Supporting Information

Selective, High Efficiency Reduction of CO₂ in a Non-Diaphragm-Based Electrochemical System at Low Applied Voltage

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1. Water content analysis by Karl Fischer coulometry

Figure S1. Concentrations of water generated from the dissolved 0.2 M KOH or 0.2 M NaOH with methanol (115 mL) at 25°C.

Figure S1 is the result of the analysis of water concentrations after the dissolution reaction of 0.2 M KOH or 0.2 M NaOH with methanol using a Karl Fischer Coulometer. Dissolution of KOH with CH$_3$OH produced a higher water concentration in comparison to that of CH$_3$OH and with CH$_3$OH.
2. GC-MSD analysis results

Figure S2. GC-MSD chromatogram for reduction in 0.2 M KOH at a CO$_2$ flow rate of 50 mL·min$^{-1}$ and applied voltage of 0.5 V at 25°C.

Figure S2 is presents a product analysis using GC-MSD. Other than the final product, CH$_4$, only methyl ester was determined. The non-diaphragm electrochemical system produces only H$_2$ and CH$_4$. The same products were determined for reaction times of 1 to 5 h.
3. Analysis of CH$_4$/H$_2$ according to reaction time

Figure S3. Comparison of CH$_4$/H$_2$ production over time in a non-diaphragm-based electrochemical system at a CO$_2$ flow rate of 50 mL·min$^{-1}$ and applied voltage of 0.5 V at 25°C with different electrolytes. (a), CH$_4$ concentration (GC-FID); and (b), H$_2$ concentration (GC-TCD).

Figure S3 presents the analysis of concentrations of CH$_4$/H$_2$ according to the reaction time. The pattern is nearly as constant as a steady state, and the products differ according to additional electrolytes (NaOH and KOH). As shown in Figure S3, CH$_4$ is the main product when NaOH is used as an electrolyte, while H$_2$ is the main product when KOH is used as an electrolyte. The results indicate that using NaOH and KOH may select the type of product. Only CH$_4$ and H$_2$ are the products throughout the CO$_2$ reduction reaction, as shown in Fig S2, and we thus confirm the advantage of a non-diaphragm-based electrochemical system.
4. Methanol production according to reaction time

Figure S4. Comparison of methanol concentration produced in non-diaphragm-based electrochemical system at a CO$_2$ flow of 50 mL min$^{-1}$ and applied voltage of 0.5 V at 25°C with different electrolytes: 0.2 M KOH (inverted triangles) and 0.2 M NaOH (closed circles).

Figure S4 documents the CH$_3$OH concentrations over time after the application of voltage. At 1 h, the CH$_3$OH concentration decreases due to dissolution reaction with NaOH and KOH. However, CH$_3$OH is not degraded electrochemically because the concentration is constant with the extended reaction time.