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Porous ferroelectrics for energy harvesting applications

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Abstract. This paper provides an overview of energy harvesting using ferroelectric materials, with a particular focus on the energy harvesting capabilities of porous ferroelectric ceramics for both piezo- and pyroelectric harvesting. The benefits of introducing porosity into ferroelectrics such as lead zirconate titanate (PZT) has been known for over 30 years, but the potential advantages for energy harvesting from both ambient vibrations and temperature fluctuations have not been studied in depth. The article briefly discusses piezoelectric and pyroelectric energy harvesting, before evaluating the potential benefits of porous materials for increasing energy harvesting figures of merits and electromechanical/electrothermal coupling factors. Established processing routes are evaluated in terms of the final porous structure and the resulting effects on the electrical, thermal and mechanical properties.

1 Introduction

Interest in energy harvesting from ambient sources has grown in recent years with advances in microelectromechanical systems (MEMS) and wireless electronics [1–3]. Batteries are the current power source of choice for wireless sensors but their finite lifetime can quickly add to the maintenance cost of systems. Coupled with the fact that they are often used to monitor largely inaccessible and/or hostile areas, frequent replacement can be a difficult, time-consuming and expensive procedure. The ability to scavenge energy from the surrounding environment, be it through solar, thermoelectric, pyroelectric or piezoelectric devices, offers a potential mode of powering small-scale electronic devices without the need for cables to supply power or replacement of batteries. Alternatively, energy harvesting could be used to recharge batteries, significantly extending their lifetime and reducing problems associated with disposal [4]. Ferroelectric materials are of particular interest for energy harvesting due to their ability to convert energy from mechanical vibrations through the piezoelectric effect or from temperature fluctuations via the pyroelectric effect.

Ambient vibrations tend to coexist with the requirement to monitor structural health of components, meaning there is a vast resource of potentially harvestable energy that could be recaptured through piezoelectric devices. This area has received

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great interest in recent years, and as such a number of reviews are available that cover the various considerations that must be taken into account when designing a piezo-harvester [3,5,6]. Similarly, waste heat is a necessary by-product of all thermodynamic cycles implemented in power, refrigeration and heat pump processes. As one of the potential technologies for thermal energy harvesting, pyroelectric energy conversion is of interest since it offers a novel way to convert waste heat into electricity by alternatively heating and cooling a pyroelectric material. This approach has also attracted much interest in fields such as low-power electronics and wireless sensors [7–9].

There has been limited progress with respect to the properties of the active material in piezo- and pyroelectric devices since the discovery of lead zirconate titanate (PZT) with a composition close to the morphotropic phase boundary (MPB); single crystals such as lead magnesium niobate-lead titanate (PMN-PT) can exhibit piezoelectric coefficients an order of magnitude higher than PZT [10] but tend to be significantly more expensive to process than ceramic materials, as well as having size and shape limitations. In certain applications, such as SONAR and ultrasound imaging that exploit the piezoelectric effect, and thermal imaging using the pyroelectric response, the introduction of porosity has been found to yield beneficial properties, which will be discussed in detail later. However, the effect of porosity on the energy harvesting capabilities of ferroelectric materials has not been studied in depth. The potential benefits of controlled porosity will be discussed in this article for both piezoelectric and pyroelectric energy harvesting, as will processing routes for forming porous ferroelectrics and the resulting effects on properties due to the interconnected structure of the active and the passive phases.

2 Piezoelectric energy harvesting

Over the past two decades many examples of potential applications for piezo-harvesters have arisen in the form of concepts and prototypes to convert mechanical vibrations into useful electrical energy. Structural monitoring devices, such as sensors in rail sleepers [11] and tire pressure monitors [12], are subjected to vibrations in their ambient environment, allowing them to self-power their operation and wirelessly transmit information. Other examples of prototype piezo-harvesters include fitting multiple piezoelectric devices into the sole of a shoe [13] or into the straps of a backpack [14], recapturing energy from pressure fluctuations in fluids [15,16], powering bio-MEMS inside the human body [17], using a piezoelectric membrane to convert acoustic energy to electrical energy in a thermoacoustic generator [18], as well as acoustic wave nanogenerators [19,20].

The effective design of a piezoelectric harvester requires consideration and, in the final stages, optimisation of each component of the conversion system, from the input mechanical energy and how this is driven through the active material, to the output electrical signal and how this is converted to useful electrical power. The characteristics of the active material should also be considered so as to maximise the energy generated due to an applied mechanical stress. To do so with regards to energy harvesting requires a general understanding of the piezoelectric effect, which will now be described.

2.1 Piezoelectric effect

The piezoelectric effect, first discovered by Jacques and Pierre Curie in 1880, is the change in electric polarisation of a material due to an applied pressure. This change in

polarisation leads to equal and opposite electrical charges forming on parallel surfaces generating a potential difference across the bulk material. This is known as the direct piezoelectric effect and is the basis for piezoelectric energy harvesting, as this voltage can be used to drive a current in an external circuit. Under short circuit conditions, which are the standard for measuring piezoelectric properties, the magnitude of charge developed, or the dielectric displacement, D_i , is proportional to the applied stress, σ_j , such that:

$$D_i = d_{ij}\sigma_j \quad (1)$$

where d_{ij} is the piezoelectric strain coefficient and the subscripts denote the direction of response (i) and application (j), using matrix notation. Alternatively, applying an electric field over a piezoelectric material induces a strain, which is the basis for actuating devices. This is known as the converse effect:

$$x_m = d_{im}E_i \quad (2)$$

where x is strain, E is electric field and the subscripts i and m denote application and response, respectively. High strain coefficients are desirable for actuator applications where large displacements are required. In applications that require the generation of a large voltage, such as a sensor, the open circuit voltage coefficient, g_{ij} , is of greatest importance:

$$g_{ij} = \frac{d_{ij}}{\varepsilon_{33}^\sigma} \quad (3)$$

where ε_{33}^σ is the permittivity of the material at constant stress. Piezoceramics can be classed as ‘hard’ or ‘soft’, which describes the ease of domain motion and is therefore linked to the degree to which a material can be polarised. ‘Hard’ materials are difficult to polarise, exhibiting low d_{ij} coefficients but higher g_{ij} values due to having lower permittivity, whereas ‘soft’ materials are characterised by high d_{ij} values but low g_{ij} due to high permittivities.

2.2 Piezoelectric energy harvesting figures of merit (FOMs)

Many vibration sources that arise in ambient environments, for example those associated with transport or industrial machinery, are low frequency (relative to the resonant frequency of ceramic materials) and random (in terms of frequency and amplitude), making it difficult to design for operation at one specific frequency. At a low frequency and off-resonance, a piezoelectric ceramic can be assumed to behave as a parallel plate capacitor [21]. Equations for the energy density of a material due to an applied stress, in terms of d_{ij} and g_{ij} , can be derived from simple capacitance equations. Starting with energy stored in a parallel plate capacitor, $U = 0.5CV^2$, where C is capacitance and V is applied voltage, the energy density, u , of a piezoelectric is given by:

$$\begin{aligned} u &= \frac{1}{2}d_{ij} \cdot g_{ij} \left(\frac{F}{A}\right)^2 \\ &= \frac{1}{2} \frac{d_{ij}^2}{\varepsilon_{33}^\sigma} \left(\frac{F}{A}\right)^2 \end{aligned} \quad (4)$$

where F is force and A is the area over which it is applied. Energy harvesters may work in either direct excitement mode (i.e. force is applied from the source directly

to the material along the poling axis), 33, or bending mode [3] (e.g. using a mass cantilever system), 31, and energy harvesting FOMs can be defined accordingly [22]:

Direct mode:

$$FOM_{33} = \frac{d_{33}^2}{\varepsilon_{33}^\sigma} \quad (5)$$

Bending mode:

$$FOM_{31} = \frac{d_{31}^2}{\varepsilon_{33}^\sigma} \quad (6)$$

The change in energy density gives the total amount of potential energy available for harvesting and it is therefore of interest to maximise these parameters.

The electromechanical coupling coefficient, k^2 , is related to the efficiency that a piezoelectric converts energy. For harvesting applications (given here for direct mode) a high FOM is desirable for a high coupling coefficient as:

$$k_{33}^2 = \frac{d_{33}^2}{\varepsilon_{33}^\sigma \cdot S_{33}^E} \quad (7)$$

where S^E is the elastic compliance of the material measured at constant electric field. Both these terms need to be optimised to maximise the capabilities of a piezoelectric used in an energy harvesting device.

When harvesting on-resonance a different FOM is defined for bending mode as [23]:

$$FOM_{on-resonance} = \frac{k_{31}^2 \cdot Q_m}{S_{11}^E} \quad (8)$$

where Q_m is the mechanical quality factor, which describes the damping behaviour of a system at the resonant frequency [24]. A high Q_m is favourable for on-resonance harvesters as only a small amount of the input energy is dissipated. However, when the input signal is random, a material with a high Q_m would only harvest energy in a narrow frequency range, thereby limiting its effectiveness. Materials with lower Q_m values are likely to perform better than those with high Q_m when used for broadband energy harvesting as they can operate over a larger frequency range.

The dielectric loss of a material, $\tan \delta$, is the amount of input energy dissipated due to internal losses that occur during a change in polarisation. In all piezoelectric energy harvesters, a low $\tan \delta$ is favourable so as to increase electromechanical coupling, k^2 [23], and therefore the efficiency of conversion from mechanical to electrical energy.

Research into maximising these parameters has so far focussed on careful control of the composition of materials to obtain high d_{33} or d_{31} values and low permittivities in PZT-P(ZN)N (Pb[(Zn_{0.4}Ni_{0.6})_{1/3}Nb_{2/3}]O₃) ceramics [25,26], as well as the evaluation of common commercial materials for their energy harvesting potential using the previously discussed FOMs [22,23]. The trade off between high piezoelectric strain coefficients and low permittivities has also been described at a system level, where it is found smart geometries of the active material can improve the performance of mass cantilever systems through a reduction in the capacitance [27,28]. As yet, little research has focussed on the use of porous ferroelectrics for energy harvesting, despite the potential for a high energy harvesting FOM due to reduced permittivity caused by the introduction of porosity. This may be due to a simultaneous reduction in strain coefficient, d_{ij} , and an increase in compliance, S^E . However, through careful control of microstructure via the processing route it may be possible to limit the

negative effects so as to improve the piezoelectric energy harvesting capabilities of the materials.

3 Pyroelectric energy harvesting

The pyroelectric effect, discovered before piezoelectricity with the first scientific account by Louis Lemery published in 1717, although others had observed the phenomena earlier [29], was used by the Curie brothers to help determine the mechanism for the piezoelectric effect. Pyroelectric materials produce power from temperature fluctuations (dT/dt) and therefore have similarities to piezoelectric harvesters that convert mechanical oscillations ($d\sigma/dt$) into electricity. If a pyroelectric is heated ($dT/dt > 0$) there is a decrease in its spontaneous polarisation as dipoles lose their orientation due to thermal vibrations. This fall in the polarisation level leads to a decrease in the number of free charges bound to the material surface. If the material is under short circuit conditions an electric current flows between the two polar surfaces of the material. Similarly, if the pyroelectric is cooled ($dT/dt < 0$) the dipoles regain their orientation leading to an increase in the level of spontaneous polarisation, thus reversing the electric current flow under short circuit conditions as free charges are attracted to the polar surfaces. The change in polarisation, ΔP , due to a change in temperature, ΔT , depends on the pyroelectric coefficient, p , of a material such that [29]:

$$\Delta P = p\Delta T \quad (9)$$

As in piezoelectric materials, it is of interest to use materials with high pyroelectric coefficients for energy harvesting applications, which is demonstrated by examining the FOMs.

3.1 Pyroelectric energy harvesting FOMs

FOMs have been derived for the selection of pyroelectric materials based on consideration of the thermal and electrical circuits employed [7]. The FOMs are based on the generation of maximum current or voltage for a given power input for applications such as thermal imaging sensors [8,9,30].

To obtain a high voltage responsivity (F_v) due to a given input power, the following FOM should be maximised [31]:

$$\begin{aligned} F_v &= \frac{p}{c_E \cdot \epsilon_{33}^\sigma} \\ &= \frac{p}{\rho \cdot c_p \cdot \epsilon_{33}^\sigma} \end{aligned} \quad (10)$$

where c_E is volume specific heat capacity, c_p is specific heat capacity and ρ is density.

High current responsivity (F_i) is required to maximise performance of infrared detection devices and is characterised by the following FOM [31]:

$$\begin{aligned} F_i &= \frac{p}{c_E} \\ &= \frac{p}{\rho \cdot c_p} \end{aligned} \quad (11)$$

The two FOMs above are often used for selection of materials for heat and infrared detection, but these are not to be confused with energy harvesting applications where generated power is of interest, as is the efficiency of the conversion of thermal to electrical energy.

Pyroelectric energy harvesting-specific FOMs have been proposed [32–34], including an electrothermal coupling factor that has been defined to estimate the effectiveness of thermal harvesting [32]:

$$\begin{aligned} k^2 &= \frac{p^2 \cdot T_{hot}}{c_E \cdot \varepsilon_{33}^\sigma} \\ &= \frac{p^2 \cdot T_{hot}}{\rho \cdot c_p \cdot \varepsilon_{33}^\sigma} \end{aligned} \quad (12)$$

where T_{hot} is the maximum working temperature. An energy harvesting FOM, F_E , has been proposed as [33]:

$$F_E = \frac{p^2}{\varepsilon_{33}^\sigma} \quad (13)$$

which has been widely used for materials selection and materials design [29, 35, 36]. A modified version that includes heat capacity is [34]:

$$F'_E = \frac{p^2}{\varepsilon_{33}^\sigma \cdot c_E^2} \quad (14)$$

To achieve a better performance for pyroelectric harvesting, it is necessary to increase F_E or F'_E , which requires a combination of properties, such as high pyroelectric coefficient, p , low permittivity, ε_{33}^σ , and low volume heat capacity, c_E .

The piezo- and pyroelectric materials for energy harvesting display certain similarities with regards to their respective FOMs, in that increases can be achieved by maximising the piezo-/pyroelectric coefficient whilst reducing the permittivity. There are a number of ways to enhance the functional performance of a dense material, including chemical modification (doping, substitution), the utilisation of promising perovskite components for the construction of phase diagrams and the employment of the single crystals and polymers. Due to the complexity of developing new formulations and the high cost, low Curie temperature and poor mechanical properties of single crystals, the applications of the above materials are limited. Porosity offers a relatively low-cost alternative to increasing FOMs through a reduction in both permittivity and heat capacity, as will be explained in the next section.

4 Ferroelectricity

Ferroelectric materials have the ability to maintain a spontaneous polarisation, the orientation of which can be electrically switched [37]. This means that they exhibit both piezoelectric and pyroelectric properties as applying a force to or changing the temperature of a poled ferroelectric will change the magnitude of the polarisation, which, as described earlier, can be used to extract usable electrical energy. This phenomena arises from the crystal structure in which a non-centrosymmetric unit cell creates an electric dipole. All ferroelectrics exist in a paraelectric state above the Curie temperature, where a phase transition results in no electric dipole, giving the upper limit of their functional properties. Ferroelectric ceramics, such as PZT, exhibit excellent piezo- and pyroelectric properties and are therefore of great interest

for all applications that utilise these effects. Ferroelectricity can also exist in crystalline polymers, with PVDF (polyvinylidene fluoride) of particular interest due to its functional properties, flexibility and processability [38]. Ferroelectric materials are a sub-group of pyroelectric materials, and all pyroelectric materials are piezoelectric [3].

As sintered, ferroelectric ceramics have a random orientation of domains (sub-grain regions with aligned dipoles) giving an overall polarisation of zero. Poling the material by applying a large electric field aligns the domains over the bulk material resulting in a net polarisation that remains when the field is removed. Applying a significantly large electric field in the opposite direction can reverse the direction of polarisation, leading to the characteristic hysteresis behaviour observed in all ferroelectric materials [37]. Heating above the Curie temperature causes a phase change to a centrosymmetric crystal structure, resulting in the loss of piezo- and pyroelectric properties. When cooled below the Curie temperature ferroelectrics must be re-poled to restore their functional properties as domains again orientate randomly in their lowest stress configuration. PZT exhibits high functional properties as the composition is tailored close to the MPB so that two phases coexist in normal operating conditions, across a wide range of temperatures, greatly increasing the polarisability of the material. The high degree of polarisation, coupled with a relatively high Curie temperature (up to $\sim 400^\circ\text{C}$), makes PZT the material of choice for most actuator and transducer applications, as well as being frequently employed in pyroelectric thermal imaging devices.

4.1 Porous ferroelectric ceramics

Traditional processing routes have strived to obtain ceramics with very high relative densities ($>95\%$) so as to maximise the mechanical properties, with porosity usually considered as a defect. Many functional properties, such as piezo- and pyroelectric coefficients in ferroelectrics, are also maximised when the relative density is close to maximum [39]. However, by introducing a second phase, either as porosity or polymer, it is found that certain coupled properties, such as the longitudinal and transverse piezoelectric effects, can be tuned somewhat independently of one another [40,41]. The majority of research into porous piezoelectrics has been focussed in the field of ultrasonic transducers and low frequency ($<100\text{kHz}$) sensing devices such as hydrophones [42–44]. Most of the research into porous pyroelectrics has occurred in the last 15 years and has focussed on improving thermal imaging devices alongside side energy harvesting capabilities [45–47].

The connectivity of a ferroelectric composite determines the electrical, mechanical and thermal properties [48]. Newnham et al. [40,41] defined the connectivity of a material with respect to the dimensionality of the interconnection of the individual phases, so that a two-phase material can be described by two numbers, the first of which refers to the piezoactive phase and the second to the passive phase. For example, PZT with 3-0 connectivity would have a continuous ceramic phase with isolated porosity. Although originally defined for piezocomposites, this notation is now commonly used for general composite engineering. The final connectivity of a porous ceramic is determined by the processing route. Fig. 1 shows a selection of common two-phase structures that can be achieved using the methods described in Section 4.2.

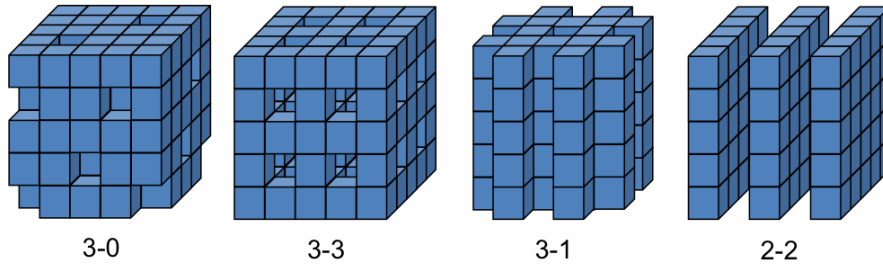


Fig. 1. Examples of common connectivities of biphasic composites, e.g. ferroelectric ceramic-air materials, adapted from [48]. The first number refers to the connectivity of the ceramic phase (in blue) and the second to the connectivity of the porosity (represented as gaps in the structures).

4.1.1 Effect of porosity on piezoelectric properties

Introducing porosity into piezoceramics is found to improve the hydrostatic response, measured by hydrostatic strain coefficient, d_h , and the hydrostatic voltage coefficient, g_h [40, 44]. Perovskite piezoelectric ceramics, such as PZT, are characterised by a longitudinal and a transverse coefficient, d_{33} and d_{31} , respectively, and the hydrostatic strain coefficient can be written in terms of these: $d_h = d_{33} + 2d_{31}$. In dense ferroelectric materials $d_{31} \sim \frac{1}{2}d_{33}$ leading to $d_h \sim 0$. Introducing porosity enables a partial decoupling of the longitudinal and transverse reactions so that d_{31} tends toward zero as porosity is increased to approximately 60vol%, with only a relatively small reduction in d_{33} [49]. Therefore, by introducing a second inactive phase into the piezoelectric material, a significant increase in the hydrostatic strain coefficient can be attained.

With regards to piezoelectric energy harvesting, the resulting structure must ensure that d_{33} maintains a high value, as the reduction in d_{31} has no benefit for direct mode harvesters and means that porous materials will not operate effectively in bending mode. This can be seen in Fig. 2, where data from past research into porous ferroelectrics for hydrophone applications has been reanalysed in terms of FOM_{33} and FOM_{31} . The benefits in direct mode are shown, with increases in FOM_{33} of >300%, whereas introducing porosity is found to significantly decrease the bending mode response, FOM_{31} . Elastic compliance data are not readily available and so the electromechanical coupling coefficients of porous materials could not be analysed in the same way.

The hydrostatic voltage coefficient, g_h , is given by the term $g_h = d_h/\epsilon_{33}^\sigma$. Dense ferroelectrics exhibit high permittivities that reduce the voltage output due to an applied stress. The permittivity of ferroelectric ceramics is significantly reduced by the introduction of an inactive second phase as there is a lower volume of easily polarisable material within the composite. Therefore, the voltage generated due to hydrostatic pressure is increased in porous ferroelectrics, compared to their dense counterparts, through the combined reduction in ϵ_{33}^σ and the increase in d_h . Examination of Eq. (4-7) shows that lowering the permittivity is also of interest for maximising the energy harvesting capabilities of ferroelectric ceramics.

The acoustic impedance of a material, Z_A , determines the ratio of energy transmitted and reflected at the interface between the receiver and the surrounding environment [50]. In sensing devices such as hydrophones, impedances of devices should be closely matched to their working environment to ensure efficient energy transfer from one medium to another [39]. Water and biological tissue have an acoustic

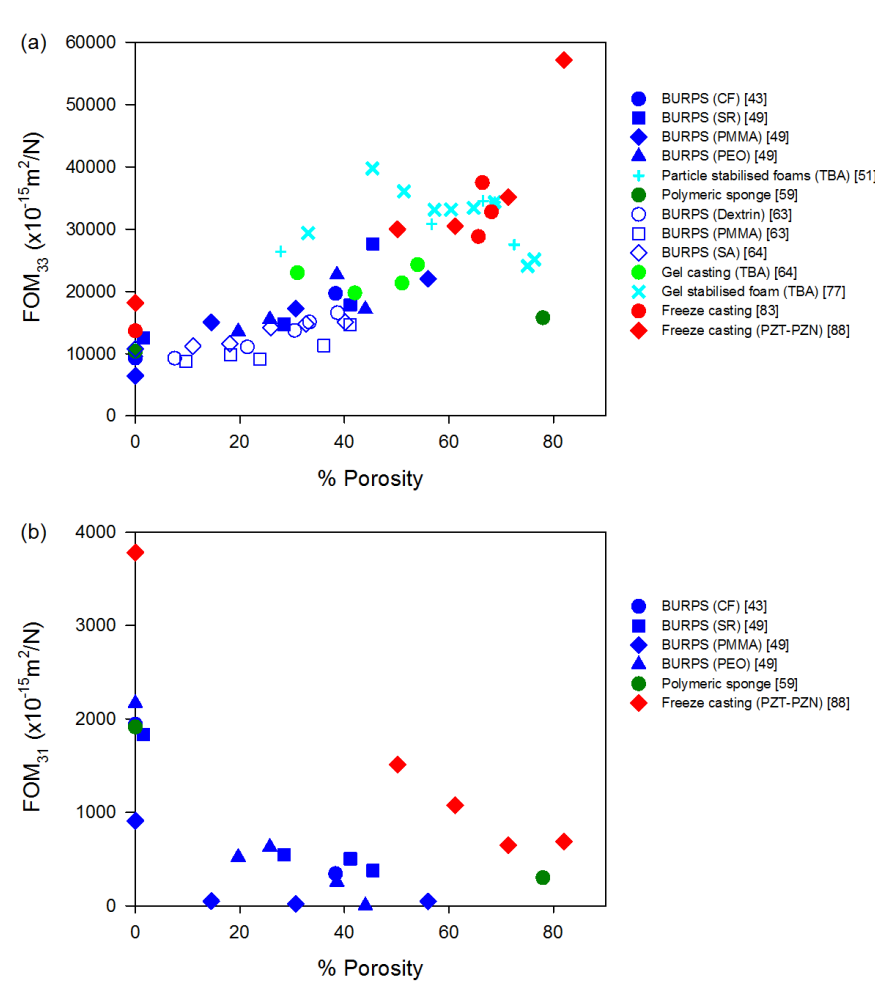


Fig. 2. Reanalysed data from literature of (a) FOM_{33} as a function of porosity and (b) FOM_{31} as a function of porosity. Improvements of $>300\%$ are possible for linear vibration harvesting, highlighting the potential for energy harvesting. A decrease in FOM_{31} can be seen with increasing porosity, due to a corresponding decrease in d_{31} , meaning that porous materials would function less well in vibration harvester geometries that operate in bending mode without extra considerations for the placement of electrodes. Data are described in terms of processing route with PFA given in brackets, where CF is corn flour, SR is self-raising flour, PMMA is poly(methyl methacrylate), PEO is poly(ethylene oxide), SA is stearic acid and TBA is tert butyl alcohol.

impedance of around 1-1.5 Mrayls and dense PZT has an impedance of around 30 Mrayls [49]. Introducing porosity reduces this value significantly, with impedances below 2 Mrayls reported for $\sim 70\%$ porous PZT [51], therefore providing a much better acoustic matching of piezoelectric devices when used in water, such as hydrophones, or on biological tissue, such as ultrasound scanners. This would also be advantageous for vibration or pressure fluctuation harvesting in these environments.

Another potential benefit of porosity for low frequency, off-resonance energy harvesting is the lower mechanical quality factors, Q_M , that porous ferroelectrics exhibit compared to dense ones [12, 52, 53]. A low Q_M material, such as porous PZT, has a

broader peak at resonance than dense PZT, making it more suited for broadband energy harvesting at lower frequencies, i.e. the conditions for which the piezoelectric FOMs in Section 2.2 are derived.

The dielectric loss, $\tan \delta$, of a piezoelectric, is important for the efficient operation of transducers, such as energy harvesters, as it is related to the amount of energy dissipated during the energy conversion process. Several studies have found that introducing porosity can reduce $\tan \delta$ compared to dense materials [54–56], which would be advantageous for increasing the conversion efficiency of devices using porous piezoelectrics as the active material.

The benefits of porous ferroelectric ceramics for applications such as hydrophones have been established over the past 30 years, with their superior hydrostatic response, improved acoustic matching and overall device sensitivity shown in numerous studies. In certain circumstances, such as in bending mode or on-resonance harvesters, dense ferroelectric ceramics offer a better route to high conversion efficiencies than porous materials. However, porous piezoceramics show promising properties for energy harvesting under certain conditions (low frequency, random excitation) due to their low permittivity coupled with relatively high d_{33} values, as well as exhibiting low dielectric loss, $\tan \delta$, and mechanical quality factors, Q_m .

4.1.2 Effect of porosity on pyroelectric properties

As well as reducing the permittivity of ferroelectric ceramics, which has advantages for both piezo- and pyroelectric harvesting, the introduction of porosity also reduces the volume specific heat capacity, which has benefits for increasing pyroelectric FOMs (Eq. (10-14)). The main application of pyroelectric materials is in infrared imaging devices, the principles of which are essentially the same as those required for energy harvesting. Three types of porous pyroelectric material have been explored for energy harvesting applications, including thin films [45,57] with high FOMs resulting from the decreased heat capacity; bulk functionally graded materials (FGM) consisting of a porous layer with controlled porosity, which allows more control over the permittivity and heat capacity of the material [46,47]; and uniform porous ferroelectric ceramics [58].

Lang et al. [58] observed that both piezoelectric and pyroelectric FOMs are improved in porous ferroelectric ceramics as a result of the reduced relative permittivity in porous PZT with 3-0 and 3-3 connectivities prepared by the burned out polymer spheres (BURPS) process (detailed in Section 4.2.2). It was reported that uniformly porous structures of pyroelectric ceramics have higher pyroelectric responsivities than the dense materials. Since porosity also decreases the volume heat capacity it leads to an improvement of the thermal response; however, it also decreases the electrical resistivity and pyroelectric coefficient [45]. This complex relationship between pyroelectric, dielectric and thermal properties means that there is potential to tune the porosity to achieve the optimum response for a given application. However, due to the poor mechanical properties of unaligned porous structures the machinability of such materials is relatively poor, limiting their use in devices for generating electric power from thermal fluctuations.

Controlling the porous structure is of interest for both piezo- and pyroelectric energy harvesting applications as it can give control over properties that affect FOMs. The processing route used to form porous ferroelectric materials ultimately determines their structure and functional properties, so an understanding of the strengths and limitations of the different methods available is important when designing a material for piezo- or pyroelectric energy harvesting. These will now be discussed with a focus on bulk porous ceramics.

4.2 Processing of porous ferroelectrics

4.2.1 Coral replamine

The initial work into piezocomposites used a coral replamine technique, whereby a cubic coral structure was impregnated under vacuum with wax [40]. The coral was dissolved away using acid to leave a wax negative that was then filled with PZT-slip, before drying and sintering to remove the wax and densify the PZT regions. The resulting structure had large pores that were then filled with epoxy resin, resulting in 3-3 connectivity, i.e. complete connectivity of both the PZT and epoxy phases. The large pore size increased the flexibility of the ceramic and an increase in hydrostatic strain and piezo- and pyroelectric voltage responses were noted. By heavily straining this material the PZT coral structure was cracked, isolating ceramic regions from one another, thereby creating a flexible 0-3 structure [41]. This simple method was used to evaluate the effect of introducing a second phase into a piezoelectric material, and succeeded in exhibiting the benefits for applications where a hydrostatic stress is applied. However, this method is not easy to scale up and so other methods for creating porous ceramics have been devised.

Most macroporous ceramic structures can be back-filled with a polymer phase to improve the mechanical properties of the material. Whilst using a polymer second phase does improve the hydrostatic piezoelectric properties, porous piezoelectric ceramics exhibit enhanced performance in terms of d_h and g_h compared with ceramic-polymer composites [59].

4.2.2 Burned out polymer spheres (BURPS)

The BURPS process is a method for creating 3-3 structures with relative ease and low cost [60]. A pore-forming agent (PFA) is added to the ceramic powder before the pressing stage and is burned out during the sintering process. The BURPS process can also be adapted for tape casting ceramics [47, 50], allowing scale-up of manufacturing as well as the manufacture of thick films in the range of 5-200 μm , which are also of interest for energy harvesting [61]. Sintering profiles are usually adjusted to include a dwell stage at the temperature at which the PFA sublimes. BURPS provides some control over the pore structure as the pore size is closely correlated to the size of the additive. Various studies have assessed the performance of different pore formers, such as poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), self-raising flour, dextrin and poly(vinyl alcohol) (PVA) [49, 62, 63], with the main difference in structure resulting from pore size and morphology. A draw back of the BURPS process is that cracking of the ceramic bridges between the pores often occurs, thought to be due to aggressive burn off of the volatile species [64], which may reduce both mechanical and piezoelectric properties. Cracking has also been reported in samples using PMMA as a pore former, thought to be caused by relatively high stiffness of the PFA that leads to spring back after pressure has been released in the pressing stage, resulting in cracks perpendicular to the pressing direction [49, 62]. A limit to the amount of porosity obtainable, particularly for large, macro-PFAs, is usually 60-70% due to severe reduction in structural integrity above this point [59].

A limited degree of control over pore anisotropy and alignment is possible using the BURPS process by using irregular shaped PFAs [54, 64]. However, these tend to align perpendicular to the pressing direction, which is usually also the poling direction, and are found to lower both permittivity and piezoelectric coefficients. Modelling studies have shown that elongated pores aligned to the poling axis exhibit superior d_{33} coefficients in 3-3 structures compared with those aligned perpendicular to the

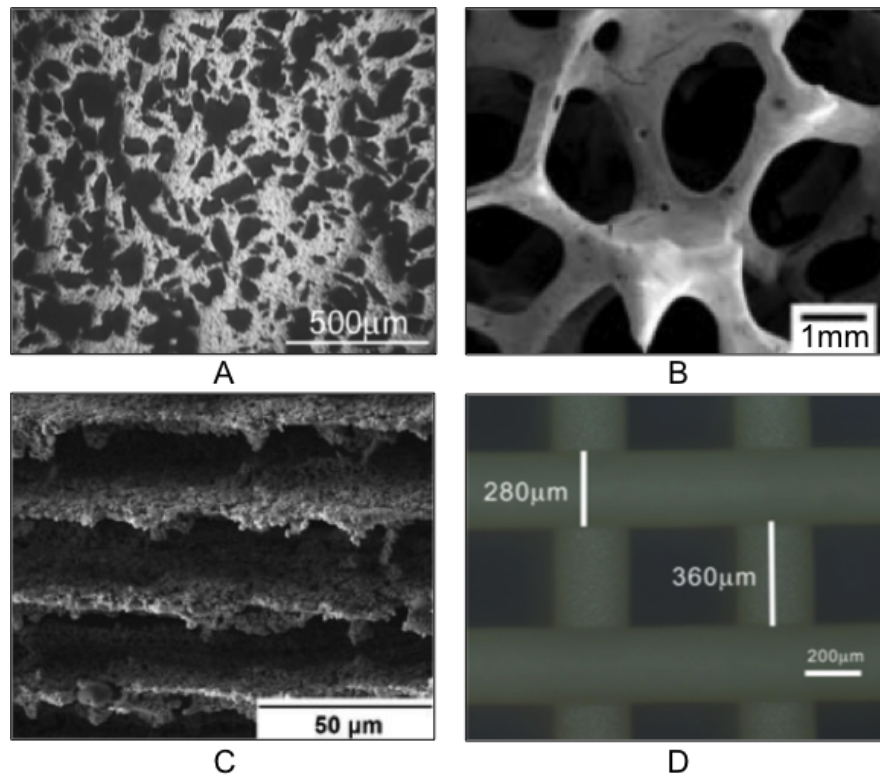


Fig. 3. Porous microstructures formed using different processing routes including (A) 3-3 porous PZT formed via BURPS process with PMMA as PFA [63], (B) $\sim 80\%$ porous PZT formed via polymeric sponge method with 3-3 connectivity [59], (C) freeze cast alumina exhibiting 2-2 nacre-like structure aligned parallel to the poling direction [66] and (D) 3D printed ‘woodpile’ structure [67].

poling direction, although were also predicted to exhibit higher permittivities [65]. It is likely that pore morphology could have a significant effect on energy harvesting capabilities of porous ferroelectric ceramics, however more sophisticated processing techniques are required to achieve desired structures.

4.2.3 Polymeric sponge

The effect of elongated pores aligned parallel to the poling direction has been studied by creating such structures via the polymeric sponge method [59,68]. In the most basic method, a sponge is impregnated with ceramic slip before sintering removes the polymer, leaving a densified ceramic foam structure in its place. This comes under the broader category of sacrificial template methods [39]. By stretching and clamping the ceramic-soaked sponge during sintering the pores can be aligned, thereby providing a route to tailor the fraction of material in the polarisation direction and influencing the piezoelectric properties and permittivity [68]. The effect of pore morphology is discussed further in Section 4.2.8. This method was useful for evaluating the effect of pore anisotropy on piezoelectric properties [59], however incomplete sintering can

lead to cracking in the ceramic struts, reducing the structural integrity and limiting its use for wider applications.

4.2.4 Gel casting

Gel casting was developed to form dense ceramics with superior shape retention from green to sintered form [69] but was adapted to synthesise porous materials with relatively high mechanical strength [70]. Ceramic powder is mixed with organic monomer binder and a dispersant in a solvent to form a slip. A commonly used pore former in gel casting is tert-butyl alcohol (TBA) [71–74]. An initiator is added to begin polymerisation of the monomer, leading to in-situ formation of gel spheres that burn out during sintering, leaving spherical pores. Research into gel casting piezocomposites has been a reasonably recent phenomena and a comparison between gel casting and BURPS processes has shown gel casting to be advantageous, mainly due to the more uniform, spherical pores that can be obtained [64]. This will be discussed in more detail in Section 4.2.8 in terms of structural effects on electromechanical properties.

More recently, gel casting has been used in combination with the direct foaming method [51] and freeze casting [75]. In the direct foaming method, porosity is generated by mechanically frothing a ceramic slurry suspension to introduce air bubbles, prior to sintering [76]. This is a relatively low-cost method of forming porous ceramics but thermodynamic instability can cause a large distribution in pore sizes that may be mechanically unfavourable. Gel casting is used to increase the stability of foams, leading to a more even pore size distribution [77].

The processing methods described above are all used to generate 3-3 porosity, tending towards 3-0 as porosity levels are decreased, with pores randomly distributed through the bulk (schematics shown in Fig. 1). As has been shown previously in Section 2.2, piezoelectric ceramics for energy harvesting should ideally have the lowest possible compliance. There is an almost linear relationship between porosity and compliance in 3-3 ceramics [58,63]. One possible way of improving the mechanical properties of porous ceramics is to utilise structures with the ceramic phase aligned in the direction in which the material is stressed.

4.2.5 Freeze casting

Freeze casting is a method for forming porous ceramics that has come to attention in the 15 years [78] and has the capability to form complex pore structures [79,80]. Ceramic powders are mixed with dispersant and a solvent and cooled from one side to stimulate directional freezing of the solvent, which grow in dendrites that form at the cooled surface. These dendrites form the template for the porous structure. During solidification, ceramic particulates are forced into the channels between the crystallising solvent, leaving behind high density channels also aligned in the direction of freezing [81]. The freezing vehicle is then removed at low pressure so as not to degrade the unsintered ceramic. The resulting structure can be thought of as 3-1, with a fully interconnected ceramic phase containing isolated pore channels (see Fig. 1), or 2-2, with a nacre-like structure (as shown in Fig. 3). For a given porosity, freeze cast ceramics exhibit superior mechanical properties to 3-3 structured materials when force is applied in the direction of alignment [82], which would be favourable for energy harvesting because of an increased electromechanical coupling coefficient, as well as making it easier to further process and handle the materials.

Freeze casting allows good control over porosity, simply by adjusting the solid loading in the slip [79,81,83,84]. Altering the freezing agent can change the shape of

the pore channels; camphene can yield pores with a near-circular cross section [81], whereas water tends to form flat ellipsoidal pores [56] and TBA produces hexagonal channels [85]. Freezing vehicles that allow room temperature processing, such as near-eutectic naphthalene-camphor, have also been investigated [86]. The width of the pore channels [85] and ceramic walls [80] can be controlled by altering the degree of undercooling and the size of the ceramic particles in the slip [66]. Freeze casting is a promising processing route for piezocomposites as it enables control over the microstructure through relatively easy changes in freezing agent, solid loading and freezing temperature that may have benefits for the electromechanical properties. It may also allow high levels of porosity to be achieved (>80%) [80], whilst maintaining structural integrity.

Porous PZT with a 2-2 structure formed by freeze casting [87] has been found to exhibit higher a pyroelectric coefficient and a lower permittivity than that found in 3-3/3-0 PZT structures made using a BURPS process by Lang et al. [58]. The aligned structure may yield improved thermal properties for pyroelectric harvesting as well as superior compressive strengths (250-300%) [87] that have been found for these structures compared with 3-3 ceramic-air composites.

Most of the work on freeze cast porous ceramics has been on non-ferroelectric material systems, although in the last few years freeze casting has been shown to work with barium titanate [55,56], PZT [53,88] and PZT-lead zinc niobate (PZN) [84]. Notable results include reported d_{33} values of 81.8-93% of the dense value despite the porosity being over 65% [88], with d_{33} values at around 75% of dense values reported elsewhere for 82% porous samples [84]. This is typically much better than would be expected with 3-3 samples made by the BURPS process which often exhibit d_{33} values <60% of the dense value for similar levels of porosity [49]. However, the permittivity of porous materials usually correlates somewhat with the piezoelectric strain coefficient, and is therefore often found to be higher in freeze cast materials.

4.2.6 Printed porous structures

Another relatively recent development in the production of porous ceramics is the use of 3D printing technology, although it may be referred to under a number of different names, such as fused deposition technology (FDM) or solid freeform fabrication (SFF), for example [48,89]. Ceramic slurry is mixed with a thermoplastic binder to make the filament, which is printed to form the desired structure. The green structure is then sintered to remove the thermoplastic and densify the ceramic phase. This can be used to form complex geometries and connectivities and, although early attempts led to relatively coarse (>250 μm) structures, advances in the technology mean microscale separations are possible [67]. Also, the use of 3D printing in combination with electrospinning technology can be used to form structures with nanoscale piezoelectric filaments [90]. Excellent control over the structure can be achieved using these methods so that good quality 3-1, 1-3 or 2-2 piezocomposites could be formed with properties tailored for energy harvesting.

4.2.7 Nanostructured porous materials

Advances in nanotechnology offer a route to form nanoscaled piezoelectric and ferroelectric structures for energy harvesting [91]. Currently the research has mainly focussed on materials such as piezoelectric zinc oxide [19] and ferroelectric lithium niobate [92] that exhibit the potential for high temperature operations and harvesting of acoustic energy. Production routes include the vapour-liquid-solid (VLS) process

and photolithography to form arrays of nanowires on a conductive substrate such as gold. Materials such as lithium niobate exhibit ferroelectric properties to much higher temperatures, with a Curie temperature in excess of 1000°C , than more commonly used ferroelectric ceramics such as PZT and barium titanate, but have a significantly lower permittivity in their pure form ($\epsilon_r < 100$), and therefore introducing porosity into structures is going to have less beneficial effect for energy harvesting. PZT nanowire arrays have been produced using a hydrothermal process [93], which has applications in the miniaturisation of harvesting devices and shows that high performance ferroelectric ceramics can be processed in this way.

Microporous PVDF thick films have also been investigated for their pyroelectric energy harvesting capabilities [45, 57]. Films $\sim 50\mu\text{m}$ thick were formed by hot-pressing a PVDF pellet before curing to remove volatiles and solvents, which yield a porous structure. These exhibited improved pyroelectric FOMs and electrothermal coupling coefficients than commercially available pure films. Similarly, 0-3 PZT-PVDF thick films formed using a spin casting process have been shown to have comparable pyroelectric FOMs to pure PZT thick films [94].

There has been increasing interest in the development of 0-3 piezocomposites using ceramic nanoparticles (NPs) embedded in an active PVDF matrix [95, 96] for small, flexible devices. Porosity, generated using sugar as a PFA, has been found to enhance the performance of the composites by increasing the compliance of the PVDF [95], which may increase the stress transfer into the ferroelectric NPs. Introducing porosity may also enhance the piezoelectric behaviour as the micropores effectively form electret arrays [97]. This work, still in its early stages, has shown the potential for using porous PVDF films for energy harvesting, although interestingly the mechanism of enhanced performance appears different from that seen in porous piezoceramics, as it is not generally associated with a decrease in the permittivity.

4.2.8 Effect of pore morphology on properties

Pore size in 3-3 piezocomposites has been found to have little effect on the piezoelectric properties [49, 62], although macroporous structures have been found to exhibit lower permittivities than microporous ones [98]. The effect of pore size on the mechanical compliance has not been studied in detail, although there is some evidence to suggest that pore size has no effect on the Young's modulus of the material [63]. However, the general trend of an increase in compliance with increasing porosity is well established [50, 63].

Pore shape can have an effect on both the piezoelectric and mechanical properties. In the BURPS process, irregular pore shape can either be caused by an irregular shaped pore former or due to smearing of a soft volatile agent during pressing. In both cases, the long axis of the pores is usually aligned perpendicular to the pressing direction [54, 64]. The use of stearic acid as a pore former leads to irregular pore formation, with the relative permittivity being lower as a result [64], possibly due to stress concentrations leading to depolarising effects. The Young's modulus of materials with spherical pores has been found to be higher than materials with irregular pores, again thought to be because of stress concentrations [54].

4.2.9 Sintering temperature

A number of studies, using the different processing methods described above, have investigated the effect of sintering temperature on piezoelectric properties [50, 71, 73, 99]. In all cases, increasing the sintering temperature results in a denser microstructure, and therefore higher piezoelectric coefficients and permittivity, nullifying the

positive effects of porosity with regards to energy harvesting and SONAR applications. The sintering temperature can be used as a mode of controlling the porosity in the structure rather than altering the level of PFA in BURPS [99] and could also be applied to tape/freeze casting. Altering the sintering temperature alongside other processing variables could be used to give added control over porosity volumes. An increase in grain size may be associated with higher piezoelectric coefficients [100] but this is difficult to achieve without also increasing density, which is likely to be associated with an increase in permittivity and is therefore unfavourable for ferroelectric ceramics for energy harvesting. At this stage the focus should be on understanding the structural relationships between the ceramic and the air phase, as this is likely to have a greater effect on overall performance, before considering the grain size when attempting to optimise the system.

5 Conclusions

Introducing porosity into ferroelectric materials, particularly high performance ceramics such as PZT, has the capability to increase both piezo- and pyroelectric off-resonance energy harvesting FOMs. High levels of porosity lead to a significant reduction in permittivity, which is of interest for both piezo- and pyroelectric energy harvesting, as well as reducing the volume specific heat capacity, which is favourable for pyroelectric harvesting. Lower Q_m values exhibited by porous piezoceramics also increase their appeal for broadband, off-resonance energy harvesting. However, the complex balance of properties required for high electromechanical and electrothermal coupling coefficients mean that porous structures must be carefully engineered to achieve the desired properties such as high d_{33} and low compliance and permittivity for piezo-harvesters, and high p , low heat capacity and low permittivity for pyro-harvesters.

Data from previous studies, presented in Fig. 2, has shown the potential for using porosity to increase piezoelectric harvesting FOMs, but more research is required to fully understand the effects this has on mechanical properties, in particular. Porosity has a detrimental effect on mechanical properties, even for freeze cast materials with excellent alignment of the ceramic phase. The significance of this effect needs to be investigated with regards to the electromechanical coupling coefficient, in which high FOMs are desirable but also low compliances, which will only be achievable in terms of porous ferroelectrics if careful attention is paid to the final structure of the material.

A variety of processing routes are available to produce ferroelectrics with complex structures that are suited to harvesting energy from thermal fluctuations and mechanical vibrations. The most promising of these includes freeze casting, which enables good alignment of both ceramic and porous phases thus yielding good properties tailored for energy harvesting, and new developments in printed and nanotechnology that may allow even better control over structure as well as enabling the production of very small energy harvesting devices.

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