Z02-4813 - *(Invited)* Synthesis of TiO_2-Based for Electrocatalysts CO_2 Reduction Using in-Liquid Plasma Method and Control of Their Reduction Properties

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1050 - 1120

Room 305A (Level 3, Hawaii Convention Center)

Abstract

Introduction

In recent years, there has been growing interest in converting carbon dioxide (CO_2), a greenhouse gas, into a valuable resource. The electrolytic reduction method, which uses only water and electricity, offers a particularly clean approach to CO_2 conversion. Its high conversion efficiency at ambient temperature and pressure, facilitated by gas diffusion electrodes (GDE), makes it a promising option for widespread adoption. Electrocatalytic CO_2 reduction using GDE selectively yields carbon monoxide, ethylene, and formic acid with Ag, Cu, or Sn catalysts, respectively 1). These catalysts are often supported on conductive carbon black (CB), valued for its high electrical conductivity and porosity. However, CB-based catalysts encounter challenges like redox-induced degradation and high CO_2 overvoltage.

So, we turned to plasma in liquid as a new method for making electrocatalysts. Plasma in liquid is generated by subjecting a metal in solution to high-frequency, high-voltage conditions. This process enables the sputtering of metal onto powder samples dispersed in solution, with the metal surface instantly heated to high temperatures. This process can improve electrochemical properties like oxygen deficiency 2). Consequently, plasma treatment in liquid presents an opportunity to utilize highly durable and chemically resistant metal oxides as catalyst base materials.

The objective of this study was to synthesize a new catalyst for electrocatalytic CO_2 reduction using titanium dioxide as the catalyst base via in-liquid plasma. Titanium dioxide offers advantages of affordability, durability, and chemical resistance. Moreover, oxygen-deficient TiO_2 with enhanced conductivity finds application as a base material for batteries.

Experimental

In the experiments, high-frequency high voltage (4 kV, 100 kHz, 0.5 μs-Pulse Width) was applied under the same conditions to various metal electrodes in a 5.0 wt%-NH_4 solution (200 mL) containing dispersed TiO_2 (P25: 0.5 g) to generate plasma in the liquid. Common plasma electrodes included tungsten (W), silver (Ag), and copper (Cu). Each gas diffusion electrode (GDE) was

prepared by washing the powder after in-liquid plasma treatment with pure water, followed by spray coating on a gas diffusion layer with Nafion dispersion as a binder. Electrocatalytic CO_2 reduction was evaluated in a conventional three-chamber gas diffusion cell at 500 mA/cm^2 for 10 minutes. The CO_2 supplied to the gas chamber was collected in a Tedlar bag, and the CO_2 reduction products were analyzed by gas chromatography.

Results and Discussion

Figure shows the CO_2 reduction products and Faraday efficiency of P25 treated with various liquid plasma electrodes. In pristine P25, small amounts of CO and CH_4 were detected due to the redox cycle of Ti^{4+} and Ti^{3+}. The use of tungsten (W), silver (Ag), and copper (Cu) as in-liquid plasma electrodes increased the production of H_2, CO, and CH_4, respectively. The difference in conversion can be attributed to the fact that the amount of etched Cu is less than that of Ag. Additionally, black nanoparticles were dispersed in the filtered solution when Ag was used, while the solution turned a clear blue color with Cu, suggesting the formation of a complex with ammonia. Generally, oxidized metal nanoparticles are synthesized when plasma is generated in solution. In this study, since an alkaline solution was used, it can be considered that the oxidized Ag nanoparticle surfaces were reduced, resulting in highly dispersed reduced Ag nanoparticles being deposited. In contrast, the generated Cu nanoparticles impregnated TiO_2 by dissolving in ammonia and exhibited catalytic activity. CH_4 significantly affects Faraday efficiency relative to the amount produced because CO and H are two-electron reactions, while CH_4 is an eight-electron reaction, requiring four times as many electrons. Although C_2H_4 is produced by Cu nanoparticles at sufficient current density, the present results show increased CH_4 production. This may be due to TiO_2 promoting the hydrogenation of CO_2 before Cu forms the C-C bond. Further investigation is required.

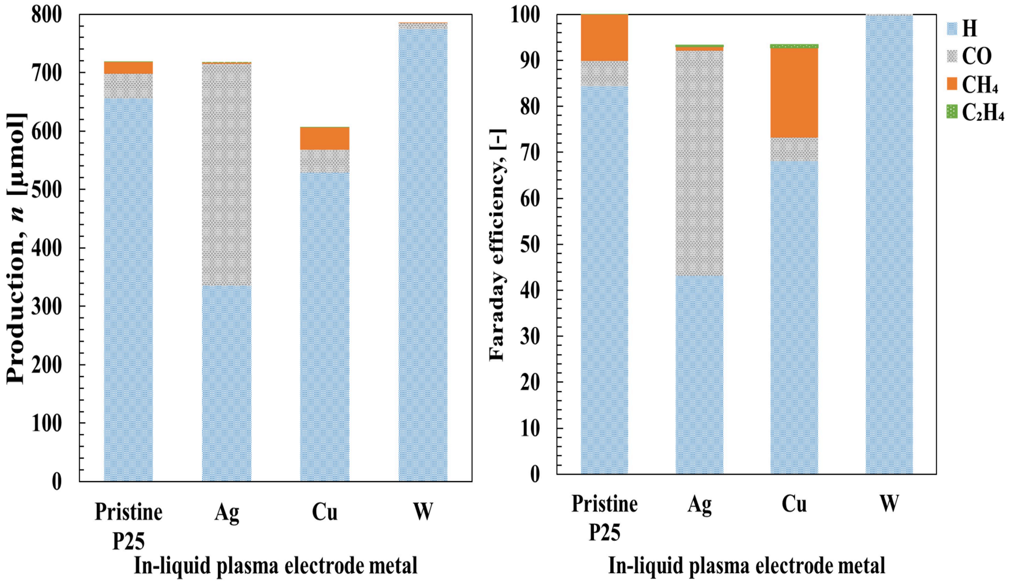
Conclusions

In this study, TiO_2 underwent treatment with various in-liquid plasma electrodes for electrocatalytic CO_2 reduction. As a result, changing the electrode allowed for successful support of metal nanoparticles on TiO_2, resulting in selectivity of CO_2 reduction products. During the presentation, we will discuss the comparison with conductive carbon black (CB) and the changes in electrocatalytic CO_2 reduction characteristics under different plasma conditions in liquid. Compared to pristine P25, the production of CO increased by 9.5-fold from 40 to 380 μmol, and CH_4 increased by 2.0-fold from 20 to 40 μmol.

Reference

1) Sassenburg *et al., ACS Appl. Energy Mater*., 5, 5, 5983 (2022).

2) Takagi *et al., Sci. Total Environ.,* 902 (13), 166018 (2023).



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