Synergistic Effect of Ag Decorated In-Liquid Plasma Treated Titanium Dioxide Catalyst for Electrocatalytic CO_2 Reduction Application

*<u>Kai Takagi [1, 2]</u>, Yuvaraj M. Hunge [3], Izumi Serizawa [2], Chiaki Terashima[1, 3]
[1]Graduate School of Science and Technology, Tokyo University of Science (TUS), 2641, Noda, Chiba 278-8510, Japan [2]ORC Manufacturing Co. Ltd., Japan [3]Research Institute for Science and Technology, TUS, Japan
*7222704@ed.tus.ac.jp (Business e-mail: k-takagi@orc.co.jp)

Keywords: Titanium Dioxide, In-liquid Plasma, Reduction Sintering, Electrocatalytic CO_2 Reduction, Noble Metals

The conversion of carbon dioxide (CO_2) into a useful resource by electrolytic reduction has been actively studied. Although conductive carbon can improve the selectivity of reduction products by loading auxiliary catalysts such as gold or lead, it is not durable enough. Therefore, we have focused on titanium dioxide (TiO_2), because of its unique properties such as non-toxicity, abundance in nature, good chemical stability during redox reactions, an inexpensive and highly durable. In this study, we examined the applicability of oxygen-deficient TiO_2 obtained by in-liquid plasma treatment(1) as catalyst support in the electrolytic CO_2 reduction.

The cyclic voltammograms of GC electrodes coated with P25, P-P25, B-P25 and CB are shown in Fig. 1. P25 that has been oxygen-deficient using hydrogen reduction sintering (B-P25) and carbon black (CB) were selected for comparison, respectively. Plasma treatment was performed by dispersing 2.0 g of TiO_2 particles (P25) in a 5 %-NH_4OH solution (200 ml) and applying an alternating pulse electric field (peak voltage 4 kV, frequency 100 kHz, pulse width 0.5 μs) to a tungsten rod electrode placed in the solution with a distance of 1 mm between electrodes. Cyclic voltammograms of P25 showed redox peaks at -1.15 and -0.95 V, which corresponds to the conversion of $Ti^{4+} \rightarrow Ti^{3+}$ and $Ti^{3+} \rightarrow Ti^{4+}$ respectively. In the case of P25, hydrogen production was not observed in the potential range 0 to -2.0 V. Interestingly, redox peaks were observed in P25, while it is not detected in P-P25. In addition, the current density in P-P25 increased significantly from -0.87 V, and large amounts of hydrogen gas bubbles were deposited on the electrode surface. Similar to P25, TiO_2-derived redox peaks were observed in B-P25 with a small shift in redox peaks, along with the peak area also decreasing. Current density (-30 mA/cm^2) is increased in B-P25 as compared to P25. The hydrogen production potential of P-P25 was shifted towards positive than that of B-P25 with high Ti^{3+} content.

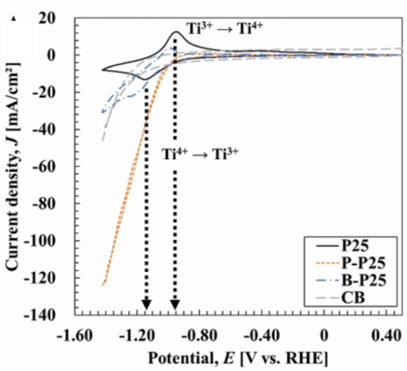

Fig. 1 Cyclic voltammograms of GC electrodes coated with P25, P-P25, B-P25 and CB.

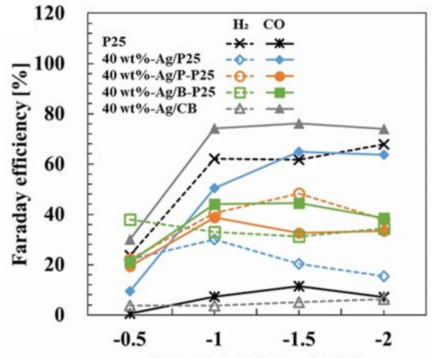

Fig. 2 Faraday efficiency of each sample calculated during electrocatalytic CO_2 reduction.

Faraday efficiency was measured using P25, P-P25, B-P25, and CB samples loaded with 40 wt% silver nanoparticles (AgNPs) and presented in Fig. 2. The silver-loaded sample was airbrushed onto a commercial gas diffusion electrode (1.0 mg/cm^2), and electrolytic CO_2 reduction was performed using a gas diffusion cell in 1.0 M KOH electrolyte. The electrode area of the working electrode was 0.5 cm^2. All gases were collected and measured by gas chromatography. P25 loaded with AgNPs showed a significant increase in CO production and Faraday efficiency was comparable to CB. TiO_2 may be the best catalyst because it produces CO and H_2 in a constant ratio. The amount of H_2 production was increased by the treatment of in-liquid plasma and the sintering process. This is because W derived from the liquid plasma electrode (during the plasma treatment) adhered to the P25 surface and hydrogen production was enhanced by the reduction of TiO_2. The use of TiO_2 as catalyst support suggests the possibility of controlling H_2 and CO production at arbitrary ratios using the TiO_2 after the in-liquid plasma and reductive sintering treatments.

References
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