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## **PROGRAM**

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### Driving the Pathway of CO<sub>2</sub>RR by Controlling Water Concentration in Ionic Liquids

Primaggio S. Mantovi<sup>1</sup>, Leonardo D. de Angelis<sup>1</sup>, Jean C. da Cruz<sup>1</sup>, Maykon L. Souza<sup>2</sup>, Susana I. C. Torresi<sup>1</sup>, Liane M. Rossi<sup>1</sup>, Fabio H. Barros de Lima<sup>2</sup>, Roberto M. Torresi<sup>1</sup>

Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, 05508-000 São Paulo (SP), Brasil.

<sup>2</sup>Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trab. São Carlense 400, 13566-590, São Carlos (SP), Brasil.

#### primaggio@usp.br

CO<sub>2</sub>, a major greenhouse gas linked to global warming, can serve as a reagent for producing valuable molecules<sup>1</sup>. Electrocatalysis is a promising approach for CO<sub>2</sub> reduction under ambient conditions, using water to hydrogenate molecules<sup>2</sup>. However, this field faces the challenge that water also contributes to energy losses via the Hydrogen Evolution Reaction (HER)<sup>3</sup>. Ionic Liquids (ILs), molten salts at room temperature, have shown the ability to expand the Electrochemical Stability Window (ESW), enabling the possibility to work at more negative potentials<sup>4</sup>. This study demonstrates that by controlling water concentration in ILs, it is possible to mitigate the HER and to control CO<sub>2</sub>RR pathways. For instance, it was possible to apply -1.6 V vs Fc/Fc<sup>+</sup> with 20 mmol L<sup>-1</sup> of water and achieve approximately 13% of faradaic efficiency (FE) for H<sub>2</sub>. Also, comparing the products distribution, when applying -0.9 and -1.0 V vs Fc/Fc<sup>+</sup> with 80 mmol L<sup>-1</sup> of water, as shown at Figure 1B, it is possible to drive the CO<sub>2</sub>RR toward methanol and methane production. In contrast, with 20 mmol L<sup>-1</sup>, represented by Figure 1A, at the same potentials, these two products practically disappear, indicating that the intermediate \*CHO is less favorable in this situation.

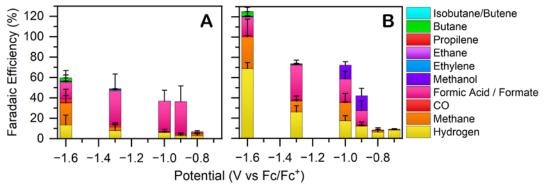


Figure 1: Faradaic efficiencies for different products from -0.7 to -1.6 V vs Fc/Fc<sup>+</sup> with (A) 20 mmol L<sup>-1</sup> and (B) 80 mmol L<sup>-1</sup> of water. The selected potentials were applied for 3 hours, and the products were determined by NMR-H and GC-FID/TCD for liquid and gaseous molecules, respectively.

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