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## 2 **Integrating Pd-Doped Perovskite Catalysts with Ceramic Hollow** 3 **Fibre Substrate for Efficient CO Oxidation**

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19

## Abstract

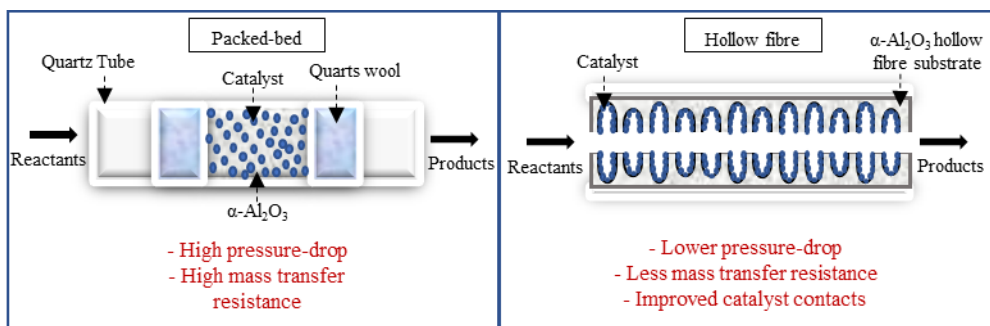
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Doping Pd into perovskite catalysts helps to reduce light-off temperatures, improve thermal-chemical stability and lowered catalyst cost by decreasing Platinum Group Metals (PGMs). In this study,  $\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$  (LFMPO) and  $\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$  (LFCPO) were synthesised, characterized and evaluated for catalytic treatment of automotive emissions, using CO oxidation as the model reaction. Such catalysts were further incorporated inside micro-structured ceramic hollow fibre substrates, and compared with a packed bed configuration by light-off temperatures. Performance evaluations suggest that, LFMPO deposited inside the hollow fibre substrate could be light up at 232 °C, which is 10 °C lower than a packed-bed counterpart with the same amount of catalyst (5 mg) and GHSV of  $\sim 5300 \text{ h}^{-1}$ . While excessive incorporation of the catalyst (10 mg) generates significantly higher transfer resistance, which impairs catalytic performance of hollow fibre reactors, with CO conversion per gram of catalyst reduced from 0.01 mole  $\text{g}^{-1}$  to 0.0051 mole  $\text{g}^{-1}$ .

*Keywords:* Catalytic Converter, Ceramic Hollow Fibre, Perovskite Catalyst, Palladium, CO Oxidation, Light-off Temperature

37 **Graphical Abstract**

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## 42 1. Introduction

43

44 Noxious gases such as carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), and hydrocarbons  
45 (HCs) can be released from internal combustion engines due to incomplete combustion, which  
46 needs to be thoroughly treated for compliance with regulatory standards established [1]. As a  
47 common and efficient practice, exhaust systems involve catalytic converters as a core  
48 component, which enable catalytically conversion of noxious emissions into non-harmful  
49 species. Catalytic converters normally consist of three essential components: i) a monolithic  
50 substrate, ii) a washcoat layer with a high surface area, and iii) catalytic active metals,  
51 conventionally Platinum Group Metals (PGM) catalysts. Despite of significantly successful  
52 application of this technology, exhaust gases from gasoline combustion engines can reach  
53 temperatures of up to 1000 °C, leading to severe sintering of washcoat oxide,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [2], due  
54 to irreversible phase transition from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> under elevated temperatures. This  
55 significantly reduces surface area of the washcoat layer in which metal catalysts are dispersed,  
56 and consequently reduce catalytic performance and efficiency of catalytic converters As a  
57 result, a highly thermally and chemically robust catalytic washcoat is always essential to good  
58 long-term performance of catalytic converters.

59

60 In addition to long-term stability, scarcity of PGMs and their price volatility belong to a second  
61 challenge of catalytic converter technology [3]. These challenges have also sparked a lot of  
62 research with the aim to reduce the dependability on PGMs, and to formulate supported PGM  
63 catalysts with better thermal stability. Among the various catalyst technologies available for  
64 substituting PGMs, perovskite catalysts are attracting more and more research interest, due to  
65 the unique regenerative properties of perovskites reported in letters to Nature regarding their  
66 potential applications in exhaust treatment [4]. Other attractive characteristics of perovskite

67 catalysts include good flexibility and adaptability in their composition, thermal stability,  
68 abundant availability, and most importantly, much lower costs than PGMs, which also enables  
69 the use of this type of material for numerous applications other than exhaust treatment [5,6].  
70 And similar to other reactions, the highly defective perovskite structure enables rapid exchange  
71 between oxygen atoms from surface carbonate and perovskite lattice oxygen, which enables  
72 efficient CO oxidation although detailed mechanism can be subject to chemical compositions  
73 of perovskites. A typical perovskite structure follows a  $ABO_3$  formulation, with a large cation  
74 at a 12 coordinated A site, 6 smaller cations in the B site and an anion, most often oxygen [7].  
75 In order to tailor the properties of a perovskite oxide, the A site and B site can be substituted  
76 by various elements. However, B site substitution normally has a more significant impact on  
77 the material properties, such as catalytic activity, and affects oxygen vacancy, which is  
78 important in altering the other properties of perovskites [8–11]. Till date, out of the many  
79 options of transition-based metal perovskites, lanthanum based perovskites have shown higher  
80 reactivity for an oxidation process, when coupled with Co, Mn, Fe, Cr or Ni in their B sites  
81 [12].

82

83 Tanaka et al. investigated regeneration ability of a perovskite, which responded in accordance  
84 with environmental input [13,14]. This enables the perovskite framework to accommodate  
85 metals that can also migrate from one site to another [4,15–18]. For example, the status of Pd  
86 inside the lattices of a perovskite changes reversibly between oxidation and reduction  
87 atmospheres, which benefits its long-term catalytic performance for exhaust treatment [10].  
88 Such a change in the status of Pd suppresses the growth of Pd particles, which is usually caused  
89 by the sintering effects of conventional catalysts such as Pd/ $\gamma$ -alumina. As a result, doping Pd  
90 into perovskite will improve the long-term stability of the catalysts, while also using much  
91 lesser amounts of PGMs than conventional catalysts for exhaust treatment. Although

92 perovskites without PGMs are catalytic active to CO oxidation, the doping of Pd can effectively  
93 reduce light-off temperatures (Table 1). This is mainly due to increased concentration of  
94 oxygen vacancy which facilitates oxygen transport from catalyst bulk to surface [19–23].  
95 Moreover, perovskite is subject to sulphur poisoning [24], which can be effectively delayed by  
96 doping Pd [25].

97

98 Despite aforementioned advantages of perovskite catalysts, their specific surface area is  
99 normally much smaller than conventional washcoat materials. This creates challenges in the  
100 potential applications of perovskites, since a larger amount of such catalysts have to be used in  
101 order to compensate for the high surface area required for a sufficiently good reaction  
102 efficiency. To address a challenge of this nature, a more advanced substrate enabling intensified  
103 interactions between the catalyst and reactants is necessary. In one of our previous studies, the  
104 potential of using a micro-structured ceramic hollow fibre substrate for a new catalytic  
105 converter design has been proved [26]. This new design offers a greater accessible surface area  
106 that originates from the unique microchannel structure inside the substrate, which also  
107 facilitates the deposition of different catalysts. Intensified transfer processes inside such  
108 substrates significantly increase catalyst utilisation, which is key to addressing the low specific  
109 surface area of perovskite catalysts. As a second benefit of depositing perovskite catalyst into  
110 such substrates, conventional washcoating materials are not needed, which ease the issue of  
111 sintering of washcoat layers, a main reason of the reduced performance of a conventional  
112 catalytic converter.

113

114 In this study, two different types of perovskites,  $\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$  (LFMPO) and  
115  $\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$  (LFCPO) were synthesised using a sol-gel method via citrate  
116 complexation. These perovskite catalysts were deposited inside a hollow fibre substrate, with

117 no washcoat materials, for catalytic conversion of CO, and compared with conventional packed  
118 bed reactor. This study presents research, conducted for the first time, into the incorporation of  
119 a perovskite catalyst without any washcoat layer, into a hollow fibre substrate for catalytic  
120 converter applications. Effects of catalyst packing inside hollow fibre substrates on CO  
121 oxidation was also outlined.

122

123

## 124 **2. Experimental**

125

### 126 **2.1 Materials**

127

128 Lanthanum (III) nitrate hydrate 99.9% trace metals basis, iron (III) nitrate nonahydrate,  $\geq$   
129 99.95% trace metals basis, manganese (II) nitrate hydrate 98%, cobalt (III) nitrate hexahydrate,  
130 and palladium (II) chloride 99.999% were purchased from Sigma-Aldrich. Hydrochloric acid  
131 37% vol%, ethanol absolute, AnalaR NORMAPUR, Assay (V/V) 99.95%, and ethylene glycol  
132 (Assay on anhydrous substance min. 98% and citric acid anhydrous (ACS Reagent  $\geq$  99.5%))  
133 were purchased from VWR.  $\gamma$ -Alumina powder ( $\text{Al}_2\text{O}_3$ ) with a surface area of  $100 \pm 30 \text{ m}^2 \text{ g}^{-1}$   
134 and  $\alpha$ -alumina ( $\text{Al}_2\text{O}_3$ ) powder (1  $\mu\text{m}$ , 99.9% metal basis, surface area 6 –8  $\text{m}^2 \text{ g}^{-1}$ ) were  
135 purchased from Inframat Advance Materials. All chemicals were used as supplied.

136

### 137 **2.2 Catalyst Preparation**

138

139 Two perovskite oxide catalysts,  $\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$  (LFMPO) and  $\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$   
140 (LFCPO), were synthesised by a sol-gel method via citrate complexation (Figure 1).  
141 Stoichiometric amounts of lanthanum, iron, manganese or cobalt nitrate were dissolved in a  
142 solution of de-ionised water (5 ml) and ethanol (15 ml). The stoichiometric ratio was calculated

143 on the basis of 4 mmol of lanthanum. The mixture obtained was treated in an ultrasonic bath  
144 for 15 minutes, to ensure uniform mixing of the chemicals.

145

146 Meanwhile, palladium (II) chloride was added into a hydrochloric acid solution (0.05 M) at a  
147 molar ratio of 1:1.5(PdCl<sub>2</sub>:HCl), which was heated at 80 °C for 30 minutes until a clear solution  
148 was obtained. It was then mixed with the metal nitrate solution and further treated in an  
149 ultrasonic bath for 30 minutes. Subsequently, an aqueous solution containing excessive citric  
150 acid (115% of the total moles of metal cations) was added, which enabled the complexation of  
151 metal cations after being stirred for one hour. The mixture obtained was continuously stirred  
152 and treated at 80 °C overnight to obtain the precursor powder, prior to a second drying at 80 °C  
153 for eight hours to remove remaining moisture. The precursor powder was then calcined at 700  
154 °C for four hours, as shown in Figure 1. The catalyst obtained was then ground into fine  
155 particles for characterizations and tests.

156

157 Meanwhile, catalysts consisting of 0.075 wt.% palladium supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were prepared  
158 by a wet incipient impregnation method. In a general process, a palladium chloride solution  
159 was mixed with  $\gamma$ -Alumina powder, stirred for one hour, dried overnight at 120 °C, and calcined  
160 for one hour at 500 °C, or 700 °C for four hours to obtain the catalysts.

161

### 162 **2.3 Incorporation of Perovskite Catalysts into Hollow Fibre Substrates**

163

164 Incorporation of catalysts into alumina hollow fibre substrates, which were prepared through a  
165 phase-inversion assisted extrusion process, has been described in our previous work [26]. For  
166 preparation of a hollow fibre substrate, a uniform slurry consisting of poly(methyl  
167 methacrylate) (PMMA) binder, N-Methyl-2-pyrrolidone (NMP) solvent, Arlacel P135



168 dispersant, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder was prepared. It was then extruded through a spinneret,  
169 together with a second stream of internal coagulant, into an external water bath to form the  
170 precursor hollow fibre substrates. The precursor hollow fibre was then straightened, dried at  
171 room temperature, cut, and finally sintered at 1500 °C to obtain the alumina hollow fibre  
172 substrates. Incorporation of catalysts into hollow fibre substrate has been described in  
173 Supplementary Information of our earlier work [26]. In general, 50 mg of perovskite catalyst  
174 was first dispersed inside 500 ml of distilled water (ultrasonic bath for one hour). The mixture  
175 was then pumped through hollow fibre substrates with pre-determined length for a certain  
176 period of time, and dried at 150 °C for one hour. Weight increment due to catalyst deposition  
177 was measured and recorded, before a second cycle of catalyst incorporation. This process was  
178 repeated until the target loadings of perovskite catalyst were obtained. No extra secondary  
179 oxide / washcoat layer was used in this study.

180

## 181 **2.4 Characterisation**

182

183 A morphology evaluation of hollow fibre substrates was carried out at different magnifications  
184 using a JOEL JSM-5610 scanning electron microscopy (SEM). Brunauer-Emmett-Teller  
185 (BET) was used to investigate the surface area of catalysts and catalyst/hollow fibre composite,  
186 and performed via a Micromeritics TRISTAR Surface area analyser using N<sub>2</sub> as the non-  
187 corrosive gas. Prior to the analysis, samples were dried overnight at 110 °C. A porometer  
188 (Porolux 100) and gas permeation tests (hollow fibre samples of 25 mm long) were used to  
189 investigate the effect of the catalyst deposition on the transport process of CO oxidation. Phase  
190 composition of the perovskite catalysts were analysed via a PANalytical X-ray diffractometer  
191 (XRD). Crystallite size was calculated by using the Scherrer equation below:

192

193 
$$D = \frac{K\lambda}{\beta \cos \theta} \quad (\text{Eq. 1})$$

194

195 Where  $D$  = the average thickness in a vertical direction of the crystal face,  $K$  is Scherrer  
196 constant,  $\lambda$  is the wavelength of X-ray,  $\beta$  is the half high width of the diffraction peak of the  
197 sample,  $\theta$  is the Bragg diffraction angle.

198

## 199 **2.5 Performance evaluation – CO oxidation**

200

201 CO oxidation was used to evaluate the catalytic performance of the perovskite catalysts and  
202 the perovskite/hollow fibre structured composite, which also facilitated the comparison with  
203 our earlier work which involved Pd/ $\gamma$ -alumina as the catalyst. Two different catalyst packing  
204 configurations were chosen (Figure 2). For the packed-bed configuration, 5 mg of perovskite  
205 catalyst (average particle size of 5  $\mu\text{m}$ ) was mixed with 200 mg of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder (particle  
206 size of  $\sim 1 \mu\text{m}$ ), before being loaded into a quartz tube and secured by quartz wool at both ends  
207 of the catalyst bed. The catalyst bed was approximately 20 mm in length. For the structured  
208 configuration,  $5 \pm 0.5$  mg of catalyst was deposited into alumina hollow fibre of 50 mm long,  
209 which weighed at approximately  $200 \pm 10$  mg. The hollow fibre sample was mounted into the  
210 quartz tube connected to a metal coil to pre-heat the gaseous reactants to the reaction  
211 temperature. The quartz tube was placed horizontally in a furnace (Vecstar Furnace,  
212 VCTF/SP). Mass flow controllers (Model 0154, Brooks Instrument) were used to control the  
213 gas flow into the system. A mixture of air and CO (10% CO in 90% Argon) at a ratio of 1:1  
214 was fed into the reactor system, which represents the lean-burn condition with an excess of  
215 oxygen. The flow rate of the feed gas was calculated to achieve a space velocity GHSV of  $\sim$   
216  $5300 \text{ h}^{-1}$ . An on-line gas chromatograph (Varian 3900) was connected to the outlet stream to  
217 analyse the effluent. The reaction temperature was gradually increased, and the sampling was

218 taken after thirty minutes of temperature stabilisation intervals. A series of reaction  
219 temperatures were used, from room temperature until 100% of the CO conversion. The  
220 conversion of CO was calculated based on the equation below (Eq. 2)

221

$$222 \quad \% \text{ conversion of CO} = \frac{C_{CO \text{ inlet}} - C_{CO \text{ outlet}}}{C_{CO \text{ inlet}}} \times 100\% \quad (\text{Eq. 2})$$

223

224 Where  $C_{CO \text{ inlet}}$  and  $C_{CO \text{ outlet}}$  are the CO concentrations at the inlet and outlet of the system,  
225 respectively. The details of the reaction test set up has been described in our previous study  
226 [26].

227

228

### 229 **3. Results and Discussion**

230

#### 231 **3.1 Phase composition of perovskite catalysts**

232

233 Figure 3 shows the XRD pattern of the LFMPO and LFCPO, which were calcined at 700 °C  
234 for four hours and have an orthorhombic crystal structure. The XRD patterns also indicate that  
235 a calcination temperature of 700 °C can enable good transformation of the synthesised  
236 perovskites [27]. Further reducing the calcination temperature helps to reduce grain size of  
237 perovskites, which can benefit catalytic reactions by providing larger catalytic areas. However,  
238 phase segregation can occur at 660 °C [28], which changes catalyst composition and impairs  
239 catalytic performance as a consequence. As a result, 700 °C was used for calcination of LFMPO  
240 and LFCPO in this study.

241

242 The XRD patterns in Figure 3 indicate that there is a small peak at the  $2\theta$  value of  $33^\circ$ , which  
243 is next to the main perovskite peak of LFMPO and LFCPO. This small peak indicates the  
244 presence of PdO [29], as a result of incomplete integration of Pd into perovskite oxides. If a  
245 calcination temperature higher than  $700^\circ\text{C}$  was used, a full integration of Pd can be possible  
246 [29]. However, it should be noted that full integration of Pd into perovskite lattices may retard  
247 catalytic performance, compared to Pd supported on perovskites which is more active due to  
248 easier interactions with reactants [30,31]. In contrast to washcoat materials such as  $\gamma\text{-Al}_2\text{O}_3$ ,  
249 perovskites are thermally more robust. Integrating Pd with perovskite is thus expected to have  
250 less problems of catalyst sintering as  $\gamma\text{-Al}_2\text{O}_3$ , benefiting life-time of catalysts.

251

252 As a common washcoat material with high surface area,  $\gamma\text{-Al}_2\text{O}_3$  is well-known for its  
253 microstructural evolution when exposed to high temperatures. This is due to phase transitions  
254 from  $\gamma$  to the meta-stable  $\delta$ - $\theta$ , and finally thermodynamically-stable  $\alpha$  phase, which results in  
255 the densification of washcoat layers, reduction in the specific surface area and consequently in  
256 deteriorating catalytic performance. For example, 5mg of 0.075 Pd/  $\gamma\text{-Al}_2\text{O}_3$  synthesised at 500  
257  $^\circ\text{C}$  was deposited inside ceramic hollow fibre substrates, which increased BET surface area of  
258 the composite, as shown in Table 2. While after thermal treatment at  $700^\circ\text{C}$ , a reduction of  
259 12.3 % in specific surface area can be observed. Here, the cations and anions in the  $\gamma\text{-Al}_2\text{O}_3$   
260 undergo rearrangement until they reach a dense corundum structure where the rearrangements  
261 result in the loss of support surface area [32]. In contrast, perovskite catalysts with fully a  
262 developed phase structure (Table 1) have no such problems. But due to the low specific surface  
263 area (Table 2) and potential reactions between perovskites and  $\gamma\text{-Al}_2\text{O}_3$  that impairs catalytic  
264 performance [33,34], perovskite catalysts are deposited inside hollow fibre substrates made of  
265  $\alpha$ -alumina and with a unique bi-modal pore structure in this study.

266

267

268

### 269 **3.2 Micro-structure of perovskites/hollow fibre substrate**

270

271 Figure 4 (a) presents a cross-section of the hollow fibre substrate with a bi-modal pore structure  
272 [35], which consists of packed-pores of approximately 200 nm and many oriented  
273 microchannels for which perovskite catalysts were deposited. LFMPO (Figure 4 (b)) and  
274 LFCPO (Figure 4 (c)) catalysts were deposited on the micro-channels and show an average  
275 particle size of approximately 5  $\mu\text{m}$ , which is much larger than the  $\alpha$ -alumina used for preparing  
276 the hollow fibre substrates.

277

278 Morphologies of hollow fibre substrates deposited with  $5 \pm 0.5$  mg of perovskite catalysts are  
279 displayed in Figure 5. As seen in a(i) and a(ii), hollow fibre substrates have open microchannel  
280 ends at the inner surface that is approximately 40  $\mu\text{m}$  in diameter. Substrates of this type could  
281 provide a GSA value of approximately  $40.7 \text{ cm}^2\text{cm}^{-3}$ , which is the same as that of a  
282 conventional monolith of 750 CPSI (GSA of  $40.2 \text{ cm}^2\text{cm}^{-3}$ ) [26]. A deposition of  $5 \pm 0.5$  mg  
283 of perovskite catalysts maintains good microchannel openings at both the inner surface and  
284 cross-section, as shown in Figure 5(b(i), b(ii), c(i) and c(ii)), by forming a thin catalyst layer  
285 along the surface of the microchannels. This is critical to the efficient interaction between the  
286 gaseous reactants and catalysts deposited inside the hollow fibre substrate [36].

287

288 By increasing the amount of perovskite catalysts to approximately 10 mg, catalyst particles  
289 start to form mini-packed-beds inside the microchannel of hollow fibre substrates. As can be  
290 seen in Figure 6, approximately 50% of the microchannel volume is filled by the LFMPO  
291 catalyst, with the microchannel endings at the substrate's inner surface remaining open (a(i)

292 and a(ii)). In contrast, the microchannel is largely filled with the LFCPO catalyst, which also  
293 blocks the microchannel endings at the inner surface of the substrate (b(i) and b(ii)). An  
294 increasing amount of perovskite catalyst inside the hollow fibre substrates provides more active  
295 sites for the catalytic reaction to proceed, which is supposed to benefit the conversion of CO in  
296 this study. Meanwhile, the formation of mini-packed-beds (Figure 6) indicates a higher transfer  
297 resistance compared to the catalyst layer in Figure 5, which retards the access of CO to the  
298 active sites of perovskite catalysts and consequently reduces the efficiency of the reaction.

299

### 300 **3.3 Evaluation of catalytic performance - CO oxidation**

301

302 Two reactor configurations were employed in this study to investigate the catalytic  
303 performance of perovskite catalysts, which include a conventional packed-bed reactor as the  
304 benchmark of catalyst performance, and a second hollow fibre reactor which can potentially  
305 be developed into a new generation of catalytic converter for automotive emissions control,  
306 due to its structural advantages over ceramic monoliths reported in our earlier work [26].

307

#### 308 **3.3.1 Packed bed reactor**

309

310 A packed-bed configuration is commonly used for investigating catalyst performance, due to  
311 an irregular flow through the voids of packing, where it creates a turbulent mixing at Reynolds  
312 numbers lower than conservative domains. This enhances the fluid transport through the  
313 braiding effect and increases contact with the catalyst through enhanced diffusion [37]. For the  
314 packed bed reactor in this study, 5 mg or 10 mg of perovskite catalysts were mixed with 200  
315 mg of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and packed inside a quartz tube reactor. Figure 7 represents the CO conversion  
316 as a function of operating temperatures, with the corresponding values of T<sub>50</sub> (the light-off

317 temperature at 50% of CO conversion) listed in Table 3. As can be seen, LFMPO shows a  
318 conversion of CO higher than LFCPO at temperatures over 200 °C, which is in line with the  
319 higher surface area of LFMPO (Table 2). In addition, since the catalytic process can be altered  
320 by modifying the interactions between the B-site species and the oxygenated species in the  
321 perovskite lattice, the change in oxygen vacancy concentration alters the catalytic activity.  
322 From a material point of view, Mn has a higher number of oxidation states than Co. This  
323 contributes to a higher synergistic activity brought about by Mn substitution. By doubling the  
324 amount of catalyst inside the packed-bed reactor,  $T_{50}$  of LFMPO reduces from 242 °C to 213  
325 °C, with LFCPO reduced from 252 °C to 235 °C (Table 3), which is still higher than commercial  
326 counterparts. However, the better thermal stability of perovskite catalysts would enable them  
327 to be placed closer to the engine to maintain a good catalytic performance, although this is not  
328 perfect to cold start.

329

### 330 **3.3.2 Packed bed reactor vs hollow fibre reactor**

331

332 For hollow fibre reactors, the reaction of CO oxidation was performed by maintaining the same  
333 conditions as the packed bed reactors, in terms of the amount of perovskite catalyst and the  
334 space velocity (GHSV of  $\sim 5300 \text{ h}^{-1}$ ). For hollow fibre reactors with 5 mg of perovskite  
335 catalysts (Figure 8 and Table 4), LFMPO shows higher conversion of CO than LFCPO, and  
336 this is in line with a packed bed reactor (Figure 7). Moreover, the hollow fibre reactor shows a  
337 light-off temperature lower than that of the packed bed counterpart. For instance, the light-off  
338 temperature of LFMPO shifted from 242 °C in packed-bed to 232 °C in the hollow fibre reactor  
339 (Table 4).

340

341 In contrast to a packed-bed reactor, in which the reactants “flow through” the porous bed, a  
342 hollow fibre reactor has a very different flow pattern. Instead of “flowing through”, the bulk of  
343 the reactants flow along the length of the direction of the hollow fibre substrate, relying on a  
344 much slower diffusion process in the radial direction, for accessing the catalyst that is  
345 deposited. As a result, the reduction in the light-off temperature is mainly due to the structural  
346 advantages of hollow fibre substrates, together with the formation of a thin catalyst layer along  
347 the microchannels inside the substrate (Figure 5). This enables better and more uniform access  
348 of the reactants to the perovskite catalysts deposited, with less transfer resistance and agreeing  
349 well with our previous studies [26].

350

351 By increasing the amount of catalyst to 10 mg, mini-packed-beds are formed inside the  
352 microchannels (Figure 6). It is interesting to see that hollow fibre reactors performed worse  
353 than packed bed counterparts (Figure 9 and Table 5). With the same amount of catalysts  
354 involved, the light-off temperatures increased from 215 °C of packed-bed to 222 °C of hollow  
355 fibre reactor for LFMPO, while the one for LFCPO increased from 237 °C to 245 °C (Table 5).  
356 By comparing the CO oxidation results in Figures 7 - 9, it is quite obvious, that the formation  
357 of the mini-packed-beds inside the microchannels significantly increase the diffusion resistance  
358 in the radial direction of the hollow fibre substrates, which reduces the efficiency of catalyst  
359 utilization and consequently increases the light-off temperature.

360

361 To further understand how transfer hindrance affects the conversion of CO, which relies on the  
362 format of perovskite catalyst packing inside the microchannels of the hollow fibre substrate,  
363 gas permeation tests were performed and the results illustrated in Figure 10. As can be seen,  
364 the permeation flux for the hollow fibre reactors with 5 mg catalysts is significantly higher than  
365 the one with 10 mg of catalysts. Furthermore, the permeation flux of LFMPO-10 mg is almost



366 double the one of LFCPO-10 mg, which agrees well with Figure 6 (a-ii) and (b-ii). This also  
367 indicates that, an excessive catalyst deposition does not work for the hollow fibre reactor  
368 design, since the actual catalyst involved in the reaction is reduced due to the significantly  
369 increased transfer resistance. In this study, for the hollow fibre reactor with 5 mg of perovskite  
370 catalysts, 0.01 mole of CO was oxidized per gram of catalyst involved. This value was reduced  
371 significantly to 0.0051 mole g<sup>-1</sup> for the hollow fibre reactor with 10 mg of catalyst, representing  
372 a nearly 50% reduction in catalyst utilization.

373

374

#### 375 **4. Conclusions**

376

377 LaFe<sub>0.7</sub>Mg<sub>0.225</sub>Pd<sub>0.075</sub>O<sub>3</sub> and LaFe<sub>0.7</sub>Co<sub>0.225</sub>Pd<sub>0.075</sub>O<sub>3</sub> with a orthorhombic structure were  
378 synthesised in this study. These catalysts were then deposited inside hollow fibre substrates for  
379 CO oxidation, the results of which were compared with packed-bed reactors. Results of CO  
380 oxidation suggests that incorporation of 5 mg LFMPO and LFCPO catalyst into the hollow  
381 fibre could be light-up at 232 °C and 248 °C, respectively, which is 3% lower than the packed-  
382 bed counterpart with the same amount of catalyst at GHSV of ~ 5300 h<sup>-1</sup>. Further incorporation  
383 of a 10 mg catalyst inside the hollow fibre resulted in a lowered catalyst utilization, where the  
384 moles of CO converted per unit mass of catalyst reduced from 0.01 mole g<sup>-1</sup> for 5mg catalyst  
385 to 0.0051 g<sup>-1</sup> for the 10 mg catalyst. This is mainly due to the higher mass transfer resistance  
386 when micro-channels were filled with perovskite particles. As a result, a better approach of  
387 forming a thin catalytic layer along the surface of micro-channels will be the key to improving  
388 performance of catalytic hollow fibre investigated in this study.

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390

391 **Acknowledgements**

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394 gratitude to the Minister of Higher Education, Malaysia and the Universiti Teknologi Malaysia  
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396

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523



524 **Highlights**

- 525 - Pd-doped perovskite catalysts efficient for catalytic converter.
- 526 - Integration of perovskite catalyst into micro-structured ceramic hollow fibre without
- 527 additional washcoating materials.
- 528 - Greater catalyst utilisation at low precious metal content.
- 529 - Excessive catalyst deposition created high mass transfer resistance.

530

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533 **Table 1** Comparison of light-off temperature for CO oxidation with different perovskite  
534 catalyst

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536 **Table 3** Light-off temperatures of CO oxidation for packed-bed reactors

537 **Table 4** Light-off temperature of CO oxidation for packed-bed (5mg of catalyst mixed  
538 with 200mg of  $\alpha$ -alumina) and hollow fibre reactor (5mg of catalyst deposited  
539 in 50mm of hollow fibre)

540 **Table 5** Light-off temperature of CO oxidation for packed bed (10mg of catalyst mixed  
541 with 200mg of  $\alpha$ -alumina) and hollow fibre reactor (10 mg of catalyst deposited  
542 in 50mm hollow fibre substrate)

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**Table 1**

547

<b>Catalyst</b>	<b>Catalyst amount (mg)</b>	<b>Reactor configuration</b>	<b>T<sub>50</sub> (°C)</b>	<b>Reference</b>
LaFe	75	Packed-bed	270	[38]
LaFe <sub>0.94</sub> Pd <sub>0.06</sub> O <sub>3</sub>			240	
LaFe <sub>0.74</sub> Cu <sub>0.2</sub> Pd <sub>0.06</sub> O <sub>3</sub>			240	
LaSrCuO <sub>4</sub>	250	Packed-bed	220	[19]
LaSrCu <sub>0.9</sub> Pd <sub>0.1</sub> O <sub>4</sub>			200	
LaFe <sub>0.6</sub> Co <sub>0.4</sub> O <sub>3</sub>	100	Packed-bed	285	[23]
LaFe <sub>0.57</sub> Co <sub>0.38</sub> Pd <sub>0.05</sub> O <sub>3</sub>			142	
LaFeO <sub>3</sub>	100	Packed-bed	535	[39]
LaFe <sub>0.9</sub> Pd <sub>0.1</sub> O <sub>3</sub>			495	
LaMnO <sub>3</sub>			485	
LaMn <sub>0.9</sub> Pd <sub>0.1</sub> O <sub>3</sub>			425	
LaFeO <sub>3</sub>	100	Packed-bed	330	[40]
LaFe <sub>0.97</sub> Pd <sub>0.03</sub> O <sub>3</sub>			230	
LaFeO <sub>3</sub>	100	Packed-bed	249	[12]
LaFePd <sub>0.05</sub> O <sub>3</sub>			150	
LaMnO <sub>3</sub>			249	
LaFePd <sub>0.05</sub> O <sub>3</sub>			170	
LaCoO <sub>3</sub>			190	
LaCoPd <sub>0.05</sub> O <sub>3</sub>			155	

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549

**Table 2**

550

<b>Sample</b>	<b>S<sub>BET</sub> (m<sup>2</sup>g<sup>-1</sup>)</b>	<b>Average Crystallite Size (nm)</b>	<b>XRD Crystal Structure</b>
LaFe <sub>0.7</sub> Mn <sub>0.225</sub> Pd <sub>0.075</sub> O <sub>3</sub>	20.69 ± 0.09	24.01	Orthorhombic
LaFe <sub>0.7</sub> Co <sub>0.225</sub> Pd <sub>0.075</sub> O <sub>3</sub>	10.73 ± 0.05	27.88	Orthorhombic
Alumina Hollow Fibre	1.42 ±	-	-
Substrate	0.01	-	-
5mg 0.075 Pd/ γ-Al <sub>2</sub> O <sub>3</sub> hollow fibre composite, Calcination at 500 °C	4.55 ± 0.01	-	-
5mg 0.075 Pd/ γ-Al <sub>2</sub> O <sub>3</sub> hollow fibre composite, Calcination at 700 °C	3.99 ± 0.01	-	-

551

552

**Table 3**

553

<b>Catalyst</b>	<b>Condition</b>	<b>T<sub>50</sub></b> <b>(°C)</b>
$\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$	5 mg	242
$\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$	10 mg	213
$\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$	5 mg	252
$\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$	10 mg	235

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**Table 4**

556

<b>Catalyst</b>	<b>Condition</b>	<b>T<sub>50</sub></b> <b>(°C)</b>
$\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$	Packed-bed	242
$\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$	Hollow Fibre	232
$\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$	Packed-bed	252
$\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$	Hollow Fibre	248

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**Table 5**

560

<b>Catalyst</b>	<b>Condition</b>	<b>T<sub>50</sub></b> <b>(°C)</b>
$\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$	Packed-bed	215
$\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$	Hollow Fibre	222
$\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$	Packed-bed	237
$\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$	Hollow Fibre	245

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562

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564

565 **Figure 1** Experimental steps of preparing perovskite catalysts

566 **Figure 2** Reactor configuration

567 **Figure 3** XRD diagram of  $\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$  and  $\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$  calcined  
568 at  $700^\circ\text{C}$  for four hours

569 **Figure 4** SEM images of a) cross-section of hollow fibre substrate, b)  
570  $\text{LaFe}_{0.7}\text{Mn}_{0.225}\text{Pd}_{0.075}\text{O}_3$  and c)  $\text{LaFe}_{0.7}\text{Co}_{0.225}\text{Pd}_{0.075}\text{O}_3$  catalyst deposited inside  
571 hollow fibre substrate.

572 **Figure 5** SEM images of (a) substrate without catalyst; (b) substrate with 5mg LFMPO  
573 catalyst; (c) substrate with 5mg of LFCPO catalyst. (i) top-view of substrate  
574 inner surface and (ii) side-view of substrate cross-section

575 **Figure 6** SEM images of (a) substrate with 10mg LFMPO catalyst; (b) substrate with  
576 10mg of LFCPO catalyst. (i) top-view of substrate inner surface and (ii) side-  
577 view of substrate cross-section

578 **Figure 7** Light-off temperature of CO oxidation for packed bed reactors

579 **Figure 8** Light-off temperature of CO oxidation for packed-bed (5mg of catalyst mixed  
580 with 200mg of  $\alpha$ -alumina) and hollow fibre reactor (5mg of catalyst washcoated  
581 in 50mm of hollow fibre)

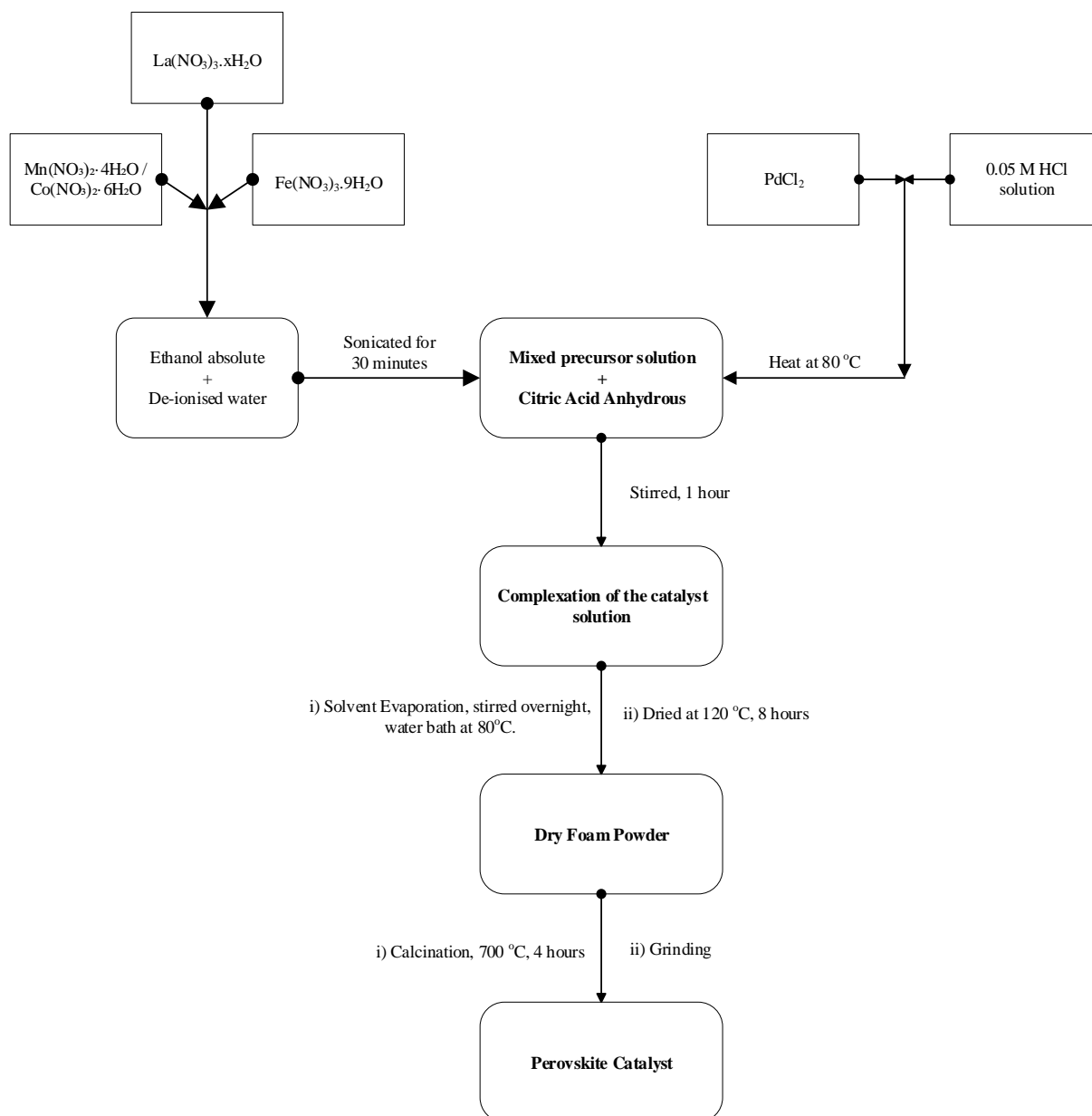
582 **Figure 9** Light-off temperature of CO oxidation for packed-bed (10mg of catalyst  
583 supported on 200mg of  $\alpha$ -alumina) and hollow fibre (10mg washcoated on  
584 50mm of hollow fibre)

585 **Figure 10** Gas permeation tests of hollow fibre substrates deposited with different amount  
586 of catalysts

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Figure 1



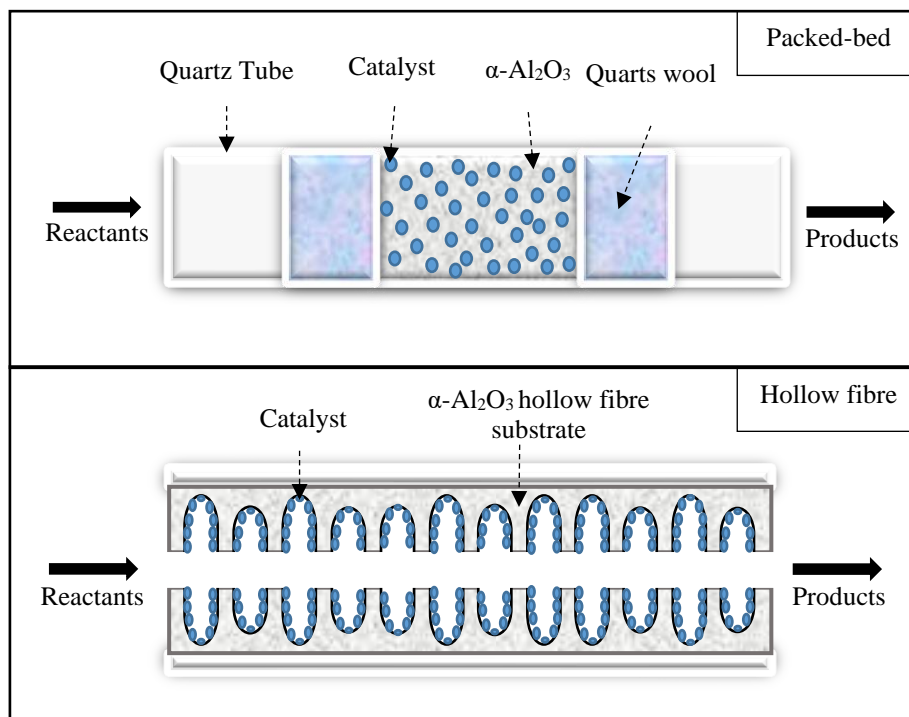
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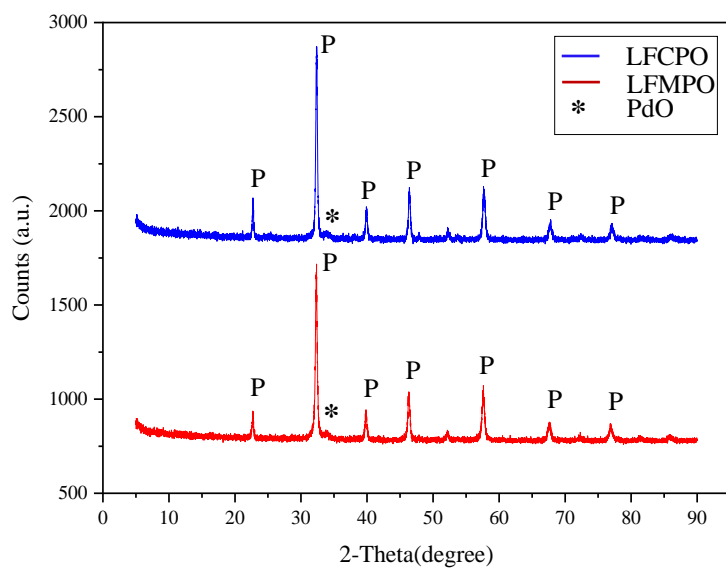
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Figure 2



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Figure 3



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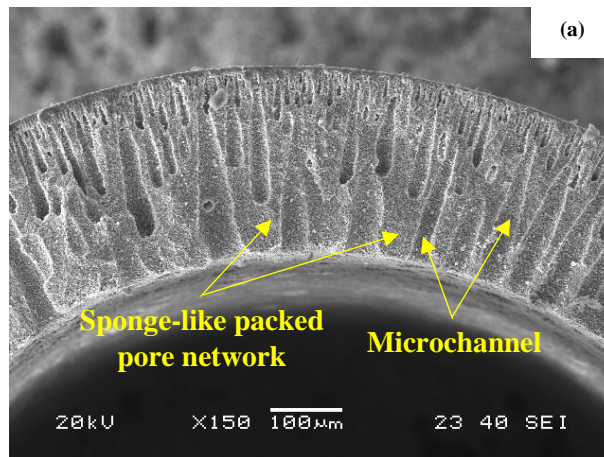
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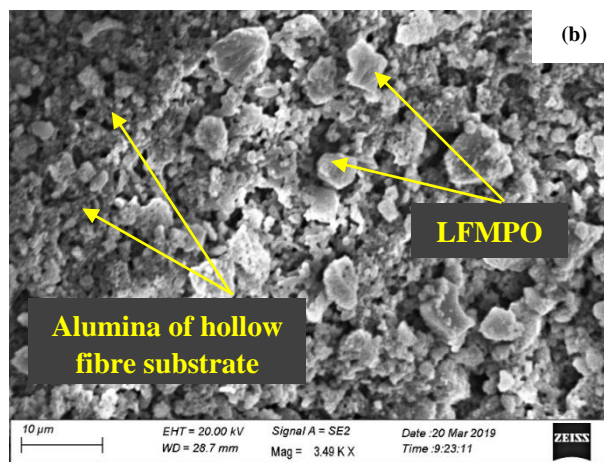
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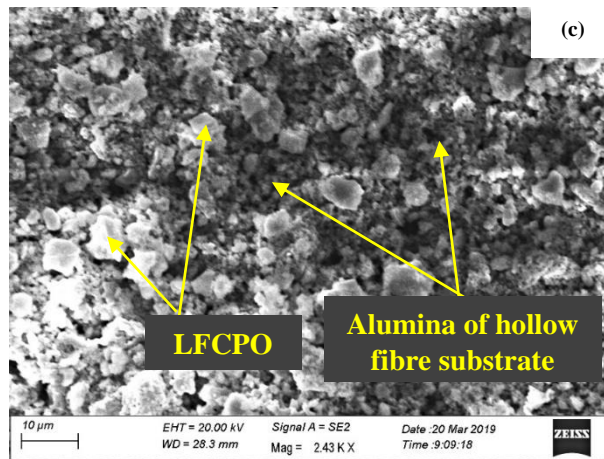
Figure 4



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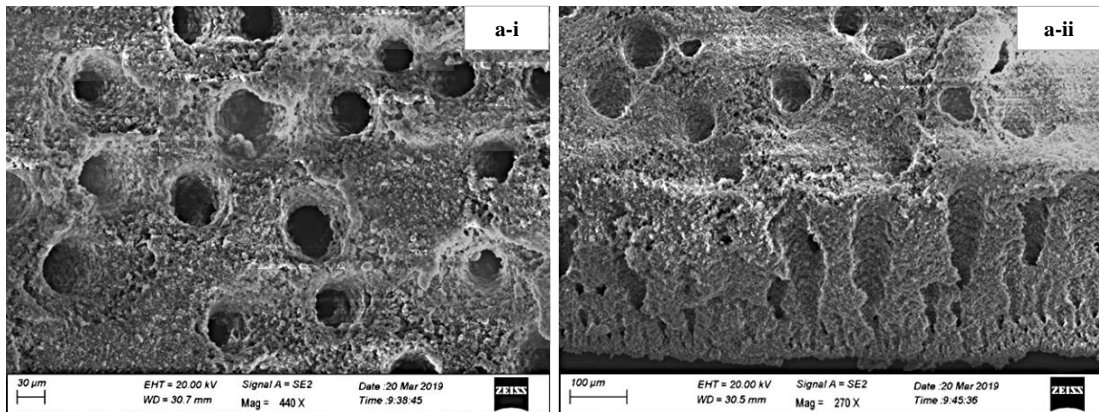
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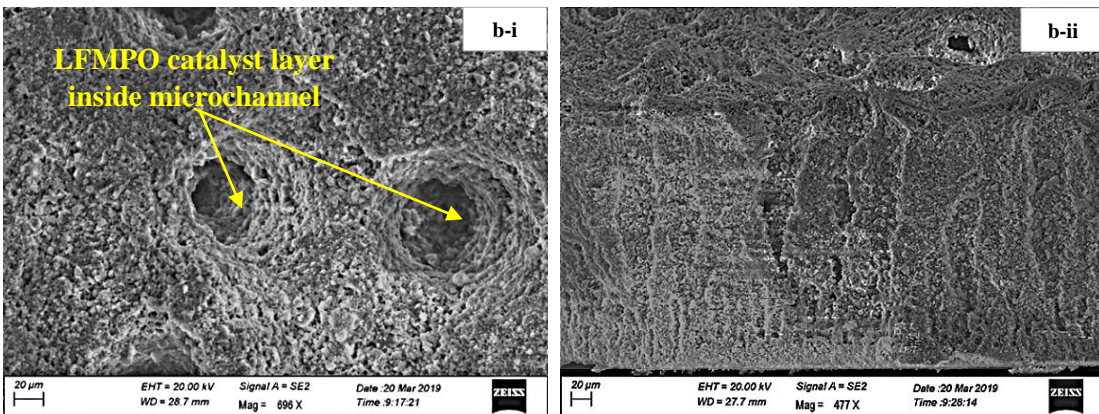
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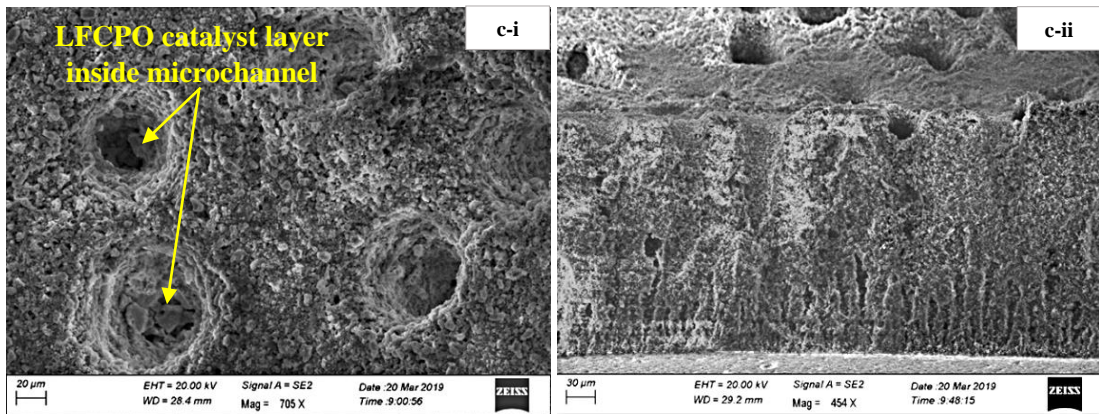
Figure 5



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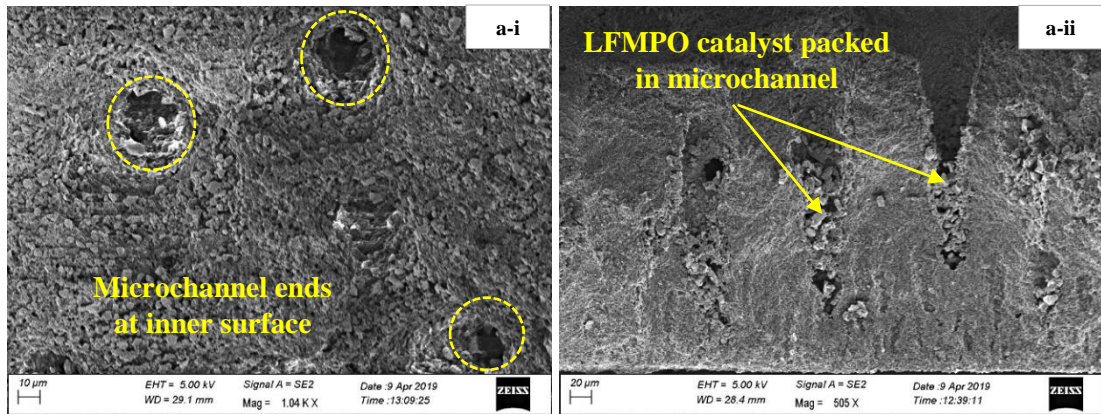
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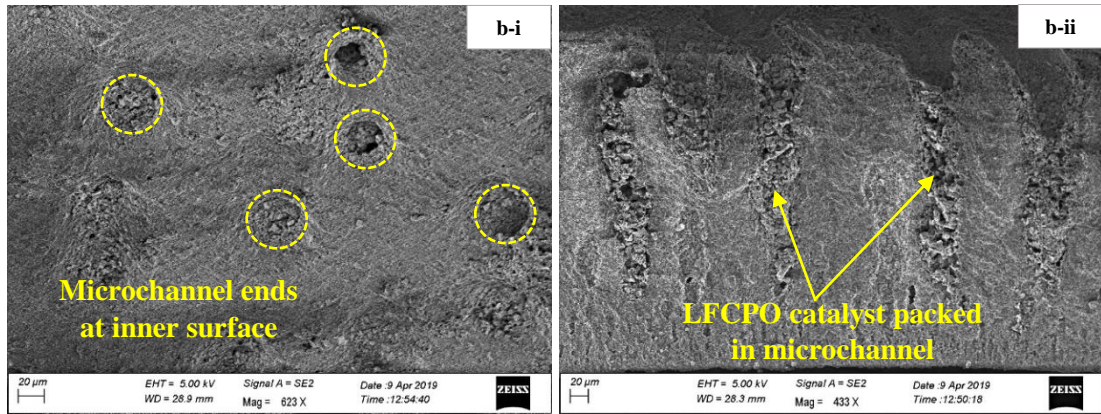
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Figure 6

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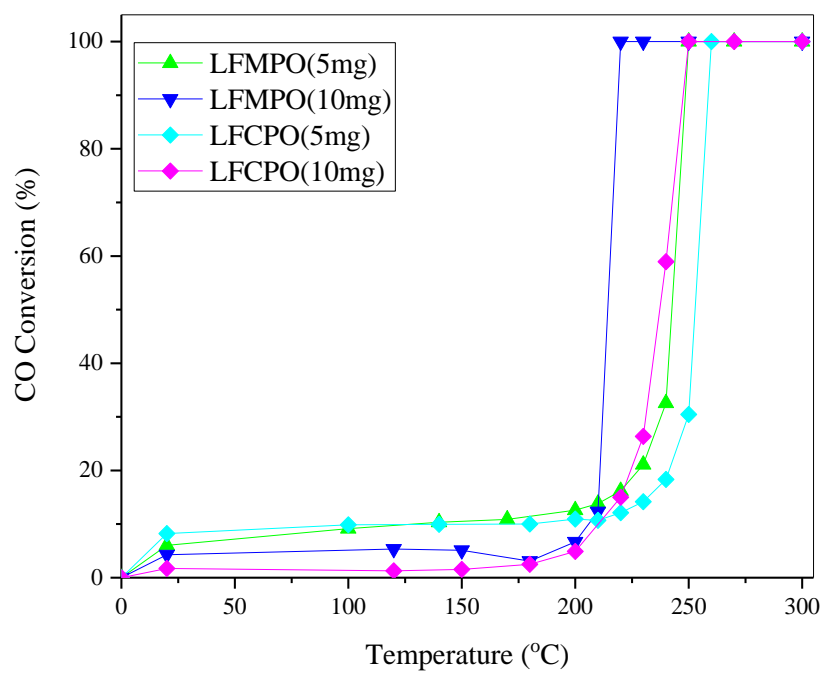
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Figure 7



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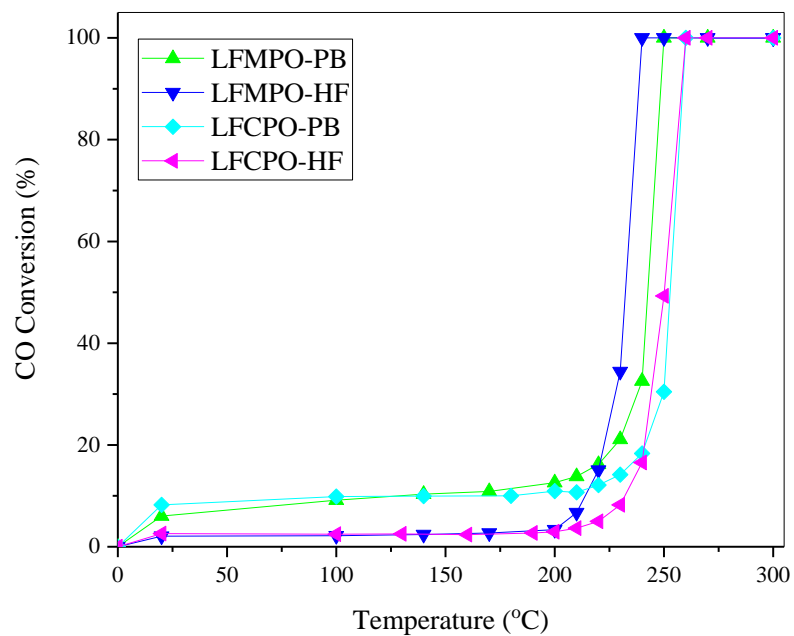
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Figure 8



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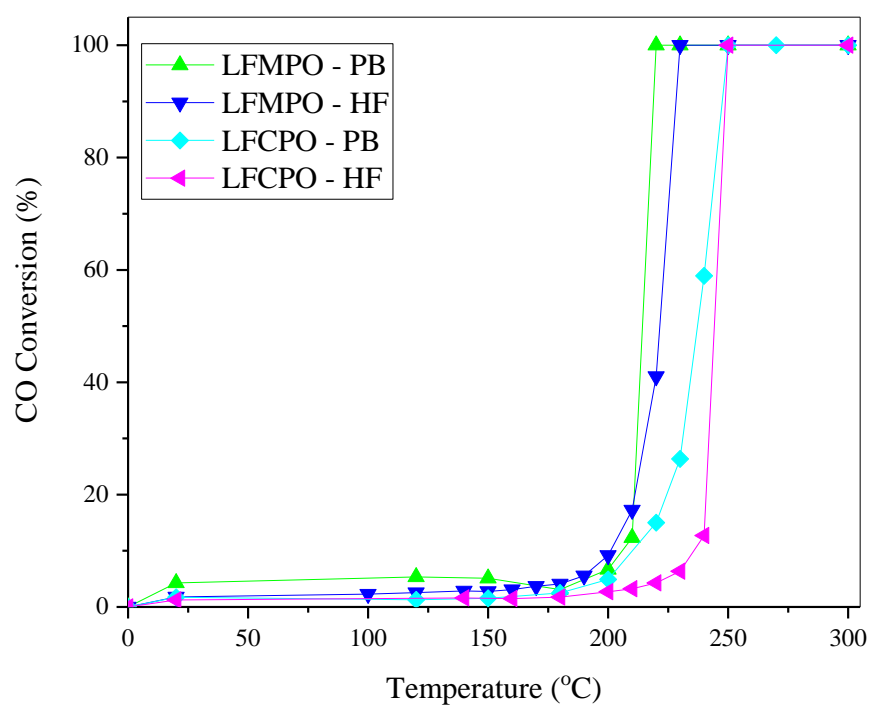
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Figure 9



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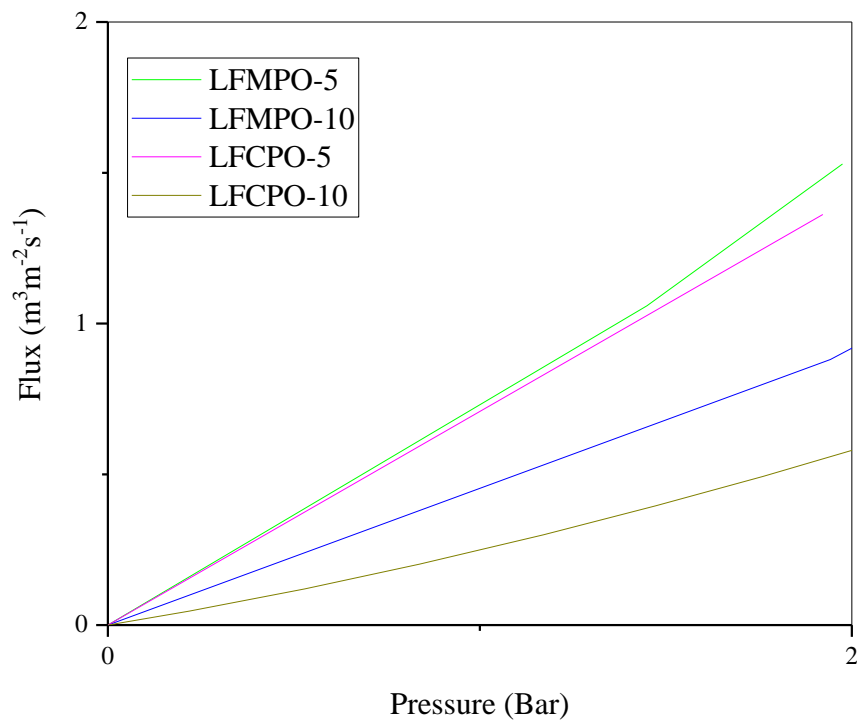
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**Figure 10**



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