

Supporting Information

Design of Laccase-Metal Organic Frameworks based Bioelectrodes for Biocatalytic Oxygen Reduction Reaction

Snehangshu Patra,^{ζ,⊥,‡,♯} Saad Sene,[‡] Christine Mousty,[◊] Christian Serre,[‡] Annie Chaussé,^{ζ,⊥}
Ludovic Legrand,^{*,ζ,⊥} Nathalie Steunou^{*,‡}

^ζCNRS UMR 8587 Bd François Mitterrand 91025 Evry, France

[†]Université d'Evry, Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement
(LAMBE), Université Evry, Université Paris Saclay, Bd François Mitterrand 91025, Evry,
France.

[‡]Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles St Quentin en
Yvelines, Université Paris Saclay, 45 avenue des Etats-Unis 78035 Versailles Cedex. France.

#Present address : Center for Excellence in Green Energy and Sensors Systems (CEGESS),
Indian Institute of Engineering Scence and Technology (IEST), Shibpur, Howrah, 711103, West
Bengal, India;

[◊]Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, UMR-
CNRS 6296, BP 10448 F-63000 Clermont-Ferrand, France.

Corresponding author

E-mail : ludovic.legrand@univ-evry.fr; nathalie.steunou@uvsq.fr

Calculation of Diffusion coefficient

The diffusion coefficient was calculated according to the Randles-Sevcik Equation,

$$I_p = 0.4463 nFAC \left(\frac{nF}{Rt} \right)^{1/2} D^{1/2} \vartheta^{1/2}$$

Where I_p =Current (Ampere), n =number of electron transferred, F = Faradaic Constant ($C.mol^{-1}$), A =Area of the electrode (cm^2), C = Concentration of the species ($mol.cm^{-3}$) assuming a film thickness of about $0.6 \mu m$, R = Gas constant ($J.K^{-1}.mol^{-1}$), T = Temperature (K) D = Diffusion coefficient ($cm^2.s^{-1}$), v =Scan rate ($V.S^{-1}$).

$$\frac{I_p}{A} = 0.4463 \times 1 \times 96485 \times C \times D^{1/2} \times \vartheta^{1/2} \left(\frac{1 \times 96485}{8.314 \times 298} \right)^{1/2}$$

$$\frac{I_p}{A} = \text{Slope of current density versus sweep rate}$$

$$= 268722.16 \times C \times D^{1/2}$$

$$\text{Anodic slope} = 0.031 A.cm^{-2} (\vartheta \times S^{-1})^{-\frac{1}{2}}$$

$$\text{Cathodic slope} = 0.017 A.cm^{-2} (\vartheta \times S^{-1})^{-1/2}$$

$$268722.16 \times C \times D^{\frac{1}{2}} = 0.031 A.cm^{-2} (\vartheta \times S^{-1})^{-\frac{1}{2}}$$

$$D_{anodic} = 1.2 \times 10^{-8} cm^2 S^{-1}$$

$$D_{cathodic} = 0.4 \times 10^{-8} cm^2 S^{-1}$$

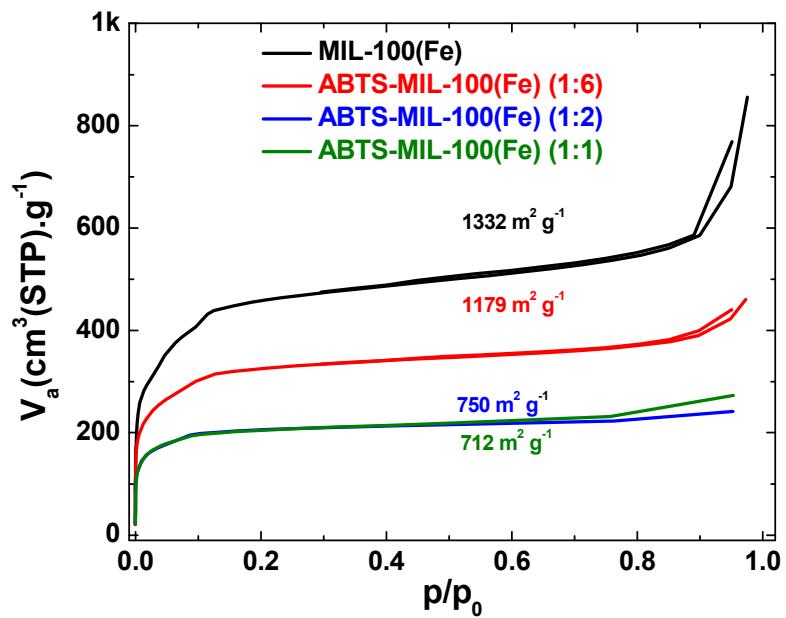


Figure S1. N₂-adsorption isotherm data recorded before and after the encapsulation of ABTS in the pores of MIL-100(Fe).

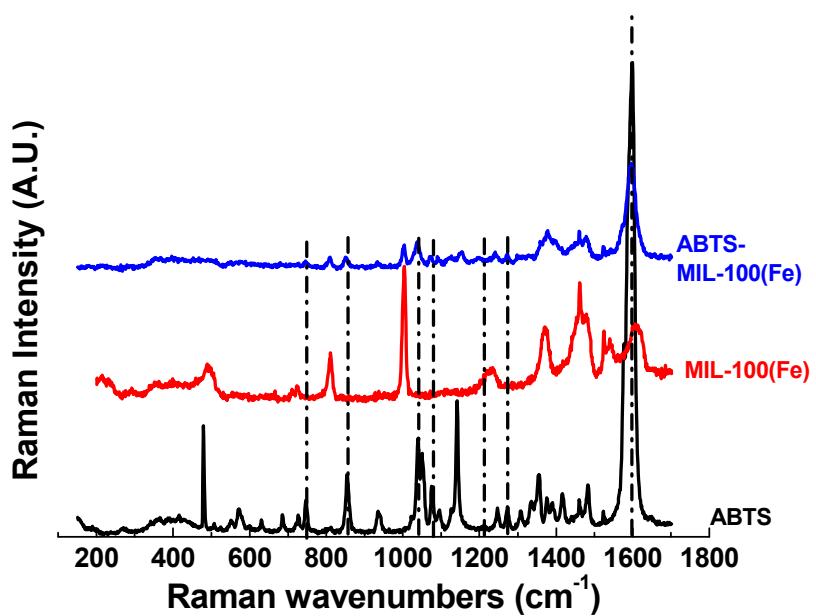


Figure S2. Micro-Raman spectra of ABTS, MIL-100(Fe) and MIL-100(Fe)-ABTS.

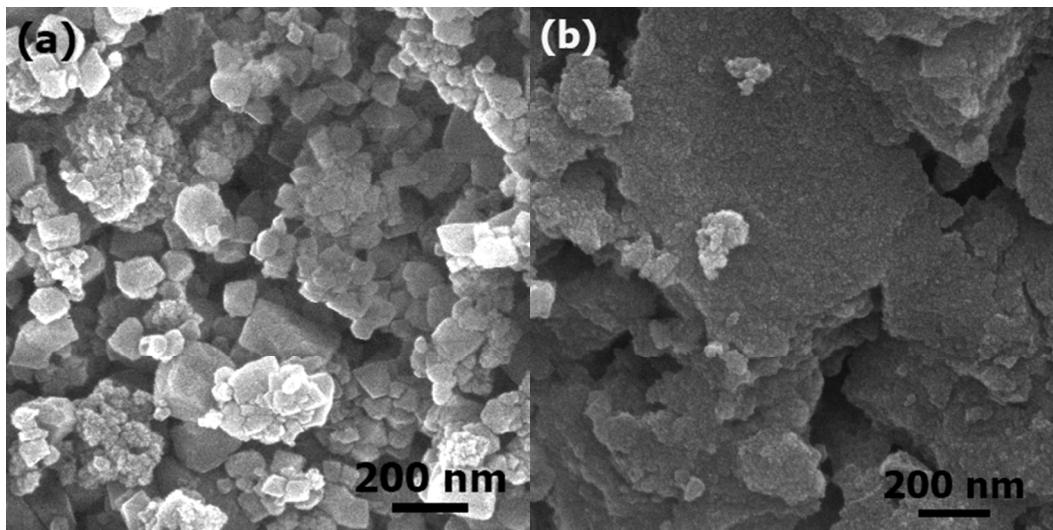


Figure S3. SEM images of MIL-100(Fe) (a) before and (b) after ABTS impregnation.

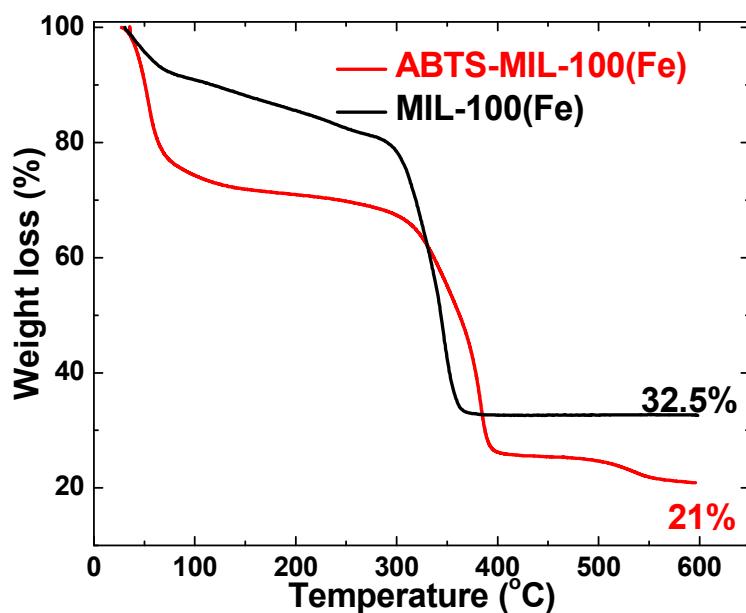


Figure S4. TGA of ABTS, MIL-100(Fe) and MIL-100(Fe)-ABTS.

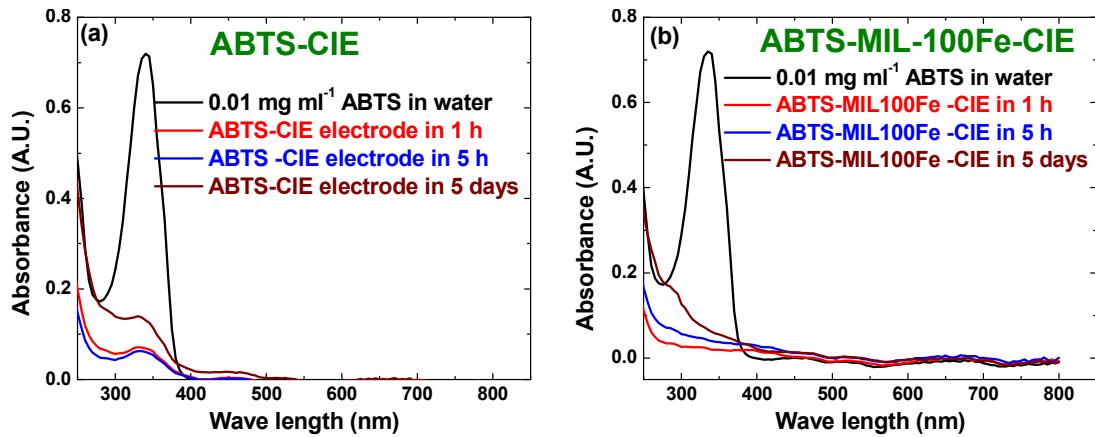


Figure S5. Comparison of UV-Visible spectra of (a) ABTS-CIE and (b) ABTS-MIL-100(Fe)-CIE electrode soaked in 0.1 M acetate buffer of pH=5.1 for a time period as mentioned in the legend of the graphs.

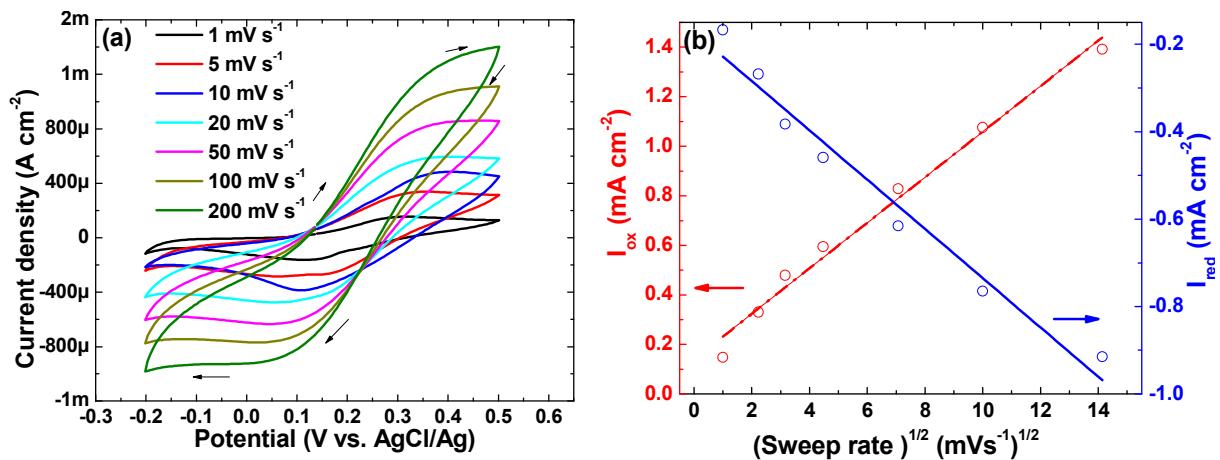


Figure S6. (a) Cyclic voltammograms of the ABTS-MIL-100(Fe)-CIE modified SS electrode at various sweep rates of 200, 100, 50, 20, 10, 5, and 1 mV/s in 0.1 M acetate buffer of pH=5.1 (b)Oxidation and reduction peak current density as a function of $(\text{sweep rate})^{1/2}$. Arrow indicates the direction of potential sweep.

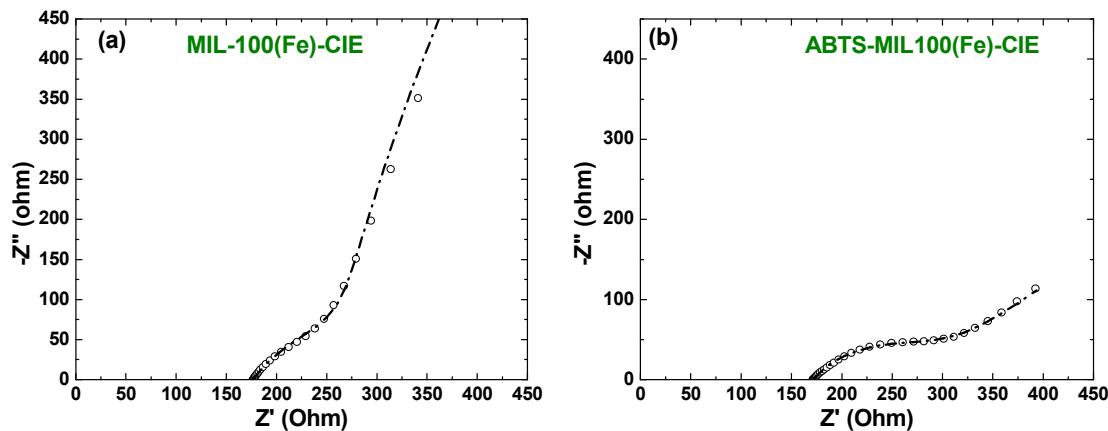


Figure S7. Impedance spectrum of (a) MIL-100(Fe)-CIE and (b) ABTS-MIL100(Fe)-CIE, at open circuit potential ($\sim 0.1\text{V}$ vs. AgCl/Ag) in 0.1 M acetate buffer of pH=5.1.

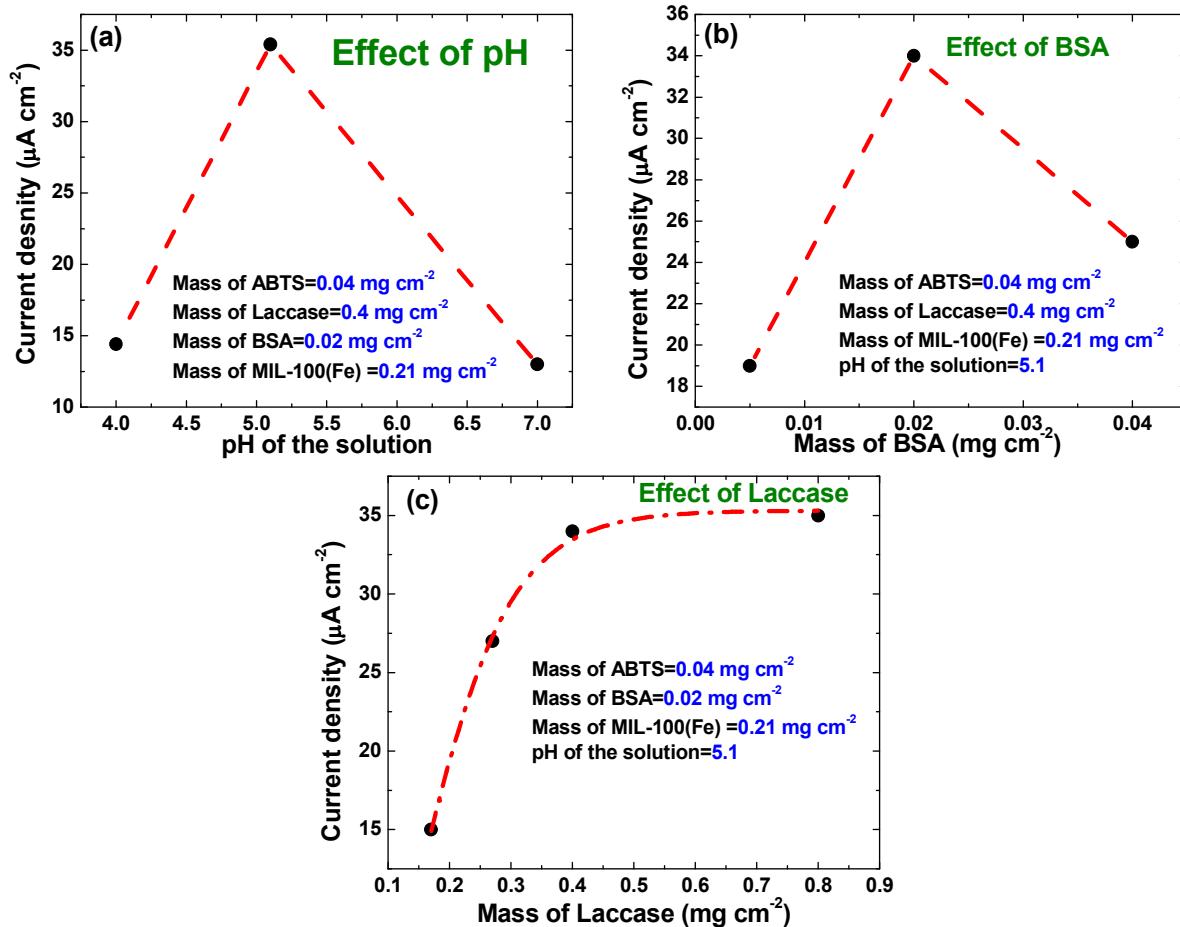


Figure S8. Current density of Lac-ABTS-MIL-100(Fe)-CIE for the electrocatalytic reduction O_2 as function of (a) pH of the electrolyte, mass of (b) Bovine serum albumin (BSA), (c) Laccase at $E_{\text{app}}=0.160\text{ V}$.

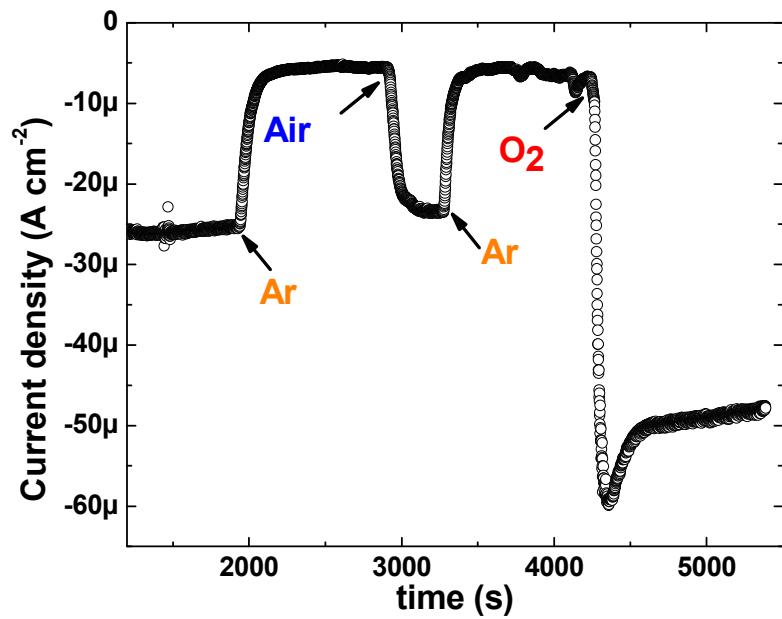


Figure S9. Chronoamperometry of Lac-ABTS-MIL-100(Fe)-CIE modified SS electrode at 0.16V vs. Ag/AgCl in 0.1 M acetate buffer of pH=5.1.