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Carbon Dioxide Reduction to Alcoholson Perovskite-Type $\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$ Electrodes

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The electrochemical carbon dioxide reduction to produce acetaldehyde, methanol and ethanol is investigated by using perovskite type electrode ($\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$). The experiments were performed under 100 mA/cm^2 and -2 to -2.5 V vs. Ag/AgCl . The highest faradaic efficiencies for methanol, ethanol, acetaldehyde were 11.6, 15.3, and 6.2%, respectively. The experimental data demonstrated that the capability of the perovskite type oxide for the electrode of electrochemical carbon dioxide reduction to produce alcohols was superior to other metal electrode.

Key words : Perovskite, Electrode, Alcohol Formation, Electrochemical Reduction, Carbon Dioxide Fixation.

1. INTRODUCTION

There exist many incentives for the development of new technologies that would use carbon dioxide as a chemical raw material for the synthesis of useful fuels and chemical feed stocks. The study of electrochemical carbon dioxide reduction to produce hydrocarbons is one of the interesting field of carbon dioxide recycling (Sullivan, 1994).

Considerable effort (Hori et al., 1987; 1989; Ikeda et al., 1989; Kim, 1988) has been conducted over the last several years directed toward promoting the electrochemical carbon dioxide reduction to produce hydrocarbons at various operating conditions. Numerous papers have been published in connection with electrochemical reduction of carbon dioxide. They reported that methane, carbon monoxide, formate, ethane, ethylene and alcohols were selectively produced in the cathodic reduction of carbon dioxide on metal electrodes (Cu, Hg, Au, Ag, Zn, Cd, Sn and In) in aqueous inorganic salt solutions.

Hori et al. (1988) reported that methane, ethy-

lene and alcohols such as ethanol and propanol were produced in high faradaic efficiencies on Cu-electrode. After this report, many following researches were performed in batch reactor type cell. Recent work by M.Schwartz et. al. (1993) and others have shown that copper had revealed high electrocatalytic activity for both CO_2 and CO reduction to hydrocarbons and alcohols. In many cases, the copper electrocatalysts have been utilized in the form of metal plates. The major products of electrochemical carbon dioxide reduction, are carbon monoxide, methane and ethylene. However, Schwartz et al. (1993) have presented the results for electrochemical carbon dioxide reduction to produce ethanol and n-propanol by using perovskite-type electrocatalysts. The transition-metal based perovskite oxides have been previously examined as catalysts for the heterogeneous catalyzed synthesis of alcohols from synthetic gas. Bourzutschky et al. (1990) concluded that both Cu⁰ and Cuⁿ⁺ were required for alcohol synthesis, whereas metallic copper alone would only promote hydroca-

rbon formation.

In this communication, we present the experimental results of the electrochemical carbon dioxide reduction to produce alcohols on perovskite-type electrodes, $\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$, which contains copper in the perovskite B lattice site.

2. EXPERIMENTAL

2.1 Perovskite powder and electrode fabrication

The perovskite oxide was synthesized by the amorphous citrate sol-gel method. The metal nitrates and citric acid which is equivalent to the metal ion mole number were weighed and then dissolved in distilled water. The mole composition of La : Sr : Cu was 0.9 : 0.1 : 1. After mixing the metal nitrate solution, the pH of solution was controlled by NH_4OH . The aqueous mixture was evaporated at 70~80°C in a rotary evaporator until viscous liquid (precursor) was obtained. The viscous citrate precursor was dried in vacuum oven for one day. After the drying process, the precursor was grinded and calcined at two experimental conditions; 500°C for 12hours and at 800°C for 12hours. Fine powder precursor was obtained after drying process. The crystal structure and yield of perovskite were confirmed using XRD (Rigaku Co, scan rate 5° mm, Cu target, angle 15° ~80°) and SEM (Hitachi Inc.). Electrodes were made by sintering at 900°C after cold pressing (disk type, 10 mm dia. 1 mm thickness) of perovskite powder described in the above procedure.

2.2 Electrolysis

The electrochemical reduction of carbon dioxide was potentiostatically conducted by using an all-acrylic batch type electrolytic cell with the perovskite-type electrode in KOH electrolyte. Fig. 1 shows the schematic diagram of batch type electrochemical carbon dioxide reduction cell. In order to minimize the alcohol oxidation, the catholyte compartment was separated from the anolyte compartment with a cation exchange membrane (Nafion 117).

A perovskite-type oxide was chosen as working electrode (cathode). The electrode was polished and washed thoroughly with distilled water before use. The electrode potential was measured vs. Ag/AgCl. The platinized Platinum (99.99%) foil was used as a counter electrode (anode). The aqueous electrolyte (0.5 mol KOH) prepared from reagent grade chemicals (WAKO PURE CHEMICALS CO.) and distilled water was purified by pre-electrolysis for 8 hours.

Carbon dioxide was fed to the carbon dioxide saturation reservoir at a constant flow rate (20 ml/min). After the electrolyte was deaerated by carbon dioxide bubbling for 1 hour, the saturated electrolyte solution was circulated in electrolysis cell. The electrolysis was carried out in a cell by using potentiostat/galvanostat (EG&G PARC 362).

2.3 Product Analysis

Electrolysis product contained in liquid phase (electrolyte) were analyzed by Hewlett Packard 5890-II gas chromatograph equipped with a TCD/FID detector and HPLC (Waters model 510 pump) equipped with UV detector.

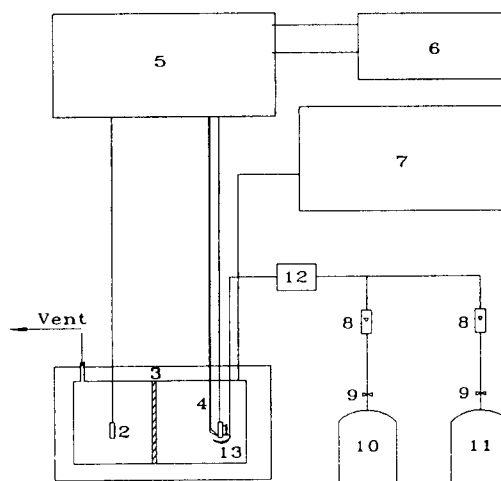


Fig. 1. Schematic diagram of experimental apparatus for the batch cell system. (1. Cathode 2. Anode 3. Membrane separator 4. Reference electrode 5. Potentiostat 6. Recorder 7. Gas Chromatograph 8. Flow meter 9. Regulator/Valve 10. N_2 bomb 11. CO_2 bomb 12. CO trap 13. Diffuser)

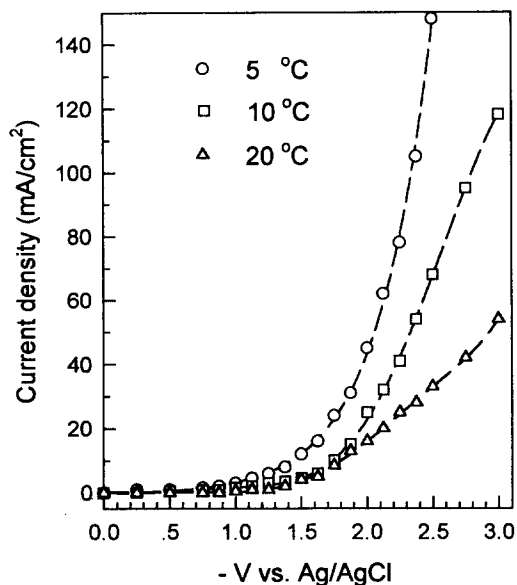


Fig. 2. Voltammograms for the electrochemical carbon dioxide reduction on perovskite ($\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$) electrodes as a function of reduction potential and operating temperature.

3. RESULT

3.1 Current-Voltage Characteristics

We obtained a series of *i*-*V* voltammograms of various temperature and electrolyte concentration. Fig. 2 shows the effects of operating temperature on the *i*-*V* voltammograms of electrochemical carbon dioxide reduction. The data were obtained in the potentiostatic mode by using surface pretreated perovskite electrode. The electrolyte was gently stirred by the magnetic bar. Vigorous magnetic stirring of the electrolyte had a negligible effect on the current-voltage results.

The pattern of *i*-*V* curve for the perovskite electrode showed a similar features in most conditions.

Under the potential of $-1.0 \sim -1.5$ V vs. Ag/AgCl, current density was constant with potential change. Above the potential of -1.5 V vs. Ag/AgCl, the current density was increase rapidly with the increase of potential. The intermediate change of $-1.0 \sim -2.0$ V vs. Ag/AgCl in Fig. 2 refers to the hydrogen evolution and electrochemical carbon dioxide reduction current. Also, the rapid curve over -2.0 V vs. Ag/AgCl in Fig. 2 mainly refers to the hydrogen evolution current.

Kim (1996) reported that, the current density of electrochemical carbon dioxide reduction on Cu electrode was raised with the operating temperature. On the contrary, the current density of electrochemical carbon dioxide reduction on perovskite electrode was decreased with the operating temperature. At the potential of -2.0 V vs. Ag/AgCl, the current density of electrochemical carbon dioxide reduction at 5°C , was 3 times higher than that of 20°C .

3.2 Current-Voltage Characteristics

Table 1 shows the faradaic efficiencies for the liquid products at the $\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$ electrodes as a function of reduction potential and temperature. They were calculated based on the number of electrons required for the formation of one molecule of the products from CO_2 : 2 for HCOO^- , 6 for CH_3OH , 12 for $\text{C}_2\text{H}_5\text{OH}$ and 18 for $\text{C}_3\text{H}_7\text{OH}$. The faradaic efficiencies of formation of methanol at -2.0 and -2.5 V vs. Ag/AgCl are shown in Fig. 3. The faradaic efficiency of methanol increased clearly at 30°C . The increase in the faradaic efficiency for methanol formation indicates that its rate increases faster with temperature than competing reactions, e.g. hydrogen evolution, and so must have a

Table 1. The faradaic efficiencies for the liquid products of electrochemical carbon dioxide reduction on perovskite ($\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$) electrodes as a function of reduction potential.

Potential V vs. Ag/AgCl	Faradaic Efficiency (%)				
	Acetaldehyde	MeOH	EtOH	iso-PrOH	n-Proh
-2	5.75	1.56	15.18	1.69	0.46
2.5	6.11	0.81	6.16	1.42	0.02
-3	4.60	0.61	4.64	1.07	0.01

5°C , 0.5M KOH electrolyte

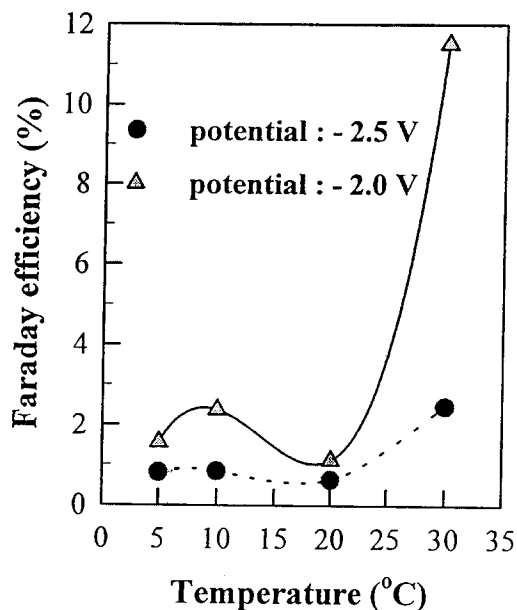


Fig. 3. The effect of temperature on the faradaic efficiency of methanol formation (-2.0 , -2.5 V vs. Ag/AgCl, 0.5M KOH electrolyte).

higher activation energy.

The effect of temperature on the faradaic efficiency of ethanol formation at -2.0 and -2.5 V vs. Ag/AgCl are shown in Fig. 4. The faradaic efficiency of ethanol was decreased with temperature rise. The formation behavior of ethanol was inverse to the formation behavior of methanol. K. W. Frease (1991) reported that methanol was produced on the Cu_2O electrode and ethanol was not produced. In contradiction to his result, M.Schwartz et. al. (1993) reported that ethanol was produced on the perovskite-PTFE porous gas diffusion electrode and methanol was not produced. In Fig 3. and Fig 4., both kind of alcohols were produced in our experiment. It seems that, the difference of M.Schwartz et. al. (1993) and our experimental data was depend on the electrode geometry.

The effect of temperature on the faradaic efficiencies of acetaldehyde formation at -2.0 and -2.5 V vs. Ag/AgCl are shown in Fig. 5. The curves of faradaic efficiencies of methanol and acetaldehyde

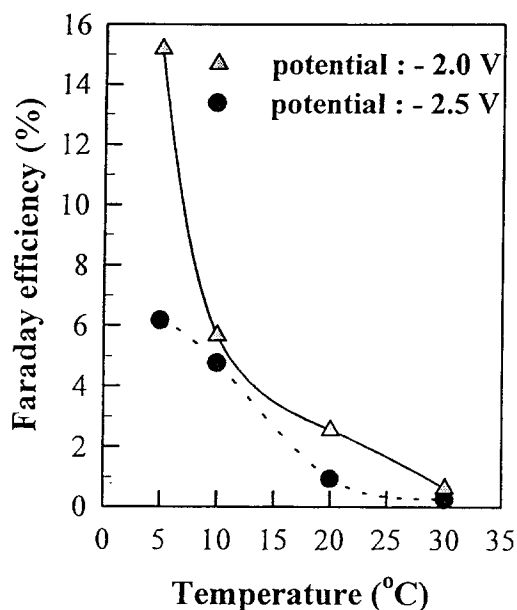


Fig. 4. The effect of temperature on the faradaic efficiency of ethanol formation (-2.0 , -2.5 V vs. Ag/AgCl, 0.5M KOH electrolyte).

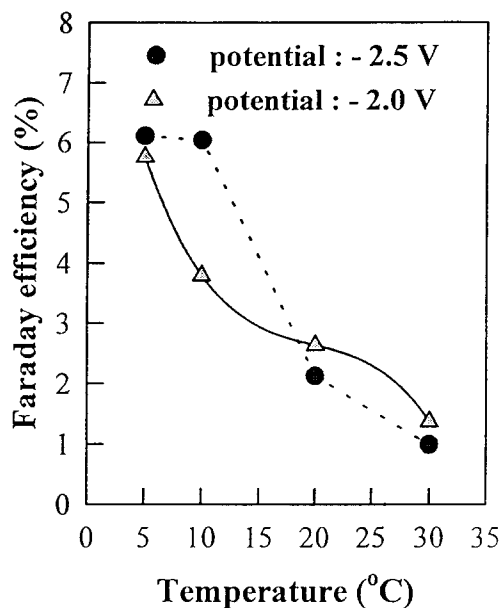


Fig. 5. The effect of temperature on the faradaic efficiency of acetaldehyde formation (-2.0 , -2.5 V vs. Ag/AgCl, 0.5 M KOH electrolyte).

show that the rate of methanol formation was deeply dependent on the rate of acetaldehyde formation. Therefore it was suggested that acetaldehyde was an intermediate product of carbon dioxide to methanol formation process. The more experimental data were needed to conclude the formation mechanism of carbon dioxide to produce alcohols. However, we can expect that the performance of electrochemical carbon dioxide reduction to produce alcohols on perovskite ($\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$) electrode was higher than Cu or Cu_2O electrode.

4. CONCLUSION

The electrochemical carbon dioxide reduction to produce alcohols was investigated by using perovskite type electrode ($\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$). The results of our experiment were summarized belows;

1. The highest faradaic efficiencies for methanol, ethanol, acetaldehyde were 11.6, 15.3, and 6.2%, respectively.
2. The acetaldehyde was an intermediate product of carbon dioxide to methanol formation process.
3. The performance of perovskite type oxide for the electrode of electrochemical carbon dioxide reduction to produce alcohols was superior to other metal (e.g. Cu) electrode.

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페로브스카이트 ($\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$) 전극에서 이산화탄소의 전해환원에 의한 알콜류 생성

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페로브스카이트 ($\text{La}_{0.9}\text{Sr}_{0.1}\text{CuO}_3$) 전극을 이용하여 이산화탄소를 메탄올, 에탄올등의 알콜류와 아세트알데히드로 전해환원하였다. 전해환원 실험은 전류밀도 100 mA/cm^2 그리고 환원 전위 -2 to -2.5 V vs. Ag/AgCl 에서 수행하였다. 실험결과 메탄올은 11.6%, 에탄올은 15.3% 그리고 아세트알데히드는 6.2%의 최고효율을 나타내었다. 따라서 페로브스카이트 전극은 알콜생성 면에서 기타 다른 금속전극에 비하여 매우 우수한 효과를 보여주었다.