Fundamental effect of electrolyte composition over photoelectrochemical processes

The rapid utilization of fossil fuels escorted by an excess of CO_2 emissions has led to global energy and environmental crisis. Economically viable CO_2 reduction would be a critical turnover in research, as it has the potential to fulfil a substantial need for clean energy. Herein, we provide the experimental proof for enhancement of the CO_2 reduction efficiency and selectivity from the SEI (semiconductor-electrolyte interface) side through the use of carbonates, borates, and alkali cations as the electrolyte as well as an overview of the latest developments on Cu2O based PEC CO2 reduction for solar fuel production. Cu2O is a low- cost semiconductor and one of the most promising candidates for PEC CO2 RR. We propose a very facile electrodeposition method, which offers a high level of reproducibility and the possibility of using a new electrode in each experiment in order to follow the phenomena occurring in the double layer during the photocatalytic run. In this way, we could correlate the final CO 2 RR performance with a reorganization of the cations and anions near the photocatalyst surface. It is shown in literature that that factors such as: carbonate concentration, local pH, the presence of alkali metal cations, the geometry of the anionic group, CO 2 solubility, conductivity as well as pH changes along with the number of H + in the electrolyte, play a significant role in regulating the partial CO 2 RR current. Additionally, the specific interaction between the alkali cation and geometry of the anionic group contributes to the formation of a kind of a “rigid layer” within the double diffusion, close to the photocatalyst surface layer, which accounts more for an apparent CO 2 RR current than the decrease in the finite Warburg element, which is a central key parameter for the diffusion coefficient values. This mechanism might provide useful information for creating further experimental design and the new pathways for addressing highly efficient PEC systems.