

Reactions of carbon dioxide on an electro-chemical interface from computer simulations: Comparison with Au(111)

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The chemical transformation of CO₂ into more valuable chemicals is a lucrative way to harness and store the energy from renewable sources for later use. The electro-chemical route, using molten carbonates as the electrolyte, has been explored as one efficient alternative to achieve this transformation. Recently the reduction of CO₂ into CO was investigated in eutectic molten carbonate Li₂CO₃-K₂CO₃-Na₂CO₃ on a working electrode of gold plate [1]. Subsequently the dynamics of the relevant molecular and atomic species in a prototype carbonate were studied using the atomistic molecular dynamics simulations based on the density functional theory to describe the interactions between the atoms [2]. Key results were the repeated association and dissociation reactions of CO₂ with a carbonate ion CO₃²⁻ into the pyrocarbonate species C₂O₅²⁻, CO₂ + CO₃²⁻ ↔ C₂O₅²⁻, and the solvation dynamics of the oxalate C₂O₄²⁻, which was found to enhance the transformation CO₂ into CO in the experiments [1]. Here we extend the previous simulations by including a model electrode, Au(111) surface, explicitly in the simulation. We estimate the reaction barriers both in the pure electrolyte and in the vicinity of the surface. Interestingly the CO₂ is bound to the substrate in the presence of the electrolyte at the elevated temperature used in the experiments, thus enabling the electronic activation and reactivity of the CO₂, whereas it is weakly bound at the clean substrate in the vacuum environment. We also explore the reactions involving the oxalate specie and the binding of the CO molecule onto the substrate. We compare the results to the ones obtained on the static Au(111) surface without the electrolyte, and present simulated scanning tunnelling microscope images of the adsorbed species.

[1] D Chery, V Albin, A. Meléndez-Ceballos, V Lair, M Cassir, *International Journal of Hydrogen Energy* **41**, 18706 (2016).

[2] Antoine Carof, François-Xavier Coudert, Dario Corradini, Dominika Lesnicki, Elsa Desmaele, Rodolphe Vuilleumier, *International Journal of Hydrogen Energy* **46**, 15008 (2021).