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ORIGINAL PAPER

Fouling resistant nitrogen doped carbon powder with amino-tri-methylene-phosphate cathode for microbial fuel cell

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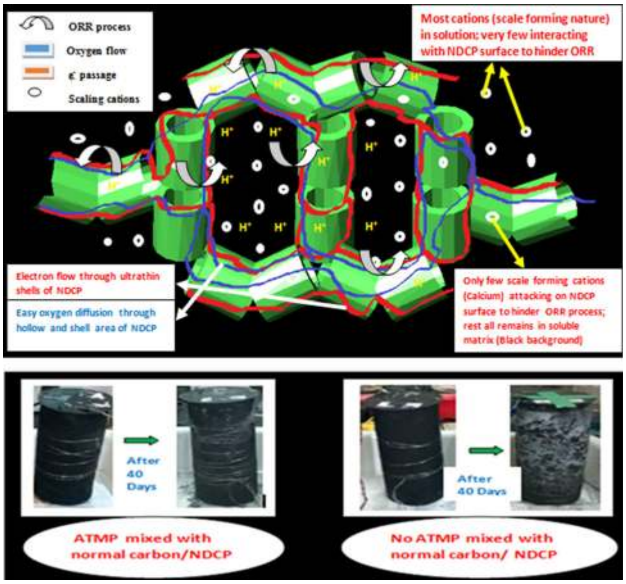
Abstract Long term stable performance of a microbial fuel cell (MFC) is difficult to achieve because of scale formation on cathode. Nitrogen doped carbon powder (NDCP) was used as cathode along with amino-tri-methylene-phosphate (ATMP) as an anti-scaling agent in a MFC. Maximum power density of 66 mW/m^2 obtained in the MFC using NDCP as cathode, was 2.2 times higher than that obtained with simple carbon powder. High electroactive surface area and meso-porous structure of the NDCP improved electrochemical performance of the MFC having NDCP cathode. After 40 days of operation, the maximum power density decreased by only 12.5% in the MFC using NDCP and having ATMP in its cathode as compared to a 55.6% decrease in the MFC using only carbon powder in cathode due to fouling. Ultrathin shell structure of NDCP catalyst molecules, as evident from transmission electron microscopy (TEM) images, ensured high catalyst performance providing good electron transfer for enhancing oxygen reduction reaction (ORR). Less deposition of calcite molecules on cathode surface, illustrated via X-ray diffraction (XRD) after 40 days of operation, clearly reveals high anti-fouling property of ATMP as a cathode material. ATMP being a commercial anti-scaling agent has inherent chelation properties to stop chemical fouling and thus helped in demonstrating stable long term performance of cathode in the MFCs. NDCP along with ATMP could be used for fabrication of a cost effective fouling resistant cathode for long term use by increasing ORR in MFCs to achieve stable power generation by minimizing scale formation on cathode and effective wastewater treatment simultaneously.

Graphical abstract



Keywords Cathode fouling · Microbial fuel cell · Nitrogen doped carbon · Oxygen reduction reaction

Introduction

Ability of microbial fuel cells (MFCs) to simultaneously generate electricity while treating wastewater has made it an attractive option for sustainable wastewater treatment. However, efficiency of a MFC still needs considerable

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improvement and fabrication cost of it needs to be reduced to consider it as a commercially viable option. Power production in a MFC mainly depends on its configuration, electrode material and proton exchange membrane (PEM), type of substrate and inoculum used, and operating conditions such as temperature and pH [1]; and it is limited by the overpotential of oxygen reduction reaction (ORR) at the cathode [2]. To reduce the production cost of MFC, expensive PEM has been replaced by clay-ware ceramic separator and it has been used by several researchers [1, 3]. Air cathode MFCs are more sustainable than aqueous cathode MFCs, because the former use passive oxygen transfer to provide oxygen at the cathode as an electron acceptor [2].

To reduce overpotential of ORR, catalyst is often used on cathode [4]. Platinum (Pt) is the most expensive and frequently used catalyst [2]. The catalysts generally used in air cathode MFC can be grouped into three types: noble metal catalyst, non-noble metal catalyst and modification of carbon materials [4]. Nitrogen doped carbon powder is also reported to have high catalytic activity for ORR [2, 5].

Fouling of air–cathode and consequent deterioration in cathode performance is a typical problem faced by researchers [6]. In particular, while using air cathode MFC with ceramic separators, the problem of fouling of cathode due to scaling is more pronounced [7]. The most common reason for fouling is scaling due to deposition of organic and inorganic materials and biofouling [8]. A thick layer of carbonate forms as a consequence of the alkalinity, induced by the ORR on cathodes operated for long time in MFCs, which deactivates the cathodic reaction sites of the MFC [9, 10]. Although some attempts have been made to remove biofouling [7], but researchers such as Choi, Chae [11] observed that biofouling has less influence on deterioration of performance of MFC. Very few studies have focused on inorganic scale formation on cathode surface and its removal.

In the present study, the feasibility of using nitrogen doped carbon powder (NDCP) as cathode and amino-tri-methylene-phosphate (ATMP) as anti-scaling agent (ASA) in a cylindrical clay-ware MFC for long term stable electricity generation with simultaneous accomplishment of wastewater treatment has been investigated. The electrocatalytic activities of the NDCP and ATMP were studied using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) and then the performance of the MFCs using these materials was evaluated and compared in terms of wastewater treatment, Coulombic efficiency, electricity generation and polarization behaviours.

Materials and methods

Synthesis of nitrogen doped carbon powder (NDCP)

Carbon powder (Vulcan XC, 200 mg) was immersed in 1 M di-ammonium hydrogen phosphate solution and it was sonicated for an hour before stirring the same for 24 h at room temperature. The solution was filtered using glass fibre filter paper (0.45 μ) and the filtrate was kept in hot air oven at 106 °C for 12 h. After drying, it was kept in muffle furnace at 480 °C for 3 h, where a fine layer of NDCP was obtained. Finally 6 M HCl solution was added to the powder to remove any impurities, if present, and it was pressure filtered using glass fibre filter paper of pore size 0.45 μ. The filtrate thus obtained was further rinsed with de-ionized water till the filtered solution became neutral. The solid pellets recovered were dried in oven at 120 °C for 24 h.

MFC construction

Four single chambered MFCs were fabricated using cylindrical clay-ware pots having anodic chamber volume of 300 mL. Carbon felt (Zoltex panex 35®, Inc., USA) of projected surface area of 224 cm^2 was used as the anode material in all the MFCs, placed on the inner side of the clay-ware cylinder wall facing the solution side. SS 316 grade stainless steel wire woven as a mesh in the felt was used as anodic current collector.

The various cathode materials impregnated over the air side of the clay-ware cylinders were (1) Vulcan XC (CB) with anti-scaling agent (ASA) and amino-tri-methylene-phosphate (ATMP) (2) Nitrogen doped treated carbon powder (NDCP) with ATMP, (3) Vulcan XC (CB) without ASA, and (4) Nitrogen doped treated carbon powder without ASA (i.e. ATMP), (Table 1). Normal carbon powder or nitrogen doped carbon powder was coated using a spray gun on the air facing side of the respective MFCs with a loading of 0.5 mg/cm^2. Vulcan XC carbon powder (95 mg) was mixed with 3 mL of 5% ATMP solution and 10 mL of acetone for ASA-CB cathode in MFC-1. For ASA-NDCP cathode of MFC-2, Vulcan XC carbon powder was replaced with NDCP. Similarly, Vulcan XC carbon powder with same loading rate as above was added to 10 mL acetone without ATMP solution, to prepare ink for cathodes of MFC-3 and NDCP was added to acetone without ATMP for making cathode of MFC-4 (Table 1). Polydimethyl siloxane (PDMS) of volume 0.76 mL and strength 5% was added to each of the ink solutions as the binder material and finally the ink solution volume was made up to 25 mL using acetone. The prepared solution was sonicated for 2 h before it became ready for spraying

Table 1 Cathode description of MFCs used in the study

MFC	Cathode type	Anti-scaling agent	Proton mass transfer coefficient × 10^6 (cm/s)
MFC-1	CB (Vulcan XC) + ASA	ATMP (5%, 3 ml sol)	3.98
MFC-2	ASA + NDCP	ATMP (5%, 3 ml sol)	5.83
MFC-3	CB (Vulcan XC)	No ASA	1.75
MFC-4	NDCP	No ASA	2.83

on the air facing side of the clay-ware cylinder. After spraying with the prepared ink, the cylinders were heat treated in oven at 105 °C for 10–15 min to remove any volatile organic matter, if present. Stainless steel wire (SS 316) was used as the cathodic current collector and it was wrapped uniformly along the external surface of the inked cylindrical clay-wares. Finally, the electrodes were connected through concealed copper wires through an external resistance of 100 Ω.

Operation of MFCs

For inoculum, 30 mL of mixed anaerobic sludge collected from septic tank was used in the anodic chamber after heating it for 15 min [12]. The sludge contained 15 g/L of volatile solids. For the feed, synthetic wastewater having chemical oxygen demand (COD) of 3000 mg/L was used, where acetate acted as a carbon source. The acetate medium also contained (per gram of COD) $NaHCO_3$, 1500 mg; NH_4Cl, 318 mg; $CaCl_2 \cdot 2H_2O$, 250 mg; $MgSO_4 \cdot 7H_2O$, 64 mg; K_2HPO_4, 27 mg; and KH_2PO_4, 9 mg. Trace metals were added as $FeSO_4.6H_2O$, 10.00 mg/L; $MnSO_4$, 0.526 mg/L; $ZnSO_4 \cdot 7H_2O$, 0.106 mg/L; H_3BO_3, 0.106 mg/L; and $CuSO_4 \cdot 5H_2O$, 4.5 µg/L, $CoCl_2$, 105.2 µg/L, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 105.2 µg/L. All four MFCs were operated for 12 cycles with each cycle being of 4 days. All MFCs were operated under temperature range of 35–39 °C, and fresh feed was given after the end of every cycle by decanting 50 mL of anolyte.

Analysis and calculation

Performance of MFC was measured in terms of voltage and current generated using data acquisition unit (Agilent technologies, Malaysia). Each day open circuit voltage (OCV) and operating voltage (OV) were measured. For OCV measurement, resistance was disconnected from the working/operating circuit for 1.5 h and reading was noted followed by the anode potential measurement using Ag/AgCl reference electrode (+197 mV vs. SHE, Bioanalytical Systems Inc., USA). Power was calculated by the formula $P = VI$, where P is Power in mW, V is voltage in mV and I is current in A. The Coulombic efficiency (CE) was calculated as the part of coulombs actually transferred to the anode to that of theoretically present in the substrate for current generation over the time period as given by Eq. 1.

$$\mathrm{CE} = M \int_0^{tb} \frac{I dt}{Fbv \Delta \mathrm{COD}} \tag{1}$$

where, $M = 32$, the molecular weight of oxygen; I, is the current generated; F is Faraday's constant; $b = 4$, is the number of electrons exchanged per mole of oxygen; v is the volume of liquid in the anodic compartment; and Δ COD is the change in COD over time tb.

After six cycles, when operating cell potential got stabilized, polarization analysis was done by varying external resistance from 10,000 to 10 Ω using resistance box (GEC 05 R Decade Resistance Box, India). Internal resistance of MFCs was measured by determining the slope of voltage vs. current plot [13]. Polarization was repeated when fouling started to occur on the cathodes after ten cycles of operation.

Oxidation reduction property of the cathode was studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) tests for these four MFCs using AUTOLAB (AUT58696, Metrohm) and NOVA 1.9 software. Scanning rate for voltammetry was kept at 10 mV/s. The impedance measurements were carried out in a frequency range of 100 kHz to 100 mHz with an AC signal of 5 mV amplitude. 1 M KCl solution was used as the catholyte solution for performing CV, LSV and EIS for cathodic half-cell. Cathode acted as the working electrode, Ag/AgCl electrode (+197 mV vs. SHE, Bioanalytical Systems Inc., USA) was used as reference electrode and a platinum wire was used as the counter electrode. The catalyst material was characterized by electro diffraction spectroscopy (EDX), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) adsorption isotherm tests and cathode scaling was quantified by X-ray diffraction (XRD) analysis. Wastewater COD, volatile solids (VS) of sludge and pH were measured as per Standard Methods [14]. Proton mass transfer coefficients for the different separators, after coating with different carbon powders, were abiotically determined with one chamber filled with de-ionized water (pH ≈ 6.8) and using 0.1 M NaOH solution with pH of

10.5 in other chamber as described by Ghadge and Ghangrekar [15].

Results and discussion

Characterization of catalyst

The structure of the NDCP catalyst composite is imaged by TEM (Fig. 1). It is evident from the TEM images that NDCP possesses a typical core–shell type structure. During the mixing process of the Vulcan XC-72R carbon powder in di-ammonium hydrogen phosphate solution (nitrogen source), the filtrate exposure at high temperature could be the reason for nitrogen atom encapsulating the catalyst surface. Framework of structure is indicated in Fig. 1c, where the nanoparticle molecules are interconnected with each other via the thin shells of each molecule of approximate thickness of 5 nm. Such unique structure of the catalyst possessing ultrathin shell, might be useful in achieving excellent cycling stability, which makes the structure suitable for electrode materials for longer period of operation. EDX scans confirmed that NDCP consists only of carbon (89.10%), nitrogen group (4.25%), and oxygen (6.65%). BET test indicated that NDCP had a surface area of around 211 m^2/g.

Wastewater treatment and Coulombic efficiency

The average soluble COD removal efficiencies were 81.01 ± 4.35, 76.01 ± 3.08, 80.94 ± 2.99 and 77.84 ± 4.70% for MFC-1, MFC-2, MFC-3 and MFC-4, respectively (Fig. 2a). These results indicate that nitrogen doping on the cathode did not influence the COD removal efficiency much. Similar trend was observed by Ahn et al. [2], who used meso-porous nitrogen-rich carbon as cathode catalyst and compared its performance with platinum and observed that COD removal was almost same for all cathodes.

The CE was 13.06 ± 2, 17.34 ± 4, 10.12 ± 1, and 15.78 ± 3% for MFC-1, MFC-2, MFC-3, and MFC-4, respectively (Fig. 2a). CE in MFC-3 using untreated carbon powder was similar to previously reported values obtained by Chatterjee, Ghangrekar [16], where clay-ware air–cathode MFCs were used. Use of anti-scaling agent ATMP in MFC-1 resulted in significantly higher CE than MFC-3, because of good proton conductivity of ATMP maintained by the acid functional group in it. Also, use of ATMP increased the operating voltage in MFC-1 when used with normal carbon powder by around 23% as compared to MFC-3. Maximum CE in MFC-2 can be attributed to two kinds of mechanism, one being proton conduction via H^+-$H_2PO_4^-$ or H^+-HPO_4^{2-}, second being that, as ATMP molecule was protonated by di-ammonium hydrogen phosphate doped in carbon powder, more ATMP molecules participated into the proton conduction gateway [17]. Advantage of using NDCP is evident from the CE difference obtained in MFC-3 and MFC-4. The procedure used for nitrogen doping also activated the carbon powder and increased active surface area for ORR. The increased CE in MFC-4 than MFC-3 and MFC-2 than MFC-1, highlights the importance of chemical activation due to nitrogen doping and increase in active surface area for ORR [17].

Electricity generation

Stable operating voltage was obtained in all four MFCs after 8 days of operation (Fig. 2b). Maximum OV of 259 ± 11 mV was observed for MFC-4, where treated carbon powder was used as the cathode material without anti-scaling agent (Table 2); which was almost 1.5 times higher than MFC-3 where carbon powder without any treatment was used as the cathode material. Use of ATMP though increased the operating voltage in MFC-1 when used with normal carbon powder, but its use reduced the operating voltage when used with NDCP in MFC-2 to some extent. Lowest operating voltage was observed in MFC-3 using normal carbon powder as cathode without having any anti-scaling agent. This voltage is similar to previously reported values obtained from clay-ware air–cathode MFCs [7].

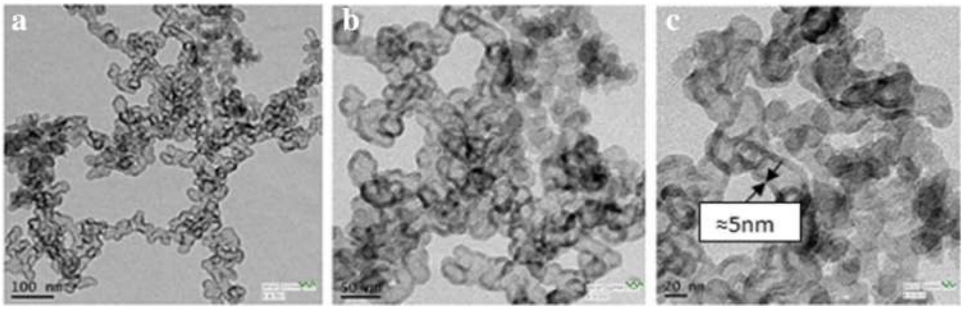


Fig. 1 TEM image of **a** 100, **b** 50, **c** 20 mm scale (indicated inside figure) of NDCP catalysts, respectively

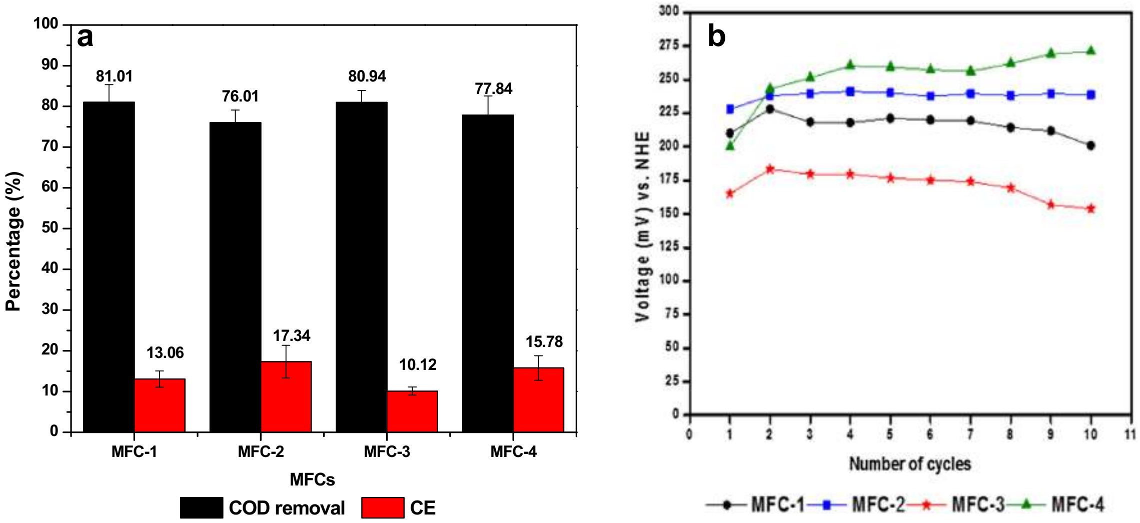


Fig. 2 **a** COD removal and CE of MFCs, **b** Operating Voltage of the MFCs

Table 2 Performance of the MFCs

Parameters	MFC-1	MFC-2	MFC-3	MFC-4
Operating voltage (mV)	221.38 ± 6.86	241.75 ± 7.10	174.56 ± 8.46	258.89 ± 11.18
COD removal	81.01 ± 4.35%	76.01 ± 3.08%	80.94 ± 2.99%	77.84 ± 4.70%
Coulombic efficiency (CE)	13.06 ± 2.08%	17.34 ± 4.13%	10.12 ± 1.11%	15.78 ± 3.28%
Max. power density after six cycles	33 mW/m^2	48 mW/m^2	30 mW/m^2	66 mW/m^2
Max. power density after ten cycles	30.02 mW/m^2	41.55 mW/m^2	13.47 mW/m^2	34.51 mW/m^2
Internal resistance after six cycles	47.80 Ω	42.78 Ω	67.50 Ω	20.09 Ω
Internal resistance after ten cycles	65.43 Ω	59.21 Ω	102.07 Ω	42.86 Ω

Polarization and internal resistance

Polarization was carried out twice, first after six cycles of operation and the second one after visible scale formation on cathode after 10 cycles of operation. Voltage response was recorded by varying external resistance from 10,000 to 10 Ω. In the first polarization, maximum power density of 66 mW/m^2 was achieved in MFC-4 followed by 48 mW/m^2 in MFC-2, which was 2.2 and 1.6 times higher than the control MFC-3 (30 mW/m^2), respectively (Fig. 3a). Significantly low power density of MFC-1 and MFC-3 using carbon powder without nitrogen doping as compared to MFC-4, where cathode was made of NDCP without ATMP, indicates the benefits of using NDCP as cathode material. This higher power production in MFC-4 is due to the high electroactive surface area of the N-doped carbon powder and also because of the meso-porous structure development as reported by Wen, Wang [18] resulting in a fast rate ORR. It is clear that cathode potentials of the MFCs followed practically comparable trend as power density curve and anode potentials were almost in the same range (Fig. 4), signifying that cathode performance was the key aspect causing varying performance of the MFCs. Cathode potentials in the MFC without nitrogen doped carbon powder as cathode dropped very promptly through polarization, whereas the potential of the nitrogen doped cathodes were not affected that much. This indicates that nitrogen doped carbon can reduce the overpotential for electrochemical reaction. The better performance in nitrogen doped cathodes can be ascribed to the formation of ORR active sites for pyridinic N and pyrrolic N [5, 19].

The internal resistances obtained from voltage-current graph during polarization were 47.80, 42.78, 67.50 and 20.09 Ω, respectively, for MFC-1, MFC-2, MFC-3 and MFC-4 after six cycles. The internal resistance of MFC-2 and MFC-4 were found to be comparatively lower than MFC-1 and MFC-3 due to higher proton transfer rate process of nitrogen doped carbon powder used in cathode. After ten cycles of operation, internal resistance of MFC-4 still remained lowest among all. These values increased by

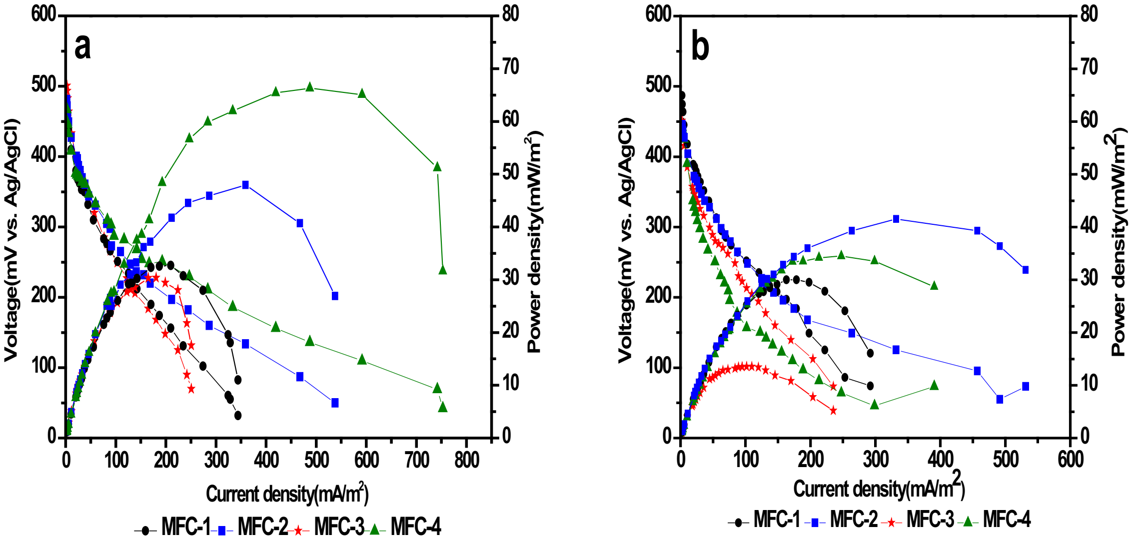
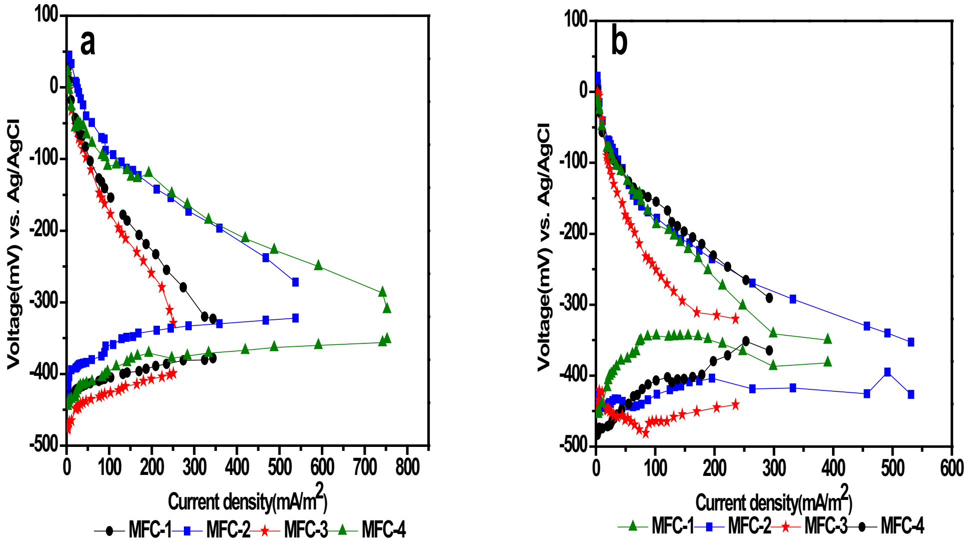


Fig. 3 Polarization curve obtained after **a** six cycles, **b** ten cycles, respectively

Fig. 4 Electrode potentials obtained after **a** six cycles, **b** ten cycles, respectively



36.8, 38.4, 51.2, and 113.3% for MFC-1, MFC-2, MFC-3 and MFC-4 respectively. Low internal resistance values for MFC-1 and MFC-2 as compared to MFC-3 and MFC-4 proves better co-ordination of using anti-scaling agent with carbon particles (treated or untreated), which is also evident from the fact that the fouling or scale formation that occurred over the cathode surface of MFC-1 and MFC-2 were significantly lower than that in MFC-3 and MFC-4.

After ten cycles of operation, maximum power densities were 30.02, 41.55, 13.47 and 34.51 mW/m^2 for MFC-1, MFC-2, MFC-3 and MFC-4, respectively (Fig. 3b). As compared to 6th cycle, power densities were found to be reduced by 47.71% in MFC-4 and 55.6% in MFC-3 after ten cycles due to fouling of the cathode. Power density performances were almost similar in MFC-1 and MFC-2, where anti-scaling agent was used in the cathode, with only 9 and 12.5% decrease in their values after ten cycles of operation as compared to value observed after six cycles. These results strengthen the fouling resisting properties of ATMP. White patches were observed to be formed on the surface of the cathodes of MFC-3 and MFC-4 after 7th or 8th cycle, indicating inorganic fouling in the membrane (picture shown in graphical abstract). This fouling can cause physical blockage to cation transfer, which can in turn cause decrease in power production [20]. Fouling is the formation of an impenetrable film on reactive surface due to accumulation of bacteria, biofoulants and cations, resulting in increased internal resistance of the MFCs (Table 2). Similar increase in internal resistance was observed by Choi, Chae [11] and they attributed this increase in resistance to high concentration of cation deposition on membranes. ATMP being a commercial anti-scaling agent has inherent chelation properties to stop this deposition of chemicals by keeping the ions in solution form; thus cathode performance in the MFCs using ATMP in cathode did not decline notably with time.

Linear sweep voltammetry

To evaluate the ORR on the cathode surface of the MFCs, LSV test was performed. The test was carried out twice, one after the end of 6th cycle (Fig. 5a) and the other after the end of 10th cycle (Fig. 5b) to study the change in the performance of ORR on cathode surface due to fouling. The first LSV showed higher current response for MFC-2 and MFC-4, where ASA + NDCP and NDCP were used as the cathode material respectively. Peak current response of 0.502 A/m^2 was obtained in MFC-4 followed by 0.411 A/m^2 in MFC-2. The peak current responses of these MFCs were 2.2 and 1.8 times higher than the control MFC-3 using carbon powder without anti-scaling agent. Also, the onset potential (where ORR commenced) of MFC-4 and MFC-2 were found to be 0.25 and 0.2 V, respectively, which was 6.25 and 5 times greater than the control MFC-3 (0.04 V) and MFC-1 (0.14 V), respectively. This positive potential shift of the nitrogen doped carbon powder cathode implies an enhanced catalytic activity for ORR [21]. The range of current response (difference between higher value and lower value) of 0.896 A/m^2 and 0.824 A/m^2 over the potential range of −0.9 to +0.6 V was also higher for MFC-4 and MFC-2, respectively, than the control MFC-3 (0.706 mA/m^2) and MFC-1 (0.753 mA/m^2). Pyridinic N and pyrrolic N at the N-doped carbon surface can efficiently create active sites for ORR [19]. Carbon atoms neighbouring N-atoms incorporated due to doping, possess a substantially high positive charge density to equipoise the strong electron affinity of the nitrogen atom. This nitrogen-induced charge delocalization also changes the adsorption of oxygen on carbon powder, which effectually weakens the O–O bonding to facilitate ORR [5].

The improved catalytic property of NDCP can be ascribed to the effective heat treatment used for N-doping, which increased specific surface area (SSA). High SSA increases the electrolytic ion activity and allows passage of oxygen molecule for ORR thereby improving performance of the cathodes using NDCP [18]. After 10 cycles of operation, MFC-3 and MFC-4, where ASA was not used in the cathode, showed significant deterioration in the performance of ORR due to blocking of active ORR sites because of fouling [22]. Reduction in the peak current density for MFC-1, MFC-2, MFC-3 and MFC-4 after 10th cycle (40 days of operation) was 11, 4, 18, and 30%, respectively, compared to that with 6th cycle (24 days). This performance of ATMP as an anti-fouling or anti-scaling agent is much better than that observed by Ma, Wang [23], who used PVDF membrane as separator to avoid fouling, but observed a 30% decline in peak current density just after 25 days of operation. Many compounds and ions in the anolyte precipitate on cathode surface, after migrating through the PEM. Consumption of protons and production of hydroxyl ions at the cathode surface results in increase of pH, which can lead to severe fouling of the cathode surface by precipitation of hydroxides of the cations migrated from the anolyte. The value of the interfacial pH depends on the balance between the rates of proton consumption and proton transport to the surface [24]. Proton mass transfer of the membrane cathode assemblies of MFC-1 and MFC-2 (Table 1) was significantly higher than that of MFC-3 and MFC-4, leading to a better pH balance and improved resistance to fouling.

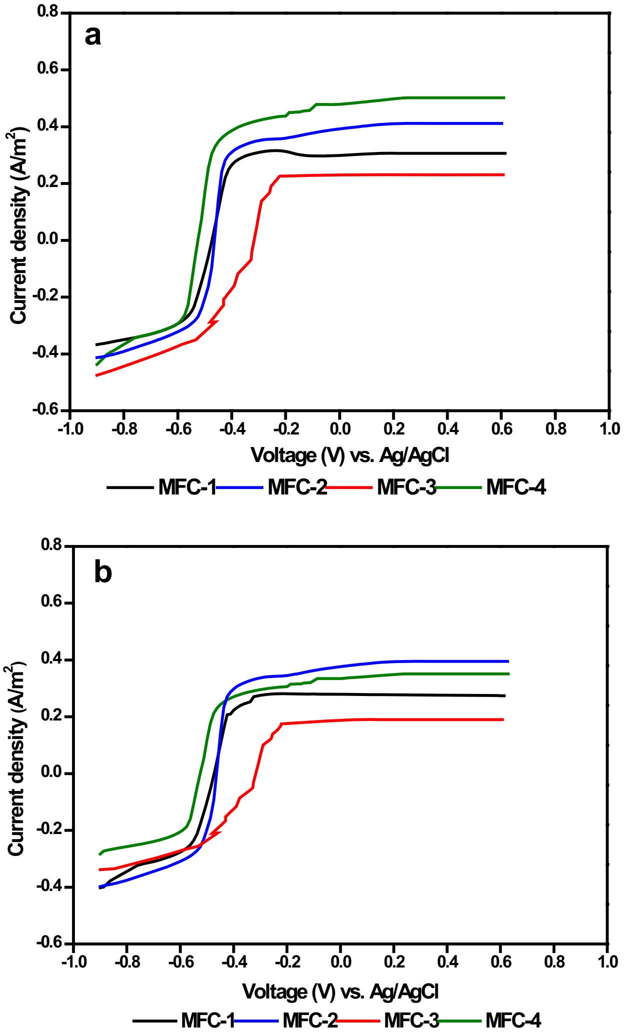


Fig. 5 Linear Sweep Voltammetry obtained after **a** six cycles, **b** ten cycles, respectively

Cyclic Voltammetry

Cyclic voltammetry test was done to study the mechanism of cathodic reactions and ORR [21]; and this test was done at the scan rate of 10 mV/s to check the reduction capability of the treated carbon powder as the cathode material after 6th cycle of operation (Fig. 6a). Two reduction peaks were obtained for MFC-4, one at the voltage of −0.48 V and the other at +0.68 V at the current response of −2.6 and 1.9 A/m^2, respectively, while other MFCs produced only single reduction peak at 0.50, 0.55, 0.50 V for MFC-1, MFC-2 and MFC-3, respectively. This indicates high ORR property of NDCP. MFC-2 and MFC-4, where NDCP was used as the cathode material, were observed to respond with much higher current in the positive range of voltage than MFC-1 and MFC-3. The peak current of CV in the MFCs using treated carbon powder cathode was higher than those where carbon powder without any treatment was used as cathode. Also, reduction peaks (at −0.25 V) with the nitrogen doped cathodes (for both MFC-2 and MFC-4) were much higher than that of normal carbon cathodes, after 10 cycles of operation, demonstrating NDCP cathode had a higher faradic charge capacity, which is known to be related to the electrode surface area [25]. After 10 cycles (Fig. 6b), for potential window −0.43 to −0.1 V, the reductive current density response increased for both MFC-2 and MFC-4 as compared to that obtained after six cycles. Reductive current response (for same potential window) for these MFCs registered highest values among all, where NDCP cathode material was used, indicating higher catalyst performance responsible for enhancing ORR process for long term performance. Also, reductive current density response for MFC-1 was observed better than MFC-3, indicating increased ORR process for cathode where untreated carbon is used with ATMP. Overall, cyclic voltammograms revealed better electrochemical behaviour in the nitrogen doped carbon cathodes and the full picture can be attributed to improved electrical conductivity and increased active reaction surface area [26–28].

Electrochemical Impedance Spectroscopy

Nyquist plots for the cathodes of the MFCs after 6th and 10th cycle that is before and after fouling are shown in Fig. 7 and different resistances such as solution resistance (R_s), charge transfer resistance (R_{ct}) and diffusion resistance (R_d) are reported (Table 3). Charge transfer resistance in the 6th cycle of operation for MFC-3, containing only normal carbon powder, was 19.7 Ω. Use of nitrogen doped carbon in MFC-4 reduced this resistance to 1.57 Ω. Also the use of ASA in MFC-1 decreased R_{ct} by a significant amount (as compared to MFC-3, the control) to about 9.79 Ω. The use of NDCP with ASA (MFC-2) was able to maintain similar charge transfer resistance (1.86 Ω) as compared to MFC-4 (1.57 Ω). Charge transfer resistance is inversely proportional to reaction rate [20], thus a higher R_{ct} value indicates a lower cathodic ORR. This clearly indicates good catalytic behaviour of NDCP when used as cathode material and it is also responsible for better ORR rates for the reason mentioned above. The diffusive resistances too showed a similar trend as R_{ct} and it was the least for MFC-4 with NDCP in its cathode. The charge transfer resistance was maximum among R_s, R_{ct} and R_d in MFC-1 (Table 3), whereas in MFC-2 and MFC-4 using NDCP, diffusion resistance was the limiting resistance. Diffusion resistance is the electronic resistance of the current

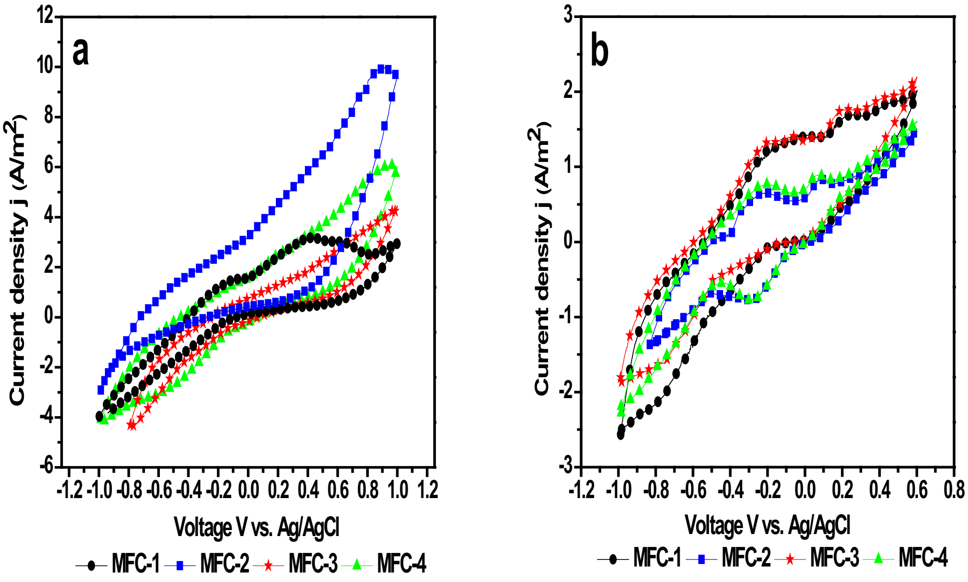


Fig. 6 Cyclic Voltammetry obtained after **a** six cycles, **b** ten cycles, respectively

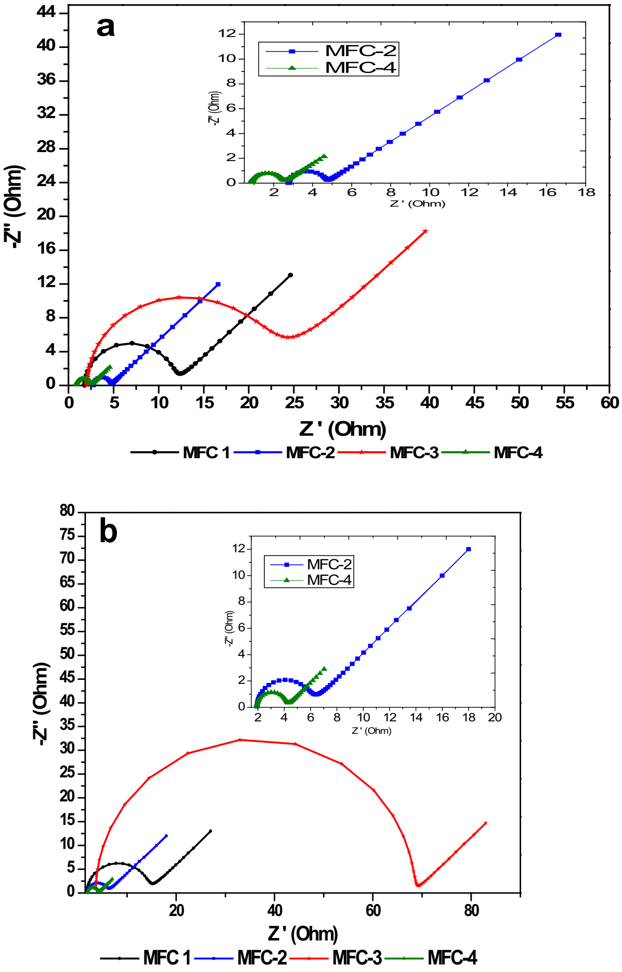


Fig. 7 Electrochemical impedance spectroscopy analysis of the cathodes **a** after six cycles, **b** after ten cycles, respectively

Table 3 Nyquist plot data for the MFCs

	MFC	R_s (Ω)	R_{ct} (Ω)	R_d (Ω)
Cycle 6	MFC-1	1.83	9.79	4.62
	MFC-2	2.78	1.86	4.24
	MFC-3	2.07	19.7	20.2
	MFC-4	0.87	1.57	2.40
Cycle 10	MFC-1	1.89	12.2	10.53
	MFC-2	1.92	2.22	3.24
	MFC-3	3.64	64.6	16.45
	MFC-4	1.94	3.98	7.41

collector and contact resistances and R_d of air–cathodes exhibited decreasing trend after nitrogen doping on carbon powder. This indicated that doping was able to enhance the surface conductivity. However, higher R_d than R_{ct} or R_s in MFC-2 and MFC-4 indicates that a better current collector like sock net as used by Chatterjee and Ghangrekar [16] will further improve the performance of the MFCs.

Table 4 Data from XRD analysis of the catalyst

MFCs	Angle (2θ)	Intensity	Cathode material
MFC-1	29.406	1878	CB + ASA
MFC-2	29.406	1016	NDCP + ASA
MFC-3	29.406	9022	CB only
MFC-4	29.406	5302	NDCP only

Charge transfer resistance (R_{ct}) after ten cycles increased for both MFC-3 and MFC-4 by around 228 and 154%, respectively, from their respective values after 6th cycle, where ASA was not used in MFCs; whereas, these resistance values increased by only 24.6 and 19.35% for MFC-1 and MFC-2, respectively, wherein ASA was used in the cathode. This indicated that, not only NDCP (as discussed above) is responsible for efficient ORR but the interaction of the catalyst with ATMP molecules, which reduces fouling and gives a better long term performance, also plays a part. The only possible reason for increase of charge transfer resistance as well as the diffusive resistance of cathodes without the use of anti-scaling agent was fouling of the cathodes. Layer formed by deposition of alkali salts on cathode reduces the contact of oxygen to the cathode active reaction sites as indicated by the increase in diffusion resistance (Table 4) after long term operation [18].

Quantification of scale formation

XRD analysis of the scrapped cathode material was done using PANalytical X‘pert high score plus software for each MFC after 10 cycles of operation (Fig. 8). This was required to know the amount of scale formation on the cathode surface in the form of $CaCO_3$ compound (calcite). The quantity of scale formation was assumed to be directly proportional to the intensity of $CaCO_3$ compound (reference code: 00-005-0586) analysed via XRD at $2\theta = 29.406°$ (indicated by black arrow inside figure). The intensity of $CaCO_3$ was found to be increasing significantly when the anti-scaling agent ATMP was not used in the cathode material made either with carbon black or with the NDCP (Table 4). The intensity of $CaCO_3$ reduced by 79.18% with anti-scaling usage along with carbon black and by 88.73% with its usage along with NDCP. This proves the effectiveness of ATMP as an anti-scaling agent over air cathode surface of MFCs and versatility of NDCP in suppressing the scaling effects further.

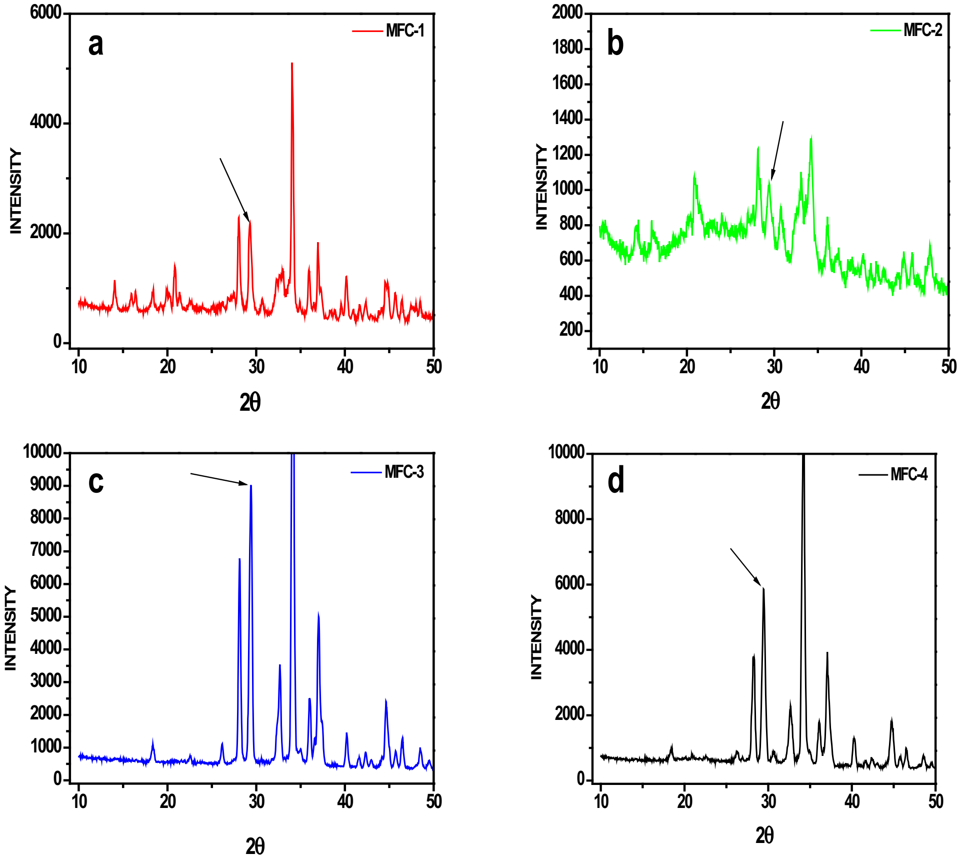


Fig. 8 XRD analysis of the outer scrapped cathode material for **a** MFC-1, **b** MFC-2, **c** MFC-3, **d** MFC-4, respectively

Conclusions

Nitrogen doped carbon powder was used as cathode catalyst along with amino-tri-methylene-phosphate as an anti-scaling agent in a MFC. It was found successful in increasing electrochemical activities thereby enhancing ORR for the cathodes, accompanied with good power performance and offering promising wastewater treatment simultaneously. TEM image showed NDCP catalyst with ultrathin shell structure, which is responsible for improved performance of cathode by maintaining good electron flow for ORR. Presence of ATMP in the cathode significantly reduced the scale formation on cathode surface thus increasing longevity of MFC performance. Electrochemical analysis proved better ORR for cathodes having NDCP. In future, to achieve long term stable improved cathodic performance, nitrogen doping along with ATMP can offer a promising solution to enhance electricity generation in MFC in a more economical and sustainable way.

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