Supplementary Information

Rhodium-based cathodes with ultra-low metal loading to increase the sustainability in the hydrogen evolution reaction

Gema Pérez¹, Guillermo Díaz-Sainz¹, Lucía Gómez-Coma¹, Lucía Álvarez-Miguel², Aymeric Garnier², Nolwenn Cabon³, Alfredo Ortiz¹, Frederic Gloaguen², Inmaculada Ortiz^{1*}

¹Department of Chemical and Biomolecular Engineering, University of Cantabria. Av. Los Castros 46, 39005 Santander, Spain.

²UMR 6521, CNRS, Université de Bretagne Occidentale, CS 93837, 29238, Brest, France

³UMR 6226, CNRS, Université de Rennes 1, Campus Beaulieu, 35042 Rennes, France

*Corresponding author: ortizi@unican.es

Synthesis of 5,6-diamino-1,10-phenanthroline

All the syntheses were carried out using standard Schlenk techniques from commercial analytical-grade chemicals used without further purification. Solvents were purified and dried by passing through a MBraun MPSP-800 column and collected under nitrogen gas. Deionized water was dispensed from a Millipore Milli-Q purification system.

1,10-Phenanthroline-5,6-dioxime (phendioxime) and 5,6-diamino-1,10-phenanthroline (phendiamine) were synthesized under inert atmosphere following a literature procedure [2] (Figure S1). Briefly, phendione (0.42 g, 2 mmol), hydroxylamine hydrochloride (0.49 g, 7 mmol) and barium carbonate (0.59 g, 3 mmol) were refluxed in ethanol (30 mL) overnight. After removal of the solvent under reduced pressure, the residue was treated with HCI (0.2 M, 40 mL). The mixture was stirred for 30 minutes and filtered. A light-yellow solid was collected, washed successively with water, ethanol and ether, and dried under vacuum at 80°C to give phendioxime (ca. 0.46 g, 95% yield). Phendioxime (0.40 g, 1.6 mmol) and Pd/C powder (0.40 g, 10% in weight of Pd) were dispersed in N₂-purged dry ethanol and heated to reflux. A solution of hydrazine hydrate (3.5 mL) in ethanol (15 mL) was added dropwise over a period of 1 hour.



Figure S1. Synthesis of 5,6-diamino-1,10-phenanthroline.

The resulting mixture was subsequently refluxed overnight. The hot mixture was then then filtered on Celite. The solid filtrate was washed 3 times with hot ethanol (20 mL), dried under vacuum, triturated to water (30 mL) and left overnight at 4 °C. A yellow solid was collected by filtration, washed with cold water and dried to give phendiamine (ca. 0.28 g, 83% yield).

Synthesis of [RhCp*Cl(phendiamine)]Cl

[RhCp*Cl₂]₂ (0.62 g, 0.1 mmol) and 5,6-diamino-1,10-phenanthroline (phendiamine, 0.42 g, 0.2 mmol) were dissolved in methanol (15 mL) under inert atmosphere (Figure S2) [3]. After stirring for 1 hour, the orange-red solution was concentrated under reduced pressure. The addition of ether gave a microcrystalline solid identified as [RhCp*Cl(phendiamine)]Cl (0.87 g, 85% yield).



Figure S2. Synthesis of [RhCp*Cl(phendiamine)]Cl.

Synthesis of Rh-complex/Vulcan XC-T2

The grafting of the Rh complex on carbon black (Vulcan XC-72) was achieved by means of a pyrazine link [1], i.e. the condensation of two adjacent carboxyl groups on the carbon surface with the two amine groups of the phenanthroline ligand of the Rh complex. As a result, to increase the amount of grafted Rh complex, the amount of "oxidized groups" on the carbon surface must be significantly increased by reaction with an oxidant [4]. Here, Vulcan XC-72 (0.8 g) was dispersed in a solution of HNO₃ (40 mL, 30% in weight). The mixture was refluxed for 4 hours and then filtered using a Büchner funnel equipped with a PTFE filter (TF200). The collected grey solid was successively washed with water, ethanol and ether and dried under vacuum.

¹H NMR analysis

1H NMR (400 MHz, DMSO-d6) δ 9.03 (d, J = 4.9, 2H, H2,9), 8.86 (d, J = 8.6, 2H, H4,7), 8.00 (d, J = 8.8, 2H, H3,8), 5.83 (s, 4H, NH2), 1.69 (s, 15H, CH3Cp*).



Figure S3. ¹H RMN spectra (400 MHz) of [RhCp*Cl(phendiamine)]Cl in DMSO-d6.

Grafting of [RhCp*Cl(phendiamine)]Cl on oxidized Vulcan XC-72

Activated Vulcan XC-72 (0.415 g) dispersed in DMF (100 mL) was added under inert atmosphere to a solution of [RhCp*Cl(phendiamine)]Cl (0.041 g) in DMF (40 mL) (Figure S4). The mixture was stirred and heated at 110°C overnight. The solid fraction in the mixture was collected using a Büchner funnel and thoroughly washed with ethanol until it became colorless, indicating that physisorbed Rh complexes were completely removed. The powder was then stirred in HCl (0.1 M, 20 mL) for 4 hours to cleave bonds to monoamine linked complex. The Rh/Vulcan XC-72 electrocatalyst (95% yield) was finally collected by filtration, washed with water and ethanol and dried under vacuum.



Figure S4. Condensation of the two-amine groups of the phenanthroline ligand of the Rh complex with two adjacent carboxyl groups on the carbon surface.

ICP-MS analysis

Digestions of the Rh/Vulcan samples (10 mg) were performed at 105°C for 4 h in a closed Teflon screw-cap vials (30 mL, Savillex) with 1 mL nitric acid (65% wt., Merck suprapur) and 0.25 mL hydrogen peroxide (30% wt. Merck suprapur). The measurement of Rh concentrations (103Rh isotope) was then conducted on diluted mixtures (2.6% HNO3) using an ICP-quadrupole mass spectrometer (X-series II, Thermo Scientific) with a H2 collision cell. Three Rh standard solutions were used (i.e. 11.74, 2.384 and 0.4443 mg·L⁻¹). These solutions, also in 2.6% HNO3, were prepared from a 1000 mg·L⁻¹ stock solution (Sigma Aldrich). For each step (powder weighing, addition of nitric acid and hydrogen peroxide, sample dilution and standard preparations) a Kern ABT-120 balance with a precision of 0.01 mg was used to accurately calculate the Rh concentrations in the standards and samples.

XPS spectra

	RI	1	Rh/C Sample 2			
Cycle	Name	Position	% Atom rel.	Name	Position	% Atom rel.
С	C-C, C-H	284.6		С-С, С-Н	284.6	
	C 1s	285.5	92.1	C 1s	285.6	
	C 1s	286.7		C 1s	286.6	02.2
	C 1s	288.4		C 1s	288.3	92.2
	C 1s	290.8		C 1s	290.9	
	C 1s	293.7		C 1s	294.0	
0	O 1s	531.6	5.7	O 1s	531.6	
	O 1s	533.4		O 1s	533.4	5.5
	O 1s	536.1		O 1s	536.4	
N	N 1s	400.2	1.2	N 1s	400.2	1.3
Rh*	Rh (3d 5/2)	310.3	0.4	Rh (3d 5/2)	310.3	0.4
	Rh (3d 3/2)	314.8	0.4	Rh (3d 3/2)	314.8	0.4
Cl	Cl (2p 3/2)	198.3	0.4	Cl (2p 3/2)	198.2	0.4
	Cl (2p 1/2)	200.0	0.4	Cl (2p 1/2)	200.0	0.4
S	S (2p 3/2)	164.0	0.2	S (2p 3/2)	164.0	
	S (2p 1/2)	165.3		S (2p 1/2)	165.2	0.2
	S 2p	168.2		S 2p	168.2	

Table S1. Detailed data about the results achieved in the XPS spectra of different Rh/C samples.





Figure S5. Representative EDX spectra of a Rh/C sample. Note that the weight ratio Rh/C is not that in the actual sample because the Rh/C powder was dispersed on an adhesive carbon tape for SEM-EDX measurements.

SEM images



Figure S6. SEM image (A) along with the composition distribution in N (B), Cl(C) and Rh (D). The scope magnification is 350 times. The width and the height of the image are 352.5 and 264.4 μ m, respectively, corresponding to a ratio μ m/pixel of 0.7.'

Tafel plot analysis



Figure S7. Tafel plot calculated from the amperometric curves shown in Figure 4 of the manuscript.

Table S2. Hydrogen flow rate, geometric current density and cell voltage values obtained from the polarization curves of each cathode tested in the PEM electrolyzer at $50 \,^{\circ}$ C.

	Geometric current density (A·cm ⁻²)	Cell voltage (V)					
Hydrogen flow rate (mL·min ⁻¹)		Rh/C- GDE 0.0066 mg Rh·cm ⁻²	Rh/C- GDE 0.0044 mg Rh·cm ⁻²	Pt/C- GDE 0.4 mg Pt·cm ⁻²	CPt/C- GDE 0.3 mg Pt·cm ⁻²	MEA 0.3 mg Pt·cm ⁻²	
10	0.04	1.62	1.71	1.54	1.52	1.50	
12	0.08	1.71	1.81	1.58	1.58	1.54	
16	0.12	1.76	1.89	1.62	1.63	1.58	
23	0.16	1.78	1.94	1.66	1.67	1.62	
29	0.2	1.82	2.00	1.69	1.71	1.66	
36	0.24	1.85	2.04	1.71	1.76	1.69	
40	0.28	1.87	2.09	1.74	1.80	1.72	
49	0.32	1.90	2.13	1.77	1.83	1.75	
55	0.36	1.93	2.16	1.79	1.87	1.78	
66	0.40	1.95	2.21	1.82	1.91	1.81	
72	0.44	1.96	2.24	1.85	1.95	1.84	
78	0.48	1.98	2.28	1.87	1.98	1.87	

Table S3. Hydrogen flow rate, geometric current density and cell voltage values obtained from the polarization curves of each cathode tested in the PEM electrolyzer at $70 \,^{\circ}$ C.

	Geometric current density (A·cm ⁻²)	Cell voltage (V)				
Hydrogen flow rate (mL∙min ⁻¹)		Rh/C- GDE 0.0066 mg Rh•cm ⁻²	Pt/C- GDE 0.4 mg Pt∙cm ⁻²	CPt/C- GDE 0.3 mg Pt·cm ⁻²	MEA 0.3 mg Pt·cm ⁻²	
10	0.04	1.58	1.44	1.50	1.46	
12	0.08	1.65	1.47	1.54	1.50	
16	0.12	1.70	1.50	1.58	1.54	
23	0.16	1.73	1.53	1.61	1.57	
29	0.2	1.76	1.56	1.63	1.59	
36	0.24	1.78	1.58	1.66	1.62	
40	0.28	1.80	1.61	1.68	1.65	
49	0.32	1.82	1.64	1.70	1.67	
55	0.36	1.84	1.67	1.73	1.70	
66	0.40	1.86	1.69	1.75	1.73	

72	0.44	1.88	1.72	1.77	1.75
78	0.48	1.91	1.75	1.79	1.78

Supplementary Information References

- S. Bodige, F.M. MacDonnell, Synthesis of free and ruthenium coordinated 5,6diamino-1,10- phenanthroline, Tetrahedron Lett. 38 (1997) 8159–8160. https://doi.org/10.1016/S0040-4039(97)10223-4.
- U. Kölle, M. Grützel, Organometallic Rhodium(III) Complexes as Catalysts for the Photoreduction of Protons to Hydrogen on Colloidal TiO2, Angew. Chemie Int. Ed. English. 26 (1987) 567–570. https://doi.org/10.1002/anie.198705671.
- M.N. Jackson, C.J. Kaminsky, S. Oh, J.F. Melville, Y. Surendranath, Graphite Conjugation Eliminates Redox Intermediates in Molecular Electrocatalysis, J. Am. Chem. Soc. 141 (2019) 14160–14167. https://doi.org/10.1021/jacs.9b04981.
- [4] N. Zhang, L.Y. Wang, H. Liu, Q.K. Cai, Nitric acid oxidation on carbon dispersion and suspension stability, Surf. Interface Anal. 40 (2008) 1190–1194. https://doi.org/10.1002/sia.2864.