

Supporting Information

Metal Organic Framework Derived Rare Earth Metal (Ce-N-C) based Catalyst for Oxygen Reduction Reaction in Dual Chamber Microbial Fuel Cells

Shaik Ashmath¹, Hao Wu¹, Shaik Gouse Peera^{1,*} and Tae-Gwan Lee^{1,*}

Department of Environmental Science, Keimyung University, Daegu 42601,
Republic of Korea

***Correspondence: S. G. P (gouse@kmu.ac.kr); T. G. L (wateree@kmu.ac.kr)**

S1. Physical and electrochemical characterizations

Particle size, graphitic nature of the Ce/N-C and NC catalysts are studied by using powder X-ray diffraction (XRD, Rigaku (D/Max-2500) diffractometer) analysis with Cu-K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The morphology of the Ce/N-C and NC catalysts are studied by scanning electron FESEM (Hitachi SU8220) and transmission electron microscope (FETEM, Titan G2 ChemiSTEM Cs Probe (FEI Company, The Netherlands). The oxidation state of Ce and identification of different bonding of N and C are examined by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer.

S2. Electrochemical Characterizations of the Ce/N-C and NC catalysts

Electrochemical studies of the Ce/N-C and NC catalysts are studied in a traditional three electrode system with glassy carbon electrode (effective surface area of 0.1257 cm^2) as working electrode, graphite rod and saturated calomel electrode as counter and reference electrodes, respectively. The electrochemical studies were performed by using Biologic instruments SP-150e, potentiostat/galvanostat in 0.1 M HClO_4 . For rotating disk studies, catalyst (Ce/N-C and NC catalysts or Pt/C) ink is made by dispersing 4 mg of the catalyst in 1 mL of ethanol: water mixture (1:3) and the solution is ultrasonicated for 30 mins , to which a Nafion solution ($5 \text{ wt.}\%$) of $15 \text{ }\mu\text{l}$ is added and further ultrasonicated for 30 mins . A $14 \text{ }\mu\text{l}$ of the resultant catalyst ink is deposited in the glassy carbon electrode and then allowed it to dry at room temperature (catalyst loading: $560 \text{ }\mu\text{g cm}^{-2}$). For comparison, the Pt/C catalyst ($10 \text{ wt}\%$) with a catalyst loading of $110 \text{ }\mu\text{g cm}^{-2}$ is also deposited on the GCE.

The ORR electrochemical tests were performed by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Before the electrochemical tests, the electrolyte 0.1 M HClO_4 solution is saturated with N_2/O_2 gas. The CV and LSV curves were recorded in the potential range of $0-1.2 \text{ V}$ vs. RHE with a scan rate of 50 and 10 mV s^{-1} , respectively. For Koutechy-Levich (K-L) plots, the LSV curves were recorded at different rotations speeds from 800 to 2400 rpm . The number of electrons transferred in ORR process at different electrode potentials are calculated from the slopes of Koutechy-Levich (K-L) plots i.e plots of j^{-1} vs. $\omega^{-1/2}$ using the following questions.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} \quad (1)$$

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (2)$$

$$B = 0.62 n F C_{\text{O}_2} D_{\text{O}_2}^{2/3} \nu^{-1/6} \quad (3)$$

where j is measured current density, j_L is diffusion-limiting current density, j_k is kinetic current density, ω is angular velocity (rad s^{-1}). B is a parameter calculated from the equation (3); “ n ” is number of electrons transfer per O_2 molecule, F is Faraday constant ($96,485 \text{ C mol}^{-1}$), C_{O_2} is the concentration of oxygen in electrolyte $1.26 \times 10^{-6} \text{ mol cm}^{-3}$, D_{O_2} is diffusion co-

efficient of oxygen in the solution ($1.93 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$) and ν is kinematic viscosity of 0.1 M aqueous HClO_4 electrolyte ($\nu=0.001009 \text{cm}^2 \text{s}^{-1}$). The number 0.62 is adopted when the rotation speed is expressed in rad s^{-1} . The stability of the Ce/N-C and Pt/C catalysts have been carried out by potential cycling of the working electrode by recording repeated cyclic voltammograms between 0 to 1.0 V vs. RHE for 5000 at the scan rate of 50mV s^{-1} . To assess the degradation of the catalysts, the LSVs were recorded after stability test in O_2 saturated 0.1 M HClO_4 electrolyte with a scan rate of 10mV sec^{-1} . All the potential was represented on relative hydrogen electrode (RHE) scale for convenience.

S3. Microbial fuel cell operation

The MFC reactor used was a dual chamber glass reactor with a volume capacity of 250 mL each (with a working volume of 200 mL). The carbon brush was used as an anode. The as received carbon brush was washed with ethanol and water to remove any dust and impurities. The two glass chambers are separated by a proton exchange membrane (Nafion 117). The as received membrane was pre-treated in 30wt% H_2O_2 , then in 0.5 M H_2SO_4 and finally in deionized (DI) water. Each step is performed for 1 h at 80°C . The pre-treated membrane is then stored in DI until use. The cathode used was a commercial GDL (geometric area = $2.6 \times 5.5 \text{cm}$). The cathode catalyst Ce/N-C and Pt/C in the form of catalyst ink is deposited onto the GDL. The cathode catalyst ink is prepared by dispersing $\sim 50 \text{mg}$ of the Ce/N-C catalyst in isopropyl alcohol (10 ml) and ultrasonicated for 30 mins, to which 30 wt.% of Nafion (5 wt.%, i.e 300 mg) solution is added and further ultrasonicated for 30 mins to obtain the final catalyst ink. The catalyst ink is then coated onto the GDL by using paint brush layer by layer until a desired catalyst loading 2.5mg cm^{-2} (when electrodes reached an excess weight of 35.75mg from those of initial weight (corresponding to 2.5mg cm^{-2} catalyst loading), for both Ce/N-C and Pt/C catalyst while 0.5mg cm^{-2} in case of Pt/C catalyst is achieved. The two MFC chambers were coupled with the Nafion 117 membrane, and two chambers are filled with 200 mL of the buffer solution (pH=7) on both sides. The anode chamber consists of 20 mM sodium acetate + 2M Glucose solution. The cathode is purged continuously with atmospheric air with the help of an air pump at a controlled flow rate ($\sim 10 \text{ml min}^{-1}$). In this work, we have “utilized bacterial seed sample”, from sewage water, collected from the local drainage as the source of bacteria. A sample of 10 mL sewage drainage water sample is added to the anodes of fresh MFC set up, allowing the bacteria to culture naturally in the anode chamber. Sewage water is a good source of mixed bacterial strains and mimics the most realistic wastewater treatment applications. In addition, as a source of carbon, we add 20 mM sodium acetate every alternative day to the anode chamber and allow the bacteria to grow. Over the course of time, bacteria attaches the carbon brush fibers and grow continuously, forming a biofilm. The biofilm formation can be assessed from the fact that the OCV slowly rises and reaches the maximum after a period of time. After reaching a steady and stable OCV, then the polarization curves were recorded. The anode and cathodes are connected to the potentiostat to monitor the open circuit voltage. The polarization curves were recorded by linear sweep voltammetry at a scan rate of 1mV sec^{-1} . The current density and power densities were normalized according to the cathode geometric area and volume of the anolyte. For the TOC measurements, 5 mL of the

analyte is taken at a specified intervals and diluted to 30 mL with distilled water and the samples are stored in a refrigerator and later sent to the TOC analysis. The MFC is operated with 100 Ω resistor and an ample of solution from the anode chamber is collected at specified intervals and analyzed for TOC measurements.

S4. Instrumentation used for RDE/MFC studies are as follows

Electrochemical Studies - SP-150e, potentiostat/galvanostat provided by the BioLogic company. France

For rotating measurements - RRDE-3A Rotating Ring Disk Electrode Set up - provided by the BioLogic company. France

Glass Carbon Electrode – Provided by the BioLogic company. France

Saturated Calomel Electrode – BioLogic company. France

High Purity Graphite Rod Electrode – Obtained from AliExpress, Mainland China

Carbon Brush - Obtained from AliExpress, Mainland China

Gas diffusion layers - Obtained from AliExpress, Mainland China

Nafion 117 - Obtained from AliExpress, Mainland China

Glass Dual Chamber Microbial Fuel Cell Set up - Obtained from AliExpress, Mainland China

S5. Justification for using Graphite rod as counter electrode

The primary reason for this decision lies in the inherent limitations associated with using traditional Pt counter electrodes under these conditions.

In acidic electrolytes, there is a significant risk that Pt wire may dissolve, leading to the formation of Pt ionic species ($\text{Pt}^{\text{n}+}$). These species can subsequently redeposit on the working electrode. This redeposition poses a particular problem when evaluating the ORR activity of non-precious metal catalysts, in fact even other electrochemical reactions such as HER, OER etc. The presence of Pt atoms on the working electrode can artificially enhance ORR activity measurements, thus confounding the true performance of the non-precious metal catalysts.

To circumvent this issue, researchers have increasingly adopted graphite-based counter electrodes, which do not dissolve or redeposit under acidic conditions, even if dissolves it only contributes the carbon into CO_2 , not any species that can contribute to the ORR activity. This approach ensures that the ORR activity measured is solely attributable to the non-precious metal catalysts under investigation, thereby providing more accurate and reliable results. Consequently, the use of graphite counter electrodes has become the standard practice in RDE studies aimed at assessing non-precious metal catalysts.

By using a graphite rod, we maintain the integrity of our measurements and uphold the precision necessary for evaluating the true catalytic activity of the materials in question.

S6. Biofilm monitoring via OCV measurement over time:

Microbial fuel cells (MFCs) energy generation depend on electron transfer from bacterial cells to carbon-based electrodes. This electron transfer requires bacteria to attach to the carbon electrodes via cell walls or flagella. Here, we explain the process and evidence for uniform biofilm formation on carbon brush fibers.

Bacteria attach to the pre-treated carbon brush electrode in the anode chamber over time. Once bacteria stick to carbon brush fibers, they multiply to form a biofilm. After biofilm formation, bacteria oxidize organic matter, releasing electrons and protons for the cathode oxygen reduction reaction (ORR). The MFC's open circuit voltage (OCV) gradually rises, indicating bacterial attachment and biofilm formation. After bacteria form a biofilm on carbon electrodes, the OCV rises and stabilizes, indicating electron transfer. The anode chamber lacks mediators and electron receivers, so bacteria suspended in the solution away from the carbon brush cannot transfer electrons. Biofilm formation is confirmed by this OCV trend.

SEM imaging of the biofilm on carbon fibers would be more conclusive than indirect evidence of bacterial attachment and biofilm formation from OCV's gradual increase and stabilization. SEM imaging before and after OCV stabilization can confirm bacterial attachment and biofilm uniformity.

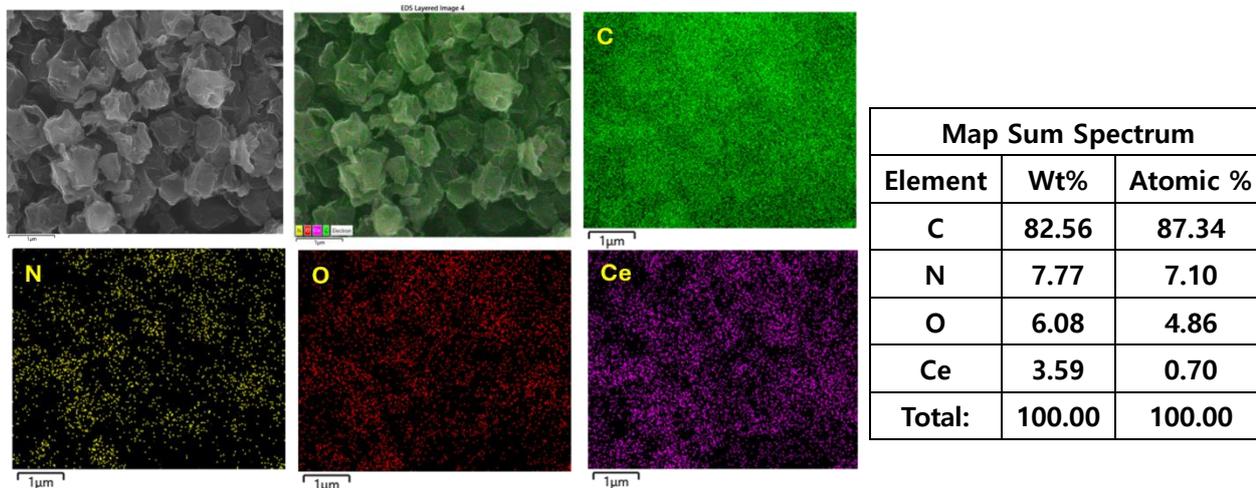
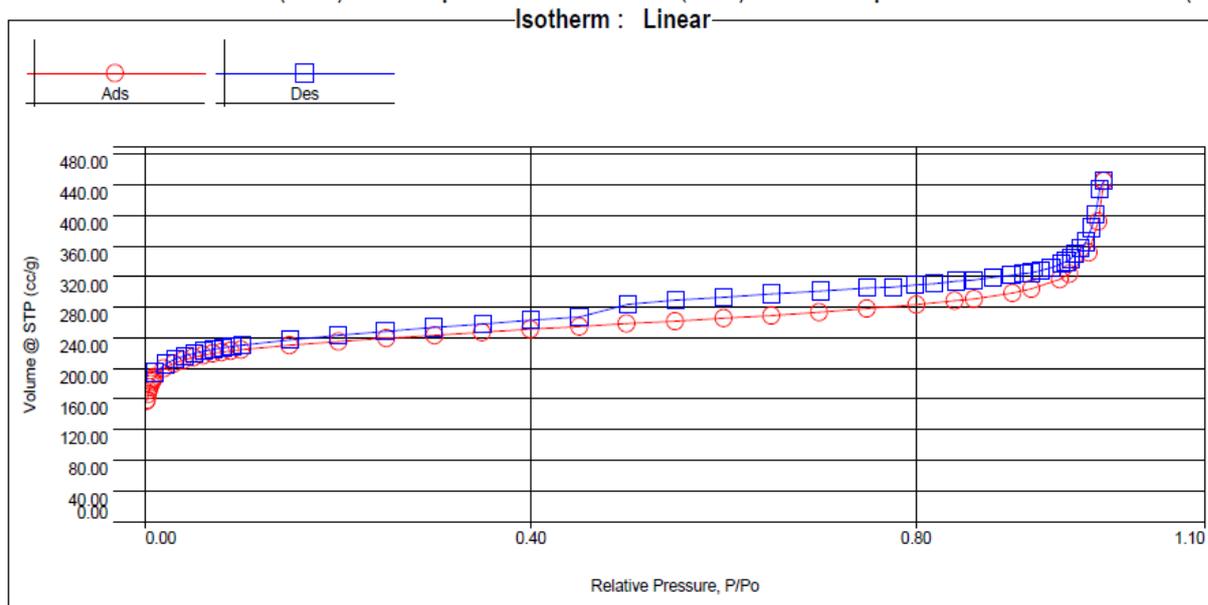


Figure S1. SEM images of Ce/N-C catalyst and the EDS elemental mapping, along with the tabular column report the atomic %t collected for each element in the catalyst, including Ce.

As per the reviewer's suggestion, we have now freshly synthesized Ce/N-C catalysts and conducted SEM analysis. The elemental mapping from the SEM-EDS analysis clearly indicates a dense distribution of Ce, suggesting a sufficient amount of Ce in the catalysts (Figure. R1). We have now added fresh images to the supporting information of the article. It can be seen that the Ce/N-C sample contains a sufficient amount of Ce atoms.



Analysis		Report	
Operator:	operator	Date:	9/28/2022
Sample ID:	B1	Operator:	operator
Sample Desc:		Filename:	QW1_220928_01_2022-09047-KMUniv-B1.QPS
Sample weight:	0.0477 g	Comment:	
Analysis Time:	1099.0 min	End of run:	9/28/2022 17:40:16
Void Vol.:	He Mode, Cell: 9mm large bulb	Run mode:	Standard
Cold Zone Vol.:	26.4326	Warm Zone Vol.:	13.5656
Thermal delay:	30 sec	He evac time:	3 min
Outgas Time:	15.0 hrs	Outgas Temp:	100.0 C
Analysis gas:	Nitrogen	Bath Temp:	77.3 K
Press. Tolerance:	variable/0.050 (ads/des)	Equil time:	80/80 sec (ads/des)
		Equil timeout:	variable/variable sec (ads/des)



Analysis		Report	
Operator:	operator	Date:	9/28/2022
Sample ID:	B1	Operator:	operator
		Filename:	QW1_220928_01_2022-09047-KMUniv-B1.QPS
		Date:	2022/09/29

MBET summary	
Slope =	3.844 1/g
Intercept =	4.215e-03 1/g
Correlation coefficient, r =	0.999996
C constant =	912.818
Surface Area =	905.030 m ² /g

Figure S2. N₂ adsorption/desorption isotherms of Ce/N-C-3 catalyst

Analysis
Operator: operator Date: 9/28/2022
Sample ID: B1 Filename: Report
Operator: operator Date: 2022/09/29
QW1_220928_01_2022-09047-KMUniv-B1.QPS

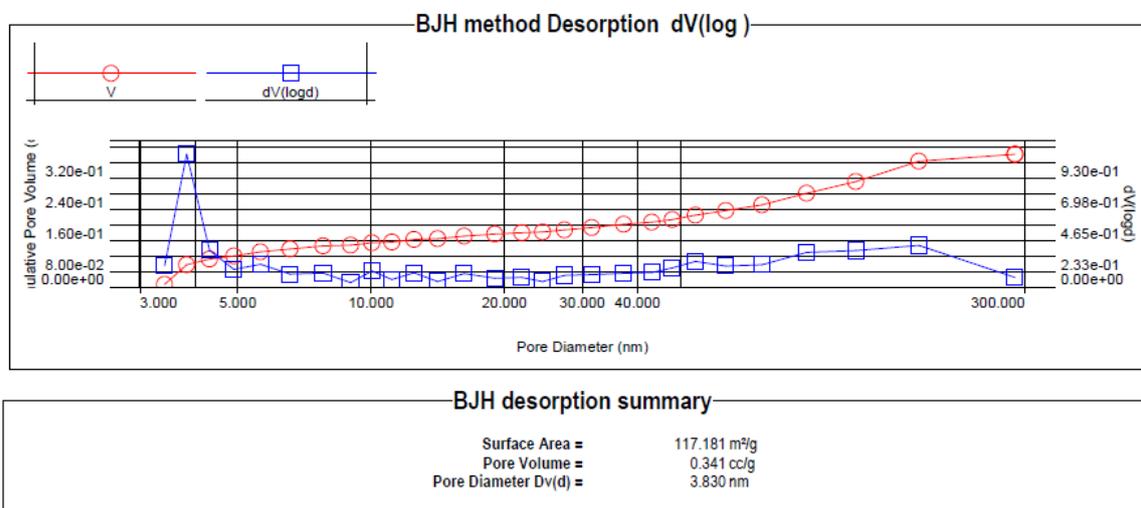


Figure S3. BJH desorption summary and the pore size distribution analysis of the Ce/N-C-3 catalyst

The BET analysis of the Ce/N-C-3 catalyst (Figure S2 and S3) and found that it has a surface area of $\sim 900 \text{ m}^2 \text{ g}^{-1}$ and BJH pore size distribution analysis reveals most of the pores in the catalyst are in the range of 3 – 5 nm, with an average pore diameter of 3.8 nm which is within mesoporous range. Therefore, it confirms that the Ce/N-C-3 catalyst has mesoporous range as we described in the text.