Supporting Information

Understanding the Impact of N-Arylpyridinium Ions on the Selectivity of CO$_2$ Reduction at the Cu/Electrolyte Interface

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Fig. S 1: Custom-built two-compartment cell setup. A carbon rod was used as the counter electrode. 10 mL of an aqueous solution of KHCO₃ (0.5 M) was used as the anolyte. 17 mL of the same solution was used for the catholyte. The catholyte was purged at 5 sccm with a fine-porosity gas dispersion tube to ensure saturation of the solution with CO₂ or Ar. A teflon-coated magnetic stir bar was used to stir the catholyte at 900 rpm. Before each experiment, the Cu surface was fully reduced by cycling the potential between −0.6 V and −1.2 V vs Ag/AgCl at 10 mV/s in Ar saturated electrolyte. Without returning to open circuit, the potential was maintained at −0.6 V while the catholyte was purged with the gas of interest. After 20 minutes, the reference spectrum was collected and then a 0.5 ml aliquot of electrolyte containing T-Pyr, P-Pyr, or pyridine was added to the catholyte. The potential was maintained at −0.6 V for two more minutes to allow the additives to mix into the electrolyte, directly followed by the electrochemical experiment.
Fig. S 2: (A) IR spectra of the Cu/electrolyte interface in the presence of 10 mM P-Pyr in CO$_2$-saturated 0.5 M KHCO$_3$ during the CV in Figure 1 of the main text and (B) a repeated experiment. The main organic film features at 1610 and 1511 cm$^{-1}$ are consistent with the ring stretch of the pyridyl moiety of the film dimer.$^{2,3}$ A reversibly appearing peak at 1599 cm$^{-1}$ that reaches the maximum intensity at $\approx -1.1$ V is attributed to pyridinium ions that adsorb/desorb or change their orientation.
Fig. S 3: (A) IR spectra of the Cu/electrolyte interface in the presence of 10 mM T-Pyr in CO$_2$-saturated 0.5 M KHCO$_3$ during the CV in Figure 1 of the main text and (B) a repeated experiment.
Fig. S 4: IR spectrum of the unmodified Cu/electrolyte interface at $-1.1$ V in CO$_2$-saturated 0.5 M KHCO$_3$ during the CV in Figure 1 of the main text.
Fig. S 5: IR spectrum of a 10 mM aqueous solution of K$_2$CO$_3$. The spectrum of pure water served as the reference spectrum.
Fig. S 6: SEM images of Cu foils. (A) Pristine copper surface, (B) P-Pyr-derived film on Cu, (C) T-Pyr-derived film on Cu. The organic films were deposited during a CV under conditions as those employed for SEIRAS (Figure 2 of the main text). The films were deposited on a 1 cm$^2$ Cu foil. After removal of the electrode from the catholyte, the films were rinsed with deionized water, gently dried with N$_2$, and placed into a N$_2$-flushed container before SEM images were taken. A JEOL JSM-6340F Scanning Electron Microscope was used for all measurements.
Fig. S 7: IR spectra of CO$_{\text{atop}}$ at saturation coverage on Cu (solid line) in CO$_2$ saturated 0.5 M KHCO$_3$ while the potential was held at $-1.1$ V. While maintaining the potential, the purging gas was then switched to Ar, lowering the surface coverage of CO (dashed line) with a corresponding peak intensity of $\approx 1/5$ saturation coverage.
Fig. S 8: (A) IR spectrum of a 10 mM aqueous solution of pyridine with the spectrum of pure water used as the reference spectrum. B\textsubscript{2} and A\textsubscript{1} indicate in-plane vibrations perpendicular and along the C\textsubscript{2}-axis of pyridine. (B) IR spectrum of the Cu/electrolyte interface with 10 mM pyridine at $-1.1$ V in CO\textsubscript{2}-saturated 0.5 M KHCO\textsubscript{3}. The peaks with A\textsubscript{1} symmetry at $\approx 1480$ and $\approx 1600$ cm\textsuperscript{-1} are present during the CV, whereas the B\textsubscript{2} symmetry peak at $\approx 1444$ cm\textsuperscript{-1} is not. This observation supports end-on adsorption of pyridine on the copper electrode.\textsuperscript{4}
Fig. S 9: $^1$H NMR (400 MHz) spectrum of T-Pyr taken in D$_2$O.
Table S 1: Ratios of the signal intensities for CH₄, H₂, and C₂H₄ in the presence of T-Pyr versus those for unmodified Cu at an applied potential of −1.63 V (−1.0 V vs RHE). The electrochemical cell, electrolyte, and stirring conditions (900 RPM) were identical to those of the SEIRAS experiments. A planar polycrystalline Cu foil was used as the working electrode. GC-MS (Shimadzu QP2010 Ultra, with Carboxen 1010 PLOT column) was used for product analysis after 15 min of electrolysis. No CH₄ was detected in the presence of T-Pyr.

<table>
<thead>
<tr>
<th>T-Pyr/Unmodified Cu</th>
<th>CH₄</th>
<th>H₂</th>
<th>C₂H₄</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.37</td>
<td>0.62</td>
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References


