**High-rate and efficient ethylene electrosynthesis using a catalyst:promoter:transport layer**

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**ABSTRACT**

**Carbon dioxide (CO2) electroreduction to valuable chemicals such as ethylene is an avenue to store renewable electricity and close the carbon cycle. Membrane electrode assembly (MEA) electrolyzers have attracted recent interest in light of their high stability, and despite low productivity: a modest partial current density in CO2-to-ethylene conversion of approximately 100 mA cm-2. Here we present an adlayer functionalization catalyst design: a catalyst:tetrahydro-phenanthrolinium:ionomer (CTPI) interface in which the catalytically-active copper is functionalized using a phenanthrolinium-derived film and a perfluorocarbon**-**based polymeric ionomer. We find, using electroanalytical tools and operando spectroscopies, that this hierarchical adlayer augments both the local CO2 availability and the adsorption of the key reaction intermediate CO on the catalyst surface. Using this CTPI catalyst, we achieve an ethylene Faradaic efficiency of 66% at a partial current density of 208 mA cm-2 – a two-fold increase over the best prior MEA electrolyzer report – and an improved full-cell energy efficiency of 21%.**

**TOC GRAPHIC**



The electrochemical CO2 reduction reaction (CO2RR) offers storage of intermittent electricity from solar and wind in the form of fuels and value-added chemicals,1–3 enabling further penetration of renewables in the transportation and chemical industries.4–8

Implementation of CO2RR will require high productivity to reduce capital cost, and high energy efficiencies (EE) to reduce operating cost. Techno-economic assessments further emphasize the need for high activity in generating high-value CO2RR products, such as ethylene, well beyond the 100 mA cm-2 threshold.9,10 Conventional H-cells deliver current densities of only tens of mA cm-2 due to CO2 mass transport limitations in aqueous solutions.11,12

Introducing CO2 in the gas phase enables facile CO2 mass transport from the bulk to the local electrode by decreasing the thickness of the diffusion layer from tens of micrometers to tens of nanometers, permitting CO2RR current densities above 100 mA cm-2.13–15 In such a flow-cell configuration, a gas diffusion electrode (GDE) separates gas-phase CO2 from either alkaline or neutral electrolyte.16,17 However, ohmic loss across the neutral electrolyte that extends between cathode and anode leads to a high overpotential when the current density is high, limiting EE.18 Though the use of alkaline electrolyte increases ionic conductivity and enables higher current densities and EEs,17 the formation of carbonate salt from the reaction of CO2 with alkali electrolyte wastes reactant CO2, reduces system stability, and increases cost.8

Membrane electrode assembly (MEA) electrolyzers form an integrated layered stack by removing the catholyte and merging the cathode:ion-exchange membrane:anode **(Figure 1a)**.16–20 MEAs developed for fuel cells and water electrolyzers and achieved current densities >1 A cm-2.21–23 However, with present day MEAs, CO2RR activities towards ethylene are still limited to approximately 100 mA cm-2.18,24,25

Here we present hierarchical adlayer – a catalyst:tetrahydro-phenanthrolinium:ionomer (CTPI) structure – that enables high-rate and efficient electrosynthesis of ethylene in an MEA electrolyzer. In this design, the catalytically-active copper is modified by a phenanthrolinium-derived molecular film and a perfluorocarbon based polymeric ionomer.This hierarchical adlayer augments simultaneously the availability of reactant CO2 and the binding strength of \*CO, a key intermediate along the pathway to ethylene.26,27 These two factors contribute to current densities and EEs in CO2RR.

We achieve as a result ethylene partial current densities greater than 200 mA cm-2 – a two-fold enhancement in rate compared to the best prior reports in MEA electrolyzers.18,24 We do this with an ethylene Faradaic efficiency (FE) of 66% and a full-cell EE of 21% – the highest selectivity, and the highest efficiency, reported for MEA-based CO2RR electrolyzers.

We sought to diagnose the origins of low current densities in MEA electrolyzers. Using polycrystalline Cu (150 nm thick) sputtered on a porous polytetrafluoroethylene (PTFE, average pore size of 450 nm) gas diffusion layer **(Figure S1)** as the cathode (Cu/PTFE), iridium oxide supported on a titanium mesh as the anode, and an anion exchange membrane (AEM) as the solid-state electrolyte, we assembled the MEA **(Figure S2)** and explored the CO2RR performance at the voltage range of -3 V – -4.5 V. Both total current density and ethylene FE increase with increasing voltage, and the peak ethylene FE reaches 45% at -3.8 V. This trend results in a peak ethylene partial current density of ~75 mA cm-2 **(Figure 1b)**. The limiting current density was positively correlated with the partial pressure of CO2 supplied **(Figure S3)**, suggesting that mass transport of CO2 could be limiting the reaction rate. The full-cell EE was 14% based on Equation (1):

Equation (1)

where *E*° is 1.15 V, the thermodynamic potential for the overall reaction 2CO2 + 2H2O → C2H4 + 3O2.

It is suggested that the CO2 concentration decreases rapidly at the gas/liquid/solid three-phase interface **(Figure 1c)**: since CO2RR uses water as the proton source26 and generates local hydrated OH-, a significant portion of the catalyst surface is likely inaccessible to CO2,28,29 and the competing HER dominates in these areas **(Figure 1d)**.

We took the view that CO2RR kinetics would increase if the transport of CO2 to catalyst surfaces was unimpeded by OH-/H2O, i.e. with separate gas and ion/liquid transport channels that improve CO2 transport and avoid consumption of CO2 by OH-. We took inspiration from the role of ionomers in the enhancement of oxygen reduction reaction (ORR) kinetics in fuel cells through concurrent transport of reactants, by-products and charged species,30,31 and explored the viability of ionomers on CO2RR performance of Cu catalysts. We reasoned that the hydrophobic and hydrophilic segments of the ionomer would allow the transport of gas and hydrated ions, respectively.32

We formed nm-thick polymeric films via the spray-coating of an ionomer solution onto the Cu/PTFE substrate and tested CO2RR performance (**Figure S4** for the morphology). A short-side-chain (SSC) perfluorocarbon polymer32,33 **(Figure 1b)** was used as the ionomer. It is composed of a hydrophobic PTFE backbone and a hydrophilic side chain terminated by sulfonic acid. We found that the SSC extends the ethylene partial current density to 280 mA cm-2 **(Figure 1b and S5)**. The increased current density is attributed to increased CO2 transport achieved by the separation of CO2 and ion/H2O pathways. As in prior reports,32,34 a much larger portion of the catalyst becomes accessible to gas (CO2) via a hydrophobic backbone while the transport of ions/H2O is retained within hydrophilic side chains **(Figures 1e and 1f)**. This effect is akin to the well-coordinated, simultaneous transport of O2 and proton/H2O transports in fuel cells.30,31 The length of the side chain in the ionomer does not markedly affect the productivity of ethylene from CO2RR **(Figure S6)**. Although the partial current density for ethylene is increased to >200 mA cm-2, the ethylene FE around 52% is only slightly higher than that of the reference Cu/PTFE case, and the high (-4.5 V) potential required **(Figures 1b and S5)** renders a low full-cell EE <15%. We realized that, at the optimum voltage for the reference Cu/PTFE, -3.8 V, the FE towards CO for the SSC-modified Cu is 25% while that for the Cu/PTFE is 13%. Converting the excess CO to ethylene while maintaining a similar applied voltage would improve EE.

We sought to introduce a further adlayer on catalyst surfaces with an organic film functioning similar to pyridinium-derived films.24,35 We postulated that conformal hierarchical deposition of such a layer together with SSC ionomer on the Cu surface – without disrupting SSC benefits and blocking the catalytically active sites **(Figure S7)** – may optimize the binding of \*CO, and therefore promote CO-to-ethylene conversion **(Figure 2a)**.

We electro-reduced N,N’-ethylene-phenanthrolinium dibromide onto the Cu/PTFE catalyst to form a 20±5 nm continuous and conformal film **(Figure S8)** comprising primarily the 4,4' and 2,2' dimeric structures **(Figure 2b and S9)**, in accordance with previous findings on polycrystalline copper.35 While it is possible that during extended storage the molecular film composition evolves **(Figure S9)**, for example via partial oxidation, its CO2RR performance is high even after a period of weeks. We then spray-deposited the electrode with a 15±5 nm SSC ionomer layer, and the resulting electrode possessed a similar morphology to the unmodified Cu/PTFE **(Figures 2c, S1 and S10)**.

We found that the phenanthrolinium-derived molecular film enables an improved ethylene FE. Applying the optimal tetrahydro-phenanthrolinium loading to the Cu/PTFE surface **(Figure S11)**, we achieved an ethylene FE of 58% at an applied voltage of -3.7 V **(Figures 2d and S12)**. The increased ethylene FE at the expense of CO FE **(Figure S12)** is consistent with the prior report.24 Due mainly to the improved FE, the full-cell EE improved from 14% for the reference Cu/PTFE, to 18%.

Although the ethylene FE is high for the tetrahydro-phenanthrolinium-modified Cu/PTFE catalyst, the partial current density was capped at around 110 mA cm-2, in agreement with the picture of limited CO2 transport. To recover the already-achieved high current density observed in the SSC-modified Cu/PTFE case, we re-introduced the outermost SSC layer to the tetrahydro-phenanthrolinium-modified Cu/PTFE catalyst (see **Figures 2c and S13** for the SEM images). We found that the FE and partial current density towards ethylene are increased, especially at the applied voltage region where the CO2RR is otherwise limited by CO2 mass transport, as in the case of tetrahydro-phenanthrolinium-modified Cu/PTFE electrode **(Figure 2e)**. By optimizing the tetrahydro-phenanthrolinium loading and the hierarchical ordering in the tetrahydro-phenanthrolinium/SSC film **(Figures S14 and S15)**, we achieved (at -4.4 V) a peak ethylene FE of 69% with a partial current density of 304 mA cm-2, both of which are the highest performance metrics for CO2RR MEA electrolyzers to date. The full-cell EE is 18%, a similar value to that achieved by the tetrahydro-phenanthrolinium-modified Cu, due to the compromise between increased ethylene FEs and simultaneously increased applied potentials.

By performing electrochemical impedance spectroscopy (EIS) measurements, we found that modification of the Cu/PTFE electrode with tetrahydro-phenanthrolinium or together with SSC ionomer does not substantially change the resistances at the interface **(Table S1)**, thus yielding similar cell resistances overall **(Figure S16).**

This tetrahydro-phenanthrolinium molecule was reported in a recent flow cell electrolyzer study, with operating current densities lower than 10 mA cm-2,35 and has not been applied to GDE-based CO2RR MEA electrolyzers. To clarify the CO-adsorption enhancing role of the tetrahydro-phenanthrolinium in this new system, we used CO as a probe molecule and carry out the CO reduction reaction (CORR) using 3 M KOH as the anolyte, a condition that has been proven to promote CORR.36,37 We found that the tetrahydro-phenanthrolinium-modified Cu/PTFE shows a higher ethylene FE **(Figure 2f)** and partial current density **(Figure 2g)** in both cases, with and without the SSC layer. We note also that the SSC ionomer layer promotes higher current densities, benefiting from the improved availability of CO near the active sites, akin to the case of CO2.

Using *in situ* Raman spectroscopy, we found that the tetrahydro-phenanthrolinium increases the ratio of atop- to bridge- bound CO from 0.14 on Cu to 0.51 **(Figure 2h)**, an optimum value we found previously24 that resulted in a low activation barrier for C–C coupling, the first step in CORR.26,27,38 We further confirmed that the modification of the tetrahydro-phenanthrolinium on Cu does not promote CO2RR through the tuning of Cu’s electronic structure, a finding we concluded from the unaltered Cu L-edge soft X-ray adsorption spectroscopy (XAS) on the tetrahydro-phenanthrolinium deposited Cu/PTFE upon one-hour electrolysis at an applied voltage of -3.7 V **(Figure 2i)**.

We sought further to improve current densities at similar, if not increased, EEs. A prior report18 has shown that a lower CO2 partial pressure favours the ethylene selectivity, which the authors attributed to a high local pH by mitigating the reaction of OH- with excess CO2. However, at the relatively high current densities tested here, lowering CO2 partial pressure decreases current density due to less reactant CO2 availability. Instead, we extended the developed CTPI architecture into three dimensions by establishing a tetrahydro-phenanthrolinium:ionomer hierarchy together with Cu nanoparticles (NPs) on a Cu/PTFE substrate **(Figures 3a and 3b)**: more active sites lead to higher current densities per geometric area and thus meanwhile consume more CO2 by CO2RR, resulting in less CO2 “free” to react with OH-.

We spray-coated a homogenous dispersion of Cu NPs, tetrahydro-phenanthrolinium, and SSC ionomer, onto the Cu/PTFE substrate (see **Figure S17** for the morphology and microstructure of the mortem electrodes). The tetrahydro-phenanthrolinium precursor was electro-dimerized *in situ* when CO2RR was initiated in the MEA **(Figure S18)**, establishing a highly porous catalyst comprised of Cu NPs:tetrahydro-phenanthrolinium:SSC ionomer **(Figure S19)**. The X-ray photoelectron spectroscopy (XPS) peaks corresponding to S2p, N1s, F1s, and Cu2p confirm the presence of each component in the Cu NPs:tetrahydro-phenanthrolinium:SSC catalyst upon completion of CO2RR **(Figure 3c)**. The N1s spectrum consist of two peaks located at 400.2 eV and 402.5 eV, indicating that the tetrahydro-phenanthrolinium includes tertiary amine and quaternary ammonium, consistent with the prior report.35 The thickness of sputtered Cu, loadings of Cu NPs, and the ratios among Cu NPs, SSC ionomer and tetrahydro-phenanthrolinium, were optimized (**Figures S20-S23)**. We observed the typical gas and liquid products for CO2RR with a total FE of ~100% **(Figure S24)**.

We investigated the electrochemical performance of the 3D CTPI catalyst in an MEA electrolyzer in neutral media. The electro-dimerized molecular film resulted in an increased ethylene FE compared to the control samples **(Figure 3d)**. The working principle is similar to the planar CTPI catalyst – the tetrahydro-phenanthrolinium promotes ethylene selectivity via favourable conversion of CO **(Figure S25)**, and the SSC ionomer enables higher reaction rates by enhanced CO2 transport.

The extended reaction interface provided by the 3D catalyst yielded improved reaction rates compared to its 2D counterpart at lower full-cell voltages **(Figures 3e and S25)**, reaching an ethylene partial current density of 208 mA cm-2 at only -3.9 V. In contrast, the 2D catalyst provides 97 mA cm-2 at the same potential. The full-cell EE is 21% for the 3D CTPI catalyst, slightly higher than the best prior value in MEA electrolyzers,24 but along with a 2.8x larger current density.

We further assessed the performance of 3D CTPI catalyst under challenging conditions: a diluted CO2 stream;39 a direct intake of flue gas;10,40 and a variable CO2 feed rate.17 We simulated the dilution of CO2 streams (down to 10%) via co-feeding with N2. The 3D CTPI catalyst maintained ethylene partial current densities >120 mA cm-2 – along with EEs over 20% – at all concentrations including 10% CO2 **(Figures 4a and S26)**. Markedly, it yields an ethylene FE of 69% at -3.7 V at a 40% CO2 concentration, corresponding to a full-cell EE of 22%. We further assessed the 3D CTPI catalyst using a simulated flue gas composed of CO2 (15.1%), O2 (3.99%), CO (190 ppm), SO2 (698 ppm) and N2 (balance). The 3D CTPI catalyst yields FEs towards ethylene of 22% at -3.8 V, whereas the reference Cu/PTFE provides an ethylene FE below 5% across -3 V – -4.0 V **(Figure S27)**. The direct intake of flue gas decreases selectivity toward CO2RR at the current densities investigated **(Figure S28)**. This is ascribed to the parasitic ORR,41 which is thermodynamically more favourable than CO2RR by more than 1 V, as well as the poisoning of catalysts by SO2.42

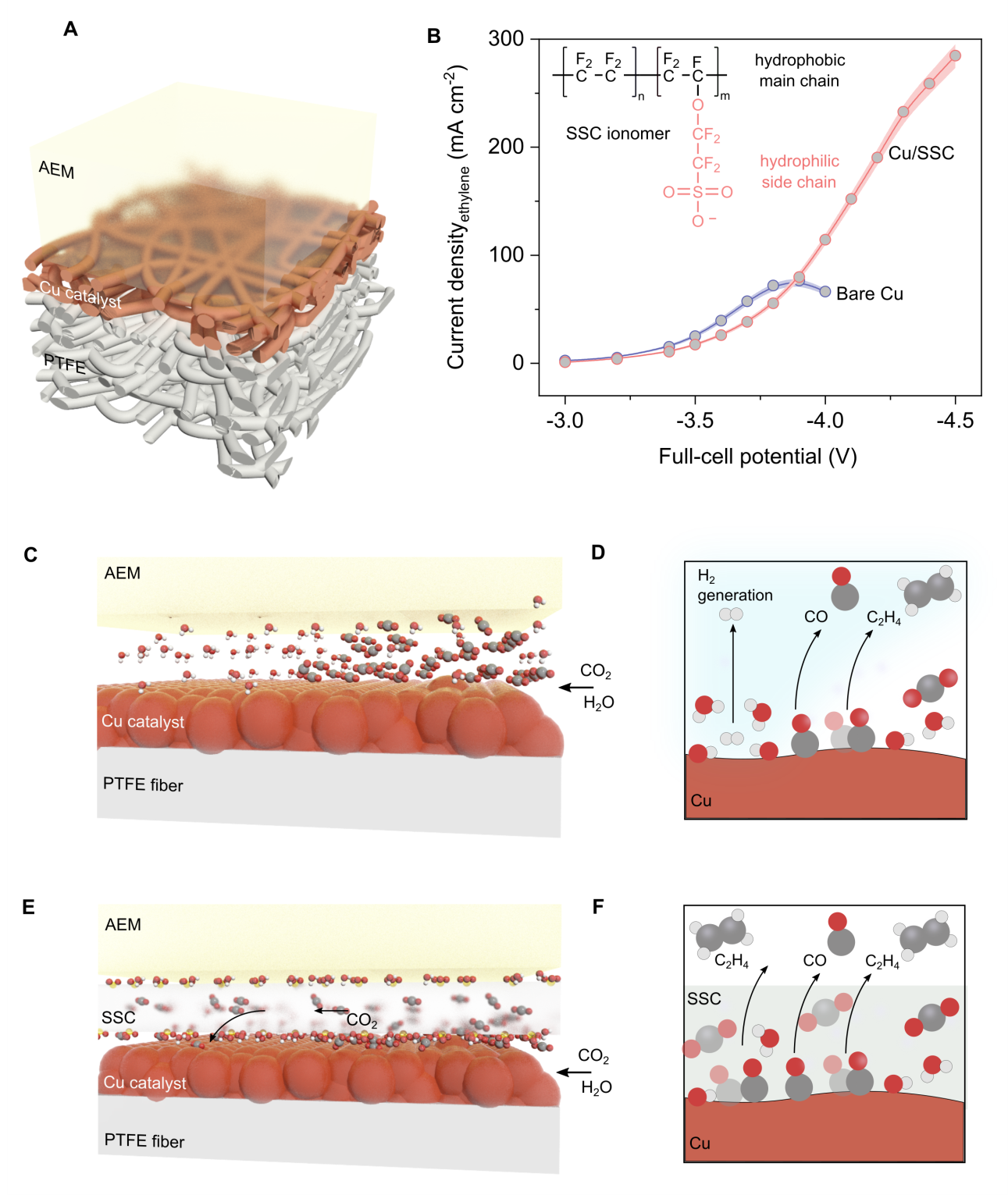
We varied the CO2 flow rate 25-fold (80 to 3 sccm) while performing CO2RR with the 3D CTPI catalyst at a constant current density of 300 mA cm-2. The ethylene FE reached a peak of 67% at ~30 sccm **(Figures 4b and S29)**. Lower flow rates reduced the selectivity, although ethylene production continued with an FE of ~28%, for the lowest CO2 flow rate of 3 sccm. At this low CO2 flow rate, the 3D CTPI produced an outlet gas stream with 37% ethylene (molar ratio) **(Figure 4b)**. The comparative value at 80 sccm is 1%. The production of concentrated CO2RR products reduces downstream product separation/purification costs.6,19

The 3D CTPI catalyst was stable – presenting an average ethylene FE of 63% at a constant current density of 220 mA cm-2 for over 100 hrs of continuous operation **(Figure 4c)**. We found that the catalyst maintained its morphology and microstructure following the extended electrosynthesis **(Figure S30)**.

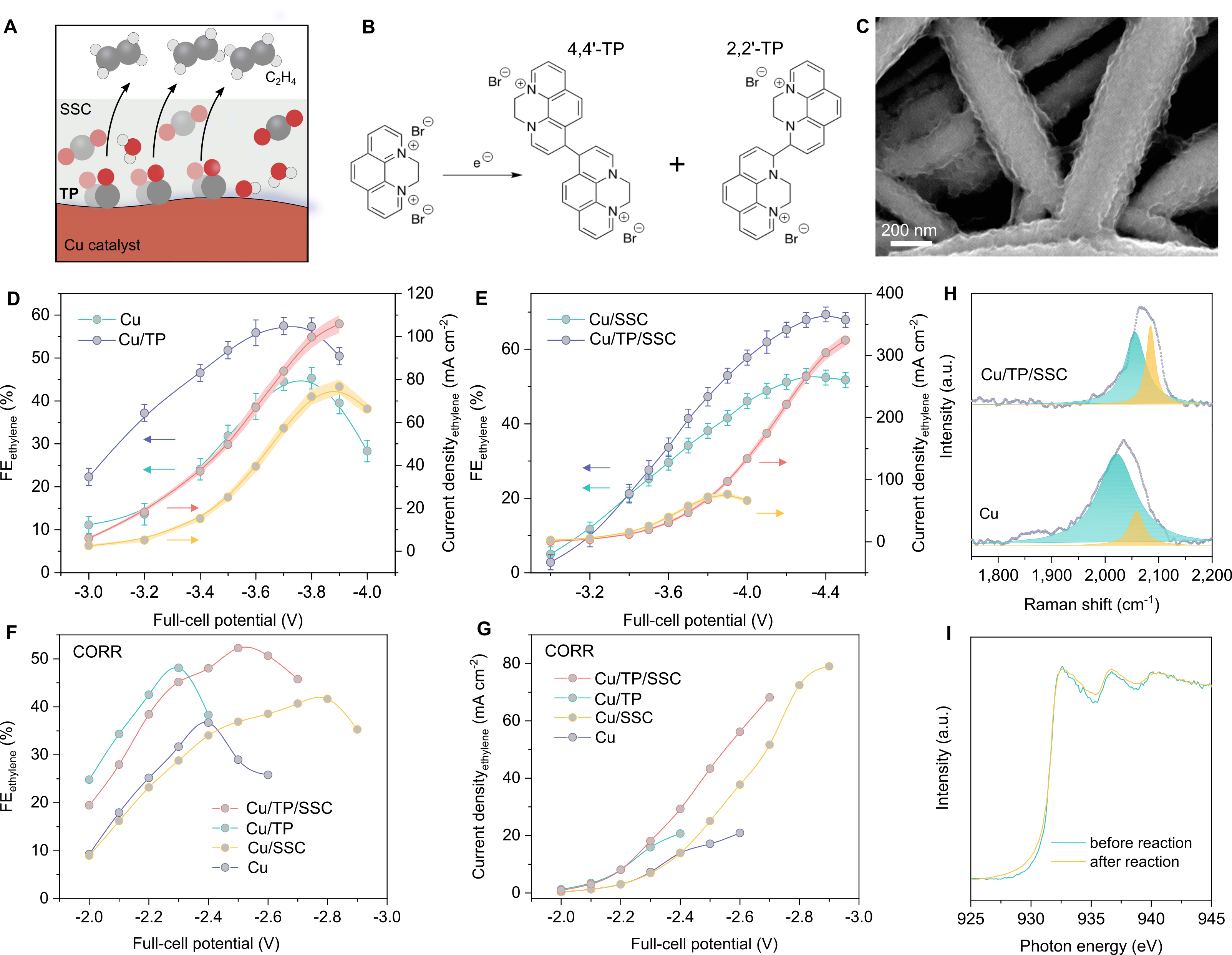
By comparing the performance metrics presented herein with literature benchmarks **(Figure 4d)**, we conclude that the 3D CTPI catalyst offers a means to achieve efficient, high-rate CO2-to-ethylene conversion in MEA electrolyzers.

In summary, this work devises a hierarchical adlayer structure that enables stable, selective CO2-to-ethylene conversion at high productivity and EE. Benefiting from the catalyst:tetrahydro-phenanthrolinium:ionomer augmentation, the structure offers improved CO2 availability and optimized adsorption of a key intermediate, CO. In an MEA electrolyzer this strategy achieved an ethylene FE of 66% at partial current densities >200 mA cm-2 and full-cell EE of 21%. The tetrahydro-phenanthrolinium-augmentation approach extends the boundaries of what can be achieved in today’s CO2RR MEA electrolyzers and sets out a path for future development.

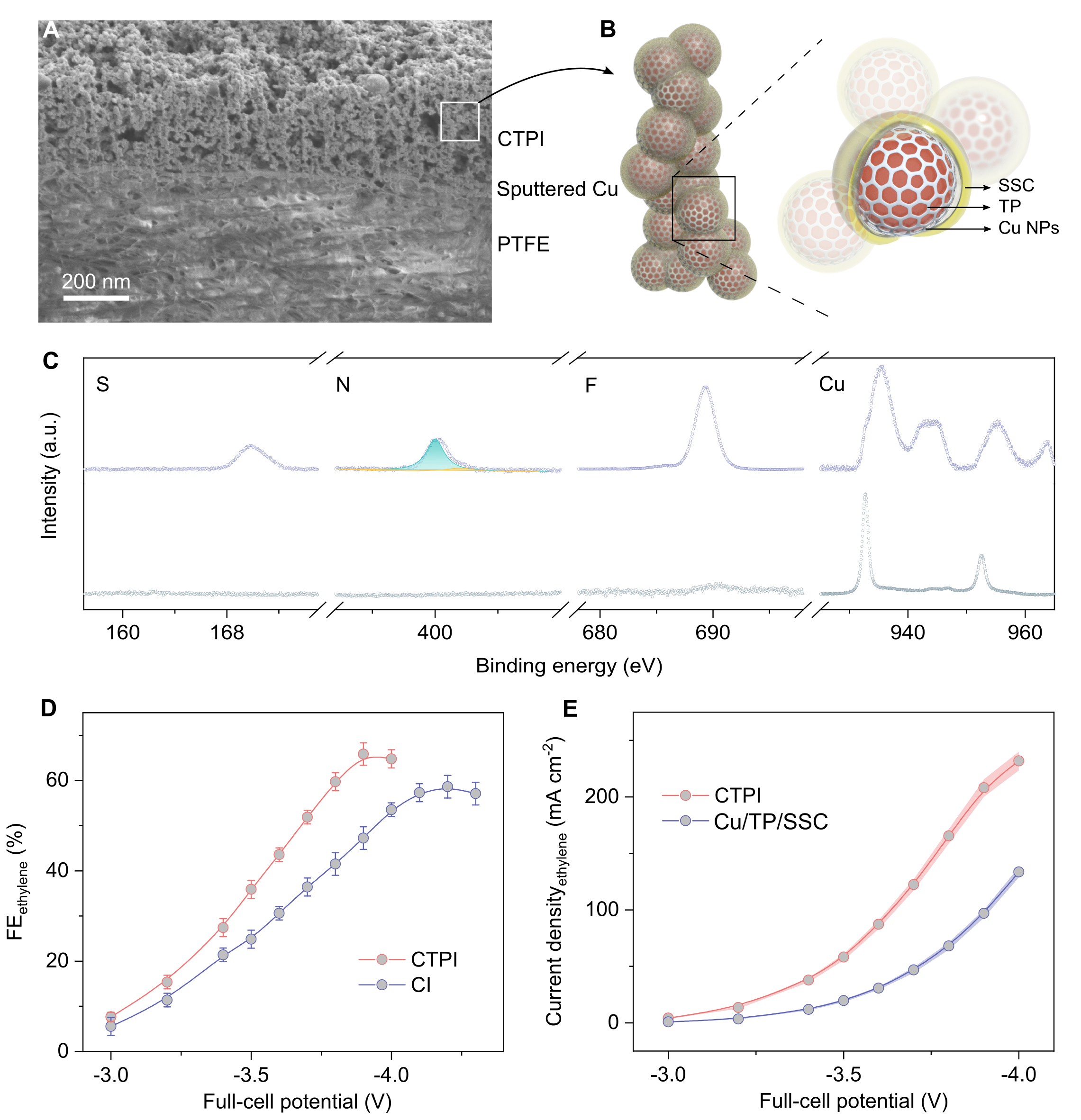
**FIGURES**



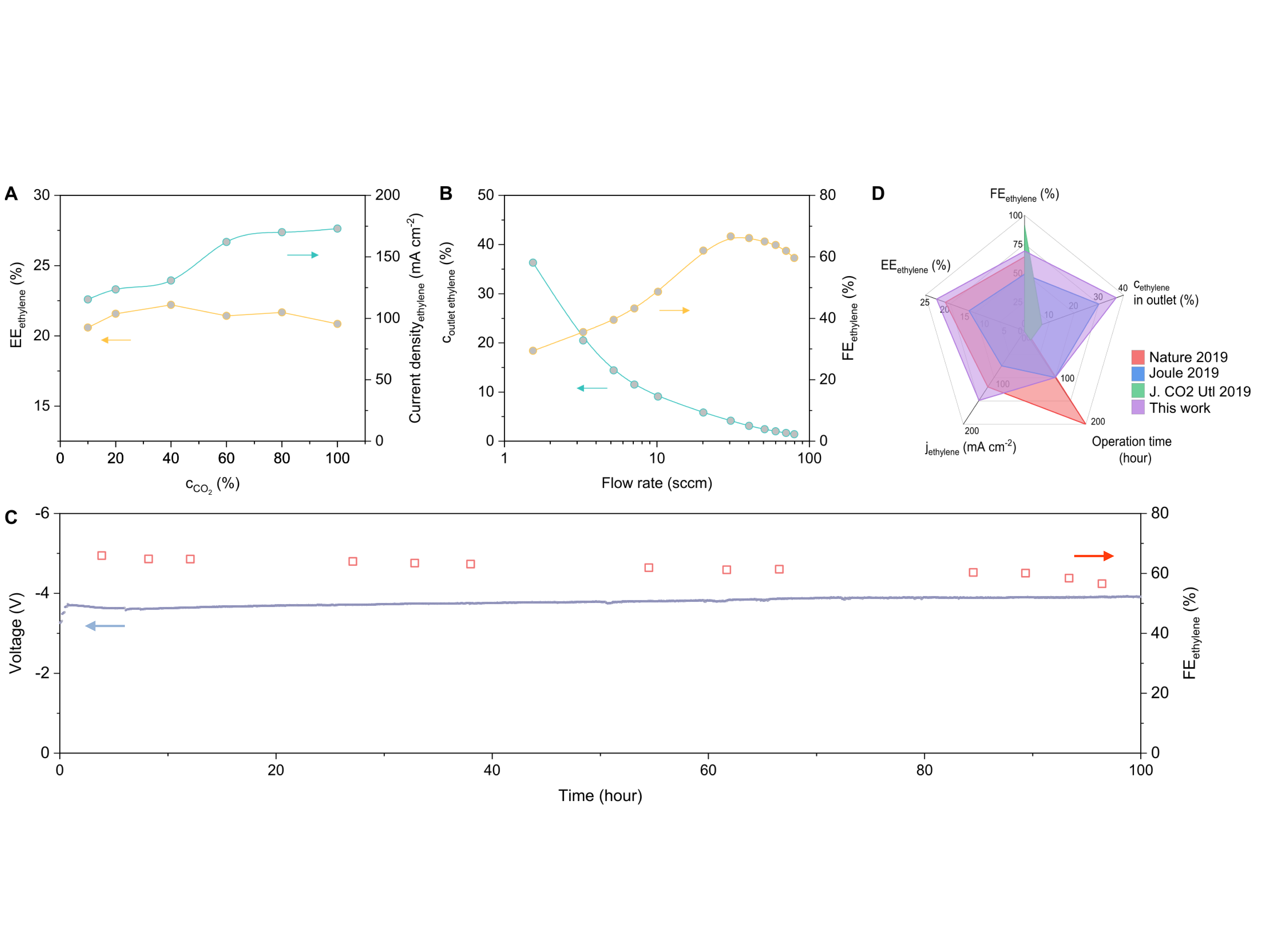
**Figure 1. Ionomer-augmented CO2 availability in an MEA electrolyzer. (A)** Cu/PTFE electrode and its interface with the AEM. **(B)** Ethylene partial current densities under a range of applied voltage for bare Cu/PTFE, and SSC-modified Cu/PTFE electrodes. Inset B describes the chemical structure of the SSC ionomer. The SSC is comprised of hydrophobic PTFE backbone and hydrophilic side chain terminated by sulfonic acid. Full-cell potentials are presented without iR compensation. The CO2RR electrolysis was operated using CO2 with a flow rate of 80 sccm, 0.1 M KHCO3 anolyte with a flow rate of 20 mL min-1. **(C)** Limited CO2 availability on unmodified Cu surface. The schematic illustrates the local CO2 and H2O transport for a single Cu/PTFE fiber in the cross-sectional direction. **(D)** Competition between the CO2RR and HER on unmodified Cu surface.The limited CO2 availability surface dominates the competing HER over CO2RR at elevated current densities. **(E)** Enrichment of CO2 species in the local reaction environment enabled by SSC ionomer conformably surrounding Cu surface. The schematic illustrates the local CO2 and H2O transport for a single Cu/PTFE fiber coated with the SSC ionomer in the cross-sectional direction. **(F)** Dominancy of the CO2RR over the HER upon SSC ionomer modification. Note: SSC stands for SSC ionomer.

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**Figure 2. CO2-to-ethylene conversion in an MEA electrolyzer. (A)** Hierarchical tetrahydro-phenanthrolinium:ionomer modified Cu/PTFE surface allows more CO2 and \*CO. **(B)** Electrodimerization of the phenanthrolinium into the 4,4' and 2,2'-tetrahydro-phenanthrolinium dimeric structures. **(C)** SEM images of tetrahydro-phenanthrolinium/ionomer on Cu/PTFE. **(D)** Ethylene FE and partial current density for unmodified Cu/PTFE (yellow line) and tetrahydro-phenanthrolinium-modified Cu/PTFE (red line). **(E)** Ethylene FE for SSC-modified Cu/PTFE, and ethylene FE and partial current density for tetrahydro-phenanthrolinium/SSC-modified Cu/PTFE (red line), and ethylene partial current density for unmodified Cu/PTFE (yellow line). Full-cell potentials of the CO2RR electrolysis are presented without iR compensation. The CO2RR electrolysis was operated using CO2 with a flow rate of 80 sccm, 0.1 M KHCO3 anolyte with a flow rate of 20 mL min-1. **(F)** Ethylene FE for unmodified Cu/PTFE, SSC-modified Cu/PTFE, tetrahydro-phenanthrolinium-modified Cu/PTFE, and tetrahydro-phenanthrolinium/SSC-modified Cu/PTFE for CO-to-ethylene conversion. **(G)** Ethylene partial current density for unmodified Cu/PTFE, SSC-modified Cu/PTFE, tetrahydro-phenanthrolinium-modified Cu/PTFE, and tetrahydro-phenanthrolinium/SSC-modified Cu/PTFE for CO-to-ethylene conversion. Full-cell potentials of the CORR electrolysis are presented without iR compensation. The CORR electrolysis was operated using CO with a flow rate of 80 sccm, 3 M KOH anolyte with a flow rate of 20 mL min-1. **(H)** Raman spectra of tetrahydro-phenanthrolinium/SSC ionomer modified Cu/PTFE and unmodified Cu/PTFE (the areas highlighted in blue and yellow indicate the bridge and atop adsorptions of CO on the Cu surface, respectively). **(I)** XAS spectra of the tetrahydro-phenanthrolinium/SSC-modified Cu/PTFE. Note: TP and SSC stand for tetrahydro-phenanthrolinium and SSC ionomer, respectively.



**Figure 3. 3D CTPI catalyst enables selective and efficient CO2-to-ethylene conversion in an MEA electrolyzer. (A)** Cross-sectional SEM image of the tetrahydro-phenanthrolinium/SSC ionomer hierarchy established together with Cu NPs on a Cu/PTFE substrate. **(B)** Schematic illustration of the tetrahydro-phenanthrolinium/SSC ionomer hierarchy on Cu NPs. **(C)** XPS spectra of the 3D CTPI catalyst. **(D)** Ethylene FE for 3D CTPI (tetrahydro-phenanthrolinium/SSC-modified Cu NPs on Cu/PTFE) and 3D CI (SSC modified-Cu NPs on Cu/PTFE) for CO2-to-ethylene conversion. **(E)** Ethylene partial current density for 3D CTPI (tetrahydro-phenanthrolinium/SSC-modified Cu NPs on Cu/PTFE) and 2D CTPI (tetrahydro-phenanthrolinium/SSC-modified Cu/PTFE (Cu/TP/SSC)).Full-cell potentials are presented without iR compensation. The CO2RR electrolysis was operated using CO2 with a flow rate of 80 sccm, 0.1 M KHCO3 anolyte with a flow rate of 20 mL min-1.



**Figure 4. Applied CO2RR performance of the 3D CTPI catalyst in an MEA electrolyzer. (A)** Full-cell EEs and ethylene partial current densities as a function of CO2 concentration in a diluted CO2 stream. **(B)** Ethylene concentrations in the cathode outlet and FEs as a function of CO2 flow rate.The CO2RR electrolysis was operated using CO2 with a flow rate of 80 sccm, 0.1 M KHCO3 anolyte with a flow rate of 20 mL min-1. **(C)** Extended CO2RR performance of the 3D CTPI catalyst at a constant current density of 220 mA cm-2 and with a feeding gas of CO2:N2 (40%:60%) at a flow rate of 80 sccm. The anolyte was 0.1 M KHCO3 with a flow rate of 20 mL min-1. Blue line represents the voltage recorded during the extended CO2RR experiment (primary y-axis). Each red square represents the ethylene FE averaged from three independent measurements (secondary y-axis). **(D)** Comparison of the performance metrics of the MEA electrolyzer based on 3D CTPI catalyst with literature benchmarks (for each report, the plotted values are those from the longest duration test).

**ASSOCIATED CONTENT**

**Notes**

The authors declare no competing financial interest.

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**Supporting Information**

Experimental details and additional data. The Supporting Information is available free of charge on the ACS Publications website.

**AUTHOR CONTRIBUTIONS**

D.S. and E.H.S. supervised the project. A.O. conceived the idea and carried out the electrochemical experiments with advice from F.L.. A.T. and A.R.H. synthesized and characterized the tetrahydro-phenanthrolinium. A.O. carried out Raman and EIS measurements. Y.W. and A.O. carried out SEM imaging. F.L. and S.F.H. designed the XAS measurements. S.F.H. performed the XAS measurements. X.W. performed the NMR analysis and provided help in EIS measurements. B.C. and Y.W. performed the TEM analysis. J.W. performed XPS measurements. M.L., J.L., and Z.W. provided help in electrochemical experiments. A.O. and F.L. wrote the manuscript. F.P.G.A. provided help in manuscript writing. All authors discussed the results and assisted during manuscript preparation.

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