

## 論文の内容の要旨

論文題目 A Comparative study of novel materials for electrochemical reduction of CO<sub>2</sub> in aqueous solutions

(電解液中二酸化炭素の電気化学還元に適した新規材料の比較検討)

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Carbon dioxide (CO<sub>2</sub>) is the main greenhouse gas emitted through human activities and is also present in the atmosphere as part of the Earth's carbon cycle. There is a natural carbon cycle which exists between the soil, plants and oceans but the increased human activities over the centuries have started to alter this carbon cycle. The addition of more CO<sub>2</sub> to the atmosphere and its impact on our planet necessitates finding novel and efficient materials which can convert CO<sub>2</sub> into valuable chemicals. This process dubbed as 'Artificial Photosynthesis' essentially replicates the use of sunlight towards the generation of value-added chemicals and thus helps to capture the energy in chemical bonds, a form of energy that can be readily stored and transported and can help to mitigate the challenges posed to climatic cycle by CO<sub>2</sub>.

In the light of this objective, my first doctoral study was to reduce CO<sub>2</sub> under natural intermittent solar irradiation in order to observe its impact on the progression of CO<sub>2</sub> reduction with time. A novel Maximum Power Point Tracking circuit, working on Perturbation and Observation algorithm was employed to track and transfer the optimum V,I values on to the EC cells. The bulk metal electrodes of tin and gold were used to produce formic acid and carbon-monoxide, respectively. The maximum Solar-to-CO<sub>2</sub> reduction of about 4.3% efficiency was achieved. The affect of current

density on the faradaic efficiency of CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) was studied along with the analysis of each individual sections in the solar-to-fuel scheme.

The next chapter changed the focus from bulk metal to metal nanoparticles. Copper (Cu) and Gold (Au) were chosen as the target materials for the nanoparticles. Au mainly produces CO as a result of CO<sub>2</sub>RR and since CO acts as an intermediate specie for the generation of higher-order carbon products, copper was also chosen due to its higher propensity towards electron-intensive reactions. Arc Plasma Deposition (APD) technique was used to deposit the nano-sized particles on the surface of the substrate since the APD technique is characterized by highly ordered deposition of nanoparticles. The first phase of the study employed the conducting FTO glass as the substrate material. The nanoparticles were co-deposited in order to allow a composite reaction for the CO<sub>2</sub> reduction. The FTO-based electrodes were able to generate formic acid as a result of CO<sub>2</sub>RR with a faradaic efficiency of up to 60%. FTO suffered surface deterioration during the experiments however the results did demonstrate improved activity towards CO<sub>2</sub>RR and so the second half of this study focused on a more stable, metal-based substrate of In-Sn alloy. Exclusive deposition of Cu and Au was also carried in addition

to the co-deposition so that the individual roles of the Cu and Au nanoparticles could be determined. The results reflected that Cu nanoparticles were the most active towards increasing the faradaic efficiency as well as the production rates for formic acid during CO<sub>2</sub>RR.

Since a great deal of research has been reported on metal catalysts, our subsequent focus shifted towards the use of new materials that are abundantly available in foreseeable future so as to ensure elemental sustainability for long-term commercial use of CO<sub>2</sub> reduction. Chalcogenide sulfide glass was chosen as the working electrode material for the reduction of CO<sub>2</sub>. The experimental data from these samples showed that due to their amorphous structure, chalcogenide glasses were not active for photocatalytic reduction, possibly because of high recombination rate. The IV data from the bulk sulphides reflected that the current generation was directly proportional to the area of the ohmic contact between the copper wire and sample surface. Furthermore, the CO<sub>2</sub> reduction sites also seemed to be proportional to the distance from the ohmic contacts and meant that the surface further away from the ohmic contact, visually showed lesser formation of bubbles. The only product from CO<sub>2</sub>RR was the gaseous CO, which formed at a maximum faradaic efficiency of about 15%. The next half of this study used the particle form of the same glass structures and was formed by crushing the bulk material into micron-sized particles. These particles were then stirred in nafion and

ethanol solution. The resulting mixture was drop casted onto a Carbon Paper (CP) substrate and then left to dry. CP along with being hydrophobic, is very conductive and hence an ideal choice for a substrate. The experimental results showed that the product selectivity had changed and formic acid with up to 26% faradaic efficiency was observed for this particle-based chalcogenide electrode.

The sulfide chalcogenides were found to be active for CO<sub>2</sub>RR but in order to increase the product selectivity, our research direction switched to chalcogenide oxide materials that were reported to be more stable than sulfides. Cuprous oxide was employed since it is a stable oxide form of Cu and has been shown to generate a product range different from metals. The gas phase analysis after the experimental results showed presence of ethylene (C<sub>2</sub>H<sub>4</sub>) along with hydrogen and CO while formic acid was observed during the liquid phase analysis. Methane was interestingly not observed and this demonstrated that the use of micron-sized catalyst particles on carbon paper had an impact on the adsorption of certain transitory species during CO<sub>2</sub> reduction which in turn affected the reduction mechanism of CO<sub>2</sub> and thus the selection of end-products.

Another chalcogenide oxide material tested was Co<sub>3</sub>O<sub>4</sub> since Co has two different oxidation states within its oxide structure and this could impact the charge transfer mechanism and hence CO<sub>2</sub> reduction. Acetic acid and formic acid were observed as a result of CO<sub>2</sub>RR however the results remained inconsistent and it was our conclusion that the redox couple mechanism of the catalyst was responsible for reducing CO<sub>2</sub> which caused inconsistency in results.

The final study during this doctoral research was conducted in collaboration with a commercial company JXTG, to test a homogeneous charge transfer mechanism using redox couple reactions. The idea was to exploit the redox differential between the different oxidation states of the metal ions for efficient transfer of electrons as this allowed the surface area for charge transfer to become more abundant and homogeneous. The results of the study are not discussed in the dissertation due to terms of agreement with the sponsor company.

In summary, this doctoral research explored the usability of bulk and nano-range metal catalysts along with new and novel chalcogenide-based electrode structures for electrochemical reduction of CO<sub>2</sub>. The results report various different products with different level of selectivity and reasonable faradaic efficiency. We hope that this work can pave the way for the selective reduction of CO<sub>2</sub> on a commercial scale.