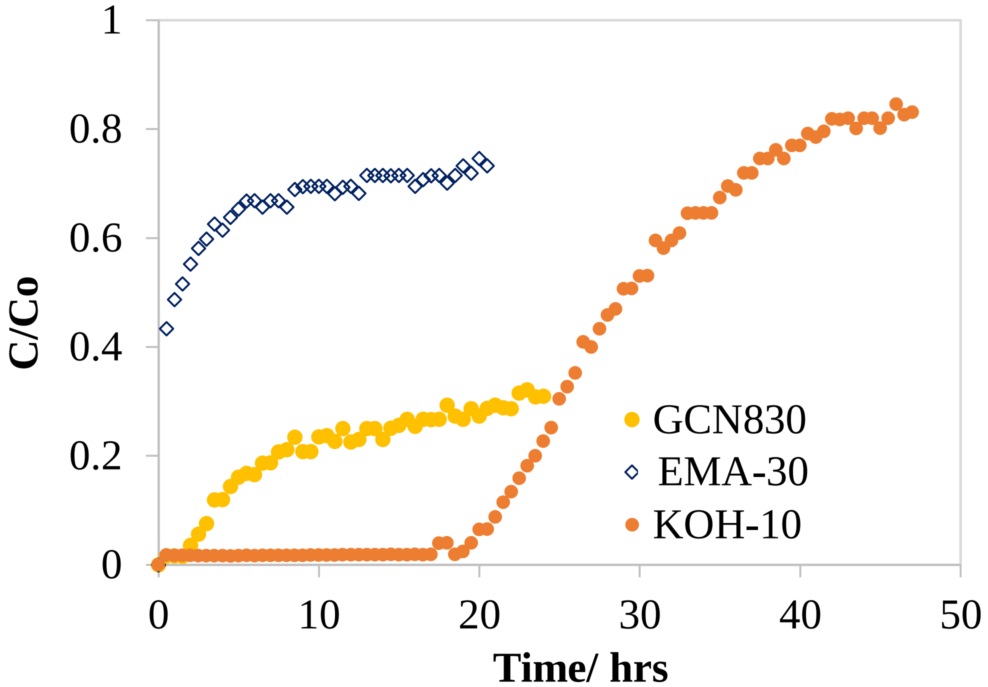
EMA sorbent performed better than the 10 wt% KOH-AC impregnated activated carbon material.

Severa, G., et al., SO_2 sorption by activated carbon supported ionic liquids under simulated atmospheric conditions. Chemical Engineering Journal, 2015. **265**: p. 249-258.

Results: Comparison of NO_2 Sorption by EMA and 10 wt% KOH-AC

Experimental conditions:

- ❖ 30 LPM purified air
- ❖ 5 ppm NO_2
- ❖ 50 % RH @ 25 °C.

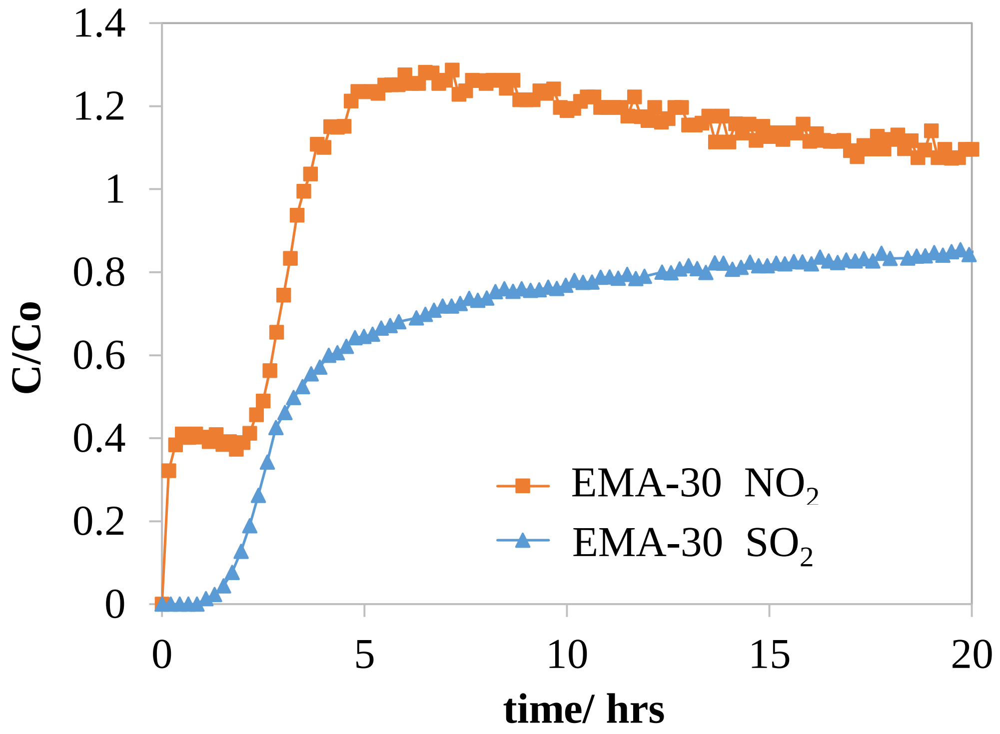


EMA shows poor NO_2 sorption compared to 10 wt% KOH and pure activated carbon.

Results: Mixed Gas Contaminant Studies SO_2 and NO_2 Selectivity

Experimental conditions:

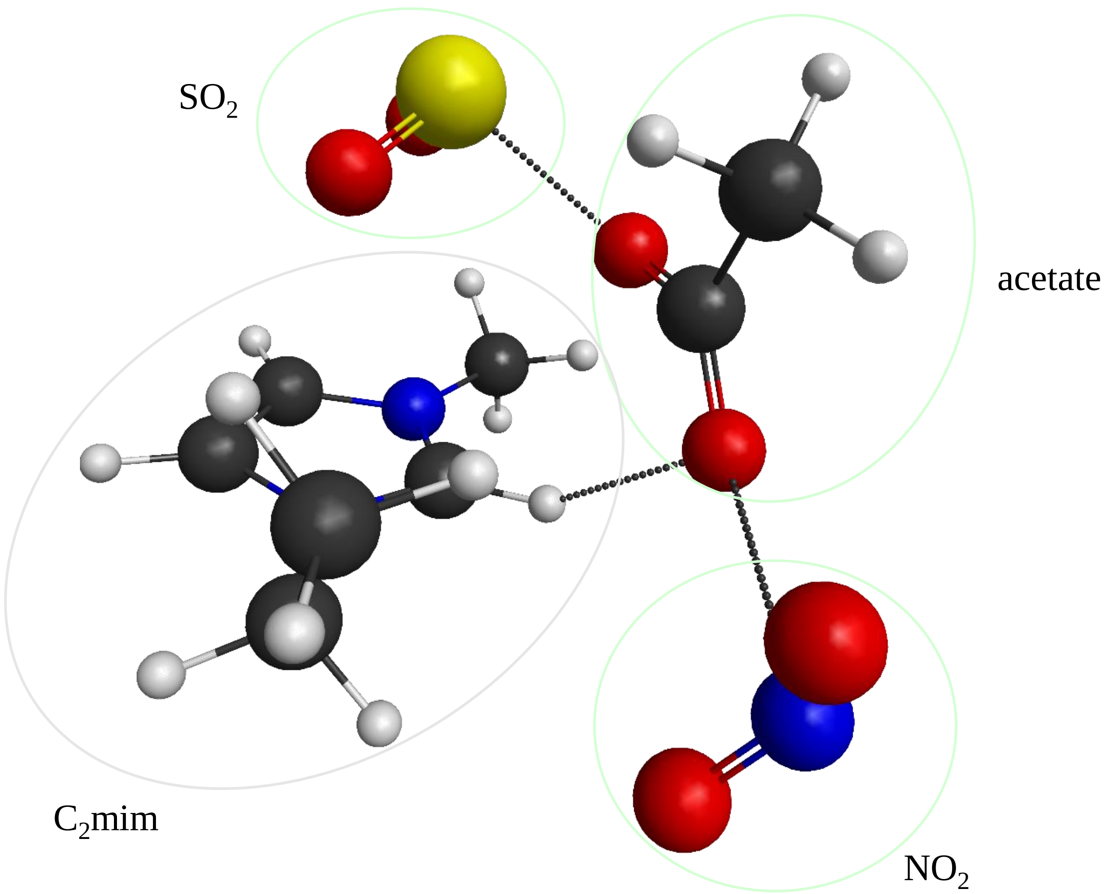
- ❖ 30 LPM purified air
- ❖ 5 ppm SO_2 and 5 ppm NO_2
- ❖ 50 % RH @ 25 °C.



EMA shows higher selectivity and sorption performance for SO_2 compared to NO_2.

Results: DFT Molecular Modelling

GAMESS
DFT: B3LYP
6-311G basis set

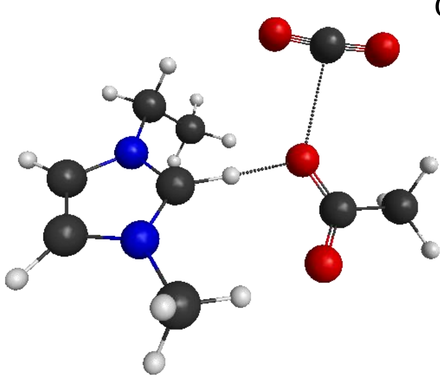


Determine ionic liquid, $[C_2mim][Ac]$, binding affinity for SO_2 and NO_2.

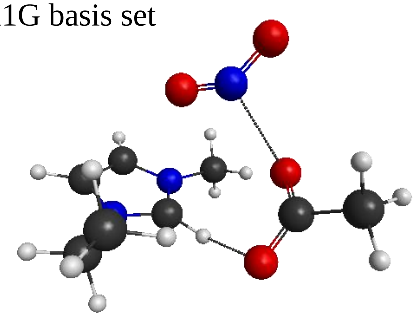
Results: Interaction of the Ionic Liquid $[C_2mim][Ac]$ with SO_2 or NO_2

$[C_2mim][Ac]$: Stronger SO_2 binding compared to NO_2

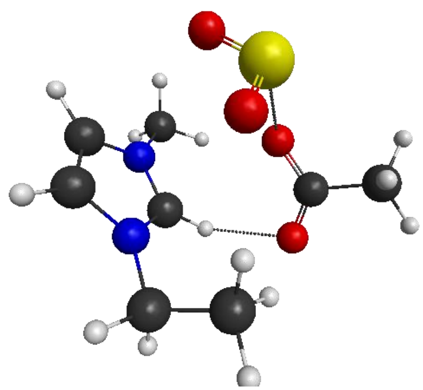
GAMESS DFT: B3LYP
6-311G basis set



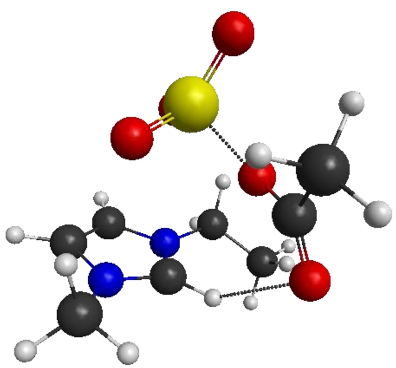
(a) CO_2



(b) NO_2



(c) SO_2



(d) SO_3

Atom colors: black (**C**), blue (**N**), red (**O**), yellow (**S**) and white (**H**).

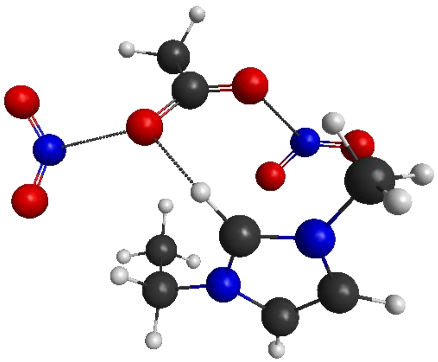
Lower SO_2 binding enthalpy compared to NO_2

Adsorbate XO_n on $[C_2mim][Ac]$	ΔH (298 K)	ΔG (298 K)
CO_2	-34	-3
NO_2	-30	5
SO_2	-99	-48
SO_3	-184	-127

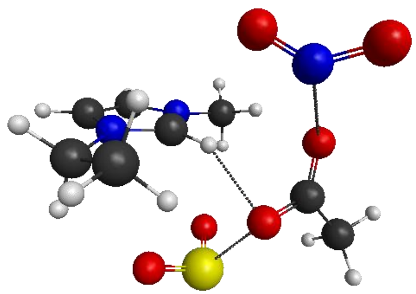
Adsorption enthalpies and Gibbs energies (in kJ/mol) for XO_n binding

Results: Simultaneous Interaction of the ionic liquid $[C_2mim][Ac]$ with SO_2 and NO_2

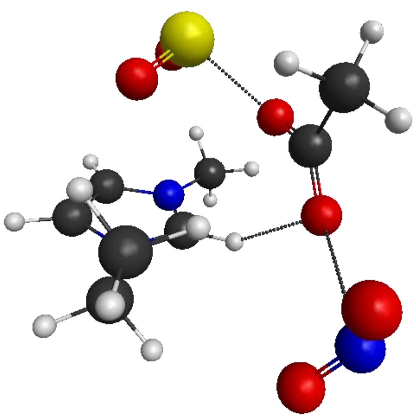
Higher affinity for SO_2 than NO_2 for ionic liquid $[C_2mim][Ac]$



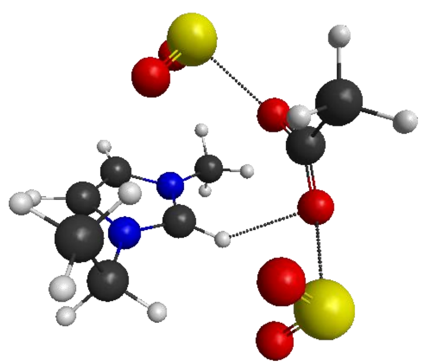
(a) $NO_2{\cdot}NO_2$



(b) $NO_2{\cdot}SO_2$



(c) $SO_2{\cdot}NO_2$



(d) $SO_2{\cdot}SO_2$

Atom colors: black (**C**), blue (**N**), red (**O**), yellow (**S**) and white (**H**).

$[C_2mim][Ac]$: Stronger SO_2 binding compared to NO_2

Substrate	Adsorbate YO_2	ΔH (298 K)	ΔG (298 K)
$[C_2mim][Ac]$	1st NO_2	-30	5
$[C_2mim][Ac]{\cdot}NO_2$	2nd NO_2	-41	11
$[C_2mim][Ac]{\cdot}SO_2$	2nd NO_2	-31	12
$[C_2mim][Ac]$	1st SO_2	-99	-48
$[C_2mim][Ac]{\cdot}NO_2$	2nd SO_2	-91	-34
$[C_2mim][Ac]{\cdot}SO_2$	2nd SO_2	-71	-25

Adsorption enthalpies and Gibbs energies (in kJ/mol) for YO_2 binding with $[C_2mim][Ac]$ and $[C_2mim][Ac]{\cdot}XO_2$ where X and Y are N or S atoms

Conclusion: Main Takeaways

- Supported ionic liquids absorbents can perform greater than potassium hydroxide-activated carbon materials.
- Potential for synergistic SO_2 sorption by ionic liquid and activated carbon support.
- Possible to determine mechanisms of SO_2 sorption by ionic liquids materials using a combination of techniques.
- Important to evaluate potential ionic liquids absorbent materials under simulated real world conditions.
- Computational work confirm experimental data of higher selectivity for SO_2 compared to NO_2 by EMA ionic liquid.

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Thank You

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