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.

![Experimental setup diagram]

**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$_2$O catalyst layer, (10) SPE, (11) Pt/C catalyst layer, (12) anode gas diffusion layer, (13) anode vent (O$_2$ and unreacted H$_2$O), (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$_2$H$_6$ 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$_2$H$_6$) also were detected. It may be noted that there was no interference of the CH$_4$ from the reactor and methane form methanizer (which was obtained from CO and CO$_2$ conversion), because these CH$_4$ reach FID at different times. The liquid products like CH$_3$OH and higher alcohols were analyzed by GC with packed column (Porapak-Q) using FID.
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:

(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 25 min 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 4.52 mA 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$_2$H$_6$ with the maximum efficiency of 17.06% at 2.25V.
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