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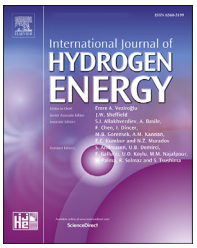

Synthesis of bimetallic iron ferrite $Co_{0.5}Zn_{0.5}Fe_2O_4$ as a superior catalyst for oxygen reduction reaction to replace noble metal catalysts in microbial fuel cell

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ABSTRACT

A low-cost electrochemically active oxygen reduction reaction (ORR) catalyst is obligatory for making microbial fuel cells (MFCs) sustainable and economically viable. In this endeavour, a highly active surface modified ferrite, with Co and Zn bimetal in the ratio of 1:1 (w/w), $Co_{0.5}Zn_{0.5}Fe_2O_4$ was synthesised using simple sol-gel auto combustion method. Physical characterisation methods revealed a successful synthesis of nano-scaled $Co_{0.5}Zn_{0.5}Fe_2O_4$. For determination of ORR kinetics of cathode, using $Co_{0.5}Zn_{0.5}Fe_2O_4$ catalyst, electrochemical studies viz. cyclic voltammetry and electrochemical impedance spectroscopy were conducted, which demonstrated excellent reduction current response with less charge transfer resistance. These electrochemical properties were observed to be comparable with the results obtained for cathode using 10% Pt/C as a catalyst on the cathode. The MFC using $Co_{0.5}Zn_{0.5}Fe_2O_4$ catalysed cathode could produce a maximum power density of 21.3 ± 0.5 W/m^3 (176.9 ± 4.2 mW/m^2) with a coulombic efficiency of 43.3%, which was found to be substantially higher than MFC using no catalyst on the cathode 1.8 ± 0.2 W/m^3 (15.2 ± 1.3 mW/m^2). Also, the specific power recovery per unit cost for MFC with $Co_{0.5}Zn_{0.5}Fe_2O_4$ catalysed cathode was found to be 4 times higher as compared to Pt/C based MFC. This exceptionally low-cost cathode catalyst has enough merit to replace costly cathode catalyst, like platinum, for scaling up of the MFCs.

Introduction

Cathode reduction kinetics bring severe restriction in the performance of microbial fuel cells (MFCs) [1]. Among the various terminal electron acceptors (TEA), like, $KMnO_4$ [2], $[FeCN]_6^{2-}$ [3] etc., oxygen is found to be the most suitable TEA in MFCs because of high oxidation potential, environment friendliness and abundant availability in nature [4,5]. Cathodic overpotential loss during oxygen reduction reaction (ORR) [6] and a high cost of noble cathode catalysts (e.g. Platinum) [7], which is popularly used for enhancing the ORR kinetics, are serious drawbacks for field scale sustainable application of MFCs. Abundant availability on the earth, low cost and high activity of transition metal ($Co^{2+/3+}$, $Fe^{2+/3+}$, $Mn^{3+/4+}$, $Ni^{3+/4+}$, Ti^{4+} etc.) oxides [8] for ORR are attracting the attention of

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researchers to investigate catalytic activity of these catalysts for application in MFCs. Transition metal oxides are gaining popularity among researchers, to be used as cathode catalyst in MFCs, to demonstrate high ORR rate and reduce fabrication cost of MFC.

It was observed that bi- or tri-metal oxides with spinel structure show excellent catalytic activity towards ORR [9] due to their variable valence states and redox stability [10]. Cobalt Sulfide Porous Nanocubes [11], Carbon nanosheets [12], Zn-MOF [13] etc. are previously used and reported as efficient ORR catalyst for fuel cell applications. Zinc is also used as popular electrode material [14]. CoO nanosheets [15] and $CoFe_2O_4$ nanoparticles [16] were previously tested as a cathode catalyst in MFC and the power density of 1650.1 ± 36.2 mW/m^2 and 1770.8 ± 15.0 mW/m^2, respectively, were reported; which was noted to be considerably higher as compared to MFC using no catalyst on cathode (741.5 ± 8.5 mW/m^2). Similarly, $ZnO/ZnCo_2O_4$ nanoparticles [17] were also previously regarded as a good catalyst for ORR. Cobalt, Zinc and Iron transition metals have seven, ten and six electrons in their respective external 3d orbital and electron sharing of d block electron clouds in these three transition metals in $Co_{0.5}Zn_{0.5}Fe_2O_4$ increase the intermolecular electron mobility, which assists to reduce ORR overpotential. In $Co_{0.5}Zn_{0.5}Fe_2O_4$ framework, cations of zinc and iron occupy the space via two types: (1) tetrahedral and (2) octahedral, making spinel type of structures. Based on these arrangements, spinals are divided into three types. Zn occupies tetrahedral places and Fe occupies octahedral places in normal spinel. Zn occupies octahedral sites together with other half of Fe atoms on tetrahedral sites in case of inverse spinel. Both Zn and Fe occupy both tetrahedral and octahedral sites in mixed or random spinel. In addition, cobalt was impregnated into this structure to improve the intermolecular electronic mobility and redox property [18] of $Co_{0.5}Zn_{0.5}Fe_2O_4$.

In this research, surface modified ferrite nanoparticles with cobalt and zinc were synthesised via simple sol-gel auto combustion method and as-synthesized materials was characterised using X-Ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) to identify phase orientation and particle distribution. Applicability of this cathode catalyst in MFC was investigated in terms of power density, wastewater treatment and coulombic efficiency (CE) by comparing this catalyst with the MFC having Platinum (Pt/C) (10% Pt loading) catalyst, which was traditionally used as cathode catalyst in MFCs and a control MFC with only acetylene black coated on cathode surface. The performance of catalysts was evaluated, to understand the overpotential loss to execute ORR, using cyclic voltammetry (CV) analysis and electrochemical impedance spectroscopy (EIS).

Materials and methods

Combustion synthesis of cobalt zinc ferrite nanoparticles

Cobalt zinc ferrite ($Co_{0.5}Zn_{0.5}Fe_2O_4$), cobalt ferrite ($CoFe_2O_4$) and zinc ferrite ($ZnFe_2O_4$) nanoparticles were synthesized via sol-gel combustion process using analytical grade iron nitrate ($FeNO_3$, $9H_2O$), cobalt chloride ($CoCl_2$, $6H_2O$), zinc nitrates ($ZnNO_3$, $6H_2O$), and urea $Co(NH_2)_2$ (Sigma Aldrich, USA) and all reactions were carried out under air medium. All the chemicals were mixed based on the proper stoichiometric composition. In brief, 40 ml of 2 M $Fe(NO_3)_3.9H_2O$, 64 ml of 0.5 M $Co(NO_3)_2.6H_2O$, 16 ml of 0.5 M $Zn(NO_3)_2.6H_2O$ and 40 ml of 6.67 M $CO(NH_2)_2$ were prepared and mixed properly with magnetic stirrer with 500 rpm for 30 min. The light red solution of above mixture was heated at 100 °C on a hot plate until dark gel type viscous liquid was obtained. The dark gel was calcined at 440 °C for 30 min in muffle furnace and at this temperature an ignition of the gel occurred by liberating grey smoke. After 30 min of ignition, the temperature was further increased to 800 °C and the material was kept for another 2 h at this temperature for proper impregnation of transition metals in ferrate structural framework. The dried gel burnt completely to form a loose powder having magnetic properties [19]. This material was washed with ethanol and water to remove the impurities. Final product was then dried at 100 °C for 24 h in hot-air oven and stored in dry place for further use.

Catalyst ink preparation

Five cathodes were fabricated using synthesized $Co_{0.5}Zn_{0.5}Fe_2O_4$ catalyst, $CoFe_2O_4$ and $ZnFe_2O_4$ catalysts. Catalyst ink was prepared using poly(dimethylsiloxane) (PDMS) solution as a binder. The proportions of different materials used for fabrication of cathodes are elaborated in Table 1. These materials were mixed together under ultrasonic bath operated at 120 kHz ultrasound frequency for 2 h to obtain a homogenous ink-based solution. The above ink-based solution (either $Co_{0.5}Zn_{0.5}Fe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$ or Pt/C or no catalyst) was sprayed over clean piece of carbon felt (Nickunj Catalysing Transformation, India) of dimension 20 cm × 6 cm using highly pure compressed N_2 gas. Finally, fabricated cathodes were dried in hot-air oven at 100 °C for 1 h before installing them on the respective MFCs. Felts were pre-treated with sequential washing using 1 N HNO_3, 30% ethanol and deionised water vigorously to reach neutral pH and dried in hot air oven at 100 °C [20]. Two reference control electrodes having Pt/C (10% weight basis) and only acetylene black (1 mg/cm^2) as catalyst layer were also prepared, following similar procedure, for performance comparison. A 0.5 mg/cm^2 loading of Pt/C (0.05 mg/cm^2 of Pt metal) was maintained on the cathode.

Catalyst characterization

The XRD technique was conducted for crystallographic phase identification of as-synthesized $Co_{0.5}Zn_{0.5}Fe_2O_4$ (CoZnFe-S), $CoFe_2O_4$ (CoFe), $ZnFe_2O_4$ (ZnFe) and the performance results were compared with the commercially available $Co_{0.5}Zn_{0.5}Fe_2O_4$ (CoZnFe-P) (SRL, India). Diffraction patterns were acquired in X'Pert pro diffractometer (PANalytical, The Netherlands) with Cu-Kα irradiation ($\lambda = 0.1541$ nm) under 2θ value ranging from 20° to 70° at a scanning rate of $0.12^{\circ}s^{-1}$. Surface morphology was examined in field emission scanning electron microscopy (FESEM, MERLIN-ZEISS, Germany); whereas the lattice imaging and selected area electron diffraction (SAED) was performed in transmission electron microscopy (TEM, JEOL, JEM-ARM200FTH, Japan). The

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