The electrochemical conversion of CO₂ to methane provides a means to store intermittent renewable electricity in the form of a carbon-neutral hydrocarbon fuel that benefits from an established global distribution network. The stability and selectivity of reported approaches reside below technoeconomic-related requirements. Membrane electrode assembly-based reactors offer a known path to stability; however, highly alkaline conditions on the cathode favour C-C coupling and multi-carbon products. In computational studies herein, we find that copper in a low coordination number favours methane even under highly alkaline conditions. Experimentally, we develop a carbon nanoparticle moderator strategy that confines a copper-complex catalyst when employed in a membrane electrode assembly. In-situ XAS measurements confirm that increased carbon nanoparticle loadings can reduce the metallic copper coordination number. At a copper coordination number of 4.2 we demonstrate a CO₂-to-methane selectivity of 62%, a methane partial current density of 136 mA cm⁻², and > 110 hours of stable operation.
The electrochemical CO₂ reduction reaction (CO₂RR) enables the storage of intermittent renewable electricity while utilising CO₂ emissions[1-7]. Methane (CH₄) has the largest heating value of 55.5 MJ kg⁻¹ (ref. 6) among CO₂RR products, and is the main component of natural gas, well-known for clean and efficient combustion[7-8]. Natural gas provides 24% of global energy, and the infrastructure for CH₄ storage, transportation and consumption is established worldwide[9-11]. Thus, the electrochemical conversion of CO₂ into CH₄ offers a means to close the carbon cycle at a scale relevant to the global carbon challenge (Fig. 1a).

The application of CO₂ electrolysis requires catalysts and systems that operate at current densities over 100 mA cm⁻², exhibit high selectivity, and operate for long lifetimes[12-17]. Prior electrochemical CO₂ methanation catalysts have incorporated sputtered copper (Cu) nanoparticles[9], Cu-based alloys[18], covalent triazine framework Cu (ref. 19) and Cu-complexes[20]. These approaches have increased CH₄ selectivities, albeit at low current densities and short run times. CO₂ electrolyser incorporating membrane electrode assemblies (MEA) have recently demonstrated significant advancements in reaction stability, current density and scale-up potential[21,22]. The anion exchange membrane also provides a highly alkaline environment at the cathode that has been used extensively to promote C-C coupling and multi-carbon product formation on Cu catalysts[23-25].

Here we report a low coordination Cu catalyst approach for stable and selective electrochemical CO₂ methanation in an MEA. We identify, using density functional theory (DFT) calculations, that the reaction energy for the hydrogenation of the ∗CO intermediate, essential for CH₄ generation, is minimised when lowering the global coordination number of Cu from 7.5 to 3.0. To achieve and maintain low coordination number Cu in an MEA, we design a carbon nanoparticle (CNP) moderator strategy. The CNP isolate and prevent the agglomeration of low coordination number Cu clusters formed during the in situ reduction of a Cu-complex, copper(II) phthalocyanine (CuPc). With a Cu coordination number of 4.2, as verified by in situ extended X-ray absorption fine structure (EXAFS), we achieve a high CO₂RR to CH₄ Faradaic efficiency (FE) of 62% with a CH₄ partial current density of 136 mA cm⁻² and 110 h of stable electrolysis at 190 mA cm⁻².

Results and discussion

DFT calculations. We employed a mechanistic CO₂RR study to explore the key methanation pathways on Cu catalysts. CO adsorbed on the electrode surface (∗CO) is a crucial reaction intermediate toward most C₁ and C₂ products (Fig. 1b)[26,27]. The adsorbed ∗CO intermediate faces two diverging pathways leading to different products. In the first option, the ∗CO intermediate undergoes electrochemical hydrogenation to ∗CHO, embarking on the CH₄ pathway[28]. Alternatively, the ∗CO can couple in a purely chemical manner (no electron transfer is involved) with another ∗CO to produce ∗OCCO, subsequently leading to C₂ products, such as C₂H₄[29]. This C-C coupling step is enhanced by the highly alkaline conditions of MEA-based electrolyzers[21,24].

We applied DFT calculations to predict the effect of Cu coordination number on hydrogenation and C-C coupling. To accurately represent low values of atomic coordination, nanoparticles were used to simulate the Cu active sites. Based on these models, we investigated the reaction energy for the hydrogenation of the ∗CO to ∗CHO (Fig. 1c). The reaction energy for ∗CO to form ∗CHO via the hydrogenation step is significantly reduced at low coordination numbers, reaching −0.93 eV at a global coordination number of 3.0, a trend consistent with previous reports[30]. We then investigated the reaction energy associated with C-C coupling of the ∗CO intermediate toward ∗OCCO (Fig. 1d). The reaction energies for ∗CO to form an ∗OCCO intermediate via C-C coupling did not change significantly with coordination number. Similarly, the adsorption of H⁺ to ∗H (on the pathway to hydrogen evolution)
Fig. 2 Effect of the CNP to CuPc ratio on CO2RR methanation performance. Schematic of the atomic agglomeration (marked with orange arrows) from CuPc reduction a without CNP and b with CNP. c Current-voltage characteristics for samples with different CNP to CuPc ratios. d The maximum FE toward CH4 and C2H4 for samples with different CNP to CuPc ratios when operating between full cell voltages of −3.6 and −4.4 V. Error bars represent the standard deviation of three independent measurements.

The product distributions obtained during steady-state operation are shown in Supplementary Fig. 2 for all samples. Among the products, CH4 is furthest along the C1 hydrogenation pathway26. With C2H4 being the dominant C2 gas product from CO2RR, its selectivity is an indicator of C–C coupling. The selectivities of CH4 and C2H4 provide an indication of the degree of hydrogenation vs. C–C coupling for comparison with our DFT predictions. To account for the effect of the applied voltage on CO2RR selectivity, we plotted the peak FE values for CH4 and C2H4 within the voltage window of −3.6 to −4.4 V (Fig. 2d). We found that increasing the proportion of CNP in the catalyst composition increased CH4 production. The ratio of 7:1 was the exception to this trend, as all CO2RR product FEs, including CH4 and C2H4, decreased while the hydrogen evolution increased (Supplementary Fig. 2b). As the CNP active sites increased relative to that of the Cu, more H2 production is expected because CNP active sites cannot perform CO2RR and instead produce H2 (Supplementary Fig. 2). A lower density of Cu sites thus lowers CO2RR activity. This suggested a trade-off between methanation and reduced CO2RR activity as the ratio of CNP to CuPc was increased. The highest FE toward CH4, 62%, was exhibited by the 4:1 sample at −4.00 V and 220 mA cm−2 (liquid product analysis shown in Supplementary Fig. 3). Of the five samples, this 4:1 sample also demonstrated the highest peak CH4 to C2H4 FE ratio of 5.5, highlighting the ability of low coordination Cu states to encourage hydrogenation.

In situ mechanistic investigations. To examine the effect of CNP on the Cu coordination number, we investigated the chemical structure at 200 mA cm−2, the current density that corresponds to the maxima of CH4 selectivity for the samples studied, with in situ X-ray absorption spectroscopy (XAS). Three representative samples were analysed using this approach: CuPc only, 1:1, and 4:1 ratios of CNP to CuPc, respectively (see Supplementary Note 1).

We carried out in situ Cu K-edge X-ray absorption near edge structure (XANES) spectra to probe the oxidation state of Cu in our CuPc complex. To investigate the structural stability of the

Electrochemical reduction of CO2).
These results confirmed experimentally the DFT prediction that Cu catalysts with low atomic coordination numbers can boost CO₂RR methanation.

Ex situ mechanistic investigations. To further investigate the catalytic mechanism, we examined the chemical structure ex situ using X-ray photoelectron spectroscopy (XPS). The highest CH₄ selectivity performance sample (4:1 ratio of CNP to CuPc) was analysed and compared to its pre-electrolysis state. Since XPS is an ex situ measurement, we expected some oxidation of the Cu sample during the sample disassembly, preparation, and transport. The deconvolved N 1s peaks demonstrate the N–Cu bond in the CuPc molecular structure was decomposed irreversibly (Fig. 4a and Supplementary Fig. 10 and Supplementary Table 3). The deconvolved Cu 2p peaks show that the CuPc molecules were reduced to the metallic Cu (0) state, and most do not revert back to CuPc after the electrolysis (Supplementary Fig. 11). The post-electrolysis X-ray diffraction (XRD) results of the samples demonstrated a decrease in the CuPc characteristic diffraction patterns, compared to the pre-electrolysis states, further confirming CuPc decomposition (Supplementary Fig. 12). These XPS and XRD findings support the conclusion of the in situ XAS measurements, namely that metallic Cu is derived during CO₂RR and does not revert to CuPc.

Scanning electron microscopy with secondary electrons (SEM) and backscattered electrons (BS), and transmission electron microscopy (TEM) were employed to investigate the morphological changes of the pre- and post-electrolysis catalyst samples. The visual absence of large particle formations in the SEM and BS images of the pre- and post-electrolysis samples suggest no large metallic Cu agglomerates were formed during electrolysis (Supplementary Fig. 13). Energy dispersive X-ray (EDX) mapping and spectroscopy results proved the Cu element is evenly distributed on the GDE (Supplementary Figs. 14, 16 and Supplementary Table 4). STEM/EDX and TEM images taken pre- and post-electrolysis also support the claim that Cu...
nanoclusters (~2–5 nm) were formed during the reaction (Supplementary Figs. 16, 17).

**Stability and performance comparison.** To investigate the electrochemical stability of our low coordination Cu catalyst, we performed extended electrolysis galvanostatically at a current density of 190 mA cm\(^{-2}\) (Fig. 4b). To prevent salt accumulation in the gas diffusion layer (GDL) micropores and maintain CO\(_2\) mass transport through the GDL, every 2 h we briefly injected DI water into the cathode flow channel (see current fluctuations on Fig. 4b). Every ~24 h additional anode electrolyte, 0.05 M KHCO\(_3\), was provided to maintain the original electrolyte mass transport through the GDL, every 2 h we briefly injected DI water into the cathode flow channel (see current fluctuations on Fig. 4b). Every ~24 h additional anode electrolyte, 0.05 M KHCO\(_3\), was provided to maintain the original electrolyte volume. The low concentration of electrolyte was chosen to minimise potassium cation crossover and subsequent salt formation\(^{11,42}\). Over the course of the experiment, an average CH\(_4\) selectivity of 56% was achieved, and the non-iR compensated full cell voltage exhibited only a minor change, from −3.9 to −4.2 V. In contrast, applying this strategy in a flow cell configuration with liquid catholyte provided only 2 h of continuous operation prior to flooding (Supplementary Fig. 18), a failure mode typical of these systems\(^{22,43}\).

We showcase the performance achieved in this work in the context of three metrics essential for industrial implementation of CO\(_2\)RR: current density, product selectivity, and stability (Fig. 4c). Compared to the highest current density CH\(_4\)-focused literature, this work outperformed other catalysts in CH\(_4\) selectivity and stability. None of the literature reports in Fig. 4c are from MEA-based electrolysers because this work marks the first MEA system capable of selective (e.g., >50%) CH\(_4\) production from CO\(_2\) (refs. 21,44,45). The highest FE towards CH\(_4\) reported to-date in an MEA is 32%, less than half of the peak methane FE reported in this work\(^{45}\).

In summary, we studied the critical mechanism pathways for CO\(_2\)RR methanation and multi-carbon production on Cu catalysts. We found low coordination numbers to be beneficial for reducing the hydrogenation energy requirement toward CH\(_4\), counteracting the traditionally low energy requirements for C–C coupling found in MEA systems due to the high basic alkaline conditions found on the cathode. Guided by this finding, we designed a low coordination Cu catalyst, synthesised with CNP additives, which encase and better distribute Cu clusters to prevent excessive agglomeration, for use in an MEA system. This catalyst-system combination converted CO\(_2\) to CH\(_4\) at a FE of 62% and a partial current density of 136 mA cm\(^{-2}\). The same catalyst operated for 110 h at a current density of 190 mA cm\(^{-2}\) with an average FE of 56%. The stability of this strategy is a significant advance toward electrochemically derived renewable methane.

**Methods**

**DFT calculations.** We performed DFT calculations with the Vienna Ab Initio Simulation Package (VASP) code\(^{46,47}\). The exchange correlation energy was modelled by using Perdew-Burke-Ernzerhof (PBE) functional within the generalised gradient approximation (GGA)\(^{48}\). The projector augmented wave (PAW) pseudo-potentials\(^{49}\) were used to describe ionic cores. The cutoff energy of 500 eV was adopted after a series of tests. A Methfessel-Paxton smearing of 0.05 eV to the orbital occupation is applied during the geometry optimisation and for the total energy computations. In all calculations, the atoms at all positions have convergence was 10\(^{-5}\) eV using the Normal algorithm. A 4-layer (4 × 4) Cu (111) supercell was built to simulate the exposed surface of Cu while ensuring a vacuum gap of 15 Å. The Cu active sites with various coordination numbers were constructed via creating Cu vacancies on the surface or subsurface. We first ran the adsorption calculations, the top three layers are fully relaxed while the other layers are fixed at the tested lattice positions. All reaction energy calculations were described in Supplementary Note 3.

**Electrode preparation.** The cathode GDE were prepared by airbrushing catalyst inks with a carrier gas of nitrogen. The catalyst ink was prepared with 30 mL ethanol (Greenfield Global Inc., >99.8%), 150 mL Nafion (Fuel Cell Store D521 Alcohol based 1100 EW, 5 wt%) and catalytic material. The catalytic material
quantities varied by sample. For example, the sample containing only CuPc was made with 14 mg of CuPc (Sigma–Aldrich 546682, ≥99%). Similarly, the catalytic materials for CNP-CuPc ratios of 1:1, 2:1, 4:1, 7:1 and CNP only were made with 14 mg CNP (Alfa Aesar 39372, 75 mg g⁻¹) + 14 mg of CuPc, 14 mg CNP + 7 mg CuPc, 14 mg CNP + 3.5 mg CuPc, 14 mg CNP + 2 mg CuPc and 14 mg CNP + no CuPc, respectively. The catalyst ink mixtures were sonicated for 5 h, and then sprayed on a gas diffusion carbon paper (Fuel Cell Store Sigraet 39 BC, with microporous layer) with a 25 μL cm⁻². After spraying thoroughly, the GDE was dried for 24 h at room temperature (~20 °C). The anode electrode was prepared by dip-coating iridium chloride (Alfa Aesar, IrCl₃·xH₂O 99.8%) on titanium support (0.002 cm²). Catalyst surface morphology was imaged by a Hitachi S-5200 electron microscope (SEM; Hitachi, Tokyo, Japan). Catalyst surface morphology was imaged by a Hitachi S-5200 field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) equipped with a Gatan 689 energy-dispersive X-ray spectrometer (Gatan, Pleasanton, CA, USA) to determine the nanoscale composition of the catalysts. Microscopy images were taken at an accelerating voltage of 15 kV.

Characterisation. Catalyst surface morphology was imaged by an Hitachi S-5200 SEM at 10 kV and JEOI JEM-2010 HRTEM at 200 kV. Elemental analysis was performed with a field-emission scanning electron microscope (FE-SEM; JEOI JSM-6700F) equipped with an energy-dispersive X-ray spectrometer (EDX, Oxford Instruments X-Max 150) and X-ray diffraction. Quantitative X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha spectrophotometer with a monochromated Al Kα X-ray radiation source.

Electrochemical reduction of CO₂. All CO₂RR experiments were performed using an MEA electrolyser with an active area of 5 cm² (Supplementary Fig. 19). During a CO₂RR experiment, the aqueous 0.05 M KHCO₃ solution was bubbled through water for humidification. The CO₂RR gas products were analysed in 1 mL volumes using a gas detector (TCD) and a cubic centimetre per minute (sccm), was bubbled through water for humidification. Faradaic efficiency (FE) of CO₂RR gas product was calculated by the following equation:

\[ FE_{\text{gas}} = \frac{x_i \times z_i \times F \times P_o}{RT} \times \frac{1}{I_{\text{outlet}}} \times 100\% \]  

where \( x_i \) is the fraction of gas product \( i \), \( z_i \) is the number of electrons required to produce one molecule of product \( i \), \( F \) is the Faraday Constant, \( P_o \) is atmosphere pressure, \( R \) is the ideal gas constant, \( T \) is the temperature, and \( I_{\text{outlet}} \) is the total current. The FE of CO₂RR liquid product was calculated by the following equation:

\[ FE_{\text{liquid}} = \eta_i \times \frac{z_i F}{Q} \times 100\% \]  

where \( \eta_i \) is the number of moles of liquid product \( i \), and \( Q \) is the cumulative charge as the liquid products were collected.

Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions

D.S. and E.H.S. supervised the project. Y.X. designed and carried out all the experiments. F.L. designed and analysed the sample characterisation. A.X. carried out the DFT simulation. Y.X., F.L. and J.P.E. analysed the experimental data and prepared the manuscript. C.M.G., C.P.O., S.L. and R.K.M. designed and performed the stability test. S. P.H., F.L., X.W. and J.A. performed and analysed the in situ and ex situ XAS measurements. J.W. performed the XPS measurements. Y.Liu. performed XRD measurements and data analysis. Y.Li., J.L., J.E.H. and Y.W. contributed to data analysis and manuscript polishing. All authors discussed the results and assisted during manuscript preparation.

Competing interests

The authors declare no competing interests.

Additional information

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