The evolution of Bi-based electrocatalysts during CO_2RR: Post-mortem and Operando investigations

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Electrochemical reduction of CO_2 to valuable chemicals and fuels has emerged as a promising approach to the net-zero emission target [1]. The p-block metals are selective for converting CO_2 to HCOOH, which enable to close the cycle of CO_2 and HCOOH for renewable energy storage [2]. Recently, bismuth (Bi)-based electrocatalysts have received intensive attention, due to their low toxicity and relatively high stability beyond good selectivity and activity for the CO_2RR [3]. Many studies focus on the structure and composition effects of Bi-base electrocatalysts on the CO_2RR performance. Several active species, including metallic Bi, Bi_2O_3, $(BiO)_2CO_3$, have been reported. However, the evolution of the composition and structure of Bi-based electrocatalysts happens during the reaction, which makes significant impacts on the overall performances. Thus, intensive post-mortem or in situ / operando investigations are required to clarify the reaction mechanisms.

In this work, Bi-based gas diffusion electrodes (Bi-GDEs) have been developed for operando Raman measurements. Operando Raman spectroscopy reveals that Bi_2O_3 undergoes chemical and electrochemical reactions in CO_2 saturated $KHCO_3$ solution during CO_2RR. Bi_2O_3 reacts chemically with CO_3^{2-} forming $(BiO)_2CO_3$ which has a layered structure. $(BiO)_2CO_3$ passivates the surface, and it can be electrochemically reduced to metallic Bi at a potential more negative than –0.56 V vs. RHE. Once metallic Bi exists on the surface, the CO_2RR happens, indicating that metallic Bi is active for the reaction. The evolution of nanoparticulate Bi_2O_3 to layered $(BiO)_2CO_3$, and then to Bi nanoflakes has significantly expanded the surface area of electrodes, elevating the geometric current density. The Bi-GDEs show excellent $HCOO^-$ selectivity of larger than 90% at potentials in a wide potential range, and a high current density of 108 $mA \cdot cm^{-2}$ at –1.2 V [4]. Bi-based electrocatalysts have different evolution pathways in acidic and alkaline environment, which determine the equilibrium potentials for Bi_2O_3 reduction to metallic Bi, and the morphology of electrodes. The deep understanding of the evolution of Bi-based electrocatalysts in Bi-GDEs will bring further improvements to enable its implementation in the CO_2 conversion at large scales.