Supplementary Information

Effect of Polarization on Kinetic Overpotential of CO2R Products on Copper:

The computed polarization losses and the corresponding equilibrium potentials were subtracted from the applied potential to obtain the intrinsic activity or overpotentials of various reactions of copper shown in Figure S1a. The plots shown in Figure S1a are shifted horizontally by a fixed value (according to the equilibrium potentials) in Figure 12. Additionally, there is an extra shift of the Tafel plots due to polarization losses for applied voltages < -1V in Figure S1a. According to Figure S1a, the onset overpotentials (for a current density of 0.056 mA cm^{-2}) are -0.668 V for hydrogen, -1.114 V for methane, -0.972 V for ethylene, -0.8692 V for ethanol, -0.666 V formate, and -0.676 V for CO.

Figure S1b shows the equilibrium potential of methane, the polarization loss and the kinetic overpotential with respect to the applied voltage. The equilibrium potential of methane (solid red line) is not parallel to hydrogen, due to decrease in concentration of CO_2 at cathode (as shown in Figure 12). The polarization loss at the cathode is given by the net decrease in the equilibrium potential of the reaction due to the increase in the pH at the cathode. Consequently, the applied voltage in Figure S1b is a sum of polarization loss and kinetic overpotential. Therefore, the kinetic overpotential decreases with increasing applied voltage as the polarization losses become significant below -1 V.

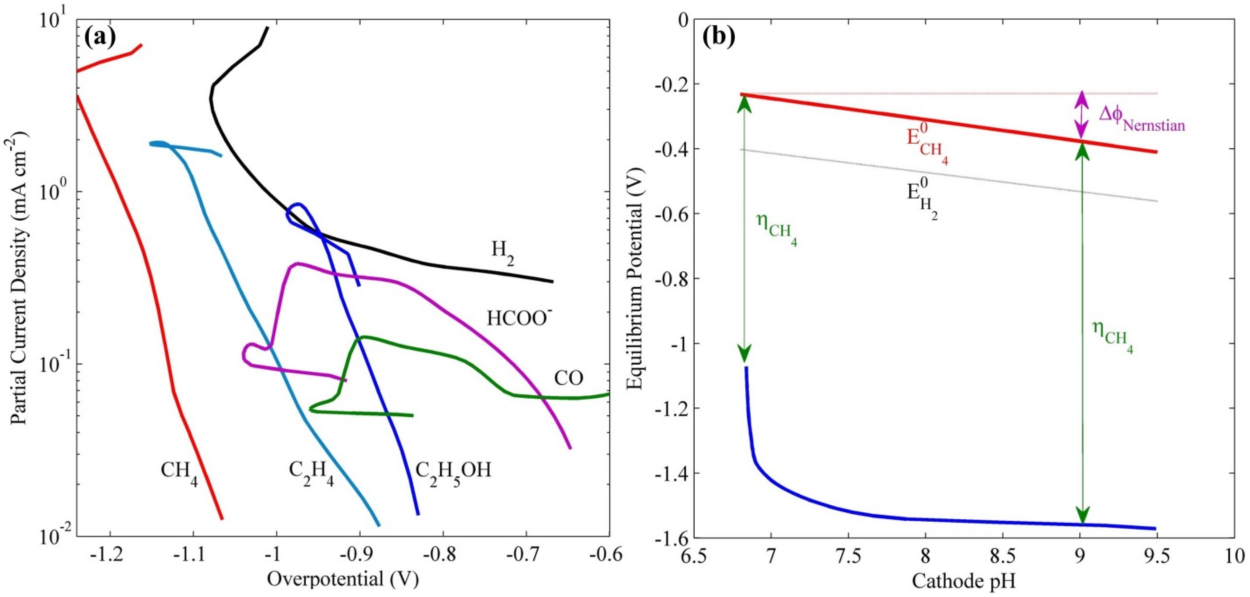

Figure S1 (a) Partial current density versus kinetic overpotential for CO2RRs on Cu after subtraction of polarization losses and the equilibrium potential for each product from the applied voltage. (b) Plot of equilibrium potential of methane versus the cathode pH. The kinetic overpotential decreases with increasing negative bias (past -1.4 V vs SHE) due to increase in the polarization losses. Note a slight decrease in the equilibrium potential of methane formation is due to decrease in the CO_2 concentration at the cathode as shown in Figure 12.