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A Structural Transition in an Ionic Liquid Controls CO₂ Electrochemical Reduction

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Electrochemical cell preparation: Ag and Ionic liquid

The polycrystalline Ag electrode (99.999% Accumet Materials Co.), was mechanically polished using successively finer Al₂O₃ lapping films (Mark V Laboratory), 12 μm, 9 μm, 7 μm, 5 μm, 3 μm and 1 μm grades, followed with 0.3 μm Al₂O₃ paste (Buehler) until a mirror-like surface was achieved. Then the electrode was twice sonicated for 10 minutes with ultrapure Milli-Q water, with rinsing in between. The electrode was dipped in H₂SO₄ for 5 s, then sonicated and rinsed with Mili-Q water. An ultrapure water drop was placed on the electrode surface to keep it free from contaminants during electrochemical cell assembly. The reference electrode was Ag/AgCl from BASi Inc. The counter-electrode was a Pt wire that was H₂ flame-annealed, washed with Mili-Q water and electrochemically polished (0.1 M H₂SO₄, 50 cycles from -0.2 V to -1.5 V at 50 mV/s with Ar bubbling).

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The cell parts, except the CaF_2 window, were washed with detergent and water and sonicated for 15 minutes. They were rinsed with deionized water and sonicated with acetone for 15 minutes. Then they were again rinsed with deionized water, cleaned for at least 12 h with concentrated H_2SO_4 and Nochromix (Fisher), and finally boiled in ultra-pure water (Mili-Q, 18.2 M Ω) 3 times and dried in clean air.

The ionic liquid EMIM- BF_4 (98% Sigma-Aldrich) was Ar-bubbled for at least 30 min before each experiment, and no further purification was done. This RTIL is hygroscopic, and it picks up water from the environment. No attempt was made to remove the water since, as shown previously, a small amount of water is needed for high Faradaic efficiency.¹ We carried out a Karl-Fischer titration (KFT) of the Ar-purged EMIM- BF_4 . KFT is a universal method for measuring the water content in all types of substances, such as chemicals and foods. This method works over a range of concentration from ppm to 100%, and for bound and free water. The coulometric titration determined the EMIM- BF_4 contained 0.3 mol% of water. For the CO_2 reduction experiments, CO_2 was bubbled for at least 1 hour, but during the cyclic voltammetry scans the CO_2 was stopped to avoid producing bubbles in the optical path.

Ag/AgCl reference electrode calibration in ionic liquid (EMIM- BF_4)

The reference electrode (RE) was Ag/AgCl in 3M saturated KCl (MF-2021 BASi, Inc.). Ferrocene (Fc) was used as an internal reference electrode as previously described²⁻³, to calibrate the Ag/AgCl reference electrode in the presence of the RTIL (room-temperature ionic liquid), EMIM- BF_4 . The ferrocene/ferrocenium (Fc/Fc^+) redox couple (2.5 mM) in 0.1M tetrabutylammonium perchlorate (TBPA) in acetonitrile (ACN) is well known, and the redox potential in this system was compared to the potential using the room-temperature ionic liquid

(RTIL), EMIM-BF₄.³ Pt and Ag were used as working and counter electrodes, respectively. The sweep rate was 100 mV s⁻¹, and both electrolytes were Ar-purged for at least 30 minutes prior to the cyclic voltammetry measurements. The average potentials at the peak were 461 mV and 322 mV for the TBPA/ACN and EMIM-BF₄, respectively, versus Ag/AgCl. Previous studies reported similar values for the Fc/Fc⁺ couple in TBPA/ACN vs Ag/AgCl of 410 mV,⁴ and 450 mV.⁵ According to our calibration procedure, all the measured potentials versus our Ag/AgCl RE should be offset by +139 mV (Figure S1).

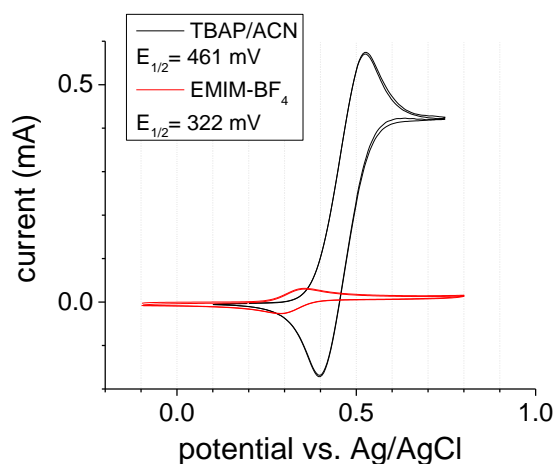


Figure S1. Cathodic and anodic waves of the Fc/Fc⁺ couple in TBPA/ACN and EMIM-BF₄

Capacitance Experiments

The interfacial potential-dependent capacitance was measured by a phase-sensitive detection technique. An AC sine wave at excitation frequency $\omega = 25\text{Hz}$, 50 mV amplitude peak-to-peak and initial phase of zero was provided by using the potentiostat-galvanostat Autolab PGSTAT100, in the AC voltammetry mode.⁶ The potential-dependent capacitance of the Ar-saturated electrolyte was similar in form to the capacitance of CO₂-saturated electrolyte, but with CO the absolute capacitance decreased by 60%. A minimum was found around -0.579

V, which can be assigned to the potential of zero charge (pzc). This measured value is close to what was previously found using EMIM-BF₄ with Au, -0.51V.⁷

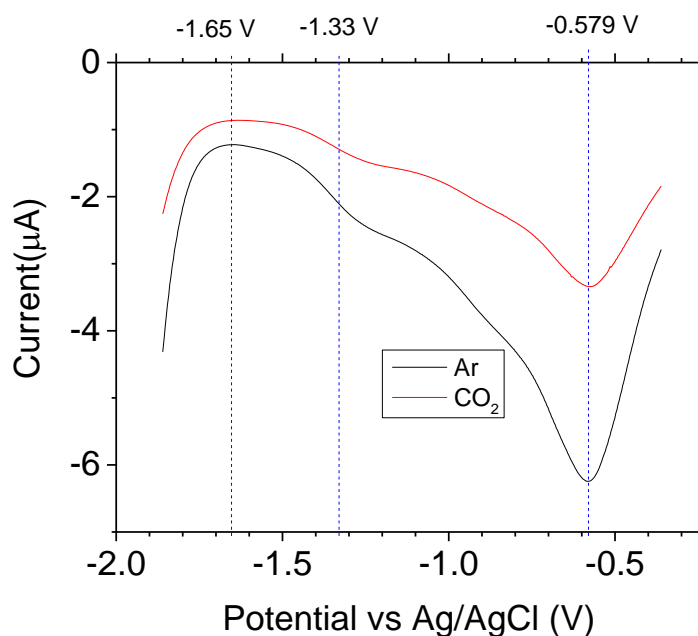


Figure S2. Capacitance measurements Ar- and CO₂- saturated EMIM-BF₄ on poly Ag. Excitation frequency 25 Hz, amplitude 50mV.

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