Nanorods of cerium oxide as an improved electrocatalyst for enhanced oxygen reduction in single-chambered microbial biofuel cells

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Abstract

This paper reports the synthesis and utilization of cerium oxide (CeO₂) nanorods as a cathode catalyst and a potential, low-cost replacement of platinum for microbial biofuel cells (MBFCs). The nanorod electrocatalyst had exhibited significant improvements over Pt nanoparticles in terms of forward and backward onset potentials and peak current densities, electronic conductivity, charge transfer resistance, stability in 0.1 M phosphate buffer solution, and cost. It had also demonstrated a more stable forward peak current density at the 100th steady cycle, as well as, higher current density values up to 7,200 s. In addition, the synthesized CeO₂ nanorods also produced ~10³ times higher exchange current density over the synthesized Pt nanoparticles. Furthermore, in a single-chamber MBFC, the CeO₂ nanorods exhibited higher open circuit voltage (+0.80 V after 14 days), and output current (3613 mA/m² at +0.3 V) and power (1084 mW/m²) densities in comparison to Pt nanoparticles.

1. Introduction

‘Energy’ and ‘environment’ are, at present, two of the most prominent challenges globally. There is a pressing need for increasing energy availability, and high concerns regarding the health of the environment [1, 2]. Microbial biofuel cells (MBFCs) are promising sources of energy with minimal environmental footprint [1]. MBFCs are multiutility devices, owing to their primary applicability in: (a) production of alternative energy from cheapest available fuel (for example, household, municipal and industrial effluent/sewage) [1, 3, 4], (b) treatment and purification of the employed effluent wastewater [1, 5, 6], (c) production of biohydrogen by microbial electrolysis cells [1, 7, 8], and (d) water desalination by microbial desalination cells [1, 9]. Other secondary applications of MBFCs include biosensing, useful chemical production, and metal and nutrient recovery from wastewater [10–12]. Owing to these significantly advantageous features of MBFCs, it is critical that these promising devices get developed into commercially viable products with widescale utility. To move forward, the rather lackluster performance of MBFCs in comparison to other important fuel cell devices, such as hydrogen fuel cells, direct methanol fuel cells and solid oxide fuel cells, that are already in developed and/or commercialized stages, must be first addressed. This work is aimed at enhancing the oxygen reduction efficiency of the cathode catalyst, an area that has been identified as seriously problematic in MBFCs, under neutral pH.

In a typical MBFC, organic matter in the fuel present in the anode compartment get oxidized by microorganisms, followed by subsequent reduction of a terminal electron acceptor (e.g. oxygen) at the cathode.
Conventionally, platinum (Pt) is used as the cathode electrocatalyst owing to its excellent catalytic properties toward oxygen reduction [14–16]. However, in the prevalent operating conditions present within the cathode chamber of an MBFC, Pt metal catalyst exhibits slow oxygen reduction reaction (ORR) kinetics [17]. This, in turn, results in loss of potential at the cathode, leading to generation of low current and power outputs [18]. Moreover, Pt is a high-cost noble metal with limited availability [19–21], which seriously questions the commercial viability of MBFCs using Pt electrocatalysts [13]. Therefore, there is a critical need to find a more efficient and lower cost alternative material that can replace the traditionally used Pt metal as the ORR catalyst in MBFCs.

Recent research activities in the field of ORR, in general, indicate a paradigm shift towards utilization of transition metal oxide catalysts [22–24], due to their superior catalytic activity and significantly lower cost compared to Pt and Pt-based catalyst systems [17, 25]. For instance, in case of metal oxide catalysts, the oxygen gets attached to the metal and helps in oxidizing the intermediates formed during ORR [26]. This, in turn, results in eliminating or minimizing the catalyst poisoning, as presented in the following reactions [26]:

\[
\begin{align*}
    \text{MO}_x + \text{H}^+ + e^- & \rightarrow \text{MO}_{x-1}\text{OH} \\
    2\text{MO}_{x-1}\text{OH} + \text{O}_2 & \rightarrow [(\text{MO}_{x-1}\text{OH})\text{O}_{\text{ads}}]_2 \\
    [(\text{MO}_{x-1}\text{OH})\text{O}_{\text{ads}}]_2 + e^- + \text{H}^+ & \rightarrow (\text{MO}_{x-2}\text{OH})\text{O}_{\text{ads}} + \text{H}_2\text{O} + \text{MO}_x \\
    (\text{MO}_{x-1}\text{OH})\text{O}_{\text{ads}} + e^- + \text{H}^+ & \rightarrow \text{MO}_x + \text{H}_2\text{O}
\end{align*}
\]

where, M stands for transition metal.

Noble metals, doped with metal oxides (like MnO2, TiO2, WO3, CeO2 and Fe2O3), have been reported to exhibit remarkable improvements in the performance of the overall catalyst systems [27]. For example, a Pt-CeO2/graphene nanosheet catalyst, containing 7 wt% of CeO2, demonstrated superior electrocatalytic activity towards ORR in comparison to both the CeO2/graphene nanosheet and the Pt/graphene nanosheet catalysts [28]. In another study, incorporation of 1 wt% of CeO2 within a Pt/C cathode catalyst produced higher power density (i.e. 130 mW cm\(^{-2}\)) than that exhibited by the unmodified Pt/C catalyst (i.e. 103 mW cm\(^{-2}\)) [29]. Zhang et al [30] reported that hydrothermally synthesized β-MnO2 can generate a maximum power density of 4660 W m\(^{-2}\), when employed as a cathode catalyst in MBFCs. Similarly, octahedral molecular sieve MnO2 cathode catalyst, synthesized hydrothermally and doped with Cu, showed a maximum power density value of 1980 W m\(^{-2}\) in MBFCs [31]. Furthermore, use of iron phthalocyanine, modified with cobalt oxide in an MBFC cathode, resulted in enhancement of the ORR activity, producing a maximum power density value of 654 ± 32 mW m\(^{-2}\). This value was 37% higher than that realized upon employment of carbon-supported iron phthalocyanine [24].

Herein, the chemical synthesis of unsupported cerium oxide (CeO2) nanorods (NRs) and their electrocatalytic efficacy toward ORR in 0.1 M phosphate buffer solution, as well as, in a practical single-chambered MBFC have been reported. The results obtained have been compared with synthesized and commercial Pt nanoparticles (NPs), as well as, commercial CeO2 NPs under similar operating conditions. It was intuited that apart from the use of low-cost CeO2 as a replacement of costly Pt, removal of the supporting matrix from the cathode catalyst system will ensure reduction of both the cost and the complexity of the system. This will, in turn, help in realizing a catalyst system with high performance-to-cost ratio.

2. Material and methods

2.1. Synthesis of Pt NPs and CeO2 NRs

CeO2 NRs and Pt NPs were synthesized from their respective precursor salts, i.e. cerium sulfate (Ce(SO4))\(_2\), Sigma Aldrich, St. Louis, MO, USA) and chloroplatinic acid (H\(_2\)PtCl\(_6\), Arora Matthey Ltd, Kolkata, WB, India). The salts were first ultrasonically dispersed separately in mixtures of milli-Q water and isopropanol (1:1) (Merck Millipore, Burlington, MA, USA) for 10 min. This was followed by addition of sodium hydroxide (Merck Millipore) in order to increase the pH of the salt solution to 8. Subsequently, 20 ml of 0.2 moll\(^{-1}\) of NaBH\(_4\) (Merck Millipore) solution was added dropwise to this solution mixture. After the addition of NaBH\(_4\) solution for 30 min, the solution was left under stirring for another 1 h. After cooling, the catalyst was washed with deionized (DI) water in order to ensure complete removal of chloride ions. The final dried catalyst particles were obtained upon vacuum drying at 25 °C for 24 h. A schematic representation of the synthesis of CeO2 NRs is shown in scheme S1 (supplementary materials) is available online at stacks.iop.org/MRX/7/015514/mmedia.

For comparing the performance of the synthesized catalysts with that of the commercial ones, CeO2 NPs (Particle size <25 nm) and Pt NPs (99.8 weight%, Particle size <50 nm) were purchased from Sigma Aldrich.
2.2. Preparation of electrode for electrochemical measurements
Graphite rod electrode, having 0.12 cm$^2$ geometrical area, was first cleaned by ultrasonic treatment. This was followed by subsequent covering of the outer surface of the electrode with a sheet of Teflon ensuring that the bottom surface was left uncovered. 10 $\mu$l dispersion, each of Pt NPs and CeO$_2$ NRs, was then separately casted on the smooth round surface of the electrodes in order to maintain a catalyst loading of 1 mg cm$^{-2}$. These dispersions were prepared by adding specific predetermined quantities of the Pt NPs and the CeO$_2$ NRs, separately, in mixtures of 0.5 ml of milli-Q water and 0.5 ml of isopropanol, followed by a period of 30 min of ultrasonication. Subsequently, the casted electrodes were dried for 1 h, followed by a further casting of 5 $\mu$l of Nafion solution (5 wt%) (Sigma Aldrich) on the electrode surface. A further drying of these catalysts-coated electrodes at 25 °C for 24 h ensured completion of the electrode preparation process [32, 33].

2.3. Electrochemical measurements
Cyclic voltammetric (CV) and chronoamperometric (CA) analyses of the prepared catalyst-coated electrodes were carried out at a temperature of 25 °C, by using a computer-aided potentiostat/galvanostat instrument (G600 Gamry Instrument Inc., Warminster, PA, USA). The tests were performed in a two-chambered glass cell, fitted with a conventional three-electrode assembly; whereby, the prepared graphite electrodes functioned separately as the working electrode, a Pt wire was employed as the auxiliary electrode and Hg/Hg$_2$SO$_4$ (0.5 M) performed the role of the reference electrode. Cyclic voltammograms were recorded in O$_2$ saturated 0.1 M phosphate buffer solutions, within the potential range of −0.8 V to +0.8 V and at a scan rate of 50 mVs$^{-1}$. All cyclic voltammograms were realized after a steady profile was obtained. Multiscan CV and CA were also performed in order to gauge the stability and performance of the electrodes [34].

2.4. X-ray diffractometric (XRD) analysis
XRD patterns of the prepared catalyst nanoparticles were recorded on an x-ray diffractometer (Philips Analytical PW 1710, Almelo, the Netherlands), using a CuK$\alpha$ radiation ($\lambda$ = 1.541 Å) within the range of 10° to 100° and at a fixed scan rate of 1° min$^{-1}$.

2.5. Field emission scanning electron microscopic (FESEM) analyses
Morphological investigations were performed on a field emission scanning electron microscope (Zeiss SUPRA 55 VP-41-32 instruments, equipped with the smart SEM version 5.05 Zeiss software, Oberkochen, Germany).

2.6. Electrochemical impedance spectroscopic (EIS) measurements
EIS measurements were carried out at 25 °C in a three-electrode cell (Dr Bob’s cell, Gamry Instrument Inc.), which was attached to the computer-aided potentiostat/galvanostat. A catalyst-loaded glassy carbon electrode (3 mm in diameter) (Gamry Instrument Inc.), a Pt wire (Acharaya Scientific Equipment, Rajarhat, WB, India) and an Ag/AgCl electrode (Pine Research Instrumentation, Durham, NC, USA) containing 4 M KCl solution were utilized as the working, the counter and the reference electrodes, respectively. These measurements were performed by employing an amplitude of 5 mV within the frequency range of 30 kHz to 30 mHz and at a potential of −0.3 V. The resistances offered by the cells were evaluated from the obtained Nyquist plots [20].

2.7. Pre-treatment of the membrane and the electrodes
Pre-treatment of the employed Nafion-117 membranes (M/S Anabond Sainergy Fuel Cell India Pvt. Ltd, Chennai, TN, India) were carried out by first immersing the membranes in a 5 M H$_2$O$_2$ solution (30% solution) (Merck Millipore), followed by further treatment with a 30% H$_2$SO$_4$ (Merck Millipore) solution for 2 h under stirring condition [35, 36]. These treated membranes were then cleaned with DI water in order to preserve their pH neutrality. The membranes were then dried naturally under ambient conditions for 24 h [37, 38].
Carbon cloths (Zoltek Corporation, Bridgeton, MO, USA), having fixed surface areas of 16 cm$^2$, were dipped in DI water and kept overnight in order to neutralize the effect of any unwanted ions that may be present to enhance the attachment of microbes.

2.8. Preparation of the catalyst ink and fabrication of membrane electrode assemblies (MEAs)
The catalyst inks were prepared from the synthesized nano electrocatalysts (i.e. Pt NPs and CeO$_2$ NRs) by mixing each catalyst in 1:1 DI water/isopropanol solution and 5% Nafion solution, separately [39, 40]. Each mixture was, in turn, ultrasonically dispersed for 30 min in order to form fine catalyst slurry, which was then coated on the carbon cloth. A fixed catalyst loading of 3 mg cm$^{-2}$ was employed on the cathode surface. The prepared electrodes were subsequently dried at 25 °C for 24 h. Finally, the MEAs were prepared by placing the pre-treated Nafion-117 membrane between the carbon cloth electrodes, followed by hot pressing at a temperature of 125 °C to 130 °C by applying a pressure of 6.89 MPa [41].
2.9. Preparation of bacterial culture and inoculum

Microbes were isolated from a fed batch MBFC, which underwent operation for 6 months with municipal wastewater. Incubation for 48 h was followed by selection and inoculation of the different microbial colonies. The inoculated step was performed in a sterile solution, which contained nutrient broth. The individual microbial colonies were allowed to grow for a period of 24 h to 48 h, at a temperature of 37 °C, under anoxic conditions. The grown microbial culture was subsequently introduced into the single-chambered MBFC through the available sampling ports [42].

2.10. MBFC construction and operation

In order to compare the fuel cell performances of the four different cathode catalysts, i.e. commercial Pt NPs, synthesized Pt NPs, commercial CeO2 NPs and synthesized CeO2 NRs, four separate single-chambered MBFC reactors were employed. These MBFCs (air-cathode) were fabricated from cylindrical plexiglass tube (Acharya Scientific Equipment), each possessing an inner volume of 150 ml (inner diameter: 3 cm, length: 8 cm). The chambers, after treatment in an autoclave, were assembled with the MEA. The attachment of the respective MEA was done on one end of a chamber with rubber gasket and silicon glue. The entire anode chamber (volume: 150 ml) was filled with microbial culture. The sampling ports were sealed with sterile cotton and silicon adhesive in order to prevent contamination of the anolyte. The current collector aluminum sheets, each having rectangular shape with one extended end, were placed on either side of the electrodes. The extended ends were used for establishing connections with a multimeter (Fluke Corporation, Everett, WA, USA). All fuel cell measurements were performed at 25 °C [43].

3. Results and discussion

3.1. XRD analyses

The XRD patterns obtained for the CeO2 NRs and the Pt NPs are shown in figure 1. The diffraction peaks obtained for the CeO2 NRs at 2θ values of 29.33°, 34.13° and 56.18° represent the (111), (200) and (311) planes of CeO2 NRs, respectively [44, 45]. Further, the strong diffraction peaks obtained for the Pt NPs at 2θ values of 39.81°, 45.78°, 66.71° and 80.55° correspond to the Pt(111), Pt(200), Pt(220) and Pt(311) facets, respectively [46, 47].

3.2. FESEM analyses

Figures S1(a) and (b) (supplementary materials) represent the FESEM images of the synthesized Pt NPs captured under two different magnifications (i.e. 80,000 × and 1,60,000 ×, respectively). The FESEM images of the synthesized CeO2 NRs are presented in figures S1(c) and (d) (supplementary materials), respectively, with 1,00,000 × and 1,20,000 × magnifications. It is evident from the images that while the Pt NPs are devoid of any particular or distinct shape, the CeO2 NRs exhibit rod like structure, with an average width of 6 nm to 10 nm and length of 300 nm to 400 nm. It has been suggested that because of a) higher active surface area leading to availability of higher number of active catalytic sites and b) good interconnectivity leading to better electronic conduction one dimensional materials possess higher catalytic properties over other materials [48, 49].
Therefore, it was interesting to explore whether this one-dimensional nanorod morphology of CeO₂ imparts higher electrocatalytic efficiency over that of the Pt NPs.

3.3. BET analyses
BET surface areas of CeO₂ NRs and Pt NPs have been determined from nitrogen adsorption isotherms (Quantachrome Instruments, version 11.03) (table 1). It was observed that CeO₂ NRs exhibited higher BET surface area (i.e. 271 m² g⁻¹) compared to that of Pt NPs (i.e. 193 m² g⁻¹). It was hypothesized that nanorod shape of CeO₂ could be responsible for its higher surface area. CeO₂ NRs also demonstrated higher pore radius and pore volume of 52 Å and 1.04 cm³ g⁻¹, respectively. This type of porous rod-shaped CeO₂ could be effective as cathode catalyst in MBFC because of its higher surface area [50].

3.4. CV analyses
For the purpose of determining the ORR catalytic activities of the prepared and purchased electrocatalysts, CV analyses in the three electrode Dr Bob’s cell was performed. Figures 2(a) and (b) present the CV curves (representing the 1st steady cycle) of the synthesized Pt NPs, the synthesized CeO₂ NRs, the commercial Pt NPs and the commercial CeO₂ NPs obtained in N₂ and O₂ saturated 0.1 M phosphate buffer solution respectively. Small anodic and cathodic peaks have been observed at potentials of +0.45 V and −0.05 V, respectively, in case of the synthesized Pt NPs. The intensities of these peaks were found to be flattened for the prepared CeO₂ NRs in N₂ saturated 0.1 M phosphate buffer solution (figure 2(a)). On the other hand, the commercially purchased CeO₂ NPs exhibited no such characteristic peak; while a small forward peak was observed at +0.75 V for the commercial Pt NPs. Therefore, from figure 2(a), it can be concluded that the CeO₂ NRs demonstrate superior inert behavior in N₂ atmosphere than the Pt NPs.

In figure 2(b), it was observed that in case of the synthesized CeO₂ NRs, the forward peak potential (Eᶠ) underwent a higher positive shift (∼50 mV) over that of synthesized Pt NPs (table 2). The prepared CeO₂ NRs exhibited a backward peak potential (Eᵇ), i.e. the cathodic peak, at a potential of ∼0.20 V. A negative shift of ∼150 mV was also thus obtained upon using the CeO₂ NRs compared to the Pt NPs for the ORR. This backward peak was very small in the case of the Pt NPs while it was not even observed for the CeO₂ NRs (figure 2(a)). This observation indicates that reduction of O₂ took place in presence of the catalyst. Again, it was realized that inertness towards the ORR was higher for the CeO₂ NRs than for the Pt NPs, since no characteristic cathodic peak was realized for the CeO₂ NRs in N₂ saturated 0.1 M phosphate buffer solution. In addition, the onset potential observed for the CeO₂ NRs and the Pt NPs for the reduction peak were almost equal, i.e. at the potential of ∼0.20 V. Moreover, the half-wave potential (Ehf-wheel) for the reduction region, i.e. the potential at the current density value of id/2 [51], obtained for the CeO₂ NRs and the Pt NPs were −0.05 V and 0.00 V, respectively. This result also implied a negative shift of ∼50 mV in favor of the CeO₂ NRs. Furthermore, the backward capacitive peak current density (Iac) obtained for the CeO₂ NRs was −7.95 mACm⁻², which was

| Catalysts | BET surface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Pore radius (Å) |
|-----------|--------------------------|----------------------|----------------|
| Synthesized Pt NPs | 193 | 0.35 | 31 |
| Synthesized CeO₂ NRs | 271 | 1.04 | 52 |

Table 1. BET adsorption isotherms and different parameters of the synthesized CeO₂ NRs and Pt NPs.
higher than the value produced by the Pt NPs (i.e. $-5.90 \text{ mAcm}^{-2}$) (table 2). It should be noted that, when the backward Faradic peak current density ($I_{B(F)}$) was taken into account, the synthesized CeO$_2$ NRs exhibited $-0.35 \text{ mAcm}^{-2}$ lesser current density than the Pt NPs. However, although the CeO$_2$ NRs produced slightly lesser $I_{B(F)}$ value, its overall $I_B$ was higher compared to that of the Pt NPs. Again, the potential lower cost of the CeO$_2$ NRs compared to the Pt NPs indicated that the CeO$_2$ NRs have comparatively advantageous cost-effective electrocatalytic activity towards ORR. The nanorod morphology of CeO$_2$, which resulted in higher surface area, can be attributed for this superior activity towards ORR [52]. In comparison, the commercial CeO$_2$ NPs exhibited no sharp peak (just a hump) for ORR along with the production of the capacitive and the Faradic $I_B$ values of $-5.90 \text{ mAcm}^{-2}$ and $-2.00 \text{ mAcm}^{-2}$, respectively (table 2). This implies very poor electrocatalytic activity of the commercial CeO$_2$ NPs towards ORR. On the other hand, the commercial Pt NPs showed both the capacitive and Faradic $I_B$ values of $-6.00 \text{ mAcm}^{-2}$. Note that although the Faradic $I_B$ value obtained for the commercial Pt NPs was higher compared to that of the other catalysts studied here, especially to that of the synthesized CeO$_2$ NRs, the latter is much more cost-effective. Again, the specific ordered crystal structure of CeO$_2$ NRs efficiently improves its molecular adsorption properties and electronic conductivities; thus, resulting in its good exhibition of efficacy as the cathode catalyst [53].

CV curves, representing the 100th steady cycle of all systems in O$_2$ saturated 0.1 M phosphate buffer solution, are shown in figure 3. The $I_{B(C)}$ for the synthesized Pt NPs and CeO$_2$ NRs increased to $-6.10 \text{ mAcm}^{-2}$ and $-8.10 \text{ mAcm}^{-2}$, respectively. In addition, the $I_{B(F)}$ value obtained for the synthesized Pt NPs and CeO$_2$ NRs were $-5.10 \text{ mAcm}^{-2}$ and $-4.60 \text{ mAcm}^{-2}$, respectively (table 3). On the other hand, the commercial CeO$_2$ NPs exhibited very low capacitive and Faradic $I_B$ values of $-4.00 \text{ mAcm}^{-2}$ and $-1.30 \text{ mAcm}^{-2}$, respectively. It was realized that although the commercial Pt NPs produced lower $I_{B(C)}$ value of $-7.20 \text{ mAcm}^{-2}$, it demonstrated a superior $I_{B(F)}$ ($-6.20 \text{ mAcm}^{-2}$) compared to the other catalysts studied here. This observation provided evidence towards the capability of the synthesized CeO$_2$ NRs in retaining, as well as, increasing the generated current density for a longer period [54]. In addition, in the 100th steady cycle, the forward peak current density ($I_F$) of the synthesized Pt NPs got flattened and almost disappeared. In comparison, the prepared CeO$_2$ NRs produced a higher $I_F$ value of $+7.20 \text{ mAcm}^{-2}$ than the Pt NPs (table 3). Therefore, the synthesized CeO$_2$ NRs showed comparable electrocatalytic activity towards ORR with respect to the Pt NPs. In general, the ORR follows the mechanistic pathway as presented below [55]:

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**Table 2. Summary of different parameters obtained from the 1st steady cycle of the CV curves.**

| Catalysts          | $E_C$ (V) | $E_R$ (V) | $I_F$ (mA cm$^{-2}$) | $I_{B(C)}$ (Capacitive current) (mA cm$^{-2}$) | $I_{B(F)}$ (Faradic current) (mA cm$^{-2}$) |
|---------------------|-----------|-----------|----------------------|-----------------------------------------------|----------------------------------------------|
| Synthesized Pt NPs  | +0.45     | −0.05     | +4.90                | −5.90                                         | −5.75                                         |
| Synthesized CeO$_2$ NRs | +0.50     | −0.20     | +6.00                | −7.95                                         | −5.40                                         |
| Commercial Pt NPs   | +0.40     | −0.05     | +5.75                | −6.00                                         | −6.00                                         |
| Commercial CeO$_2$ NPs | +0.50     | −0.15     | +1.00                | −5.90                                         | −2.00                                         |

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**Figure 3.** Cyclic voltammograms representing the 100th steady cycle of all the studied catalysts in O$_2$ saturated 0.1 M phosphate buffer solution at the scan rate = 50 mVs$^{-1}$.
where, ‘*’ denotes an active site.

### 3.5. POTENTIODYNAMIC POLARIZATION STUDY

In order to compare the kinetic activities of the synthesized and the commercial catalysts toward ORR, Tafel polarization analysis of the catalysts were executed following linear Tafel relation as follows [46, 56]:

\[
E = E_0 - \frac{2.303RT}{F} \log i + \frac{2.303RT}{F} \log i_0
\]

The different parameters obtained from the equation are provided in table 4, and the Tafel plots for the four catalysts have been presented in figure 4. From these potentiodynamic measurements, the Tafel slopes for the synthesized and the commercial catalysts were obtained (figure 4). The exchange current densities (I₀) for the catalysts were obtained by extrapolating the linear fitted Tafel line to the point where the overpotential value equals zero. The Tafel slope, which represents the number of electron transfer per oxygen molecule in ORR, was higher for the prepared CeO₂ NRs in comparison to the other catalysts studied here. The synthesized CeO₂ NRs also exhibited a higher value of I₀, i.e. $1.86 \times 10^{-9}$ mA cm⁻². The I₀ values obtained for the prepared and the commercial Pt NPs were between 100 to 1000 times lower compared to the CeO₂ NRs. At neutral pH, ORR follows a four-electron transfer mechanism by lowering the yield of peroxide produced. Again, a lower exchange current density has also been observed at neutral pH, as compared to the acidic or the basic pH. This is because of

### Table 3. Summary of different parameters obtained from the 100th steady cycle of the CV curves.

| Catalysts       | Eᵢ (V) | Eₐ (V) | Iᵢ (mA cm⁻²) | Iₑᵢ₋₋₀ (Capacitive current) (mA cm⁻²) | Iₑᵢ₋₋₀ (Faradic current) (mA cm⁻²) |
|-----------------|--------|--------|--------------|--------------------------------------|-----------------------------------|
| Synthesized Pt NPs | +0.30  | −0.00  | +1.75        | −6.10                                | −5.15                             |
| Synthesized CeO₂ NRs | +0.65  | −0.25  | +7.20        | −8.10                                | −4.60                             |
| Commercial Pt NPs | +0.35  | 0.00   | +2.80        | −7.20                                | −6.25                             |
| Commercial CeO₂ NPs | +0.60  | −0.20  | +2.00        | −4.00                                | −1.30                             |

### Table 4. Tafel slope, intercept and exchange current densities obtained from cyclic voltammetric studies at 1 mVs⁻¹.

| Catalysts       | Tafel slope (V dec⁻¹) | Intercept (V) | Exchange current density, I₀ (mA cm⁻²) |
|-----------------|-----------------------|---------------|---------------------------------------|
| Synthesized Pt NPs | -0.46                 | −5.02         | $1.65 \times 10^{-12}$                |
| Synthesized CeO₂ NRs | -0.62                 | −5.01         | $1.86 \times 10^{-9}$                 |
| Commercial Pt NPs | -0.54                 | −5.04         | $8.41 \times 10^{-11}$                |
| Commercial CeO₂ NPs | -0.34                 | −5.02         | $1.15 \times 10^{-16}$                |

![Figure 4](https://example.com/figure4.png)

Figure 4. Tafel plots for all the studied catalysts obtained from cyclic voltammetric studies in 0.1 M phosphate buffer solution at a scan rate of 1 mVs⁻¹.

O₂ → O₂* → OOH* → O* + OH* → 2OH* → 2H₂O

HOOH* ↔ H₂O₂

where, ‘*’ denotes an active site.
the limitations of the transfer of electrons to the protons and the hydroxyls; since, these two species are present in much lower concentrations at neutral pH, compared to the acidic or the basic pH [57].

3.6. CA analyses
The CA curves obtained for the ORR at +0.3 V versus Hg/Hg₂SO₄ on graphite electrodes modified individually with the synthesized and the commercial catalysts are shown in figure 5. The current dropped initially for all the modified electrodes owing to the formation of double layer and generation of the reactive intermediates during ORR [25, 58]. For the synthesized Pt NPs, the current drop took place up to 100 s, followed by a stable current density of about −6.15 mA cm⁻² up to 7200 s. In comparison, the commercial Pt NPs exhibited a current density of −4.95 mA cm⁻² at 7200 s. This supports that the stability of the commercial Pt NPs is much higher compared to the synthesized Pt NPs, possibly owing to the agglomeration of the latter. The current density obtained for the commercial CeO₂ NPs dropped rapidly, with a very low current density of −4.20 mA cm⁻² after 7200 s. On the other hand, the current density of the CeO₂ NRs decreased rapidly for the first 900 s followed by a gradual decrease up to the measured 7200 s, with a final exhibited value of −4.20 mA cm⁻². Thus, the improvement of the current density of the CeO₂ NRs was 32% and 16% compared to the prepared and the commercial Pt NPs, respectively.

3.7. EIS analyses
Impedance data was analysed by fitting to the equivalent circuit shown in figure 6(a). In these circuits, Rₛ, CPE and Rₜ represent the solution resistance, a constant phase element corresponding to the double layer capacitance and the charge transfer resistance associated with the ORR, respectively. Nyquist plots, obtained for the synthesized and the commercial nanocatalysts in O₂ saturated 0.1 M phosphate buffer solutions at 25 °C are presented in figure 6(b). The resultant impedance obtained for the synthesized CeO₂ NRs was lower than that obtained for the other catalysts. This result suggests that the conductivity of the synthesized CeO₂ NRs is comparatively higher than that of the commercial and the synthesized Pt NPs. The Pt NPs exhibited a higher Rₜ value (table 5), which was responsible for the deactivation of the reaction kinetics [59, 60]. The significant decrease in the charge transfer resistance (Rₜ) for the CeO₂ NRs indicates an improvement in the charge transfer kinetics on the CeO₂ NRs in phosphate buffer solution (table 5). On the other hand, a comparatively higher value of Rₛ obtained for the commercial CeO₂ NPs implies poor charge transfer kinetics, as well as, poor conductivity in phosphate buffer solution. It can be suggested that the difference in the resistance values observed for the commercial CeO₂ NPs and the synthesized CeO₂ NRs is the result of their morphological differences.

3.8. Analyses of the open circuit voltage (OCV)
The potential difference or voltage that exists between the cathode and anode of the cell in disconnected condition is the OCV of the cell [61, 62]. The OCV of the single-chambered MBFCs, comprising of the synthesized cathode nanoelectrocatalysts, was measured without application of any external resistance. The obtained results are presented in figure 7. With increase in time, the OCV of both MBFCs increased and reached their respective maximum values. The oxidation of the fuel substrate by the microorganisms is a comparatively slower process than any chemical oxidation reaction. As a result, it usually takes an adaption time of ~2 days to 3 days for improving its metabolic activity. After this adaption time, a linear increase in the OCV was realized. The
OCV of the MBFC that contained the synthesized Pt NPs reached a maximum value of +0.70 V on the 14th day of its operation. This MBFC maintained its OCV peak from the 12th to the 15th day of its operation. In comparison, the MBFC employing the commercial Pt NPs and CeO$_2$ NPs as cathode catalysts exhibited maximum OCV values of +0.80 V (14th day of operation) and +0.50 V (15th day of operation), respectively.

For comparison the MBFC based on the synthesized CeO$_2$ NRs exhibited a maximum OCV value of +0.80 V on the 14th day of its operation and maintained its OCV peak from the 12th to the 18th day of its operation. AgNPs/rGO and AgNPs synthesized by Sun et al exhibited comparable OCV of +0.78 V and +0.61 V, respectively [63]. The higher OCV of CeO$_2$ NRs for a longer period of time is again consistent with their improved performance in MBFCs.

### 3.9. Analyses of the MBFC performance

The electrochemical studies presented so far on the synthesized and the commercial nanocatalysts at 25 °C suggest that the CeO$_2$ NRs cathode catalyst possessed better electrocatalytic activity compared to the synthesized Pt NPs cathode catalyst. Although the $I_{RFP}$ value for both the synthesized and the commercial Pt NPs were higher compared to the synthesized CeO$_2$ NRs, the overall current density, stability, resistance and cost made the

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**Figure 6.** (a) Equivalent circuit for the ORR and (b) Nyquist plots obtained for all the studied catalysts at $-0.3$ V (versus Ag/AgCl) at 25 °C.

**Table 5.** EIS parameters obtained from the impedance curves of the studied cathode catalysts.

| EC/EIS parameters | Synthesized Pt NPs | Synthesized CeO$_2$ NRs | Commercial Pt NPs | Commercial CeO$_2$ NPs |
|-------------------|-------------------|------------------------|-------------------|------------------------|
| $R_s$ (Ω)         | 1.9               | 2.6                    | 2.1               | 2.0                    |
| $R_{ct}$ (Ω)      | 20.3              | 18.1                   | 18.9              | 25.4                   |

**Figure 7.** OCVs obtained for all the studied cathode catalysts in single-chambered MBFCs.

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synthesized CeO₂ NRs a superior cathode catalyst. Based on these promising results, the practical applicability of CeO₂ NRs as cathode catalyst was finally tested in a single-chambered MBFC. For comparison, three other single-chambered MBFC, composed of the commercial Pt NPs, the synthesized Pt NPs and the commercial CeO₂ NPs cathode catalysts, were operated under similar operating conditions. The four MBFCs were operated in batch modes for about 30 days using mixed microbial cultures as the substrate. The polarization curves and power density plots from these four MBFCs are shown in figure 8. External resistances ranging from 10 MΩ to 1 Ω were applied in order to evaluate the performance (power densities and current densities) of the MBFCs. The MBFC containing the synthesized Pt NPs as the cathode catalyst exhibited a maximum current density of 2857 mAm⁻² at +0.3 V, and a corresponding maximum power density of 857 mWm⁻². On the other hand, the MBFC employing the commercial Pt NPs as the cathode catalyst exhibited a maximum current density of 3097 mAm⁻² at +0.3 V and a corresponding maximum power density of 929 mWm⁻². In comparison, the MBFC containing the commercial CeO₂ NPs as the cathode catalyst exhibited a very low maximum current density value of 1351 mAm⁻² at +0.3 V with a corresponding power density value of 405 mWm⁻². In contrast, the MBFC based on the CeO₂ NRs showed a maximum current density value of 3613 mAm⁻² at +0.3 V and corresponding power density value of 1084 mWm⁻². Sun et al synthesized a silver nanoparticles/reduced graphene oxide composite, which produced a maximum power density of 474.5 mWm⁻², in comparison to the pristine silver nanoparticles that showed a maximum power density of 186.7 mWm⁻² in phosphate buffer solution (pH = 7) [63].

3.10. Cost analysis
The superior catalytic performance of the synthesized CeO₂ NRs cathode catalyst over that of the Pt NPs cathode catalyst in MBFCs has been unambiguously established in this work. However, another critical aspect is the cost involved in the synthesis of the new catalyst, since, as noted in the introduction section, an alternative catalyst should not only demonstrate higher efficiency but also possess significantly lower cost compared to the traditionally used Pt cathode catalyst system. Therefore, a preliminary cost analysis of the catalyst materials has been performed. The overall expense involved in the synthesis of the catalyst nanoparticles, taking into account the cost of the chemicals used and the energy consumption during the entire process (i.e. reduction, ultrasonication, stirring, filtration, cooling, washing and drying) for CeO₂ NRs was in the range US$ 7 to 10 per gram. On the other hand, the cost of the synthesized Pt NPs was in the range US$ 30 to 33 per gram. Again, the cost of the commercially purchased Pt NPs [Sigma Aldrich (St Louis, MO, USA), CAS Number 7440-06-4] was US$ 197 per gram. Finally, the cost of the commercially purchased CeO₂ NPs (Sigma Aldrich (St Louis, MO, USA), CAS Number 1306-38-3) was US$ 13 per gram. Therefore, a considerable reduction in the cathode catalyst cost can be realized upon using the CeO₂ NRs in place of the commercially available Pt NPs.

4. Conclusions
The synthesized cathode electrocatalyst, CeO₂ NRs, demonstrated superior electrocatalytic activity and stability, in terms of forward peak current density, over that of the synthesized and the commercial Pt NPs, as well as, the commercial CeO₂ NPs, owing to their nanorod morphology that exhibited enhanced electrochemically active surface area and reduced impedance. In addition, the prepared low-cost CeO₂ NRs, when employed as a cathode...
catalyst in a single-chambered MBFC, also showed improvements in the generation of OCV and the output current and power densities in comparison to the commercial and the synthesized Pt NPs, as well as, the commercial CeO₂ NPs.

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Declarations of interest

None.

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References

[1] Dutta K and Kundu P P 2018 Progress and Recent Trends in Microbial Fuel Cells 1st edn (Amsterdam: Elsevier) (https://doi.org/10.1016/C2016-0-04695-4)
[2] Dutta K and De S 2017 Aromatic conjugated polymers for removal of heavy metal ions from wastewater: a short review Environ. Sci. Water Res. Technol. 3 793–805
[3] RabaeY and Verstreeete W 2005 Microbial fuel cells: novel biotechnology for energy generation Trends Biotechnol. 23 291–8
[4] Das S, Dutta K and Rana D 2018 Polymer electrolyte membranes for microbial fuel cells: a review Polym. Rev. 58 610–29
[5] Zhang F, Ge Z, Gimaud J, Hurst J and He Z 2013 Long-term performance of litre-scale microbial fuel cells treating primary effluent installed in a municipal wastewater treatment facility Environ. Sci. Technol. 47 6941–8
[6] Kumar S S, Kumar V, Malvan S K, Sharma J, Mathimani T, Maskarenj M S, Ghosh P C and Pugazhendhi A 2019 Microbial fuel cells (MFCs) for bioelectrochemical treatment of different wastewater streams Fuel 254 115520
[7] Logan B E, Call D, Cheng S, Hamelers H V M, Sletet J, H J, Jeremiase A and Rozendal R A 2008 Microbial electrolysis cells for high yield hydrogen gas production from organic matter Environ. Sci. Technol. 42 8630–40
[8] Kumar G, Mathimani T, Rene E R and Pugazhendhi A 2019 Application of nanotechnology in dark fermentation for enhanced biogas production using inorganic nanoparticles International Journal of Hydrogen Energy 44 13106–13
[9] Mehanna M, Saito T, Yano T, Hickner M, Cao X, Huang X and Logan B E 2010 Using microbial desalination cells to reduce water salinity prior to reverse osmosis Energy Environ. Sci. 3 11114–20
[10] Chang I S, Jang J K, Gil G C, Kim M, Kim H J, Cho B W and Kim B H 2004 Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor Biosens. Bioelectron. 19 607–13
[11] Heijne A T, Liu F, Weijsen D V D, Weijma J, Buisman C J N and Hamelers H V M 2010 Copper recovery combined with electricity production in a microbial fuel cell Environ. Sci. Technol. 44 6376–81
[12] Kumar S S, Kumar V, Kumar R, Malvan S K and Pugazhendhi A 2019 Microbial fuel cells as a sustainable platform technology for bioenergy, biosensing, environmental monitoring, and other low power device applications Fuel 255 115682
[13] Dutta K and Kundu P P 2014 A review on aromatic conducting polymers-based catalyst supporting matrices for application in microbial fuel cells Polym. Rev. 54 401–35
[14] Cheng S, Liu H and Logan B E 2006 Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Naion and PTFE) in single chamber microbial fuel cells Environ. Sci. Technol. 40 364–9
[15] Logan B E, Hamelers B, Rozendal R, Schroder U, Keller J, Freguia S, Aelterman P, Verstreeete W and RabaeY K 2006 Microbial fuel cells: methodology and technology Environ. Sci. Technol. 40 5181–92
[16] Neelakandan S, Kanagaraj P, Nagendran A, Rana D, Matsuura T and Muthumeenal A 2015 Enhancing proton conduction of sulfonated poly (phenylene ether ether sulfone) membrane by charged surface modifying macromolecules for H₂/O₂ fuel cells, Renew. Energ. 78 306–13
[17] Wang B 2005 Recent development of non-platinum catalysts for oxygen reduction reaction J. Power Sources 152 1–15
[18] Yu E H, Cheng S, Scott K and Logan B 2007 Microbial fuel cell performance with non-Pt cathode catalysts J. Power Sources 171 275–81
[19] Das S, Dutta K, Shul Y G and Kundu P P 2015 Progress in developments of inorganic nanocatalysts for application in direct methanol fuel cells Crit. Rev. Solid State Mater. Sci. 40 316–57
[20] Das S, Dutta K and Kundu P P 2016 Sulfonated polypropylene matrix induced enhanced efficiency of Ni nanocatalyst for application as an anode material for DMFCs Mater. Chem. Phys. 176 143–51
[21] Das S, Dutta K, Kundu P P and Bhattacharya S K 2018 Nanostructured polyaniline: an efficient support matrix for platinum-ruthenium anode catalyst in direct methanol fuel cell Fuel Cells 18 369–78
[22] Wu Z S, Yang S, Sun Y, Parvez K, Feng X and Mullen K 2012 3D nitrogen-doped graphene aerogel-supported Fe₃O₄ nanoparticles as efficient electrocatalysts for the oxygen reduction reaction J. Am. Chem. Soc. 134 9082–5
[23] Ishihara A, Ohgi Y, Matsuzawa K, Mitsushima S and Ota K-I 2010 Progress in non-precious metal oxide-based cathode for polymer electrolyte fuel cells Electrochim. Acta 55 8003–12
[24] Ahmed J, Yuan Y, Zhou L and Kim S 2012 Carbon supported cobalt oxide nanoparticles–iron phthalocyanine as alternative cathode catalyst for oxygen reduction in microbial fuel cells J. Power Sources 208 170–5
[25] Morozan A, Jousselme B and Palacin S 2011 Low-platinum and platinum-free catalysts for the oxygen reduction reaction at fuel cell cathodes Environ. Sci. 4 1238–54
[26] Liu X-W et al 2010 Nano-structured manganese oxide as a cathodic catalyst for enhanced oxygen reduction in a microbial fuel cell fed with a synthetic wastewater Water Res. 44 5298–305
[27] Liew K B, Daud W R W, Ghasemi M, Leong J X, Lim S S and Ismail M 2014 Non-Pt catalysts as oxygen reduction reaction in microbial fuel cells: a review Int. J. Hydrogen Energy 39 4870–83
[28] Yu S, Liu Q, Yang W, Han K, Wang Z and Zhu H 2013 Graphene–CeO$_2$ hybrid support for Pt nanoparticles as potential electrocatalyst for direct methanol fuel cells Electrochim. Acta 94 245–51
[29] Yu H B, Kim J H, Lee H I, Schiob M A, Lee J, Han J, Yoon S P and Ha H Y 2005 Development of nanophase CeO$_2$–Pt/C cathode catalyst for direct methanol fuel cell J. Power Sources 140 59–65
[30] Zhang L, Liu C, Zhuang L, Li W, Zhou S and Zhang J 2009 Manganese dioxide as an alternative cathodic catalyst to platinum in microbial fuel cells Biosens. Bioelectron. 24 2825–9
[31] Li X, Hu B, Subi P, Rei Y and Li B 2011 Electricity generation in continuous flow microbial fuel cells (MFCs) with manganese dioxide (MnO$_2$) cathodes Biochem. Eng. J. 54 10–5
[32] Mukherjee P, Roy P S, Mandal K, Bhattacharjee D and Bhattacharya S K 2015 Improved catalysis of room temperature synthesized Pd–Cu alloy nanoparticles for anodic oxidation of ethanol in alkaline media Electrochim. Acta 154 447–55
[33] Mandal K, Bhattacharjee D, Roy P S, Bhattacharya S K and Dasgupta S 2015 Room temperature synthesis of Pd–Cu nanoalloy catalyst with enhanced electrocatalytic activity for the methanol oxidation reaction Appl. Catal. A 492 100–6
[34] Chowdhury S R, Mukherjee P and Bhattacharya S K 2016 Palladium and palladium-copper alloy nano particles as superior catalyst for electrochemical oxidation of methanol for fuel cell applications Int. J. Hydrogen Energy 41 17072–83
[35] Dutta K, Das S and Kundu P P 2016 Polyamine nanowhiskers induced low methanol permeability and high membrane selectivity in partially sulfonated PVdF–co–HFP membranes RSC Adv. 6 107069–d–HFP membranes RSC Adv. 6 107069–d–HFP membranes
[36] Dutta K, Das S and Kundu P P 2016 Effect of the presence of partially sulfonated polyamine on the proton and methanol transport behavior of partially sulfonated PVdF membrane Polym. J. 48 301–9
[37] Dutta K, Das S and Kundu P P 2016 Highly methanol resistant and selective ternary blend membrane composed of sulfonated PVdF–co–HFP, sulfonated polyamine and nafion J. Polym. Sci. 133 43294
[38] Das S, Kumar P, Dutta K and Kundu P P 2014 Partial sulfonation of PVdF–co–HFP: a preliminary study and characterization for application in direct methanol fuel cell Appl. Energy 113 169–77
[39] Das S, Dutta K and Kundu P P 2016 Electrocatalytic potential of sulfonated polypropylene-supported Ni–Ag towards methanol oxidation in acidic medium 21st Century Energy Needs – Materials, Systems and Applications (ICTPCEN) (India: Khuragpur) (https://doi.org/10.1109/ICTPCEN.2016.0852738)
[40] Das S, Dutta K and Kundu P P 2015 Nickel nanocatalysts supported on sulfonated polyamine: potential toward methanol oxidation and as anode materials for DMFCs J. Mater. Chem. A 3 11349–57
[41] Kumar V, Nandy A, Das S, Salahuddin M and Kundu P P 2015 Performance assessment of partially sulfonated PVdF–co–HFP as polymer electrolyte membranes in single chambered microbial fuel cells Appl. Energy 137 310–21
[42] Nandy A, Kumar V, Mondal S, Dutta K, Salah M and Kundu P P 2015 Performance evaluation of microbial fuel cell: effect of varying electrode configuration and presence of a membrane electrode assembly New Biotechnol. 32 727–81
[43] Papiya F, Nandy A, Mondal S and Kundu P P 2017 Co/C$_x$/Al$_2$O$_3$–GO nanocomposite as cathode electrocatalyst for superior oxygen reduction in microbial fuel cell applications: the effect of nanocomposite composition Electrochem. Acta 254 1–13
[44] Jiang H, Yu C, Huang Z and Zhu H 2009 Oxide (SnO$_2$, CeO$_2$, Co$_3$O$_4$, and NiO)–promoted Pt/C electrocatalysts for PEMFCs J. Electrochem. Soc. Trans. 17 347–58
[45] Sisubalan N, Ramkumar V S, Pugazhendhi A, Karthikeyan C, Indira K, Gopinath K, Hameed A S H and Basha M H G 2018 ROS-mediated cytotoxic activity of ZnO and CeO$_2$ nanoparticles synthesized using the Rubia cordifolia L leaf extract on MG-63 human osteosarcoma cell lines Environ. Sci. Pollut. Res. 25 10482–92
[46] Banik S, Mahajan A, Chowdhury S R and Bhattacharya S K 2016 Improved and synergistic catalysis of single-pot-synthesized Pt–Ni alloy nanoparticles for anodic oxidation of methanol in alkalai RSC Adv. 6 93490–501
[47] Das S and Kundu P P 2015 Pt–Ru/Al$_2$O$_3$–C nanocomposites as direct methanol fuel cell catalysts for electrooxidation of methanol in acidic medium RSC Adv. 5 93539–46
[48] Zhou Z–Y, Tian N, Li J–T, Broadwell I and Sun S–G 2011 Nanomaterials of high surface energy with exceptional properties in catalysis and energy storage Chem. Soc. Rev. 40 4167–85
[49] Liu J et al 1998 Fullerene pipes Science 280 1233–6
[50] Papiya F, Das S, Pattanayak P and Kundu P P 2019 The fabrication of silane modified graphene oxide supported Ni–Co bimetallic electrocatalysts: a catalytic system for superior oxygen reduction in microbial fuel cells Int. J. Hydrogen Energy 44 25874–93
[51] Wu G, More K L, Johnston C M and Zelenay P 2011 High-performance electrocatalysts for oxygen reduction derived from polyamine, iron, and cobalt Science 332 443–7
[52] Kumar P S M, Thiripuranthagan S, Imai T, Kumar G, Pugazhendhi A, Vijayan S R, Esparza R, Abe H and Krishnan S K 2017 Pt nanoparticles supported on mesoporous CeO$_2$ nanostuctures obtained through green approach for efficient catalytic performance toward ethanol electro–oxidation, ACS Sustain. Chem. Eng. 5 11290–9
[53] Wang Y, Li J and Wei Z 2018 Transition–metal–oxide–based catalysts for the oxygen reduction reaction J. Mater. Chem. A 6 8194–209
[54] Cao R, Thapa R, Kim H, Xu X, Kim M G, Li Q, Park N, Liu M and Cho J 2013 Promotion of oxygen reduction by a bio-inspired tethered iron phthalocyanine carbon nanotube-based catalyst Nat. Commun. 4 2076
[55] Gu W, Hu L, Li J and Wang E 2018 Recent advancements in transition metal–nitrogen–carbon catalysts for oxygen reduction reaction Electrochim. Acta 30 1217–28
[56] Mahajan A, Banik S, Roy P S, Chowdhury S R and Bhattacharya S K 2017 Kinetic parameters of anodic oxidation of methanol in alkalai: effect of diameter of Pd nano–catalyst, composition of electrode and solution and mechanism of the reaction Int. J. Hydrogen Energy 42 21623–78
[57] Rojas-Carbonell S, Artysuschkova K, Serov A, Santoro C, Matanovic I and Atanasov P 2018 Effect of pH on the activity of platinum group metal–free catalysts in oxygen reduction reaction ACS Catal. 8 3041–53
[58] Sidik R A, Anderson A B, Subramanian N P, Kamaruguru S P and Popov B N 2006 O$_2$ reduction on graphite and nitrogen–doped graphene: experiment and theory J. Phys. Chem. B 110 1787–93
[59] Bondarenko A S, Stephens I E L, Hansen H A, Pérez-Alonso F J, Tripkovic V, Johansson T P, Rossmeisl J, Nørskov J K and Chorkendorff I 2011 The Pt(111)/electrolyte interface under oxygen reduction reaction conditions: an electrochemical impedance spectroscopy study Langmuir 27 2058–66

[60] Genies L, Bultel Y, Faure R and Durand R 2003 Impedance study of the oxygen reduction reaction on platinum nanoparticles in alkaline media Electrochim. Acta 48 3879–90

[61] Qi Z and Buelte S 2006 Effect of open circuit voltage on performance and degradation of high temperature PBI-H3PO4 fuel cells J. Power Sources 161 1126–32

[62] You S, Zhao Q, Zhang J, Jiang J and Zhao S 2006 A microbial fuel cell using permanganate as the cathodic electron acceptor J. Power Sources 162 1409–15

[63] Sun H, Xu K, Lu G, Lv H and Liu Z 2014 Graphene–supported silver nanoparticles for pH-neutral electrocatalytic oxygen reduction IEEE Trans. Nanotechnol. 13 789–94