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Ferroelectricity in biological building blocks: Slipping on a banana peel?

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Ferroelectricity in biological system has been anticipated both theoretically and experimentally over the past few decades. Claims of ferroelectricity in biological systems have given rise to confusion and methodological controversy. Over the years, a "loop" of induced polarization in response to a varying applied electrical field and a consequent polarization reversal has prompted many researchers to claim ferroelectricity in biological structures and their building blocks. Other observers were skeptical about the methodology adopted in generating the data and questioned the validity of the claimed ferroelectricity as such, "loop" can also be obtained from linear capacitors. In a paper with somewhat tongue-in-cheek title, Jim Scott showed that ordinary banana peels could exhibit closed loops of electrical charge which closely resemble and thus could be misinterpreted as ferroelectric hysteresis loops in barium sodium niobate, BNN paraphrasing it as "banana". In this paper, we critically review ferroelectricity in biological system and argue that knowing the molecular and crystalline structure of biological building blocks and experimenting on such building blocks may be the way forward in revealing the "true" nature of ferroelectricity in biological systems.

Keywords: Ferroelectricity; piezoelectricity; pyroelectricity; biological materials; ion channel; voltage gating.

1. Introduction

Biological systems, such as bone, have long been known as piezo- and pyro-electric in the classical sense. As such, they fall into the group of polar dielectrics — materials that can be polarized by an electric field due to induced dipole moments or the rotation of internal electrical dipoles.

In a direct current (dc) electrical field, positive charges are pushed in the direction of the electrical field while negative charges are pushed in the opposite direction. Hence, the centers of gravity of net positive and negative charges in the material do not coincide, thus giving rise to polarization due to the creation of an electrical dipole. Polarization is the measure of net dipole moments in a given volume of a material. All dielectrics such as glass, ebonite, mica, rubber, wood and paper are, more or less, electrostrictive with a deformation that is quadratically related to the electrical field that has caused the deformation in the first place. Another class of dielectric that is relevant here are electrets, which possess quasi-permanent charge or polarization.[1] Two-sided metallized electrets contain large quasi-permanent dipole moments resulting, e.g., from ferroelectric polarization.

Crystalline piezoelectrics lack an inversion center in the unit cell. As a result, they deform linearly in response to an applied electric field (converse effect) and vice versa (direct effect). A subset of piezoelectrics, pyroelectrics, possesses a spontaneous polarization in the structure. This polarization can give rise to a compensative charge in the electrodes attached to them when there is a change in temperature.

Ferroelectric materials are a subgroup of piezoelectric and pyroelectric materials. In ferroelectrics, the spontaneous polarization is retained even when the applied electric field is removed, and the polarization can be reversed with the application of an electric field in the opposite direction to the original applied field. Ferroelectricity is often claimed in a material if one finds a closed loop of electrical polarization (P) that can be traced as the applied electric field (E) to the materials is cycled.

The polarization (P) versus applied electrical field (E) P–E as a closed loop was reported by Vasalek in 1920 on Rochelle's salt as a "dielectric anomaly". Rochelle's salt is a double salt of tartrate ($KNaC_4H_4O_6{\cdot}4H_2O$) first made in c. 1675 by Pierre Seignette, an apothecary of La Rochelle, France. Pierre Curie and Jacques Curie demonstrated in 1880 piezoelectric effect in tourmaline, quartz, topaz, cane sugar and Rochelle salt. French physician and chemist Linné, described pyroelectricity of tourmaline *lapis electricus* in 1747.[2]

2. Slipping on a Banana Peel

In 2008, Scott compared the P–E loops obtained from a (002)-oriented film of BNN (nicknamed as "banana"), which

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is widely accepted as being ferroelectric, with the "cigar"-shaped P–E loop obtained from a banana peel.[3] Cigar-shaped loops are typical of lossy dielectrics and do not represent, in the classical sense, ferroelectric behavior. Anomalous dielectric loop can also rise from Schottky-like electrodes on many nonferroelectric materials.

The use of a banana peel as an example of ordinary household objects or fruits and vegetables that are nonferroelectric materials is interesting. A banana peel is composed of several building blocks, including carbohydrates (~60%), cellulose-based fibers (~30%), water, proteins and fat. Individually, these constituents may or may not be ferroelectric. The questions that are needed to be asked in the beginning, however, are whether these building blocks were piezo- or pyro-electric and if so, how their individual piezoelectric or pyroelectric behavior impacts the ferroelectric polarization of the banana peel.

Since the publication of relatively weak piezoelectricity in wood, silk and bone in the 1950s, the field of piezoelectricity in biological materials has advanced considerably.[4] Figure 1 summarizes piezo- and pyro-electric effect found in biological building blocks.

Biological constituents and building blocks include water, organs, tissues, cells, macromolecules (e.g., proteins, nucleic acids and polysaccharides) and small organic molecules (e.g., fatty acids sugars, amino acids and nucleotides). Macromolecules and small organic molecules are generally asymmetric and can retain the asymmetry when crystallized. This, however, does not necessarily mean that asymmetric molecules will universally crystallize into an asymmetric structure. A polar asymmetric molecule can interact with a partner molecule to form a "synthon" that will form a crystal structure with an inversion center. Similarly, racemic mixtures of asymmetric amino acids have been found to crystallize into an asymmetric structure and exhibit polar nature.[5]

Classical piezo/pyro- or ferro-electric measurements are seldom conducted on the isolated crystalline/molecular forms of biological building blocks due to the absence of suitable material and the need of electroding. Single crystals of these molecules are very difficult to electrode in a conventional way. Conductive micro- or nano-probes have often been used to measure piezoelectricity in these single crystals. In some cases, measurements can be made either by sandwiching polycrystalline aggregates or a film between two conducting plates[6] or depositing films on interdigitated electrodes (IDEs).[7,8] Any firm contact between the electrode and film/aggregate is challenging in many cases, thus the presence of any Schottky barrier is very probable when dealing with these materials. Optical measurements such as second harmonic generation (SHG) can be used for contactless measurements.[8] Interpretation of the data to retrieve quantitative piezoelectric coefficients is not trivial and a one-to-one correspondence between acoustic and optical measurements are still elusive, however.[9]

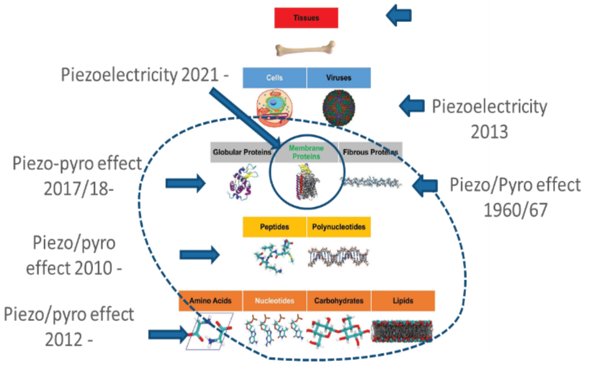

Fig. 1. Biological building blocks that have been found piezo- and/or pyro-electric. Whether they are ferroelectric will need to be experimentally established, adapted from Ref. 5.

Water is ubiquitous and essential in biological systems. In addition to the water that surrounds biological systems, there is bound and structural water that is integral to the supramolecular structure of biological building blocks. For example, water confined within the nanoscale cavity has been found to govern polarization-related properties of self-assembled diphenylalanine peptide nanotubes[10] known to demonstrate ferro-, pyro- and piezo-electricity. These nanotubes mimic the structure of β-amyloid fibrils, which are known biomarkers of the onset of Alzheimer's disease. Collective response of water dipoles to an external electric field rendered high pyro- and piezo-electric activity and nonlinear optical effects in these peptides.

Interestingly, the permittivity of free water can drop by nearly 20–30 times when water is bound or loosely bound in the surroundings of a biological building block. Measuring ferroelectricity, or, for that matter, piezo- and pyro-electricity using conventional electrodes, is not straight forward. If the measurement is made at room temperature, or in ambient conditions, water evaporation could become an additional complexity. Perhaps one may need to accept water as a fact of "life" and expect that it would interfere with measurement. Unlike classical measurements of ferro-, pyro- and piezo-electricity in conventional polar dielectrics such as barium sodium niobate (banana) where presence of water would be seen as a great nuisance, we must expect water to play a role in biological systems. The trick in separating "the wheat" from "the chaff", perhaps, lies in not avoiding water but in knowing what water can do to the electrical measurement in question.

3. Lossy Dielectric versus Ferroelectricity in Biological Structures

Paradoxically, most of the molecular building blocks that make up banana peels have crystalline or partially crystalline structures that lack an inversion symmetry and should be piezoelectric. Piezoelectricity is the pre-requisite of ferroelectricity. Biopolymers such as carbohydrates, cellulose, proteins have been demonstrated to be piezoelectric. Water in the form of ice structure is also piezoelectric. Even fat molecules can form noncentrosymmetric crystal structures. Some of these building blocks have also been found to be pyroelectric.

It is still possible that the organization of these building blocks can be isotropic so that a banana peel, as-a-whole, may not be ferroelectric. In ferroelectric ceramics, individual building blocks are piezo- and pyro-electric but the aggregate is isotropic and hence shows no macroscopic piezo- or pyro-electricity. However, such isotropic aggregate can be electrically "poled" to render ferroelectric nature to the macroscopic body. Textured ceramics are shown to be ferroelectric and, by extension, piezo- and pyro-electric, as they retain the anisotropy.

A cursory look at the banana peel will reveal its fibrous texture, so macroscopically it should be anisotropic. Regardless of whether its building blocks are ferroelectric or not, what really matters here is how to they exist in a complex system with hierarchical structure. The building blocks could well aggregate into a heterogeneous ferroelectret that displays ferroelectric behavior despite the building blocks not being ferroelectric themselves.

In his experiment, Scott took a small section of banana skin and electroded using silver paste.[1] We can safely assume that the peel section contained water, which would significantly cause leakage current to result in a *P–E* loop that resembles a lossy dielectric. We too have observed charge leakage in macroscopic measurements of ferroelectricity in nanocrystalline hydroxyapatite deposited on *n*-type silicon wafer.[11] The leakage charge was much smaller, and a true ferroelectric nature of the hysteresis was found when we used a much smaller, nanoscale probe in a piezo-force microscopy (PFM) set up. Similar results were obtained from glycine and peptide crystals when PFM was used as an experimental technique for ferroelectric measurements.

Scott is however correct in stating that the cigar-shaped *P–E* loop should not be seen as a proof of ferroelectricity. The pre-requisite of ferroelectricity is that the material must be both pyro- and piezo-electric. All ferroelectric materials are pyro- and piezo-electric, but the reverse is not true. If the symmetry does not allow pyroelectricity, true ferroelectricity should not be expected as only a subset of pyroelectric materials is actually ferroelectric. This means that the cigar-shaped *P–E* loop reported by Lemanov and his colleagues[12] does not necessarily preclude ferroelectric switching in pressed powder of DNA as long as DNA showed piezo- and pyro-electricity and the ability to be poled.

The ability to "pole" a piezo/pyro-electric material has long been taken to be an additional test of ferroelectric nature, especially, of composites and aggregates. Electrically poled materials can also be electrets[1] and show ferro-, pyro- and piezo-electricity. The true ferroelectric nature will depend on the symmetry, poling and switching of polarization. In this way, the *P–E* loop tracing should be applied only if the biological material in question has shown piezo- and pyro-electricity.

4. Pyroelectricity in Biological Building Blocks

The study of pyroelectricity in biological building blocks has been remarkably rare. The dual ability of PFM in carrying out both converse piezoelectricity measurement and *P–E* loop tracing is a convenience, which has triggered studies in piezo- and ferro-electricity in biological materials. This convenience is not as easily shared in scanning probe measurements of polarization as a function of temperature. It is not, however, impossible to investigate pyroelectricity in biological building blocks using scanning probe measurements and other techniques.

Table 1 lists pyroelectric figures of merits of a few biological materials. Figure 2 shows a comparison of figures of merits such as maximum voltage output, F_v = pyroelectric coefficient/(specific heat capacity × permittivity of the material) and maximum power output, F_W = pyroelectric coefficient^2/(specific heat capacity^2 × permittivity of the material). We can notice that lysozyme can generate a few orders of magnitude of higher voltage and power when compared to

Table 1. Pyroelectric constants of materials. Data from various sources.

	Pyroelectric coefficient (μC/m^{2}K)	Specific heat capacity (×10^6 J/m^{3}K)	Dielectric constant
Ceramics	3000	3	1000–10,000
Polymers	25	2.8	10–15
Triglycine sulfate	1000	2.6	7
Collagen	0.004	2	3
Peptide nanotubes	2	2.5	3
Glycine	20	2	2.5
Bone	0.003	0.88	7
Hydroxyapatite	400	5	12
Lysozyme	1400	2	2

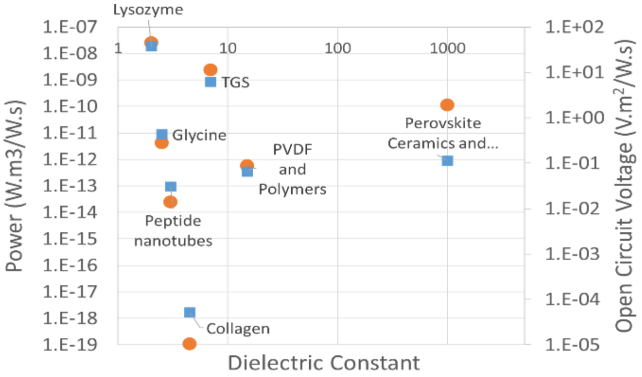

Fig. 2. Pyroelectric energy conversion figures of merits for various materials: open circuit voltage (squares) and power output (circles). Data plotted are based on those in Table 1.

ceramics. However, the stability of lysozyme will need to be addressed before any technical applications.

Another important aspect of piezo-, pyro- and ferro-electric nature of biological building blocks such as proteins is that the assigned symmetry in protein data bank (PDB) or crystallography database can suggest a chiral symmetry (allowing only piezoelectricity and antiferroelectric polarization). Such materials may change crystal symmetry when handling real-life conditions. This has been observed in lysozyme which changed symmetry from a chiral to a polar class, and exhibited pyroelectricity[8] and ferroelectricity.[13]

Pyroelectricity in biological materials is significant as it establishes the presence of spontaneous polarization in biomolecular aggregates in various hierarchical forms. On the other hand, the presence of a spontaneous polarization makes them a candidate for showing switchable polarization, i.e., ferroelectricity.

This can have significance on both biological processes and technical applications. For example, pyroelectric energy generators made of conventional lead-zirconate-titanate (PZT) ceramic films (pyroelectric coefficient 800 μC/m^{2}K) generated 15–22 volts, drove a liquid crystal display for over 60 s and charged a lithium–ion battery to light a light emitting diode.[14] Appropriate engineering of pyroelectric biologicals can replace toxic lead from many such applications.

5. Physiological Significance

A number of pyroelectric biological materials and building blocks have already shown ferroelectric behavior. Physiological roles of ferro-, pyro- and piezo-electricity have widely been speculated in the literature ever since piezoelectricity in bone was discovered. In 1988, Leuchtag proposed a ferroelectric channel unit within the glycoprotein sodium (Na) channel to be in a ferroelectric state in a membrane at resting potential.[15]

Electrophysiological experiments combined with molecular biology approach have won the Nobel Prize in Medicine of 2021.[16] The work revealed data on pressure-sensing proteins Piezo 1 and Piezo 2, and heat sensitive TRPV1 and TRPM8 receptors. These membrane proteins should also exhibit piezoelectricity in line with the proton pump cytochrome C oxidase, which is a membrane protein. While the shear piezoelectricity dominated piezoelectricity in cytochrome C oxidase, a small longitudinal piezoelectricity has also been detected suggesting a lowering of symmetry that allows pyroelectricity.[5] This can potentially show ferroelectricity if the polarization is switchable.

In 1974, Mascarenhas argued that the piezoelectric potential was too low in comparison to other stress-generated potentials, e.g., streaming potential in physiological systems.[17] While stress-generated potentials are generally considered important for mechanotransduction in physiological systems, piezo-, pyro- and ferro-electricity of cellular building blocks are currently not considered significant. In nonexcitable cells residing in intervertebral discs, the magnitude of piezoelectricity has been found to be significant enough to activate voltage-gated ion channels.[18] This finding may have important implications for how "all-or-nothing"-type ion-selective gating actually occurs in intercellular transport.

Leuchtag cited experimental observations of current–voltage hysteresis, voltage-dependent birefringence, single-channel currents, "gating" currents, heat and cold block of excitability, electromechanical and thermoelectric responses, and nonlinear ion conduction to find quantitative agreement with the estimated magnitude of the surface charge of the channel assuming ferroelectric polarization.[13] Switching of electron beam poled domains in ferroelectric hydroxyapatite nanocrystalline film showed coulombic interactions with globular protein lysozyme.[19] The fact that a cell membrane works as a leaky capacitor gives little hope that a cigar-shaped *P*–*E* loop would be a compelling experimental evidence of ferroelectric polarization in the classical sense. Piezoelectric hysteresis studied on tetragonal lysozyme showed two different states: ferro/piezo-electric and nonferro-piezoelectric states.[13] Besides, a classical symmetrical ferroelectric *P*–*E* loop representing two thermodynamically equivalent equilibrium states may not be experienced in biological building blocks, which are zwitterionic and capable of hydrogen bonding. As a result, the polarization of the building blocks may prefer one direction of polarization with respect to the other.

6. Contribution of Professor Reimund Gerhard-Multhaupt and Conclusions

Learned societies and their leaderships are very important especially when current dogma and state of the art are challenged. Through his long-standing leadership in various capacities of the IEEE Dielectric and Electrical Insulation Society (DEIS) and International Symposium on Electrets (ISE), Professor Gerhard-Multhaupt encouraged understanding ferroelectricity, pyroelectricity and piezoelectricity in biological system in their classical sense. His paper on electrets with quasi-permanent charge or polarization facilitated understanding electret nature and charge injection. Professor Gerhardt has extended a huge help in understanding charge injection by corona discharge, which will facilitate technical use of ferroelectric biomaterials. Professor Gerhard-Multhaupt extended his technical assistance to build a corona poling set up for Professor Sidney Lang, Ben-Gurion University of the Negev during the realization of European Commission FP7 project BioElectricSurface, which was led by the author. Such assistance and support were critical in advancing the understanding of the phenomenology of ferroelectricity in biological materials.

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