Solubility of Carbon Dioxide in Mixtures of Polymer/Ionic-Liquid

Tung S. Nguyen, Shayan Kaviani, Siamak Nejati

Department of Chemical & Biomolecular Engineering, University of Nebraska – Lincoln

University of Nebraska Lincoln | Nebraska Center for Energy Sciences Research

Nebraska Public Power District

Introduction

Energy consumption worldwide grew by 2.3% in 2018, nearly twice an average rate of growth since 2010. Consequently, global energy-related Carbon Dioxide (CO_2) emissions increased to 33.1 Gt CO_2 and hit a new record (highest since 2013). The global average annual CO_2 concentration in atmosphere averaged 407.4 ppm in 2018.

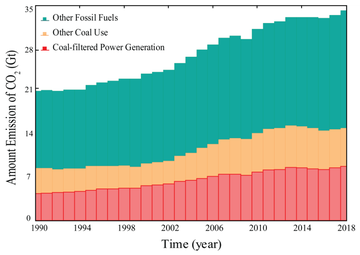

Figure 1: Global energy-related Carbon Dioxide (CO_2) Emissions statistics, 1990 – 2018 [1].

This research investigates the solubility of CO_2 in 1-ethyl-3-methyl-imidazolium bis (trifluoromethanesulfonyl) imide ([EMIM][Tf_2N]) / Poly(Vinylidene Fluoride-co-hexafluoropropylene) (PVDF-HFP) composite thin films on Quartz Crystal (QC), using a novel technique based on adsorption on Quartz Crystal Microbalance (QCM).

Ionic Liquids (Ils) have been introduced as novel solvents and are being explored for CO_2 capture due to their unique properties: high CO_2 solubility, nonvolatility, high thermal stability, and tunability of structure for a wide range of operating condition.

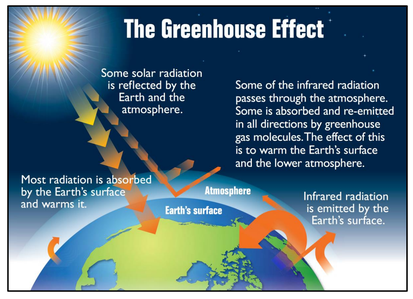

Figure 2: The Greenhouse Effect Explained [2].

Materials and Methods

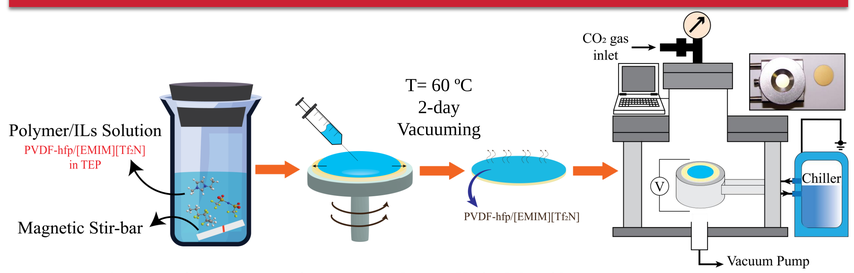

Figure 3: Schematic of preparations of PVDF-HFP/[EMIM][Tf_2N] thin film on QC (left); Experimental setup used for the evaluation of sensor performances (right).

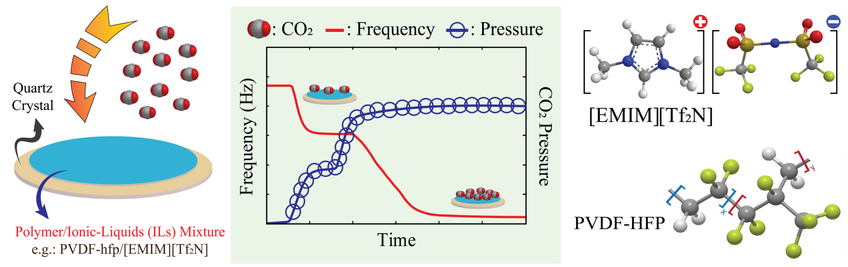

Figure 4: Schematic of evaluating Solubility of CO_2 on thin film of PVDF-HFP/[EMIM][Tf_2N] coated on Quartz Crystal (left); PVDF-HFP/[EMIM][Tf_2N] structures (right).

Results

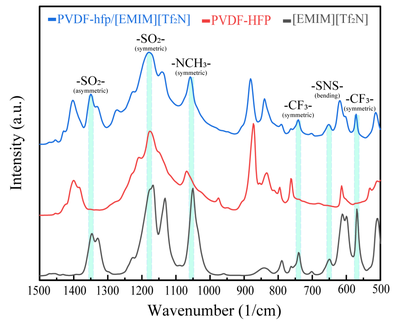

Figure 5: Fourier-transform Infrared Spectroscopy (FITR) of [EMIM][Tf_2N], PVDF-hfp, and PVDF-hfp /[EMIM][Tf_2N].

- Amount of adsorbed CO_2 mole on a coated thin film is valuated by the quotient of mass, from *Eq. 1* [4], and molecular weight of gas.
- Mass of coated thin film is measured with the high 0.0001-mg precision Microbalance.

$$\frac{m_{CO_2}}{m_{film}} = \frac{f_{wet\ film} - f_{dry\ film}}{f_{dry\ film} - f_{crystal}} \quad (1)$$

- We successfully spin-coated thin, ranged from 300–500 nm, films PVDF-hfp / [EMIM][Tf_2N] on Quartz Crystal and confirmed its characterization via ATR-FTIR.
- The CO_2 solubility is evaluated under isothermal conditions under different Compositions of Polymer/ Ionic Liquid (IL) and Gas Pressure.
- Frequency of empty, dry, and wet film on QC are observed to measure adsorbed weight of CO_2.

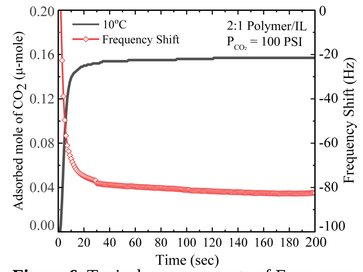

Figure 6: Typical measurements of Frequency of PVDF-HFP/[EMIM][Tf_2N] and Adsorbed mole of CO_2.

Discussions and Conclusion

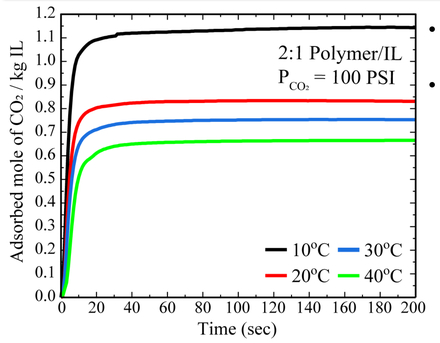

Figure 7: Adsorbed mole of CO_2 at 100 PSI with 4 different range of temperature

- Based on Henry's law constant, gas solubility, dissolved in Polymer/IL, is proportional to its partial pressure applied on the thin film. Henry's constant increases with increase in temperature, which delivers a decrease in gas solubility.

- Adsorbed mole of CO_2, per kg of IL, reaches largest at the lowest temperature.
- Furthermore, under isothermal condition, gas solubility increases as an amount of adsorbed mole of CO_2, per kg of IL, increases.

$$K_H = P_{sat}\alpha_i \ (2)$$

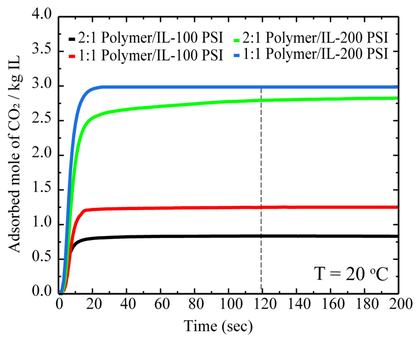

Figure 8: Adsorbed mole of CO_2 at different Pressures and Compositions under Isothermal conditions.

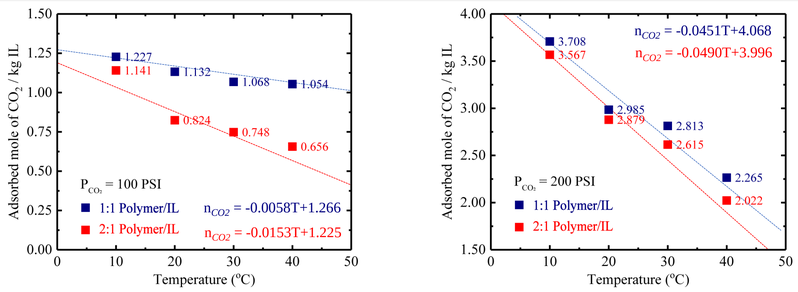

Figure 9: Adsorbed mole of CO_2, per kg IL, on different film compositions and at different pressures

- Gas sorption isotherms in 1:1 and 2:1 Polymer/IL composites show trends of decreasing gas solubility with increases of temperature, depicted in **Figure 9.** This is due to a decreases in volume of gas adsorbed on the coated thin film surface.

Conclusions

- Gas solubility in PVDF-HFP/[EMIM][Tf_2N] thin film coated on Quartz Crystal is successfully evaluated at four different temperatures with two different pressures.
- The highest adsorbed mole of CO_2 is 3.708 per kg IL valuated at 200 PSI and 10ºC, and the lowest value is 0.656 mol of CO_2 per kg IL at 100 PSI and 40ºC. These results follow Henry's law sorption isotherm conditions.

Future Works

Gas solubility, under isothermal conditions, is further studied by evaluating the effects of thin film thickness, varied compositions, and material of Polymer/Ionic Liquids, with Fick's Diffusion and Henry's Law fitting models.

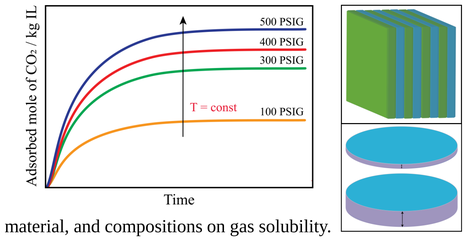

Figure 10: Study of Effect of film thickness, material, and compositions on gas solubility.

Acknowledgements

Authors would like to acknowledge Mahdi Ghaleni for help with QCM setup and give gratitude to the kind support by Nebraska Public Power District (NPPD) through the Nebraska Center for Energy Sciences Research (NCESR) at the University of Nebraska-Lincoln.

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