

学位論文の要旨

学位論文題目: Catalyst development for electro-catalysis of carbon dioxide reduction (二酸化炭素の電気化学還元触媒の開発)

専攻: ナノ新機能物質科学

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Carbon emissions have aroused tremendous environmental problems, such as global warming, ocean acidification, climate change, and so on. Carbon dioxide (CO₂) is the most important greenhouse gas. Its concentration of atmospheric exceeded 400 ppm from 2016, which added to concerns about the immense potential scale of economic, social, and ecological damages. Therefore, the development of strategies and technologies to effectively reduce CO₂ emissions has attracted great attention. The different proposed technologies follow one of two major approaches: to capture and geologically sequester CO₂, or to convert CO₂ into chemicals and fuels. The chemical conversion and utilization of CO₂ into high value-added chemicals and fuels are a more attractive and promising solution. Among all of the chemical conversion routes including thermal/electro/photo-catalytic strategies, the electrochemical CO₂ reduction reaction (CRR) into value-added chemical feedstocks offers a sustainable route toward carbon-neutral in the future due to its ambient operating temperature and pressure, and its effective control of the target product through adjustment of the applied potential. Especially, electricity can be generated from renewable energy sources such as solar and wind energies. It is reasonable to believe that the price of electricity by renewable energy is lower and lower with the continuous development of renewable energy technology in the future.

Many heterogeneous catalysts have been developed for the clean, efficient transformation of CO₂ to high value-added products to date, based on a multiple-electron transfer mechanism involving transfer of 2, 6, 8, or 12 electrons, such as carbon monoxide (CO), methane (CH₄), formate, and C₂ products (*i.e.*, ethylene and ethanol), that of them are the most important building block in chemical industry, and possess a

large market. In general, the catalysts currently being employed are still not active enough and have insufficient catalytic selectivity and stability. This is attributed to that CO₂ is a thermodynamically stable molecule with low reactivity. CO₂ activation has to overcome a high barrier, and the chemical utilization of CO₂ constitutes a significant challenge. The other hand, the reaction mechanisms are still under debate. So, these problems urge us to investigate the CO₂ conversion and develop high efficiency electrocatalyst.

Currently, copper is still the main metal that can effectively catalyze CRR to C₂ products, owing to the specific binding energy of *CO intermediate. Among all the copper-based catalysts, Cu₂O is considered optimal due to its better selectivity towards C–C coupling which is attributed to its controllable defects, morphology and so on. In Chapter 1, Cu₂O nanoparticles with rough surface and abundant oxygen vacancies were facilely prepared by using an ionic liquid, [Omim]Cl (1-octyl-3-methylimidazolium chloride), as a bifunctional structure-directing agent, where the [Omim]⁺ played a role of surfactant to adjust the morphology of Cu₂O and the Cl⁻ facilitated the formation of oxygen vacancies by coordination with Cu⁺. The obtained Cu₂O nanoparticles were further dispersed on the home-made graphite nanosheets to fabricate a composite catalyst. By adjusting the content of [Omim]Cl, the optimum catalyst of Cu₂O/ILGS-400 performed the best performance with a faradic efficiency (FE) of 62.4% for C₂ products (ethylene and ethanol) with 0.1 M KHCO₃ as electrolyte at -1.15 V (*vs.* RHE) in an H-cell. To overcome the low current density of CRR in the H cell, a home-made flow cell was established to enhance the mass transport of CO₂. An excellent catalytic performance with high FE of C₂ (78.5 ± 2%) and commercial-level current density (123.1 mA cm⁻²) at -1.1 V (*vs.* RHE) for 100 h in a flow cell. *In-situ* surface-enhanced Raman spectroscopy and density functional theory (DFT) computations proved the special structure of Cu₂O strengthened the adsorption of intermediates (CO₂^{*}, CO*) and the following C–C coupling reaction, thus remarkably promoting the formation of C₂ products. This work affords a novel strategy to synthesize metal oxide with controllable morphology and defects for electrochemical applications.

Among commodity chemicals, formate is noted for its nontoxicity, safety,

transportability, and broad applications, which is also a hydrogen carrier for transportation. From CRR to formate is also a superior pathway, which has been investigated due to high selectivity. However, the double high index of current density and FE in CRR is a great challenge. In Chapter 2, carburized indium oxide nanorods ($\text{In}_2\text{O}_3\text{-C}$) was synthesized by pyrolysis of MOFs precursor [MIL-68 (In)]. The electronic structure of In was regulated and the localization of negative charges was increased on the surface of $\text{In}_2\text{O}_3\text{-C}$ catalyst, resulting in high FE of 97.2% at -1.0 V vs. RHE and above 90% in a wide potential range of 500 mV using the H cell. Furthermore, it reached a current density of $-1.0 \text{ A}\cdot\text{cm}^{-2}$ in the flow cell for producing formate efficiently. The carbon atoms embedded into the In_2O_3 lattice were able to regulate the electronic structure of In and increased the localization of negative charges on the surface of In_2O_3 , resulting in enhanced activity and selectivity simultaneously for CRR to formate. The whole reaction path from CO_2 to formate on $\text{In}_2\text{O}_3\text{-C}$ was investigated by DFT computations, *in-situ* attenuated total reflection surface-enhanced infrared adsorption spectroscopy and 2D/3D surface-enhanced Raman spectroscopy. This work gives new light on developing high-performance CRR catalysts with high selectivity under large current density.

Therefore, two new electro-catalysts were designed, synthesized and applied to CRR, which exhibited the excellent performance about ethylene, ethanol, and formate. And a preliminary study is made with these catalysts in the ampere-level current state. The development of high efficiency electro-catalysts provided a new view in identifying the active sites and the pathways to the low carbon products for CRR.

【審査結果要旨】

(学位申請者 王 文行)

当学位審査委員会は本論文を詳細に審査し、かつ論文審査会を令和5年8月8日公開で開催し、その発表と質疑応答について審査した。その審査結果を下記のようにまとめる。

二酸化炭素の電気化学還元は再生エネルギー電気を使い、二酸化炭素と電気化学セルの水溶液から各種化学品とエネルギー製品を温和な温度と圧力条件下で合成する方法である。

本論文は緒言、第一章、第二章、まとめから構成される。緒言は二酸化炭素の電気化学還元の最新動向に関する紹介である。

第一章は塩素系イオン液体を利用して、グラファイト・ナノシートに担持された亜酸化銅系複合電極触媒を調製した。この電極と0.1M炭酸水素カリウム電解質水溶液から構成されたセルにおいて、CO₂からのエチレンとエタノールの直接合成では62.4%のファラデー効率を実現した。さらに物質移動効率が向上された連続フロー型セルに応用し、上記反応を78.5%のファラデー効率と実用レベルの高い電流密度(123.1mA/cm²)で100時間以上安定運転した。量子化学計算とその場でのラマン分光の解析によって、塩素イオンに誘発された銅系電極の表面配位欠陥濃度に支配される中間生成物の吸着速度とC-C結合速度が合成速度向上の鍵であることは明らかになった。

第二章はMOF(金属錯体フレームワーク)前駆体を生かして、炭化インジウム酸化物ナノロッド電極を調製した。二酸化炭素還元によるギ酸の合成において、97.2%のファラデー効率を実現した。さらに物質移動効率が向上された連続フロー型セルに応用し、この合成反応を実用レベルの高い電流密度(1A/cm²)で100時間以上安定運転した。各種分光解析および量子化学計算をもって、これらの反応のメカニズムを解明した。

最後に上記内容のまとめも記載してある。

上記の内容は国際学術専門誌に原著論文2報として掲載された。

当審査委員会は以上を総合的に判断した結果、審査論文は、エネルギー、環境、電気化学、触媒化学諸分野において、学術的価値のある知見を与えたと判断し、博士の学位論文として十分な価値を有し、博士の学位を授与するに値する論文であると判定した。