

Porous Al₂O₃ catalyst carrier by 3D additive manufacturing for syngas reforming

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A disk-shaped ceramic catalyst made by 3D printing (3DP) is used to reform syngas. We select two Al₂O₃ powders (α - and high-surface-area θ -Al₂O₃) and polymeric binders for preparing the 3DP feedstock. Catalyst stacked Al₂O₃ disks are made by kneading the polymers with ceramic powders and extruding to produce filaments, which are melted and used for 3D additive manufacturing (AM). The processing parameters (sequence of addition, viscosity of the feedstock, etc.), the phase transformation of the θ -powder, and catalytic properties of the made carrier are examined. The made alumina disks were densified to a relative density (RD) of 40%–65%. Two porous disks were coated with catalyst NiO and CeO₂, and used to reform syngas made from waste paper. The best case reforms the CH₄ content in the syngas from 25.7% down to 0.15% or lower. The reformed gaseous fuel is suitable for solid oxide fuel cells (SOFCs).

Key words: Al₂O₃, catalyst, 3D printing, additive manufacturing, feedstock.

Introduction

Fused deposition modeling (FDM) is one of the popular methods widely known in 3D additive manufacturing (AM) [1–3]. This is partially due to its simpler equipment and lower cost of operation compared to other techniques, e.g. selective laser sintering (SLS). However, most ceramics and refractory metals are limited [4, 5] to high melting temperatures and are hardly made directly by FDM. Thus, we require different manufacturing methods to the reports in the literature [3–10]. A new module, called the Melt Extrusion (ME) module, was proposed and practiced using ceramic/polymer filaments in our previous work [11]. Pure polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) are currently made into a filament shape and then fed into equipment to fabricate plastic parts by FDM. The filaments are curled into an easily portable coil and continuously fed into a hot nozzle to produce 3D parts of complex design [11–13].

Hwang *et al.* [13] demonstrated Fe or Cu powder compounds with ABS to form composite filaments, which is used it to fabricate circuits and electromagnetic devices by FDM. Lewis and Smay [14] took different media, aqueous ink with polyethylene imine (PEI)-coated silica, and printed the parts for tissue engineering scaffolds. Very limited FDM researches have been

reported using composite materials, of which ceramic powder was mixed with polymer and then the materials were used as the 3DP feedstock.

Ceramic feedstock kneaded with several polymer additives are currently used in ceramic injection molding (CIM). CIM has been rapidly developed due to strong demand in the past two decades because of the needs of the reproducibility of near-net-shape ceramic pieces [15]. The development of a powder/polymer blend in past decades has established an important background for the need of feedstock in 3D printing.

For formulating the polymer carrier used in precision injection molding (PIM), there are three basic ingredients, primary (backbone) binder, plasticizer (low molecular weight wax), and surfactant [15, 16]. Our previous work [11] used formulations, containing Al₂O₃, maleic acid-PP (MA-PP), and other polymeric materials, to achieve acceptable flexibility of made filaments and debinding behavior of the Al₂O₃ feedstock.

This study continues our previous investigation on the use of high-purity Al₂O₃, but the one with high-specific surface area powder is used as a catalyst carrier. The other objective concerns the test of reforming syngas from paper waste. Since different city wastes produce various types of syngas as a fuel for solid oxide fuel cell (SOFC), one of the compositions of the syngas CH₄ is detrimental to the anode [17]. The fuel gas needs reforming.

Based on previous results and previous accomplishments on the gasification of various biomass and city wastes [18],

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we examine the effects on the property change of alumina powders, the formation of catalyst carrier, and reforming performance of syngas from a waste paper (recovered from paper cup) in this study. Detailed phase transformation of the $\theta\text{-Al}_2\text{O}_3$ powder and the surface area reduction of the powder, etc., are also studied. Besides, an in-house ME module is used to produce a porous carrier in a disk shape to understand the potential of the reforming of the syngas from municipal waste.

Experimental Method

Sample preparation

Two alumina powders are used. One is α -phase (99.5% pure, P172SB, Gardanne, France) with an average particle size of $0.5\ \mu\text{m}$ and specific surface area of $5.0\ \text{m}^2\text{g}^{-1}$. The other is θ -phase (99.96% pure, APA-0.2, Ceralox, US) $0.06\ \mu\text{m}$ in size with a surface area of $35\ \text{m}^2\text{g}^{-1}$.

Previous works [11, 16] identified two polymer systems, polypropylene grafted with maleic acid (MA-PP, ACROS, Belgian), and ethylene vinyl acetate (EVA, UE633, USI Corp, Taiwan) as the binders for the alumina powder feedstock. Paraffin wax (PW, 140F, Taiwan Wax, LTD., Taiwan) and stearic acid (SA, ACROS, US) are used as plasticizer and surfactant, respectively. Flexible, homogeneous polymer blends containing Al_2O_3 powder (α - or $\theta\text{-Al}_2\text{O}_3$) are prepared by two efficient kneading processes, either with or without the twin-rolling step. The feedstock is then extruded to produce filaments of 1–2 mm diameter. To improve the physical properties of the filament, including flexibility, the dispersion of powder and addition sequence of the ingredients are tested.

Powder, MA-PP and EVA are the three major ingredients for the sequence test. Previous results [11]

showed only those filaments containing EVA in quantities of 30–40 wt% or 50–60 wt% on the basis of MA-PP+EVA+PW possessed appropriate flexibility for 3D additive manufacturing. We use a similar sample abbreviation as before [11], defining two formulations, $\theta\text{E60-40}$ and AE40-50 , for this study, which mean using either α - or θ -phase powder, EVA in 60 or 40 wt% comparing to (MA-PP+EVA), Al_2O_3 loading in 40 or 50 vol%, respectively. Similar processing conditions were used for preparing the filaments, of which the formulations are shown in Table 1.

Three kneading processes (P1, P2 and P3) are described below. The powder was heated first to $200\ ^\circ\text{C}$ for 10 min, and then binders were added in the sequence of either PP + EVA (P1), or PP first, then EVA (P2), or EVA first, then PP (P3) kneading for 60 min at $180\ ^\circ\text{C}$ [15]. PW and SA (see Table 1) were added after the binders were all kneaded for 60 min. The feedstock was blended and cooled in a kneader, then granulated to small chips of ca. 5 mm in a cross section. Part of the reported data in this study used the other feedstock, where the granulates were kneaded again by a twin-roll mixer (Bellaform, Germany) in

Table 1. Formulation of two alumina feedstocks.

Ingredient	$\theta\text{E60-40}$	AE40-50
Al_2O_3 loading	40 vol% (72.9 wt%)	50 vol% (81.7 wt%)
MA-PP/EVA (wt%)	40/60	60/40
PW/binder/SA (wt%)	20/70/10	20/75/5
Binder: MA-PP	7.59 wt%	8.25 wt%
EVA	11.39 wt%	5.5 wt%
PW	5.42 wt%	3.67 wt%
SA	2.71 wt%	0.92 wt%

Density of $\theta\text{-Al}_2\text{O}_3 = 3.58\ \text{gcm}^{-3}$, $\alpha\text{-Al}_2\text{O}_3 = 3.95\ \text{gcm}^{-3}$, MA-PP = $0.901\ \text{gcm}^{-3}$, EVA = $0.938\ \text{gcm}^{-3}$, PW = $0.80\ \text{gcm}^{-3}$, and SA = $0.847\ \text{gcm}^{-3}$.

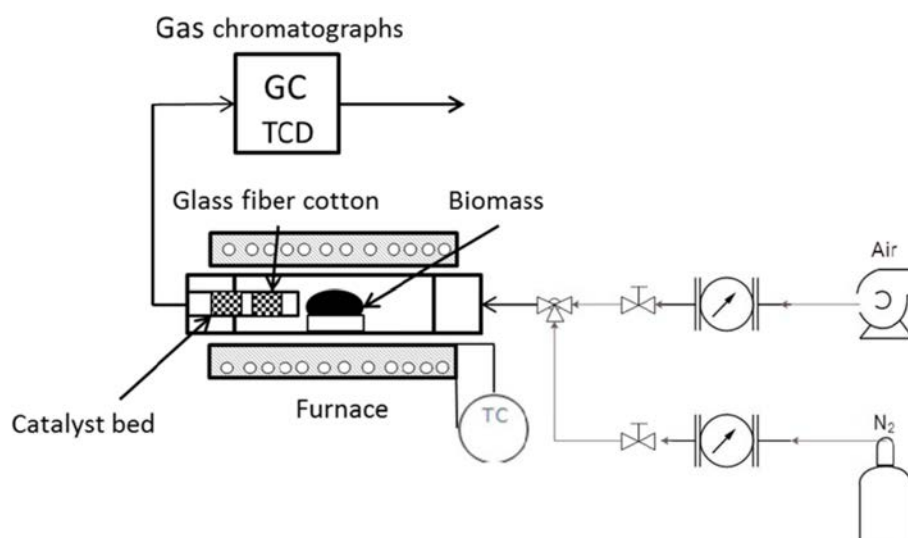


Fig. 1. Schematic diagram of the gasification/reforming test. Glass tube located at the center of the furnace is 2.16 cm in diameter, hosts biomass, glass filter cotton, and catalyst tube containing Ni + $\text{CeO}_2/\text{Al}_2\text{O}_3$ disks.

selected conditions to prepare the feedstock to achieve the best dispersive condition.

The feedstock was extruded by a single screw extruder (Barbender, Germany) to filaments in a ca. 1.5 mm diameter. One filament at a time was fed into a 3D printer (FDM series, Li-Huey, New Taipei city, Taiwan) and the green parts in a disk-shape of $\phi = 43$ mm and a thickness of 1.0 mm were printed out. The disks then went through solvent debinding, thermal debinding, and sintering at 1100 °C for 1 hr to 12 hrs. Following optimization the processing conditions of the formulation, the disks were densified to a sintered density better than 52% theoretical density (T.D.) [19].

The porous Al_2O_3 disks were repeatedly infiltrated with 0.1 M $\text{Ce}(\text{NO}_3)_3$ and then 0.1 M $\text{Ni}(\text{NO}_3)_2$ solutions. After the absorbed nitrates were calcined at 800 °C in air, the gain mass was the produced NiO or CeO_2 . The filtration was repeated until the mass ratio of $\text{NiO} \cdot \text{CeO}_2 \cdot \text{Al}_2\text{O}_3$ reached 1.0 : 1.0 : 10. The syngas was produced from a mixture of waste paper with 10 mass% K_2CO_3 , which was used to reduce the tar content in the syngas [18]. The proximate analysis results of waste paper were as follows: moisture 5.2%, fixed carbon 16.2%, ash content 0.8%, volatile content 77.9% and low heat value (LHV) 18.6 MJ kg^{-1} . The paper/ K_2CO_3 mixture would be dried at 130 °C to remove the adsorbed water before being placed in an 800 °C-preheated gasifier. Details of the reforming test equipment are shown in Fig. 1, consisting of a box furnace, glass tube and reaction bed for filtering of tar, solid particles, and reforming of syngas.

Characterization

Bending test of feedstock was conducted to measure the bending angle of the filaments just about to break. 35 ° bending angle of a 50 mm long filament is the minimal angle needed for a filament fed into the printer. The viscosity of the melted feedstock was measured by a viscometer (B-one touch, Lamy Rheology Instrument, French) at 200 °C. The microstructures of the raw feedstock, filaments and sintered Al_2O_3 parts were characterized by scanning electron microscope (SEM, JEOL Japan).

Phase transformation of the Al_2O_3 was detected by an X-ray diffractometer (TTRAX3, Rigaku, Japan). The specific surface area of the powder was determined by the instrument (Tristar, Micrometry, US) and compared to our previous report [20]. The gas content of syngas, including CH_4 , CO, H_2 , was quantified by a gas chromatographer (GC2000, China Chromatography Co., Taiwan).

Rectangular test-bars made from feedstock and sintered samples for 4-point bending flexural-strength test were prepared in a size of $4.0 \times 5.0 \times 40$ mm³. Averages of at least three pieces of data or completion of 10 data tests for estimating standard deviation were conducted. The fracture surface of the feedstock was

observed to estimate the dispersive index (D_s) defined as below [16].

$$D_s = 1 - \phi_a = 1 - \frac{1}{A_0} \sum_{i=1}^N A_i \quad (1)$$

where ϕ_a is the fraction of agglomerates/polymer blend, A_0 is the total analysis area, A_i is the area of each agglomerate i .

Results and Discussion

Feedstock properties

The content of EVA at a level of $\geq 30\%$ was reported for the feedstock to have appropriate flexibility [11]. Besides, the feedstock made from the low-surface-area α -alumina powder was more flexible than that from the θ -powder. Therefore, AE60-xx was first selected as the following test object of filament flexibility. Fig. 2 shows the bending angle of the filaments made from different solid contents of α - Al_2O_3 powder in the AE60 feedstock. All samples meet the requirement of the bending angle $\geq 35^\circ$ for feeding to most of 3D printer. The filaments made by P2 process show a higher bending angle and better flexibility than the other samples.

The dispersion condition of the feedstock is one of the important properties. Fig. 3 shows one typical fractured surfaces of the AE40-50 feedstock, imaging by either secondary electron (SE) or backscattering electron (BE) conditions. The residual polymeric regions have irregular features in darker contrast in Fig. 3(b), and the brightest contrast (hardly observed in this magnification) is the sub-micrometric Al_2O_3 particles. The area of each polymeric regions is colored red (Fig. 3(c)) and represents a non-homogeneously mixed

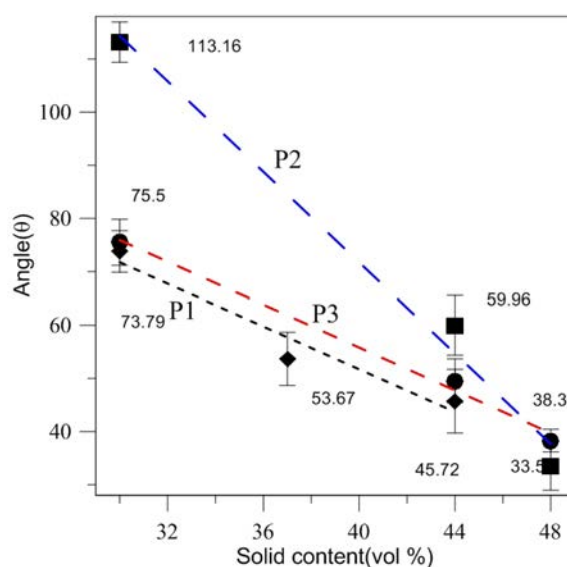


Fig. 2. Bending angle of filaments (AE60-xx) as a function of solid content of the α - Al_2O_3 powder used to prepare filaments by three kneading sequences.

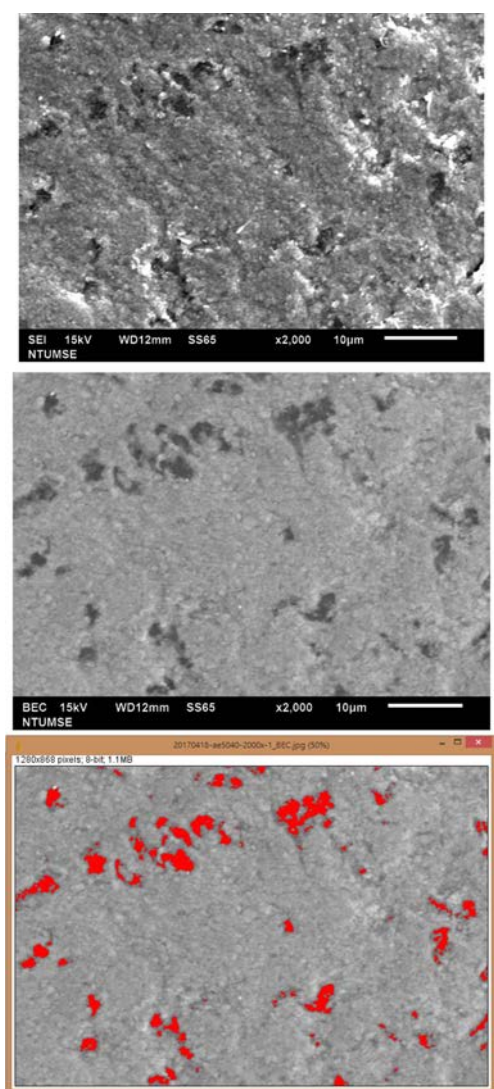


Fig. 3. SEM of the fractured surface of AE40-50 feedstock imaged by (a) secondary electron (SE) imaging, (b) back scattered (BS) imaging, and (c) the polymeric regions are marked. The area can be counted by image analyzer program and get the dispersive index.

polymer blend. The D_s of this sample is 0.89 ($f_a = 11\%$). This high D_s value is rarely seen in the series prepared by the σ -kneader. The compatibility of three polymer blend MA-PP/EVA/Wax is considered. The paraffin wax cannot be adapted to the feedstock rich in MA-PP due to the compatibility issue (one is hydrophilic, the other is hydrophobic). The wax is not able to be dissolved in EVA/MA-PP blend, and possibly form a fibrous wax-phase in the MA-PP/EVA/PW/SA system. Some of the fibers are often seen in θ E60-40.

Fig. 4 shows the microstructure of the fracture surfaces of various feedstocks without twin-rolling step. Most of the Al_2O_3 particles in the feedstock are in a dispersive state, but some of agglomerated particles in bright features in Figs. 4(a), (d), and (g) are in various degrees of agglomeration. The area (A_i) of the

polymer blend/ Al_2O_3 agglomerates can be statistically sum-up to give dispersive index (D_s) as Eq. (1). Following analysis of the SEM micrographs, the D_s of each feedstock is reported in Fig. 5.

The D_s of AE60-xx samples is included in the shaded area, in the range of 0.65 to 0.95 as the solid content of 30% to 48% in Fig. 5. High D_s indicates a better dispersion condition of the fine Al_2O_3 particles/polymer in the feedstock. As the solid content is increased to 48%, D_s is close to 1.0. Figs. 4 & 5 shows feedstock of 30 vol% Al_2O_3 loading by P2 has a D_s of ca 0.7, but no significant differences among three feedstocks as the solid content with 48 vol%. As a consequence, a high solid loading (40 vol% or higher), appropriate EVA/MA-PP ratio (AE30 ~ AE 40, and AE60) are promising formulations. Besides, the D_s of the feedstock is also strongly controlled by a twin-rolling step, achieving good dispersion of Al_2O_3 powder in the polymer blend. Two cases ($D_s = 0.944$ and 0.958) of good feedstock are prepared and shown in Fig. 5.

Previous research [11] showed the ceramic parts made by AE60-48 could be typically sintered to 85% theoretical density (T.D.). Moreover, the AE60-50 alumina samples if kneaded by the twin-rolling step could be sintered to nearly full density (98.5% T.D.) by 1500 °C in 1 hr. However, the case of θ E60-40 used for ceramic carrier needs uniform porosity to carry the catalyst for reforming syngas. Below, we use a similar formulation and kneading design to effectively prepare the feedstock and porous ceramic disks.

Two granulated feedstocks are shown in Fig. 6. The apparent viscosity of two Al_2O_3 feedstocks and one ABS testing at 200 °C was measured and reported in Fig. 6(c). Three samples show a pseudo-plastic flowing behavior, and the viscosity of both Al_2O_3 feedstocks is less than that of ABS, which is often used as a standard plastic filament for a 3D FDM printing machine and normally extruded at temperatures of 200-260 °C. Two alumina feedstocks can be extruded at lower pressure than that of ABS.

Sintering and fracture strength

One of the objectives of this study is to form a porous catalyst carrier with an appropriate strength. Therefore, the sintering test of the Al_2O_3 aims to find the sintering temperature with limited densification but retaining continuous porosity [19]. Under the requirements, at least 30% porosity and limited neck-growing between Al_2O_3 particles are selected as the objective properties for the ceramic carrier.

Fig. 7 shows the relative sintered density (RD) of the θ - Al_2O_3 disks. The RD is typically in the range of 41%-44% T.D. while being sintered at ≤ 1050 °C for 1 hr. But the density apparently increases if the temperature is higher than 1050 °C. The density profiles of the

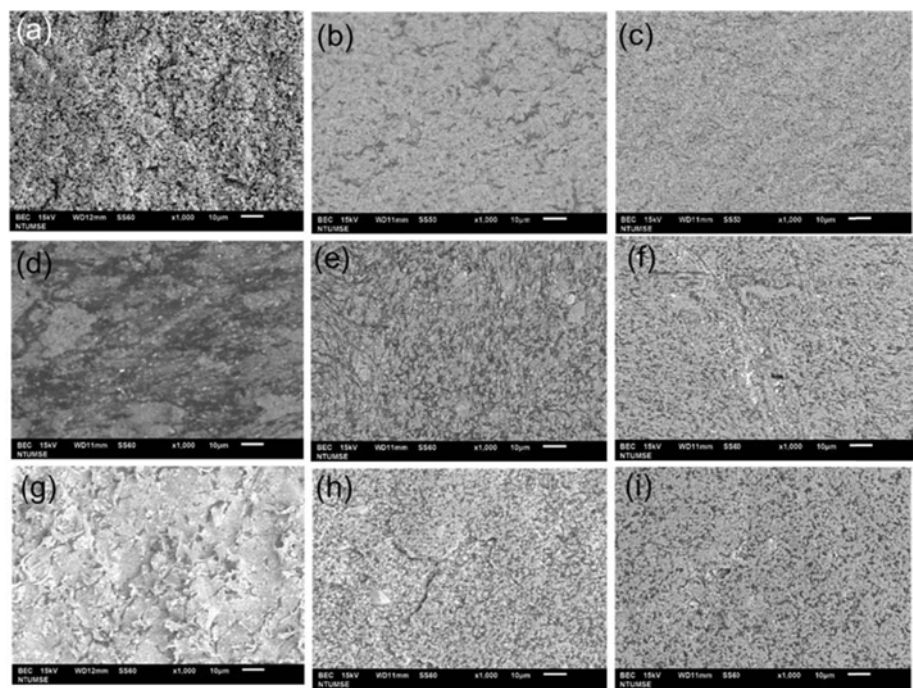


Fig. 4. SEM micrographs showing the fracture surfaces of the feedstock imaging by back scattering electron. (a) P1AE60-30, (b) P1AE60-44, (c) P1AE60-48, (d) P2AE60-30, (e) P2AE60-44, (f) P2AE60-48, (g) P3AE60-30, (h) P3AE60-44, and (i) P3AE60-48.

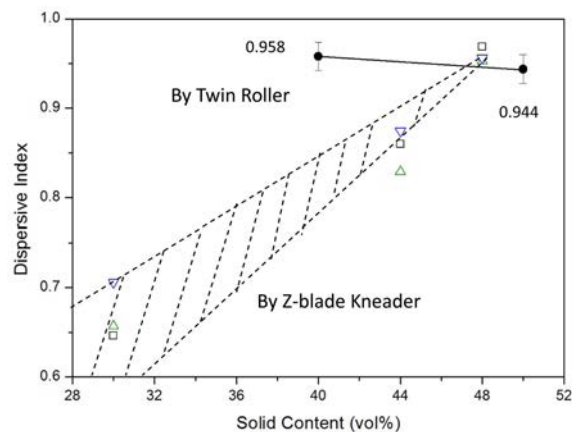


Fig. 5. Dispersive index (D_s) plotted against solid content of the feedstocks, AE60-xx prepared in previous figure. The solid symbols (●) show the samples kneading by P3 and twin-rolling step. Two D_s values (0.944 and 0.958) are an average of 20 data and showing a standard deviation of 1.6%.

feedstock θ E60-40 and AE50-40 undergo different steps after sintering at $> 1050\text{ }^{\circ}\text{C}$ and $> 1100\text{ }^{\circ}\text{C}$, respectively. The temperature of the density transition is around $1100\text{ }^{\circ}\text{C}$, implying the starting point of mass diffusion of the alumina particles. Therefore, a temperature of $1100\text{ }^{\circ}\text{C}$ was selected to achieve limited ($< 5\%$) densification for the following sintering practice.

To improve fracture strength, the sintering time of θ E60-40 samples was extended from 1 hr to 12 hr at $1100\text{ }^{\circ}\text{C}$. Fig. 8 shows the sintering density and the flexural strength of the porous Al_2O_3 bend-bars. The strength and RD of the bend-bars at $1100\text{ }^{\circ}\text{C}$ for 4 h is $6.0 \pm 1.5\text{ MPa}$ and 48% T.D., respectively, which are

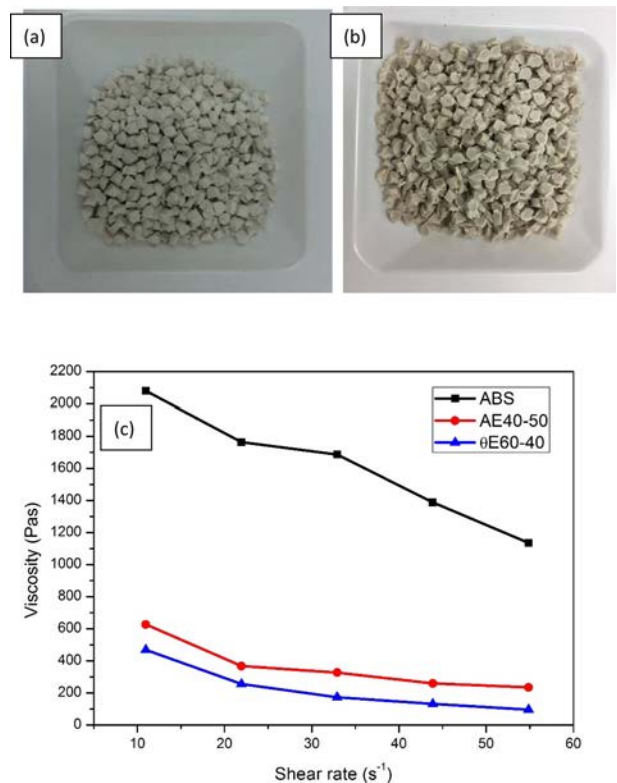


Fig. 6. Pictures of granulated (a) AE40-50 and (b) θ E60-40 feedstocks, and (c) apparent viscosity curves of two feedstocks plotted against shear rate tested at $200\text{ }^{\circ}\text{C}$, comparing to the viscosity of ABS tested in same conditions.

good enough for the applications of porous carrier going through the processing steps of NiO-CeO_2 dip-coating and reforming of syngas.

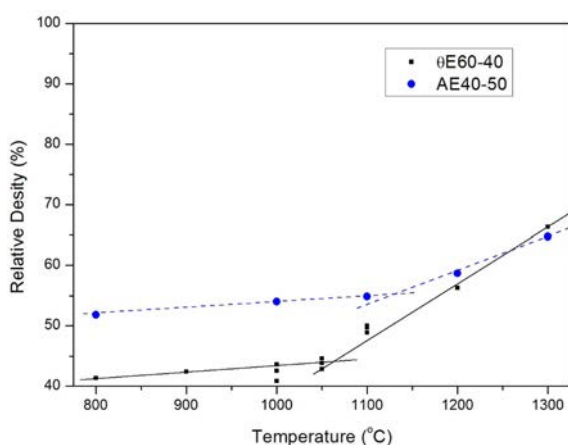


Fig. 7. Sintering density plotted against sintering temperature of two alumina samples made from the feedstock either AE40-50 or $\theta\text{E60-40}$.

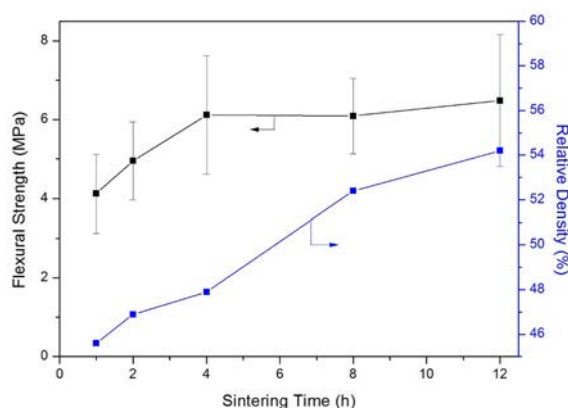


Fig. 8. Average fracture strength with standard variation of 1σ and relative density of $\theta\text{E60-40}$ samples sintered at 1100 °C for various periods.

Phase transformation and additive manufacturing of Al_2O_3 disks

The phase transformation of the $\theta\text{-Al}_2\text{O}_3$ powder to α -phase strongly affects the surface-area of the made carrier. About 10 wt% α -phase in the θ -phase matrix is maintained if the $\theta\text{-Al}_2\text{O}_3$ goes through the heat treatments at 800 °C holding up to 200 min, or 1000 °C up to 2 hrs [20]. However, the α -phase becomes the dominating phase of sintering at 1100 °C for 1 h to 4 h. The phase transition of θ to α is rapid, and likely loses its specific surface area at 1100 °C. At this temperature, the powder transforms to the α -phase and reduces the specific surface area to a level less than $10\text{ m}^2\text{g}^{-1}$ (Fig. 9), which is still high for adsorbing fine-grain catalyst.

The schematic diagrams of the printing Al_2O_3 carrier in a disk shape are shown in Fig. 10. The disks with shallow ditches in a radial direction are made by 3D printing and designed to easily stack-up. One made Al_2O_3 disk is shown in Fig. 10(c). In the reforming test, several disks are stacked together to have the same mass (30 ± 3 g) as the comparable case, containing the $\gamma\text{-Al}_2\text{O}_3$ balls used in our previous test [18].

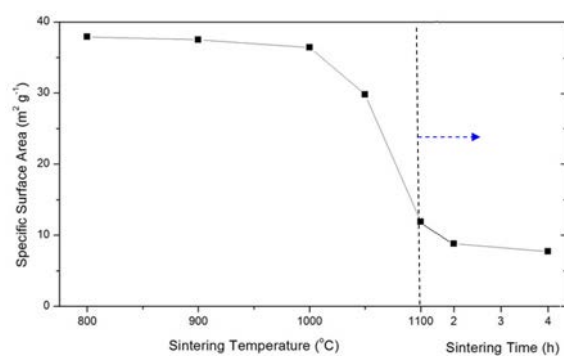


Fig. 9. Specific surface area of $\theta\text{-Al}_2\text{O}_3$ samples calcining at selected temperatures 800 °C-1100 °C for 1 h, then holding at 1100 °C for 1 h to 4 h.

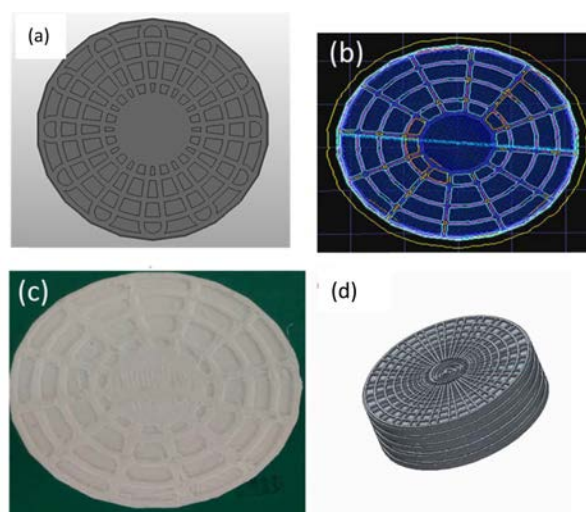


Fig. 10. (a) Schematic CAD model of printed item, (b) walking path of extruded nozzle, (c) photos of printed Al_2O_3 disk in a resolution of 0.15 mm, (d) stacked disks used as Ni-CeO₂ carrier.

Table 2. Gas compositions of waste paper after gasification in different catalytic conditions.

Waste paper RT-800 °C	CH ₄	CO	H ₂
Without K ₂ CO ₃ [5]	25.7%	51.7%	22.6%
With K ₂ CO ₃ [5]	20.6%	46.9%	32.4%
Without K ₂ CO ₃ , then reforming with the carrier ($\theta\text{E60-35}$)	7.1%	23.1%	69.8%
With K ₂ CO ₃ , then reforming with the carrier ($\theta\text{E60-40}$)	0.15%	48.8%	51.0%
With K ₂ CO ₃ , then reforming with the carrier ($\theta\text{E60-35}$)	ND* ¹ ($<0.1\%$)	54.8%	45.2%

*¹ND: below the detectable level of 0.1%.

Reforming by (Ni-CeO₂)/ Al_2O_3

The reforming of syngas was conducted into two stages [18]; the first was gasifying the waste paper with/without K₂CO₃, the other was reforming the syngas using stacked disks ($\theta\text{E60-35}$ and $\theta\text{E60-40}$). The results of the gas composition after reforming are shown in Table 2. The syngas prepared from the

mixture of the waste paper and K_2CO_3 showed a lower CH_4 content (20.6%) than the one without K_2CO_3 (25.7%). In addition, an improvement in H_2 content (from 22.6% to 32.4%) was also noted.

Additional comparison is shown in the last two cases in Table 2. The syngas produced by the help of K_2CO_3 were reformed by two $\theta E60$ -xx disks (with $NiO-CeO_2$ catalyst). The reforming by $NiO-CeO_2$ on $\theta E60$ -35 disks was able to reduce the CH_4 content to 7.1%, and increase H_2 content to 69.8%, simultaneously. The reforming of CH_4 in the syngas was apparent by the catalyst. The gas composition of the parallel experiments appears to have very low CH_4 content, to the level of 0.15% or a non-detectable (ND) level. In those two cases, the reforming of CH_4 was nearly complete, and transformed to CO and H_2 gaseous fuels. The performance of the catalytic design shows low CH_4 content and the gaseous fuel prevents carbon deposition at the anode side of SOFC. Therefore, the syngas reformed by the disks made by 3D-AM is favored as a feeding fuel for SOFC.

Conclusions

Flexible, homogeneous polymeric feedstocks containing $\theta-Al_2O_3$ powder of high specific surface area were used to prepare filaments for 3D printing. The disk-shaped catalyst carriers are made by precise 3D additive manufacturing and coated with a $NiO-CeO_2$ fine catalyst. The optimized formulation of $\theta E60$ -40 is proposed following approval by this study. The additive sequence of powder/MA-PP/EVA (P2 sequence) and two-step kneading (σ -kneading followed twin-rolling step) are able to disperse the powder in the polymer blend in a powder content from 35 wt% to 50 wt%. The dispersive index (D_s) of the feedstock is in the range of 0.95 ± 0.02 , implying optimal dispersion property of the feedstock can be achieved.

The disks made by 3D AM of $\theta E60$ -40 show precise patterns with shallow ditches. The porous disks following binder burnout and sintering at 1100 °C for 4 hr retained appropriate high-surface-area conditions and strength. Before coating, the disks kept ca. 60% ~ 52% porosity and were strong enough to undergo the coating of $NiO + CeO_2$ catalyst and reforming steps.

The reforming of CH_4 in the syngas from the gasification of waste paper is greatly improved by using the $NiO-CeO_2$ on the Al_2O_3 disks. The reforming

capability of the disks with the catalyst is better than that of other comparable cases, reducing the CH_4 content in syngas to a level of 0.15% or less.

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