Journal of Power Sources 390 (2018) 45–53

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

MnO$_x$-based electrocatalysts for enhanced oxygen reduction in microbial fuel cell air cathodes

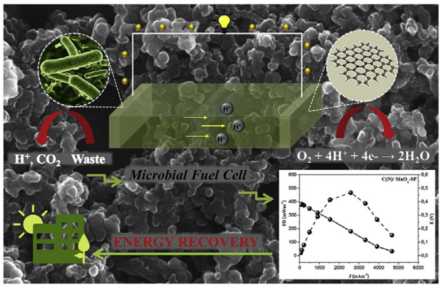
Fatemeh Shahbazi Farahani[a,b], Barbara Mecheri[b,*], Mir Reza Majidi[a,**], Maida Aysla Costa de Oliveira[b], Alessandra D'Epifanio[b], Francesca Zurlo[b], Ernesto Placidi[c,d], Fabrizio Arciprete[c], Silvia Licoccia[b]

[a] *Dept. of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, 51664 Tabriz, Iran*
[b] *Dept. of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy*
[c] *Dept. of Physics, University of Rome Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy*
[d] *CNR-ISM, Via Fosso del Cavaliere 100, Rome, Italy*

HIGHLIGHTS

- Electrocatalysts based on manganese dioxide and nitrogen-doped carbon (C(N)/MnOx).
- C(N)/MnOx as oxygen reduction reaction catalysts at cathodes of microbial fuel cells (MFCs).
- High and stable power generation.
- Cost reduction and improved performance with respect to Pt-based MFCs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Manganese dioxide
Nitrogen-doped carbon
Oxygen reduction reaction
Air cathode
Microbial fuel cell

ABSTRACT

Multivalent MnO$_x$ supported on nitrogen-doped carbon (C(N)/MnO$_x$-SP) and reduced graphene oxide (rGO(N)/MnO$_x$-SP) is fabricated via a solid state method. The synthesized catalysts are characterized by X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FE-SEM), and X-ray photoelectron spectroscopy (XPS) to get insights on crystalline structure, morphology and surface chemistry. The electrocatalytic activity toward oxygen reduction reaction (ORR) is evaluated by cyclic voltammetry, hydrodynamic voltammetry with rotating disk electrode, and electrochemical impedance spectroscopy in neutral media. As compared to rGO(N)/MnO$_x$-SP, C(N)/MnO$_x$-SP shows higher performance toward ORR, due to the interplay of surface chemistry and morphology. C(N)/MnO$_x$-SP is assembled as cathode of a single-chamber microbial fuel cell (MFC) fed with sodium acetate as fuel. The MFC performance is evaluated by measuring power generation and acquiring voltage generation cycles in long-term operation mode. MFCs assembled with C(N)/MnO$_x$-SP exhibits a peak power density of 467 mWm^{-2}, slightly higher than that of reference Pt/C (446 mWm^{-2}). The obtained results indicate that C(N)/MnO$_x$-SP is a viable catalyst for MFC cathodes owing competitive price and high performance in terms of power generation and stability of voltage cycle.

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: barbara.mecheri@uniroma2.it (B. Mecheri), majidi@tabrizu.ac.ir (M. Reza Majidi).

https://doi.org/10.1016/j.jpowsour.2018.04.030
Received 29 January 2018; Received in revised form 26 March 2018; Accepted 7 April 2018

1. Introduction

Microbial fuel cell (MFC) is a bioelectrochemical system which has attracted increasing attention during the past decade since it converts chemical energy stored in organic compounds to electrical power and simultaneously treats wastewater [1–3]. However, the widespread diffusion of MFCs is constrained because of durability issues and high cost of materials, mainly arising from the use of platinum as catalyst for the oxygen reduction reaction (ORR) occurring at the cathode side.

A viable approach for reducing costs, while enhancing ORR, is the use of platinum group metal (PGM) free catalysts. Previous literature reports have shown that PGM-free catalysts obtained by supporting transition metal, such as Fe and Co, on different carbon supports can be used as cathode in MFCs, achieving an electrochemical performance comparable to that of Pt [4–8]. Also, thanks to low cost, natural abundance, environmental friendly nature, and good electrochemical properties, electrode materials based on manganese dioxide (MnO_2) have been tested at the cathode side of MFCs [5,6]. ORR activity and the overall electrochemical performance was found to be strongly dependent on size, morphology, crystal structure, surface chemistry, and surface area [7–11].

MnO_2 can be synthesized following diverse strategies, including sol-gel process, microwave heating, and precipitation/ion-exchange, obtaining materials with different structure, surface area, and hydration degree [12–14]. Generally, MnO_2 exists in three crystallographic forms, *i.e.* α-, β-, and γ-MnO_2, which correspond to differently connected [MnO_6] octahedral frameworks, resulting in different morphologies and pore structures [15–20].

However, MnO_2 has an intrinsic low electrical conductivity and suffers from agglomeration and dissolution issues, which limits its activity as ORR catalysts. Supporting MnO_2 on highly conductive materials, such as graphene and graphene oxide, carbon black, carbon nanotubes, and activated carbons is a widely recognized strategy for overcoming the above-mentioned drawbacks [21,22].

Electronic conductivity, catalytic activity, and anchoring of the metal particles can be further enhanced by heteroatom functionalization of the carbon support [23–25]. In particular, carbon materials show a nitrogen-doping-enhanced ORR activity in neutral and alkaline environment, due to improved adsorption of oxygen and decomposition of peroxide intermediate [26–30]. In fact, there are two possible ways of oxygen reductions that can take place: oxygen can be reduced to water by direct 4-electron pathway or to peroxide by 2-electron pathway, following a pH-dependent mechanism as illustrated in Table 1. For achieving high power performance in MFCs and avoid peroxide formation, the direct 4-electron pathway is a mandatory requirement of ORR catalysts [28].

Nitrogen-doping of carbon supports can be thus considered as an efficient way to improve MFC performance of previously reported MnO_2-based cathodes [31–36].

In this work, we report a strategy to develop a novel multivalent MnO_x supported on either nitrogen-doped carbon black or nitrogen-doped graphene oxide to be used at the cathode side of MFCs, for enhancing power generation, stability, and reducing costs. To the best of our knowledge, electrocatalysts based on multivalent MnO_x supported on *N*-doped carbon have not been yet investigated in air-cathode MFCs.

Table 1
ORR pathways and standard reduction potentials.

Reaction Mechanisms	Reaction	pH	E^0 (vs SHE)
4e pathway (direct)	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	alkaline	0.401 V
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	acidic	1.229 V
2e pathway (peroxide)	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$	alkaline	−0.065
	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $H_2O_2 + 2H + 2e^- \rightarrow 2H_2O$	acidic	0.670

2. Experimental

2.1. Materials preparation

XC-72R Carbon Vulcan (C) was obtained by Cabot Corporation. It was modified by a two steps treatment with nitric acid and ammonia gas, according to previous reports [37], obtaining a material labeled as C(HNO_3) and C(N), respectively.

Graphene oxide was synthesized through electrochemical exfoliation of graphite in aqueous solution of LiCl, as previously reported [38]. *N*-doping and reduction of GO was further carried out by a thermal treatment in a flow of anhydrous ammonia into a tubular oven at T = 400 °C (heating rate of 5 °C/min) for 4 h, obtaining a sample labeled as rGO(N).

MnO_x was supported on C(N) and rGO(N) by a solid state method. In a typical preparation, 4.16 mmol of either C(N) or rGO(N), 0.0416 mmol $Mn(Ac)_2{\cdot}4H_2O$, and 0.0277 mmol $KMnO_4$ (Mn^{+2}:Mn^{+7} = 3:2) were mixed together in an agate mortar and ground for 20 min. The powder was then transferred to a glass vial, capped and kept at T = 180 °C for 8 h. The resulting powder was cooled and thoroughly washed with distilled water and ethanol four times, and then dried at 60 °C for 4 h. Finally, the obtained samples were calcined at 400 °C for 90 min, and labeled as C(N)/MnO_x-SP and rGO(N)/MnO_x-SP, respectively.

2.2. Materials characterizations

To verify the crystalline structure, X-ray diffraction (XRD) was performed by using Philips PW1730 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406$ Å).

The morphology of the materials was investigated by scanning electron microscopy (SEM). All images were acquired using a Leo Supra 35 field-emission scanning electron microscope (Carl Zeiss, Oberkochen, Germany).

Raman Spectroscopy was performed with a DXR Raman Microscope (Thermo Scientific) using laser excitation wavelength of 532 nm with a 10 X objective. Laser power was maintained at 0.1 mW.

X-ray Photoelectron Spectroscopy (XPS) was performed using an Omicron DAR 400 Al/Mg Ka nonmonochromatized X-ray source, and a VG-CLAM2 electron spectrometer. Samples were dispersed in ethanol to a 1 $mgmL^{-1}$ content and deposited on silicon wafer.

The electrochemical tests to evaluate ORR activity of the different catalysts were carried out by Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Hydrodynamic Voltammetry with a Rotating Disc Electrode (RDE) model 636A (Princeton Applied Research, Ametek). All electrochemical tests were performed with a VMP3 Potentiostat (Bio Logic Science Instruments) connected to a computer through EC-lab V10.18 software. Fitting and analysis of the EIS data were done by ZView software. 100 mM neutral phosphate buffer (PBS) saturated with either nitrogen or oxygen was used as electrolyte. A three electrode cell was used, using saturated calomel electrode (Amel 303/SCG/12), Pt wire (Amel 805/SPG/6J), and a glassy carbon disk (0.196 cm^2 area) modified with catalyst layer as the reference, counter, and working electrode, respectively. To prepare catalysts ink, 4 mg catalyst was dispersed in 455 μL of a mixture of ethanol, water and 5.0 wt% Nafion (Aldrich) with volume ratio 5.4:2.7:1. Then 7 μL of catalyst ink was deposited on the GC electrode to 0.31 $mgcm^{-2}$ catalyst loading.

CV experiments were performed in the potential range +1.1 V ÷ −0.8 V (versus SCE) with scan rate in the range of 10–80 mVs^{-1}. Linear sweep voltammetry (LSV) with RDE electrodes was carried out at different rotation rates by sweeping the potential from −0.4 V ÷ −1 V (versus SCE) at 10 mVs^{-1}. EIS spectra were recorded at E = −0.3 V