STUDY OF THE IMIDAZOLIUM-BASED IONIC LIQUID – Ag ELECTRIFIED INTERFACE ON THE CO_2 ELECTROREDUCTION BY SUM FREQUENCY SPECTROSCOPY.

NATALIA GARCIA REY, DANA DLOTT, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

Imidazolium based ionic liquids (ILs) have been used as a promising system to improve the CO_2 electroreduction at lower overpotential than other organic or aqueous electrolytes[1]. Although the detailed mechanism of the CO_2 electroreduction on Ag has not been elucidated yet, we have developed a methodology to study the electrified interface during the CO_2 electroreduction using sum frequency generation (SFG) spectroscopy in combination with cyclic voltammetry[2]. In this work, we tuned the composition of imidazolium-based ILs by exchanging the anion or the functional groups of the imidazolium. We use the nonresonant SFG (NR-SFG) to study the IL-Ag interface and resonant SFG (RES-SFG) to identify the CO adsorbed on the electrode and monitor the Stark shift as a function of cell potential. In previous studies on CO_2 electroreduction in the IL: 1-ethyl-3-methylimidazolium tetrafluorborate (EMIM-BF_4) on Ag, we showed three events occurred at the same potential (-1.33 V vs. Ag/AgCl): the current associated with CO_2 electroreduction increased, the Stark shift of the adsorbed atop CO doubled in magnitude and the EMIM-BF_4 underwent a structural transition[3]. In addition, we also observed how the structural transition of the EMIM-BF_4 electrolyte shift to lower potentials when the IL is mixed with water. It is known that water enhances the CO_2 electroreduction producing more CO[4]. Moreover, the CO is adsorbed in multi-bonded and in atop sites when more water is present in the electrolyte.

[1]Lau, G. P. S.; Schreier, M.; Vasilyev, D.; Scopelliti, R.; Grätzel, M.; Dyson, P. J., New Insights into the Role of Imidazolium-Based Promoters for the Electroreduction of CO_2 on a Silver Electrode. J. Am. Chem. Soc. 2016, 138, 7820-7823. [2]García Rey, N.; Dlott, D. D., Studies of Electrochemical Interfaces by Broadband Sum Frequency Generation. J. Electroanal. Chem. 2016. DOI:10.1016/j.jelechem.2016.12.023. [3]García Rey, N.; Dlott, D. D., Structural Transition in an Ionic Liquid Controls CO_2 Electrochemical Reduction. J. Phys. Chem. C 2015, 119, 20892–20899. [4]Rosen, B. A.; Zhu, W.; Kaul, G.; Salehi-Khojin, A.; Masel, R. I., Water Enhancement of CO_2 Conversion on Silver in 1-Ethyl-3-Methylimidazolium Tetrafluoroborate. J. Electrochem. Soc. 2013, 160, H138-H141.