Supporting information

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

Bertrand Reuillard,[a] Matias Blanco,[b] Laura Calvillo,[b] Nathan Coutard,[a] Ahmed Ghedjatti,[a] Pascale Chenevier,[c] Stefano Agnoli,[b] Michal Otyepka,[d] Gaetano Granozzi[c] and Vincent Artero[a]*

a. Univ. Grenoble Alpes, CEA, CNRS, IRIG, Laboratoire de Chimie et Biologie des Métaux, F-38000 Grenoble.

b. Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova.

c. Univ. Grenoble Alpes, CEA, CNRS, IRIG, SYMMES, F-38000 Grenoble.

d. Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Palacký University Olomouc, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic

*Corresponding author: vincent.artero@cea.fr

Table of content

Experimental section

Materials and reagents

Dry (distilled) EtOH was used for the ligand synthesis. Dry solvents (MeOH, Et_2O 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 $P_2{}^{Cy}N_2{}^{Arg}$ 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% HNO_3 under reflux at 100°C, to convert the –CN groups into –CO_2H 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 cm^2) 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 cm^2 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 H_2PtCl_6 in H_2O. Once the film was dried, a chronoamperometry at -0.2V vs RHE was carried out for 1 min in 0.5M H_2SO_4. After rinsing of the electrode with deionized water, the GDL|GA|Pt was characterized in fresh H_2SO_4 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 cm^2) 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/Hg$_2$SO$_4$ (0.5 M H$_2$SO$_4$, from ALS) reference electrode was used in acidic conditions (0.5 M H$_2$SO$_4$). All experiments were carried out in electrolyte degassed with argon and with a constant flow of argon or H$_2$ 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 sp^2 component, whereas symmetrical Voigt functions were used for the sp^3 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:

$$x_0 = \sum_i \frac{x_i}{n} \quad \sigma = \sqrt{\sum_i \frac{(x_i - x_0)^2}{(n-1)}}$$

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 sp^2	C sp^3	C-OH/ C-N	Epoxide	C=O	O-C=O
GA	284.5 eV 1.2 62.2 %	285.6 eV 1.2 14.9 %	286.5 eV 1.2 7.5 %	287 eV 1.2 4.4%	288.0 eV 1.2 1.1 %	288.8 eV 1.0 9.9 %
GA/NiArg	284.5 eV 1.2 20.2 %	285.4 eV 1.3 32.5 %	286.5 eV 1.3 25.2 %	/	287.8 eV 1.3 14.3 %	289.0 eV 1.3 7.8 %

*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
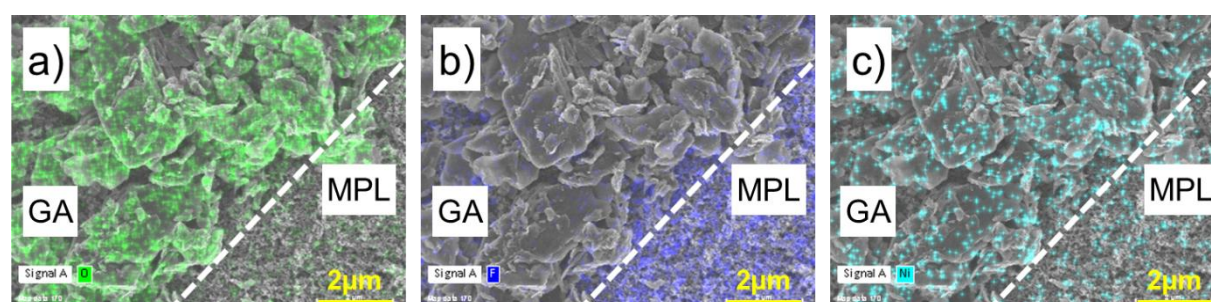

*Figure S2: EDX mapping of a GDL|GA (0.4 mg cm^{-2}) film modified with **NiArg** highlighting: a) the oxygen b) the fluorine and c) the nickel content after modification with 5 mM of **NiArg**.*
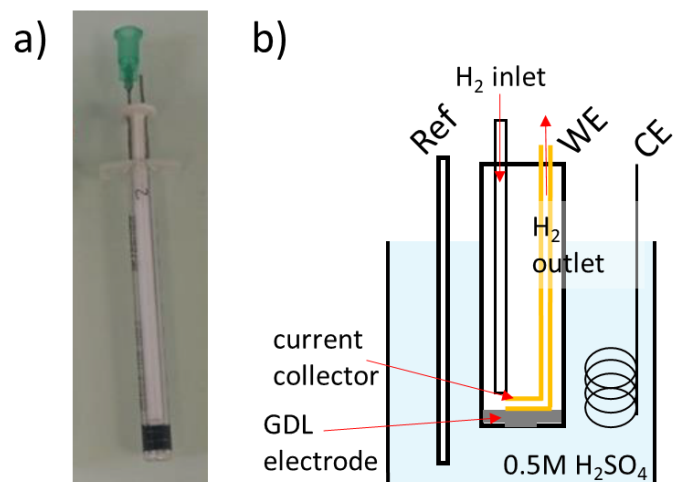
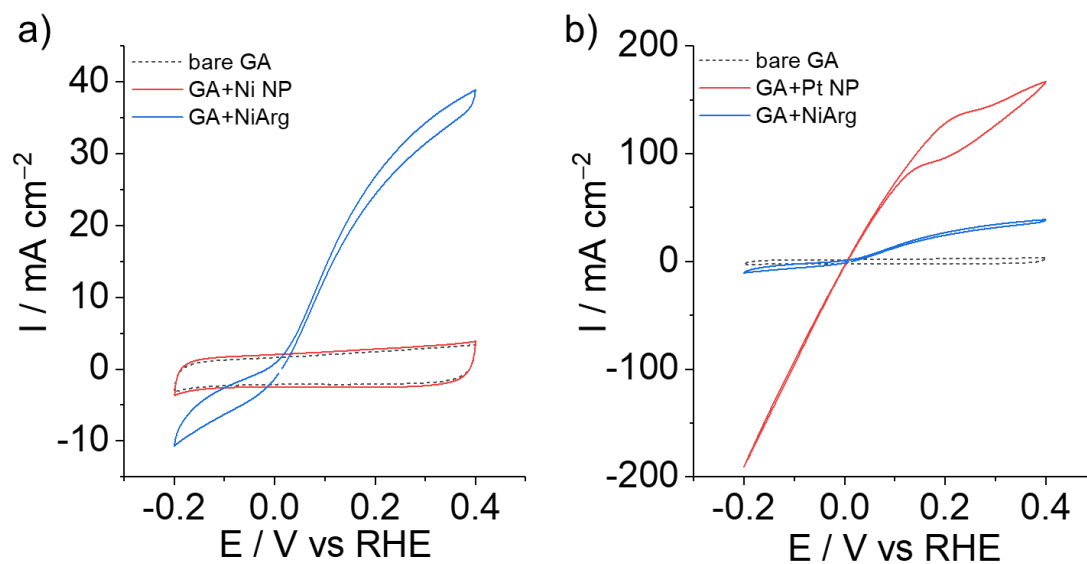*Figure S3: a) picture of the homemade breathing electrode b) scheme of the 3-electrode setup used in the study*

*Figure S4: CV traces of a) GDL|GA electrodes (0.4 mg cm^{-2}) unmodified (black dash trace), modified with 5 μL of Ni NP solution in EtOH (red trace) or with 2 μL 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 μL 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}) (v = 20 mV s^{-1})*
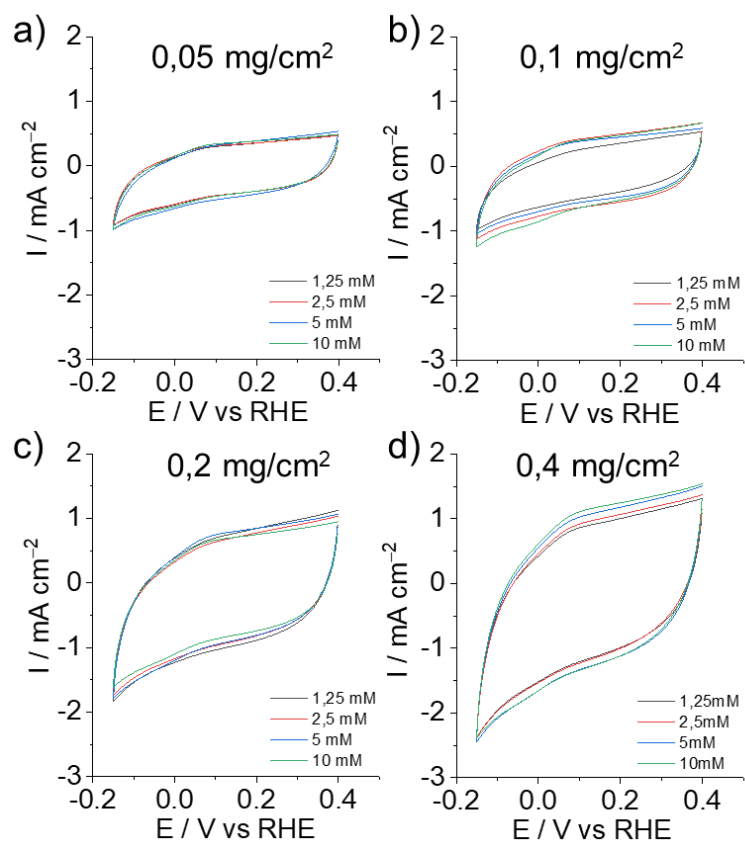
*Figure S5: CV traces of a) GDL|GA (0.05 mg cm^{-2}) b) GDL|GA (0.1 mg cm^{-2}) c) GDL|GA (0.2 mg cm^{-2}) and d) GDL|GA (0.4 mg cm^{-2}) electrodes with different catalyst loadings (2 µL of 1.25; 2.5; 5 and 10 mM of **NiArg**) in 0.2 M potassium phosphate under argon (v = 20 mV s^{-1})*
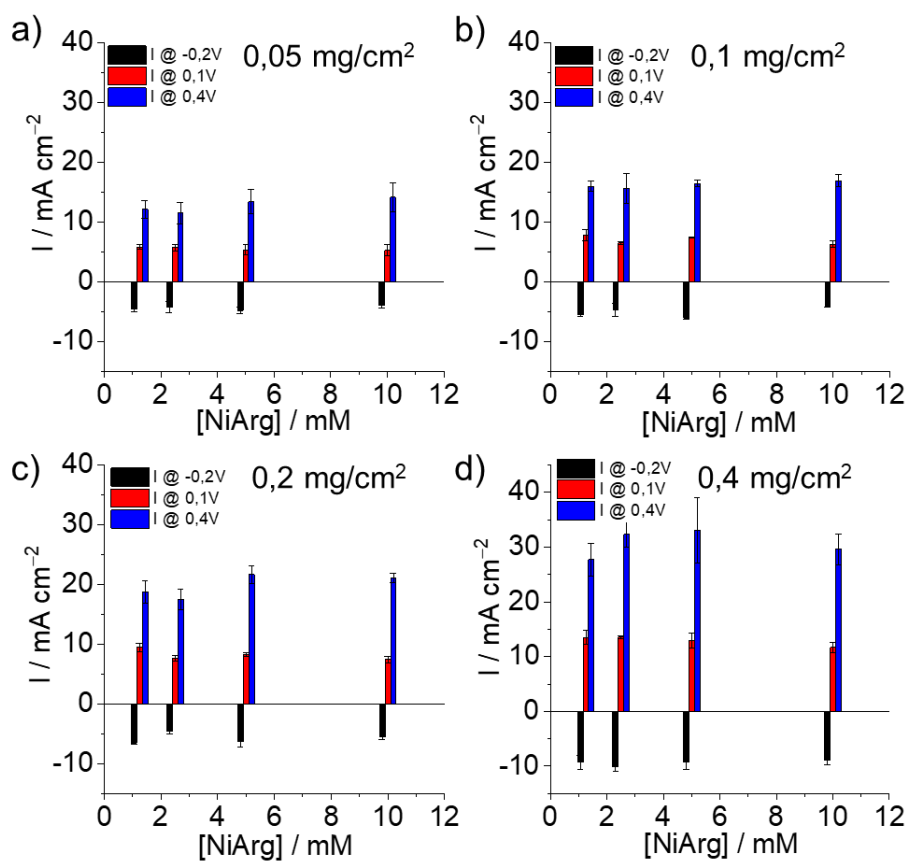
*Figure S6: current densities for HER at -0.2 V vs RHE and for HOR at 0.1 and 0.4 V vs RHE for the different GDL|GA electrodes with a) 0.05 mg cm^{-2} GA b) 0.1 mg cm^{-2} GA c) 0.2 mg cm^{-2} GA and d) 0.4 mg cm^{-2} GA modified with different **NiArg** concentration solutions (1.25; 2.5; 5 and 10 mM) 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}) (v = 20 mV s^{-1})*
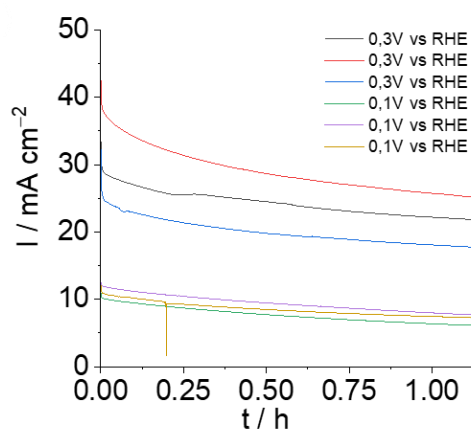

*Figure S7: CPE triplicates of the GDL|GA|**NiArg** modified electrodes at 0.3V (red, black and blue traces) and 0.1V (green, purple and gold trace) in 0.5 M H$_2$SO$_4$ under argon and with a constant flow of H$_2$ at the back of the GDL (5 mL min^{-1})*
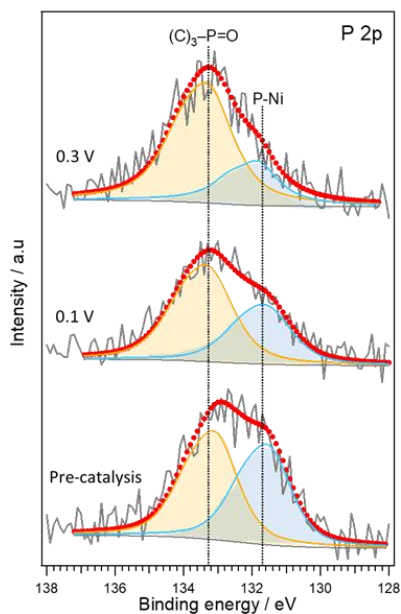
Figure S8: P 2p XPS region of GA|NiArg modified electrode before and after 1 of electrolysis at 0.1 or 0.3V vs RHE in 0.5 M H$_2$SO$_4$ with a constant flow of H$_2$ at the back of the GDL (5 mL min^{-1})

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.

End of Electronic Supporting Information