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Finite element modelling of bilayer porous PZT structures with improved hydrostatic figures of merit

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Abstract— A finite element model is presented in which bilayer lead zirconate titanate (PZT) structures that are formed from a dense layer and a porous layer are investigated for their hydrostatic sensing properties. The model simulates the poling of the porous ferroelectric material to determine the distribution of poled material throughout the structure. The fraction of PZT successfully poled is found to be closely related to resulting piezoelectric and dielectric properties of the composite. Structures with high layer porosity (>40 vol.%) and porous layer relative thickness (>0.5) were found to have a significantly improved hydrostatic piezoelectric coefficient, d_h , hydrostatic voltage coefficient, g_h , and hydrostatic figure of merit, $d_h.g_h$. The highest $d_h.g_h$ of $7.74 \times 10^{-12} \text{ m}^2/\text{N}$ was observed in the structure with a porous layer relative thickness of 0.6 and porosity of 60 vol.%, which was more than 100 times higher than that for dense PZT ($d_h.g_h = 0.067 \times 10^{-12} \text{ m}^2/\text{N}$) and over three times that of PZT with 60 vol.% porosity with 3-3 connectivity ($d_h.g_h = 2.19 \times 10^{-12} \text{ m}^2/\text{N}$). The results demonstrate the potential for layered porous materials for use in hydrophones.

Keywords—piezoelectric, hydrophones, PZT, finite element

I. INTRODUCTION

Ferroelectric ceramics have long been of interest for both sensor and transducer applications due to their ability to convert mechanical or thermal energy into electrical energy, and vice versa, via the piezoelectric and pyroelectric effect [1]. The introduction of porosity as a low permittivity second phase into a ferroelectric ceramic, such as lead zirconate titanate (PZT), has been found to increase sensitivity of both mechanical and thermal sensors [2, 3]. The interconnectivity between the ceramic and porous phases determines the final mechanical, thermal and electrical properties of these composites, allowing tuning of properties depending on the desired application [4]. Despite the potential benefits of porous ferroelectric materials, the effect of porosity on the poling of these materials is only recently being understood in more detail [5].

As formed, ferroelectric materials display no piezoelectric or pyroelectric properties and so must be poled via the application of a large electric field in order to generate a net alignment of domains within the material. In porous

ferroelectrics the electric field tends to preferentially concentrate in the low permittivity pores, resulting in regions of the active material becoming difficult to pole. The degree of poling of a ferroelectric material is closely linked to the final piezoelectric and pyroelectric properties [5, 6]. By developing a better understanding of how the porous structure may affect the poling of ferroelectric materials will allow better design of these materials for their desired application.

Porous PZT ceramics have been extensively studied for low frequency ($\ll 100 \text{ kHz}$) hydrophone applications, such as sonar [7-10]. Various figures of merit have been derived to rank the performance of piezoelectric materials for these applications. Firstly, materials should have high hydrostatic piezoelectric charge coefficients, d_h , that is related to the longitudinal and transverse piezoelectric charge coefficients (d_{33} and d_{31} , respectively) by the relationship:

$$d_h = d_{33} + 2d_{31}. \quad (1)$$

Monolithic piezoceramics tend to have low d_h values as $d_{31} \sim -1/2.d_{33}$ due to crystallographic symmetry, however, the introduction of porosity decreases d_{31} whilst d_{33} maintains relatively high values up to ~50 vol.% porosity, leading to increases in d_h [2]. This is important for increasing the sensitivity of hydrophones as it leads to an increase in the hydrostatic voltage coefficient, g_h , which is related to the charge coefficient by:

$$g_h = d_h / \epsilon_{33}^\sigma \quad (2)$$

where ϵ_{33}^σ is the permittivity at constant stress. Introducing porosity reduces significantly the bulk permittivity of the composite thus further increasing g_h . A figure of merit for materials selection for hydrostatic applications is the product of (1) and (2), i.e. $d_h.g_h$. A further benefit of introducing porosity into PZT for use in hydrophones is the resulting reduction in the density of material, which leads to improved acoustic matching between water and the active material, allowing more efficient transfer of mechanical energy into the active phase.

Functionally graded structures have also received interest for hydrophone and medical transducer applications [11], whereby materials are manufactured with a porosity gradient

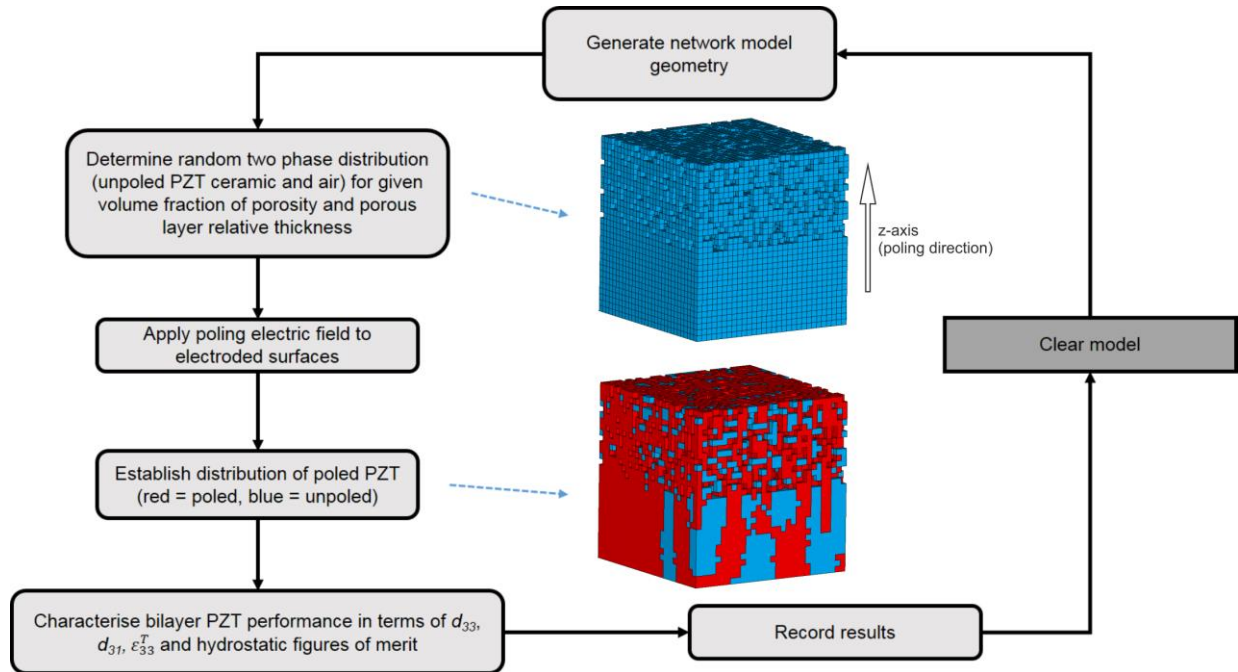


Fig. 1: Schematic diagram showing the finite element modelling process in Ansys. The upper image shows an example network of air and unpoled PZT, with the porosity concentrated into a porous layer. The lower image shows the poling distribution of unpoled (blue) and poled (red) PZT after the application of the poling field.

that acts to match the acoustic impedance between the dense piezoceramic and the media in which it is working, whilst also reducing the bulk permittivity and increasing piezoelectric anisotropy resulting in an improved piezoelectric hydrostatic response [12-14]. Another variation on this is the use of sandwich layer structures, whereby a porous interlayer is surrounded by dense outer-layers. Recent work on barium titanate sandwich structures found it was possible to increase the longitudinal piezoelectric response with increasing bulk porosity, which is a result of the complex poling behavior of ferroelectric materials with high fractions of porosity concentrated into a porous layer in the material, as well as achieving large reductions in permittivity, thus yielding improved energy harvesting figures of merit [15]. Experimental results showed that similar reductions in d_{31} could be achieved for layered porous structures as in uniform porous materials, indicating these structures may be of interest for hydrophone applications, see (1) and (2), particularly when coupled with the reductions in permittivity that were reported. Common manufacturing techniques of layered porous structures include tape casting [13, 14] and sequential uniaxial pressing of powders with varying weight fractions of pore forming agents [12, 15] prior to sintering.

In this work, finite element modelling has been used to determine the effect of bilayer structures, i.e. a dense backing layer and a porous matching layer, on the hydrostatic properties of PZT-5H, a commonly used soft PZT ferroelectric ceramic manufactured by Morgan Advanced Materials. The model simulates the poling process of layered dense-porous structures so as to obtain the hydrostatic sensing properties of interest, i.e. d_{33} , d_{31} , ϵ_{33}^{σ} , d_h , g_h and $d_h.g_h$. Previous work has demonstrated that models that do not take into account poling

distributions within porous materials, but rather assume all the material to be *fully poled* regardless of the volume and structure of porosity present, tend to overestimate the longitudinal and transverse piezoelectric response as well as the permittivity, which in turn leads to errors when calculating relevant figures of merit [5].

II. MODELLING PROCEDURE

Finite element analysis (Ansys APDL) was used to investigate dense-porous layered PZT structures. A cubic mesh was divided into 30^3 elements with a dense and a porous layer. The relative thickness of the porous layer was varied from $0 \leq t_p^{rel} \leq 1$, so that when $t_p^{rel} = 0$ the structure was fully dense and when $t_p^{rel} = 1$ the structure was fully porous (3-0 or 3-3 connectivity depending on porosity). Elements in the porous layer were randomly assigned the properties of either air or unpoled PZT, depending on the desired final porosity of the layer. The porosity of the porous layer was varied from 10 to 60 vol.%. Higher porosities were not investigated as this leads to high fractions of ‘floating’ PZT elements, i.e. those surrounded by air, that lead to frequent errors when running the model. All elements in the dense layer were assigned the properties of unpoled PZT. Electrodes were simulated by coupling the voltages of both the top surface and the bottom surface. The properties of unpoled PZT are summarized in Table 1 (from [16]).

After the network of elements had been generated an electric field (0.5 kV/mm) was applied across the geometry to simulate the poling field; this field was selected as it gave a good fit to experimental data for uniform porous structures previously [5]. After the application of the poling field the

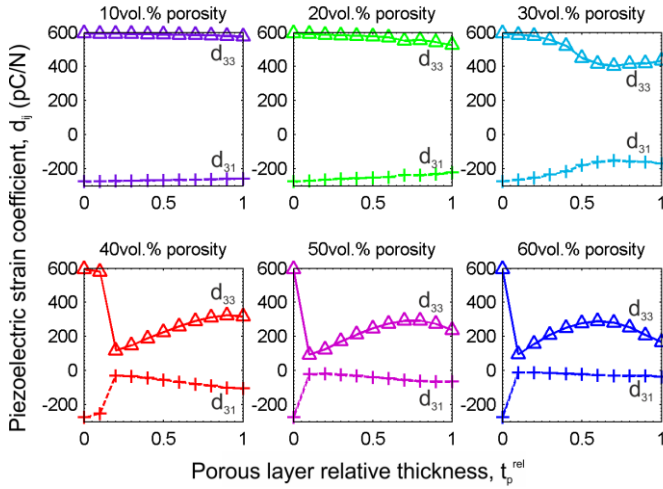


Fig. 2: Longitudinal and transverse piezoelectric strain coefficients, d_{33} (Δ) and d_{31} (+), respectively, plotted as a function of porous layer relative thickness for varying layer porosities.

local electric field in the z-direction in each PZT element was analyzed and when it exceeded the coercive field ($E_c = 0.4\text{kV/mm}$ [17]) the element was considered poled, i.e. the properties of the element were changed from unpoled PZT to poled PZT. The properties for poled PZT are summarized in Table 2 (from [17]). Once the network of air, unpoled and poled PZT elements was established, a potential difference was applied between the electrodes and the resulting strain in each direction used to calculate the effective d_{33} and d_{31} coefficients of the layered structure. The capacitance was measured from the charge that developed at the electrodes, using $C = Q/V$, and from this the effective permittivity was calculated. Data was averaged from 25 runs of each bilayer structure. A schematic of the modelling process is shown in Fig. 1.

TABLE I. MATERIAL PROPERTIES OF UNPOLED PZT-5H (FROM [16])

Material	Density (kg m^{-3})	Relative permittivity	Young's Modulus (GPa)	Poisson's ratio
PZT-5H	7500	1585	65	0.37

TABLE II. MATERIAL PROPERTIES OF POLED PZT-5H (FROM [17])

C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)
126	79.5	84.1	117	23.0
e_{31} (C m^{-2})	e_{33} (C m^{-2})	e_{15} (C m^{-2})	$\epsilon_{11}^s / \epsilon_0$	$\epsilon_{11}^s / \epsilon_0$
-6.55	23.3	17.0	1700	1470

III. RESULTS AND DISCUSSION

A. Poling and piezoelectric coefficients

The effect of porous layer porosity and relative thickness on d_{33} and d_{31} is shown in Fig. 2. At low layer porosities (≤ 30

vol.%) there is a small reduction in d_{33} and d_{31} tends towards zero with increasing porous layer relative thickness. When the layer porosity is ≥ 40 vol.% a large drop in d_{33} is observed at low porous layer thicknesses, before a gradual increase. At very high layer porosities (≥ 50 vol.%) a local maxima in d_{33} is observed before it begins to reduce as the structure approaches one with uniformly distributed porosity, i.e. no dense layer. The origin of this behavior is discussed in detail for barium titanate sandwich layer structures elsewhere and a good fit with experimental data was achieved [15], in which the presence of a dense and porous layers was found to concentrate the poling field in the low permittivity porous layer. This leads to incomplete poling in the dense layer as the layer porosity increases and a high proportion of the material in the porous layer becoming poled, as can be seen in Fig. 3 where the poled distribution can be seen for three different porous layer thickness and layer porosity is 60 vol.%. As this porous layer increases in thickness, the overall fraction of poled material also increases as there is a higher volume of PZT in the porous layer, which is subject to local electric fields that exceed the coercive field and therefore becomes poled. A drop off in d_{33} is observed as t_p^{rel} approaches unity, i.e. uniform porous structure with no dense layer, as the field is no longer sufficiently concentrated by the presence of the high permittivity dense layer and so the fraction of poled material reduces, hence the fall in d_{33} , see Fig. 2 and 3.

As the inner layer porosity increases the overall reduction in d_{31} becomes more pronounced, as in 3-3 connected porous material [2, 5]. Generally, when there is a point of inflection in the d_{33} curve as a function of porous layer thickness the same applies to d_{31} indicating that once more there is a dependence on the overall amount of material poled. However, as the overall porosity is increased there is a decoupling of stress transferred from the transverse to the longitudinal direction as high stiffness material is removed, resulting in relatively constant, low d_{31} values for $t_p^{rel} > 0.1$ at high layer porosities (>40 vol.%). This enhanced decoupling between longitudinal and transverse piezoelectric coefficients, due to the presence of porosity, is one of the reasons why porous piezoceramics gained interest as materials for hydrostatic sensors, as evaluation of (1) indicates that an increase in the charge generated due to a hydrostatic pressure is possible if d_{31} can be

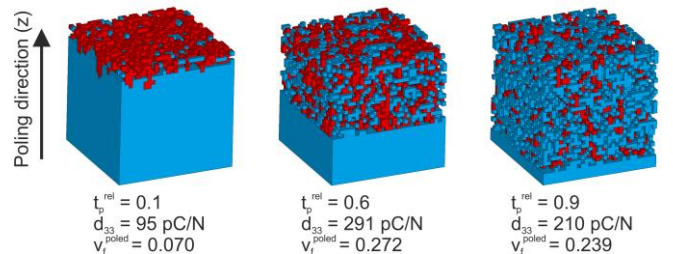


Fig. 3: Example poling maps of modelled bilayer PZT structure with 60 vol.% porosity in porous layer and varying porous layer relative thicknesses. At high porosities the poled PZT (red) is concentrated in the porous layer, whereas the dense regions remain largely unpoled (blue). Higher fractions of poled PZT result in higher d_{33} coefficients.

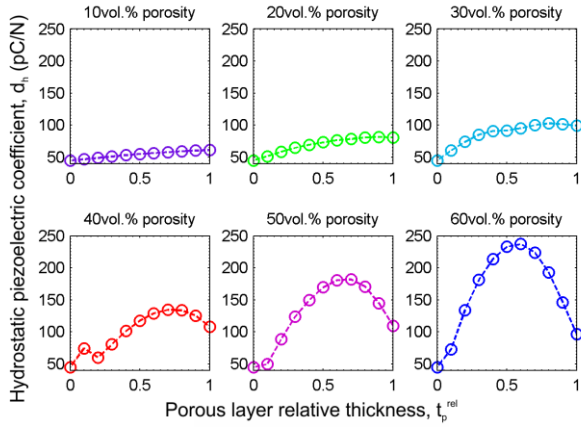


Fig. 4: Hydrostatic piezoelectric coefficient plotted as a function of porous layer relative thickness for varying layer porosity.

reduced at a faster rate than d_{33} .

The hydrostatic piezoelectric coefficient, d_h , is shown in Fig. 4 as a function of porous layer thickness and porosity. In all cases introducing a porous layer is found to increase d_h compared to fully dense PZT, however when the layer porosity is ≥ 40 vol.% an optimum porous layer thickness is observed. This is a result of the high d_{33} values for these structures that arises from the complex poling behavior and the decoupling of the longitudinal and transverse piezoelectric responses. The maximum d_h was found to be 237 pC/N for a structure with a 60 vol.% porosity layer with $t_p^{rel} = 0.7$, compared to 45 pC/N for dense PZT and 109 pC/N for uniformly porous PZT with 50 vol.% porosity, which has the highest d_h of the uniformly porous material ($t_p^{rel} = 1$).

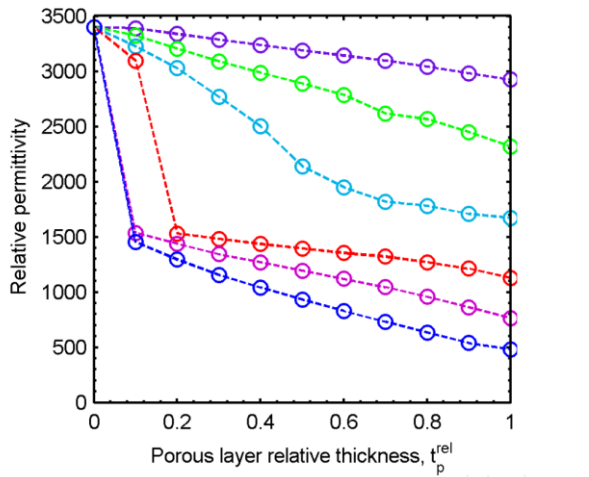


Fig 5: Effect of porous layer relative thickness on the relative permittivity of bilayer PZT with varying layer porosity.

B. Permittivity

The effect of porous layer thickness and porosity on the relative permittivity ($\epsilon_r = \epsilon_{33}^g / \epsilon_0$, where ϵ_0 is the permittivity of free space) is shown in Fig. 5. Permittivity reduces in all cases with the introduction of a porous layer as the amount of low permittivity phase increases. The degree of poling also has an effect on the permittivity as poled PZT has a higher

permittivity than when it is unpoled, which explains the steep decline in permittivity observed for structures with layer porosities ≥ 40 vol.% at low t_p^{rel} values. The layer thicknesses where these declines begin coincide with significant reductions in d_{33} that can be seen in Fig. 2. The lowest permittivity for a given layer porosity occurs when $t_p^{rel} = 0.1$ in all, i.e. uniform porous structures where the overall volume of porosity is at a maximum.

C. Hydrostatic figures of merit

The variation of the hydrostatic voltage coefficient, g_h , with porous layer thickness is shown in Fig. 6a. Increasing the porosity of the porous layer was found to increase g_h in all cases due to the increase in d_h and reduction in ϵ_r . When the layer porosity is 30 vol.% or less the uniform porous material is predicted to have higher g_h values than a bilayer structure. However, as the porosity is increased a maximum g_h value is observed when $0.5 < t_p^{rel} < 1$. The maximum g_h ($34.6 \times 10^{-3} \text{ V m}^{-1} \text{ Pa}^{-1}$) was found in the bilayer structure with 60 vol.% layer porosity and $t_p^{rel} = 0.7$, which is over 20 times that of dense PZT ($g_h = 1.50 \times 10^{-3} \text{ V m}^{-1} \text{ Pa}^{-1}$) and 1.5 times higher than uniformly porous PZT with 60 vol.% porosity ($g_h = 22.5 \times 10^{-3} \text{ V m}^{-1} \text{ Pa}^{-1}$).

The hydrostatic figure of merit, $d_h g_h$, is plotted in Fig. 6b as a function of porous layer thickness. For high layer porosities (≥ 40 vol.%) a broad peak is observed for $0.5 < t_p^{rel} < 0.9$, with the highest value predicted for 60 vol.% porous layer PZT with $t_p^{rel} = 0.7$, where $d_h g_h = 7.74 \times 10^{-12} \text{ m}^2/\text{N}$. This is a significant increase compared to dense PZT ($d_h g_h = 0.067 \times 10^{-12} \text{ m}^2/\text{N}$) and uniform porous PZT with 60 vol.% porosity, where $d_h g_h = 2.19 \times 10^{-12} \text{ m}^2/\text{N}$.

These are significant predicted increases in hydrostatic sensitivity that have not yet been demonstrated experimentally, although similar increases in energy harvesting figure of merit have been reported for barium titanate with porous layers sandwiched between dense outer-layers [15]. Previous experimental work on layered porous PZT has focused on layer porosities < 30 vol.% [12-14], however these results indicate that higher layer porosities (> 40 vol.%) may be necessary to achieve further increases in hydrostatic piezoelectric properties.

IV. CONCLUSIONS

A finite element modelling study has been presented that investigated the poling characteristics of PZT-5H with bilayer dense-porous structures. Once the distribution of poled and unpoled PZT and porosity was established the structures were characterized in terms of their piezoelectric and dielectric properties, before being evaluated in terms of relevant figures of merit for hydrophone applications. Complex poling behavior was observed that resulted in d_{33} increasing with increasing overall fraction of porosity under certain conditions, a similar phenomenon to that observed previously in barium titanate ceramics with a porous layer sandwiched between dense outer-layers [15]. The transverse coefficient, d_{31} , appeared less dependent on the fraction of material poled at high layer porosities ≥ 50 vol.% and was consistently low at high layer porosities and thicknesses, which lead to significant

increases in the hydrostatic piezoelectric response, d_h , at high

is also likely to facilitate better transfer of energy into the material if these structures were implemented in hydrophones.

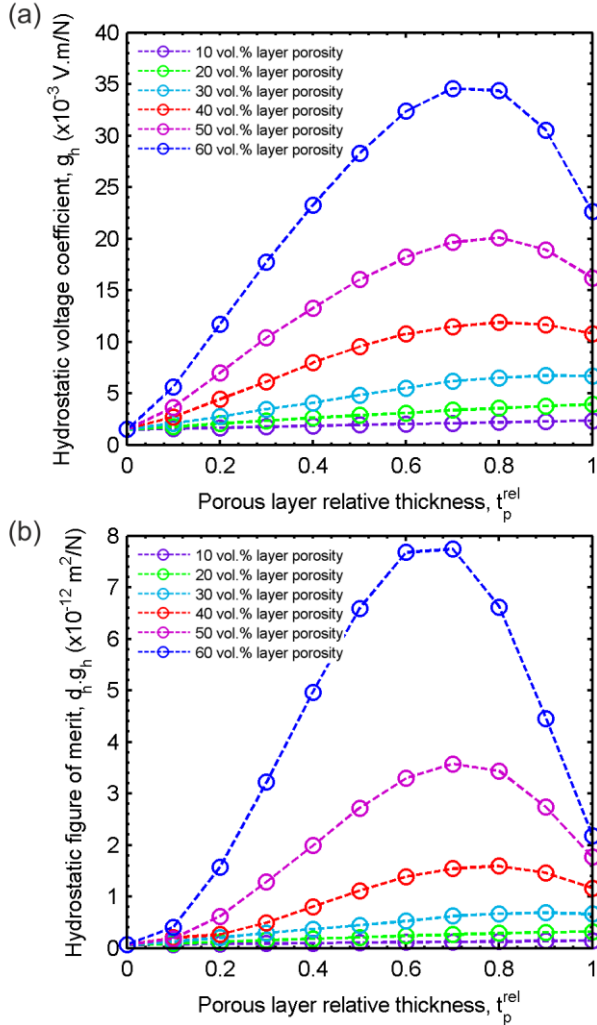


Fig. 6: Effect of porous layer thickness and porosity on (a) hydrostatic voltage coefficient, g_h , and (b) hydrostatic figure of merit, $d_h g_h$.

porous layer relative thicknesses, i.e. $t_p^{rel} > 0.5$. The highest d_h (237 pC/N) was found for PZT with a porous layer thickness of $t_p^{rel} = 0.7$ and 60 vol.% porosity, which was 20 times that of dense PZT and 1.5 times that of PZT with 60 vol.% uniformly distributed porosity.

The permittivity of the structures was found to decrease in all cases, which is beneficial for increasing the hydrostatic voltage response, g_h , and the hydrostatic figure of merit, $d_h g_h$, which are both inverse functions of the permittivity. Both g_h and $d_h g_h$ were significantly increased compared to dense PZT in structures where the porous layer is over half the total thickness of the material and when porosity in this layer exceeds 50vol.%. The highest predicted hydrostatic figure of merit ($d_h g_h = 7.74 \times 10^{-12}$ m²/N) was found when $t_p^{rel} = 0.7$ and the layer porosity was 60 vol.%, which was over 100 times that of dense PZT and almost 3.5 times that predicted for uniformly porous PZT. The use of a porous matching layer

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