Supporting Information for:

Electrochemical conversion of CO$_2$ to fuels: Tuning of reaction zone using suitable functional group in solid polymer electrolyte

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Experimental setup:

The schematic of the experimental setup used for the ERC is shown below.
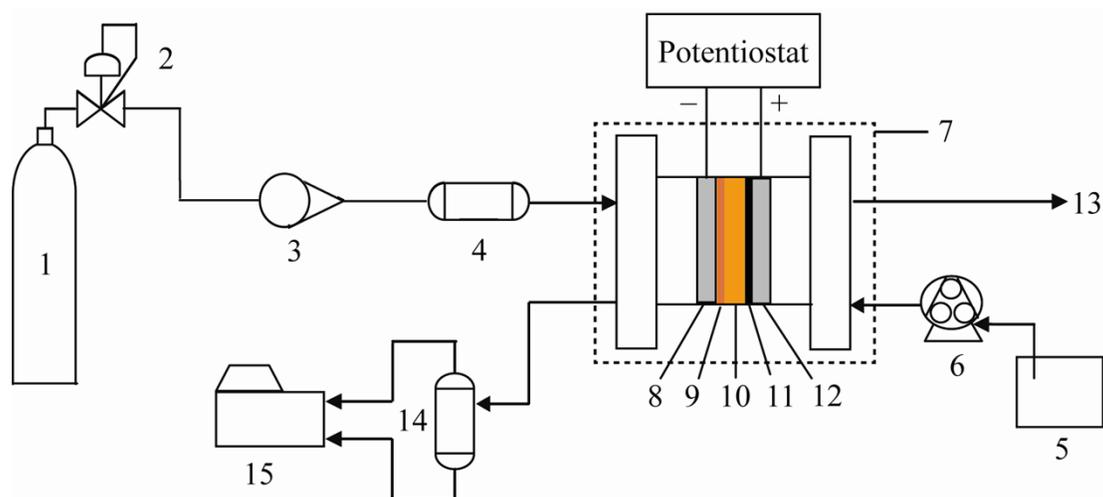
Figure S1: Experimental setup for dERC; (1) CO_2 source, (2) pressure regulator, (3) rotameter, (4) humidifier, (5) water source, (6) peristaltic pump, (7) electrochemical reactor, (8) cathode gas diffusion layer, (9) electrodeposited Cu_2O catalyst layer, (10) SPE, (11) Pt/C catalyst layer, (12) anode gas diffusion layer, (13) anode vent (O_2 and unreacted H_2O), (14) gas/liquid separator, (15) gas chromatograph.

Product Analysis:

Gas chromatography (GC):

The gaseous products were analyzed by GC with packed column (Carbosieve S-II, 3.05 m, 1/8 in., 2.1 mm) using thermal conductivity detector (TCD), and flame ionization detector (FID). Ar used as a carrier gas to take the sample in to the column, where separation of H_2, CH_4, CO, CO_2 and C_2H_6 will occur. After exiting the columns, the gas ample was first analyzed by TCD detector where H_2 and CO_2 gases were detected. Then, gas sample passes through methanizer where CO and CO_2 are converted to methane, analyzed by FID detector where the remaining hydrocarbons (CH_4, C_2H_6) also were detected. It may be noted that there was no interference of the CH_4 from the reactor and methane form methanzier (which was obtained from CO and CO_2 conversion), because these CH_4 reach FID at different times. The liquid products like CH_3OH and higher alcohols were analyzed by GC with packed column (Porapak-Q) using FID.

Gas sample
from
the reactor

H$_2$, CO$_2$ CO   CH$_4$, C$_2$H$_6$

TCD → Methanizer → FID

Carbosieve S-II column

Liquid sample
from
the reactor

Methanol

FID

Porapak-Q column
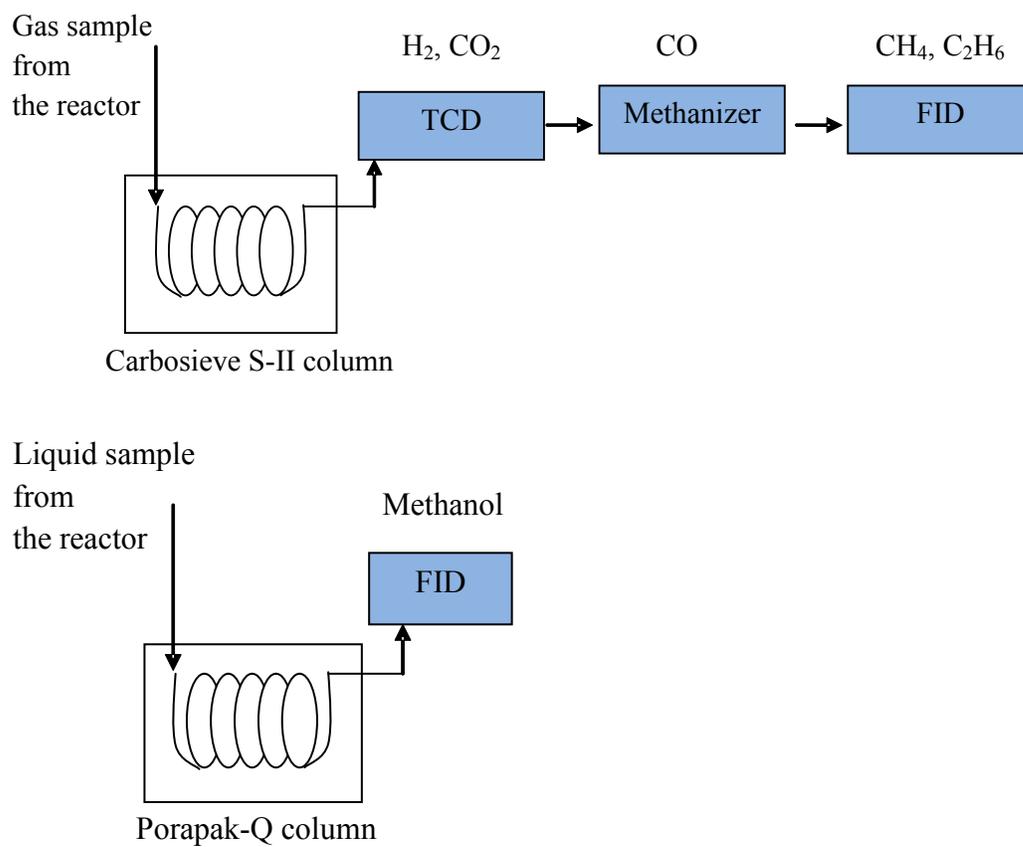
Figure S2: The flowchart of gas chromatography for gas phase product analysis and liquid phase analysis of alcohols.

Figure S3 shows the standard curves for each product prepared from the standard gas mixture.

Standard calibration curves:
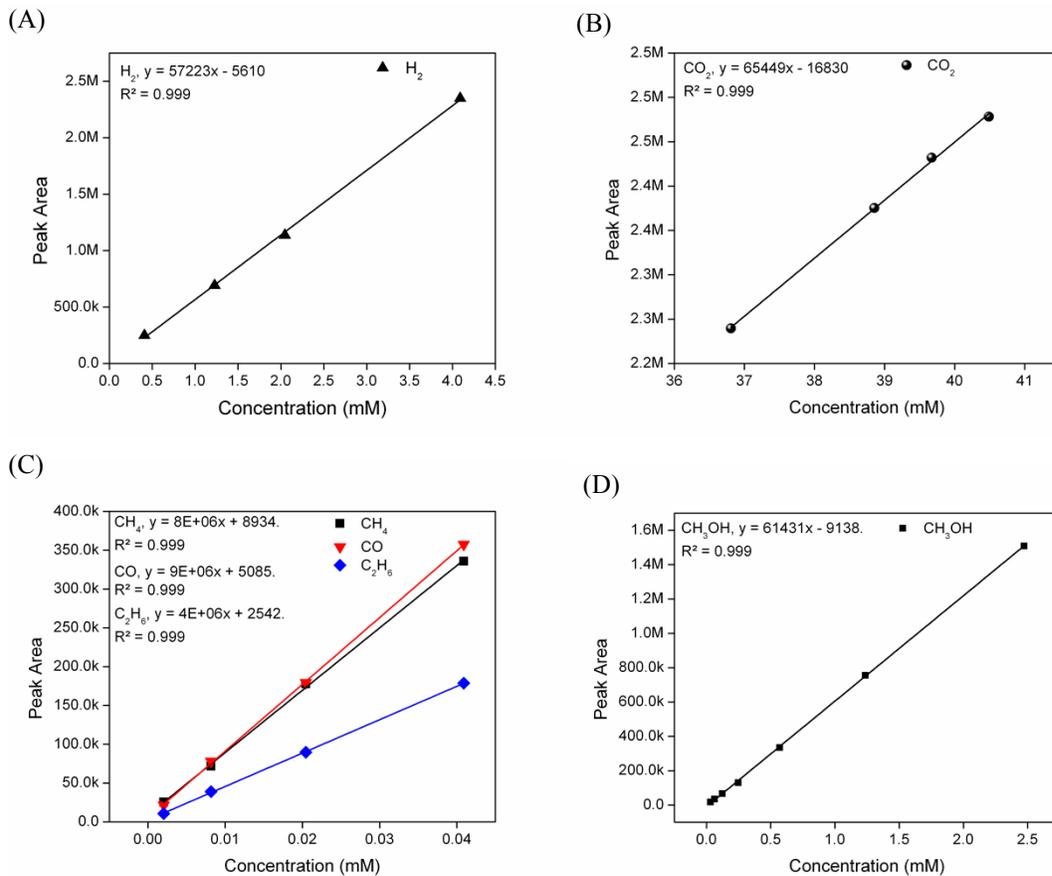
Figure S3: Standard calibration curves for (A) H_2, (B) CO_2, (C) CH_4, CO, C_2H_6, and (D) CH_3OH.

Faradaic efficiency was calculated for different ERC products obtained using PEI/PVA/KOH and QPEI/PVA/KOH after 25min of electrolysis at different voltages (Figure S4). The maximum Faradaic efficiency of CH_4 is 7.97% obtained at 2.5V at current density of $4.52mA.cm^{-2}$ in the case of PEI/PVA/KOH. It may be seen that to form any reaction product, either a potential window or a particular voltage is more favorable. However, with lowering the voltage or raising the applied voltage, the adverse effect is found for the reaction products. At higher voltages the hydrogen evolution is favoured and at lower potentials the Faradaic efficiencies for the products are generally reducing with significant hydrogen evolution. On further decreasing the potential there was no significant formation of either reaction products or hydrogen by-product. The maximum Faradaic efficiency for CH_4 was around 6% for the potential window of 2.25-2.75 V using PEI/PVA/KOH, whereas the use of QPEI/PVA/KOH suppressed the Faradaic efficiency of the CH_4 and selectively formed C_2H_6 with the maximum efficiency of 17.06% at 2.25V.

(A)
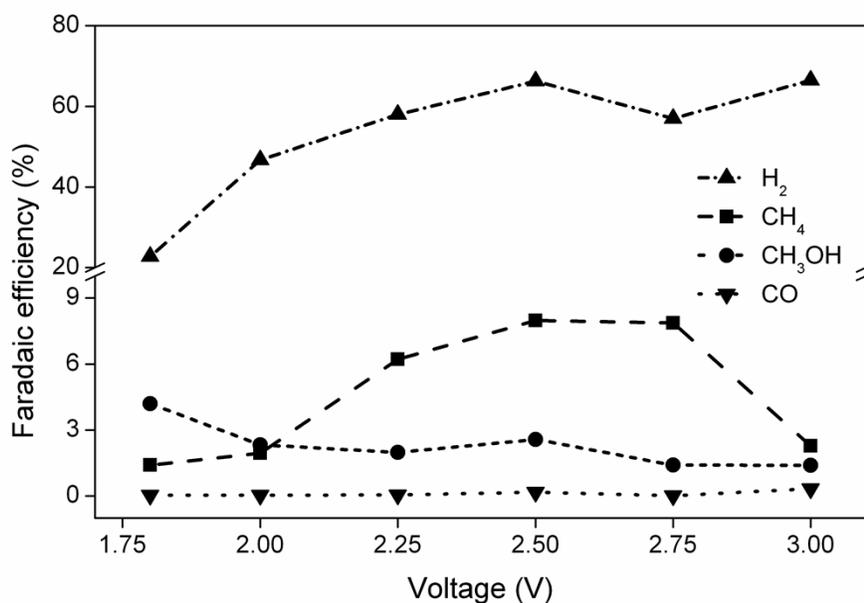
(B)
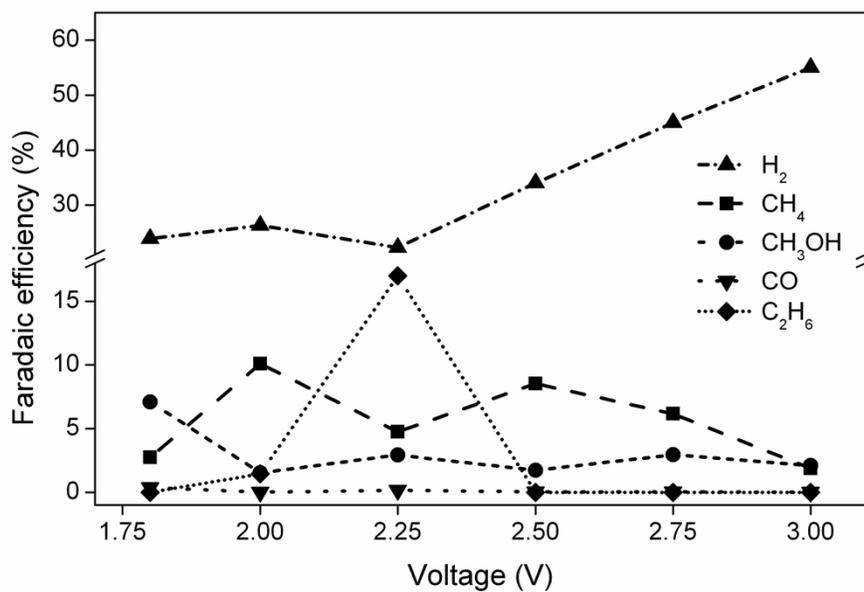
Figure S4: Faradaic efficiency obtained as a function of applied potential in the ERC using (A) PEI/PVA/KOH SPE and (B) QPEI/PVA/KOH during 25min of electrolysis