Improvement of Electrochemical Reduction of CO\(_2\) Using the Potential-Pulse Polarization Method

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ABSTRACT

Electrochemical conversion of CO\(_2\) gas emitted to the atmosphere to useful chemicals has been expected to suppress the global greenhouse effect and to conserve the natural resources. For the electrochemical reduction of CO\(_2\) on an Ag electrode, the effect of the addition of 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE) ionic liquid to the aqueous solution of 0.1 mol dm\(^{-3}\) K\(_2\)CO\(_3\) and the effect of the polarization methods, i.e., the potentiostatic polarization and the potential-pulse polarization, on the reduction efficiency were investigated. From the gas chromatography measurement, CO as the main product of CO\(_2\) reduction and H\(_2\) as a by-product of water decomposition were obtained. Faraday efficiency of CO formation obtained by the potential-pulse polarization was considerably higher than that obtained by the potentiostatic polarization. The addition of EMISE could add further improvement in the efficiency of CO formation higher than 70%. Such improvement provided by the potential-pulse polarization method and the addition of EMISE was interpreted by the depletion and recovery of the reactants on the electrode in the pulse cycle and promotion of CO\(_2\) molecular formation from HCO\(_3^-\) ions in the dense adsorption layer of EMIM cations on the electrode surface.

Keywords : Pulse Polarization, Electrochemical Reduction, Ionic Liquid, Silver Electrode

1. Introduction

Since the industrial revolution in the 18th century, the drastic increase in the consumption of coal and oil has considerably increased the concentration of carbon dioxide in the atmosphere as 400 ppm in 2016 and recognized nowadays as the dominant causes of temperature rise.\(^1\) The reduction of CO\(_2\) gas emission is, therefore, the highest priority issue from the sustainable development perspective. The CO\(_2\) capturing and storage to underground (CCS) have been investigated to reduce CO\(_2\) emission to the atmosphere.\(^2,3\) The electrochemical reduction of CO\(_2\) has also been attempted because of its simple facility comprises of electrodes and electrolyte, mild operation conditions under the atmospheric pressure, and room temperature. Although the electrochemical CO\(_2\) reduction by using electricity produced by fossil fuels does not match the energetic benefit, use of renewable energies is beneficial to leveling the energy consumption and suppress the CO\(_2\) emission. Several products of CO\(_2\) reduction, such as carbon monoxide, methane, ethylene, and methanol, were obtained respectively on the electrode catalysts of Au, Ag, Cu, and Zn.\(^4,5\) Reduction products are also affected by the polarization conditions such as the electrode potential or polarization current, the cell temperature, and the gas pressure.\(^6,8\) Among the molecular products, CO is useful as a reforming gas and a raw material for organic synthesis (C1 chemistry) to produce various compounds.\(^9,10\)

Since the CO\(_2\) molecule is thermodynamically quite stable and requires a considerably less-noble polarization potential for its electrochemical reduction, a side reaction of the electrolyte decomposition takes place simultaneously to reduce the Faraday efficiency of CO\(_2\) reduction. Improvement of the Faraday efficiency of CO\(_2\) reduction has been intensively investigated, such as the suitable crystallographic orientation of the electrode surface,\(^11\) the modification of the electrode surface with halides,\(^12\) the adjustment of the electrode morphology,\(^13\) and a choice of suitable electrolyte solvent. Recently, ionic liquids (ILs) have been used as electrolyte solutions for electrochemical processes, owing to their attractive properties such as high ionic conductivity, wide potential window, high thermal stability, and negligible volatility. Some ILs also has the ability of CO\(_2\) absorption. For example, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF\(_6\)) can absorb CO\(_2\) molecular physically with a molar fraction of 0.6 at a pressure of 8 MPa and 1-ethyl-3-methylimidazolium acetate (EMIM Ac) can absorb CO\(_2\) chemically with a molar fraction of 0.2.\(^14\) Extensive research has been, therefore, conducted on the electrochemical reduction of CO\(_2\) using IL solvents. Zhao et al.\(^15\) investigated the electrochemical reduction of CO\(_2\) using BMIMPF\(_6\) at various CO\(_2\) pressure and revealed that the Faraday efficiency of the CO formation increased by increasing the CO\(_2\) pressure. Pardal et al.\(^17\) reported that the Faraday efficiency of the CO and H\(_2\) formation in an EMIM trifluoromethanesulfonate-based electrolyte solution changed with the Zn content of the Zn-Cu electrode. The effects of the addition of ILs to the aqueous solution were also investigated.\(^17\)

In this paper, the electrochemical reduction of CO\(_2\) in the mixed electrolyte of aqueous K\(_2\)CO\(_3\) solution and 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE) was investigated. Since EMISE was reported to suppress the hydrogen evolution reaction (HER),\(^18\) it is quite attractive for the optimizing the electrolyte solutions for the electrochemical CO\(_2\) reduction. The-potential pulse polarization method was also examined because it has been used to control the kinetics of the electrochemical process in various electrochemical processes such as electrolysis and plating. In the pulse polarization applied to the electroplating of metals, the evolution of the depletion layer of the metal ions in the electrolyte solution vicinity of the substrate surface is mitigated, and thus uniform electrodeposition can be achieved. Such a strategy seems to be useful for efficient electrochemical CO\(_2\) reduction, although the effect of the potential-pulse polarization on electrochemical CO\(_2\) reduction in IL-contains electrolyte has not yet been reported.
2. Experimental

Figure 1 shows a two compartments electrochemical cell made by machining from a poly(chlorotrifluoroethylene) (Daiel®) block in which the anodic and the cathodic reactions were separated by a cation exchange membrane (Nafion™117). Potassium carbonate (>99.5%, Junsei Chemical Co., Ltd.) and 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE) (>95.0%, Sigma-Aldrich, Inc.) were used to prepare the aqueous catholyte of 0.1 mol dm$^{-3}$ of K$_2$CO$_3$ + x mol dm$^{-3}$ of EMISE ($x = 0, 1.0$). The anolyte was an aqueous solution of 0.01 vol% of H$_2$SO$_4$ (>95.0%, Junsei Chemical Co., Ltd.). The EMISE was vacuum dried at 105 °C for 24 h before the experiment. The solution in the cathode compartment was deaerated by bubbling with the Ar gas (>99.99 vol%) or CO$_2$ gas (>99.5 vol%) with a flow rate of 0.1 dm$^3$ min$^{-1}$ for more than 1 h. The pH of the catholyte after CO$_2$ gas saturation was ca. 7.1.

A working electrode of Ag plate (Ag-WE, >99.98%, Nilaco Co., Ltd.), a counter electrode of Pt plate (>99.98%, Nilaco Co., Ltd.), and an Ag/AgCl (saturated KCl) reference electrode were used for the three electrodes system. The catholyte was stirred during the electrochemical measurements. A potentiostat/galvanostat (Ivium Technologien Co., model CompactStat) was used for the electrochemical polarization. Two kinds of polarization methods were compared, the potentiostatic polarization and the potential-pulse polarization. Three cathodic polarization potentials for CO$_2$ reduction were chosen as $E_a = -1.4$ V, $-1.5$ V, and $-1.6$ V in the potentiostatic polarization method. The averaged current density $i_{av}$ for the potentiostatic polarization at each $E_a$ was calculated from the equation;

$$i_{av} = Q_i / t$$

where $Q_i$ [C] is the amount of the cathodic charge, and $t$ is the polarization period. In the potential-pulse polarization, the polarization potential was switched between the $E_a = -1.4$, -1.5, or -1.6 V for 5 s and $E_0 = 0$ V for 5 s. The duty ratio was $r = 0.5$. The net cathodic charge $Q$ of the potential-pulse polarization was calculated from the cathodic charge $Q_i$ and the anodic charge $Q_o$ as $Q = Q_i + Q_o$. The averaged polarization current $i'_{av}$ during the duty period of the potential-pulse polarization was obtained from the equation;

$$i'_{av} = Q / r t.$$

For the quantitative analysis of the products in the cathodic reduction of CO$_2$, a closed electrochemical cell saturated with CO$_2$ gas was used. The cell atmosphere with a volume of 0.5 cm$^3$ was sampled against the total gas phase of 10 cm$^3$ and supplied to the gas chromatography (GC; L.C. Science Co., model INORGA, Molecular Sieve column). In this work, only CO as a product of CO$_2$ reduction and H$_2$ as a by-product of water decomposition were detected.

The Faraday efficiencies of CO and H$_2$, $f_i$ and $f_{H2}$ [%], were calculated from the amount of the product obtained by the GC and the net cathodic charge $Q$ from the equations;

$$f_{H2} = 100 n_{H2} F / Q$$
$$f_{CO} = 100 n_{CO} F / Q$$

where $n$ [mol] is the amount of each product, $z$ is the valency of each product, and $F$ is the Faraday constant. All experiments were performed a few times to confirm reproducibility.

The solubility of CO$_2$ in a mixed solution of water and EMISE was roughly estimated as follows. First, 15 cm$^3$ CO$_2$ gas was sucked into a 20 cm$^3$ syringe, then 5 cm$^3$ of a degassed solution was added to the syringe. The syringe was shaken several times and left for 30 minutes at 293 K. From the volume loss of the CO$_2$ gas phase in the syringe, $\Delta V_{CO_2}$, caused by the dissolution in the solution phase, the solubility of dissolved CO$_2$ was calculated as,

$$s_{CO_2} = 200 P \Delta V_{CO_2} / RT$$

where $P$ is the atmospheric pressure, $R$ is the gas constant, $T$ is the experimental temperature (293 K), with the ideal gas approximation and the assumption that the partial pressure of water in the gas phase was negligible compared to the CO$_2$ gas.

3. Results and Discussion

Time-transition of the current density $i$ of Ag electrode during the potentiostatic polarization in 0.1 mol dm$^{-3}$ K$_2$CO$_3$ + x mol dm$^{-3}$ EMISE ($x = 0, 1$) solution is shown in Fig. 2(a). The current curves show the initial drop and a subsequent steady current at all potentials. Figure 2(b) shows the averaged current density $i_{av}$ at the three polarization potentials. This result shows that the $i_{av}$ increased with lowering the polarization potential, and the addition of EMISE ($x = 0$) caused an increase in $i_{av}$ at $-1.4$ V and $-1.5$ V but not at $-1.6$ V.

Figure 3(a) shows the time-transition of the current density $i$ in the potential-pulse polarization. The transition shows the initial increase of $i$ in the cathodic direction and subsequent decay during the polarization at $E_c$ and the decrease of $i$ to almost 0 mA cm$^{-2}$ at 0 V. The small decay of the anodic current observed at 0 V may contain not only the charging current of the electric double layer but also the oxidation reaction of H$_2$ or OH$^-$ produced in a previous cathodic cycle at $E_c$. Since the electric charge of the cathodic current decay at $E_c$ was significant comparing to that of the anodic charge at 0 V, it is speculated that the cathodic current decay at $E_c$ corresponds to the evolving depletion layer of the reactant in the vicinity of the electrode surface. Figure 3(b) shows the averaged polarization current $i'_{av}$ as a function of $E_c$ and concentration of EMISE. The addition of the EMISE ($x = 1$) increased the $i'_{av}$ at all $E_c$.

Noda et al. reported that the main product of electrochemical CO$_2$ reduction on an Ag cathode was CO.$^7$ Figure 4 shows the Faraday efficiency $f_{CO}$ and $f_{H2}$ under the potentiostatic polarization (a) and the potential-pulse polarization (b) in a CO$_2$-saturated 0.1 mol dm$^{-3}$ K$_2$CO$_3$ + x mol dm$^{-3}$ EMISE ($x = 0, 1$) solutions. Since the polarization current changes with the polarization potential, the polarization time was adjusted so that the cathodic charge $Q$ was about 3 C in the potentiostatic polarization and the potential-pulse polarization. In the potentiostatic polarization shown in Fig. 4(a) at $x = 0$, $f_{CO}$ increases with lowering the polarization potential from 20.0% at $-1.4$ V to 61.9% at $-1.6$ V, as listed in Table 1. The same tendency was observed at $x = 1$ that $f_{CO}$ increases with lowering the polarization potential from 40.1% at $-1.4$ V...
to 56.8% at −1.6 V. Therefore, the addition of EMISE to the K2CO3 aqueous solution considerably increases \( f_{CO} \) at −1.4 V but not at −1.5 V or −1.6 V. Figure 4(b) shows the \( f_{CO} \) obtained for the potential-pulse polarization. In all conditions, \( f_{CO} \) was considerably larger than that obtained in the potentiostatic polarization shown in Fig. 4(a). For example, at \( x = 0 \), \( f_{CO} \) was in the range from 57.7% to 69.6% and slightly increased with lowering the cathodic potential from −1.4 V to −1.6 V. When EMISE was added (\( x = 1 \)), \( f_{CO} \) was further increased to the range from 72% to 73% without potential dependence. The \( f_{CO} \) obtained by the potential-pulse polarization in the present work is higher than that obtained using the Ag electrodes,\(^5\)\(^,\)\(^20\)\(^,\)\(^21\) electrodeposited Ag catalyst,\(^22\) and similar to the value obtained by using Ag-Cu bimetallic catalyst.\(^23\)

The partial current density of CO reduction, \( i_{CO} \), and HER, \( i_{H2} \), were calculated from the \( i_{av} \) (or \( i'_{av} \)) and the Faraday efficiency of each product, \( f_{CO} \) and \( f_{H2} \), as

\[
\begin{align*}
  i_{CO} &= f_{CO} i_{av}, \\
  i_{H2} &= f_{H2} i_{av}.
\end{align*}
\]

The resultant \( i_{CO} \) and \( i_{H2} \) in various conditions are listed in Table 1 and plotted in Fig. 5. In the results of the potentiostatic polarization at −1.4 V shown in Fig. 5(a), the addition of EMISE increased \( i_{CO} \) about three times larger than that without EMISE addition, while the \( i_{H2} \) was almost unchanged. On the other hand, the effect of EMISE addition on the \( i_{CO} \) or \( i_{H2} \) at \( E_c = −1.5 \text{ V} \) or −1.6 V was unclear. In the results of the pulse polarization shown in Fig. 5(b), the \( i_{CO} \) increased considerably compared to the results of the potentiostatic polarization shown in Fig. 5(a) and the \( i_{H2} \) decreased, whether EMISE was contained or not at all potentials. Therefore, the potential-pulse polarization increased \( i_{CO} \) and decreased \( i_{H2} \), i.e., promotes the CO reduction and suppresses the HER.

The favorable effect of the EMISE addition on the electrochemical reduction of CO2 can be attributed to, for example, (i) the increase in the concentration of CO2 molecular in aqueous solution, (ii) suppression of HER, and (iii) the catalytic effect of adsorbing EMIM cations for electrochemical CO2 reduction on the Ag-WE surface. To verify the possibility (i), the solubility of CO2, \( s_{CO2} \), in three solutions, \( a-c \), were compared in Table 2. The \( s_{CO2} \) in EMISE (\( b \)) is larger than that in H2O (\( a \)) but not so much. The measured \( s_{CO2} \) in H2O + 1 M EMISE (\( c \)) is the same as that calculated from the molar fraction of H2O and EMISE (\( d \)). Since the \( s_{CO2} \) in the K2CO3 solution is considerably higher than that of pure water due to chemical equilibrium reaction, it seems reasonable that the contribution of additional EMISE to K2CO3 is negligible. For the
possibility (ii), the difference in the partial current of HER (i_{H2}) with or without EMISE addition was not significant at the same polarization potentials, as seen in Fig. 5. Therefore, the possibility (iii) is examined below. Since CO\textsubscript{2} is stable, a high overpotential is required to form a reaction intermediate for cathodic reduction. Rosen et al. proposed that EMIM cation of ionic liquid adsorbs densely on the Ag electrode surface,\textsuperscript{24} and the EMIM cation forms a complex with CO\textsubscript{2} to lower the energy state of CO\textsubscript{2}, i.e., reducing

Table 1. Average polarization current $i_{CO}$ and $i_{H2}$, faradaic formation efficiency difference of polarization mode, $f_{CO}$ and $f_{H2}$, formed on Ag-WE immersed in solution consisting of K\textsubscript{2}CO\textsubscript{3} (0.1 mol dm\textsuperscript{-3}) and EMISE electrolyte solution ($x = 0$, 1.0 mol dm\textsuperscript{-3}) saturated with CO\textsubscript{2}, under the cathodic polarization at $E_C$.

| Polarization | $x$ [mol dm\textsuperscript{-3}] | $E$ [V vs. Ag/AgCl] | $f_{CO}$ [%] | $f_{H2}$ [%] | $f_{CO}/(f_{H2} + f_{CO})$ | $i_{CO}$ [mA cm\textsuperscript{-2}] | $i_{H2}$ [mA cm\textsuperscript{-2}] | $i'_{av}$ [mA cm\textsuperscript{-2}] |
|--------------|---------------------------------|--------------------|--------------|--------------|-----------------|----------------|----------------|----------------|
| static       | 0                               | $-1.4$             | 20.0         | 66.7         | 0.23            | -0.72         | -0.14         | -0.48          |
| static       | 0                               | $-1.5$             | 50.1         | 38.3         | 0.57            | -1.46         | -0.73         | -0.56          |
| static       | 0                               | $-1.6$             | 61.9         | 22.8         | 0.73            | -3.11         | -1.92         | -0.71          |
| static       | 1                               | $-1.4$             | 40.1         | 45.0         | 0.47            | -1.13         | -0.45         | -0.51          |
| static       | 1                               | $-1.5$             | 45.8         | 37.9         | 0.55            | -1.75         | -0.80         | -0.66          |
| static       | 1                               | $-1.6$             | 56.8         | 31.6         | 0.64            | -2.96         | -1.68         | -0.94          |
| pulse        | 0                               | $-1.4$             | 57.7         | 27.4         | 0.68            | -0.62         | -0.36         | -0.17          |
| pulse        | 0                               | $-1.5$             | 64.3         | 16.7         | 0.79            | -1.54         | -0.99         | -0.26          |
| pulse        | 1                               | $-1.6$             | 69.6         | 12.2         | 0.85            | -2.96         | -2.06         | -0.36          |
| pulse        | 1                               | $-1.4$             | 72.3         | 12.4         | 0.85            | -1.04         | -0.76         | -0.13          |
| pulse        | 1                               | $-1.5$             | 72.2         | 14.9         | 0.83            | -2.14         | -1.54         | -0.32          |
| pulse        | 1                               | $-1.6$             | 73.2         | 10.9         | 0.87            | -3.28         | -2.40         | -0.36          |

Figure 5. Averaged polarization current and calculated partial current of CO and H\textsubscript{2} formation in K\textsubscript{2}CO\textsubscript{3} (0.1 mol dm\textsuperscript{-3})/EMISE ($x = 0$, 1.0 mol dm\textsuperscript{-3}) solutions at $E_C = -1.4$ V, $-1.5$ V, and $-1.6$ V for (a) potentiostatic and (b) pulse polarization.
the overpotential for cathodic reduction of CO₂.²⁵ Thus, the dense adsorption of EMISE can be regarded as the catalyst (the possibility (iii)). At −1.4 V, the addition of EMISE caused the improvement in the fCO and the increase of the fCO more than three times. However, such catalytic effect becomes invalid at −1.5 V or −1.6 V in the potentiostatic polarization. Probably, the structure of the adsorption layer of the EMIM(iso) is perturbed by the increasing HER on the surface at high polarization current.

On the other hand, the potential-pulse polarization promotes the CO₂ reduction and the HER suppression at all potentials with or without EMISE, as seen in Figs. 4 and 5. The HER and CO₂ reduction proceed competitively on the Ag electrode. Figure 6 shows the probable scheme of the competitive reactions on the Ag electrode both at the polarization potential (EC) and the resting potential (0 V) of the potential-pulse polarization. The cathodic reduction of CO₂ at EC in a weak alkaline solution proceeds as follows:

\[
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{CO} + 2\text{OH}^-.
\]  

(8)

This process causes the alkalization of local solution vicinity of electrode²⁶ and decreases the CO₂ concentration in the equilibrium of carbonic acid. As a result, the rate of CO₂ reduction decreases with the polarization time of a single pulse at EC. The depletion of CO₂ species near the electrode surface also lessens the CO₂ reduction rate, and the HER may be promoted complementary. When the cathodic reduction was interrupted by the rest period at 0 V, the local alkalization is mitigated by the diffusion of H⁺ ions from the bulk of the solution. Diffusion of the carbonic species such as HCO₃⁻ and CO₃²⁻ from the solution also mitigates the depletion of them near the electrode surface to release CO₂ by the following equilibrium reaction,

\[
\text{CO}_2\text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^-,
\]

(9)

\[
\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{OH}^-.
\]

(10)

As a result, the efficiency of the CO₂ reaction can be improved.

As seen in Fig. 5, the partial current iₜ₂ at EC = −1.4 V to −1.6 V in the potential-pulse polarization was considerably smaller than that at the same EC in the potentiostatic polarization. The H₂ad is formed by the water decomposition (H₂O + e⁻ → H₂ad + OH⁻) at EC and consumed by the HER with recombination of two H₂ad (2H₂ad → H₂). When the electrode potential moves to 0 V, the H₂ad may be re-oxidized to H₂ and detached from the electrode surface.²⁷

As a result, the HER is suppressed at the initial stage of the next cathodic pulse at EC. It is also expected from these results that the fCO can be improved further by reducing the duty ratio r of the pulse polarization. Figure 7 shows the dependence of the fCO on r of the pulse polarization measured in 0.1 mol dm⁻³ K₂CO₃ solution. In this figure, it is confirmed that the fCO increased with decreasing r as fCO = ca. 53% at r = 0.8 to fCO = ca. 70% at r = 0.2, although the averaged polarization current iₜ₂ decreased with decreasing r.

In conclusion, application of the potential pulse polarization and the addition of EMISE to the aqueous solution can improve the Faraday efficiency of electrochemical CO₂ reduction. From the speculation of current transient shown in Fig. 3, it is reasonable that the efficiencies depend not only on the duty ratio but also on the frequency. Since higher efficiency of CO formation is expected to be obtained in the conditions of the shorter rest period and polarization period to suppress the H formation, further systematic investigation to optimize the pulse polarization condition for efficient CO formation is currently undergoing.

4. Conclusion

In this paper, the effects of the polarization methods and the addition of the EMISE ionic liquid to the K₂CO₃ aqueous solution on the electrochemical CO₂ reduction on an Ag electrode were investigated. From the gas chromatography analysis, the main product of the CO₂ reduction was CO, and the side reaction of water decomposition also formed H₂. The potential-pulse polarization considerably improves the Faraday efficiency of CO formation and suppresses the HER compared with the potentiostatic polarization. This result indicates that the supply of the CO₂ released from the HCO₃⁻ ions dominant in the solution to the cathode surface determines the cathodic reduction rate, and the pulse polarization mitigates the evolution of the depletion layer of the reactant vicinity of the cathode surface. Further improvement of the Faraday efficiency of CO formation can be achieved by the addition of EMISE ionic liquid to the K₂CO₃ aqueous solution. Such improvement is thought to be provided by the complexing ability of the
EMIM cations densely adsorbed on the electrode surface to CO₂ molecular. These results clarify that the optimization of the polarization condition and electrolyte solution is quite promising for the improvement of the efficient electrochemical reduction of CO₂.

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