**Understanding of Electrochemical CO2 Reduction Reactions from Intrinsic and Extrinsic Perspectives**

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**Abstract**

Electrochemical CO2 reduction reaction (CO2RR) has emerged as a promising technology to convert atmospheric CO2 into valuable chemicals using renewable energy sources. Designing efficient electrocatalysts with high activity (current density) and selectivity (Faradaic efficiency of a specific product) requires an understanding of the underlying chemistry of how intrinsic and extrinsic properties of catalysts affect CO2RR performance. Noble metal nanoparticles which have been widely used as catalysts for CO2RR have unique intrinsic properties depending on their surface morphologies. The surface morphologies of catalysts were modified by designing their nanostructures. For example, Au nanostars having exclusive Au {321} facets represented 3.8 times higher activity for CO production than Au {111} facets. In addition, branched CuO nanoparticles showed high FEC2H4­ above 70% because of a large number of grain boundaries, which are formed during the electrochemical reduction of CuO. Besides, AuAg alloyed nanoparticles exhibited remarkably low overpotential of CO production owing to the stabilization of bi-dentate \*COOH binding on AuAg alloyed surfaces.

In the meantime, the recent advanced electrochemical cell configurations, which provide high CO2 concentration, current density, and pH make it more important to understand how microenvironments near the catalyst surface are changed depending on the cell and catalyst design. In this presentation, the changes in extrinsic factors such as CO2 concentrations, pH, and humidity were investigated depending on the catalyst thickness using computational fluid dynamics (CFD) simulations. In addition, the water transportation during CO2RR in MEA cell was studied by comprehensive deuterium-labeled experiments and CFD simulation. Besides, the cation back-diffusion from anolyte to the cathode and their effects on CO2RR in MEA cell were elucidated. Finally, from the cell resistance measurements as a function of current density, it was observed that the current limiting factor of CO2RR in MEA cell was due to the Ohmic loss originating from the high cell resistance, instead of CO2 mass transport limitation.

I hope this comprehensive understanding of intrinsic and extrinsic properties of catalysts on CO2RR performances gives valuable insights for designing highly efficient catalysts and CO2RR systems in the future.