Chapter 1

Introductory Chapter: A Brief Introduction to Porous Ceramic

Uday M. Basheer Al-Naib

Additional information is available at the end of the chapter

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1. Introduction

Porous ceramics have grown in importance in the industry recently because of their many applications like filters, absorbers, dust collectors, thermal insulation, hot gas collectors, dielectric resonators, bioreactors, bone replacement and automobile engine components [1–4]. Generally, porous ceramics have good properties such as mechanical strength, abrasion resistance, chemical and thermal stability. These porous network ceramic structures also have relatively low density, low mass and low thermal conductivity [5]. Furthermore, permeability is one of the most important properties of porous ceramics for different applications such as membranes because this property directly relates to the pressure drop during filtration. Pore size control is the one key factor in fabrication of porous ceramics [6]. As well as the size of particles and their distribution of the raw materials, manufacturing techniques, types of binder used, distribution of binder and sintering affect the final porosity and pore connectivity important factors that must be considered during the manufacturing of the porous ceramic body. Therefore, the development of porous ceramics research requires sufficient mechanical and chemical stability as well as permeability. This book covers a wide range of topics such as porous ceramic structure and properties, preparation, simulation and fabrication, 3D printer fabrication, porous ceramic composites, honeycombs, membranes, bioceramic, automotive and aerospace porous ceramic.

2. What are porous ceramics?

Porous ceramics are categorized as those ceramics having high percentage porosity between 20 and 95%. These materials composed of at least two phases like solid ceramic phase, and the gas-filled porous phase [7]. The gas content of these pores usually regulates itself to the environment, as an exchange of gas with the environment is possible through pore channels.

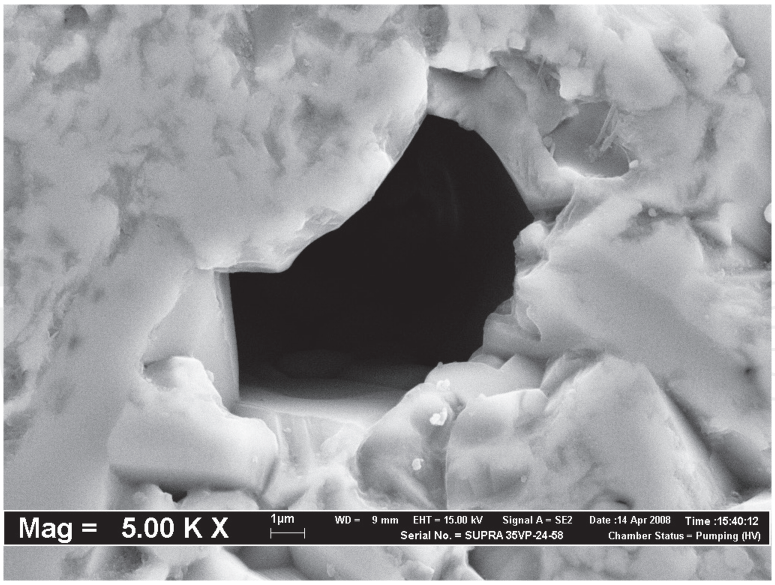

Figure 1. Magnification of a single open pore in the alumina ceramic body.

Closed pores can contain a composition of gases that is independent of the environment [8]. When porosity is determined for any ceramic body, porosity can be distinguished for several types such as open (accessible from the outside) porosity (**Figure 1**) and closed porosity. Where open porosity can be further categorized into open dead-end pores and open pore channels. The presence of porosity depends on the specific application, so a more open porosity may be needed to be permeable such as a closed porosity or filters/membrane such as thermal insulator may be wanted. The sum of the open and closed porosity is mentioned to as the total porosity [9]. If the fractional porosity of a material is relatively low, then the closed porosity will dominate; at the fractional porosity increases, the open porosity level increases.

The porous ceramics have been classified on the basis of nature of porosity, volume fraction and size of these pores [10]. The nature of porosity in natural ceramics depend on their genesis while in synthetic ceramics, it depends on their manufacturing and generally, it can be controlled. The pore size of these materials can be classified into three grades depending on the pore diameter: microporous (less than 2 nm), mesoporous (between 2 and 50 nm) and macroporous (more than 50 nm). The pore size distributions are usually measured by mercury intrusion porosimetry technique. The pore size distribution of the closed porosity is not determinable using this technique, but may occur, for example, by optical and electronic examination of a polished cross section. The pore size distribution represents the pore volume in function of pore size and commonly is given as percentage or a derivative [11].

3. Methods and techniques for fabrication of porous ceramics

In recent years, with the development of new needs and technologies, there was an increasing request for porous ceramic. Hence their fabrication methods are being widely studied and the subject of inclusive research. Partial sintering of ceramic powder compacts is one of the methods used to fabricate porous ceramic bodies, but this method mostly yields low porosities (less than 50%) and few options to significantly alter the pore size distribution [12].

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Honeycombs also with well-defined unidirectional channels can be paste extruded from a variety of ceramic powders and more complex three-dimensional porous ceramics can be made by rapid prototyping techniques, such as 3D printing. Apart from these methods, it is possible to distinguish many different types of fabrication routes (**Figure 2**) for producing

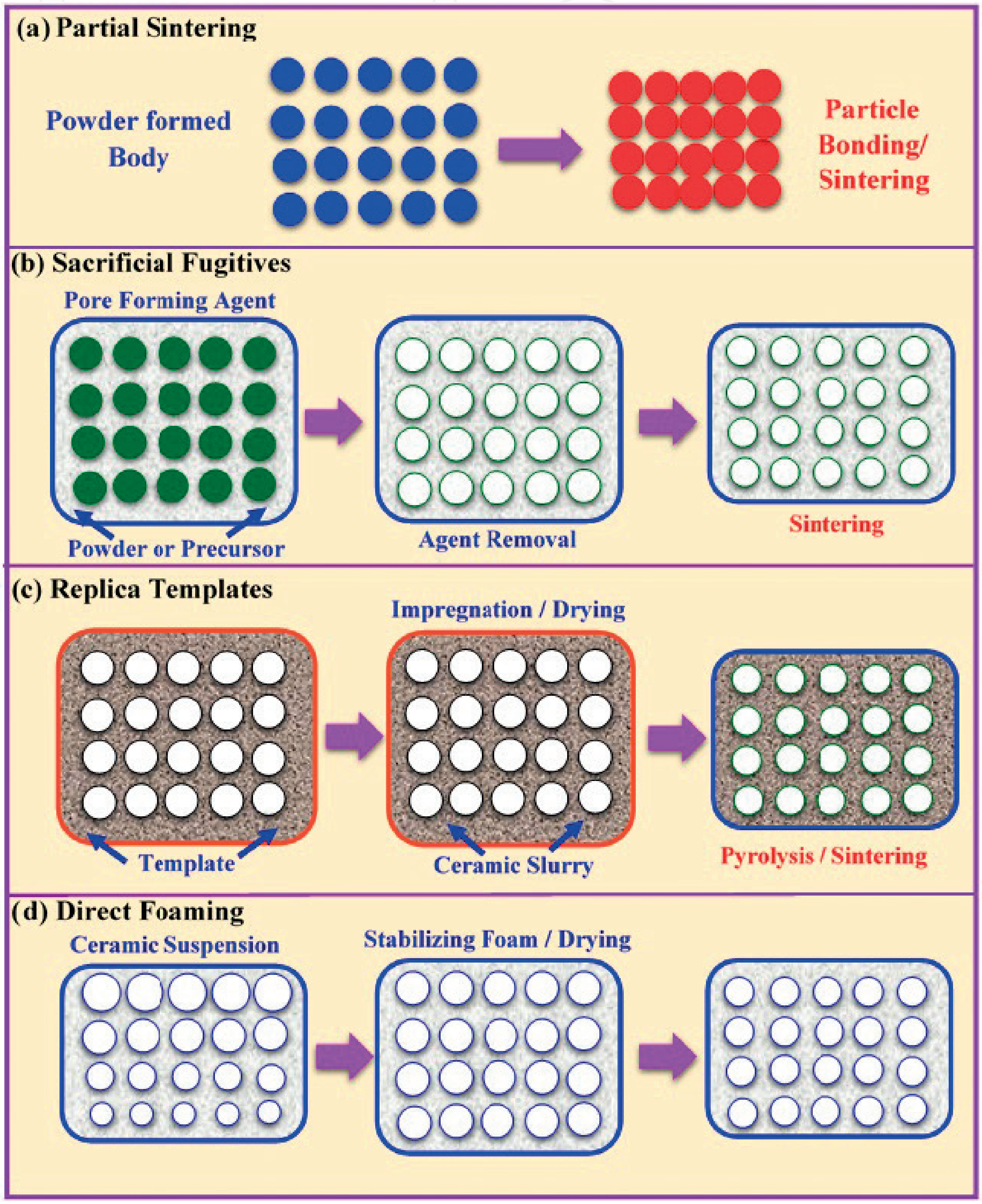

Figure 2. Schematic of porous ceramic processing methods: (a) partial sintering, (b) sacrificial fugitives, (c) replica templates, and (d) direct foaming [1].

porous ceramics such as the replica method, the sacrificial phase technique, direct foaming methods, paste extrusion and most recently developed rapid prototyping technique [13].

The fields of application and specific forms of porous ceramics are wide and varied according to their manufacturing processes [14]. Some of its useful applications are in the manufacture of filter. As these porous structures are used to filter high-pressure gas at high temperature and are used as an aid to remove the contaminants. In the field of petroleum treatment, porous ceramics are used as a substrate for catalysts in the process of filtration. They are also used in recovering hydrogen from the crude oil. Other applications are thermal insulators in filter membrane to separate metal impurities from molten metals such as steel, iron and aluminum. Today, porous ceramic structures prepared from different materials based on their application are used widely in biomedical field. For example, porous calcium phosphate materials can be used to replicate bone architecture and allow the growth of osseous tissue on an artificial substrate, thereby forming an artificial living bone structure. There porous hydroxyapatite can be used to replace bone and also as a drug delivery system [15].

4. Porous ceramic structure and properties

Porous ceramics possess a number of suitable properties, which combine the features of ceramics, and porous materials such as low density, lightweight, low thermal conductivity, low dielectric constant, thermal stability, high specific surface area, high specific strength, high permeability, high resistance to chemical attack and high wear resistance [13]. Either porous ceramics are reticulate (interconnected voids surrounded by a connection of ceramic) or foam (closed voids within a continuous ceramic matrix). Reticulated porous ceramics are usually used for molten metal, industrial hot-gas filters, catalyst supports, and diesel engine exhaust filters.

Pore size and porosity percentage are controlled by the particle size distribution of starting ceramic powders, fabrication techniques, types of binder used, concentration of binder and sintering conditions respectively [1]. Generally, the particle size of raw ceramic powder should be geometrically in the range between two to five times larger than that of pores in order to provide the desired pore size. The Porosity percentage reductions with increased making conditions such as pressure, sintering temperature and time. Furthermore, the fabrication influences such as the amount and type of additives, green densities, and sintering conditions (temperature, pressure atmosphere, etc.) significantly affect for the porous ceramics microstructures.

5. Mechanical behavior of porous ceramic

The general properties for porous ceramics can be designed for specific environmental application by controlling their composition and microstructure [16]. Changes in open and closed porosity, distribution of pore size and shapes of pore can have a main effect on the properties of porous ceramics. All of these microstructural features are in turn greatly affected by the processing way used to produce of the porous ceramic. For mechanical properties of porous ceramics, they are determined by their structural parameters, such as percentage of porosity, pore size, and shape. Furthermore, the solid microstructure phase of grain growth and solid phase continuity greatly affect the mechanical properties. Several important issues relating to the growth of the neck touching particles by surface and volume diffusion can significantly increase the mechanical properties with minimal increase in density. The microstructure in porous ceramics can be controlled not only by adjusting the particle size and shape of the initial raw powders, but also through the process of sintering.

6. Classification of porous ceramic

Classification of pores is one of the basic requirements of inclusive characterization of porous ceramics (**Figure 3**). There are different classes of pores described porous ceramic in the literature,

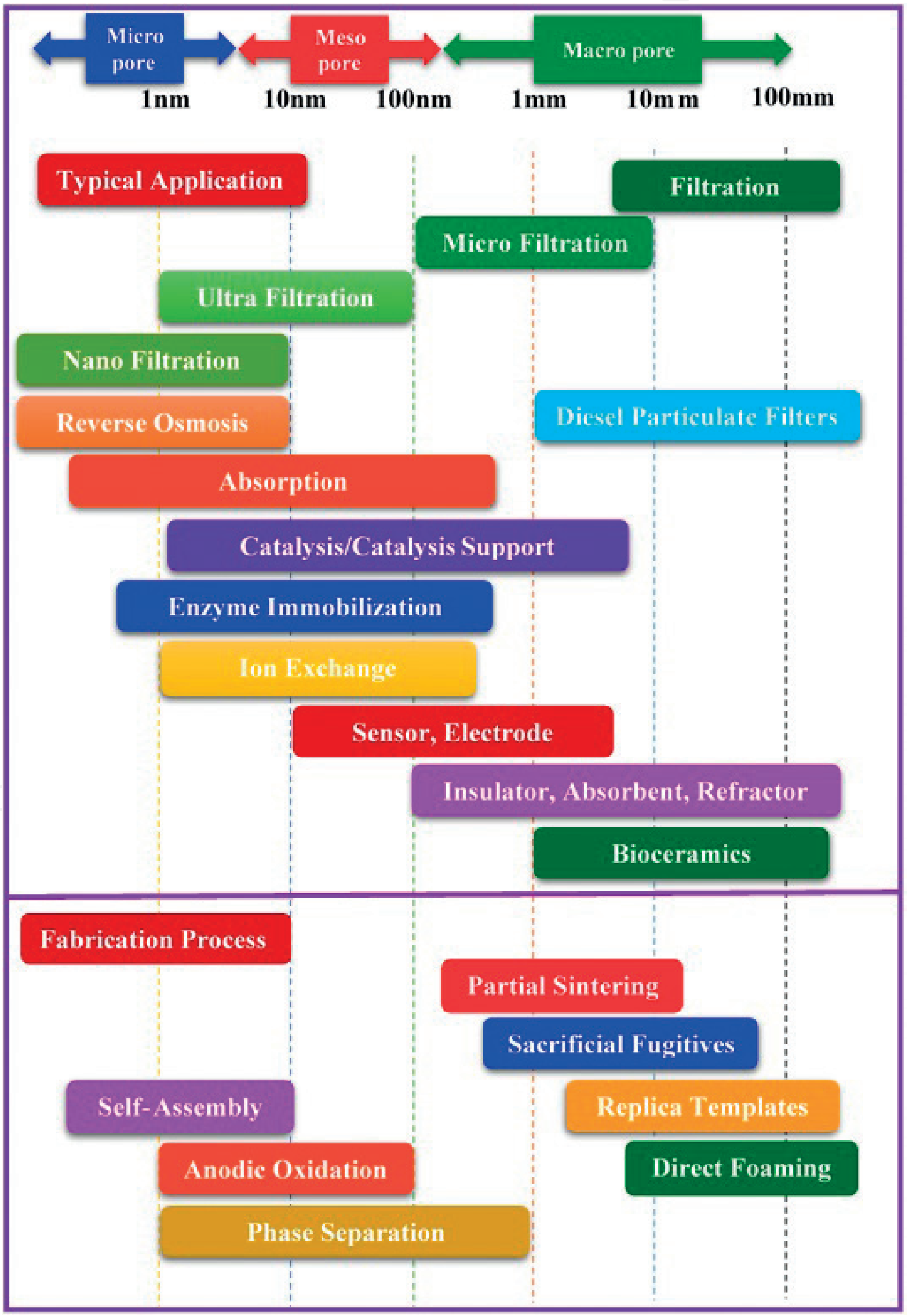

Figure 3. Schematic of classification of porous ceramic [1].

but they are difficult to give a consistent general classification of porous ceramics including catalyst carriers in various chemical processes, electrolyte carriers in fuel elements, adsorbents. As well as filtration of liquids, hot gases, melted metals and alloys, membranes for separation and purification of gas and liquids etc. The purpose of these classifications is to organize pores in classes by grouping them based on their common characteristics like structure, size, shape, accessibility etc. Therefore, porous ceramics can be classified according to the different characteristic attributes such as chemical composition of initial ceramic materials, porosity percentage, physical state of these products, refractoriness correlated to service temperatures, destination and application area [1].

7. Ceramic foams

Ceramic foams are porous brittle materials with closed, open-celled structures or partially interconnected porosity [17]. Ceramic foams are a special class of porous materials included of large voids with linear dimensions in the range between 10 and 5 mm. Foams are also called cellular ceramic materials because their structure can be represented by a lattice of a repeatable unit called "cell". They are fabricated from a broad kind of ceramic materials; specifically both oxide and non-oxide, which includes pure oxides, aluminosilicates and carbides that are being considered for the whole range of possible applications. These include filtration, catalysis, impact-absorbing structures, thermal insulation, performs for metal-ceramic composites, biomechanical implants, high specific strength materials and high efficiency combustion burners. The ceramic foams have been produced in a variety of materials with different shape sizes, densities and degree of interconnectivity. Foams or cellular are usually made with the density between 10 and 40% of theoretical and the pore sizes less than 1 mm. Ceramic foams can be made with a variety of microstructures with controlled properties through several versatile and simple methods, such as direct foaming, replica, sacrificial template techniques [5].

8. Porous ceramics using additive manufacturing techniques

The manufacturing of complex porous ceramic parts with defined microstructure is a challenge today [18]. Concerning this issue, additive manufacturing technology is a promising alternative to conventional manufacturing procedures. Various additive manufacturing technologies like laminated object manufacturing (LOM), stereolithography (SLA), fused deposition modeling (FDM), selective laser sintering (SLS) and three-dimensional printing (3D printing) have already been used to fabricate different porous ceramic shapes [19]. One of the fastest and most efficient technologies is 3D printing. The introduction of 3D printing technology into the porous ceramic industry provides greater speed and flexibility, eliminates tool constraints, needs only low cost investment, and enables the sustainability of the additive manufacturing process. The 3D printing can be used in the making of porous ceramics in a different of applications. For example, it is widely used for catalysis chemical reactors, biomedical applications and filtration technologies. It can also be used to produce porous ceramic membranes, energy storage and heat exchangers, because of the good thermal properties and relative strength of ceramic materials.

9. Porous hydroxyapatite ceramic and its biomedical applications

Hydroxyapatite (HA) porous ceramics are substitute materials for bone and teeth in repairing and regeneration applications due to their chemical and biological similarity to human hard tissue [20]. In the design of these porous ceramic for bone repairing or regeneration, it is important to control their pore structures. Pore ceramic structure can be designed using the size and morphology of the Hydroxyapatite particles that are utilized to build these porous ceramics. Porous hydroxyapatite ceramic exhibits strong joining to the bone, the pores provide a strong mechanical interlock leading to a firmer fixation of the structure. Porous hydroxyapatite is more resorbable and osteoconductive than HA dense counterpart [21]. The surface area of porous Hydroxyapatite form is greatly increased which allows more bone cells to be carried in comparison with dense hydroxyapatite. The most common techniques used to make porosity in a biomaterial are gas foaming, salt leaching, freeze-drying, phase separation and sintering depending on the material used to make the scaffold. The minimum pore size required to regenerate mineralized bone is generally considered to be around 100 μm.

10. Porous ceramics and catalyst carriers

Porous ceramics have a good activity and high absorption materials. The reaction rate and conversion increase significantly for the reactive fluid that flows through the porous ceramic networks [22]. The ceramic catalyst carrier plays a major role in promoting the chemical reaction. Due to the chemical corrosion resistance and thermal shock of porous ceramics, they can be used in highly required service conditions, like the reactor in chemical engineering and the vehicles gas exhaust treatment. As well as the fine metal particles are usually supported on the heterogeneous catalyst carriers, which are generally ceramic. Catalysis becomes also progressively more important in environmental pollution control. The catalyst effectively reduced pollution from automotive and industries applications. The ceramic used must have connected porosity and the pore size can differ between 6 nm and 500 μm. Alumina, titania, zirconia silica and silicon carbide are the most popular choices for catalyst supports. These ceramic powders are formed into a variety of shapes such as cylinder bars or hollow beads or clover-leaf shaped sections. They are then sintered to their final density. Porous ceramics also can be used as carriers in the recycling of steam, oxidation of ammonia, recombination of methane, destruction of volatile organic compounds (VOCs) by incineration and decomposition of organics by photocatalysis.

11. Porous ceramics and membranes

Porous ceramic membranes can be used to separate water, oil, liquids, solids, dust in gas, yeast or thallus and blood cells and to clarify alcohol in the food, chemical and medical industries. In addition, these membranes act as biological reactors in the recovery of fermented fluid. During the last few decades, the ceramic membrane applications have increased because of their excellent chemical, mechanical and thermal stability, and high separation efficiency [23]. High-permeability ceramic membranes can only be obtained in an asymmetric multilayer arrangement with microporus support, providing mechanical strength and reducing flow resistance. Commercially porous ceramic membranes of oxides such as alumina and zirconia are not suitable for large-scale application because these kind of oxide membranes are very expensive. Recently, the natural minerals such as zeolite, apatite, dolomite and clays have received increasing attention due to their cheap fabrication and multiple applications. The development of ceramic membranes made of natural minerals could lead to a new critical technological revolution that would add significant economic value to the natural minerals found all over the world.

12. Porous ceramics and piezoelectric materials

The piezoelectric materials contain crystalline structures that do not overlap the positive and negative charge centers, leading to bipolar moments. When subjected to mechanical vibrations or movement, the mechanical strain of this material is applied and leads to distortion of the electrode, creating electrical charge [24, 25]. The electrical energy can be harvested by storing it in capacitors or rechargeable batteries. The piezoelectric material has been widely recognized with unique electromechanical coupling properties for its potential benefits in a large number of sensors and application engines. Moreover, it has also been shown that the microstructure of a piezoelectric material can be modified by adding a second phase (as in piezoelectric composites) or by introducing porosity (as in piezoelectric foams), in order to improve the piezoelectric materials properties for specific applications [26]. For example, by introducing porosity into piezoelectric material, the signal-to-noise ratio, sensitivity properties and impedance matching can be improved, thus the piezoelectric material can be made more suitable for the applications of hydrophone.

Author details

Uday M. Basheer Al-Naib

Address all correspondence to: ummb2008@gmail.com

Faculty of Mechanical Engineering, UTM Centre for Low Carbon Transport in Cooperation with Imperial College London, Institute for Vehicle Systems and Engineering, University of Technology Malaysia, Johor, Malaysia

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