

Supporting Information

Cyclic Voltammetry using Silver as Cathode Material: A simple method for determining (Electro)-Chemical Features and Solubility Values of CO₂ in Ionic Liquids.

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1. Experimental Details

1.1. Chemicals

Carbon dioxide, CO₂, and nitrogen, N₂, were obtained from Carburos Metálicos S.A. (purity of 99.9999 %).

All the commercially available reagents, including ILs, are of the highest purity available and are used without further purification. However, since the CO₂ solubility and diffusion coefficient is dependent on the water content of the ILs [1], when required, the purchased ILs were dried under vacuum using activated molecular sieves for 72 h in order to guarantee that the amount of water present was always less than 100 ppm.

1.2. Cyclic Voltammetry Experiments

An electrochemical conical cell equipped with a methanol jacket, which makes it possible to fix the temperature by means of a thermostat, is used for the set-up of the three-electrode system. For cyclic voltammetry experiments, the working electrode is, in all cases, a silver disk of a diameter of 1.6 mm. It is polished using a 1 μm diamond paste. The counter electrode is a Pt disk of a diameter of 1 mm. All of the potentials are reported versus an aqueous saturated calomel electrode (SCE) isolated from the working electrode compartment by a salt bridge. The salt solution of the reference calomel electrode is separated from the electrochemical solution by a salt-bridge ended with a frit made of a ceramic material, allowing ionic conduction between the two solutions and avoiding appreciable contamination. Ideally, the electrolyte solution present in the bridge (pure IL in the Ionic Liquid experiments) is the same as the one used for the electrochemical solution, in order to minimise junction potentials.

Dissolved oxygen was purged by bubbling N₂ gas through the ILs solution before the electrochemical measurement of the baseline was registered. After removing all the oxygen, CO₂ was bubbled into the selected IL. A thermal mass flow meter of modular construction with a 'laboratory style' pc-board housing (EL-FLOW® Mass Flow Meter/Controller) from Bronkhorst Hi-Tec, has been used to monitor the CO₂ concentrations in the solution. Control valves are integrated to measure and control a gas flow from: lowest range 0.2 up to 10 ml/min.

The error associated with the potential values is less than 5 mV. The ohmic drop can be one of the main sources of error when ILs are used as solvents, since they are more resistive media than aprotic polar solvents with 0.1 M concentration of supporting electrolyte. In order to minimise the ohmic drop effects, the electrode used as working electrode is 1.6 mm diameter and the scan rates investigated were in the range 0.1 – 1 V s⁻¹. Positive feed-

back iR compensation was used throughout. Typically compensated resistances were 0.5-2.0 k Ω , depending on the electrode location in the electrochemical cell. [2-4]

1.3. Instrumentation

The cyclic voltammetry at low scan rates was performed using a PAR 273A potentiostat controlled by a computer. Power Suite software was used for data acquisition and data handling.

2. Cyclic Voltammograms

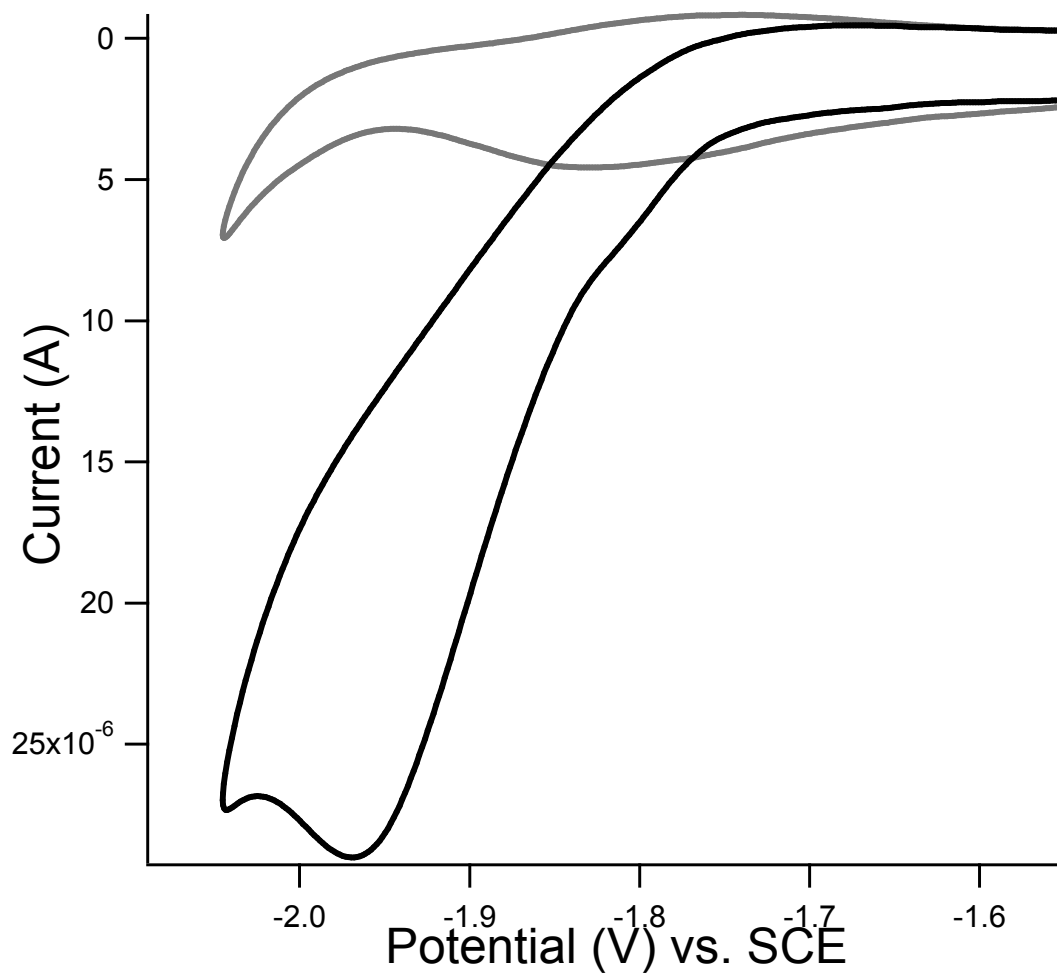


Figure S1. Cyclic Voltammograms (scan rate of 0.5 Vs^{-1}), at $25 \text{ }^\circ\text{C}$, on a silver electrode showing the base line (grey line) and the reduction of CO_2 (7.0 mM) at $25 \text{ }^\circ\text{C}$ in [EMIM] TFSI.

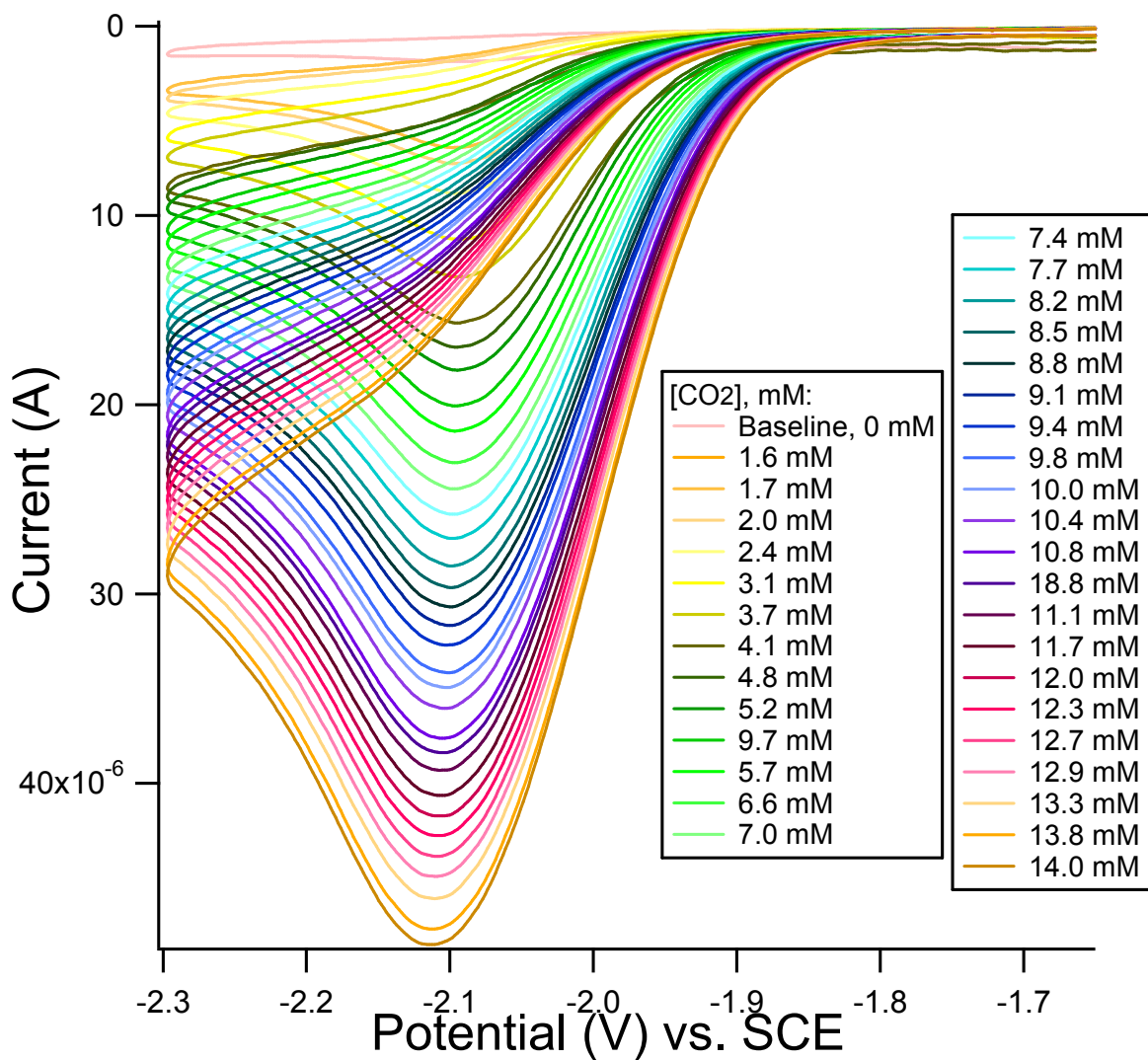


Figure S2. Cyclic Voltammograms (scan rate of 0.5 Vs⁻¹) at 25 °C on a silver electrode showing baseline and the reduction of CO₂ at different concentration in [PP13]TFSI.

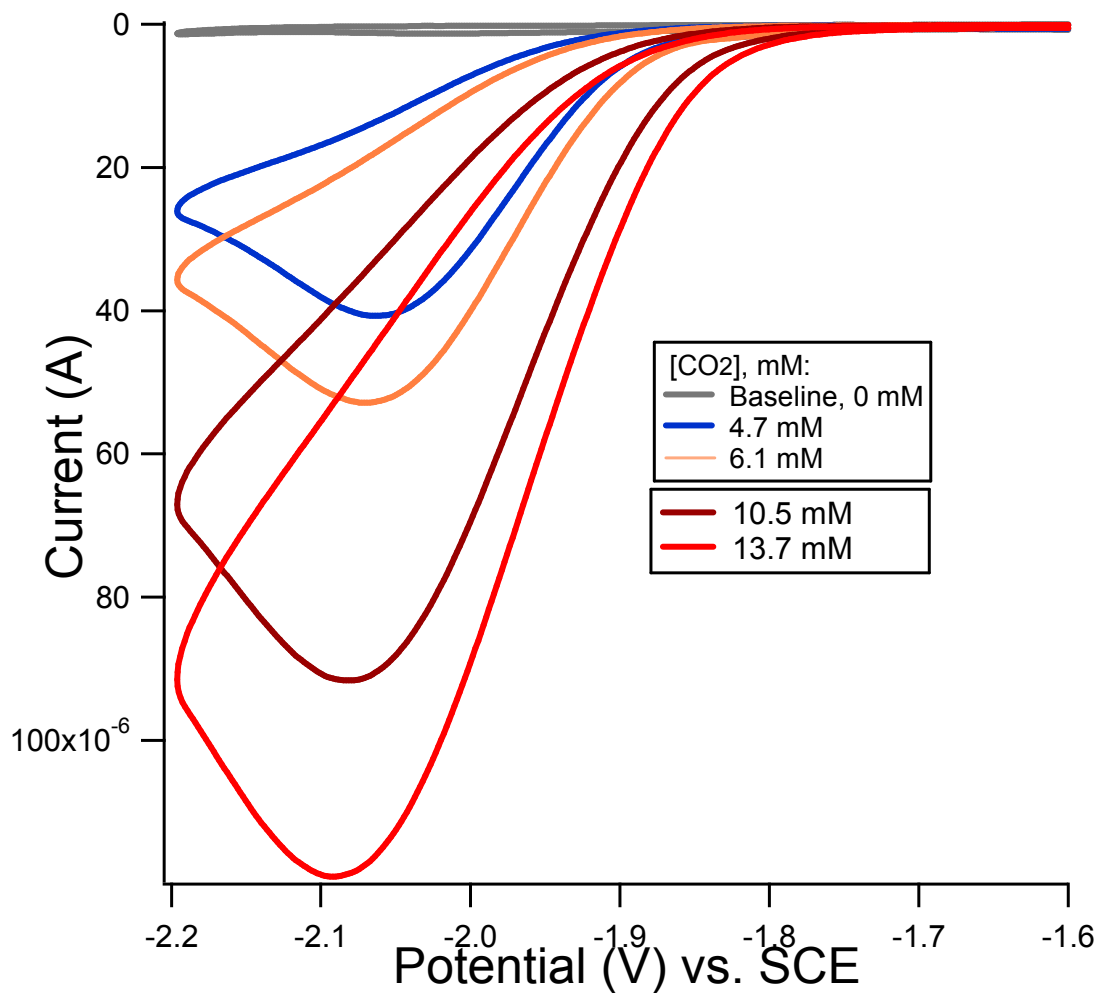


Figure S3. Cyclic Voltammograms (scan rate of 0.5 Vs⁻¹) at 25 °C on a silver electrode showing baseline and the reduction of CO₂ at different concentration in [BMPyr]TFSI.

3. References

- [1] U. Schröder, J. D. Wadhawan, R. G. Compton, F. Marken, P. A. Z. Suarez, C. S. Consorti, R. F. de Souza, J. Dupont, *New J. Chem.*, **2000**, 24, 1009
- [2] H. Cruz, I. Gallardo, G. Guirado, *Electrochim. Acta*, **2008**, 53, 5967
- [3] H. Cruz, I. Gallardo, G. Guirado, *Green Chem.*, **2011**, 13, 2531
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