Electrochemical Reduction Behavior of Carbon Dioxide on Sintered Zinc Oxide Electrode in Aqueous Solution

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The electrocatalytic properties of a sintered ZnO electrode in electroreduction of CO₂ were investigated in aqueous solutions of several potassium salts. The reduction product from CO₂ was only CO (faradaic efficiency = 70% at -1.4 V vs. Ag-AgCl in 0.1 mol/dm³ KHCO₃ solution) with a considerable amount of H₂ as a byproduct. The ZnO was found to have a higher electrocatalytic activity for CO formation than metallic Zn, since the potential showing a maximal faradaic efficiency for CO formation was nobler by 200-250 mV than that of the Zn electrode. The partial current density for CO formation on the ZnO electrode in 0.1 mol/dm³ KH₂PO₄ solution was 10 to 50 times higher than that on a Zn foil electrode. The sum of the faradaic efficiencies for CO and H₂ formation did not reach 100%, the difference from which was attributed to the faradaic efficiency for the reduction of the electrode itself. The metallic Zn thus formed on the electrode surface played no significant role in the electroreduction of CO₂.

Key Words : Carbon Dioxide, Zinc Oxide, Electroreduction, Potassium Salts

1 Introduction

Recently, the electrochemical reduction (electroreduction) of carbon dioxide (CO₂) on various metal electrodes has been investigated by many authors using of different kinds of electrodes.¹⁻⁶⁾

It is well known that conductive metal oxides have high catalytic activities for the production of Cl₂ and O₂ from NaCl solution and for the reduction of O₂.⁷⁻¹³⁾ Thus, these oxides have attracted researchers' attention as the electrode materials for the electroreduction of CO₂.^{14,15)} For example, Furuya *et al.*¹⁶⁾ reported that the gas diffusion electrodes loaded with ZnS or ZnO as a catalyst were active for CO formation from CO₂.

In previous paper^{17,18)} the authors reported that the Zn metal foil electrode reduced CO₂ in aqueous electrolytes to HCOO⁻ and CO, in the formation of which the oxide layer formed on the electrode surface played a certain role. In the present work, so that the role of the zinc oxide layer was understood, a sintered ZnO electrode was employed for the electroreduction of CO₂ in aqueous solutions of several potassium salts.

2 Experimental

Specimen electrodes were sintered polycrystalline ZnO tablets of an apparent working surface of 0.94 cm². They were prepared by iso-static pressing of ZnO powder (1.0 g) of reagent-grade (Nakarai Tesque, Inc.; >99.0%) under 147 MPa, and then sintered for 4 hours at 1473 K in air. Ohmic contacts were made with an In-Ga alloy (7 : 3 by atomic ratio). The rest of the surface was shielded by epoxy resin after connecting with a Cu lead wire. Aqueous solutions of KHCO₃ (0.1 M ; M = mol/dm³), K₂SO₄

(0.05 M), K₃PO₄ (0.1 M), K₂HPO₄ (0.05 M), and KH₂PO₄ (0.1 M) were prepared from reagent grade chemicals and doubly distilled water. Each solution was pre-electrolyzed for 12 h at a current density of 40 μ A/cm² with platinized Pt electrodes, while purified N₂ was bubbled. The pH values of the KHCO₃, K₂SO₄, K₃PO₄, K₂HPO₄ and KH₂PO₄ solutions saturated with CO₂ were about 6.8, 4.2, 6.8, 6.1, and 4.2, respectively at 298 K. A catholyte of 40 ml was degassed by bubbling purified CO₂ gas in a Pyrex cell²⁾ prior to electrochemical experiments. The electroreduction experiments were usually carried out for 40 C at 298 K by combination of a potentio/galvanostat (Hokuto Denko ; HA-301) and an electronic coulometer (Hokuto Denko ; HF-201). The electrodes were polished with alumina powder (0.05 μ m) and then etched in 2 M HCl for 30 s. They were rinsed with doubly distilled water. Cyclic voltammograms were measured between the rest potential and -1.8 V vs. an Ag-AgCl saturated KCl reference electrode at 50 mV/s under N₂ or CO₂ atmosphere in the KHCO₃ or K₂SO₄ solution immediately after the immersion of the electrode in the solution. The pH of each solution under N₂ atmosphere was adjusted to the same value as that under CO₂ atmosphere by adding an appropriate amount of 2 M H₂SO₄ solution. The electroreduction products were analyzed by gas chromatography and high performance liquid chromatography as described previously.²⁾ The X-ray diffractometry (XRD) using Cu-K α radiation (JEOL Ltd. ; JDX-7E) was carried out so that the phases of the electrode surface before and after the electrolysis were observed.

3 Results

3.1 Cyclic voltammograms and reduction products

Figure 1 shows the cyclic voltammograms on the ZnO electrode in the KHCO_3 and K_2SO_4 solutions under N_2 (dotted lines) and CO_2 atmospheres (solid lines). The reduction currents began to flow at more positive potentials and became higher at the same potentials under CO_2 atmosphere than those under N_2 atmosphere in both solutions. When the pH values were adjusted to the same ones under both atmospheres, the difference between the current under CO_2 atmosphere and that under N_2 atmosphere corresponded to the reduction current of CO_2 . The ZnO was confirmed to have a significant catalytic activity for the electroreduction of CO_2 .

Figures 2, 3, 4, 5, and 6 illustrate the faradaic efficiencies, η 's, on the sintered ZnO electrode for 40 C at 298 K for electroreduction products in the aqueous solutions of KHCO_3 , K_2SO_4 , KH_2PO_4 , K_2HPO_4 , and K_3PO_4 with respect to the electrode potential, E . In all the solutions, the electroreduction products were CO and H_2 with a trace amount (less than 0.01%) of HCOO^- . No hydrocarbon and alcohol were detected. In the KHCO_3 and K_2SO_4 solutions, the dependence on the electrode potential of the products on the ZnO electrode was almost the same as that on the zinc foil electrode; namely CO was the main reduction product, the efficiency maximum of which reached about 70% in the KHCO_3 solution at

Fig. 1 Cyclic voltammograms on the ZnO electrode in aqueous 0.1 M KHCO_3 and 0.05 M K_2SO_4 solutions under N_2 (dotted line) or CO_2 (solid line) atmosphere, respectively, at ± 50 mV/s.

Fig. 2 Faradaic efficiency for the formation of CO and H_2 and current density on the ZnO electrode in aqueous 0.1 M KHCO_3 solution as a function of the electrode potential at 298 K. (Quantity of the electricity passed : 40 C)

around -1.40 V, which was 200-250 mV nobler than that observed with Zn foil electrodes.¹⁸⁾ A considerable amount of hydrogen (5-55%) was formed as a byproduct, the potential profile of which was opposite to that of CO.

In the phosphate solutions, the production of H_2 became predominant ($\eta > 50\%$) at both ends of the potential region examined, *i.e.* $E < -1.55$ V and -1.35 V $< E$, and the efficiency for CO_2 reduction became lower than those in the KHCO_3 and K_2SO_4 solutions. The η values for CO formation on the ZnO electrode showed maxima between -1.55 and -1.35 V in all the phosphate solutions and the highest value was found to be 62.5% at -1.40 V in K_2HPO_4 . The sums of η were distributed between 50 and 80%, and did not fulfill 100% in all the solutions examined.

3.2 Comparison with metallic Zn electrode¹⁸⁾

The catalytic activity of the ZnO electrode for CO formation was found to be 10 to 50 times higher than that of the Zn electrode, taking into account the fact that the partial current density for CO formation (I_{CO}) on the ZnO electrode in the KH_2PO_4 solution was 10 to 50 times greater than that on the Zn electrode,¹⁸⁾ *e.g.* the I_{CO} values were 2.0 and 0.04 mA/cm^2 for the ZnO and Zn electrodes, respectively, at -1.40 V. The distributions of the

Fig. 3 Faradaic efficiency for the formation of CO and H_2 and current density on the ZnO electrode in aqueous 0.05 M K_2SO_4 solution as a function of the electrode potential at 298 K. (Quantity of the electricity passed : 40 C)

Fig. 4 Faradaic efficiency for the formation of CO and H_2 and current density on the ZnO electrode in aqueous 0.1 M KH_2PO_4 solution as a function of the electrode potential at 298 K. (Quantity of the electricity passed : 40 C)

Fig. 5 Faradaic efficiency for the formation of CO and H₂ and current density on the ZnO electrode in aqueous 0.05 M K₂HPO₄ solution as a function of the electrode potential at 298 K. (Quantity of the electricity passed: 40 C)

Fig. 6 Faradaic efficiency for the formation of CO and H₂ and current density on the ZnO electrode in aqueous 0.1 M K₃PO₄ solution as a function of the electrode potential at 298 K. (Quantity of the electricity passed: 40 C)

Fig. 7 Dependence of the faradaic efficiency for the formation of CO and H₂ on the quantity of electricity passed on the ZnO electrode at -1.45 V in 0.1 M KHCO₃ solution at 298 K.

reduction products in the phosphate solutions were subtly different from those obtained with the metallic Zn electrode,¹⁸⁾ where the η value for H₂ was predominant (>90% at -1.4 V) and the values for CO and HCOO⁻ formation were less than 30 and 10%, respectively, at the maximum at -1.8 V in 0.05 M K₂HPO₄.

3. 3 Stability of catalytic activity of ZnO electrode

The dependence of the faradaic efficiencies for the reduction products of CO₂ at -1.45 V in the KHCO₃ solu-

Fig. 8 XRD patterns of the ZnO electrode surface (a) before, (b) after electrolysis at -1.45 V in 0.1 M KHCO₃ solution, (c) surface electrolyzed at -1.60 V in 0.1 M KHCO₃ solution, and of (d) zinc formate dihydrate powder as the reference.

tion on the quantity of electricity passed was examined to confirm the stability of the electrocatalytic activity of the ZnO electrode, which is shown in Fig. 7. The η value for CO reached a maximum of 80% at 10 C passed, and then decreased with increasing the quantity of electricity up to 30 C, beyond which the η value was kept almost constant (65%) up to 100 C. The η value for H₂ formation showed almost the same tendency as that for CO. The η value for HCOO⁻ was below 0.01% up to 100 C. The time course of the current density of electroreduction of CO₂ at -1.45 V in the KHCO₃ solution at 298 K increased steeply up to 30 min (*ca.* 7.0 mA/cm²) and then gradually increased. It became approximately 9.5 mA/cm² after about 400 C were passed for 15 hours, *i.e.* the relatively low efficiency at the initial period of the electrolysis may be due to the low current density with a low surface area of the ZnO electrode. As the quantity of electricity passed for the experiments were usually 40 C, the current densities presented in Figs. 2, 3, 4, 5, and 6 are mean values including the initial extremely low values.

In order to realize the deficiency from 100% in the sum of faradaic efficiencies for each product on the ZnO electrode, the electrode surface was investigated by XRD before and after the electrolysis for 40C in 0.1 M KHCO₃. Figure 8 depicts the XRD patterns of the surfaces, with the pattern of zinc formate dihydrate powder as a reference. Apparently the peaks of ZnO and Zn were observed, while no peak related to zinc formate was found on the surface of the ZnO electrode after the electrolysis.

The effects of Zn produced on the surface of the ZnO electrode on electroreduction of CO₂ were also examined. The changes of the rest potential of the ZnO electrode in

the KH_2PO_4 solution (40 ml) on addition of 5 mmol of formate ions were also compared both under N_2 and CO_2 atmospheres to make clear the performance of the electrode. No difference in the rest potential was observed between both atmospheres. However, the addition of formate ions caused a significant change of the rest potential from -0.083 to -0.120 V due to the pH shift from 4.3 to 4.9 of the solution, which corresponded to the -35 mV shift of the potential.

3.4 Dependence on pH and partial pressure of CO_2

In order to elucidate the effect of pH on the electroreduction of CO_2 , the potentiostatic electroreduction of CO_2 was carried out in phosphate buffered solutions of several pH values.

Figure 9 shows the relationship between the partial current density for the formation of CO, I_{CO} , and the electrode potential. It is seen that the potential-current curves are divided into three regions, *i.e.* the Region I; -1.20 to -1.35 V, Region II; -1.35 to -1.55 V, and Region III; -1.55 to -1.70 V. In Region I, a linear relationship between the logarithm of the partial current density and the electrode potential holds at 2×10^{-2} to 1×10^0 mA/cm², its Tafel slope being about -120 mV/decade at all the pH values. I_{CO} does not depend on the pH value in Region I. In Region II, the partial current densities in log units are dependent linearly on the potential and independent of the pH values with the same trend as in Region I, except that the Tafel slopes become about -300 mV/decade. On the other hand, the current densities depend neither on the electrode potential nor on pH values in Region III, where the diffusion limit of the CO_2 might occur.

Figure 10 represents the dependence of the partial current density in the KH_2PO_4 solution for CO formation on the partial pressure of CO_2 , $P(\text{CO}_2)$, 10 at -1.30 and -1.40 V, which correspond to the potentials in Regions I and II, respectively. There is a linear relationship between the

Fig. 9 Relationship between the partial current density for the formation of CO and the electrode potential on the ZnO electrode in the potassium phosphate buffer solutions with different pH values at 298 K.

logarithms of I_{CO} and $P(\text{CO}_2)$. The slope is unity and independent of the electrode potential, E .

Based on the above results, the reaction order is regarded as one with respect to CO_2 in Regions I and II, and E , I_{CO} , m , and n values may be represented as follows.

Region I :

$$^{\text{I}}E = C_1 - (120 \pm 20) \log ^{\text{I}}I_{\text{CO}} \quad (1)$$

$$^{\text{I}}I_{\text{CO}} = C_2 (P(\text{CO}_2))^m \exp(-FE/2RT) \quad (2)$$

$$m = (\partial \log ^{\text{I}}I_{\text{CO}} / \partial \log P(\text{CO}_2))_{E, T} \quad (3)$$

Region II :

$$^{\text{II}}E = C_3 - (300 \pm 20) \log ^{\text{II}}I_{\text{CO}} \quad (4)$$

$$^{\text{II}}I_{\text{CO}} = C_4 (P(\text{CO}_2))^n \exp(-FE/5RT) \quad (5)$$

$$n = (\partial \log ^{\text{II}}I_{\text{CO}} / \partial \log P(\text{CO}_2))_{E, T} \quad (6)$$

where C_1 to C_4 denote constants, m and n the reaction orders of CO_2 for CO formation, and F , R , and T have conventional meanings.

4 Discussion

Carbon monoxide was selectively produced by electroreduction of CO_2 on the sintered ZnO electrode ($\eta = 45\text{--}70\%$ at a maximum) in aqueous potassium solutions, and HCOO^- was hardly detected. These results differ from those in the case of Zn metal electrode,^{17,18)} where the HCOO^- was produced ($\eta = 5\text{--}20\%$) together with a large amount of H_2 ($\eta = 55\text{--}95\%$) in the potassium phosphate solutions. In the case of the ZnO electrode, which was run in the KH_2PO_4 , K_2HPO_4 , and K_3PO_4 solutions with different pH values each other, no significant change in the profile of the reduction products was observed, as is apparent from Figs. 4, 5, and 6. These findings indicate that the reduction current density of CO formation on ZnO should not be influenced significantly by the pH change.

The partial current for CO formation on ZnO was significantly larger than that on Zn.¹⁸⁾ Therefore, ZnO is a fairly good electrocatalyst for CO formation. However, the sum of the faradaic efficiencies for the reduction products, CO and H_2 , did not reach 100%. The reason

Fig. 10 Relationship between the partial current density for the formation of CO at -1.30 V and -1.40 V and the CO_2 partial pressure on the ZnO electrode in 0.1 M KH_2PO_4 solution at 298 K.

may be ascribed to the partial reduction of ZnO electrode itself¹⁹⁾ or to the absorption of produced HCOO^- on the surface of the ZnO electrode.²⁰⁾ The observation of the electrode surface after the electroreduction by XRD (Fig. 8) suggested the presence of Zn and the absence of zinc formate on the surface. Therefore, the absorption of formate ions was disproved. This was also supported by the results on the rest potential observation. Namely, the shortage of the sum of the faradaic efficiencies from 100% may be caused by the reduction of the ZnO electrode itself to Zn. The amount of Zn produced was estimated to be about 17 mg after 100 C passage on the assumption of the maximum shortage value of 50%. This amount corresponded to less than 2 % of the initial weight of the ZnO electrode.

If metallic Zn affects the electrocatalytic activity, the production of HCOO^- would become higher in the electrolysis.^{17, 18)} However, the dependence of the faradaic efficiencies for the reduction products CO and H_2 on the quantity of the electricity passed was relatively constant, as is shown in Fig. 7. HCOO^- was hardly observed up to 100 C and the cathodic current was stable for more than 15 hours.

Pakhomov *et al.*¹³⁾ reported that the doping of Zn to the ZnO electrode did not affect the properties of the ZnO electrode for the electroreduction of O_2 in aqueous solutions. This was also the case in the present work, where the deposited Zn during the electrolysis did not affect the properties of the sintered ZnO electrodes for the electroreduction of CO_2 . However, the deposited Zn may partially dissolve again during the electrolysis and the resulting Zn^{2+} ions affect the formation of CO from CO_2 as was discussed in a previous paper.¹⁸⁾ Therefore, it is considered that ZnO maintains a high electrocatalytic activity for CO formation in the electroreduction of CO_2 in cooperation with Zn^{2+} ions.

According to the kinetic analysis of the reactions for the CO formation, no dependence of I_{CO} on pH values was observed in potentiostatic electrolyses. Two regions having Tafel slopes of -120 and -300 mV/decade for the $I_{\text{CO}}-E$ curves were observed. The reaction order of CO_2 on the CO formation was almost unity in both regions. Based on these results, the theoretical values of Tafel slopes, and the reaction order of CO_2 derived by the Langmuir's isotherm for the adsorption, the following scheme is proposed for the mechanism of the CO formation. Mechanism :

or

In the scheme B^- denotes an appropriate counter anion of the supporting electrolyte, $\rightarrow$ the rate determining step, and $_{(\text{aq})}$ and $_{(\text{ads})}$ The hydrated and adsorbed states, respectively.

5 Conclusion

Sintered ZnO electrodes partially covered with Zn formed during reduction processes were found to have a higher electrocatalytic activity for formation of CO from CO_2 than the metallic Zn electrodes¹⁸⁾ in aqueous potassium salt solutions. The results support the observations in the electrolysis using the Zn electrode pretreated in K_2SO_4 solution, where ZnO occurred on the surface of the electrode. The similar results were obtained by addition of Zn^{2+} ions to a KHCO_3 solution, where the efficiency for CO formation reached 70% with HCOO^- formation at a lower efficiency being accompanied. The further spectroscopic investigations should be required to identify intermediate species and pathways for CO formation on metallic and oxide electrodes.

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