論 文 の 内 容 の 要 旨

論文題目　Study of the active species and effect of CO_2 bubbling in the electrochemical reduction of CO_2 in aqueous solutions
（水溶液中の二酸化炭素の電気化学還元における二酸化炭素通気の影響と化学的活性種に関する研究）

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Solar energy is regarded as one of the most promising renewable energies to replace the fossil fuels in the 21st century. However, the solar energy is not stable and not available at night. Therefore, energy conversion, storage and transportation systems are needed for better utilizing the solar energy. Photoelectrochemical and electrochemical CO_2 reduction combining with solar energy to produce hydrocarbons and other organic chemicals, such as CH_3OH and HCOOH, are promising ways to transform and store solar energy into chemical energy. In these methods, CO_2 bubbling into the aqueous electrolytes ($KHCO_3$, KCl, etc.) is used and generally regarded as the active species. Since CO_2 can react with water to generate H_2CO_3, which further decomposes into HCO_3^- and CO_3^{2-}, the effect of CO_2 bubbling on the electrolyte and CO_2 reduction needs to be studied. Meanwhile, in the electrochemical reduction of $KHCO_3$ without CO_2 bubbling, formation of HCOOH was reported. However, both CO_2 and HCO_3^- were reported as the active species for the HCOOH production. The real active species is still not clear. Therefore, the active species in the electrochemical reduction of $KHCO_3$ and the effect of CO_2 bubbling in different solutions were studied and presented in this dissertation.

This dissertation is divided into 7 chapters, and the details are as follow:

Chap 1 is the general introduction. The background of the solar energy conversion, storage and transportation were first presented. Then, technologies and previous reports of electrochemical reduction of CO_2 in aqueous solutions were introduced. Finally, the motivations and objects of this research were given, which included investigating the active species and effect of CO_2 bubbling in the electrochemical reduction of CO_2 in aqueous solutions.

Chap 2 is the experimental section, in which the electrochemical cells, experimental setups, experimental materials and procedures, and analysis methods were presented.

Chap 3 studied the electrochemical reduction of $NaHCO_3$ and $KHCO_3$ without CO_2 bubbling using I-V measurement (products analysis is discussed in Chap 4). Voltammograms were obtained at various $NaHCO_3$ and/or $KHCO_3$ concentrations, and different temperatures on Cu working electrode. Reasons for why current density was increased by the high temperature and high HCO_3^- concentration were also thermodynamically studied.

Chap 4 analyzed the products in the electrochemical reduction of $KHCO_3$ without CO_2 bubbling and studied the active species in this reaction. Results showed that H_2 was the main products (over 90%) after 1 hour's reaction. The current increase caused by the high concentration of HCO_3^- and elevated temperature was mainly contributed by the H_2 evolution. However, the CO, CH_4 and C_2H_4 were also detected in the gas products, which had not been reported before. After examining the decomposition of HCO_3^-, results revealed that high concentration and elevated temperature strongly promoted the decomposition of the HCO_3^- into CO_2. The active species in the electrochemical reduction of $KHCO_3$ is probably the CO_2 rather than the HCO_3^-. The chemical reaction pathway of the decomposition of HCO_3^- into CO_2 was also discussed.

Chap 5 studied the electrochemical reduction of CO_2 in different electrolytes ($KHCO_3$, KCl, and KOH) under CO_2 bubbling at various conditions. The effects of CO_2 bubbling, temperature, electrolyte, applied potential, reaction time, stirring, and geometrical shape of the working electrode on the faradaic efficiency of CO_2 reduction were investigated. Results showed that the HCO_3^- concentration and the applied potential strongly affected the CO_2 reduction and product selectivity. Lower concentration (0.1 mol/L) of HCO_3^- had better performance for the CO_2 reduction than higher concentrations (0.5, 1.0, and 1.5 mol/L). The best faradaic efficiency of CO_2 reduction of 55.1% was obtained in 0.1 mol/L $KHCO_3$ at applied potential of -2.1 V (vs Ag/AgCl) on a Cu wire working electrode.

Chap 6 examined the effect of CO_2 bubbling into different solutions ($KHCO_3$, KCl, KOH, K_2CO_3 etc.) by measuring the pH changes and total carbon concentrations. The concentrations of different carbonaceous species (CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}) in these solutions before and after bubbling with CO_2 were calculated according to the experimental data. Results showed that much higher ratio of dissolved CO_2 to total dissolved carbon ($[H_2CO_3^*]$/TC) was contained in 0.1 mol/L $KHCO_3$ (23.6%) than that in 1.5 mol/L $KHCO_3$ (2.8%), which possibly promoted the CO_2 reduction.

Chap 7 summarized the results above and discussed the progresses made in this dissertation. The limitations in this dissertation and suggestions to the future works were also given in chapter 7.