Deciphering the Role of Imidazolium in Electrochemical CO₂ Reduction: Interfacial Ion Assembly Governs Reaction Pathways

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Experimental details

Chemicals

1-Ethyl-2,3-dimethylimidazolium tetrafluoroborate ([EMMIm][BF₄], >98% purity, Iolitec) and Tetrabutylammonium tetrafluoroborate ([TBA][BF₄], >99% purity, TCI) were used as purchased without further purification. HPLC grade acetonitrile and dichloromethane were from Sigma Aldrich, ethanol (200 proofs) was from Decon Laboratories Inc., methanol was from Fisher Chemicals, and diethyl ether was from Arcos Organics. 1,2,4,5-tetramethylimidazole (98%) was from TCI. Iodoethane (97%) was from Combi-Blocks. Silver tetrafluoroborate (>99%) was from Thermo Scientific. Potassium bromide was from MP Biomedicals. Silver nitrate (99.9+% metal basis) was from Alfa Aesar. 4-Mercaptobenzonitrile was from AstaTech. Deuterated acetonitrile (>98.5% atom D) was from Acros Organics. Ultrapure water (Milli-Q, \geq 18.2 M Ω cm) was used in all experiments.

Synthesis of 1-ethyl-2,3,4,5-tetramethylimidazolium tetrafluoroborate ([EM₄Im][BF₄])

 $[EM_4Im][BF_4]$ was synthesized following a reported method.¹ 1,2,4,5-Tetramethylimidazole (0.030 mol) was dissolved in 1.5 equivalents of iodoethane (0.045 mol), and the solution was heated at 40 °C. The solution solidified to a dark yellow solid after 15 min of heating, and the heating continued for 12 hours. The solid was then cooled to room temperature and washed with diethyl ether (6 × 20 mL). The washed solid was recrystallized from acetone, yielding transparent, light yellow crystals of 1-ethyl-2,3,4,5-tetramethylimidzolium iodide ($[EM_4Im]I$). The yield of $[EM_4Im]I$ was 68% (0.021 mol). $[EM_4Im]I$ (0.014 mol) was then mixed with 1 equivalent of silver tetrafluoroborate (0.014 mol) in water (28 mL). The mixture was isolated from light by wrapping the flask with aluminum foil and reacted for 18 hours under stirring at room temperature. After the reaction, the mixture was filtered and centrifuged (6000 rpm, 25 min) to remove the silver iodide precipitate. The aqueous phase was separated into three portions. Each portion was transferred to a separating funnel and extracted with dichloromethane through multiple extractions (5 × 30 mL). The dichloromethane phase was then combined and dried over anhydrous sodium sulfate. Dichloromethane was then removed through rotary evaporation (BUCHI Rotavapor R-300) and vacuum

oven, yielding $[EM_4Im][BF_4]$ in the form of white crystals. The yield of $[EM_4Im][BF_4]$ was 79% (0.011 mol). ¹H NMR spectrum of $[EM_4Im][BF_4]$ is shown in Figure S1.

Electrochemical Methods

A BioLogic VSP potentiostat was used for all electrochemical measurements except electrochemical impedance spectroscopy (EIS). EIS data was collected using a BioLogic VSP 3e potentiostat. A polycrystalline Ag disk electrode (BASi) with a diameter of 3 mm was used as the working electrode in all experiments. All current densities reported were normalized to the geometric area of the pc-Ag electrode. Before every experiment, the pc-Ag electrode was polished using 15 µm, 3 µm, 1 µm diamond polish, and finnally 0.05 µm alumina polish (BASi) until a mirror finish had been achieved. The electrode was then cleaned by ultrasonication in water. An Ag/Ag⁺ non-aqueous reference electrode was used in all experiments, and the filling solution was an acetonitrile solution of 0.1 M [TBA][BF4] and 0.01 M AgNO3. The counter electrode was a coiled platinum wire. All electrochemical measurements were performed in a two-compartment H-cell. The catholyte and anolyte chamber of the H-cell was separated by a Nafion 117 membrane that transports cations between anolyte and catholyte. The Nafion 117 membranes were activated by immersing the membranes sequentially in 3 wt% H₂O₂ (aq), water, 1 M H₂SO₄ (aq), and water, all of which were kept at 80 °C. Freshly activated Nafion membranes were rinsed thoroughly with acetonitrile and then stored in an acetonitrile solution of 0.1 M [TBA][BF₄]. To avoid cross-contamination, a different Nafion membrane was used for each ionic liquid solution. Used Nafion membranes were stored in 0.1 M acetonitrile solutions of corresponding ionic liquids when not being used. Electrolytes were purged by targeting gas (Ar or CO₂, as stated) for 10 minutes before all experiments.

During chronoamperometry (CA) measurements, the gas was continuously purged into the electrolyte at a flow rate of 9.2 sccm, and the electrolyte was stirred at 600 rpm. For steady-state analysis of current density and product selectivity, the potential on the working electrode was held at -2.5 V vs Ag/Ag^+ for 65 min. For reaction order analysis, the potential on the working electrode was held at -2.5 V vs Ag/Ag^+ for 11 min to achieve the steady state and also avoid the depletion of reactants, which may impact the kinetic results.

Chronopotentiometry (CP) measurements were conducted in the Tafel analysis of H_2 formation. During CP measurements, Ar is purged into the electrolyte at a flow rate of 5 sccm. The current passing through the working electrode was held at designated values for 8 minutes to achieve the steady state and to enable the quantification of H_2 generated.

Product Analysis

Gas products from CA and CP experiments were analyzed by an online gas chromatograph (GC, SRI Multiple Gas Analyzer #5) equipped with a thermal conductivity detector (TCD) and a flame-ionization detector (FID) coupled with a methanizer. The TCD detector was connected to a HayeSep D column, and the FID was connected to a HayeSep D and a Molesieve 5A column (Restek) in sequence. Ultrahigh purity grade He (Airgas) was used as the carrier gas. The faradaic efficiency of each gas product was calculated using the equation:

$$FE(\%) = \frac{\frac{v}{60s/min} \times \frac{y}{24,000 cm^3/mol} \times N \times F}{i} \times 100\%$$

where v is the flow rate of inlet gas in sccm, y is the concentration of product measured from GC in the unit of mole (volume) fraction, N is the number of electrons consumed to generate one product molecule (N = 2 for both CO and H₂), F = 96500 C mol⁻¹ is the Faraday constant, and *i* is the total current passing through the working electrode in the unit of ampere.

For 65 min CA measurements, the outlet gas was analyzed by the GC every 11.5 min starting from the 6 min. The steady-state current density was obtained by averaging current densities and faradaic efficiencies over 65 min of a single trial to reflect the time-dependent variations. Standard deviations of the total current density over 65 min were used as error bars.

For CP measurements used during Tafel analysis, the outlet gas was analyzed by the GC every 2 minutes, starting from 4 minutes. A steady-state potential applied was obtained by averaging the potential applied over the last 2 min. Standard deviations of the potential applied over the last 2 minutes were used as the error bars. The electrolyte was replaced, and the Ag working electrode was re-polished after the collection of three data points to minimize the influence of side product buildup on the electrode surface.

Liquid products generated during CA experiments were analyzed using a 400 MHz NMR spectrometer (Bruker Avance) with a BBFO probe. For electrolytes containing [EMMIm]⁺, catholytes after reaction were mixed with deuterated acetonitrile in a 1:1 ratio to prepare an NMR sample. The amount of formate was estimated based on the ratio between the integral of formate peak at 8.5 ppm and the sum of integrals of C4/C5-Hs of [EMMIm]⁺ at 7.3 ppm. For electrolytes of [TBA]⁺ and [EM₄Im]⁺ that do not have aromatic protons, catholytes after the reaction were mixed with deuterated acetonitrile electrolytes of 0.1 M [EMMIm]⁺. [EMMIm]⁺ introduced served as an internal reference, and the amount of formate was still estimated based on the ratio between the integrals of formate peak and C4/5H peak. The average and standard deviation (error bars) of formate FE from three CA replicates were reported.

Surface-enhanced Raman scattering (SERS) Measurements with 4-MBN probe

SERS measurements were carried out using a single-compartment PTFE liquid Raman cell with an L-shape polycrystalline Ag working electrode (Shanghai Fanyue Electronic Technology Co. Ltd). To obtain the SERS substrate, the L-shape Ag electrode was electrochemically roughened following the reported method

with modifications.² In brief, a polished L-shape Ag electrode was cycled between -0.50 V and +0.17 V versus Ag/AgCl (3M) at a scan rate of 50 mV/s in 0.1 M potassium bromide aqueous solution for three cycles under Ar purging. The electrode was held at -0.50 V vs Ag/AgCl (3M) for 10 seconds at the end of cycling to desorb bromide from the silver surface, and the electrode was vigorously rinsed with water immediately after the roughening to remove chemical and silver oxide residues. Then, the roughened L-shape Ag electrode was immersed in 0.02 M ethanol solution of 4-MBN for over 24 hours to obtain the self-assembled monolayer of 4-MBN. Before SERS measurement, the 4-MBN modified L-shape Ag electrode was rinsed with ethanol and briefly sonicated in ethanol to remove free 4-MBN.

For SERS measurement, the counter electrode was a coiled Pt wire, while the reference electrode was a non-aqueous Ag/Ag^+ (0.01 M AgNO₃) electrode. Electrolytes were purged with Ar for 20 minutes prior to all measurements. SERS spectra were collected using a Horiba LabRAM HR Evolution Raman Spectrometer with a 532 nm excitation laser and a 50× long-working distance objective. To obtain spectra of the nitrile group, the ND filter was set to 5%, the acquisition time was 1 s, and 8 scans were collected for each spectrum. The potential was swept from OCP (around -0.47 V vs Ag/Ag⁺) to -0.90 V vs Ag/Ag⁺ at a step of 0.05 to 0.03 V. The potential was held at each potential for at least 5 min to reach the equilibrium. The spectra were fitted with GaussLor method in LabSpec6, and the average Raman shift of the nitrile peaks over three spectra was reported.

Supplemental Figures



Figure S1. ¹H NMR spectrum confirms the successful synthesis of [EM₄Im][BF₄].



Figure S2. CV measurements of 0.7 M [TBA][BF₄], 0.7 M [EM₄Im][BF₄], and 0.7 M [EMMIm][BF₄] in acetonitrile under Ar purging in the absence of proton donors. The scan rate was 10 mV/s for all measurements. All electrolytes are fairly electrochemical stable within the potential range used in this study (anodic to -2.5 V vs Ag/Ag⁺).



Figure S3. CV measurements of [TBA][BF₄] electrolytes at different [TBA][BF₄] concentration with 0.05 M [Et₃NH]Cl under Ar purging. A nonmonotonic change of current density at -2.5 V vs Ag/Ag⁺ was observed, with the highest current density achieved in 0.2 M [TBA][BF₄]. Since the current density under Ar completely stems from the direct reduction of $[Et_3NH]^+$ to H₂, this trend strongly suggests the lower relative concentration of $[Et_3NH]^+$ when the concentration of $[TBA][BF_4]$ is high.



Figure S4. Partial current densities of CO₂-purge (A) [TBA][BF₄], (B) [EM₄Im][BF₄], and (C) [EMMIm][BF₄] electrolytes at different concentrations with 0.05 M [Et₃NH]Cl as the proton donor at -2.5 V vs Ag/Ag⁺. Both [EM₄Im][BF₄] and [EMMIm][BF₄] electrolytes facilitate CO₂ reduction. [EM₄Im][BF₄] electrolytes yield a higher overall CO₂ reduction rate and produce both CO and formate, while [EMMIm][BF₄] selectively produces CO at a lower overall CO₂ reduction rate.



Figure S5. Scan rate dependent CV of 0.7 M [EMMIm][BF₄]. No scan rate dependence was observed under Ar purging. Under CO₂ purging, however, the CV results show a significant dependence on the scan rate. A peak related to mass transport limitation appears. Meanwhile, the peak current density and the applied potential to achieve the peak current density both shift with the scan rate. We note that at higher scan rates (> 25 mV/s), the peak due to mass transport limitation is not observable in the potential range usually adopted (< -2.5 V vs Ag/Ag⁺) in related studies.



Figure S6. Initial CA of [EMMIm][BF₄] electrolytes at selected concentrations. The high initial current density rapidly drops to a much lower steady-state current density.



Figure S7. Scan rate-dependent CV of (A) 0.7 M [TBA][BF₄] and (B) 0.7 M [EM₄Im][BF₄] under CO₂ purging. No apparent scan rate dependence was observed for both electrolytes.



Figure S8. Initial CA of [EM₄Im][BF₄] electrolytes at selected concentrations during CO₂ reduction. No rapid drop in initial current density was observed.



Figure S9. Composition-dependent solution resistance of [TBA]/[EM₄Im][BF₄] and [TBA]/[EMMIm][BF₄] electrolytes at selected mixture concentrations. Solution resistance remains at the same scale, indicating the presence of other factors that lead to the significant or nonmonotonic change of composition-dependent current density shown in Figure 3 in the main text.



Figure S10. Partial current densities of (A) $[TBA]/[EM_4Im][BF_4]$ and (B) $[TBA][EMMIm][BF_4]$ electrolytes. Similar to single ionic liquid electrolytes, $[EM_4Im]^+$ facilitates the overall CO₂ reduction at moderate to high relative concentrations but produces both CO and formate. In contrast, $[EMMIm]^+$ leads to a compromised overall reaction rate but selectively produces CO at moderate to high concentrations.

Figure S11. Scan rate dependent CV of [TBA]/[EMMIm][BF₄] electrolytes under (A) and (B) Ar purging and (C) and (D) CO₂ purging at scan rates of (A) and (C) 10 mV/s and (B) and (D) 100 mV/s. Similarly to [EMMIm][BF₄]-only electrolytes, no scan rate dependence was observed under Ag purging. CO₂ purging introduces strong scan rate dependence at [EMMIm][BF₄] concentrations higher than 0.1 M, and the wave due to mass transport limitation becomes apparent at a scan rate of 10 mV/s.

Figure S12. Initial CA of [TBA]/[EMMIm][BF₄] at selected concentrations. A rapid drop of high initial current density was observed when the [EMMIm][BF₄] concentration exceeds 0.05 M.

Figure S13. The dependence of H_2 formation rate on [Et₃NH]Cl concentration in CO₂-purged [TBA]_{0.5}/[EM₄Im]_{0.2}[BF₄] (purple) and [TBA]_{0.5}/[EMMIm]_{0.2}[BF₄] (red) at -2.5 V vs Ag/Ag⁺. At the same [Et₃NH]Cl concentrations, the H_2 formation rate is much lower in [TBA]_{0.5}/[EMMIm]_{0.2}[BF₄], indicating the presence of [EMMIm]⁺ suppresses the adsorption of hydrogen and the reduction of [Et₃NH]⁺ to H_2 .

Figure S14. Potential-dependent SERS of the nitrile group in 0.1 M (A) [TBA][BF₄], (B) [EM₄Im][BF₄], and (C) [EMMIm][BF₄] electrolytes. The peak corresponding to the nitrile group in acetonitrile (green dashed line) does not exhibit observable shift, while the peak corresponding to the nitrile group in 4-MBN (red dashed line) redshift under cathodic applied potentials.

References

- 1. G. P. Lau, M. Schreier, D. Vasilyev, R. Scopelliti, M. Gratzel and P. J. Dyson, *J Am Chem Soc*, 2016, **138**, 7820-7823.
- 2. W. Guo, B. Liu and M. A. Gebbie, *The Journal of Physical Chemistry C*, 2023, **127**, 14243-14254.