Pyrochlore-type Bi$_2$Sn$_2$O$_7$ oxide as an electrocatalyst for carbon dioxide reduction

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Pyrochlore-type A$_2$B$_2$O$_7$ ($A = Pb, Bi; B = Nb, Ru, Sn, Ir$) oxide fine powders were synthesized by a wet-chemical method. The electrochemical reduction properties of carbon dioxide were investigated with carbon-based gas-diffusion-type electrodes loaded with various pyrochlore-type oxide catalysts. The current–voltage curves under pure CO$_2$ gas flow showed that the Sn-based pyrochlore-type oxides gave high electrocatalytic activities for the electrochemical CO$_2$ reduction. Among the pyrochlore-type oxides tested, Bi$_2$Sn$_2$O$_7$ showed the highest CO$_2$ reduction reaction which gave CO as a main product at very high concentration. XPS analyses showed that the high performance for the electrochemical CO$_2$ reduction of Bi$_2$Sn$_2$O$_7$ was come from the valence state of Sn and/or oxygen adsorption–desorption properties of the pyrochlore-type oxide.

Key-words : Pyrochlore-type oxide, Electrochemical reduction, Carbon dioxide, Gas-diffusion-type electrode, Bi$_2$Sn$_2$O$_7$

Carbon dioxide is one of the serious causes of global warming these days.$^{1,2}$ Therefore, it has been very important to reduce the amount of CO$_2$ in atmosphere by reforming CO$_2$ as effective resources, such as hydrocarbons, alcohols, CO, and etc. Electrochemical reduction of CO$_2$ has been becoming one again one of the key technologies, in the recent situation of the rapid increasing in the use of renewable electrical energy sources.

However, development of high performance catalysts is very difficult due to high values of overpotentials for electrochemical CO$_2$ reduction reactions (1, 2), and hydrogen easily evolves (3) as a byproduct due to its lower overpotential than other CO$_2$ reduction reactions, in spite of their low equilibrium potentials (1, 2).

$$\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- &= \text{HCOO}^- + \text{OH}^- \\
&= -0.43 \text{ V vs. NHE}
\end{align*}$$

$$\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- &= \text{CO} + 2\text{OH}^- \\
&= -0.52 \text{ V vs. NHE}
\end{align*}$$

$$\begin{align*}
2\text{H}_2\text{O} + 2\text{e}^- &= 2\text{OH}^- + \text{H}_2 \\
&= -0.83 \text{ V vs. NHE}
\end{align*}$$

Then it is very important to develop high performance electrocatalyst. So far, many kinds of electrode materials for electrochemical reduction of CO$_2$ have been investigated, for example, metals (Cu, Ag, Au)$^{3-6}$ organometaric compounds,$^{7-10}$ oxides (CuOx),$^{11-14}$ etc. Among the electrocatalysts investigated, mixed oxide based catalyst is promising in its chemical stability and easiness of the valence control in the ions in the oxides. So far, pyrochlore-type oxide have been studied as high active electrocatalyst for fuel cells,$^{15-17}$ oxidation catalysts of hydrocarbon,$^{18}$ unique materials for chemical sensors,$^{19,20}$ however there are few reports the use of pyrochlore-type oxides for electrochemical CO$_2$ reduction. We have been studying about pyrochlore-type oxides for the electrode materials, such as oxygen reduction reaction catalysts.$^{21-23}$ Then, we developed a wet-chemical synthesis process for pyrochlore-type oxides.$^{21}$ It revealed that some pyrochlore-type oxides had high electrocatalytic performance and they are chemically stable in both acidic and alkaline solutions. In this study, we focused on the use of some pyrochlore-type oxides for the electrochemical CO$_2$ reduction by using a gas-diffusion-type electrode which is able to apply CO$_2$ directly as gas state. Here, we tried to investigate electrocatalytic properties to CO$_2$ reduction of some pyrochlore-type oxides. It was found that Bi$_2$Sn$_2$O$_7$ showed high and unique performances.

Pyrochlore-type A$_2$B$_2$O$_7$ ($A = Pb, Bi; B = Nb, Ru, Sn, Ir$) oxide powders were synthesized by a co-precipitation method.$^{21}$ Regent grades of Pb(NO$_3$)$_2$, Bi(NO$_3$)$_3$, H$_2$O, NbCl$_5$, H$_2$O, RuCl$_3$, H$_2$O, SnCl$_2$, H$_2$O, IrCl$_4$, were used as starting materials. Stoichiometric amounts of these salts for each composition were dissolved in 150 mL distilled water. Then, 20 mL 4 mol/L NaOH was slowly added to the solution to make a precipitation which was keep at 75°C for 24 h under refluxing. The solution was then heated at 80°C with stirring to evaporate, subse-

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quently the obtained material was calcined at 450–550°C for 2h and washed with distilled water to remove NaCl and other byproducts. The obtained oxide powders were characterized by means of X-ray Diffraction (XRD) analysis (JDX3500K; JEOL) using CuKα radiation (0.15405 nm), specific surface areas were measured by Brunauer–Emmett–Teller (BET) method by using the adsorption apparatus (BELSORP-miniII; BEL). The cathodic performance of CO2 reduction was analyzed using a gas-diffusion-type carbon electrode (GDE), which consists of gas diffusion and reaction layers. The latter one consisted of a catalyst (32 wt%), a carbon (36 wt%; ECP600JD, Lion Corp.), and the Teflon (40 wt%: D-210C, Daika Ind., Ltd.). The former layer was based on a carbon (60 wt%: AB-6, Denka Co., Ltd.) and a Te on (40 wt%: ECP600JD, Lion Corp.), and the Teflon (32 wt%). These two kinds of powders were laminated and hot pressed on a nickel mesh current corrector at 20 MPa and 370°C, to make a gas-diffusion-type electrode, 15 mm in diameter and 0.4 mm thick. The cathodic polarization curves of the electrodes were measured in a 0.1 mol/L KHCO3 aqueous solution at 30°C in an electrochemical half-cell by the gas-diffusion electrode held in an acrylic holder and a Pt-plate counter electrode. Pure CO2 or N2 gases were applied at the backside of the electrode at a flow rate of 30 mL/min. The electrode potential was controlled with a potentiostat (HAL 3001; Hokuto Denko) and an Ag/AgCl as a reference electrode. The cathodic polarization curves were measured from the open circuit potential to ca. –2.00 V vs. Ag/AgCl at 50 mV and 3 min step-wise. The initial pH of the solution was about pH = 12, and after the polarization (after ca. 100 min), it was changed to about pH = 10. This change in the redox potentials with the pH change from (pH=12 to 10 is estimated as ca. 120 mV during ca. 2000 mV measurement range. Then, the change in pH of the solution in the cell did not give the large change in the redox potentials in this experiment. Products obtained in the electrolysis were analyzed by gas-chromatography (BID-GC, Tracera; Shimadzu).

XRD patterns of pyrochlore-type oxides prepared by the co-precipitation method are shown in Fig. 1. It is observed that the XRD patterns of the oxides obtained at 450–550°C could be identified as almost single-phase cubic type of pyrochlore oxides, with good agreement for the databases, such as Pb2Ru2O7: PDF:00-034-0471, Pb2Sn2O7: PDF: 01-072-0002, Pb2Ir2O6.5: PDF:01-089-0581, Bi2Ru2O7: PDF:01-081-2328, Bi2Sn2O7: PDF:01-088-0496. BET surface areas are rather high between 17–89 m2/g, as also shown in Fig. 1.

Electrocatalytic properties of various oxide-doped GDEs for CO2 reduction in 0.1 mol/L KHCO3 at 30°C are shown in Fig. 2. All GDEs showed cathodic currents and some electrodes loaded with Bi2Sn2O7 etc. gave change in I–V curve at around −1200 mV vs. Ag/AgCl. This seems the change in cathodic reactions. Among these GDEs, it seems the Ru-based oxide catalysts have high cathodic performance, however these high current densities came from hydrogen evolution reaction as shown in Fig. 3. The main product from the GDEs loaded without (carbon only) or with Bi2Ru2O7, Pb2Ru2O6.5, Bi2Nb2O7, Pb2Ir2O6.5 catalysts was hydrogen, and CO or other gases were not generated. On the other hand, it was found that the GDEs loaded with Bi2Sn2O7 or Pb2Sn2O7 gave CO product with high concentrations at the cathodic potential below −1500 mV vs. Ag/AgCl, as shown in Fig. 4. Also very small amounts (ca. 20 ppm) of HCOOH were detected during electrolysis with GDEs loaded with Bi2Sn2O7 or Pb2Sn2O7, although the exact amount could not be determined due to the detection limit of the GC. Among the oxides tested, the Bi2Sn2O7 – base electrode produced only CO at 50.4 ppm/(min·cm2) at −1500 mV vs. Ag/AgCl. Although, Faradaic efficiency to produce CO and H2 was 5 and 0%, respectively at −1500 mV vs. Ag/AgCl, selective CO2 reduction to CO was obtained with the Bi2Sn2O7 catalyst. The other loss of currents might be consumed as a non-Faradaic current to charge the GDE as a capacitor.

XPS of Bi2Sn2O7 and Pb2Sn2O7 which produce CO was analyzed to investigate the performances of Sn-based oxide catalysts. As shown in Fig. 5, adsorbed oxygen peak at around 531 eV in O 1s spectra for Bi2Sn2O7 was larger than that for Pb2Sn2O7. This showed good adsorption and desorption cycle for Bi2Sn2O7 than Pb2Sn2O7. As for Sn 3d spectra the ratio of Sn4+ /Sn3+ of Bi2Sn2O7 was higher than that for Pb2Sn2O7. This might indicate a good redox
Fig. 3. Products of carbon dioxide reduction reaction over various pyrochlore-type oxides. (a) CO production, (b) H$_2$ production.

Fig. 4. Products of carbon dioxide reduction reaction over Sn-based pyrochlore-type oxides. (a) CO production, (b) H$_2$ production.

Fig. 5. XPS spectra at O 1s and Sn 3d of Bi$_2$Sn$_2$O$_7$ and Pb$_2$Sn$_2$O$_7$ oxide powders.
cycle of Bi$_2$Sn$_2$O$_7$ for the electrochemical CO$_2$ reduction. However, further quantitative analysis for the electrode mechanism is under investigation.

In conclusions, fine powders of pyrochlore-type A$_2$B$_2$O$_7$ (A = Pb, Bi; B = Nb, Ru, Sn, Ir) oxides could be synthesized by a wet-chemical method. Carbon-based gas-diffusion-type electrode loaded with Bi$_2$Sn$_2$O$_7$ pyrochlore-type oxides showed high electrocatalytic activities for the electrochemical CO$_2$ reduction gave CO at high concentration. XPS analyses showed that the high performance should be come from its good adsorption and desorption of oxygen as well as redox cycle between Sn$^{2+}$ and Sn$^{4+}$ in Bi$_2$Sn$_2$O$_7$.

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