



Electroactive species study in the electrochemical reduction of CO₂ in KHCO₃ solution at elevated temperature

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ABSTRACT

Photoelectrochemical and electrochemical reduction of CO₂ into organic chemicals is promising for directly or indirectly transforming solar energy into chemical energy for further utilization. However, research on the electroactive species in these processes has been rather limited. In this work, we investigated possible electroactive species (CO₂ or HCO₃[−]) involved in the electrochemical reduction of KHCO₃ at elevated temperatures without CO₂ bubbling. The results showed that CO, CH₄, and C₂H₄ were produced after electrochemical reduction of 3.0 mol/L KHCO₃ at elevated temperature on a Cu electrode even without CO₂ bubbling, although their faradaic efficiencies were low (< 6 %). Measurements for CO₂ generation from the decomposition of HCO₃[−] showed that elevated temperature and high HCO₃[−] concentration strongly promoted this process. These results suggested that the in-situ produced CO₂ from the decomposition of HCO₃[−] was probably the electroactive species in the electrochemical reduction of HCO₃[−] without CO₂ bubbling. Changes of the Gibbs free energy, rate constant, and activation energy of the decomposition of HCO₃[−] into CO₂ were also investigated and calculated from the experimental data.

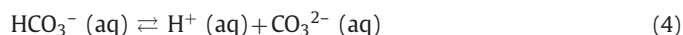
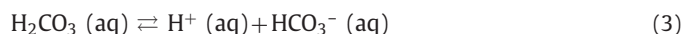
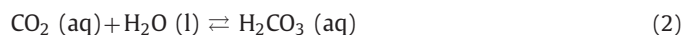
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1. Introduction

Since energy crisis is one of the most serious problems faced by human beings in the 21st century, developing renewable energies to replace the fossil fuel has been extensively studied recently. Most of the researches related to the renewable energies utilization focus on transforming the renewable energies into electricity [1–3]. Therefore, electrochemical reduction of CO₂ is an attractive method to provide human societies with fuels and chemical feedstock to realize a sustainable development powered by renewable energies [4–6]. On the other hand, reduction of CO₂ is an effective way to combat the global warming, which is caused by the increasing concentrations of atmospheric CO₂ [7,8].

In the electrochemical reduction of CO₂ in aqueous solutions, bicarbonate salt solutions are often used as supporting electrolytes, in which the major anion is HCO₃[−] [9–12]. Meanwhile CO₂ bubbling is used during these reactions and usually regarded as the

carbon source. However, CO₂ can dissolve in and react with H₂O to form H₂CO₃, which further decomposes into HCO₃[−] and CO₃^{2−}, as shown in reactions (1)–(4) [13,14]:



Therefore, there are four different carbonaceous species in the aqueous solutions: dissolved CO₂, H₂CO₃, HCO₃[−], and CO₃^{2−}. The actual electroactive species in the electrochemical reduction of CO₂ needs to be clarified in order to further study the mechanism of CO₂ reduction and improve reduction efficiency. However, there have been very few studies on electroactive species in the electrochemical reduction of CO₂.

In 1983, Hori and Suzuki reported that HCOO[−] was found in the electrochemical reduction of HCO₃[−] without CO₂ bubbling at room temperature with an Hg electrode [15]. The CO₂ dissociated from HCO₃[−] was suggested as the electroactive species for HCOO[−]

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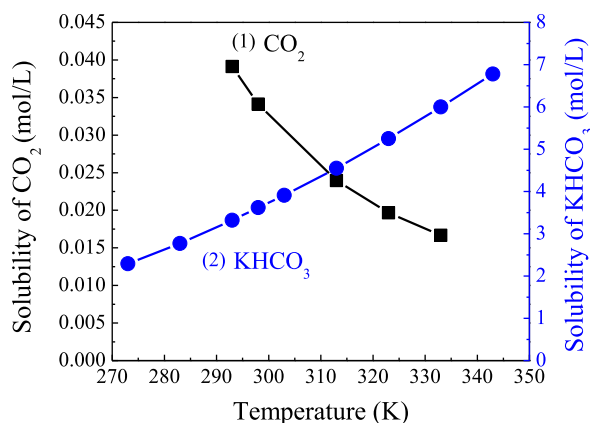


Fig. 1. Solubility of (1) CO₂ and (2) KHCO₃ in water as functions of temperature (partial pressure of CO₂: 100 kPa; data source: CRC Handbook of Chemistry and Physics (90th Edition) [18]).

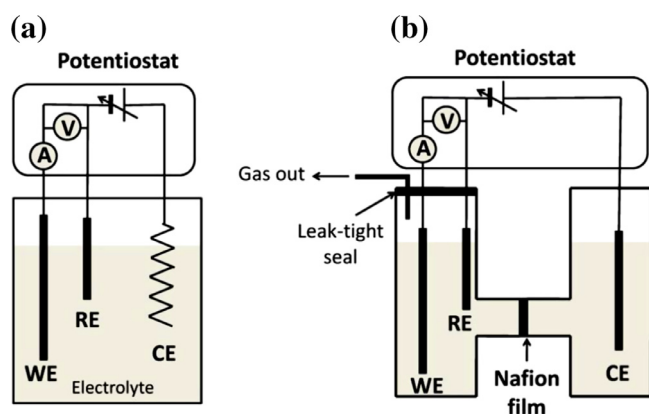


Fig. 2. Schematics of electrochemical reaction cells. (a) ALS SVC-3 Voltammetry cell, (b) H-type leak-tight cell.

production [15]. However, HCO₃[−] rather than CO₂ was recently reported as the electroactive species for HCOO[−] production in the electrochemical reduction of HCO₃[−] with or without CO₂ bubbling at Pb or Cu electrodes, respectively [16,17]. These reports lead us to conclude that the electroactive species are probably CO₂ and/or HCO₃[−]. However, the actual electroactive species is still not clear.

If HCO₃[−] is the electroactive species in the electrochemical reduction of CO₂/HCO₃[−] without CO₂ bubbling, increasing the concentration of HCO₃[−] should promote CO₂ reduction. Therefore, we investigated the electroactive species in the electrochemical reduction of CO₂/HCO₃[−] in aqueous solutions using a very high concentration of KHCO₃ electrolyte without CO₂ bubbling. Increasing the temperature of the solution reduces the solubility of CO₂ gas while improving the solubility of KHCO₃ in water, as shown in Fig. 1. Therefore, in this work, we used an elevated temperature (up to 333 K) to decrease the effect of dissolving CO₂ from the air and to make high-concentration KHCO₃ electrolytes easier to prepare.

2. Experimental

Schematic drawings of two electrochemical cells used in this research are shown in Fig. 2. Voltammetry studies of the electrochemical reduction of CO₂/HCO₃[−] were carried out in a one-compartment glass cell (SVC-3 Voltammetry cell, ALS Co., Ltd.) (Fig. 2a). A home-made leak-tight H-type glass cell (Fig. 2b) was used for further gas sample collecting experiments. The working electrode and counter electrode were separated by a Nafion

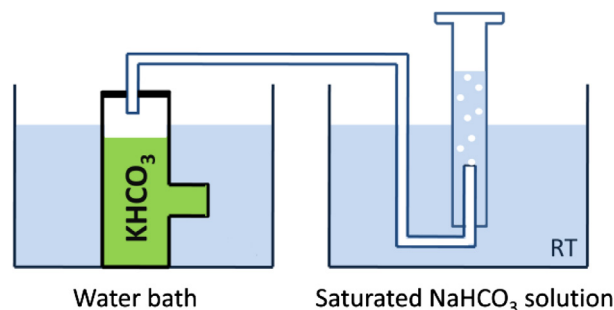


Fig. 3. Schematic of the experimental setup for measuring gas generation from the decomposition of KHCO₃ solutions (RT: room temperature (298 K); volume of KHCO₃: 35 mL).

film (DuPont: N117). A copper wire (Φ 0.5 mm, 99.999%, Nilaco) was used as the working electrode. The lengths of the working electrode were 30 and 44 mm in cells (a) and (b) with surface areas of 0.47 and 0.69 cm², respectively. The native copper oxide was removed from the wires by etching for 60 s in 0.1 mol/L aqueous HCl. The reference electrode was a standard Ag/AgCl (3.0 mol/L NaCl) electrode (RE-1B, ALS Co., Ltd.). All the potentials in this research referred to Ag/AgCl unless otherwise specified. A Pt coil (Φ 0.5 mm, ALS Co., Ltd.) and a Pt wire (Φ 0.5 mm, Nilaco) were selected as the counter electrode in cells (a) and (b), respectively. KHCO₃ (99.5%, Kanto chemical Co., Inc.) was used directly without any purification to prepare the electrolytes. The solutions were produced by mixing the chemicals with deionized water (18.2 MΩ, Organo Corporation, PRA-0015). The volumes of the electrolytes were 20 mL in cell (a) and 35 mL in both compartments of cell (b). We did not use CO₂ bubbling in this research. All the electrochemical experiments were conducted using a Solartron 1280C electrochemical system. A water bath (EWS-100RD, AS ONE Corporation) was used for temperature control. After the reactions, gas samples were collected and analyzed by an Agilent 7890A gas chromatograph equipped with a thermal conductivity detector (GC/TCD). The liquid samples were analyzed using an ion chromatography analyzer (Tosoh IC-2001, Tosoh Corporation) for confirming the HCOOH production.

The decompositions of KHCO₃ at different temperatures were measured by putting a half H-type electrochemical cell filled with 35 mL KHCO₃ solutions into a water bath and measuring the gas production as shown in Fig. 3. Since only a half H-type cell was used, the tunnel for connecting the left and right chambers of the H-type electrochemical cell was sealed by a glass plate. A PTFE (polytetrafluoroethylene) tube was used to guide the generated gas into a measuring cylinder that was vertically set upside down in a saturated NaHCO₃ aqueous solution at room temperature (298 K). The volume of the produced gas was determined from the excluded liquid volume in the cylinder.

3. Results and discussion

3.1. Voltammetric studies of electrochemical reduction of KCHO₃

The *I*-*V* measurements for the electrochemical reduction of CO₂/HCO₃[−] were conducted in 1.5 and 3.0 mol/L KHCO₃ electrolytes at different temperatures using the one compartment electrochemical cell (Fig. 2a) on a Cu working electrode. The current densities obtained at an applied potential of −1.6 V (vs. Ag/AgCl) under different conditions were recorded and are shown in Fig. 4. The current density increased with temperature in both 1.5 and 3.0 mol/L KHCO₃ electrolytes, which means that high temperature promotes current density. Compared with the effect of temperature, high KHCO₃ concentration had a greater effect in promoting

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