Supporting information

Non-covalent integration of a bio-inspired Ni catalyst to graphene acid for reversible electrocatalytic hydrogen oxidation

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Experimental section

Materials and reagents

Dry (distilled) EtOH was used for the ligand synthesis. Dry solvents (MeOH, Et₂O and MeCN), for molecular synthesis, potassium phosphate salts, nickel nanopowder (<100 nm average particle size, ≥99% trace metals basis), hexachloroplatinic acid hexahydrate, sulfuric acid (ACS reagent, 95-98%), dimethylformamide (DMF) were purchased from Sigma-Aldrich. The supporting gas diffusion layer PTFE treated were obtained from Sigracet (GDL 39BC). The synthesis and characterisation of the P₂CyN₂Arg ligand and NiArg was carried out as previously reported.¹

Graphene acid synthesis

The graphenic acid (GA) was synthesised according to the method developed by Otyepka’s group.² Very briefly, fluorinated graphite was suspended in DMF and extendedly sonicated under nitrogen atmosphere. Then the resulting suspension was reacted at 130°C with sodium cyanide, in order to promote the nucleophilic substitution of fluorine atoms with cyano groups. In a second step, the so formed cyanographene was hydrolysed in 20% HNO₃ under reflux at 100°C, to convert the –CN groups into –CO₂H groups. The resulting material was thoroughly characterised by SEM, TEM and XPS.

GDL|GA|NiArg electrode preparation

GA stock dispersion of 1 mg mL⁻¹ were prepared by sonicating 10 mg of GA in 10 mL of DMF. This dispersion were then dilute to 0.05 mg mL⁻¹ of GA in EtOH. Appropriate volumes of dispersion (10; 20; 40; 80 and 160 mL) were then filtered through vacuum filtration directly on top of a gas diffusion layer modified with a microporous layer (from Sigracet, 39BC, filtration area = 10 cm²) sitting on a PTFE membrane filter (Millipore, 0.45 μm pore size, ø = 4.7 cm, reference JHWP). This lead to the GDL|GA films with 0.05; 0.1; 0.2; 0.4 and 0.8 mg cm⁻² of GA. Electrodes were then prepared by first hole-punching a 0.125 cm² disc of GDL|GA, followed by soaking the disc in DMF for 1 minute before a thorough rinsing step in deionized water. Then, 2 μL of NiArg at given concentration in milliQ water (1.25; 2.5; 5 or 10 mM) were drop cast at the GDL|GA film surface and allowed to dry for 10 minutes. The modified electrode was then rinsed with deionized water before being tested in three-electrode configuration.

GDL|GA|Pt and GDL|GA|Ni

A Pt modified GA electrode was prepared by first drop cast of 5μL of a 2 mM solution of H₂PtCl₆ in H₂O. Once the film was dried, a chronoamperometry at -0.2V vs RHE was carried out for 1 min in 0.5M H₂SO₄. After rinsing of the electrode with deionized water, the GDL|GA|Pt was characterized in fresh H₂SO₄ 0.5M electrolyte.

Ni NP modified electrodes were prepared by deposition of 10μL dispersion of Ni NP in ethanol, which was let to dry.
Electrochemistry

Electrochemistry measurements were carried out using a Biologic SP-300 potentiostat in a three-electrode configuration using a homemade “breathing” working electrode (geometrical area = 0.05 cm²) and a platinum wire as counter electrode. An Ag/AgCl (sat. KCl, homemade) reference electrode was used in neutral pH conditions (0.2 M phosphate buffer) and a Hg/Hg₂SO₄ (0.5 M H₂SO₄, from ALS) reference electrode was used in acidic conditions (0.5 M H₂SO₄). All experiments were carried out in electrolyte degassed with argon and with a constant flow of argon or H₂ at the back of the breathing GDL working electrode, for electrochemical and electrocatalytic characterization, respectively. All cyclic voltammetry and controlled potential electrolysis were carried out in triplicates.

XPS measurements

XPS measurements were taken at RT in a custom designed UHV system equipped with an Omicron electron analyser, working at a base pressure of 10⁻¹⁰ mbar. Core-level photoemission spectra were acquired in normal emission using a dual non-monochromatized Mg Kα X-ray source (1253.6 eV). Single spectral regions were collected using 0.1 eV steps, 0.5 s collection time and 20 or 50 eV pass energy.

C 1s region was separated into chemically shifted components in order to determine the nature and amount of the oxygenated species. An asymmetrical shape was used for the sp² component, whereas symmetrical Voigt functions were used for the sp³ component and the C-O functional groups. The π-π* transition at binding energy (BE) of 290.4 eV was also included in the fit.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

The GDL|GA|NiArg films were digested by sonicating the films in 65% nitric acid for 1h and letting the resulting “disperstion” to sit overnight. The obtained solution were then sonicated for another 15 min prior to dilution of 400 µL of the digestion solution 5.6 mL of 10% nitric acid. Detection of Ni was carried out using a Shimadzu ICPE-9000 following an eight-point calibration. Each measurement was carried out in triplicate.

Treatment of Data

ICP-AES measurements on GDL|GA and GDL|GA|NiArg as well as electrocatalytic measurements (cyclic voltammetry and chronoamperometry) were carried out in triplicates. Average value and standard deviation were calculated as follow:

\[ x_0 = \frac{1}{n} \sum_{i=1}^{n} x_i \quad \sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - x_0)^2} \]

With n the number of experiments, \( x_0 \) the unweighted mean value and \( x_i \) the value of the a sample.
Supporting table and figures

| Sample        | C sp² | C sp³ | C-OH/ C-N | Epoxide | C=O | O-C=O |
|---------------|-------|-------|-----------|---------|-----|-------|
| GA            | 284.5 eV 1.2 | 285.6 eV 1.2 | 286.5 eV 1.2 | 287 eV 1.2 | 288 eV 1.2 | 288.8 eV 1.0 |
|               | 62.2 % 14.9 % | 7.5 % 4.4 % | 1.1 % 9.9 % |         |     |       |
| GA/NiArg      | 284.5 eV 1.2 | 285.4 eV 1.3 | 286.5 eV 1.3 | /       | 287.8 eV 1.3 | 289.0 eV 1.3 |
|               | 20.2 % 32.5 % | 25.2 % 14.3 % |         | 14.3 % |     |       |

Table S1: XPS data (binding energy, eV, FWHM of the component, eV and atomic %) of the C 1s region of the GA and GA|NiArg powders

| Sample       | C (at.%) | Ni (at.%) | N (at.%) | O (at.%) | F (at.%) | P (at.%) | B (at.%) |
|--------------|----------|-----------|----------|----------|----------|----------|----------|
| GA/NiArg     | 53.5     | 0.7       | 4.9      | 7.1      | 31.3     | 1.3      | 0.7      |

Table S2: Surface composition of the GDL|GA|NiArg electrode 0.4 mg cm⁻² of GA and modified with 5 mM of NiArg

Figure S1: a) and b) SEM micrographs of the GDL|GA (0.4 mg cm⁻²) porous network at different magnifications c) TEM micrograph of a GA sheet

Figure S2: EDX mapping of a GDL|GA (0.4 mg cm⁻²) film modified with NiArg highlighting: a) the oxygen b) the fluorine and c) the nickel content after modification with 5 mM of NiArg.
Figure S3: a) picture of the homemade breathing electrode b) scheme of the 3-electrode setup used in the study

Figure S4: CV traces of a) GDL|GA electrodes (0.4 mg cm\(^{-2}\)) unmodified (black dash trace), modified with 5 \(\mu\)L of Ni NP solution in EtOH (red trace) or with 2 \(\mu\)L of NiArg (5 mM in H\(_2\)O) (blue trace) and b) GDL|GA electrodes (0.4 mg cm\(^{-2}\)) modified (black dash trace), modified with electrodeposited Pt NP (red trace) or with 2 \(\mu\)L of NiArg (5 mM in H\(_2\)O) (blue trace) in 0.5 M H\(_2\)SO\(_4\) with a constant flow of H\(_2\) at the back of the GDL (5 mL min\(^{-1}\)) (\(\nu = 20\) mV s\(^{-1}\))
Figure S5: CV traces of a) GDL|GA (0.05 mg cm$^{-2}$) b) GDL|GA (0.1 mg cm$^{-2}$) c) GDL|GA (0.2 mg cm$^{-2}$) and d) GDL|GA (0.4 mg cm$^{-2}$) electrodes with different catalyst loadings (2 µL of 1.25; 2.5; 5 and 10 mM of NiArg) in 0.2 M potassium phosphate under argon ($\nu = 20$ mV s$^{-1}$)
Figure S6: current densities for HER at -0.2 V vs RHE and for HOR at 0.1 and 0.4 V vs RHE for the different GDL|GA electrodes with a) 0.05 mg cm\(^{-2}\) GA b) 0.1 mg cm\(^{-2}\) GA c) 0.2 mg cm\(^{-2}\) GA and d) 0.4 mg cm\(^{-2}\) GA modified with different NiArg concentration solutions (1.25; 2.5; 5 and 10 mM) obtained from CVs in 0.5 M H\(_2\)SO\(_4\) under argon and with a constant flow of H\(_2\) at the back of the GDL (5 mL min\(^{-1}\)) \(\nu = 20 \text{ mV s}^{-1}\).

Figure S7: CPE triplicates of the GDL|GA|NiArg modified electrodes at 0.3V (red, black and blue traces) and 0.1V (green, purple and gold trace) in 0.5 M H\(_2\)SO\(_4\) under argon and with a constant flow of H\(_2\) at the back of the GDL (5 mL min\(^{-1}\)).
Figure S8: P 2p XPS region of GA|NiArg modified electrode before and after 1 of electrolysis at 0.1 or 0.3V vs RHE in 0.5 M H₂SO₄ with a constant flow of H₂ at the back of the GDL (5 mL min⁻¹)

Supporting references
1. A. Dutta, J. A. S. Roberts and W. J. Shaw, Angew. Chem. Int. Ed., 2014, 53, 6487–6491.
2. A. Bakandritsos, M. Pykal, P. Błoński, P. Jakubec, D. D. Chronopoulos, K. Poláková, V. Georgakilas, K. Čépe, O. Tomanec, V. Ranc, A. B. Bourlinos, R. Zbořil and M. Otyepka, ACS Nano, 2017, 11, 2982–2991.