

Identifying Promising Ionic Liquids for Electrochemical CO₂ Reduction

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Electrochemical CO₂ reduction (CO₂R) is a promising technology to reduce CO₂ atmospheric concentrations by simultaneously storing renewable energy and generating high added-value products.¹ Among the many possible reaction products, the generation of syngas, *i.e.* a mixture of carbon monoxide and hydrogen, is particularly considered as it requires low energetic consumption, yet this product ensures a broad market share.² Such process usually occurs on weak CO binding catalysts, such as Au and Ag,³ and it can be particularly enhanced using ionic liquids (IL) as co-catalysts in the electrolyte.^{4,5} Earlier computational studies indicate that ionic liquids can either stabilize the CO₂ adsorbate *via* electric interaction⁶ or poison the electrocatalytic surface,⁷ thus blocking CO₂ reduction and enhancing water reduction. In our group, we recently carried out a systematic assessment of the role of different EMIM⁺/BMIM⁺-based ionic liquids for the electrochemical reduction of CO₂ on silver electrodes. Such study resulted in a joint experimental/modeling work,⁸ where some of us demonstrated that IL anions tune the ratio between the concentration of cations (EMIM⁺ or BMIM⁺) and the carbene species (EMIM⁺/BMIM⁺) in the electrolyte. Such effect can be rationalized by using few thermodynamic descriptors, such as the formation energy of EMIM⁺/BMIM⁺ species, their adsorption energy, and their ability to trap CO₂ in solution. Consequently, the ratio of cations and carbenes rules the CO₂ capture and electrochemical conversion properties of imidazolium based ILs.

Herein, we carried out a follow up of the previous study,⁸ generalizing the previously suggested descriptors to provide predictive guidelines for experimental synthesis. Screening among different IL, we confirmed that the formation energy of EMIM⁺/BMIM⁺ species is the primary driving force for enhancing water reduction. In fact, such carbenes either increase the local availability of protons to sustain hydrogen evolution (HER) or block the surface, hindering adsorption of CO₂ at the surface and thus allowing only HER to occur. Such surface blocking effect was further confirmed by in-house measurements of electrochemically active surface areas (ECSA) in presence of different IL. In addition to surface poisoning, EMIM⁺/BMIM⁺ can also trap CO₂ in solution, further hindering CO₂ reduction. Among the considered anions, acetate anion determines the lowest energy for EMIM⁺/BMIM⁺ deprotonation, consequently leading to high H₂ partial current densities and low ECSA values. Instead, triflate anion prevents the formation of carbenes and thus hinders any surface poisoning effect, enabling Faradaic efficiency toward CO behind 90%.

Overall, by generalizing the insights from the previous work,⁸ we here provide guidelines to identify the best ionic liquids out of simple thermodynamic properties. By extrapolating our results to IL not yet tested, it is possible to predict HER and CO₂R activities on silver, thus enabling a direct pathway for the experimental design of IL for CO₂R.

1. *Nat. Energy* **2019**, *4*, 732–745.
2. *Science* **2019**, *364*, eaav3506.
3. *ChemPhysChem* **2017**, *18*, 3266–3273.
4. *Science* **2011**, *334*, 643–644.
5. *J. Phys. Chem. C* **2012**, *116*, 15307–15312.
6. *ACS Catal.* **2016**, *6*, 7133–7139.
7. *J. Phys. Chem. C* **2015**, *119*, 20023–20029.
8. *Commun. Chem.* **2023**, *Just Accepted*.