Catalytic evaluation of Pd subnanoparticle in electrochemical CO_2 reduction reaction

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Keywords: *metal cluster, metal subnanoparticle, electrochemical CO_2 reduction reaction*

In recent years, the development of technologies to convert CO_2 into useful chemicals has been increasingly demanded to achieve a carbon-neutral society. Electrochemical CO_2 reduction reactions (CO_2RR) are promising methods that enable the conversion of CO_2 into CO or HCOOH under ambient conditions using renewable energy. However, suppressing the competing hydrogen evolution reaction (HER) remains a significant challenge. Pd is a catalytic element capable of converting CO_2 into CO with high Faradaic efficiency, and the relationship between its structure and CO selectivity has been extensively studied[1)]. In Pd catalysts, it is known that energetically stable terrace sites are predominant for HER, while unsaturated coordination sites such as edges and kinks are predominant for CO formation[2,3)]. Therefore, designing a Pd catalyst material consisting only of unsaturated coordination sites may allow complete suppression of HER and achieve high Faraday efficiency of CO. Metal subnanoparticles (SNPs) with a diameter of approximately 1 nm are predominantly composed of unsaturated coordination sites, making them promising catalysts for CO_2RR. However, there are no reports on the application of Pd SNP to CO_2RR, because of the difficulty of synthesizing SNPs. In this study, Pd SNP were synthesized using a dendritic polymer, phenylazomethine dendrimer (DPA-G4), as a template[4)], and their catalytic performance in CO_2RR was evaluated.

12 equivalents of $Pd(C_5H_6O_2Cl)(CH_3CN)_2BF_4$ were added to DPA-G4, allowing the accumulation of Pd complexes onto DPA-G4. Subsequently, chemical reduction with $NaEt_3BH$ was performed to synthesize Pd SNP. ADF-STEM analysis confirmed an average particle size of 0.97 ± 0.18 nm. The CO_2RR performance of Pd SNP and commercial Pd/C was evaluated using an H-cell. This presentation reports the differences in Faradaic efficiency for CO production between Pd SNP and nanoparticles.

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