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Fundamental electrical properties of ceramic electrets

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ABSTRACT

We used thermally stimulated depolarization current and potentiometer measurements to study the fundamental electrical properties, such as the surface potential, of polarized bioceramic hydroxyapatite. We demonstrate that, under certain conditions, the surface potential attributable to several overlapping electrets is given by the algebraic sum of the surface potentials of individual electrets. This can occur when the electrets are arranged in series and the components, found by resolving the polarization vector, determine the surface potential on the electrets. In addition, we prove that the surface potential is proportional to the surface charge density attributable to the electrets, and we further prove that the electrostatic shielding is caused by surrounding the electret with a conductor or a dielectric. Potentiometer measurements, obtained for different levels of shaved electret thickness, revealed that the electric field in the electret was not uniform and was stronger nearer the inner surface of the electret, as compared to the field in the bulk of the electret.

1. Introduction

An electret is defined as a material that has a quasi-permanent macroscopic electric field near its surface. This electric field can derive from a net orientation of polar groups in the material, or from a net macroscopic electrostatic charge on the material, and thus, an electret can be thought of as an equivalent of a magnet in magnetism. During the several decades since the invention of the mixture of carnauba wax, rosin, and beeswax, electrets have found an extensive use in a variety of applications, ranging from household filters and electric devices such as microphones to biotechnologies of membranes for protein separation [1,2]. Devices that build on electrets produce information signals by utilizing the interaction of the induced surface charge with the external working force. Because of their advantage in terms of mechanical flexibility and processing tractability, polymer electrets such as polyvinylidene fluoride (PVDF), polyamides, and Teflon of several types have been developed for acoustic, mechanical, and electric transducers [2–5]. Because polymers require high electric field of 10^6 V/cm, thin films are usually subjected to electric polarization. Alternatively, corona and plasma discharges are generally used for production of polymer electrets. Biological compounds also received considerable attention; proteins such as collagens are polarized to electrets because of proton displacement through molecules [6,7].

The term “electrets” was proposed over a century ago to describe a material that is the electrostatic equivalent of a magnet. However, in contrast to magnets, electrets have gained little attention as engineering materials. One reason is the limited availability of ceramic electrets, although conventional ceramic devices generally have superior mechanical properties, thermal stability, and various electric and physical functions. Few studies specifically examining ceramic electrets have been reported, and CaF_2 [8], $SrTiO_3$ [9], silica [10], and ferroelectric PZT [11] have been the subjects of these reports. Recent studies by researchers at Harvard and Princeton Universities have contributed to understanding of the nature of electrets, design and fabrication of new electret materials. The Princeton group studied liquid electrets [12,13] and the Harvard group studied ionic electrets [14]. They have presented experimental evidence and theoretical models for the formation of liquid and ionic electrets and discussed on possible applications of these electrets.

We found physically demonstrative and practically interesting characteristics of polarized hydroxyapatite (HAp) as ceramic electrets that have a structure similar to an electric double layer. We also indicated that the HAp crystal formation on polarized HAp substrates can either be accelerated or slowed, depending on the sign of electrets' surface charge, and that the grown HAp crystal has the *c*-axis orientation [15]. HAp is recognized as a quasi-one-dimensional protonic conductor, in which OH^- ions

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within the *c*-axis columns in the hydroxyapatite hexagonal structure play an important role in setting the ionic conduction properties [16]. HAp ceramic electrets are prepared at elevated temperature in the presence of an external electrical field. In the process, the ionic dipole moments become aligned in the direction of external electric field, due to the proton transport in the OH^- columnar structure [16–18]. These remarkable effects of surface electric fields due to HAp electrets have shown to have the significant effect on the crystallization of biomaterials *in vivo* and *in vitro* and on the manipulation of local biological reactions [19–25].

While investigating crystallization of biomaterial precipitated on electrets as growth substrates, we found that the electric fields attributable to HAp and yittria-stabilized zirconia electrets control the orientation of calcite crystals. We also observed that these electric fields influenced not only the nucleation of the deposit but also its subsequent growth [21,22,25]. In addition, we suggested that an electric field attributable to the electrets could be expected to have a stronger influence on crystallization as compared to the electric field produced by the localized surface charge on organic membranes. These results opened up a new strategy for crystal growth using electric fields due to electrets.

Aggressive investigations have been carried out in such areas as the crystal growth of biomaterials and the behavior of cells and microbes in the presence of limited surface electric fields produced by HAp electrets. However, as of now, a thorough explanation based on the electrical properties of HAp electrets has not been provided yet to account for the remarkable *in vivo* and *in vitro* effects of a local electric field produced by an electret.

Because the fundamental characteristics of electrets have never been presented for polymer and ceramic electrets, this report presents a detailed treatment that might help find new applications of ceramic electrets. In addition, this report provides the explanation on the remarkable effects with relevance to the electrostatics of electrets.

2. Materials and methods

2.1. Preparation and characterization of HAp substrates

HAp pellets were prepared according to a procedure described in a previous report [16,17]. The HAp powder was synthesized from analytical grade reagents of calcium hydroxide and phosphoric acid using a wet method. The powder was calcined at 800 °C for 3 h, and then pressed into a mold at 120 MPa. Dense HAp ceramic substrates of 10 mm diameter and 0.80 mm thickness were obtained by sintering the HAp pellets at 1250 °C for 2 h under a water vapor steam to avoid the dehydration of the lattice OH^- ions from the HAp structure. The HAp pellets were polarized using the following procedure. The HAp pellets were sandwiched between the two Pt electrodes and were polarized at 200, 300, and 400 °C for 1 h under an applied direct current electric field of 1, 5, and 10 kV/cm, respectively. To avoid the relaxation of polarization during the cooling process, the electrical field was maintained until the furnace cooled to a room temperature.

Analysis of the phase evolution of the HAp substrates conducted before and after the electrical polarization treatment was done using powder X-ray diffraction (XRD) measurements with Ni-filtered Cu Kα radiation, as well as Fourier transform infrared spectroscopic analyses (FTIR) performed at room temperature.

2.2. Measurements of the thermally stimulated depolarization current (TSDC)

The TSDC measurements are widely used to measure the polarization of electrets. The technique is based on the fact that an electret inserted between two electrodes generates electric current at higher temperature as the stored electricity comes out. Before the TSDC measurements were performed, short-circuiting sufficiently removed the remnant static charges from the surface. The surface charge density in the HAp electrets was estimated using TSDC measurements. The polarized HAp substrates were sandwiched between Pt electrodes. Then measurements were performed by monitoring the dissipation current density while the polarized specimens were heated in the air, at a rate of 5 °C/min, starting from room temperature and up to a temperature of 550 °C. The values of the surface charge density σ were calculated from the TSDC spectra using the equation $\sigma = 1/\beta \int J(T)\mathrm{d}T$, in which $J(T)$ is the dissipation current density measured at temperature T and β is the heating rate.

2.3. Measurements of surface potentials

The measurements of surface potentials due to electrets were conducted using a potentiometer with a vibrating circular electrode for which ϕ was either 0.65 or 10 mm. The electrets were placed between this vibrating circular electrode and a fixed counter electrode (Fig. 1a). We briefly review here the basics of this method that was first proposed by Reedy and Perlman [26]. The method is based on the knowledge of electric capacitance between a vibrating electrode and a fixed electrode. The capacitance is given in a simple equation, $C = \varepsilon A/d$, where C is the capacitance, ε is the electric permittivity of an electret, A is the area of the electrode, and d is the distance between the electrodes. As the circular electrode vibrates against the surface of a sample placed on a fixed electrode, the capacitance C changes accordingly, whereas ε and A are constant. Using the charge–capacitance relation, $Q = CV$, the changes in C can be reflected as the changes in the current flowing through a load resistor connected across the two electrodes. The amplitude of the AC voltage reflects the voltage V. In practice, a current-to-voltage circuit with a high resistance load resistor (100 MΩ) is used, and the amplified AC output is monitored using an oscilloscope. According to the capacitance equation, $C = \varepsilon A/d$, the capacitance C is inversely proportional to d. Practically, it is quite difficult to keep d constant. So, a bias method is usually employed. In this method, a bias voltage is applied to the fixed

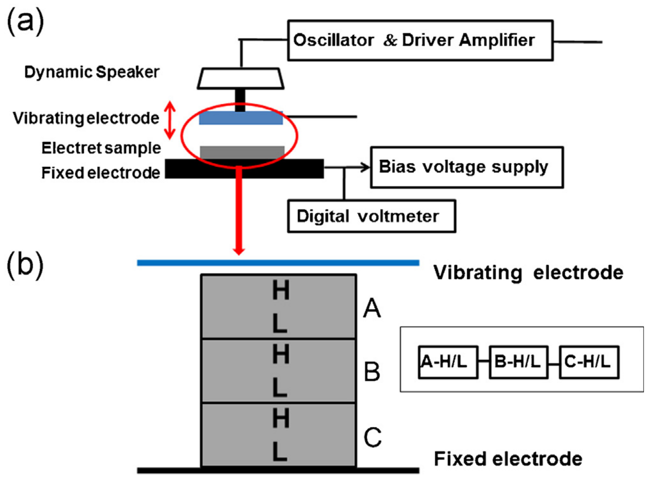

Fig. 1. (a) Schematic representation of a specific potentiometer. (b) Schematic representation of the measurements of the electric potentials attributable to three overlapping electrets, as described in Section 3.3. The inset shows the order of the three overlapping electrets drawn to the left. This schematic diagram is used in Fig. 5. In measurements obtained with the potentiometer, polarized surfaces with positive and negative surface potential were designated as the H-potential side and L-potential side, respectively. For the reference, the non-polarized surface obtained by heat treatment is designated as the 0-potential side.

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