

Exploring how cation entropy influences electric double layer formation and electrochemical reactivity

Beichen Liu, Wenxiao Guo, Seth R. Anderson, Samuel G. Johnstone, Siqi Wu, Megan C. Herrington, Matthew A. Gebbie*

Address correspondence to: gebbie@wisc.edu

Synthesis of [BisMImO][TFSI]₂:

[BisMImO][Br]₂ Preparation:

10 g (0.055 moles) of 1-methylimidazole and 30 g (0.11 moles) of 1,8-dibromooctane were added to a round bottom flask and heated to 120 °C in a silicone oil bath for 48 hours under stirring. The resulting liquid is a light brown or yellow color. After cooling to room temperature, the ionic liquid can be crystallized by gently scraping the glass or cooling further in an ice bath, at which point the ionic liquid becomes light yellow or off-white in color as a solid. It is hygroscopic and will quickly absorb water, hence acetone is used to wash the [BisMImO][Br]₂ after breaking it up into smaller pieces. This washing step is performed 3 times, or until the acetone layer remains clear and colorless. The acetone is poured off and removed using a rotary evaporator. The resulting ionic liquid should be white/off-white powder.

[BisMImO][TFSI]₂ Preparation:

5 g (15.7 moles) of [BisMImO][Br]₂ and 9.0 g (31.3 mmol) [Li][TFSI] are added to a clean round bottom flask. Approximately 30 mL of MilliQ water is added to the flask and the entire solution is stirred at room temperature for 3 hours. In this time, a separate phase containing [BisMImO][TFSI]₂ should form at the bottom of the flask. After allowing the ionic liquid phase to settle, the water layer is poured off, leaving the lightly colored, transparent [BisMImO][TFSI]₂. The ionic liquid is then washed with MilliQ water 5 times. The silver nitrate assay is used on the water supernatant after 5 washes to determine whether any halides remain. If the silver nitrate assay indicates the presence of [Br]⁻, then the ionic liquid is washed another 3 times before further testing with the silver nitrate assay.

Once the ionic liquid is washed and no longer contains halides, the ionic liquid must be purified. To do this, acetonitrile is added to the ionic liquid to decrease the viscosity. Activated charcoal is added to decolorize the ionic liquid by stirring the charcoal in the ionic liquid-acetonitrile solution for 1 day, after which the charcoal is filtered out. The ionic liquid is then passed through an alumina column containing alumina oxide and acetonitrile to filter out remaining charcoal contaminants. What results should be a colorless and transparent solution. A rotary evaporator is then used to remove the acetonitrile and the ionic liquid is dried at 80 °C for 2 days in a vacuum oven.

¹H NMR (400 MHz, CD₃CN) δ 8.43 (s, 1H), 7.38 (dt, *J* = 14.8, 1.9 Hz, 2H), 4.14 (t, *J* = 7.3 Hz, 2H), 3.85 (s, 3H), 1.84 (p, *J* = 7.3 Hz, 2H), 1.34 (s, 3H), 1.31 (d, *J* = 8.7 Hz, 1H).

Table S1. Solution resistance values obtained from EIS for [BMIm][TFSI]

Concentration	Solution resistance 1	Solution resistance 2	Average Solution Resistance	Standard Deviation
M	Ohm	Ohm	Ohm	Ohm
0.025	350.30	345.70	348.00	2.30
0.125	78.02	87.34	82.68	4.66
0.5	31.75	38.67	35.21	3.46
1	32.90	34.02	33.46	0.56
1.65	30.02	29.54	29.78	0.24
1.74	28.27	30.23	29.25	0.98

Table S2. Solution resistance values obtained from EIS for [BisMImO][TFSI]₂

Concentration	Solution resistance 1	Solution resistance 2	Average Solution Resistance	Standard Deviation
M	Ohm	Ohm	Ohm	Ohm
0.025	273.70	228.80	251.25	22.45
0.125	23.75	23.50	23.625	0.125
0.5	36.44	36.18	36.31	0.13
1	67.46	68.54	68.00	0.54
1.65	770.40	774.70	772.55	2.15
1.74	935.3	943.30	939.30	4.00

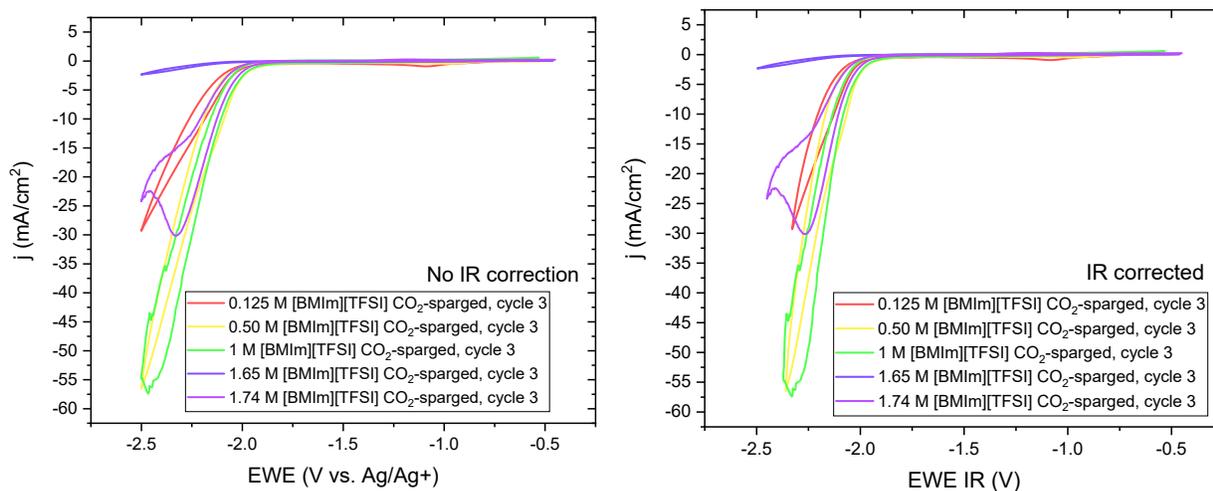


Figure S1. Representative cyclic voltammetry curves showing the results of no IR correction (left) and after IR correction (right).

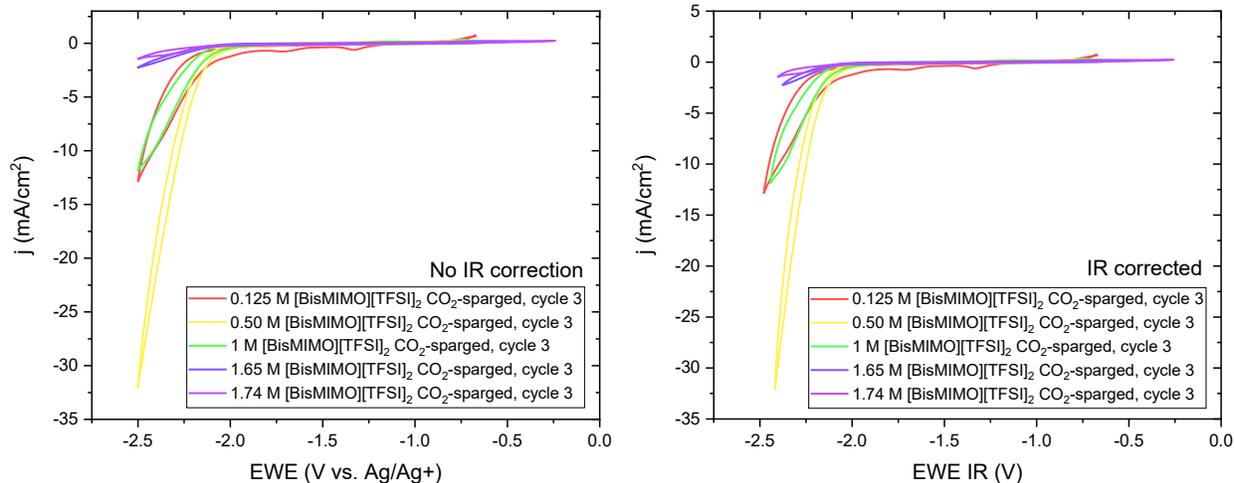


Figure S2. Representative cyclic voltammetry curves showing the results of no IR correction (left) and after IR correction (right).

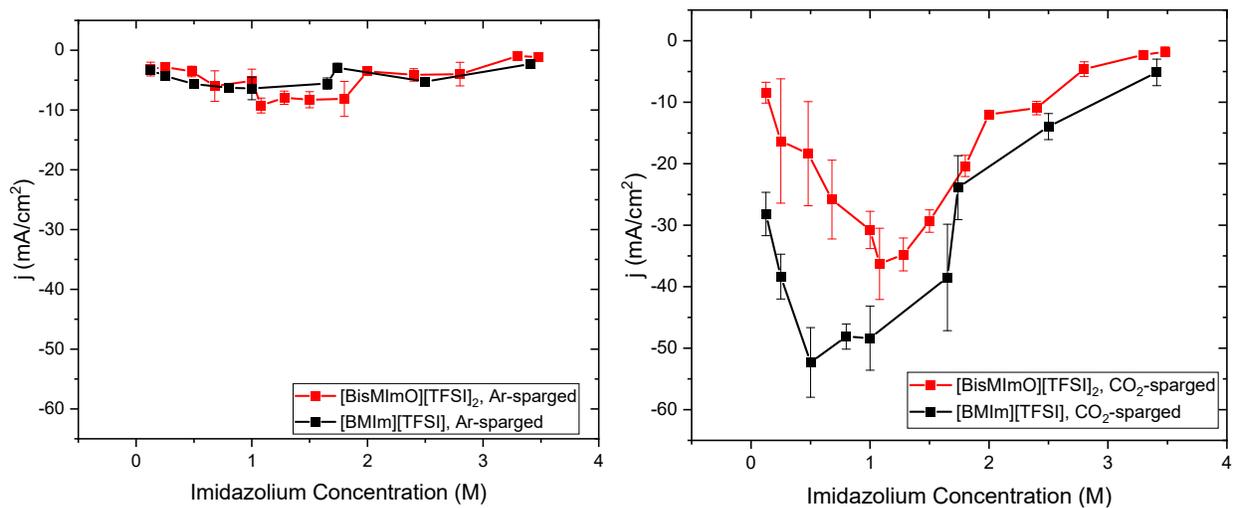


Figure S3. Ionic liquid decomposition does not account for the bulk of the current densities observed in CO₂-sparged electrolytes. Ar-sparged results (left) do not show the same non-monotonic reactivity trend nor the same current densities observed in CO₂-sparged electrolytes (right).

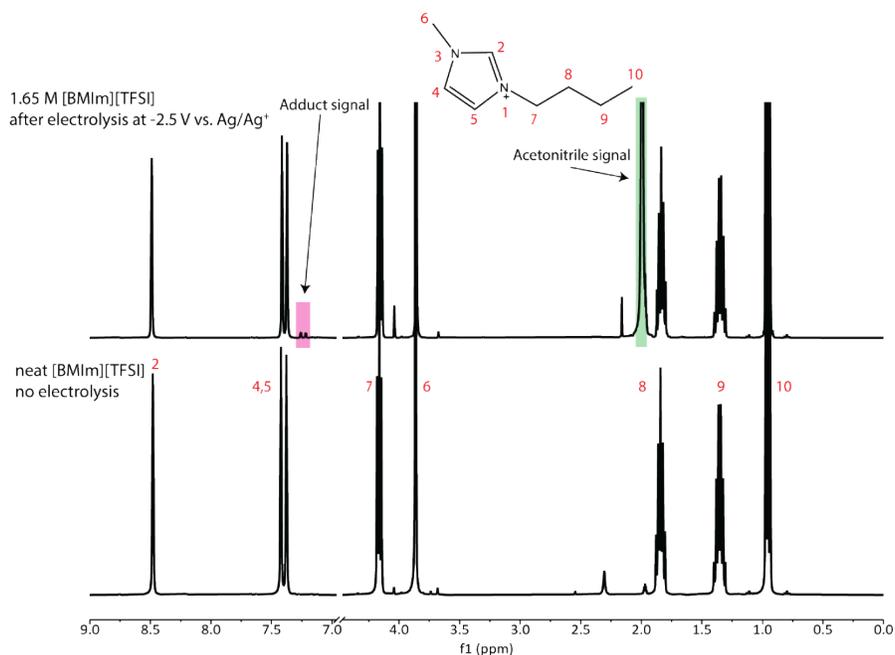


Figure S4. ^1H NMR results for 1.65 M [BMIm][TFSI] after electrolysis (top) compared to the pure ionic liquid (bottom). Other than the acetonitrile peak, the new peaks that are observed are due to the formation of imidazolium- CO_2 adduct, which causes peak splitting of the C4, C5, and C7 peaks. No peaks associated with imidazolium decomposition emerge after electrolysis.

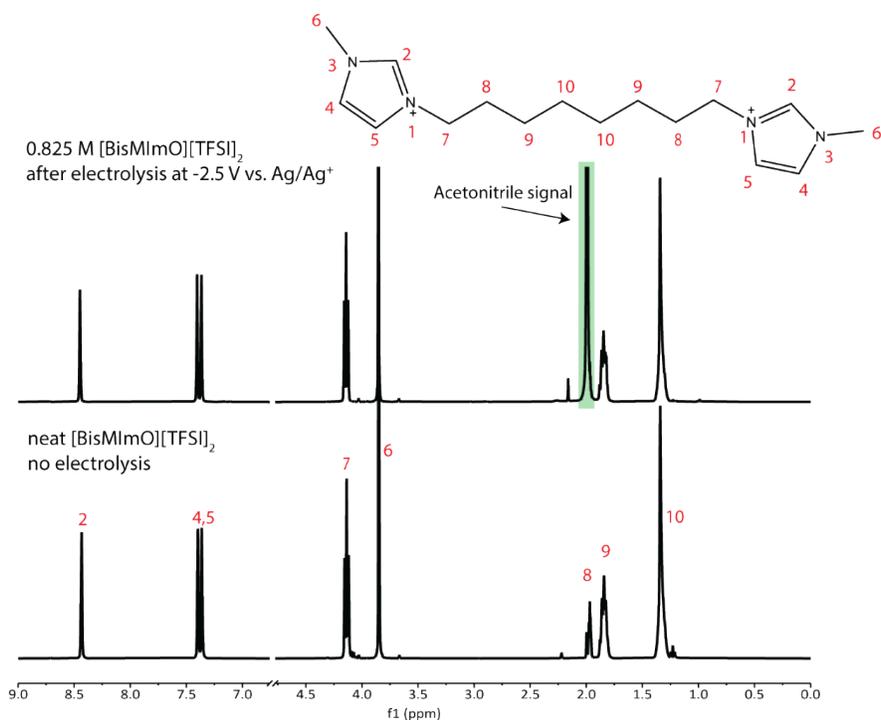


Figure S5. NMR results for 0.825 M [BisMImO][TFSI]₂ after electrolysis (top) compared to the pure ionic liquid (bottom). No new peaks emerge suggesting that ionic liquid does not decompose at -2.5 V vs. Ag/Ag^+ . Rather, the relatively diminished intensity of the C2 peak relative to the C4, C5 peaks suggest that small amounts of the carbene at the C2 position may be formed. However, due to the low current densities

in [BisMImO][TFSI]₂ electrolytes, isolating the carbene or ionic liquid decomposition products remains difficult.

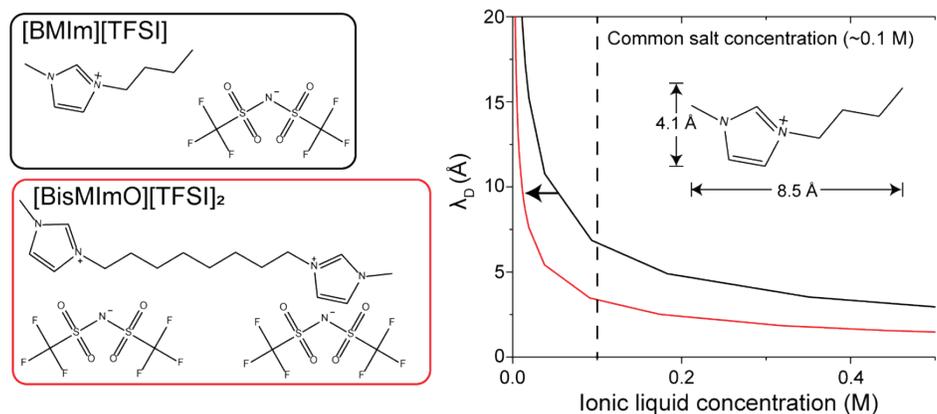


Figure S6. Predicted Debye lengths for [BMIm][TFSI] (black) and [BisMImO][TFSI]₂ (red) assuming the same dielectric permittivity values. At the same ionic liquid concentration Debye length is smaller for [BisMImO][TFSI]₂ due to the divalent nature of the cation. After approximately 0.4 M of ionic liquid, however, the predicted Debye screening length is smaller than two of the dimensions of the [BMIm]⁺ cation.

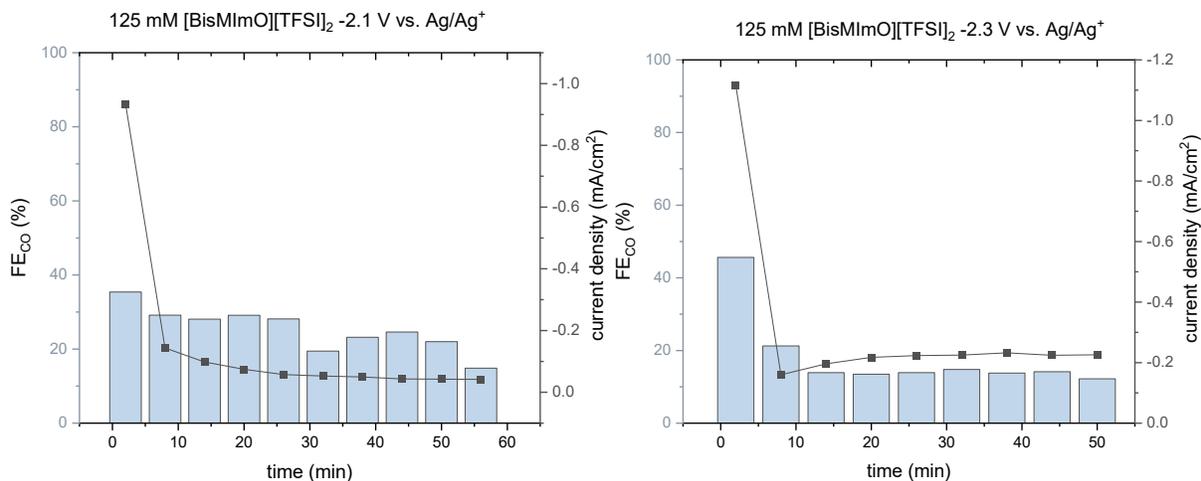


Figure S7. Potential-dependent CA results for 125 mM [BisMImO][TFSI]₂ held at -2.1 V vs. Ag/Ag⁺ (left) and -2.3 V vs. Ag/Ag⁺ (right). Within 10 minutes of applying a CO₂ reduction potential, the current density decreases dramatically due to the formation of a solid precipitate, which occludes the electrode surface.

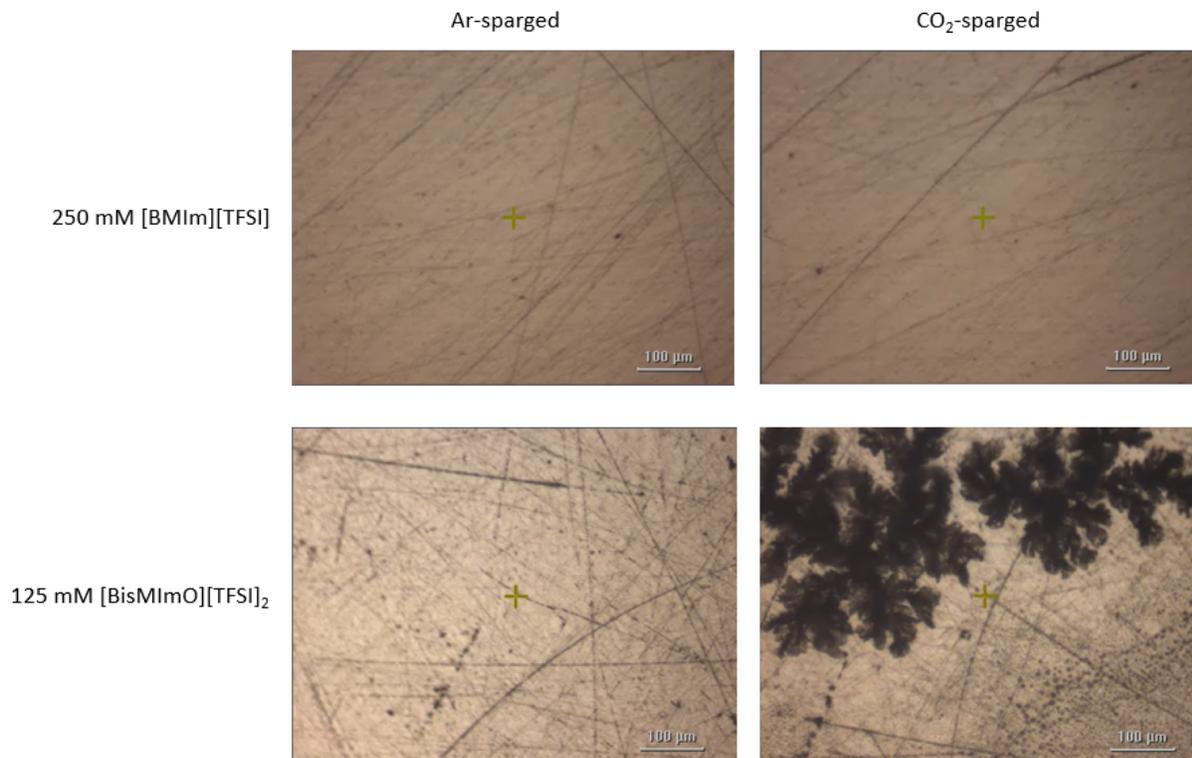


Figure S8. Images of 250 mM [BMIm][TFSI] (top row) and 125 mM [BisMImO][TFSI]₂ (bottom row) under Ar-sparged (left column) and CO₂-sparged (right column) conditions on a silver electrode surface at -2.5 V vs. Ag/Ag⁺.

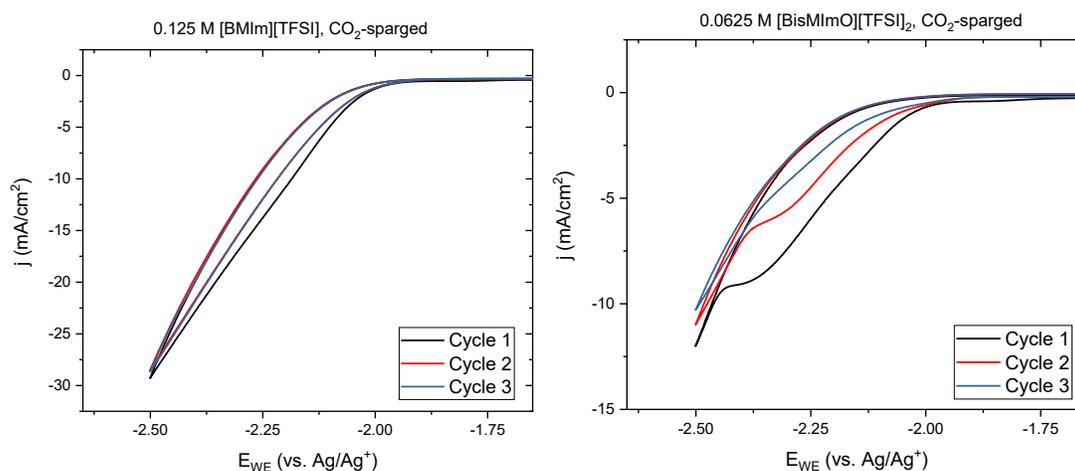


Figure S9. Cyclic voltammograms of 0.125 M [BMIm][TFSI] (left) and 0.0625 M [BisMImO][TFSI]₂ (right) under CO₂ sparged conditions. The voltammograms of 0.125 M [BMIm][TFSI] remain relatively constant over the course of 3 cycles while 0.0625 M [BisMImO][TFSI]₂ displays decreased current densities with each cycle due to the formation of small amounts of precipitates at the electrode surface.

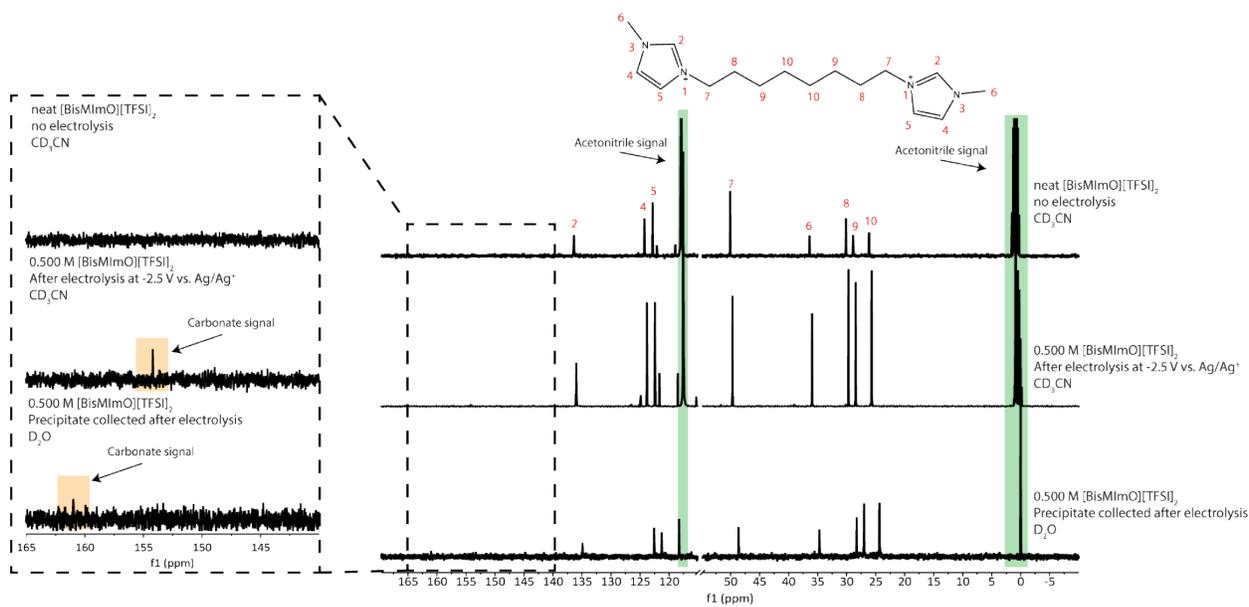


Figure S10. ^{13}C NMR results for pure $[\text{BisMImO}][\text{TFSI}]_2$ (top), 0.500 M $[\text{BisMImO}][\text{TFSI}]_2$ after electrolysis (middle), and the precipitate collected from electrolysis of $[\text{BisMImO}][\text{TFSI}]_2$ (bottom), with an inset that displays the carbonate region of the spectrum. The slight shift in the carbonate peak is attributed to the different deuterated solvents needed to solvate the analyte.

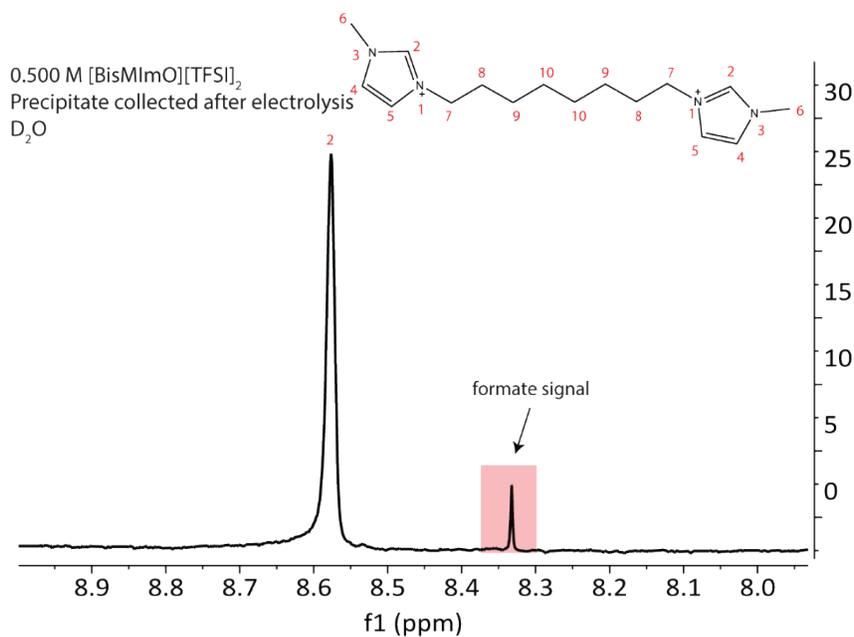


Figure S11: ^1H NMR results of the precipitate that forms in $[\text{BisMImO}][\text{TFSI}]_2$ electrolytes under CO_2 -sparged conditions, indicating the formation of formate.

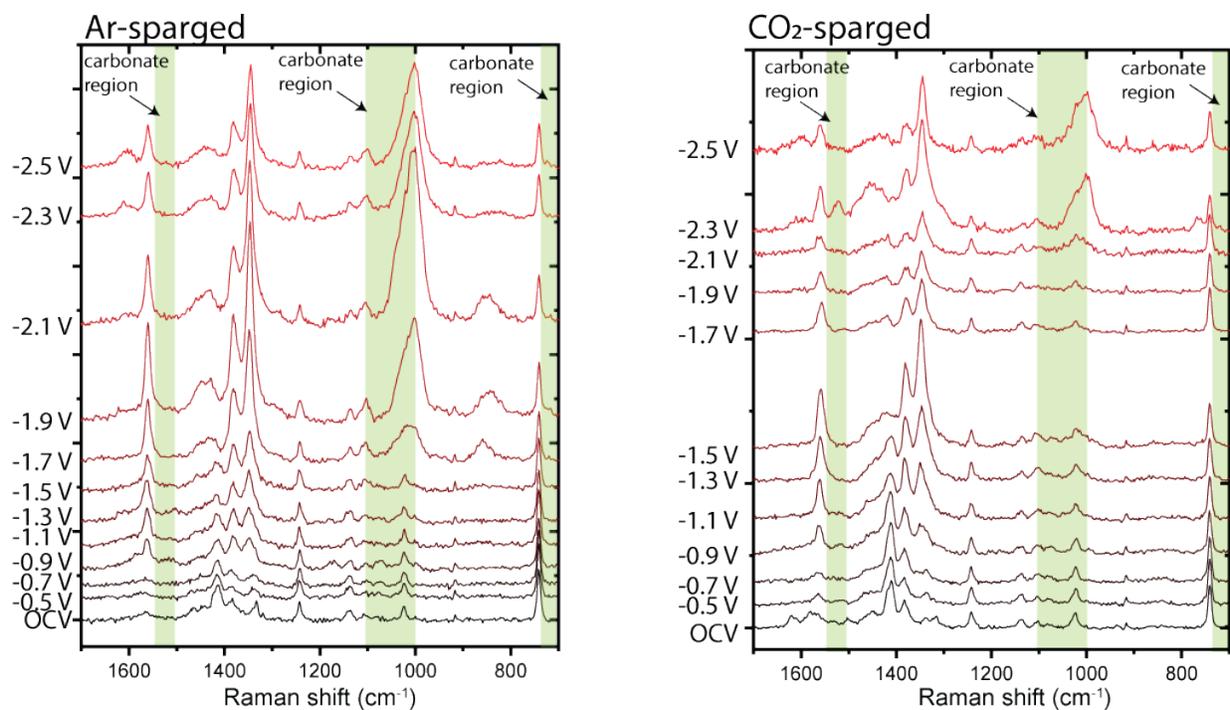


Figure S12. Representative Raman spectra of 0.825 M [BisMImO][TFSI]₂ under Ar-sparged (left) and CO₂-sparged (right) conditions. Regions associated with carbonate Raman modes are highlighted in green. The emergence of peaks in these regions associated with carbonate Raman modes under Ar-sparged conditions indicate that there is significant overlap between the carbonate and the imidazolium cation Raman modes, making carbonate identification difficult. These observations apply to both [BisMImO][TFSI]₂ and [BMIm][TFSI] electrolytes.

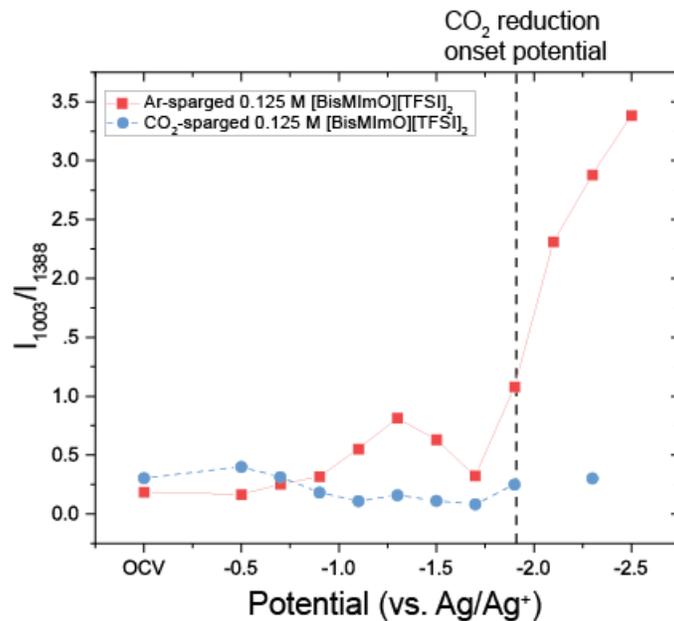


Figure S13. *In situ* SERS of 0.125 M [BisMImO][TFSI]₂ under Ar-sparged (red) and CO₂-sparged (blue) conditions. Peak ratios of 1003 cm⁻¹ and 1388 cm⁻¹ were taken to denote extent of alkyl chain organization. We note that the disappearance of the 1003 cm⁻¹ peak under CO₂-sparged conditions indicates the alkyl chain aggregation behavior we observe under Ar is disrupted due to the dynamic nature of the CO₂ reduction double layer.

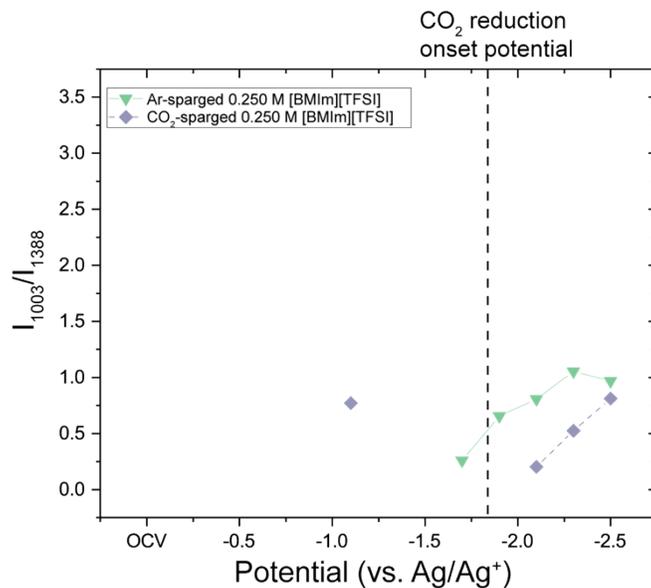


Figure S14. Potential-dependent *in situ* SERS of 0.250 M [BMIm][TFSI] under Ar- (green) and CO₂-sparged (purple) conditions. The noticeable lack of the 1003 cm⁻¹ peak indicates that there is no significant aggregation of the alkyl chain in [BMIm][TFSI] electrolytes.

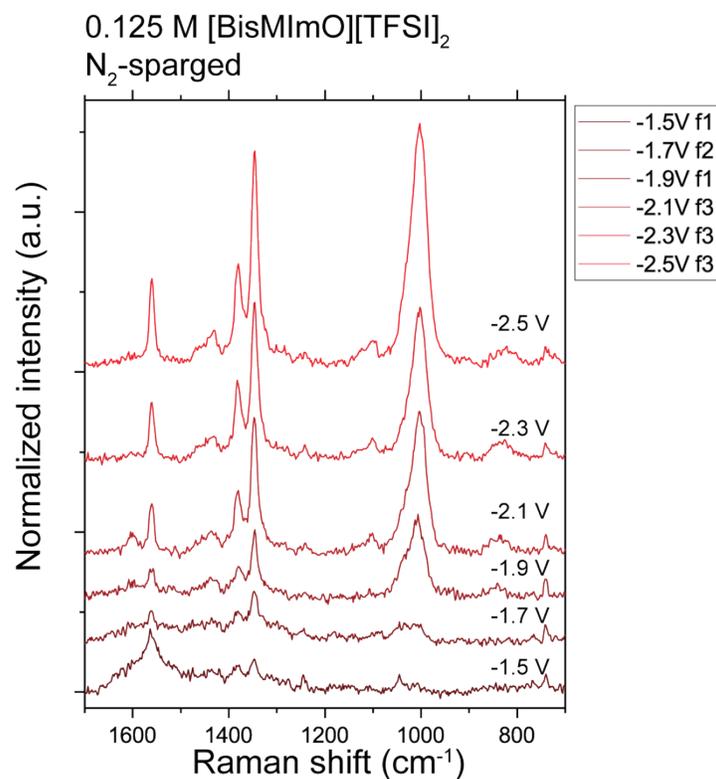


Figure S15. Potential-dependent *in situ* SERS of 0.125 M [BisMImO][TFSI]₂ under N₂-sparged conditions, which demonstrates the emergence of the 1003 cm⁻¹ peak at -1.9 V vs. Ag/Ag⁺ under inert conditions and suggests that there is a noticeable difference between interfaces in which a reaction such as CO₂ electroreduction occurs, and an inert interface.



Figure S16. Picture of the electrode surface when a potential is stepped to -2.7 V vs. Ag/Ag⁺ (left) showing the formation of solid precipitate that, when exposed to ambient humidity, forms an orange film (right).

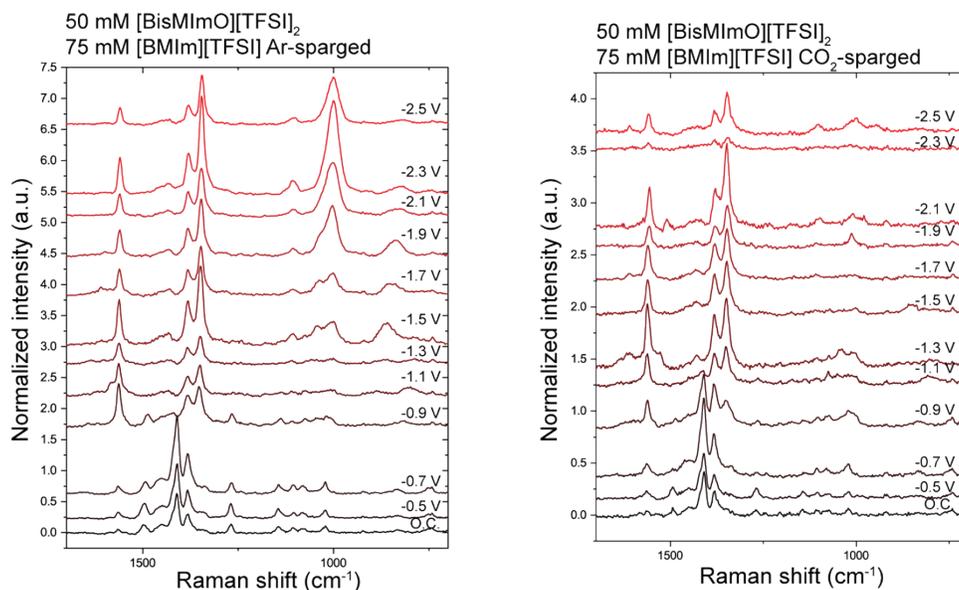


Figure S17. *In situ* SERS spectra of an electrolyte mixture containing 50 mM [BisMImO][TFSI]₂ and 75 mM [BMIm][TFSI] in acetonitrile either sparged with Ar (left) or CO₂ (right). In the Ar-sparged case, the emergence of a pronounced peak at 1003 cm⁻¹ indicates the presence of [BisMImO][TFSI]₂, as the same peak is not observed in [BMIm][TFSI]-only solutions. In CO₂-sparged solutions, the peak does not appear, which aligns with observations made in CO₂-sparged [BisMImO][TFSI]₂-only electrolytes.

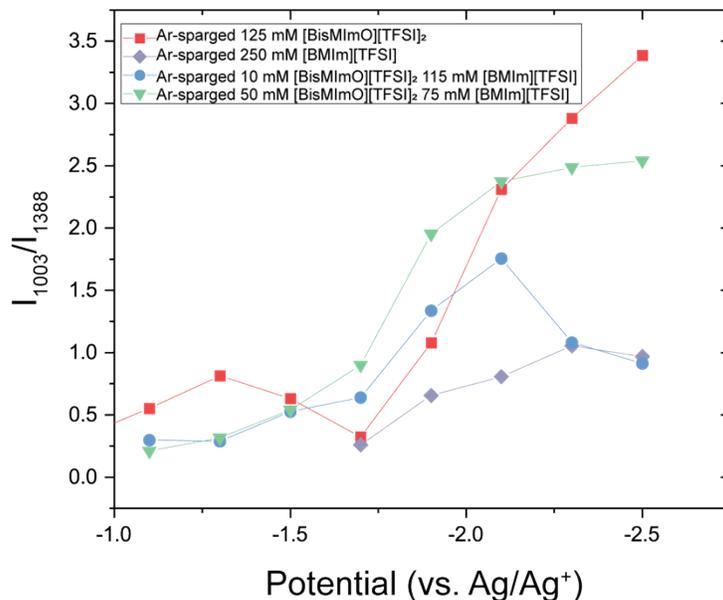


Figure S18: Peak ratios of 1003 cm⁻¹ and 1388 cm⁻¹ peaks of ionic liquid mixtures containing [BisMImO][TFSI]₂ under Ar-sparged conditions. Compared to 125 mM [BisMImO][TFSI]₂ (red) and 250 mM [BMIm][TFSI] (purple), electrolytes containing a mixture of the two show that as the concentration of [BisMImO][TFSI]₂ increases from 10 mM (blue) to 50 mM (green), the potential-dependent ratio of the two peaks becomes more like that of the [BisMImO][TFSI]₂-only electrolyte, suggesting enhanced accumulation of the [BisMImO][TFSI]₂ at the interface.

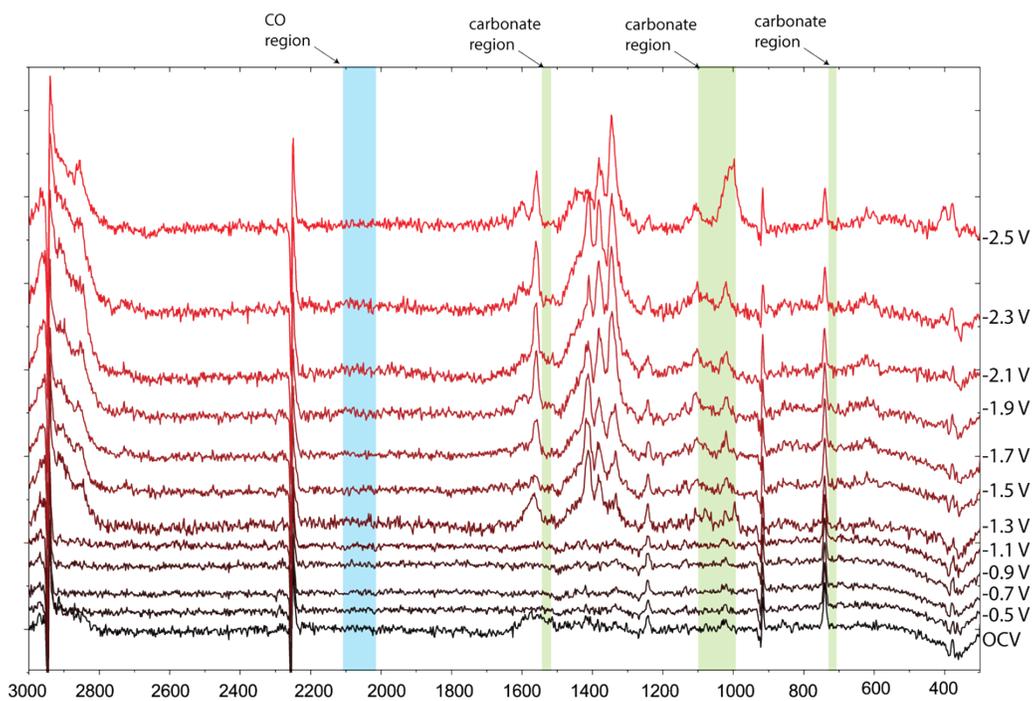


Figure S19: Full SERS spectra of CO_2 -sparged 1.65 M [BMIm][TFSI] with regions where the carbonate (green) and CO (blue) Raman modes would appear.

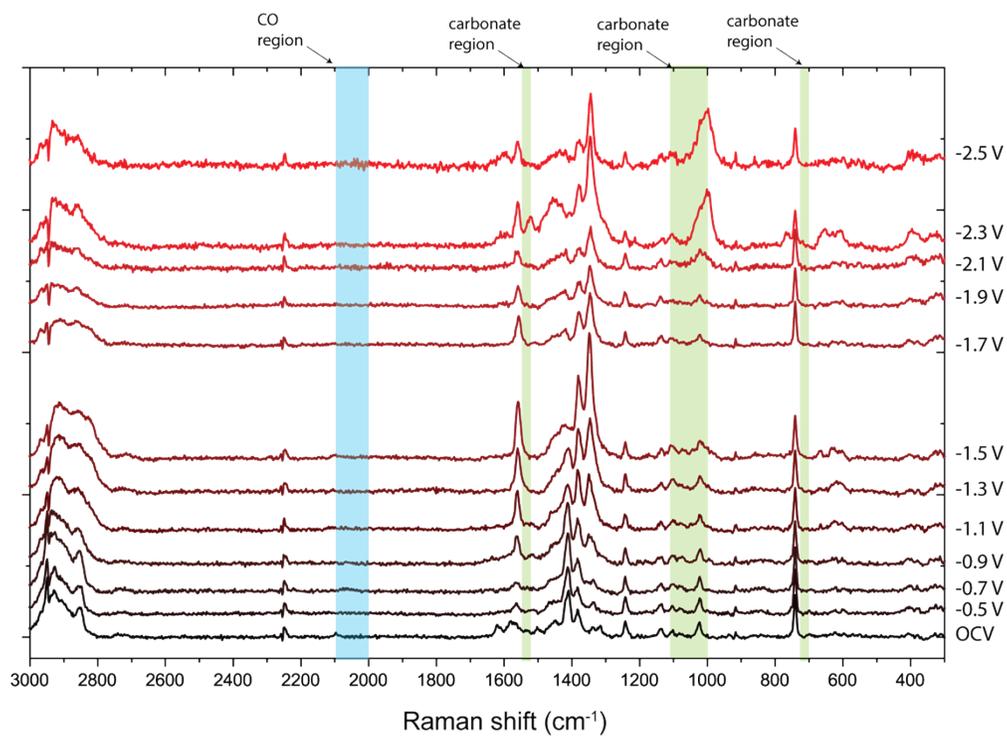


Figure S20: Full SERS spectra of CO₂-sparged 0.825 M [BisMImO][TFSI]₂ with regions where the carbonate (green) and CO (blue) Raman modes would appear.