

EFFECT OF MOLECULAR WEIGHT ON PROTON EXCHANGE MEMBRANES AND ITS APPLICATIONS WITH DIFFERENT DESIGN OF DUAL CHAMBERED MICROBIAL FUEL CELLS

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ABSTRACT

Proton exchange membranes (PEMs) were prepared with varying molecular weight (M.W.) of polyethylene glycol (PEG) (200/1500/6000) along with polyvinyl alcohol (PVA), orthophosphoric acid (OPA) and chitosan (CS) by physical blending and casting method. Ion exchange capacity (IEC) and water uptake of the membranes were found to decrease with increasing the molecular weight of PEG. The maximum power density, current density, an open-circuit voltage (OCV) were 5.28 mW/m², 3.88 mA/m² and 0.74 V observed in cylindrical shape microbial fuel cells (CYMFCs). While the power density, current density, and open-circuit voltage (OCV) of rectangular shape microbial fuel cells (REMFCs) were 61.93 mW/m², 106.48 mA/m² and 1 V, respectively. In this work, we have optimized the molecular weight of PEG in the synthesized of PEMs and compared the performances of prepared membranes in two different designs of MFCs. The rectangular shape MFCs performed better compared to cylindrical shape MFCs.

Keywords: Microbial Fuel Cells, Proton Exchange Membrane, Ion Exchange Capacity, Chemical Oxygen Demand.

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INTRODUCTION

Microbial fuel cells (MFCs) are bio-electrochemical reactors that can be utilized for power generation through microbial degradation of natural and inorganic contaminants in the anode compartment resulting in the production of protons and electrons.¹⁻³ The electron exchange from the anodic chamber to the cathodic chamber and generate current and the proton moves through PEM.⁴ Blended bacterial societies were utilized to achieve higher power densities contrasted with mixed culture.⁵ PEM is a standout amongst the most imperative parts in MFCs, which isolates the anode and the cathode.⁶ Wu et al.⁷ discussed PEG by varying molecular weight effects (200 to 1000) with the high organic component, a negatively charged hybrid sol-gel precursors (PEO-[Si(OEt)₃]₂SO₂H). They have found IEC values of the hybrid materials decreased from 1.5 to 0.3 meq/g. Bella et al.⁸ used PVA, sulfamic acid (SA), and poly (oxyethylene) (POE) as precursors in the synthesis of PEM. MFC connected with PVA-SA-POE based membrane was a maximum open-circuit voltage (OCV) value of 516 mV and a maximum current and power density of 1.72 A/m³ and 7.16 W/m³ respectively. But, it was still lower than the MFC connected with Nafion 117. Dharmadhikari et al.⁹ used PEG-200/PVA/OPA/CS based PEMs and obtained the maximum result in rectangular shape MFCs. The maximum power and current density of 63.3 mW/m² and 107.3 mA/m² respectively. The maximum OCV value was 1.07 V, which infers the membrane performance as best. Dharmadhikari et al.⁹ varied the composition of PVA and optimized the composition to obtain the best performance of PEM. PEG can be used as a plasticizer in PEMs owing to their exciting feature low toxicity and having cost.⁸ Polyvinyl alcohol (PVA) can be used as a hydrophilic agent for PEM.¹⁰ Orthophosphoric acid (OPA), an alternative to sulfonic acid, has properties like excellent thermal, chemical and electrochemical strength in energy unit application.^{9,11} Chitosan (CS) is a low cost



biopolymer that can provide chemical stability and electronic properties to the membranes.^{10,12} Prepared membranes were characterized for scanning electron microscope (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. Water uptake and ion exchange capacity (IEC) of the synthesized membranes were measured. Incorporated films were successfully utilized in the MFCs setup, and the execution of the membrane layer was assessed by estimating the values of current density, power density, open-circuit voltage (OCV) of MFCs, and chemical oxygen demand (COD) evaluation of synthetic wastewater.

EXPERIMENTAL

Materials

Polyethylene glycol of different Mw of 200, 1500 and 6000 were purchased from RANKEM India; Polyvinyl alcohol (PVA), potassium di-hydrogen orthophosphate and sodium hydroxide were purchased from Merck, India; Moreover, sulfuric acid, acetone and orthophosphoric acid (OPA) were procured from Fisher Scientific, India; glutaraldehyde and graphite powder were obtained from Loba Chemie, India; dextrose anhydrous purified, potassium dichromate, calcium chloride, magnesium sulphate heptahydrate, ammonium chloride were purchased from Merck, India all the reagents and chemicals were used as received. Distilled and deionized water was used for all the experimental runs.

Synthesis of Membranes

PEG (200/1500/6000), PVA and OPA were employed to synthesize PEM and were denoted as M-1, M-2, and M-3 membranes, respectively. *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylmethanamide (DMF) were used as organic solvents further mixed in the equal volume ratios of 1:1. The mixture for M-1 (PEG-200/PVA/OPA/CS) was maintained at a temperature of 95±5°C using a hot plate with continuous stirring for 4 h, to dissolve the powder utterly within membrane solution. M-2 (PEG-1500/PVA/OPA/CS) and M-3 (PEG-6000/PVA/OPA/CS) were maintained at a temperature mentioned above with continuous stirring for 4 h for homogeneous mixing of precursors. Finally, the prepared mixture was cast onto three different glass petri-dishes up to the pre-determined mark and dried in ambient temperature for 4 h. The thickness of synthesized PEMs was measured with a digital screw gauge (Mitutoyo, Japan) and found to be 0.20±0.001 mm. The dried membranes were immersed into the cross-linking solution, consisting of 1.5 wt.% glutaraldehyde (GA), 0.5 wt.% of sulfuric acid, 48 wt.% of acetone and rest of deionized water, for 24 h. Subsequently, cross-linked membranes were washed with deionized water to remove the extra amount of glutaraldehyde from the surface of membranes.¹³

CHARACTERIZATION

Fourier Transform Infrared Spectroscopy (FTIR)

The synthesized membranes were characterized using FTIR (Bruker, Alpha Model). A small piece of the prepared membrane was used for analysis with attenuated total reflection (ATR) mode. An FTIR spectrum was obtained in the range of 4000 and 500 cm⁻¹.

Water Uptake

Water uptake of the synthesized membranes was calculated using equation (1):

$$\text{Water uptake (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

Where, W_d is the weight of dried membrane and W_w is the weight of the wet membrane.¹⁴

Ion Exchange Capacity (IEC)

The ion exchange capacity (IEC), with units meq/g of the dry polymer membrane, was calculated using equation (2):

$$IEC = \frac{a \times b}{m} \quad (2)$$

Where, IEC is the ion exchange capacity in meq/g, a is the volume of NaOH consumed in ml, b is the concentration of NaOH in normality and m is the weight of dried membrane in gm¹⁵.

Performance of MFCs

Calculations of Power and Current Density

The potential difference across the MFCs was measured with a digital multimeter. The generated current was measured by connecting various resistances (1000 Ω) to the MFCs, by Ohm's law. The current density was calculated by dividing the current by effective area of an anode. The power density was calculated using the following equation (3):

$$P = \frac{R \times I^2}{A_n} \quad (3)$$

Where, R is the applied external resistance (ohms), I is the current (amps), and A_n is the effective area of an anode (m^2).¹⁶

Measurement of COD

COD in the sample was calculated using equation (4):

$$C O D (m g / l) = \frac{(A - B) \times M \times 8000}{V_{sample}} \quad (4)$$

Where, A is the volume of FAS consumed for titration of blank solution (ml), B is the volume of FAS consumed for titration of the sample (ml), M is the concentration of FAS in molarity, and V_{sample} is the volume of sample (ml).¹⁷

Construction of Cylindrical MFCs

Three numbers of cylindrical shaped with polyacrylic material dual-chambered microbial fuel cells were fabricated for this study. MFC consists of two chambers viz., anodic compartment, and a cathodic compartment, each having the capacity of 1 L. The dimensions of the cylindrical shape MFCs were height 15 cm and diameter 9.2 cm. Synthetic wastewater sample was prepared in the laboratory as per the literature¹⁸, and rod-shaped carbon electrodes were used as anode and cathode. The dimension of the carbon electrode was 1.5 cm diameter and 13.5 cm effective height. One chamber was completely covered, which served as an anodic compartment, while the other chamber was left open to the atmosphere, served as a cathodic compartment. The synthesized membrane was placed between the compartments. The effective diameter of membrane exposed to the solution was 2.5 cm, and an anode electrode effective area of 67.11 cm^2 was used for the calculation of power and current density. Synthesized membranes M-1, M-2 and M-3 were used in the fabricated batch-wise as MFC-1, MFC-2, and MFC-3, respectively. The anodic compartment was filled with 300 ml of sludge. The initial COD value of sludge was 11200 mg/l. The quantity of synthetic wastewater filled in the anodic chamber was 700 ml. The initial COD and pH of synthetic wastewater was 780mg/l and 7.1, respectively. COD of the mixture (sludge + synthetic wastewater) in an anodic chamber was found to be 7840 mg/l, which was taken as reference for the calculation purpose. Potassium permanganate ($KMnO_4$) of 0.2 g/l concentration was filled in a cathodic chamber.¹⁹ Experiments were performed at room temperature of $28 \pm 2^\circ C$.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM)

The SEM images of membranes, i.e. M-1, M-2 and M-3, which was synthesized using various recipes, are shown in Fig.-1. The surface morphology shows that all constituents of the membranes were homogeneously distributed throughout the membranes without any significant migration of phase segregation.²⁰ The SEM images confirmed that pores were not substantial in synthesized membranes.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR transmittance spectra of the synthesized membranes using different compositions are presented in Fig.-2. The broad peak in between 3500 and 3000 cm^{-1} wavenumber represents -OH stretching and C-H stretching, which confirmed the presence of PVA.²¹ The peak at 1670 cm^{-1} corresponds to carbonyl

groups ($C=O$), while the peak at 1590 cm^{-1} (NH_2) represents the presence of an amine group; both the peaks confirmed the presence of chitosan at the edges.²² The C-H stretching observed at 2887 cm^{-1} was due to the presence of PEG.²³ The phosphate group peaks were found in the spectrum between $650\text{--}550\text{ cm}^{-1}$ and $1300\text{--}910\text{ cm}^{-1}$.²⁴

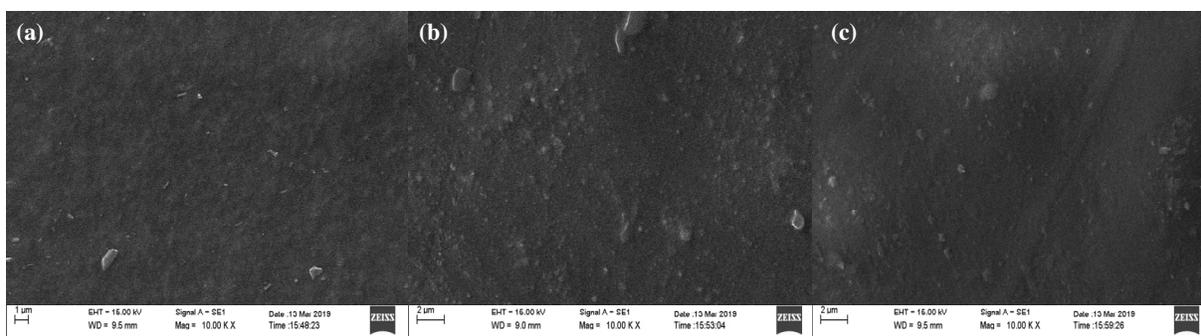


Fig.-1: SEM Images of (a) M-1 (PEG-200), (b) M-2 (PEG-1500) and M-3 (PEG-6000).

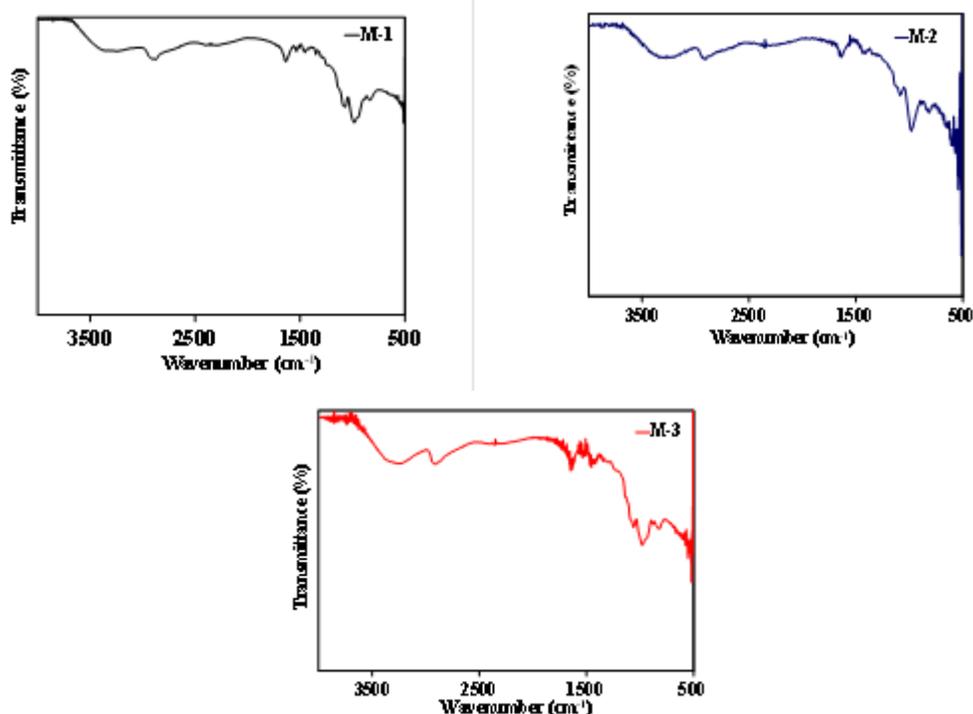


Fig.-2: FTIR Spectra of M-1, M-2 And M-3 Membranes Using Various M. W. of PEG (200/1500/6000).

Water Uptake

The water uptake of the synthesized membranes is shown in Fig.-3, and the values for M-1, M-2, and M-3 were 35.46, 31.70 and 30.3 %, respectively. The water uptake value decrease with the increasing molecular weight of PEG. The water uptake of the Nafion-117 membrane was measured as 20%.²⁵ On comparing the water uptake with pristine Nafion-117; the values of water uptake for synthesized membranes were slightly higher. This might be due to the hydrophilic nature of PVA.²⁶ Water uptake of M-1 membrane found to be higher due to the low Mw of PEG-200 present in M-1 in comparison with M-2 (PEG-1500) and M-3 (PEG-6000) membranes. The higher value of water uptake signifies a higher ion exchange capacity (IEC).

Ion Exchange Capacity (IEC)

IEC is a measure of the relative concentration of acid groups within PEMs, and the values are shown in Fig.-3. The ion content is characterized by the mass of dry membrane per molar equivalents of ion

conductor. Fig.-3 shows the ion exchange capacities of three synthesized membranes having IEC of 1.465, 1 and 0.91 meq g⁻¹, respectively. The reason behind this the increment in Mw of PEG it was prepared high-density PEMs. So the high-density membranes decrease the water uptake, lower value of water uptake signifies the lower value of IEC.²⁰ The IEC for Nafion-117 membrane was 0.90 meq/g.²⁷ The IEC values of the synthesized membrane were higher than the IEC of the Nafion 117 membrane.

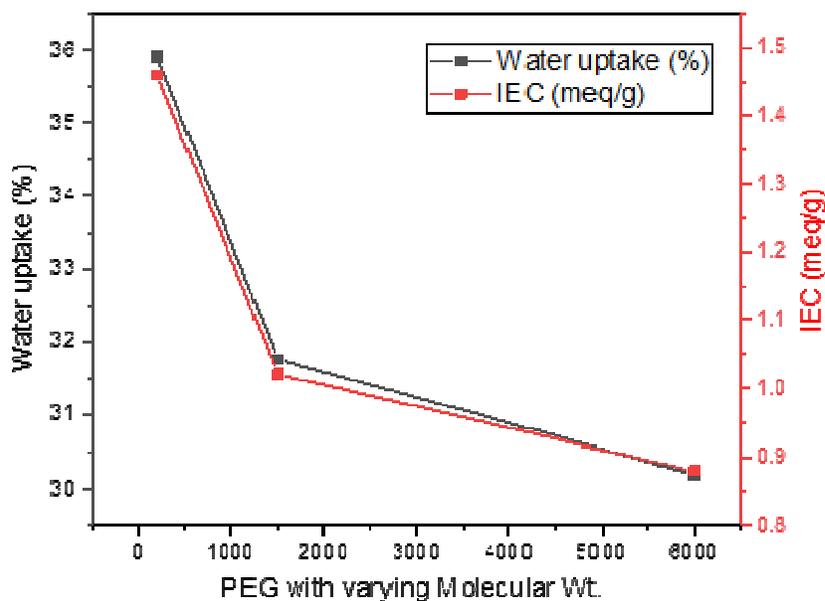


Fig.-3: Water Uptake (%) Vs. IEC (meq/g) With Various M.W. Of PEG (200/1500/6000) Used In M-1, M-2 and M-3 Membranes.

Performance of the MFCs

The open-circuit voltage (OCV) of the MFCs with different membranes was measured at a steady-state (SS) condition, and the results are presented in Fig.-4. In a typical plot of OCV vs. time, there are three stages, viz., microbial growth, energy production, and microbial death. The OCVs of MFC-1, MFC-2 and MFC-3 were 0.74, 0.59 and 0.52 V, respectively. The reason for this order might be the ion exchange capacity of membranes. The power density curves of microbial fuel cells with various synthesized membranes, while the other factors were constant, are presented in Fig.-5. From Fig.-5, it is clearly seen that the power density trend for MFC-1, MFC-2 and MFC-3 passes through a maximum and then drops because of microbial oxidation of organic and inorganic contaminants present in wastewater. This trend matches well with the data of reported literature.²⁸ The performance of MFC-1 with M-1 membrane showed a better performance with other MFCs having M-2 or M-3 membrane. The maximum values correspond to the membrane without fouling. However, the values of power densities for M-1, M-2, and M-3 were reduced to 5.28, 2.17 and 2.07 mW.m⁻², respectively. The reduction in the power density might have occurred due to the fouling of the membrane and the design of MFCs.^{29,30} The polarization curves, voltage vs. current density, of various synthesized membranes in MFCs are shown Fig.-6. The reduction in the overpotentials, particularly the ohmic overpotential, was caused by the higher ion exchange capacity of the M-1 membrane. The overpotential of M-2 and M-3 membranes were less than the overpotentials of M-1, that membrane resulted in better performance and a lower potential loss.

COD removal

The COD removal (%) with time is shown in Fig.-7. The MFCs connected with M-1, M-2, and M-3 yielded 81, 82 and 88% COD removal, respectively. Oxygen diffuses relatively rapidly through the M-1 membrane (synthesized with low Mw of PEG) from cathode to anode in comparison with M-3 (high M.W. PEG). This transfer of oxygen (O₂) might be due to the crossover problem of membrane. Hence,

the COD reduction was lower with the M-1 membrane. However, in the case of membrane synthesized with a high Mw PEG content (M-3), the diffusion of oxygen was lowered, which resulted in a higher COD reduction.

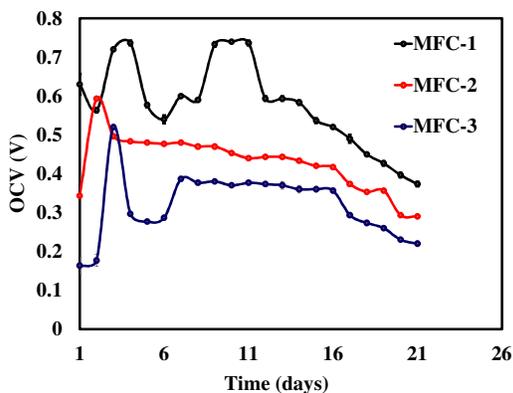


Fig.-4: OCVs of MFC-1, MFC-2 And MFC-3 Using Various Membranes

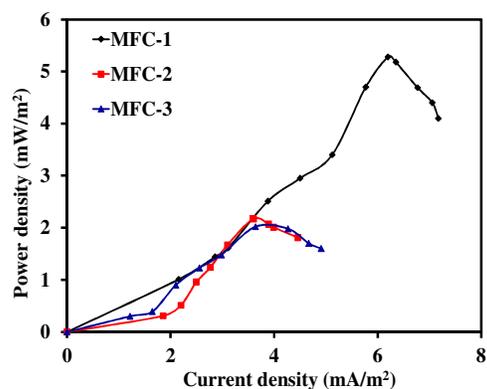


Fig.-5: Polarization Curve of MFC-1, MFC-2 And MFC-3.

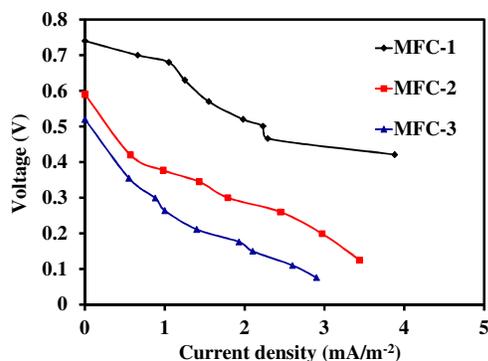


Fig.-6: Polarization Curve Of MFC-1, MFC-2 And MFC-3.

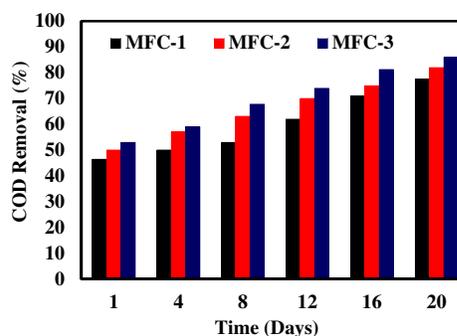


Fig.-7: COD Removal (%) Of MFC-1, MFC-2 And MFC-3 Using Various Membranes

Comparison Between Rectangular And Cylindrical Shape MFCs

Dharmadhikari *et al.*⁹ reported all parameters regarding the use of the MFCs in rectangular shape geometry. In the present case, we studied the performance of the prepared membrane using the cylindrical shape of MFC with the rectangular shape MFC. The comparison between the rectangular and cylindrical shape MFCs was based on the value of power density, current density, open-circuit voltage (OCV) and COD removal. The power density, current density and open-circuit voltage (OCV) and COD removal were 61.93 mW/m², 106.48 mA/m², 1 V, and 80% respectively, quiet higher in a rectangular shape. While the same membrane was connected with cylindrical shape MFC was generated low power density, current density, and open-circuit voltage (OCV) 5.28 mW/m², 3.88 mA/m², and 0.74 V respectively, compared than a rectangular shape. The reason behind this because of the design of MFCs.²⁹ Many factors that can affect the performance of MFCs such as crossover problem, migration of protons on the surface of PEMs, and bio-fouling, etc. One more factor which affects the performance of MFC is the MFC design. The internal resistance has been recognized as an essential parameter that determines the performance of an MFC.³¹⁻³³ The internal contributes to the polarization behavior of anode and cathode in addition to contributions from ohmic components.³⁴ The internal resistance also depends on the effective (exposure) area of the electrode. The study on rectangular shape MFCs, the effective (exposure) area of the anode in the anodic compartment, is less than the effective (exposure) area of the anode in cylindrical shape MFCs,

so the internal resistance was quite lower in rectangular shape rather than cylindrical shape.³⁵ Thus the prepared same PEMs shows different results with different designs of MFCs.

CONCLUSION

The membranes were synthesized using different molecular weights of PEG (200/1500/6000) in this study. The M-1 (PEG-200) synthesized with a low molecular weight of PEG achieves the better value of IEC and water uptake. The IEC of prepared membranes was decreased with PEG molecular weight in the range of 1.47-0.91 meq/g due to a fall in the value of water uptake range in 35.46-30 %. The MFC-1 setup using the M-1 membrane exhibited the highest value of power density, current density, and OCV. The COD removal of MFC-1 with the M-1 membrane yield a lower value. The improved performance of the M-1 membrane was due to its lower molecular weight of PEG. The comparison between the rectangular and cylindrical shape MFCs was based on the values of power density, current density, open-circuit voltage (OCV), and COD removal suggests that the rectangular shape MFCs is found to be better than the cylindrical shape MFC.

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