Electrochemical carbon dioxide reduction in ionic liquids at high pressure

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Experimental methods:

Electrochemical measurements at high pressures used a silver wire sealed within a glass capillary to minimise the exposed silver surface (7.85×10^{-3} cm^2) as the working electrode and a Pt wire counter electrode. Due to the possibility that that bulk electrolyte composition may change at elevated pressures a Ag/AgNO$_3$ reference electrode was constructed consisting of a Ag wire inserted into a AgNO$_3$ solution (10 mM, CH$_3$CN, 0.1 M TBAPF$_6$). The reference electrode was housed within thick-walled PTFE tubing and sealed with a vycor frit. The AgNO$_3$ reference electrode was tested at elevated pressure prior to use and through careful control of the rate of pressure change it was found that the AgNO$_3$ solution remained contained and that a stable potential was achieved. A schematic of the Teflon lined stainless-steel high pressure electrochemical cell is shown in figure S1. Due to the large volume of the cell the ionic liquid-water electrolyte was placed in a smaller glass beaker, placed on-top of a Teflon block. Prior to electrochemical measurements at pressure the cell was sealed and the apparatus shown in figure 1 (main paper) was purged with CO$_2$ at low pressure for at least 10 minutes. The outlet vent was then sealed and the pressure increased to be the value indicated in the paper. Once the pressure desired was reached the reciprocating pump was used to ensure thorough mixing. All electrochemical measurements shown here were carried out with the pump off.

For low-pressure studies experiments were carried out in conventional glass cells with using a silver wire working electrode (8.06×10^{-2} cm^2), silver wire pseudo reference electrode and a Pt wire counter electrode. Prior to all experiments samples were thoroughly purged (20 minutes) with either N$_2$ or CO$_2$. Bulk electrolysis experiments were carried out in a similar cell except that a Pt gauze counter electrode was used, placed behind a vycor frit to prevent product crossover with a minimum electrolysis time of 20 minutes.

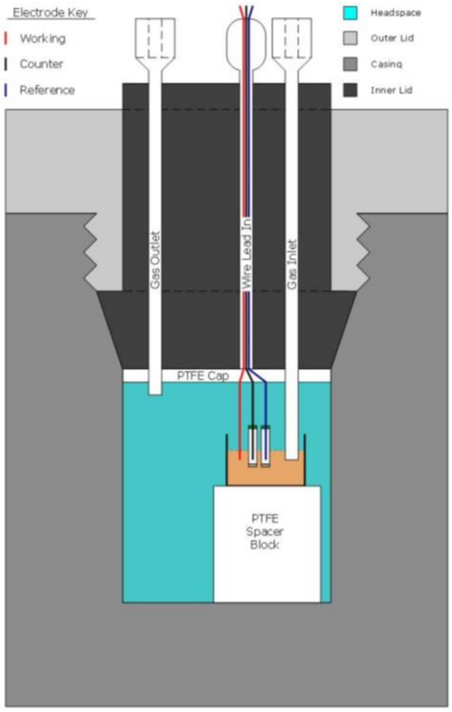

Figure S1 Schematic of the high-pressure electrochemical cell used for studies between 0.2 and 5.1 MPa.

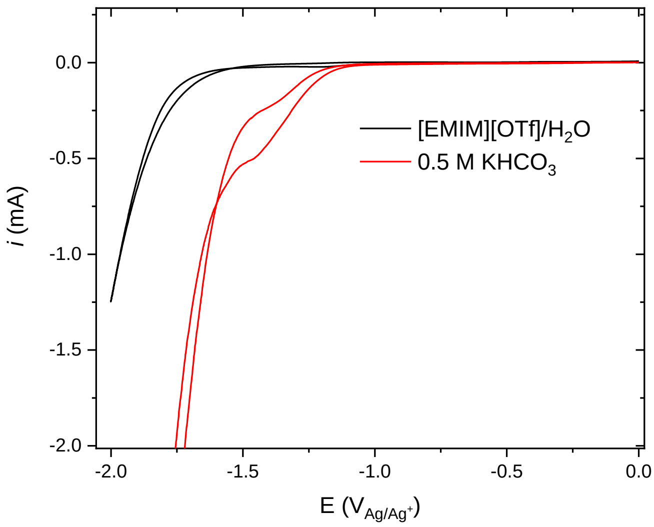

Figure S2 Electrochemistry of a silver wire recorded at 50 mV s^{-1} in the mixed ionic liquid water solvent used in the main text (black) and aqueous $KHCO_3$. Both experiments are carried out under N_2.

Table S1 Bulk electrolysis data recorded at -2.0 V in the electrolyte indicated. Experiments with ionic liquids were carried out at 20 mol% whilst the aqueous study was using 0.1M $KHCO_3$

Electrolyte	J_{avg}	Faradic Efficiency (%)		
	(mA cm^{-2})	CO	H_2	Total
EMIM-OTf/H_2O	0.22	60	34	94
EMIM-BF_4/H_2O	0.29	54	47	101
$KHCO_3$	2.92	6	99	105

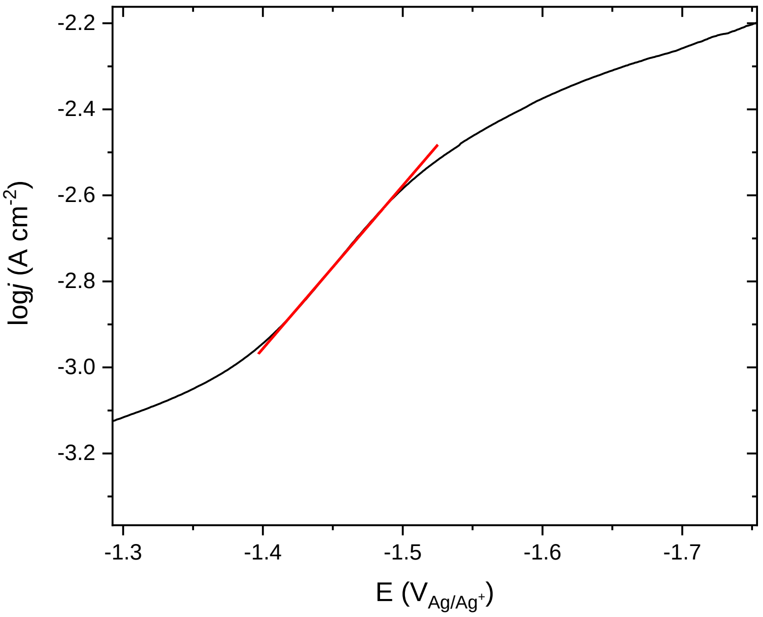

Figure S3 Plot of the logarithm of current density against applied potential showing deviation from Tafel type behaviour at potentials negative of -1.5 V for a Ag working electrode in [EMIM][OTf]/H_2O purged with CO_2 (*ca.* 0.1 MPa).

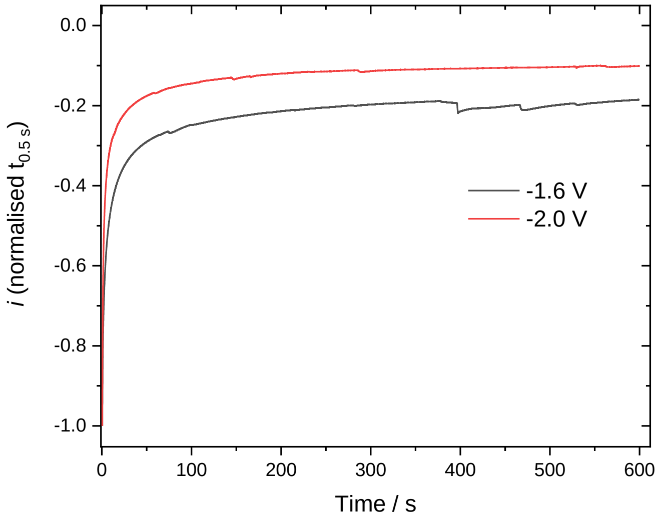

Figure S4 Chronoamperometry recorded at the potentials indicated with a Ag electrode in [EMIM][OTf]/H_2O following purging (ca. 0.1 MPa) of CO_2. The data is normalised to the current recorded 0.5 s after electrolysis starts. The raw chronoamperometry data is shown in figure S5.

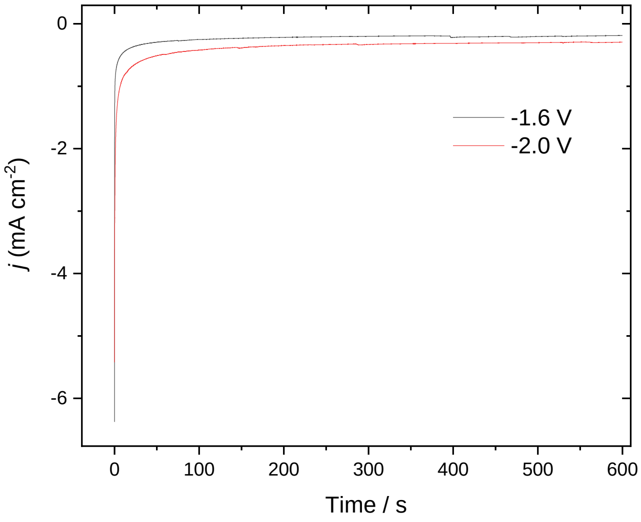

Figure S5 Chronoamperometry recorded at the potentials indicated with a Ag electrode in [EMIM][OTf]/H_2O following purging (ca. 0.1 MPa) of CO_2.

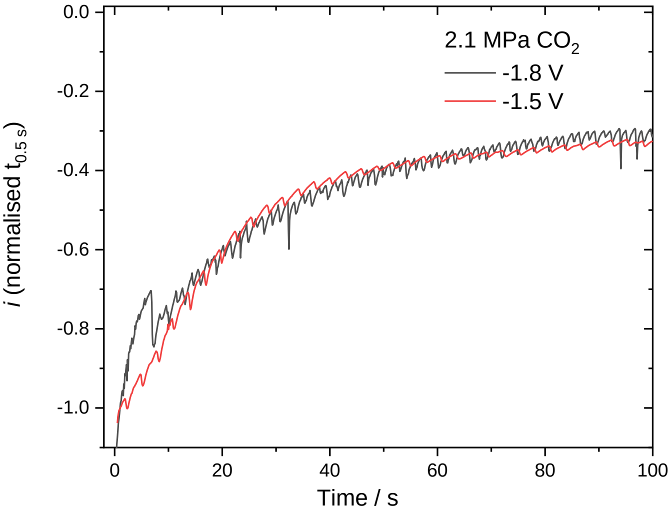

Figure S6 Chronoamperometry recorded at the potentials indicated with a Ag electrode in [EMIM][OTf]/H_2O under a 2.1 MPa pressure of CO_2. The data is normalised to the current recorded 0.5 s after electrolysis starts. The raw chronoamperometry data is shown in figure S7.

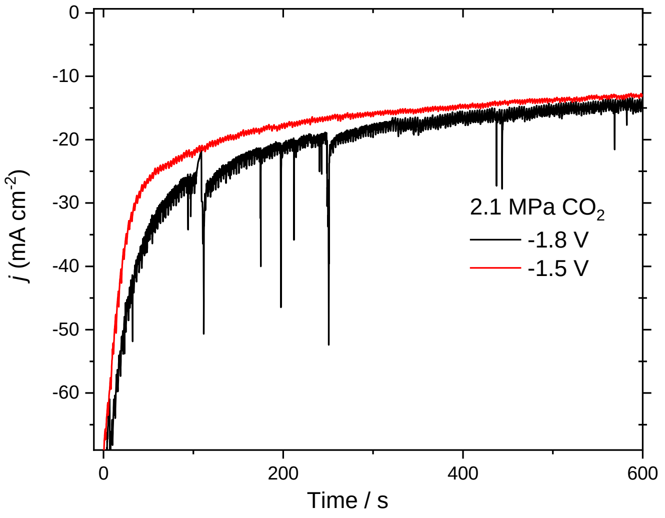

Figure S7 Chronoamperometry recorded at the potentials indicated with a Ag electrode in [EMIM][OTf]/H_2O under a 2.1 MPa pressure of CO_2.