Electrocatalytic CO₂ Reduction: Enhanced Selectivity at Low Overpotential on Anodized Silver Electrode

Li Qin Zhou, Chen Ling and Hongfei Jia*
Materials Research Department, Toyota Research Institute of North America
1555 Woodridge Ave., Ann Arbor, MI 48105, USA.
*hongfei.jia@tema.toyota.com

Introduction
Accumulation of atmospheric greenhouse gases, especially carbon dioxide (CO₂) in recent years, may trigger catastrophic climate change and endanger global sustainability. Among various potential remedies to the grand challenge of CO₂ fixation, one approach is to electrochemically reduce CO₂ to C1 products such as CO, formic acid, methanol, or methane, which can serve as feedstock to make organic materials and chemical fuels at large scale utilizing existing chemical processes. While it is preferred to conduct these processes in aqueous medium, electrocatalytic CO₂ reduction must compete with hydrogen evolution, which typically has fast kinetics and occurs at a lower electrode potential. Silver is one of a few metallic electrode materials with known selectivity for CO₂ reduction to CO. Over 80% of CO-Faraday efficiency has been reported at an overpotential of ~0.87 V,[1] but its selectivity reduces substantially when the applied electrode potential reduces. As low overpotential is essential for high energy conversion efficiency, here we report surface modification via anodization as one strategy to improve the performance of silver electrode.

Materials and Methods
Silver (Ag) plate electrodes were prepared by modifying the surface of Ag foil (Alfa Aesar, 99.999%, 0.25 mm thick) via potentiostatic anodization, which was conducted in 0.1M NaNO₃ with platinum as the counter electrode and Ag/AgCl as the reference electrode. A potential of 0.75V (vs. Ag/AgCl) was applied to the Ag plate electrodes for 5, 15 and 30 minutes respectively. Morphology of electrodes was studied on a JEOL 7800 field emission scanning electronic microscope (SEM). The structure of the samples was characterized by powder X-ray diffraction (XRD), using a Rigaku SmartLab powder diffractometer equipped with a Cu Ka radiation source. Electrocatalytic CO₂ reduction was performed in a two chamber cell separated by Naion® 117 membrane. KHCO₃ (0.1M, aqueous) was used as the supporting electrolyte. CO₂ was purged through the electrolyte for at least 15 minutes before starting each electrolysis experiment. Gas phase products were analyzed using gas chromatography (GC).

Results and Discussion
Anodization treatment significantly altered the surface morphology of silver electrodes. While the original silver foil was relatively smooth (Fig. 1a), a porous surface structure was clearly formed after anodization (Fig. 1b, c and d) for 5, 15 and 30 of treatment, respectively. Activity of the resulting electrodes for electrocatalytic CO₂ reduction was first characterized by cyclic voltammetry (CV). As shown in Fig. 2 (left), catalytic currents were significantly enhanced after anodization, and the highest value was observed from the sample subjected to 15 min of treatment. Such an improvement can be readily attributed to the formation of porous surface, resulting in larger electrochemical active surface area for the reaction. However, further tests with steady state electrolysis showed that product selectivity from the anodized electrodes was also significantly changed, which cannot be simply explained by surface roughness. Increase of CO-selectivity associated with anodization is particularly evident at lower overpotentials, with a CO selectivity of 56% for the anodized electrode vs. 4.8% for the pristine Ag foil when operated at an overpotential of 0.5 V (Fig. 2, right).

Interestingly a preferred structural orientation of (420) plane was observed for anodized electrodes by XRD (data not shown here). The correlation between the observed structural orientation and the chemistry of catalytic active site is currently under investigation.

Significance
Selectivity control is of great importance to electrocatalytic CO₂ reduction in aqueous electrolytes. We demonstrated here over 10 times enhancement of CO-selectivity at low overpotentials on silver electrodes via a facile anodization treatment. Further elucidation of the mechanism may lead to a new frontier for this research field.

Figure 1. SEM images of the pristine (a) and anodized (b, c, d) silver foil electrodes

Figure 2. Comparison of cyclic voltammograms (left) and CO selectivity (right) of pristine (0 min) and anodized (5, 15, 30 min, respectively) silver foil electrodes.

References