Supporting Information

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

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1. Water content analysis by Karl Fischer coulometry

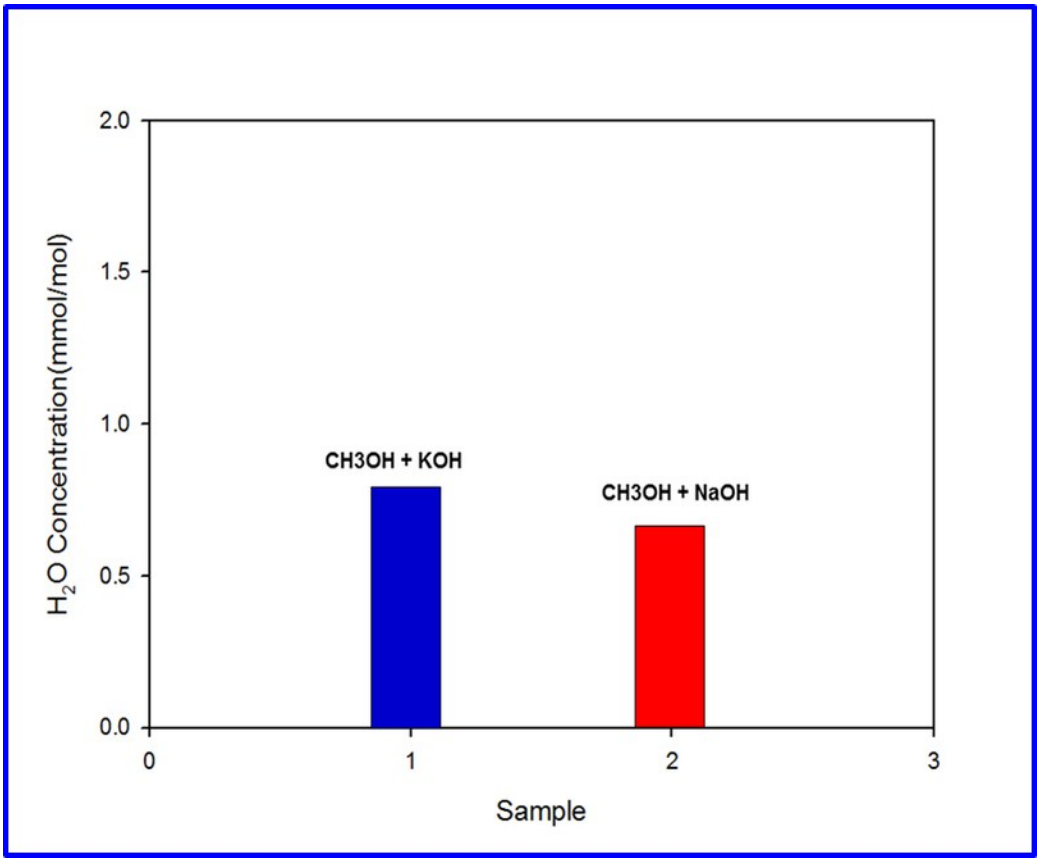

Figure S1. Concentrations of water generated from the dissolved 0.2 M KOH or 0.2 M NaOH with methanol (115 mL) at 25°C.

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_3OH produced a higher water concentration in comparison to that of CH_3OH and with CH_3OH.

2. GC-MSD analysis results

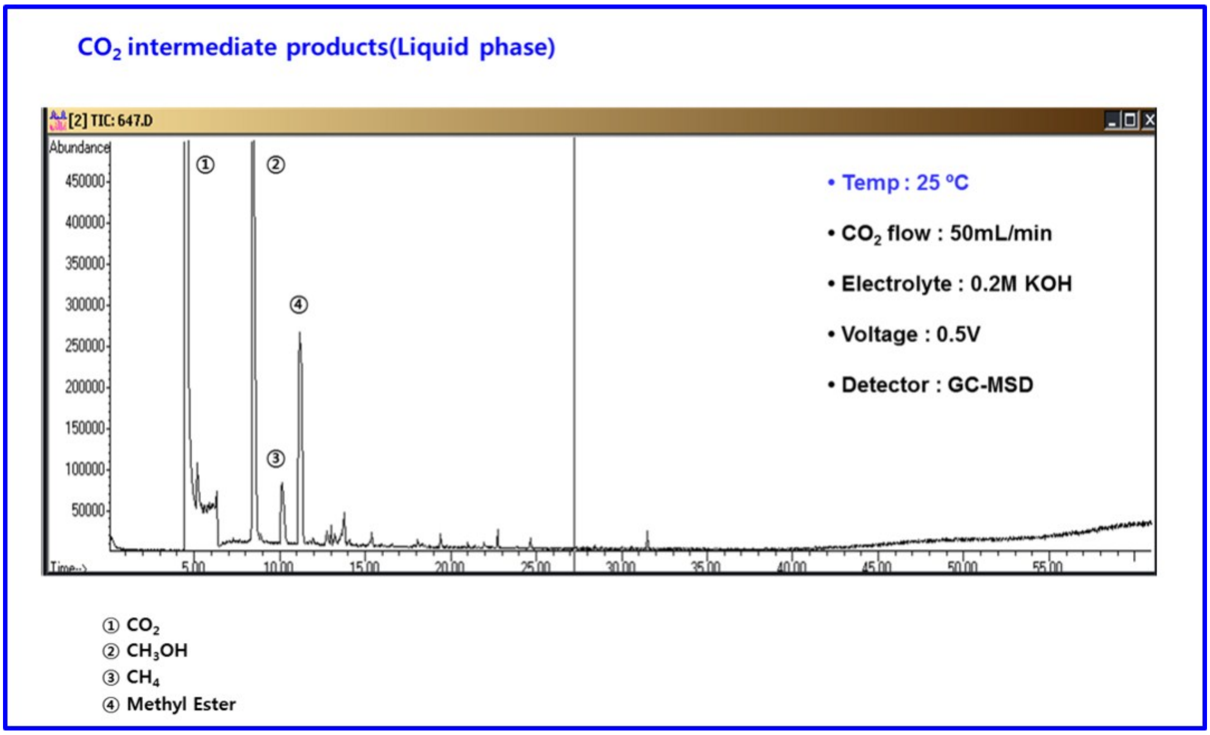

Figure S2. GC-MSD chromatogram for reduction in 0.2 M KOH at a CO_2 flow rate of 50 mL·min^{-1} and applied voltage of 0.5 V at 25°C.

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

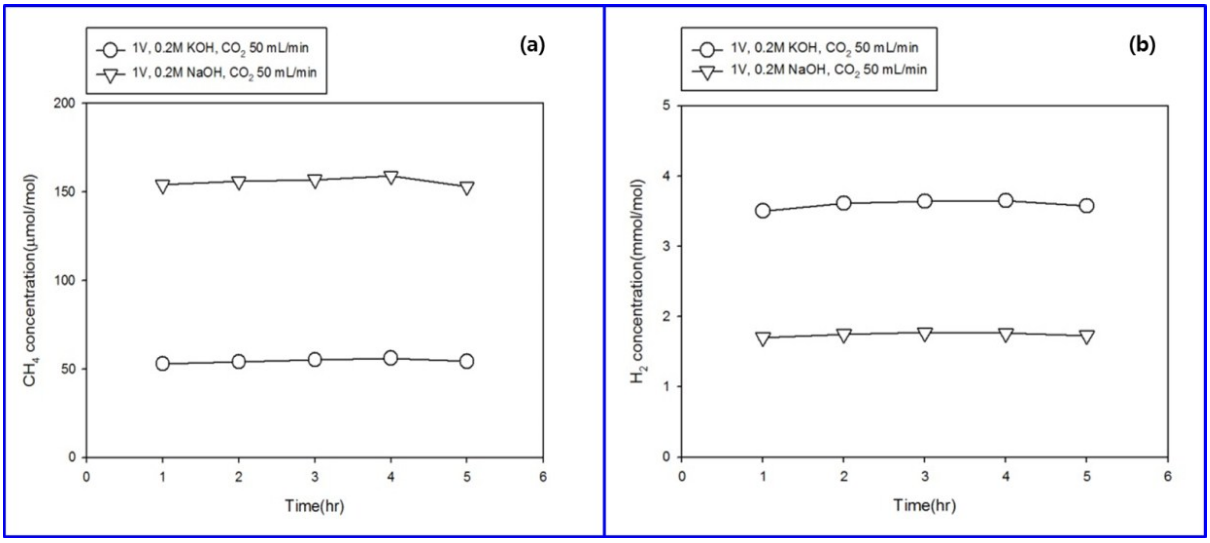

Figure S3. Comparison of CH_4/H_2 production over time in a non-diaphragm-based electrochemical system at a CO_2 flow rate of 50 mL·min^{-1} and applied voltage of 0.5 V at 25°C with different electrolytes. (a), CH_4 concentration (GC-FID); and (b), H_2 concentration (GC-TCD).

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

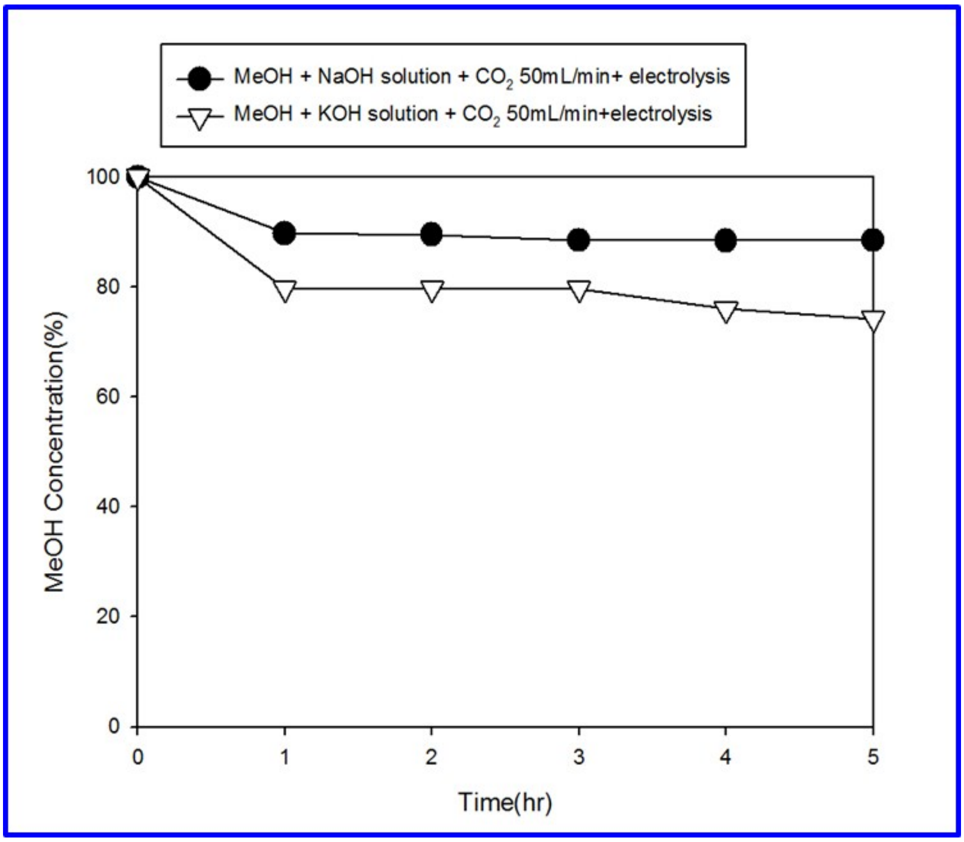

Figure S4. Comparison of methanol concentration produced in non-diaphragm-based electrochemical system at a CO_2 flow of 50 mL·min^{-1} and applied voltage of 0.5 V at 25°C with different electrolytes: 0.2 M KOH (inverted triangles) and 0.2 M NaOH (closed circles).

Figure S4 documents the CH_3OH concentrations over time after the application of voltage. At 1 h, the CH_3OH concentration decreases due to dissolution reaction with NaOH and KOH. However, CH_3OH is not degraded electrochemically because the concentration is constant with the extended reaction time.