

ELECTRETS

Permanent magnetic or electric fields are useful either for producing a mechanical movement from an electrical input or for generating an electrical response from a mechanical movement particularly in electromechanical sensor and actuator applications. The purpose of the permanent field is usually either a reduction in the magnitude of the input or an increase in the magnitude of the output. A familiar example is the enhancement of the magnetic forces in a loudspeaker or in an electric motor by a permanent magnet. Another magnetic example is the generation of a current signal from the relative movement between a permanent magnet and a coil in a dynamic microphone or in an electric generator. The underlying effect is usually called magnetic induction.

All these examples rely only on the interaction between the field and electric charges. Because magnetic fields and also electric fields interact with electric charges, the magnet producing a permanent magnetic field can be replaced, at least in principle, by a so-called electret which generates a permanent electric field. In the case of an electric field, the electric charge does not need to move to generate a field or to interact with it. Therefore, no current loops are required. If we want to miniaturize a device or reduce its complexity, the use of an electret instead of a magnet can be of great advantage. Electrets are now being employed in more and more device applications mainly for these reasons. For example, most of today's microphones are electret-condenser microphones with an electrically charged polymer-electret diaphragm or a backplate coated with a polymer electret.

HISTORICAL DEVELOPMENT AND CLASSIFICATION OF ELECTRETS

The term electret was introduced by Oliver Heaviside (1) in 1885 from a purely theoretical point of view. Analogous to the term magnet, that is, a material with permanent magnetization (oriented magnetic dipoles), Heaviside defined an electret as a material with intrinsic electrification. Because this intrinsic electrification is often more easily generated by charges than by dipoles, materials with permanently oriented electric dipoles, and also those with permanent electric excess charge are called electrets. The separation of the two possible microscopic sources can sometimes be very difficult from an experimental or a conceptual point of view.

The modern practical definition of an electret as any material with a (quasi-)permanent macroscopic electric field circumvents the difficulty that often not enough is known about the microscopic origin of the internal or external electric field. Coincidentally, the present practical definition is still basically the same as that of the electrophorus, or electrophore, first described by Johan Carl Wilcke in 1762. Before the invention of the electrochemical battery by Alessandro Volta in 1800, electrically charged insulators, such as the electrophorus, were extensively used by the natural philosophers of the eighteenth century to produce electric fields and their sometimes amusing and sometimes useful effects (2,3).

Dipole and Space-Charge Electrets

An electret is a special type of dielectric. As schematically shown in Fig. 1, it carries a (quasi)permanent excess charge, which requires that it be a very good insulator, and/or a

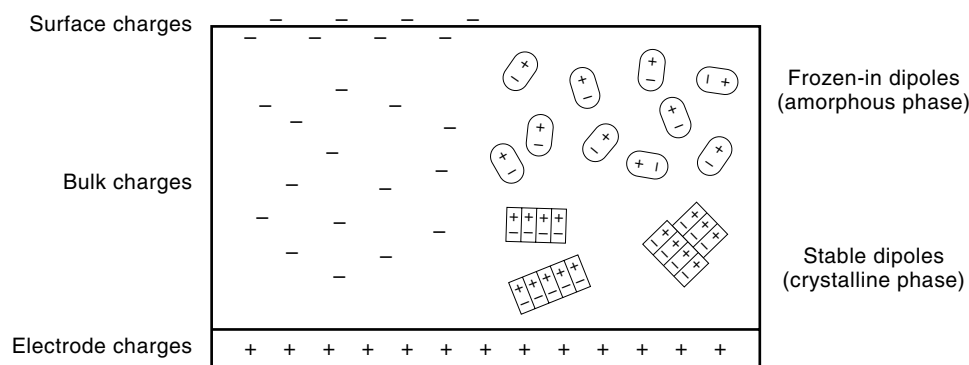


Figure 1. Schematic diagram of an electret with space charges (quasi)permanently trapped at its surface or in its bulk and/or with dipoles ordered in its crystalline phase or frozen in its amorphous phase and usually with a compensation (image) charge in its electrode(s).

(quasi)permanent preferential dipole orientation, which makes it a rather strong dielectric, that is, one with a rather high dielectric constant at high temperatures and/or low frequencies.

Whether a dipole electret is absolutely stable or only relatively stable (permanent or quasi-permanent, respectively), depends on the thermodynamic state of its material. The crystalline phase of a ferroelectric crystal, of a ceramic grain, or of a semicrystalline polymer is inherently stable at a given temperature, and so is its dielectric polarization (if there is one). On the other hand, the frozen-in dipole orientation of the amorphous phase in an inorganic glass or a glassy polymer is regarded as a supercooled liquid. The amorphous phase is in a quasi-steady state, but not in thermodynamic equilibrium, and therefore relaxes slowly (extremely slowly in a good electret around room temperature).

The stability of a space-charge electret, which contains excess charge instead of or in addition to oriented dipoles, often follows a similar rule, because the release of the excess charge is usually connected to the mobility of the atoms or molecules in the material. A more difficult case is the interfacial charge at the boundary between amorphous and crystalline regions, in, for example, semicrystalline polymer electrets. This interfacial charge, usually referred to as Maxwell–Wagner (interfacial) polarization, exhibits thermal and temporal stability that often lies somewhere between the two aforementioned situations.

Organic and Inorganic Electret Materials

More than two hundred and fifty years ago, the best electret materials were already natural substances with long chain molecules (so-called oligomers), such as resins and waxes. When Mototarô Eguchi revived the experimental research into the electrophorus (4) or electret (5) after World War I, organic materials, such as carnauba wax, were still the only available space-charge electrets of reasonable stability, and remained so during the first half of the twentieth century (6–8). With the advent of modern polymers, which usually consist of much longer macromolecules than those found in nature, it became possible to produce very stable thin-film polymer electrets for use in, for example, microphones, air filters, and ultrasonic and infrared devices (7–9). It also turned out that fluoropolymers, such as the various Teflon materials, yield the most stable charge-storing polymer electrets known to date with extrapolated lifetimes of hundreds of years (9).

The best materials for stable dipole orientation used to be inorganic crystals with piezo-, pyro-, or ferroelectric proper-

ties, such as quartz or barium titanate. Already known in China for a long time and again discovered by Jacques and Pierre Curie in 1880, monocrystals and polycrystalline ceramics of some naturally or artificially grown minerals became particularly important in developing underwater ultrasonics during the forties and fifties and laser-related electro-optics during the sixties and seventies. Inorganic ferroelectrics and inorganic dielectrics with permanent dipole polarization are sometimes also called electrets especially in the Russian tradition (10). It should be mentioned, however, that some authors (11) reserve the term electret exclusively for the thermodynamically nonpermanent quasi-steady state of waxes, resins, glassy polymers, and inorganic glasses.

The traditional division of electrets into inorganic piezo-, pyro-, or ferroelectrics and organic charge-storing materials had to be modified following two exciting developments. In 1969, after a long search for piezoelectricity in natural and synthetic polymers (12,13), Heiji Kawai discovered a strong piezoelectric effect in properly prepared polyvinylidene fluoride. This discovery was followed by the discovery of equally remarkable pyroelectricity in the same polymer by Bergman et al. at Bell Telephone Laboratories in 1971 [see Ref. (11)]. Around the same time, silicon dioxide emerged as an outstanding insulator for microelectronics and also as a very good charge-storing material (14,15). Since then, additional inorganic charge-storage materials, such as silicon nitride, silicon oxide/nitride double layers, and tantalum pentoxide, and polymeric piezo-, pyro-, and ferroelectrics, such as some copolymers of polyvinylidene fluoride, some odd-numbered polyamides, and some aromatic and aliphatic polyureas were identified. Consequently, now there are inorganic glasses and organic fluoropolymers, which are outstanding space-charge electrets, and semicrystalline polar polymers and inorganic crystals and ceramics which are important piezo-, pyro-, and ferroelectric electrets.

Bioelectrets: Biomaterials with Electret Properties

Today, the electret materials for industrial applications are usually synthetic polymers and artificially grown oxides, crystals, and ceramics. Recently, composites of inorganic crystalline particles and electrically passive or active matrix polymers also began to attract more and more interest (16). Nevertheless, the natural biopolymers and their electret properties have not been forgotten, because there are rather strong indications that charge storage and/or dipole orientation is important for some of the functions found in living species. The piezo- and pyroelectricity of various biomaterials, such as silk, wood, and bone, the triboelectricity (tendency to

accumulate electric charge during rubbing) found on hair and wool, and the effects of electric fields on bone growth or wound healing are among the bioelectret phenomena that have received attention for several decades (9,12).

In spite of quite a large number of electrical investigations into biomaterials (see (9,17–21)), it is still not clear how bioelectrets, which are usually studied *in vitro* and often even in a dry state, contribute to the life processes, *in vivo* and in a fluid environment. It is expected that the growing importance of the life sciences and the continuously improving understanding of molecular biology will also strengthen the research into and the application of bioelectrets. This exciting development would significantly benefit from increasing synergy between the various disciplines that contribute to electret science and technology (mainly physics, electrical engineering, chemistry, biology, and medicine).

Nonlinear Optical Polymer Electrets

In the early eighties, it was already recognized that dye molecules with strong nonlinear optical (NLO) properties could be incorporated into polymers which must in this case be purely amorphous so that scattering losses from crystallites are avoided. Major advantages of this approach are the choice of linear and nonlinear optical properties in already known and in newly synthesized chromophores and the ease and versatility of polymer processing. The NLO properties of the dye or chromophoric molecules originate from the strong interaction between the electric field of an optical wave and the delocalized electrons of a rather long molecule. Consequently, the strategy for obtaining a highly nonlinear optical dye is based on linking an electron-accepting group, such as the nitro group NO_2 to an electron-donating group, such as the amino group NH_2 , by a delocalized π -electron system originating from unsaturated bonds in aromatic (ringlike) and/or aliphatic (chainlike) structures (22–24). The main parameters for characterizing such an A- π -D dipole molecule are its hyperpolarizability tensor and its dipole moment. The product of the main hyperpolarizability component and the (usually parallel) dipole moment is a figure of merit for a molecule's NLO performance. The relevant molecular parameters are typically measured in solution, not in the polymer matrix.

If the dye molecules are randomly distributed (and randomly oriented) in a polymer matrix, there will be no macroscopic NLO effect, because for every microscopic chromophoric dipole, we find another with the opposite orientation so that their respective contributions cancel. A macroscopically centrosymmetrical material cannot exhibit tensor properties that require a polar axis, such as a linear electro-optic effect or other second-order optical nonlinearities. Therefore, preferential orientation of the chromophoric dipoles in the polymer matrix is necessary to arrive at a material with a well-defined polar symmetrical axis. This orientation is usually achieved by a poling process, the application of an electric field of suitable magnitude and direction to the dye-containing polymer. After poling, the orientation of the polar molecules has to be fixed by reducing the mobility of the chromophores as much as possible. The resulting quasi-permanent orientation of the dye molecules makes the polymer a molecular-dipole electret, and the techniques available for preparing and characterizing dipole electrets may be used on these nonlinear optical polymer electrets (14,19–21,25).

Several strategies have been proposed for stabilizing the orientation of the chromophore dipoles within the amorphous polymer (23–26). If the dye molecules are simply doped into the glassy polymer matrix (guest-host polymer), the polymer should have a rather high glass transition temperature so that the mobility of its macromolecules at room temperature is small and the oriented chromophore molecules are thus also restricted in their relaxation. Because the dye molecules have to be oriented during poling in the vicinity of the glass-transition temperature, however, the choice is limited by the temperature at which the chromophoric molecules begin to disintegrate. A further reduction in the chromophore-dipole relaxation rate is achieved by chemical, thermal, or radiation-induced crosslinking of the polymer matrix. Because the cross-linking often already proceeds during poling, there is competition between chromophore-dipole orientation and immobilization, which restricts the efficiency of poling. The chromophoric group can also be chemically attached to the polymer main chain via a more or less flexible spacer unit (side-chain polymer) or chemically incorporated into the polymer molecule itself (main-chain polymer). In these cases, cross-linking around or along the chromophoric units is also possible, but a suitable compromise must always be found between ease of poling and stability of the poled electret.

MANUFACTURE OF ELECTRETS: CHARGING AND POLING TECHNIQUES

Apart from single-crystal ferroelectrics with the correct polar axis, all other electrets need to be prepared by charging (separation or injection of charge carriers) or poling (orientation or reorientation of dipoles). Because both processes usually involve the application of temporary or permanent electrodes and of high electric fields and also because space-charge layers may serve as virtual electrodes to orient dipoles, charging and poling cannot always be clearly distinguished. Therefore, poling is sometimes employed as the comprehensive term for both concurrent processes. In addition to an electric field, charging and/or poling requires mobility of the charge carriers and/or dipoles, respectively. Consequently, the available charging and poling methods are usually classified according to the mechanism for achieving mobility onto, into, or inside the electret-to-be. Quite often, the resulting electrets are also named after their charging or poling technique. Thermal poling leads to thermoelectrets, and radiation charging yields radioelectrets.

The twelve charging and poling techniques (9,25) listed in Table 1 can be divided into two groups of six methods each. In the first six methods, metal electrodes provide the electric field necessary for injecting charges from the electrodes (same polarity, i.e., homo-charge) or for separating preexisting charges and for orienting molecular dipoles between the electrodes (opposite polarity, i.e., hetero-charge) (7). Figure 2 illustrates the definitions of homo- and hetero-charge in an electret. At the same time, charge and/or dipole motion in the material is facilitated by external heating, light-induced local heating, pressure-induced free-volume increase, light- or radiation-induced excitation or ionization, or very high electric fields (often leading to a controlled breakdown). In the second group, we find methods for bringing charges onto or into the electret sample by a contacting or rubbing material, an elec-

Table 1. Charging and Poling Technique for Electrets

Charging or Poling Method	Electric Field Applied with	Mobility of Charges and/or Dipoles from	Special Features and Possible Advantages
Thermal	Two metal electrodes	External heating to suitable temperature	Standard technique for glassy materials
Photothermal	Usually electrodes	Local heating with light	Optically defined 3-D patterns
Gas-assisted	Usually electrodes	Internal gas pressure	Seldom used (not simple)
Photo-induced	Usually electrodes	Optical excitation of molecules or atoms	Optically defined 3-D patterns
Radiation induced	Usually electrodes	Ionization with radiation	Radiation-induced conductivity
High-field (breakdown)	Electrodes (+dielectric)	Electric field (no heating)	Current limiter often required
Contact (friction)	Differences in work function	Local tunneling (+friction heating)	Purely mechanical procedure
Liquid contact	Polar liquid (+surface charge)	Field across liquid (sometimes +heating of sample)	Writing of patterns
Corona discharge	Corona point/control grid (+surface charge)	Corona field (sometimes +heating)	Works also with imperfect samples
Plasma	External bias or self-biasing	Plasma field (+heating)	Arbitrary surface shapes/large areas
Electron beam	Charge carriers (virtual electrode formed by charge layer)	Irradiation (+heating)	Selective across film thickness
All-optical	Electromagnetic (optical) wave	Optical excitation of molecules	Orientation of nonpolar molecules

trically biased liquid in the form of a free layer, a droplet held in a felt or cotton pad, a corona discharge in air or in another gas (27), a microwave or radio-frequency plasma, a usually monoenergetic electron beam, or the electric field of an optical wave. Because charge layers generate an electric field with which dipoles or other charges may interact, these charge-injection and charge-separation methods are often also useful for orienting dipoles. Even octupolar molecules without any dipole moment can be oriented by the technique listed last (23,24).

If the material has been softened during charging or poling by means of heat, radiation, or internal pressure, rehardening under the applied electric field is mandatory to stabilize the electret before use. In the case of thermal charging or poling, this freezing procedure is carried out by cooling under a field. Sometimes, an additional physical aging process (annealing with or without field) is employed to obtain the most stable electret possible. The details of this process depend mainly on the material's internal morphology. For some applications, patterned charging or poling in the plane of an electret or selective charging or poling across its thickness is required. Lithographically patterned electrodes, scanned photothermal or photo-induced poling, scanned liquid contacts, and electron

beams are employed to produce in-plane patterns. Absorption-controlled, photo-induced poling and energy-dependent electron-beam charging are used for poling only part of the electret thickness and for depositing space-charge layers into it. In addition, multilayer samples with differing charging or poling characteristics and combinations or sequences of the techniques described may be utilized to generate electrets with nonuniform electroactive properties, such as multimorphic ultrasound transducers or waveguide devices (9,25).

MATERIALS SCIENCE OF ELECTRETS

Although electrets (or electrophores) have been investigated for approximately four centuries (2,3), the microscopic mechanisms of charge storage and dipole orientation are still not completely clear. This is particularly true for the amorphous-phase electrets, such as inorganic glasses and glassy polymers, and for the interfacial effects near electrodes and at internal phase boundaries. Here, one of the main dilemmas stems from the small relative amount of charge or dipole orientation necessary to achieve easily detectable or useful electret properties. For example, space-charge number densities

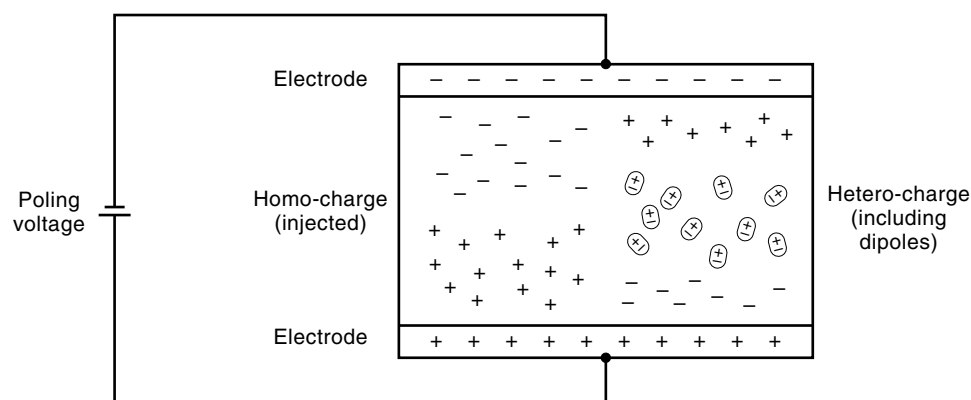


Figure 2. Homo-charge is injected into the electret from the electrodes during poling, whereas hetero-charge is separated in the electret by means of the applied field and may also consist of induced or oriented dipoles.

of 10^{15} cm^{-3} are considered very high, even though they correspond to only one excess charge per $(0.1 \text{ }\mu\text{m})^3$, that is, one charge per cube of 100 nm on each side. Contamination below the detection threshold of standard chemical analysis can quite easily reach similar densities. Nevertheless, macroscopic continuum models with localized states or local environments can be used to explain most of the relevant electret properties. This approach, however, is usually insufficient for the molecular design of new electret materials. Further research on disordered solids, molecular liquids, internal interfaces, and supramolecular environments, is required before a fuller understanding of electrets on a molecular scale becomes possible.

Material Structure and Charge Retention

Charge retention in purely amorphous or in semicrystalline electrets, such as silicon dioxide and polymethylmethacrylate or polytetrafluoroethylene, is usually described in terms of charge traps, localized states that hold excess charges for extended periods of time. The trap concept, borrowed from semiconductor physics, allows a description of trapping kinetics by rate equations and trap energies and an explanation of charge transport in insulators by trap-modulated mobility (9). Traps are usually characterized by their energy distribution and number density. Both quantities can so far be determined only indirectly from charging and discharging experiments and charge-density measurements. Charge traps have been tentatively identified with free volume, with ionic or other impurities, with crystalline-amorphous interfaces, with kinks of macromolecular chains, with chemical modifications, and with other physicochemical phenomena. Consequently, the processing of electret materials before and during charging or poling very strongly influences their electret properties (9,15). Detrapping of charges may be caused by thermal activation, high-energy photons, electron or other particle radiation, and water or other solvent molecules. All of these conductive mechanisms give some, but not a conclusive indication of the nature of the respective trap (9,28,29).

At the surface, charge trapping is strongly influenced by the surface conditions which may be described in terms of surface energy and contact angle. At least for silicon dioxide, hydrophobicity of the surface, achieved by a suitable chemical treatment, reduces surface conductivity and enhances charge stability considerably. A similar trapping mechanism may be at work on the surfaces of fluoropolymers which are usually hydrophobic to begin with (the familiar "Teflon" effect) and which up to now are the polymers with the best known charge retention, often corresponding to room-temperature electret lifetimes of centuries.

Charge-Dipole Interaction

Space charges interact with dipoles because they are sources (or sinks) of electric fields. In some polymer-electret materials, this charge-dipole interaction is significant for stabilizing the dipole orientation in the amorphous phase. Polyethylene terephthalate, polyvinyl chloride, and polyvinylidene fluoride are polymers in which such a stabilization has been discussed and probably gives rise to a detectable pyroelectric response of the oriented dipoles in the amorphous phase (9,30). It remains to be seen if the piezo- and pyroelectricity observed in

other amorphous polymers can be explained by a similar mechanism.

In several semicrystalline polymers, such as polyvinylidene and its copolymers with trifluoroethylene and with tetrafluoroethylene or some of the odd polyamides (Nylons), polar crystalline phases exhibit ferroelectricity which in turn leads to rather strong and useful piezo- and pyroelectric effects (11). The "hard" ferroelectricity of these polymers manifested by large-area dielectric hysteresis is also attributed to charge-dipole interaction because charges trapped at the crystalline-amorphous interfaces stabilize the crystalline polarization. Therefore, a larger coercive field is necessary to reverse the dipole polarization, and also to remove the trapped interfacial charges of one polarity and to move charges of opposite polarity to the interfacial traps (31,32).

CHARACTERIZATION AND PROPERTIES OF ELECTRETS

The mechanical and electrical properties of all electret materials change with temperature and pressure. In polymer electrets, the resulting effects can be particularly strong. The respective responses of an electret to temperature or pressure variations are utilized not only for device applications (see below) but also for the nondestructive or destructive characterization of electret properties and for the assessment of electret behavior under various conditions.

Effects of Temperature: Thermal Stimulation, Thermal Expansion, Pyroelectricity

A major, but usually unwanted effect of temperature on an electret is the reduction or even destruction of its space charge and/or dipole polarization. Charge detrapping, charge-carrier mobility, dipole mobility, and crystalline melting are all thermally activated processes which are strongly temperature-dependent. The resulting thermally stimulated discharge or depolarization (TSD) of electrets is a destructive technique for characterizing them (9). Depending on the particular situation, geometries with or without an air gap and circuits for measuring current or voltage are employed. Parameters, such as activation energies, detrapping or relaxation frequencies, and energy-distribution functions may be extracted from the experimental discharge or depolarization curves if additional assumptions are made. Similar and sometimes more detailed information may also be obtained from dielectric measurements at suitable frequencies and temperatures, but TSD experiments are usually faster and simpler.

Because the composition and the morphology, the mechanisms of charge retention and dipole orientation, and the spatial distribution of space charge and dipole polarization in a sample are often not known well or at all, the interpretation of TSD results is frequently rather arbitrary. For this and other reasons, the TSD techniques are now more often combined with other experiments, such as measurements of electric field or charge and polarization profiles (9,33,34). If the dynamics of a discharge or depolarization process are of interest, isothermal measurements at suitable elevated temperatures are very useful (25,32,34).

If an electret is subjected to only very small temperature changes, its space charge or dipole polarization is usually not reduced. Instead, a reversible pyroelectric effect can be detected if the electret contains oriented dipoles or if the tem-

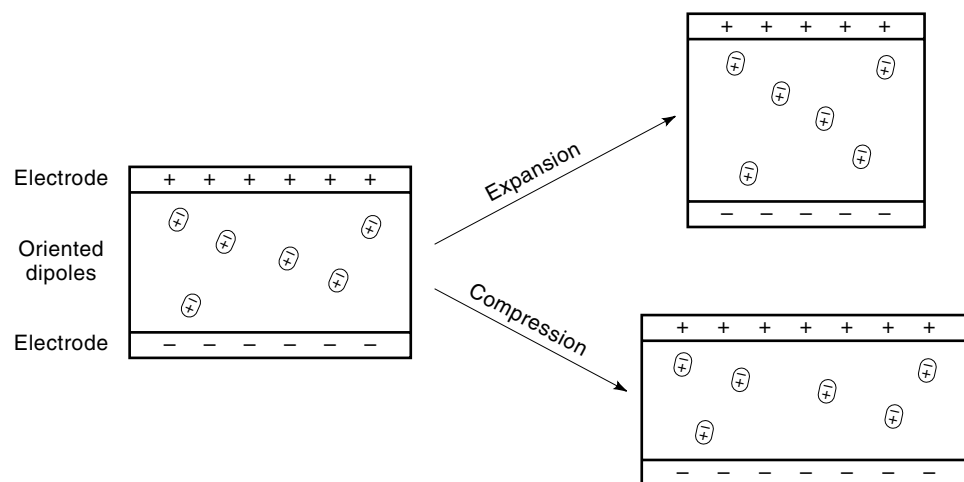


Figure 3. Because of the material's softness, piezo- and pyroelectricity in polymer electrets is often mainly a dipole-density effect, i.e., the compression or expansion of the polymer material leads to an increase or decrease, respectively, of the number of dipoles per volume and thus of the overall dipole polarization.

perature change is spatially nonuniform on the timescale of the experiment. In polar polymers, pyroelectricity is often mainly a thermal-expansion effect, that is, the density of oriented dipoles changes with temperature as schematically shown in Fig. 3. In all electrets, a spatially nonuniform time-dependent thermal expansion can be employed for probing the spatial distribution of the electric displacement or the apparent pyroelectricity between the sample electrodes (33,34). Depending on the temporal shape of the thermal excitation, there are thermal-pulse, thermal-step, and thermal-wave methods. The required timescale of a thermal probing experiment is related to the sample thickness and the desired spatial resolution. Because the nonuniform heating of an electret sample is a diffusion-controlled process, the spatial resolution decreases with distance from the heat source, and the evaluation of the experimental data requires deconvolution. Nevertheless, because of their experimental simplicity and low cost, thermal probing methods are employed quite frequently for studying space-charge or dipole-polarization profiles in electrets (9,14,33,34).

Effects of Pressure: Piezostimulation, Compression/Rarefaction, Piezoelectricity

Instead of reducing free volume and mobility in a glassy material by temperature reduction to stabilize an electret, a pressure increase may be utilized to the same end. Then charge release and dipole relaxation may be monitored during subsequent gradual pressure reduction similar to the temperature increase in a TSD experiment. This so-called piezostimulated discharge or depolarization method is rarely used, probably because of the relative difficulties in providing the required high pressures reliably and safely (9). In contrast to the previously-mentioned (Table 1) gas-assisted poling in which the electret material is expanded by pressing very small gas molecules into it, the piezostimulated technique is based on larger gas molecules which provide only external pressure to the electret material and thus compress it.

For only small pressure changes, within the elastic limits of the electret material, a reversible piezoelectric effect is observed if the electret contains oriented dipoles or if the pressure distribution is spatially nonuniform on the timescale of the experiment. Electrets with a piezoelectric effect of useful magnitude are usually also ferroelectric, that is, their dipole

polarization is thermodynamically stable and related to crystalline order (11,13,16,35). A piezoelectric effect is found, however, on any electret with oriented dipoles. In semicrystalline and amorphous electret materials, piezoelectricity is often mainly a dimensional (geometric) effect caused by a pressure-dependent change of the density of the oriented dipoles within the quite easily compressed amorphous phase (9,33) as illustrated in Fig. 3.

Because they are described by second derivatives of thermodynamic potentials such as the free energy or the free enthalpy, both pyro- and piezoelectricity must have a reverse companion effect, that is, an electrical excitation should lead to a change in temperature or entropy and to a change in mechanical stress or strain. Both the electrocaloric effect and the inverse piezoelectricity can indeed be observed, but only the inverse (or converse) piezoelectric effect is of sufficient magnitude for useful applications in transducers and actuators (11,32,35,36).

In contrast to a thermal expansion which moves through a sample because of thermal diffusion, a pressure disturbance constitutes an acoustical wave and thus propagates with the speed of sound. A propagating, spatially nonuniform compression or rarefaction can be used to probe the spatial distribution of the electric displacement or the apparent piezoelectricity between the sample electrodes (9,14,32,33). Depending on the shape of the pressure wave, there are pressure-pulse and pressure-step methods. Their short-circuit current signals are direct representations of the effective-charge distribution and of the electric-displacement profile, respectively. In comparison to the thermal probing techniques, the acoustical probing methods have the disadvantage of requiring much faster electronics and a more elaborate experimental setup but the advantage of yielding direct images of the measured distributions because of the linearity of the pressure-wave propagation. Sufficiently strong pressure pulses or steps are generated by shock tubes, high-voltage sparks, lasers, or piezoelectric plates (14). Only the last two mechanisms are still in use today (30). In a reversed electroacoustical technique, the space-charge or dipole-polarization distribution in a sample is used to launch an acoustic wave which is detected by a piezoelectric detector and whose shape directly corresponds to the distribution of interest (37). The latter method, which requires application of a strong electric pulse, has been used mainly on high-voltage insulation, not on electrets.

Effects of Radiation: Conductivity, Charging/Discharging

Ionizing radiation produces electron-hole pairs in all materials. In electrets, these electron-hole pairs provide mobile charge carriers for so-called radiation-induced conductivity. At higher photon energies, the Compton effect leads to an additional electron current. An additional electron current, the beam current, is also present in direct irradiation with electrons or other negatively charged particles. Furthermore, radiation may generate, destroy, or modify trapping sites in electret materials. All of these effects are employed to charge or to discharge electrets and to analyze their charge-storage and charge-transport behavior (9,38). Because the electric field of radiation-generated space charges interacts with the dipoles of a polar electret material, radiation charging can also be employed for dipole orientation. Electron-beam poling of piezoelectric and of nonlinear optical polymer electrets has been demonstrated (9,25).

ELECTRET APPLICATIONS

A few major electret applications are listed in Table 2. The twelve examples in the list were selected for their economic importance or because they are typical for the respective class of electrets. They are grouped according to the electret property used: charge retention (external electric field), piezoelectricity, pyroelectricity, optical nonlinearity, and external field from whatever source. Within the first two groups, the examples are given in order of importance. Apart from the listed applications which are all in industrial use or development, there are many proposed applications at various stages of implementation, ranging from ideas and concepts via patents and laboratory setups to fully developed prototypes and commercial devices (15,25,32–36). The interested reader is referred to this review literature and to the original publications cited therein for further details. Recent advances can be found in relevant conference proceedings (20,21).

Electret Transducers

Three electromechanical transduction principles are used with electrets:

1. Relative movement of an electret with a free surface and an electrode can be detected because of the voltage change across the gap between them. On the other hand, relative movement can also be generated by current- or voltage-induced electric-field variations. This principle, which works best with space-charge electrets providing large external fields, is employed mainly in electret-condensor microphones, in push-pull earphones and loudspeakers, and in microrelay switches. The basic configuration of a polymer-electret condensor microphone is shown in Fig. 4. Recently, silicon dioxide and other inorganic electrets incorporated into microelectromechanical devices more often replace polymer-electret films in mechanical setups at least for microphone and microrelay applications (9,15). Parallel instead of perpendicular movement between electret and electrode is exploited in electret slit-effect devices (9,14).
2. Direct and inverse piezoelectricity in the thickness or length-extension mode of an electret is frequently employed in such piezoelectric devices as ultrasound transmitters and detectors for underwater sound and also to some extent in microphones, headphones, and loudspeakers for audible sound. The possibility of applying polymer electrets as coatings or films allows for various transducer shapes that are useful in point hydrophones, focusing ultrasonic transducers, integrated multielement piezoelectric sensors, and ultrasonic cameras. Very thin piezoelectric films can be employed to generate and detect very high ultrasound frequencies up to several GHz. Important ultrasonic-transducer electret applications are also found in medical diagnostics and in the calibration of medical equipment (9,14,32,35,36).

Table 2. Selected Major Electret Applications

Electret Application	Required Property	Main Field(s) of Usage	Relative Advantages of Electret Use
Condensor microphone	High charge stability	Communications technology	Low cost, simple design, vibration insensitivity
Air and gas filter	Bipolar charging	Health and environment	Combination of mechanical and electrical filtering
Radiation dosimeter	Good reproducibility	Radiation protection	Low cost, simple design, continuous usage
Headphone, loudspeaker	High charge stability	Consumer electronics	Good linearity, rather flat frequency response
Photovoltaic (solar) cell	High charge stability	Energy generation	Less charge recombination, thus higher efficiency
Microrelay switch	High charge stability	Electronics technology	Reduction of driving voltage and current
Ultrasonic hydrophone	Large piezoelectricity	Medical/underwater ultrasonics	Acoustic matching to water, variable shape, low mass
Piezoelectric headphone or loudspeaker	Large piezoelectricity	Consumer electronics	Large high-frequency output, optimized directivity
Piezoelectric bending transducer	Large piezoelectric bending effect	Electromechanics	Large mechanical displacement, low drive energy
Infrared sensor	Large pyroelectricity	Safety and environment	Small thermal mass, fast response, large arrays
Optical switch	Large optical nonlinearity	Photonics technology	Fast response, good phase matching, all-optical
Healing bandage	Large external electric field	Medical therapy	Enhancement of healing speed, ease of use

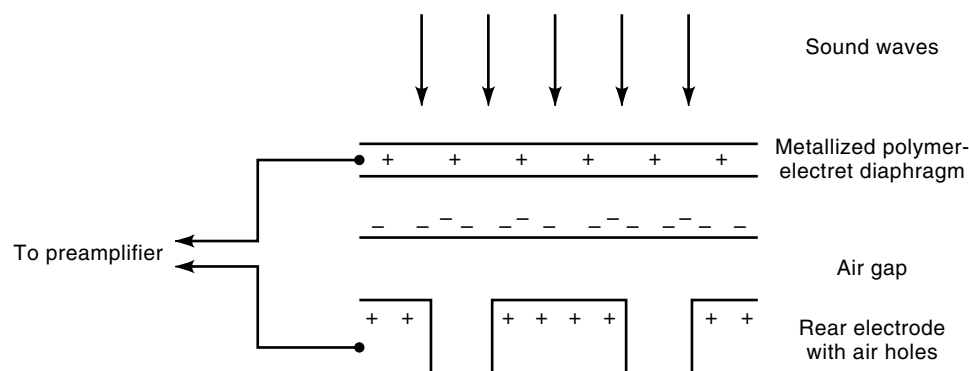


Figure 4. Schematic diagram of a classical electret-condenser microphone consisting of a metallized polymer-electret diaphragm held under slight tension over a metal backplate with holes that allow an air flow to the rear volume. The air gap is usually maintained by ridges on the rear electrode.

3. Monolithic or sandwiched monomorphs, bimorphs, etc. consist of at least two electret layers with opposite piezoelectric properties as illustrated in Fig. 5. Such elements can be used as bending devices for both electro-mechanical or mechano-electrical transduction, for example, in gas-flow sensors, nonrotating ventilators, and light shutters (9,35).

Pyroelectricity means the transduction of thermal energy from electromagnetic waves or other sources of heat into an electrical response. Pyroelectric electrets, made from the same materials and prepared in the same manner as piezoelectric electrets, are employed mainly in various types of infrared sensors for applications such as intruder alarms, driving control under fog, night vision, and energy conservation. Again, the flexibility and versatility of polymer electrets allows for advanced pyroelectric devices such as infrared arrays and cameras, focusing sensors, and microcalorimeters (33–36).

Biomedical Electrets

Because a continuously applied static electric field accelerates the healing of wounds and fractures, electret-coated bandages

and bone implants are considered useful biomedical applications and are already in practical use in several countries. Probably among the more important biomedical electret devices are the previously mentioned medical ultrasound transducers which now include catheter-tip array sensors and other imaging diagnostic tools for external or internal inspection (9,32). The same instruments may also be employed to inspect complex industrial equipment internally.

Other Applications: Air Filters, Radiation Dosimeters, Waveguide Devices

Air and gas filters are probably the electret application in which the most electret material is consumed and which earns the highest income. Such filters, now regularly found in vacuum-cleaner exhausts, air conditioners, and breathing masks, are easily manufactured from relatively inexpensive polymer electrets by a number of patented processes. They are often combined with purely mechanical filters which first eliminate the larger dust particles to increase the overall lifetime.

Radiation dosimeters do not operate primarily by radiation-induced discharge of the electret, but rather in accord

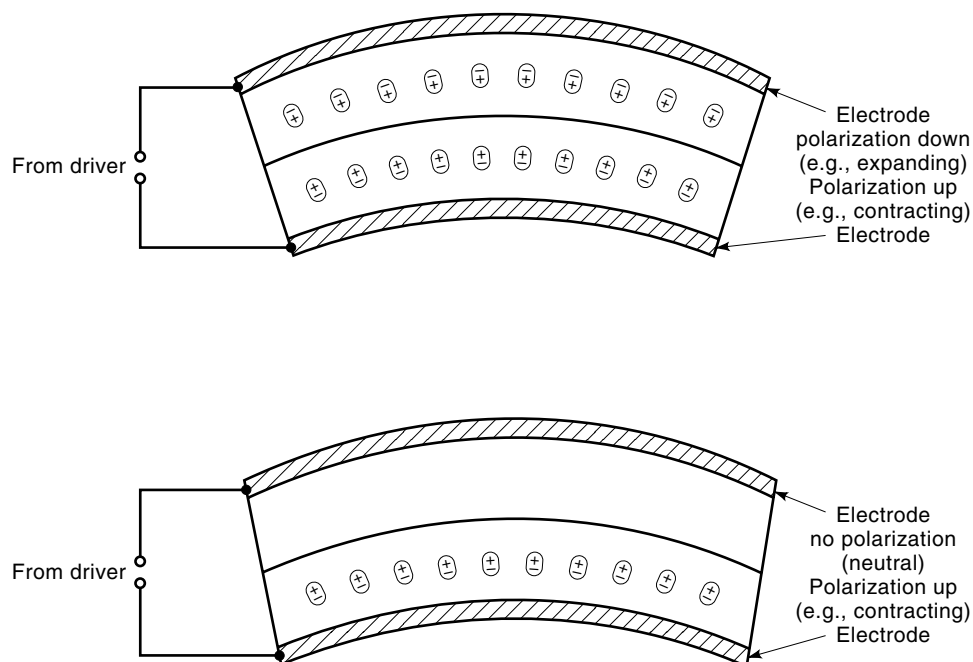


Figure 5. In a piezoelectric bimorph (top) or monomorph (bottom), the difference between the expansion or contraction of two layers with different piezoelectricity signs (one of which may be zero) leads to bending. Such double-layer arrangements consist either of two intimately bonded films or of one film with different polarizations in its upper and lower halves.

with the principle of an ionization chamber where the electret provides the bias field and the integrating device for the discharge-current spikes. Individual discharges in a suitable gas atmosphere are triggered by radiation and lead to a loss of electret charge that can be monitored by measuring the remaining surface potential of an otherwise very stable electret. Such a measurement can be made again and again so that one electret film can record the total dosage received over extended periods of time. Various absorbers, gas atmospheres, and ionization-chamber geometries may be used to tune the sensitivity of an electret dosimeter to a particular type or range of radiation.

Nonlinear optical polymer electrets have been proposed for a large variety of photonic devices including electro-optical modulators, switches, and couplers some of which are based on a waveguide interferometer. Possibly more exciting and more attractive are novel concepts for employing electrets with suitably patterned or layered dipole-orientation structures as phase-matched or quasi-phase-matched waveguide devices which permit rather efficient frequency-conversion processes. Apart from frequency doubling for second-harmonic generation and other previously known nonlinear optical effects, cascading of an up and a down conversion for an efficient all-optical switching device has been demonstrated with nonlinear optical polymer electrets. It remains to be seen if these exciting new electret materials will eventually be used in real-world applications (24,25,33).

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ELECTRETS, PHOTOCONDUCTIVE. See PHOTOELECTRETS.

ELECTRICAL AGING. See PARTIAL DISCHARGES.