Rapid communication

Large piezoelectric effects in charged, heterogeneous fluoropolymer electrets

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Abstract. Large piezoelectric $d_{33}$ coefficients around 600 pC/N are found in corona-charged non-uniform electrets consisting of elastically “soft” (microporous polytetrafluoroethylene PTFE) and “stiff” (perfluorinated cyclobutene PFCB) polymer layers. The piezoelectric activity of the two-layer fluoropolymer stack exceeds the $d_{33}$ coefficient of the ferroelectric ceramic lead zirconate titanate (PZT) by more than a factor of two and that of the ferroelectric polymer polyvinylidene fluoride (PVDF) by a factor of 20. Soft piezoelectric materials may become interesting for a large number of sensor and transducer applications, in areas such as security systems, medical diagnostics, and nondestructive testing.

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Piezoelectricity is the basis for a large number of sensor and transducer applications. Mass products emerge in security systems, medical diagnostics and nondestructive testing [1]. Basic science benefits from resonant ultrasound spectroscopy for the determination of acoustical properties of materials with sample masses of only a few µg [2]. Sensitive and low-cost piezoelectric materials are in high demand for these applications. In this rapid communication, very large piezoelectric coefficients are reported in charged heterogeneous electret films, surpassing all materials known so far. A heterogeneous two-layer electret stack, based on exceptionally stable fluoropolymer charge electrets is proposed and experimentally demonstrated. Preliminary results indicate not only very large, but also long-term stable piezoelectric effects, most promising for applications in sensor and transducer devices.

Piezoelectric material constants relate second-order symmetric tensors (stress T or strain S) to vectors (displacement D or electric field E). Since electric field and stress are independent variables easily to control experimentally, the most often used piezoelectric tensor is the third-rank d-tensor relating displacement D and stress T (direct piezoelectric effect) or strain S and electric field E (inverse piezoelectric effect) [3]:

$$d = \left( \frac{\partial D}{\partial T} \right)_E = \left( \frac{\partial S}{\partial E} \right)_T.$$

In piezoelectric sensors and thickness mode resonators, the $d_{33}$ coefficient is employed, 3 denotes the polar axis and the contracted notation is used. A necessary condition for the occurrence of piezoelectricity is the absence of a center of symmetry, piezoelectric materials are therefore intrinsically anisotropic. Large piezoelectric coefficients are usually found in ferroelectric crystals and polymers.

The most widely employed piezoelectric material, lead zirconate titanate (PZT), with a composition near the morphotropic phase boundary between the rhombohedral and tetragonal phase shows a $d_{33}$ coefficient of 220 pC/N [4]. Since the use of lead-containing materials is environmentally hazardous, the development of new piezoelectric materials is a matter of urgency. For a large number of applications, e.g. in medical ultrasound, low-density piezoelectric materials (such as polymers) are interesting, with an acoustic impedance matched to that of the human body. Unfortunately, the $d_{33}$ coefficient of 30 pC/N of ferroelectric polymers like polyvinylidene fluoride (PVDF) [5], a widely used inexpensive fluoropolymer, is only moderate in comparison to that of ceramics.

However, the basis of piezoelectric materials is broad and not limited to ferroelectrics: Piezoelectricity is observed in polar glasses, where symmetry can be broken by frozen orientation polarization [6]. In general, real charges do not contribute to the piezoelectric effect, as long as the sample is strained uniformly. Only when the material properties are nonuniform across the sample thickness, can trapped charges yield an electrical response that cannot be distinguished from a true piezoelectric signal [7]. Microscopically, this mechanism is not much different from “classical” piezoelectricity, e.g. in ceramics, with a nonuniform movement of ionic charges. Considerable interest in piezoelectric charge electrets appeared in the early seventies [8, 9], but interest faded since the coefficients found were too small for practical applications.
and “hard” polytetrafluoroethylene (PTFE) [18]. Piezoelectric $d_{33}$ coefficients comparable to PVDF were obtained, but the thermal stability of the effects was not at all satisfactory, probably because polyurethane and polypropylene are only moderate charge electrets. A large piezoelectric coefficient was estimated for highly corona charged fluoropolymer-propylene films, surprisingly for a single, “hard” polymer film [19]. A breakthrough with large piezoelectric coefficients and long-term stability may be expected by employing the best known charge electrets, like PTFE. PTFE electrets can be charged with very high charge densities and life times on the order of “centuries” at room temperature, especially for negative charging [6].

We have chosen polytetrafluoroethylene foils (Gore Tex, purchased from Goodfellow) for the “soft” electret, and perfluorinated cyclobutene (PFCB), a promising low-dielectric constant polymer (kindly provided by the Dow Chemical Company), for the “stiff” electret. Microporous PTFE [20, 21], as well as the network-forming PFCB [22] were shown to be outstanding charge electrets when charged as single layers, comparable or even superior to standard PTFE. A hybrid stack consisting of the two fluoropolymers was also found to exhibit excellent charge storage properties [21].

The “stiff” PFCB electret with a typical thickness of 10 µm is spin-coated onto a circular Al-substrate with a thickness of 2 mm and a radius of 14 mm. On the PFCB film, microporous PTFE foils are placed, with porosities of 50% (thickness of 85 µm) or 78% (thickness of 63 µm). Removal of the solvent and cross-linking of PFCB is performed at 200 °C for 6 h. After baking, the two layers are intimately connected, since part of the PFCB resin diffuses into the porous PTFE polymer. The heterogeneous nature of the structure is shown in the scanning electron micrographs of Fig. 2. The top surface (Fig. 2 left) reflects the fibrillar structure of the microporous PTFE, while the bottom surface is smooth (Fig. 2 right), as expected for the amorphous spin-on PFCB polymer.

The hybrid stack was negatively corona charged with a corona triode; the high voltage at the needle was $-7.5 \text{kV}$ and the grid voltage $-2.5 \text{kV}$. Corona charging was performed in air at 150 °C for typically 24 h. The long charging time at elevated temperature was found to be necessary in order to trap a significant amount of charge within the volume of the porous PTFE foil. The surface potential after corona charging was measured with an electrostatic voltmeter with field compensation. The surface potential after charging was typically $-1.6 \text{kV}$. Top electrodes were prepared by placing