

# Report for Long-term Overseas Training

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## Outline

I have conducted research in Prof. Marc Koper's lab from January 18<sup>th</sup> to August 31<sup>st</sup>, 2016. Prof. Marc Koper and his group plays a central role in the field of electrocatalysis, and this long-term overseas training was a wonderful chance for me to develop my skills in this field. I have summarized my main research findings as follows.

## Research Results

The electrochemical reduction of carbon dioxide to useful materials has received much attention in recent years. Potential target products include fuels such as methane ( $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ ), or chemical feedstock such as the alcohols and aldehydes which may be used for further organic chemical synthesis ( $\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$ ). However, one of the biggest challenges in this field is the simultaneous evolution of hydrogen ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  or  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ ) which drastically decreases the overall faradaic efficiency. Here, we have focused on the effects of carbon dioxide on the hydrogen evolution rate on copper electrodes, which are the materials with the highest faradaic efficiency to date.

Figure 1 shows a cyclic voltammogram of a polycrystalline copper rotating disc electrode in a pH 2.5 N  $\text{NaClO}_4$  electrolyte. Two reduction waves can be observed when the solution was saturated with argon (black lines). The wave at the positive potential leads to a plateau current which correlates to the square root of the rotation rate, indicating a mass transportation process is the limiting factor. We have ascribed this current to hydrogen evolution from proton reduction. In contrast, the current which increases from c.a. -1.1 V vs RHE (Reversible Hydrogen Electrode, all potentials hereafter will be reported vs this reference) increases after the surface proton concentration has been depleted, and therefore, we assign the origin of this current to the reduction of the water molecule itself. Noteworthy is the fact that it is this process which is specifically inhibited by the addition of carbon dioxide as can be seen from the red lines.

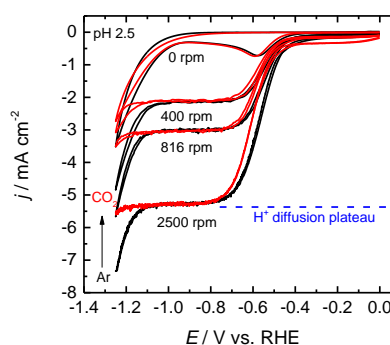


Figure 1. Cyclic voltammograms of a polycrystalline copper rotating disc electrode in argon (black) and carbon dioxide (red) atmosphere. Scan rate: 50 mV/s Electrolyte: 0.1 M  $\text{NaClO}_4$  solution (pH 2.5)

These selective, inhibitory results were also observed in a carbon monoxide atmosphere as can be seen in Figure 2. Blocking of hydrogen evolution sites due to the adsorption of carbon monoxide has been proposed in previous literature, but the active site has always been assumed to be the proton reduction site, which is indeed the lower overpotential pathway. The results in Figure 1 and 2 unequivocally show that the concentration factor in the rate equations plays a central role in determining the major reaction pathway in a real system.

Finally, carbon monoxide is known to be further reduced to products such as methane and ethane on copper electrodes. In order to confirm the existence of carbon monoxide on the surface at the negative potentials where water reduction takes place, we have measured the infrared spectra of the absorbates in an in-situ ATR-IR (Attenuated Total Reflection Infrared) configuration. When the spectrum at 0 V is taken as the reference, the carbon monoxide peak increases from -0.8 V and the intensity remains relatively constant until -1.2 V, indicating that carbon monoxide coverage does not decrease even in the potential region for water reduction. Therefore, the main inhibitor for hydrogen evolution is carbon monoxide, but contrary to popular belief, it is inhibitive for the water reduction reaction instead of the proton reduction reaction. A manuscript is under preparation based on these results.

### Acknowledgements

I express my thanks to Prof. Marc Koper for his guidance and Drs. Ioannis Katsounaros and Marta Costa-Figueiredo for their help in technical issues. This overseas training was made possible by the funding from JSPS. Finally, I thank the MERIT program and my supervisors Dr. Ryuhei Nakamura, NIMS President Kazuhito Hashimoto, Prof. Hiroshi Ishikita, and Prof. Koichi Yamashita for allowing me to spend more than half a year abroad.

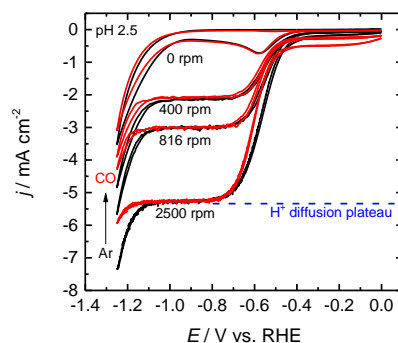


Figure 2. Cyclic voltammograms of a polycrystalline copper rotating disc electrode. All conditions are the same in Figure 1 except for the atmosphere (black: argon, red: carbon monoxide)

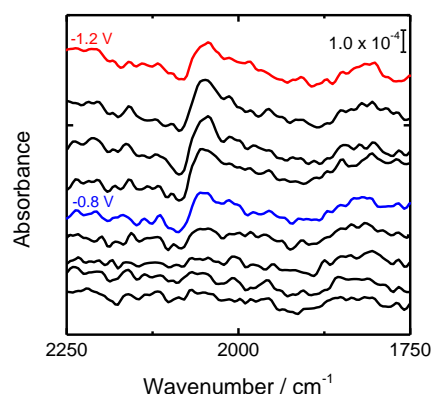


Figure 3. FT-IR spectra of a polycrystalline copper electrode on a silicon prism. Spectra are in 0.1 V intervals from -0.4 V to -1.2 V. The spectrum at 0 V was used as the reference.