3D printed honeycomb-structured $BaTiO_3$-based PTC ceramics by digital light processing for thermal management of hydrogen fuel cells

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2. Experimental

2.2. Preparation of PTC ceramic slurries

The process steps of functionalizing PTC powder are as follows: Firstly, silane coupling agent (KH560, Dongguan dinghai plastic chemical Co., Ltd., China), anhydrous ethanol, deionized water and acetic acid were mixed for 1 h according to a certain proportion. The dosage of silane coupling agent was 2 wt% of PTC powder, the ratio of anhydrous ethanol to deionized water is 9:1, and a small amount of acetic acid was added as catalyst to promote the hydrolysis. Subsequently, an appropriate amount of PTC powder was added to the mixed solution and ball-milled for 6 h. Finally, the mixed solution obtained by ball milling was dried and washed for many times to obtain PTC powder with good surface modification effect.

2.3. Fabrication of PTC ceramic samples

As shown in Fig. S1(a), the mass of PTC ceramic green body with 10 vol% PMMA and 3 vol% Al_2O_3 begins to gradually decrease when the temperature reaches approximately 300 °C and remains essentially constant after the temperature exceeds 550 °C, indicating that all organic matter within the green body has been removed.

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Therefore, the debinding and sintering curve for PTC ceramics with different PMMA and Al_2O_3 additions in Fig. S1(b) was developed based on the TG-DTA curve of the 3D-printed PTC ceramic green body with 10 vol% PMMA and 3 vol% Al_2O_3. To prevent the generation of numerous defects, a three-step heat treatment process including argon carbonization, air debinding and air sintering was adopted, with strict control over holding temperature, holding time and heating rate. During the heat treatment, PTC ceramic green bodies were debinded at 200 °C, 300 °C, 420 °C, 500 °C and 600 °C for 2 h each to steadily remove the organic matter present, with a heating rate of 0.2 °C/min. Subsequently, the debinded green bodies were heated to 1300 °C at the heating rates of 5 °C/min and 8 °C/min, followed by sintering for 30 min to obtain densified PTC ceramics. Consequently, PTC ceramics were prepared by the debinding and sintering process.

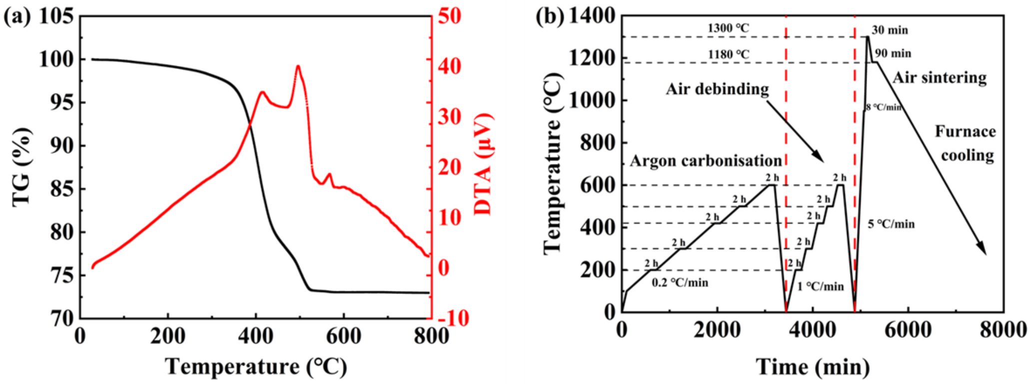

Fig. S1. (a) TG-DTA analysis, (b) debinding and sintering process of 3D printed PTC ceramic green body with 10 vol% PMMA and 3 vol% Al_2O_3.

2.4. Characterization

To thoroughly characterize the prepared ceramic slurries and the obtained PTC ceramics, extensive experimental tests and analysis were conducted. The particle size distribution of PTC, PMMA and Al_2O_3 powders was determined by the laser diffraction particle size analyzer (Mastersizer 3000, UK). The thermogravimetric and differential thermal analysis (TG-DTA) was performed on the obtained PTC ceramic green body with PMMA and Al_2O_3 addition using a thermogravimetric analyzer (Diamond TG/DTA, PerkinElmer Instruments, USA), with the temperature ranging from 25 ℃ to 800 ℃ and the heating rate of 10 ℃/min (air atmosphere). In order to characterize the curing ability of raw powders, the absorbance of raw powders and photosensitive resin at the wavelength of 200 nm to 800 nm was measured by the ultraviolet-visible-near-infrared spectrophotometer (SolidSpec-3700, Shimadzu, Japan) to indirectly obtain the UV absorptivity at the wavelength of 405 nm. The X-ray diffractometer (XRD-6100, Shimadzu, Japan) was used to analyze the phase compositions of PTC ceramic samples, with diffraction angle 2θ ranging from 10° to 80° and scanning rate of 10 °/min. Besides, the field-emission scanning electron microscope (GeminiSEM 300, Germany) was used to observe the scanning electron microscope (SEM) images of PTC ceramic samples. The relative density and apparent porosity were obtained by measuring the mass of PTC ceramic samples under different conditions according to Archimedes principle. Using the Nano Measurer software, 120 points were sampled from the SEM images of sintered PTC ceramics to calculate the grain size and pore size distribution.

Moreover, the viscosity of the made slurries with different PMMA and Al_2O_3 contents at 30 s^{-1} shear rate was measured by the rotational rheometer (MCR 302, Anton Paar, Germany) to obtain the rheological properties. The curing depth of PTC ceramic slurries under different 3D printing parameters was determined by a hand-held spiral micrometer. After coating the upper and lower surfaces of PTC ceramic samples with Ag electrodes, the electrical properties were characterized by a resistance-temperature characterization tester (AWXB R-T, China). The room temperature resistance of PTC ceramics was investigated by the low resistance tester (TH2512B, Changzhou Tonghui Electronics Co., Ltd., China). The reported results for electrical and physical properties were obtained by taking the average of five test values. The Resistance-Temperature (R-T) curves of PTC ceramic samples were recorded from room temperature to about 250 °C. Additionally, the core electrical performance parameters, such as Curie temperature, PTC jump and temperature coefficient, could be quickly and automatically sorted out by the self-built R/T characteristic test system.

3. Results and discussion

According to Lambert-Beer law, the UV absorptivity and absorbance can be converted into each other by a formula under the ideal condition of ignoring reflection, as shown in Eq. S1.

$$\alpha = 1 - 10^{-A} \quad (1)$$

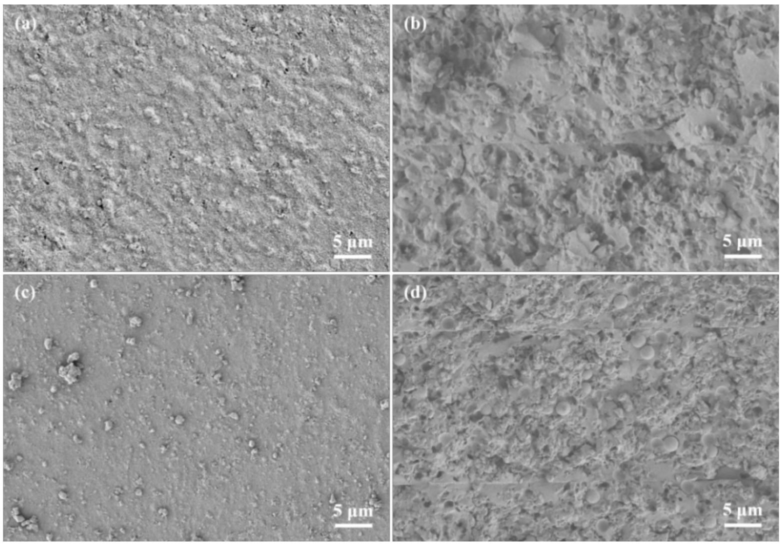

Fig. S2. SEM images of the surface and cross section of PTC ceramic green body with (a)(b) no substance added and (c)(d) 10 vol% PMMA and 1 vol% Al_2O_3 addition.

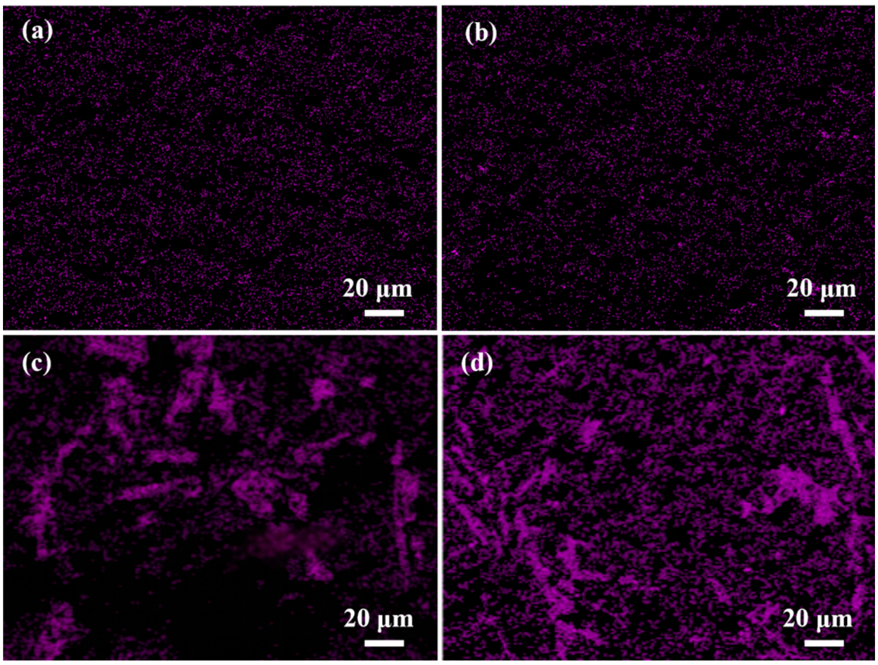

Fig. S3. SEM-EDS analysis of PTC ceramics with (a) 1 vol% Al_2O_3, (b) 2 vol% Al_2O_3, (c) 3 vol% Al_2O_3 and (d) 4 vol% Al_2O_3 addition.

Table S1. Elemental composition of PTC ceramics with 1 vol% Al_2O_3

Element	X-ray line	wt%	wt% sigma
Ba	L-series	47.85	0.39
Ti	K-series	19.94	0.26
O	K-series	14.58	0.16
Pb	M-series	16.50	0.27
Al	K-series	0.27	0.04
Si	K-series	0.09	0.04
Ca	K-series	0.77	0.08
Total		100	

Table S2. Elemental composition of PTC ceramics with 2 vol% Al_2O_3

Element	X-ray line	wt%	wt% sigma
Ba	L-series	46.97	0.45
Ti	K-series	19.68	0.30
O	K-series	16.02	0.20
Pb	M-series	14.43	0.32
Al	K-series	0.68	0.04
Si	K-series	0.62	0.05
Ca	K-series	1.60	0.09
Total		100	

Table S3. Elemental composition of PTC ceramics with 3 vol% Al_2O_3

Element	X-ray line	wt%	wt% sigma
Ba	L-series	46.22	0.41
Ti	K-series	19.38	0.27
O	K-series	16.75	0.19
Pb	M-series	11.87	0.27
Al	K-series	1.74	0.16
Si	K-series	1.48	0.05
Ca	K-series	2.56	0.08
Total		100	

Table S4. Elemental composition of PTC ceramics with 4 vol% Al_2O_3

Element	X-ray line	wt%	wt% sigma
Ba	L-series	45.78	0.44
Ti	K-series	19.11	0.27
O	K-series	18.08	0.19
Pb	M-series	8.98	0.32
Al	K-series	3.09	0.24
Si	K-series	2.27	0.05
Ca	K-series	2.69	0.09
Total		100	

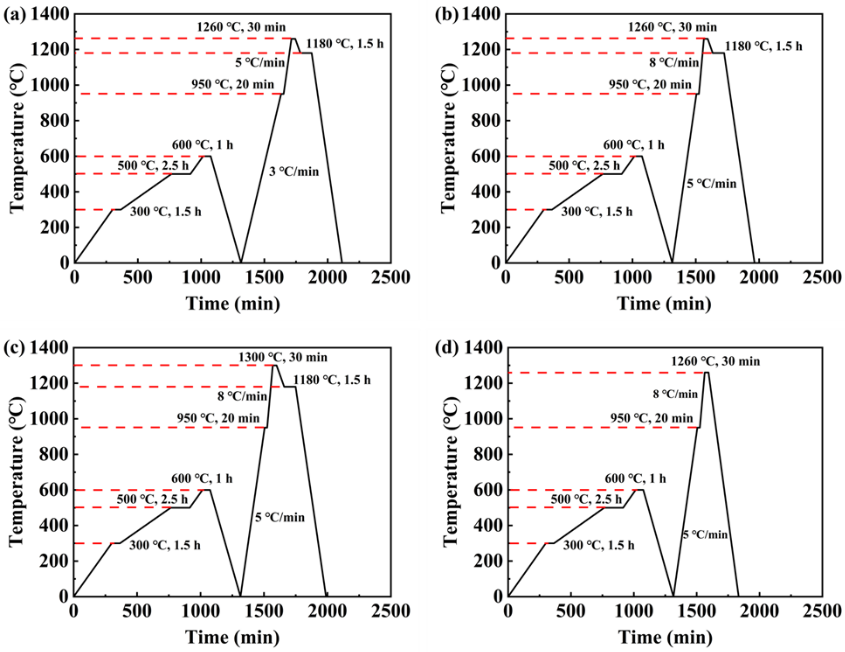

Fig. S4. Four heat treatment parameters of dry-pressed PTC ceramics: (a) I process; (b) II process; (c) III process and (d) IV process.

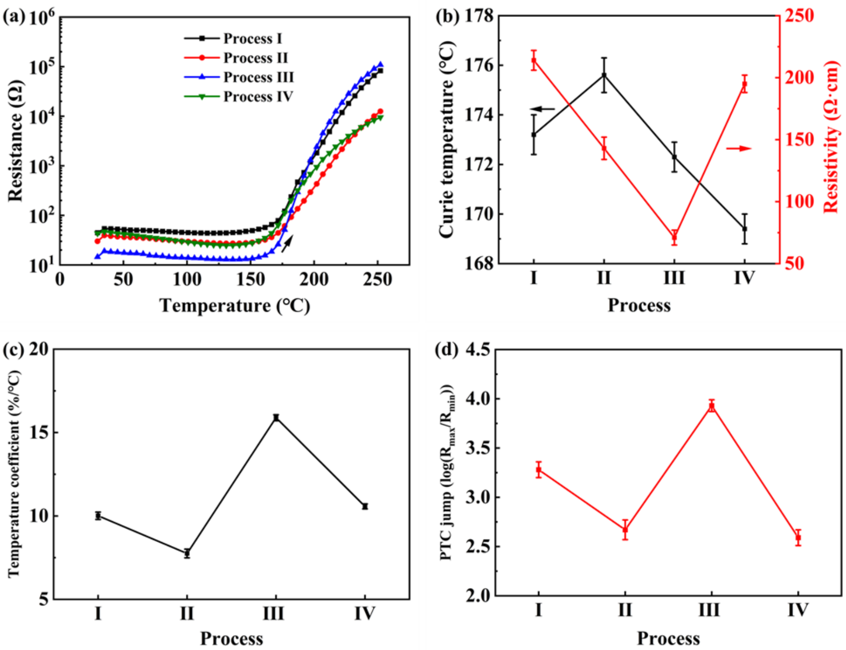

Fig. S5. (a) Temperature dependence of resistance, (b) Curie temperature and room temperature resistivity, (c) temperature coefficient of resistance (α_{10-25}) and (d) PTC jump of dry-pressed PTC ceramics prepared by different processes.

Table S5. Material and simulation parameters of PTC ceramic honeycomb structures with different porosities

Parameter	Symbol	Value	Unit
Density	rho	6.25×10^3	kg/m^3
Relative dielectric constant	ε_r	2×10^3	1
Thermal conductivity	λ	2.5	W/(m·K)
Porosity	φ	20-80 %	1
Constant pressure heat capacity	C_p	$600*(1-\varphi)$	J/(kg·K)
Thermal expansion coefficient	α	9.4×10^{-6}	1/K
Air temperature	T_{air}	20	°C
Air layer heat transfer coefficient	h_{air}	5	$W/(m^2\cdot K)$
Conductivity	σ	$1/\rho$	S/m
Voltage	U	10	V

In the table, ρ is defined as the resistivity of PTC ceramic honeycomb structure at the corresponding porosity above Curie temperature (T_c).

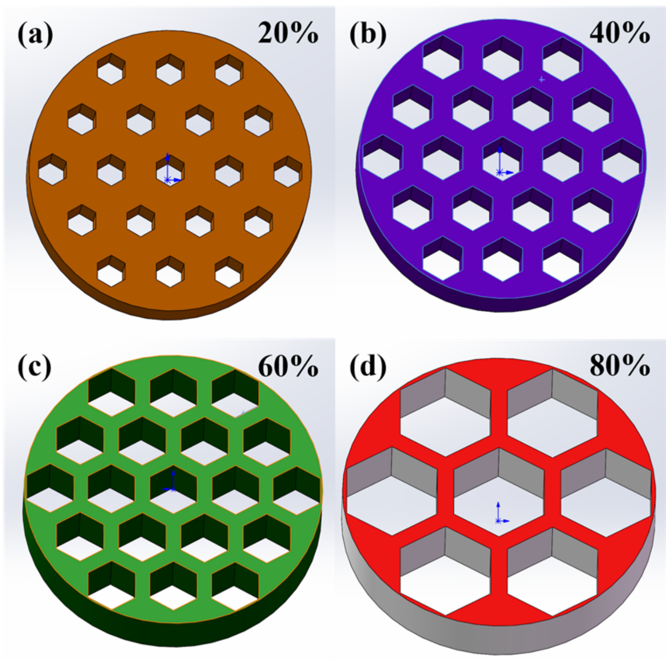

Fig. S6. 3D models of honeycomb structures with different porosities.