

Supplementary Information

Repurposing a Bioinspired NiFe Hydrogenase Model for CO₂ Reduction with Selective Production of Methane as the Unique C-based Product

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Experimental Methods:

Materials and Reagents. [LNi^{II}Fe^{II}Cp]⁺ was synthesized according to previously reported procedures.¹ CH₂Cl₂ was used as received (99.99%, HPLC gradient grade, Fisher Sci., used for electrochemical experiments). Edge Plane Graphite (EPG) discs were purchased from Pine Instruments; graphite electrodes were purchased from Aldrich or local vendors. Na₂HPO₄ and KPF₆ were purchased from Sigma Aldrich. The FT-IR data are obtained at room temperature in UATR (Universal Attenuated Total Reflection) set up of Perkin-Elmer FTIR Frontier instrument using Mercury-Cadmium-Telluride (MCT) detector. During the experiments MCT detector was kept at a temperature near 77 K by cooling with liquid N₂.

Preparation of modified graphite electrode: The graphite rod electrode (1.3 cm in diameter and 3 cm in length) purchased from Aldrich (used at Grenoble) and the graphite rod electrode (1.3 cm in diameter and 2.5 or 3.5 cm in length purchased from local vendor (used at IACS) was first sonicated in EtOH for 2 hours and then in deionized water for 1 hour (EtOH and water were replenished after each 30 min during the sonication). Then it was dried in an oven at 120 °C overnight. The cleaned and dried electrode was immersed in 0.5 mM CH₂Cl₂ solution of the catalyst (NiFeCp, Ni^{II}L^{N2S2}, [Fe^{II}(CO)(CH₃CN)₂]⁺BF₄⁻), or [(xbsms)Ni^{II}Fe^{II}Cp(CO)]⁺BF₄⁻) in a glove box under inert atmosphere. After half an hour, it was removed from the solution and dried with an N₂ stream. Finally, the surface was washed thoroughly with ethanol to remove any loosely bound catalyst on the surface, then with distilled water, and dried under N₂ flow before use in electrolysis experiments for CO₂ reduction.

Preparation of modified EPG electrode. The edge plane graphite (EPG) electrodes were freshly polished with SiC (1200 grit CarbiMet) paper after adding a few drops of EtOH, sonicated in EtOH for 2-3 mins, and washed with EtOH followed by deionized water. After such a mechanical cleaning, the EPG electrode was inserted in the ring disc holder, and 30-40 cycles were measured from +0.5 to -0.8 V vs. Ag/AgCl at a scan rate of 50 mV s⁻¹ in

pH 7 aerobic phosphate buffer 0.1M. The EPG was then thoroughly washed with deionized water and dried in the air. A 300 μ L portion of a dilute solution ($[\text{LNi}^{\text{II}}\text{Fe}^{\text{II}}\text{Cp}]^+$ \sim 0.5 mM, in CH_2Cl_2) was uniformly drop casted on a cleaned EPG disc (3.5 mm diameter). After CH_2Cl_2 evaporation, the surface was washed with CHCl_3 thoroughly and then ethanol to remove any loosely bound catalyst on the surface and washed with triple distilled water. These modified electrodes were used for measuring cyclic voltammograms.²

Cyclic voltammetry: Cyclic voltammograms were recorded on a potentiostat (CHI 700E or Metrohm Autolab PGSTAT100N) using the modified graphite electrode in pH 4 aqueous phosphate buffer 0.1 M), sweeping from 0.5 V to -1.8 V vs. Ag/AgCl (satd. KCl), with counter electrode Pt plate or larger surface area spiral Pt wire in 100 mM KPF_6 . The aqueous media was deaerated by bubbling Ar or $^{12/13}\text{CO}_2$ prior to recording the CV as appropriate. All the electrochemical experiments were performed at 20 $^\circ\text{C}$.

Controlled potential electrolysis (CPE) and gas collection: After deaerating the aqueous media with the appropriate gas (Ar, N_2 , or $^{12/13}\text{CO}_2$), the controlled potential electrolysis was performed on a (CHI 700E or Metrohm Autolab PGSTAT100N) potentiostat using the modified graphite electrode at different potentials (-1 to -1.6 V vs. Ag/AgCl (satd. KCl)) in a well-sealed two compartment electrochemical cell for 1-7 hours. The gas evolved during CPE was collected into the burette by vertical displacement of water. The volume of water displaced during the experiment is the amount of gas evolved during the experiment. The gas evolved was analyzed using (i) an Agilent GC instrument fitted with TCD (model no. 7890B, G3440B) at IACS, (ii) a Perkin Elmer Clarus 500 gas chromatograph equipped with a Clarus 560 S mass spectrometer, using helium vector gas, an ESI source, an Agilent GS-Q column, and a single quadrupole detector (in Grenoble for $^{12}\text{CH}_4$ detection), or (iii) a Clarus 500 Gas Chromatograph equipped with a Clarus SQ 8 S mass spectrometer module (electronic impact ionization, Perkin Elmer) and a Carboxen 1006 PLOT capillary column (30m x 0.32mm, fused silica; Supelco) used for the gas analysis at Grenoble (in Grenoble for $^{13}\text{CH}_4$ detection). Due to the overlap between the mass spectra profiles of $^{13}\text{CH}_4$ and H_2O at $m/z = 18, 17, 16$ and the fact it was impossible to avoid water vapor in the gaseous headspace of the CPE experimental cells, the NIST mass spectral database was used to manually subtract out the water contaminant. The raw experimental MS profile and the reproduced m/z ratios reported by NIST for H_2O (<https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Units=SI&Mask=200#Mass-Spec>) were normalized relative to the $m/z = 18$ peak, and subtracted to give the spectrum shown in Figure 3c in the main text. All the electrochemical experiments were performed at 20 $^\circ\text{C}$.

ATR-FTIR Spectroscopy: ATR-FTIR data were obtained at room temperature in UATR (Universal Attenuated Total Reflection) set up of Perkin-Elmer FTIR Frontier instrument using Mercury-Cadmium-Telluride (MCT) detector. During the experiments MCT detector was kept at a temperature near 77 K by cooling with liquid N_2 . During each experiment, the average of 1000 scans was taken.

X-ray Photoelectron Spectroscopy (XPS): The complexes were dissolved in CH₂Cl₂ (0.5 mM) and 300 μL of the solution was drop-casted prior to heterogeneous electrochemical investigations. Additional complex was removed by repeated subsequent washing with chloroform, ethanol, and water. Then bulk electrolysis (BE) experiments were carried out in pH 4 phosphate buffer 0.1 M saturated with CO₂. After BE, the electrode surface was washed with deionized water and dried under Ar atmosphere; XPS data were collected using this surface. XPS (XPS, Omicron, model: 1712-62-11) measurements were performed using a high-resolution monochromatic Mg-Kα radiation source at 1253.6 eV under 15 kV voltage and 5 mA current conditions. The XPS spectra were fitted with PickFit v4.12 software using a combination of Gaussian and Lorentzian distributions. Binding energies are referenced with respect to the adventitious carbon (C 1s BE = 284.6 eV).

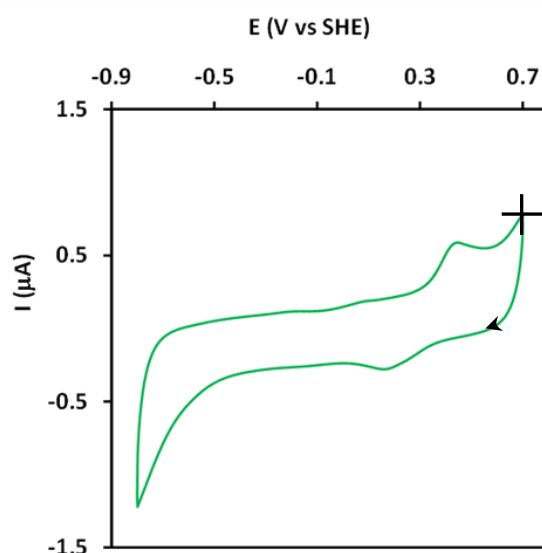


Figure S1. Cyclic voltammogram (CV) of a [LNi^{II}Fe^{II}Cp]⁺-modified EPG electrode (3.5 mm diameter) in aqueous 100 mM KPF₆ electrolyte at 50 mVs⁻¹. Ag/AgCl (satd. KCl) as reference electrode and Pt wire as counter electrode were used.

Surface coverage calculation:

Generally, the coverage of a catalyst on an electrode is estimated by taking the average of the integrated area under the corresponding oxidation/reduction wave of the respective species obtained from its cyclic voltammogram.

The experiments were repeated three times and average value are been reported here.

The value can be obtained from the equation: $\Gamma = Q/nFA$

[where Q = integrated area under the reduction/oxidation current in coulomb, n = number of electron(s) involved in the process (n=1), F = 96500 C and A = microscopic area of the disk (0.096 cm²)]

In this case, the average of the integrated area under the wave at 0.18 V vs. SHE is 5.33×10^{-8} C.

From this value, and using the above-mentioned equation, we calculated the surface coverage to be 3.46×10^{12} molecules/cm².

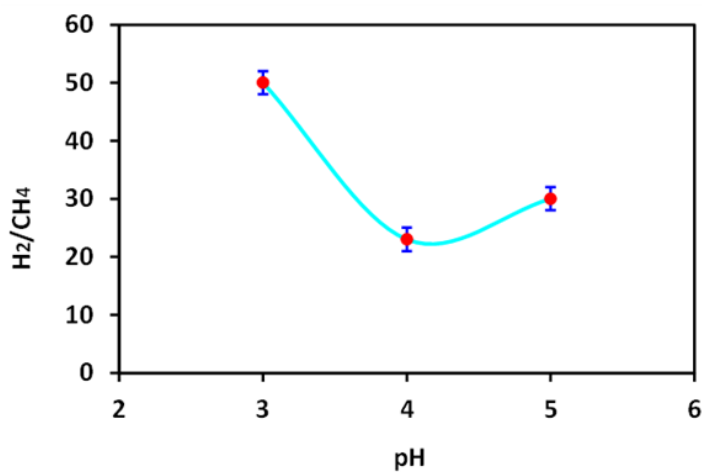


Figure S2. Plot of the changing H₂/CH₄ product ratio as a function of pH.

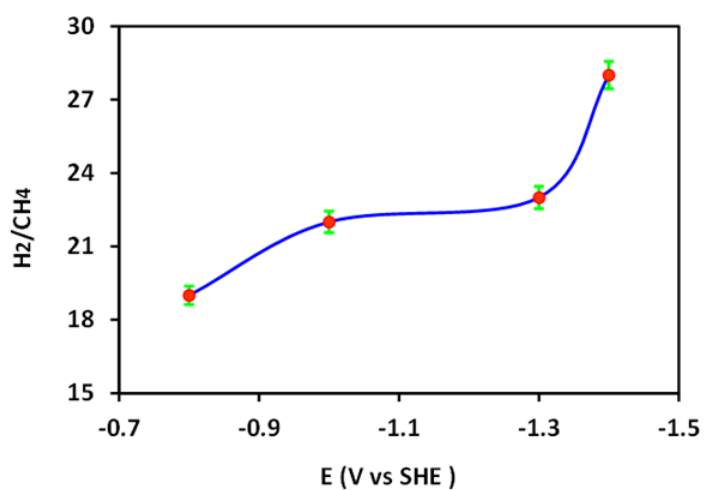


Figure S3. Plot of the changing H₂/CH₄ product as a function of the applied potential in CPE.

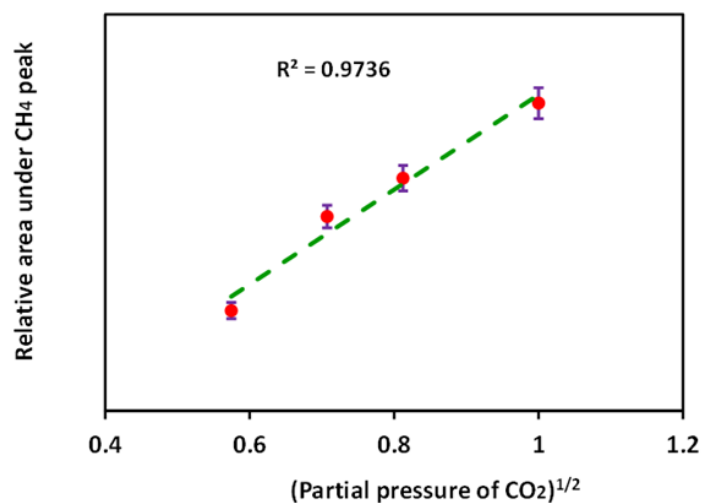


Figure S4. Plot of CH₄ production as a function of the partial pressure of CO₂ in CPE experiments with [LNi^{II}Fe^{II}Cp]⁺ at -1.3 V vs. SHE, in pH 4 phosphate buffer 0.1 M with 100 mM KPF₆ electrolyte.

Table S1.

entry	Catalyst	[CO ₂] mM	Applied potential (vs SHE)	pH	Time (h)	H ₂ /CH ₄ ratio	Faradic yield (H ₂)	Faradic yield (CH ₄)
1	NiFeCp-EPG	1.3	-1.3	4	3	29	60	8.5
2	NiFeCp-EPG	CO	-1.3	4	3	only H ₂	64	N/A
3	NiFeCp-EPG	3.9 +O ₂ ^a	-1.3	4	3	only H ₂	36	N/A

^a the electrocatalysis has been performed in the presence of air, neither the solution or the headspace have been purged with Ar.

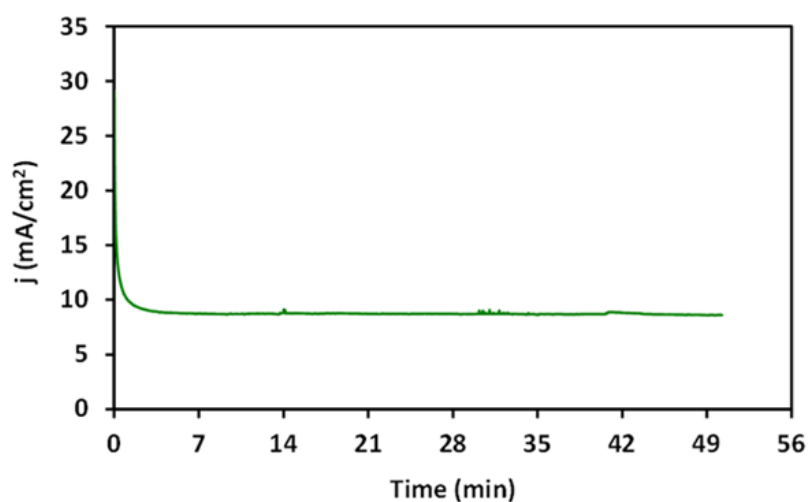


Figure S5. Chronoamperometric measurement performed on a graphite electrode (1.3 cm diameter) drop-casted with $[\text{LNi}^{\text{II}}\text{Fe}^{\text{II}}\text{Cp}]^+$ in CO_2 saturated pH 4 phosphate buffer 0.1 M at -1.3 V vs. SHE.

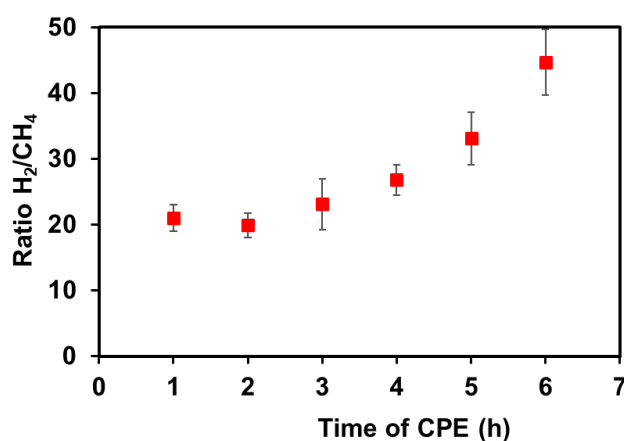


Figure S6. Changes in the H_2/CH_4 ratio produced by the $[\text{LNi}^{\text{II}}\text{Fe}^{\text{II}}\text{Cp}]^+$ -modified graphite electrode over 6 hours of CPE at -1.3 V vs. SHE in saturated pH 4 phosphate buffer 0.1 M. Aliquots of the gaseous headspace above the electrolyte were obtained and quantified by GC. Each time point was measured for at least three separate electrolysis experiments, and the pH of the solution after 6 hours had risen by ~ 0.6 pH units.

The surface coverage of the catalyst has been calculated previously.¹ Charge under the wave at 0.18 V vs. SHE is 5.33×10^{-8} C for an EPG electrode of diameter of 3.5 mm ($S = 0.096$ cm²). This yields a surface coverage of $\sim 6 \times 10^{-12}$ mol.cm⁻².

TON and TOF of CH₄

The CPE was performed at -1.3 V vs. SHE in pH 4 phosphate buffer 0.1 M, and the data showed that 14.5 C/cm² charge is consumed in 27.3 mins and 0.048 mL/cm² of CH₄ is collected.

So, in 27.3 mins, the number of molecules of CH₄ produced = $(0.048/24000) \times 6.023 \times 10^{23} = \sim 1.21 \times 10^{18}$

Therefore $\text{TON}_{\text{CH}_4} = 1.21 \times 10^{18} / 3.46 \times 10^{12} = \sim 3.5 \times 10^5$ after 27.3 mins.

and $\text{TOF}_{\text{CH}_4} = 3.5 \times 10^5 / (27.3 \times 60) \text{ s}^{-1} = \sim 214 \text{ s}^{-1}$.

The CPE was performed at -1.3 V vs. SHE in pH 4 phosphate buffer 0.1 M, and the data showed that 14.5 C/cm² charge is consumed in 27.3 mins and 1.12 mL/cm² of CH₄ is collected.

So, in 27.3 mins, the number of molecules of H₂ produced = $(1.12/24000) \times 6.023 \times 10^{23} = \sim 2.81 \times 10^{19}$.

Therefore $\text{TON}_{\text{H}_2} = 2.81 \times 10^{19} / 3.46 \times 10^{12} = \sim 8.2 \times 10^6$ after 27.3 mins.

and $\text{TOF}_{\text{H}_2} = 8.2 \times 10^6 / (27.3 \times 60) \text{ s}^{-1} = \sim 5.1 \times 10^3 \text{ s}^{-1}$.

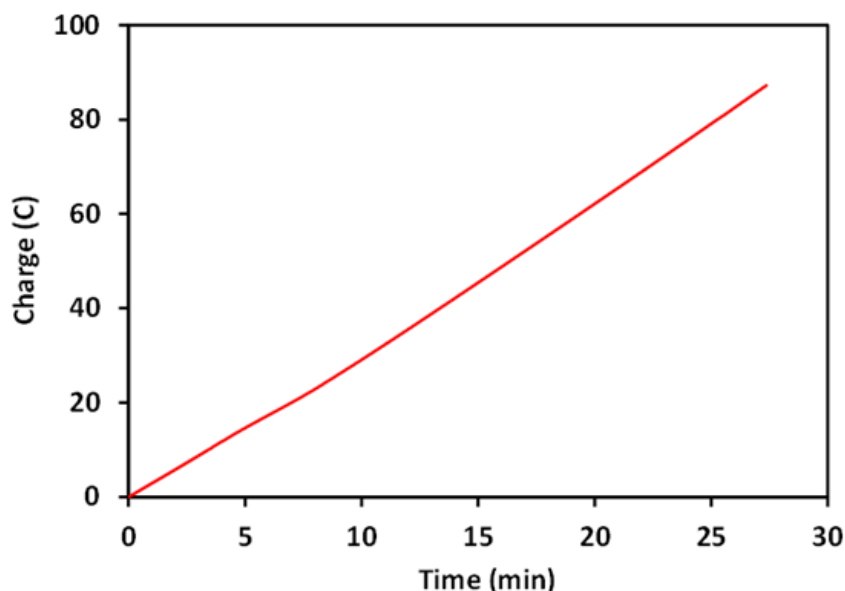


Figure S7. Control potential electrolysis measurement performed on a graphite electrode (1.3 cm diameter & 3.5 cm length) drop-casted with [LNi^{II}Fe^{II}Cp]⁺ in CO₂ saturated pH 4 phosphate buffer 0.1 M at -1.3 V vs. SHE.

Faradaic Yield FY Calculation:

Generally, FY is determined by the equation:

$$\text{FY} = 2 \times \text{amount of H}_2 \text{ produced (mol)} / (\text{Amount of charge consumed during CPE} / F) = 2F \times \text{amount of H}_2 \text{ produced (mol)} / \text{Charge consumed during CPE}.$$

During the CPE, the total charge consumed was 87 C in 27.3 mins, and 0.29 mL CH₄ gas was collected in an inverted burette set up connected to an electrolyzer cell through a channel (Figure S7).

Hence, no. of moles of CH₄ produced = 0.29/24000 mol

Therefore, the FY of CH₄ = 11.2%.

During the CPE, the total charge consumed was 87 C in 27.3 mins, and 6.71 mL H₂ gas was collected in an inverted burette set up connected to an electrolyzer cell through a channel (Figure S7).

Hence, no. of moles of H₂ produced = 6.71/24000 mol

Therefore, the FY of H₂ = 62%.

The other FY values reported herein have been calculated in a similar fashion (Table 1 and Table S1).

References:

(1) Brazzolotto, D.; Gennari, M.; Queyriaux, N.; Simmons, T. R.; Pécaut, J.; Demeshko, S.; Meyer, F.; Orio, M.; Artero, V.; Duboc, C. Nickel-centred proton reduction catalysis in a model of [NiFe] hydrogenase. *Nat. Chem.* **2016**, *8*, 1054–1060.

(2) Ahmed, M. E.; Chattopadhyay, S.; Wang, L. K.; Brazzolotto, D.; Pramanik, D.; Aldakov, D.; Fize, J.; Morozan, A.; Gennari, M.; Duboc, C.; Dey, A.; Artero, V. Hydrogen Evolution from Aqueous Solutions Mediated by a Heterogenized NiFe -Hydrogenase Model: Low pH Enables Catalysis through an Enzyme-Relevant Mechanism. *Angew. Chem. Int. Ed.* **2018**, *57*, 16001-16004.

(3) Canaguier, S.; Field, M.; Oudart, Y.; Pécaut, J.; Fontecave, M.; Artero, V., A structural and functional mimic of the active site of NiFe hydrogenases. *Chem. Commun.* **2010**, *46*, 5876-5878.