**Theoretical investigation of CO2 reduction reaction on copper and copper-tin single-atom alloys**

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Human activities, particularly excessive carbon dioxide (CO2) emission, are the main driver for rapid global environmental changes. In order to terminate the global warming trend in time, the world has to find and implement methods to reduce global CO2 emission. The electrochemical CO2 reduction reaction (RR) can relieve the global warming by recycling the excessively emitted CO2.

Utilization of appropriate electrocatalysts permits the formation of various useful and stable C1 and C2 products such as CO, HCOOH, CH4, C2H4. Our research primary focuses on CO2-to-CO conversion. Firstly, because CO in combination with H2 forms synthesis gas that is an important chemical precursor for a number of industrial processes. Secondly, an analysis of the estimated production costs and process efficiencies revealed that CO is the economically most favorable reaction products of CO2 conversion. In addition, obtaining detailed information of the CO2-to-CO RR pathway and the influence of various factors on its efficiency and selectivity will be useful for С2+ reactions as well since CO in a key intermediate a majority of C2+ reactions.

The carbon oxide and formate (HCOO-) are the first possible products of CO2 electroreduction. The reactions that produce them are competing and have different pathways. For the first one, the key steps are CO2 chemisorption and CO desorption, for the second one, the key steps are H-CO co-adsorption and HCOO- desorption.

The calculations were conducted in the framework of grand-canonical density functional theory that allows directly define an electrode potential. It was found that physisorbed CO2 has a linear configuration parallel to the substrate, while chemisorbed CO2δ- demonstrates a bent shape having chemical bonds with two top Cu/Cu or Cu/Sn atoms. We demonstrated that there is a stability inversion between CO2 and CO2δ- at approximately -0.8 V vs SHE. Thus, we might conclude that the electrode potential is responsible for the equilibrium distribution ratio between CO2 and CO2δ- facilitating the chemisorption under large negative potentials. Calculations of a charge redistribution revealed that the linear physically adsorbed configuration demonstrates nearly zero charge, whereas CO2δ- shows a strong electron-affinity properties accumulating about 0.9 electrons under the strong negative potential of -1.5 V vs SHE. In addition, the process of a partial charge transfer is potential-dependent that might explains the stabilization effect of CO2δ- under negative potentials.

Based on reaction energy diagram, obtained during the research, we can conclude that the carbon oxide desorption barrier is almost potential-independent, whereas formate desorption becomes downhill under large negative potentials which is qualitatively coincides with experiments, where the Faradic efficiency (FE) for CO decreases and Formate FE increases with the potential decrease.

Since H-CO co-adsorption is essential for the formate formation, we investigated several adsorption configurations for hydrogen and CO and found that there is no stable H-CO co-adsorption near Sn site that might explains the HCOO- inhibition in CuSn alloys with small tin concentration.