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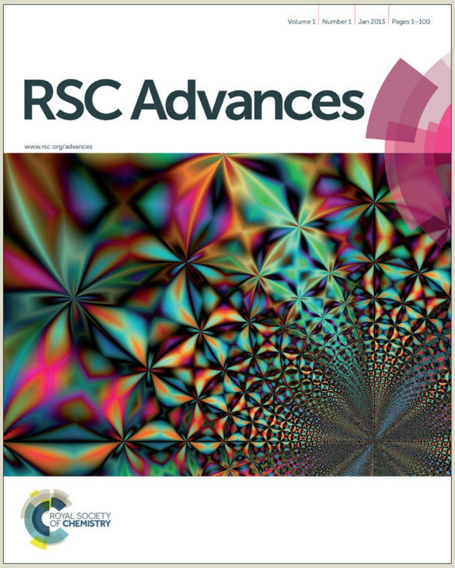

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# Selective, High Efficiency Reduction of $CO_2$ in a Non-Diaphragm-Based Electrochemical System at Low Applied Voltage

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**Abstract: In a typical electrochemical $CO_2$ reduction system, hydrocarbon products are not selectively generated when a diaphragm is used in the cell. However, without the diaphragm, $H_2$ and $CH_4$ are selectively produced with Faradaic efficiencies as high as 96.7% in methanolic NaOH and KOH electrolytes, respectively. We are the first to successfully achieve the selective production of hydrocarbon and hydrogen fuels from the electrochemical reduction of $CO_2$, which can help to meet the rapidly growing energy demands of modern society.**

The electrochemical reduction of $CO_2$ is of increasing interest as an alternative route for fuel production because of its environmental and economic benefits. Its hydrocarbon and alcohol products will become effective fossil fuel replacements as our energy resources are depleted.[1–3] $CO_2$ is a thermodynamically stable compound, and additional energy input is necessary to transform it by electrochemical reduction.[4] The reductive transformation of $CO_2$ produces a variety of products according to the numbers of generated electrons and protons. However, $CO_2$ reduction competes with hydrogen production, which occurs at a similar electrical potential.[5,6] Therefore, an overpotential is needed to accomplish the reduction efficiently.[5,6] However, this overpotential for $CO_2$ reduction results in a dramatic decrease in energy efficiency, which has led many researchers to develop methods to decrease applied voltages and increase Faradaic efficiency.[7–11] The approaches include investigations of Cu electrodes, electrolytes (*i.e.*, distilled water, organic solvents/ionic liquids), alkaline salts (*i.e.*, Li, Na, K, Rb, Cs, and Fr), photocatalysts, and biological reduction.[12–15] Despite all these efforts, there has been no report of complete $CO_2$ reduction with high Faradaic efficiency at low applied voltage. To achieve such results, we suggested an electrochemical reduction system for $CO_2$ which did not use a diaphragm, as will be discussed.[16–18] Herein, we report the selective formation of $CH_4$ and $H_2$ as the final products of $CO_2$ reduction without use of a diaphragm. This is the first example of the $CO_2$ reduction reaction under these conditions. In these experiments, we employed the alkaline salts NaOH and KOH as electrolytes for the selective generation of hydrocarbons and $H_2$ at low applied voltage.

Traditional $CO_2$ reduction is conducted in a reactor containing a diaphragm (an ion-exchange membrane), cathode (working electrode), anode (counter electrode), reference electrode, and different electrolytes within separated compartments.[19–27] In prior studies of $CO_2$ reduction, the diaphragm was used to suppress the movement of unwanted intermediates to the reduction electrode and selectively generate hydrocarbons.[28] The diaphragm was also employed to protect the reaction at the cathode from interference by oxidation products and potential electrode poisons generated by the anode.[29] However, more complex product isolation processes may be needed if various hydrocarbons, including the desired $C_1$–$C_n$ compounds, are generated, because the formation of electrons and protons on the anode in a diaphragm-containing reactor increases as the applied voltage increases.[30,31] The presumable drawbacks of CO2 reduction system without a diaphragm are uncertainty of proton sources, hard to separate target compounds from unwanted products, and occurrence of poisoned ions on Pt anode.[14,32,37] Additionally, the diaphragm, controlling the inflow of the intermediates, interferes with the flow of the electrical current generated by the two electrodes, resulting in the need for an overpotential for $CO_2$ reduction.[33] We considered that the use of a diaphragm may be a hurdle for electrochemical reduction research, and its removal may allow $CO_2$ reduction with high Faradaic efficiency at a low applied voltage. The diaphragm is suggested to be effective in controlling hydrocarbon generation beyond CO and $C_1$ compounds.[34–36] Finally, all the known processes (diaphragm-based) for the electrochemical reductive transformation of $CO_2$ to various hydrocarbons report difficulties in controlling the generation of specific products.[37]

Generally, the current density (CD) in an electrochemical reduction is significantly affected by the number of electrons and protons. Accordingly, additional voltage results in an increased CD, which accelerates the reduction.

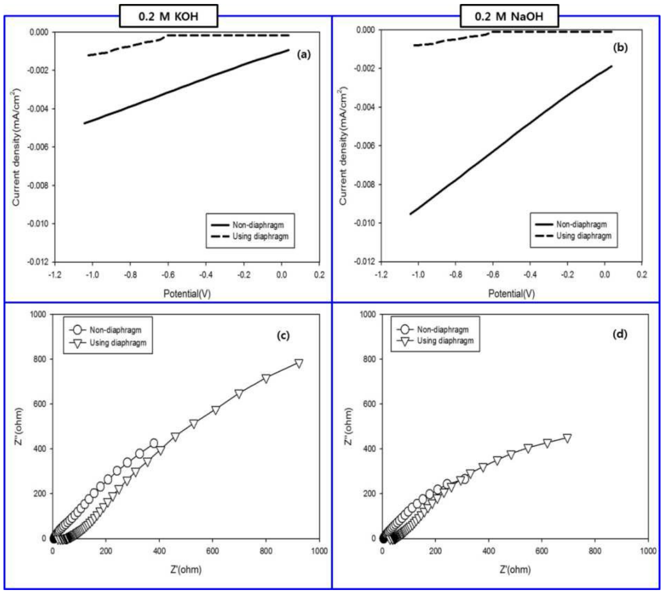

Figure 1. Cyclic voltammogram on Cu electrode at a scan rate 50 $mV \cdot s^{-1}$ and $CO_2$ flow rate of 60 $mL \cdot min^{-1}$ and 25°C with different potentials, and impedance (IMP) values at a frequency of 10,000 Hz and amplitude of 500 mV in electrochemical systems with and without a diaphragm: (a) Voltammetric curve with 0.2 M KOH electrolyte; (b) Voltammetric curve with 0.2 M NaOH electrolyte; (c) IMP with 0.2 M KOH electrolyte; and (d) IMP with 0.2 M NaOH electrolyte.

The CDs of diaphragm- and non-diaphragm-based electrochemical systems with 0.2 M KOH and 0.2 M NaOH electrolyte are shown in Figure 1(a, b). The CD in the non-diaphragm-based electrochemical system was much higher than that in the diaphragm-based cell. This trend was also evident upon increasing the potentials. The impedance (IMP) was measured to validate the generation of high CDs in the non-diaphragm-based electrochemical system. As shown in Figure 1(c, d), the impedance results demonstrate that a remarkably lowered resistance is the direct reason for the enhanced CD in the non-diaphragm-based electrochemical system in comparison to that in diaphragm-based one. Additionally, the resistance with the 0.2 M NaOH electrolyte was lower than that with the 0.2 M KOH electrolyte, which was consistent with the higher CD observed for the NaOH-based electrolyte system than that based on KOH. Clearly, the NaOH-based electrolyte produces more electrons than the KOH-based electrolyte because of its higher CD. Additionally, without a diaphragm, the electrochemical system is activated to generate electrons and protons and initiate their flow within the electrolytes.

The diaphragm in an electrochemical system exchanges the alkaline salt cations for protons; these protons are used to reduce $CO_2$ and generate hydrocarbons mixed with protons and $H_2$. In the absence of protons, the direct transfer of electrons and reduction requires an overpotential, which reduces the efficiency of the transformation. Therefore, protons play an important role in $CO_2$ reduction.[38] In the absence of a diaphragm, our electrochemical system required an intrinsic proton source. Accordingly, NaOH or KOH was used as the electrolyte and methanol was used as the electrolytic solvent. The following reaction between these components produces alkoxides and water, as previously reported:[39]

$$CH_3OH + Na(K)OH \rightarrow CH_3ONa(K) + H_2O \qquad (1)$$

Equation (1) describes the reaction of methanol and Na(K)OH upon dissolution; water then dissociates to produce hydroxyl radicals ($OH^{\bullet}$), protons, and $H_2$. Furthermore, the rate of the production of $H_2O$ with KOH is four times faster than with NaOH.[40] Thus, it is evident that the water produced via the reaction in Eq. (1) acts as a proton source in the non-diaphragm-based electrochemical system (Figure S1). It is likely that the electrochemical reduction of $CO_2$ by combining with protons ($H^+$) lowers the essential potential for the reaction. In Equations (2) to (8), formal potentials have been suggested for the standard state, defined as pH 7.0, 25°C, 1 atm, and 1 M solution.[41] As these equations show, various intermediates are formed during the reactions of protons and electrons with $CO_2$.[41] Until now, the reduction of $CO_2$ to hydrocarbons has not been selective, and was inefficient due to the generation of CO and HCOOH. High efficiency and selectivity for particular products during the reduction are strongly related to the electrodes and electrolytes. However, the previous studies were limited by the electrolyte-solubility of $CO_2$, which interferes with the reduction reaction, and the generation of CO, which can poison the electrodes. Interestingly, the previously observed CO, HCHO, and $CH_3OH$ intermediates were not formed as final products within our system. After GC-MS analysis, only $CH_4$ and methyl ester were produced in our electrochemical system and identified as intermediates (Figure S2). With this result, it is clear that the products do not influence the electrodes, confirming that the products are not affected by oxidation and/or reduction. Therefore, the main equations operating in this study are Eq. (7) and (8), and the primary products are selectively $CH_4$ and $H_2$.

$$CO_2 + e^- \rightarrow CO_2^- \qquad E^{0\prime} = -1.90\ V \qquad (2)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^{0\prime} = -0.53\ V \qquad (3)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad E^{0\prime} = -0.61\ V \qquad (4)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E^{0\prime} = -0.48\ V \qquad (5)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^{0\prime} = -0.38\ V \qquad (6)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^{0\prime} = -0.24\ V \qquad (7)$$

$$2H+ + 2e^- \rightarrow 2H_2 \qquad E^{0\prime} = -0.41\ V \qquad (8)$$

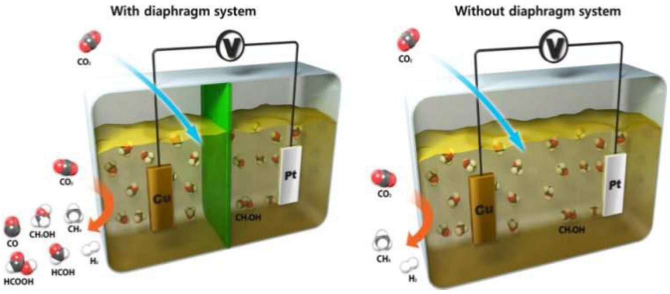

Figure 2. Schematic diagrams for the electrochemical reduction of $CO_2$ with and without a diaphragm. The products were compared according to the presence of a diaphragm under the same conditions, using methanol as solvent, NaOH/KOH electrolytes, an applied voltage range of 0.1–1 V, and a $CO_2$ input rate of 60 mL·min$^{-1}$ at 25°C.

Figure 2 illustrates the electrochemical $CO_2$ reduction systems with and without a diaphragm. It shows electrons at the applied voltage, the types of products formed in the presence or absence of a diaphragm, and the primary reaction equation for selective $CH_4$ and $H_2$ production in the non-diaphragm electrochemical reduction system. Generally, electrochemical reductions produce increased numbers of electrons and protons as the applied voltage increases. A system with or without a diaphragm would be expected to equally mediate the same electrochemical reaction. However, the $CO_2$ introduced in a diaphragm-containing electrochemical system is only supplied to the cathode reaction area, isolated by the diaphragm, where CO, $CH_3OH$, HCOOH, HCOH, and $H_2$ are produced during the reduction reaction. On the other hand, there are no isolated cathode and anode reaction areas in a non-diaphragm electrochemical system. The non-diaphragm cell freely generates the electrons and protons needed for the reduction of $CO_2$ at low applied voltage, and is the optimal system for selectively generating $CH_4$ and $H_2$.

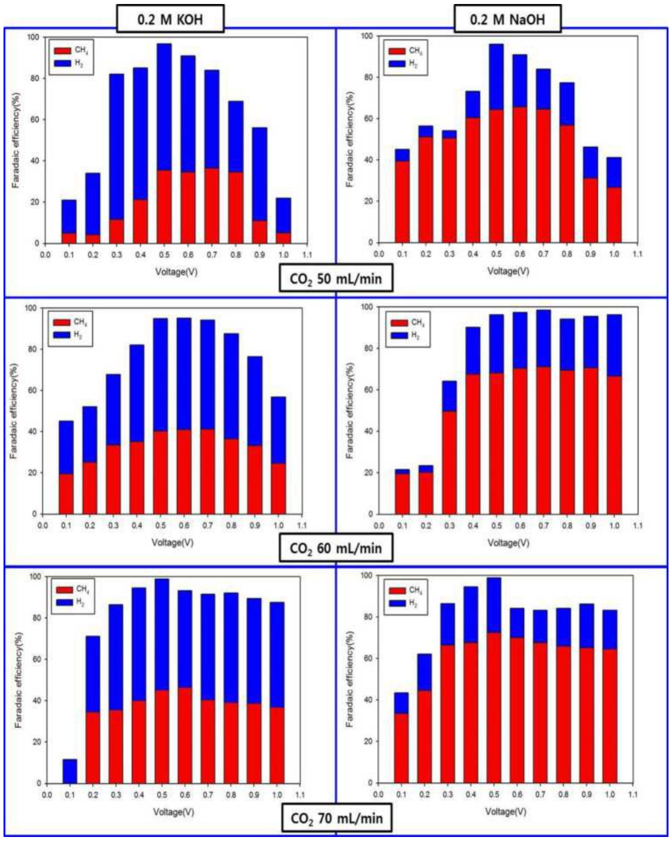

Figure 3. Faradaic efficiencies of the non-diaphragm-based electrochemical system. Comparison of Faradaic efficiencies at various $CO_2$ flow rates and applied voltages at 25°C. The left and right columns show the Faradaic efficiencies when 0.2 M KOH and NaOH electrolytes are used, respectively.

Figure 3 shows the effects of the type of electrolyte, $CO_2$ flow, and added voltage on $CH_4$ and $H_2$ generation in the non-diaphragm system, expressed as Faradaic efficiency. Only $CH_4$, $H_2$, and non-consumed reactants ($CO_2$ and gaseous methanol) were generated in the range of 0.1 to 1.0 V; this is attributed to the limited applied voltage, which might be insufficient to transform $CO_2$ to higher hydrocarbons.[42, 43] As shown in Figure 3, the Faradaic efficiency reached 96.8% ($CH_4$, 35.6%; $H_2$, 61.4%) at a 50 mL·min$^{-1}$ $CO_2$ flow rate and 0.5 V in the non-diaphragm-based electrochemical system with 0.2 M KOH electrolyte. Similarly, the Faradaic efficiency was 96.1% ($CH_4$, 64.3%; $H_2$, 31.8%) under the same conditions with 0.2 M NaOH electrolyte. The Faradaic efficiency increased in the range 0.1–0.5 V and decreased in the range 0.6–1.0 V. This reduction impaired the production of $CH_4$ and $H_2$ beyond 0.6 V at a 50 mL·min$^{-1}$ $CO_2$ flow rate. The Faradaic efficiency increased upon increasing the $CO_2$ flow rates to between 60 and 70 mL·min$^{-1}$. However, carbonate salts were formed when the flow rate was increased above 80 mL·min$^{-1}$ $CO_2$ in the 0.2 M Na(K)OH electrolyte, and the electrochemical reduction ceased. A higher Faradaic efficiency for $H_2$ production was obtained with KOH, whereas a higher Faradaic efficiency for $CH_4$ production resulted with NaOH. The non-diaphragm-based electrochemical system had higher rates of production than the diaphragm-based system. The production-rate trends are similar to those of Faradaic efficiency.

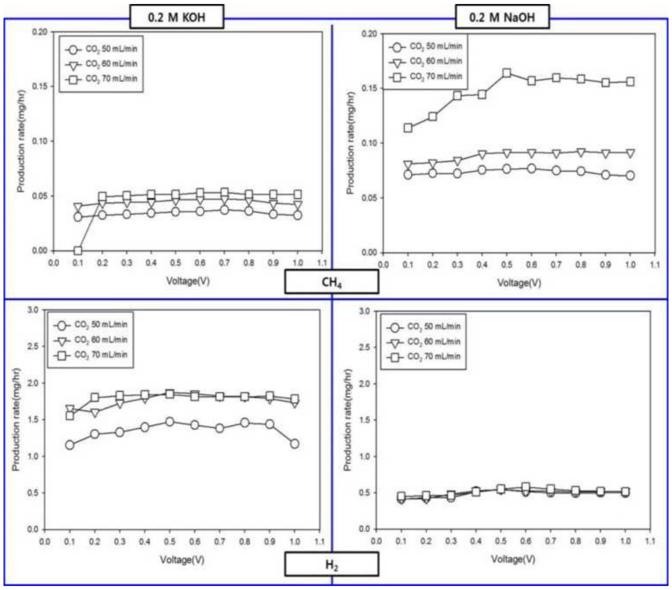

Figure 4. Production rates of $CH_4$ and $H_2$ in the non-diaphragm-based electrochemical system. The rates were measured at 25°C under various $CO_2$ flow rates and different applied voltages. The left and right columns show the production rates using 0.2 M KOH and NaOH electrolytes, respectively.

Figure 4 shows that KOH in methanol affords electrochemical reduction to $H_2$ faster than NaOH in methanol, but the higher CD in methanolic NaOH generates more $CH_4$ than KOH in methanol. This pattern is consistent with changes in the concentration of $CH_4$ and $H_2$ according to time (Figure S3). Additionally, methanol used as an electrolyte was not electrochemically degraded due to its consistent concentration during the experiment. Therefore, this demonstrates that methanol is not produced as one of intermediates in our system, which is inconsistent with Eq. (6) (Figure S4). Therefore, KOH is responsible for the higher production of $H_2$ and NaOH is responsible for the higher production of $CH_4$. Furthermore, the non-diaphragm-based electrochemical system produced not only $H_2$ and $CH_4$, but also controlled their production rates using NaOH and KOH.

Taken together, the non-diaphragm-based electrochemical system reduced the voltage required to produce $CH_4$ and $H_2$ and enhanced the Faradaic efficiency to >95%. Furthermore, it selectively produced $CH_4$ and $H_2$ when NaOH or KOH electrolytes were separately employed. In this system, oxidative gases such as CO were not produced, thereby protecting the Cu anode from decay. Accordingly, the absence of a diaphragm reduced the expected problems, including limited control of the reduction and the generation of undesirable intermediates, such as CO and formaldehyde.

## Conclusions

Removal of the diaphragm from the electrochemical reduction system eliminates the electrical resistance it would otherwise generate in the cell. The non-diaphragm system produces a higher CD in contrast to the diaphragm-containing electrochemical system, and it affords a high production rate, Faradaic efficiency, and product selectivity. The proton sources in the non-diaphragm electrochemical system are methanol and water; the latter is produced by the dissolution reactions of the alkali bases. KOH and NaOH contribute to the production of $H_2$ and $CH_4$, respectively. These findings prove the possibility that the production of $H_2$ and $CH_4$ can be controlled by using KOH and NaOH in the $CO_2$ reduction reaction.

## Experimental Section

**Electrochemical reduction.** The characteristics of the non-diaphragm-based electrochemical system for reducing $CO_2$ are as follows. The system, comprising acrylic materials, was 60 mm × 45 mm × 95 mm. $CO_2$ (99.9999% pure) was introduced at rates of 50, 60, and 70 $mL\cdot min^{-1}$ through an inlet installed at the bottom of the system using a mass flow controller (Sierra, C100L). The anode and cathode consisted of insoluble Pt and insoluble Cu plates, respectively, with dimensions of 40 mm × 40 mm × 1 mm; the two electrodes were placed at the same height with a separation of 10 mm. A standard electrode (Ag/AgCl) was placed between these two electrodes and the system was connected to an electrochemical analyzer (PAR VersaSTAT3, AMETEK). Impedance (IMP) values were measured and compared in the two electrochemical system configurations. The experiments were conducted for 5 h using 0.2 M NaOH or KOH in methanol (115 mL) as the electrolyte; methanol was used instead of water because of the higher solubility of $CO_2$ in methanol.[31]

**$H_2O$ analysis.** The water content generated in the dissolution reaction of 0.2 M NaOH or KOH in methanol (115 mL) was measured using a Karl Fischer coulometer (Metrohm, Metrohm 737, Switzerland).

**Comparison of the CDs.** For this comparison, non-diaphragm- and diaphragm (Sigma-Aldrich, Nafion membrane N117, 0.18 mm thickness)-based electrochemical systems were used. The applied voltage and generated current were measured using the electrochemical analyzer in the range 0.1–1.0 V. The diaphragm was installed in the same reactor. The atmospheric pressure was 1.2 atm.

**$CH_4$/$H_2$ production under various conditions.** An outlet and sample collection site were installed in the upper part of the system; the products in the collected samples were determined by gas chromatography (GC) with flame ionization detection (FID, Agilent HP6970) for $CH_4$ and thermal conductivity detection (TCD, PerkinElmer CALUS580) for $H_2$. The intermediate products were analyzed using a mass selective detector (MSD, Agilent HP6970). After analysis of the products, the production rates and Faradaic efficiencies were calculated.

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**Keywords**: $CO_2$ • Electrochemical Reduction • Selective • Non-diaphragm • Low voltage

## Notes and references

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## Entry for the Table of Contents

## Communication

One sentence highlight

**Electrochemical $CO_2$ reduction in a diaphragm-less cell selectively afforded $CH_4$ and $H_2$ in methanolic NaOH and KOH electrolytes, respectively.**