Supporting Information

A Highly Efficient and Stable Oxygen Reduction Reaction on Pt/CeO_x/C Electrocatalyst Obtained via a Sacrificial Precursor Based on a Metal-Organic Framework.

Yun Luo,^[a] Laura Calvillo,^[b] Carole Daiguebonne,^[c] Maria K. Daletou,^[d] Gaetano Granozzi^[b] and Nicolas Alonso-Vante^[a]*

^[a] IC2MP, UMR-CNRS 7285, University of Poitiers, 4 rue Michel Brunet, 86022 Poitiers, France.

^[b] Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy.

^[c] INSA, UMR-CNRS 6226, INSA de Rennes, 20 Avenue des Buttes de Coësmes, 35708 Rennes, France.

^[d] Foundation of Research and Technology, Hellas-Institute of Chemical Engineering Science, Stadiou Str, Platani Rion, Patras GR-26504, Greece.

*E-mail: nicolas.alonso.vante@univ-poitiers.fr

Context:

Section 1: Results of X-ray photoelectron spectroscopy (XPS).

Section 2: Results of electrochemistry for SMOF and SCNT samples.

Section 3: Accelerated stability test for SMOF-3, SCNT-2 and Pt/C (JM) samples.

Section 4: IR-drop correction for micro laminar flow fuel cell.

Section 1: Results of X-ray photoelectron spectroscopy (XPS).

Table S1-1. Analysis of the Pt 4fXPS data for the SMOF-1 and SMOF-3 materials				
	Single chemical components of the Pt 4f _{7/2} peak			
Sample	Pt ⁰	Pt ²⁺	Pt ⁴⁺	
SMOF-1	71.2 eV	72.9 eV	74.6 eV	
	1.3	1.5	1.5	
	80.5 %	11.8 %	8.0 %	
SMOF-3	71.1 eV	72.9 eV	74.7 eV	
	1.3	1.5	1.5	
	84.0 %	8.8 %	7.2 %	

Table S1-2. Analysis of the C <i>Is</i> XPS data for for the SMOF-1 and SMOF-3 materials						
	Single chemical components of the C 1s peak					
Sample	C sp ²	C sp ³	Alcohols	Carbonyl	Carboxylic	
				groups	groups	
SMOF-1	284.3 eV	285.4 eV	286.6 eV	288.0 eV	289.1 eV	
	1.1	1.4	1.4	1.4	1.4	
	60.9 %	20.4 %	7.9 %	3.5 %	7.3 %	
SMOF-3	284.4 eV	285.5 eV	286.6 eV		289.1 eV	
	1.1	1.4	1.4		1.4	
	86.3 %	8.1 %	3.1 %		2.5 %	

Table S1-3. Analysis of the Ce 3d XPS data for SMOF-1 and SMOF-3 materials				
	Single chemical components of the Ce 3d _{5/2}			
Sample	peak (Ce ³⁺)			
	f^2	f ¹		
SMOF-1	882.1 eV	886.2 eV		
	2.8	5		
	14.5 %	85.5 %		
SMOF-3	882.3 eV	886.2 eV		
	3.2	4.6		
	26 %	74 %		

Section 2: Results of electrochemistry for SMOF and SCNT samples.

Table S2. Electro	chemical surface area (E	$CSA / m^2 g^{-1}_{Pt}$) derived from	m the H _{upd} region and	
CO-stripping, as well as the geometric surface area calculated from the mean particle size.				
Sample	ECSA (H _{upd})	ECSA (CO-stripping)	Geometric surface	
			area	
SMOF-1	48 ± 3	53 ± 10	140	
SMOF-2	56 ± 2	58 ± 9	90	
SMOF-3	72 ± 5	68 ± 3	55	
SCNT-1	64 ± 4	72 ± 3	122	
SCNT-2	48 ± 3	60 ± 2	58	
SCNT-3	21 ± 2	6 ± 1	23	
Pt/C (JM)	78 ± 3	66 ± 2	133	

Section 3: Accelerated durability test (ADT) for SMOF-3, SCNT-2 and Pt/C (JM) samples in the potential interval of 0.6 – 1.0 V/RHE.



Figure S3-1. (A) CVs recorded at scan rate of 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ and (B) LSVs on RDE with rotating speed of 900 rpm at scan rate of 5 mV s⁻¹ in O₂-saturated 0.1 M HClO₄ during stability test for SMOF-3 sample.



Figure S3-2. (A) CVs recorded at scan rate of 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ and (B) LSVs on RDE with rotating speed of 900 rpm at scan rate of 5 mV s⁻¹ in O₂-saturated 0.1 M HClO₄ during the durability test for SCNT-2 sample.



Figure S3-3. (A) CVs recorded at scan rate of 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄; and (B) LSVs on RDE with rotating speed of 900 rpm at scan rate of 5 mV s⁻¹ in O₂-saturated 0.1 M HClO₄ during the durability test for Pt/C (JM).

Section 4: IR-drop correction for micro laminar flow fuel cell.

IR-drop of micro fuel cell was measured using the PEIS method with a potentiostat/galvanostat (SP-300 Biologic Science Instruments) applying a frequency of 10 kHz in a punctual measurement of the assembled micro-fluidic cell. Resistance values for cathode and anode are summarized in **Table S3**. The corrected electrodes' potential, cell potential and power density was done using equations (1 - 4).

 $E'(cathode) = E(cathode) + i(cathode) \times R(cathode)/1000$ (1)

 $E'(anode) = E(anode) - i(anode) \times R(anode)/1000$ (2)

E'(cell) = E'(cathode) - E'(anode) (3)

$$P = E'(cell) \times i \quad (4)$$

Where E' is the ohmic-drop (iR-drop) corrected potential, E recorded raw potential value, i current, R value of iR drop, P power density. The raw data without correction were shown in Figure S4.

Table S3. Values of iR-drop (Ω) for each μ LFFC assembly.							
Cathode	SMOF-1	SMOF-2	SMOF-3	SCNT-1	SCNT-2	SCNT-3	Pt/C (JM)
iR-drop	0.97	0.93	1.10	0.50	0.50	0.78	0.79
Anode:	Pt/C	Pt/C	Pt/C	Pt/C	Pt/C	Pt/C	Pt/C (JM)
	(JM)	(JM)	(JM)	(JM)	(JM)	(JM)	
iR-drop	0.70	1.00	0.92	0.70	0.97	0.85	0.92



Figure S4. (A) Corresponding representative anode and cathode non-IR corrected polarization curves of a $H_2/O_2\mu$ LFFC; and (B) cell voltage and power density curves. Pt/C (JM) catalyst was served as anode in all systems.