Introduction to vector materials science and bioengineering†

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1. Introduction

Recently, we have proved that hydroxyapatite (HA) bioceramics and 45S5-type bioglasses (BG) are excellent electrets with an outstanding chemical and biological effects [2-7]. These electrets can be prepared by electrical polarization. Conventionally polarization has been applied mainly to ferroelectric or piezoelectric ceramics, in which spontaneous dipoles are predominantly arranged in a dc field of polarization. In our study of bioceramics and bioglasses, polarization has been proved to take place due to ionic displacement to a rather long range, where ion vacancies play important roles. Due to the electrical treatment, surfaces are electrically charged, depending on the direction of applied dc field. Based on the finding of remarkable effects of polarized electrets, vector effects [1] are employed as a concept exceeding bioactivity.

This report will firstly present the concept of vector effects, and then show the electroceramic properties of HA and BG with interesting electrical properties. Their biological effects will also be demonstrated in the solidification phenomena in a simulated body fluid (SBF).

2. Concept and Definition of Vector Effects and Materials

Under certain circumstance where a force is desired to act on a targeted spot in a quasi-closed system such as human body, an external magnetic, sonic or electric field is usually applied to the whole system. The application of an external field, however, needs a continuous power supply as well as working electrodes, and to make matters worse it actually arouses some secondary competitive reactions such as dissociation of water molecules. For such situation, independently workable substances such as magnets are expected to have great benefits, because they can bring effects only to a given local spot. Such materials are expected to have useful effects in some applications of environmental devices as well as biomedical ones. Contrasting with magnets, materials with electrostatic working forces have been called electrets. Electrets also have isolated working forces, however, they have not yet been acknowledged, still less practically employed. Some physical shortage of electrostatic force such as the effective range of influence in comparison with magnetic force might be attributed to the above situation, however, it is also pointed out that an important application of electrets has not yet been invented.

In a biological condition surrounded with water, typical electrolytic substance, local electrostatic influence is sometimes desirable. Living bodies consist of lots of ionic groups including proteins and cells. In such systems, the application of external fields is limited because of side effects. Polarized HA and BG have recently been proved as the members of vector materials.

The word "vector" is commonly used in mathematics and biology. The terminology of vector is originally defined as a noun; (1)(a) a quantity that has magnitude, direction, and sense, (b) a course or compass direction especially of an airplane, or (2) an organism that transmits a pathogen. The word is also to guide (as an airplane, its pilot, or a missile) in flight by means of a radioed vector. According to the usage, we define vector, vector materials, and vector effects for materials science as: Vector is to manipulate the constituents of a living body and environmental system such as non-alive substances of ions, proteins sugars, and alive cells and bacteria, tissues and organs by biocompatible or eco materials themselves. A vector material is a material which has an ability to vector. A vector effect is an effect which a vector material brings forth.

Ceramic magnets and electrets are therefore typical vector materials after the definition. A radioactive material is another candidate of vector material because they can individually irradiate a force on its surrounding. As mentioned below, radioactive ceramics incorporated in glass beads have been applied in medical applications for cancer therapy. These materials are classified as radioactive vector ceramics. Non-polarized 45S5-type bioglass and β-tricalcium phosphate are comparatively dissolved in a body and release chemical constituents or artificial chemicals, resulting in good bone conductivity. These materials fall to chemicovector materials. Scaffolds are a kind of biovector materials which can activate surrounding cells at a desired spot through biological substances incorporated in themselves.

Such effects are expected to bring about using various kinds of energies stored in a solid, and these materials are assigned to vector materials. The family of vectors ceramicsmay be classified on the basis of the mechanisms to drive the effects. Vector ceramics are divided into two categories according to the velocity of irradiated force to penetrate through bio-interface; the lines of magnetic and electric forces or β-ray instantly traverse the interfacial zone, while released ions by dissolution gradually diffuse

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from a surface to the zone. A combination of several vector effects may amplify an effect. A variety of functional materials are under development for other vector materials such as mechanovector or optovector materials.

3. Electrical Properties of Hydroxyapatite Ceramics

In addition to the unparalleled bioactivity, HA has important and interesting properties as an electroceramic. These biomedical and electrical properties of HA are largely attributed to its stable lattice hydroxide ions, surrounded with calcium ions in the crystal structure. Prior to the present study, the dielectric measurements were carried out for understanding of the bioactive characteristics of HA.

As a result, HA ceramics were proved to exhibit dielectric characteristics below ca. 800K. At higher temperatures, HA ceramics show an unusual phenomenon of time dependent conductivity. The measured impedance of HA specimen changed with time over a wide range between 10^7 and 10^4Scm^{-1}. The time-dependent-conductivity was strongly dependent upon the water of sintering ambience; the aging was characteristic of HA sintered under a steam stream, while HA sintered in air did not show aging behavior. Then, it was considered that the electrical properties of HA can depend upon the constituents of water molecules such as H^+, OH^-, O^{2-}. It was demonstrated from a concentration cell measurement of the electromotive force generated using a hydrogen concentration cell of HA ceramic that the mass transport takes place due to the migration of protons in HA. The recent studies by the thermally stimulated current method showed that HA ceramics were polarizable at a temperature higher than the monoclinic-to-hexagonal phase transition temperature (500K). In the early stage of the study, we assumed polarization might be due to the reorientation of the lattice OH- ions along the *c*-axis. However, the assumption was inappropriate, because the relaxation was observed to take place only due to polarization conditions. Relaxation or depolarization occurs only when the strain induced by electric stress is thermally released. A measured thermally stimulated depolarized current (TSDC) confirmed that HA is polarized like ferro- or piezo-electric ceramics. Using the I-T curve, we can evaluate the stored energy in HA.

BG is also a good ionic conductor with a conductivity of the order of 10^{-4}Scm^{-1}and an activation energy of 0.6eV. As BG contains a considerable amount of sodium ions in the silica networks, the charge carriers are considered as Na^+. BG is polarized between 350 and 800K. The TSDC curves gave the stored energies of 50-200 mCcm^{-2}. Based on the results, BG is regarded as a good electret.

4. Vector effect of polarized hydroxyapatite ceramics and bioglasses in SBF

Taking the polarizability into account, we conducted a study of the vector effect on the crystal growth on HA ceramics. We observed the remarkable phenomenon on crystal growth. Here it should be noticed that bone-like crystal growth in SBF is proposed by Kokubo and his colleagues as pre-examination of bioactovity, or *in vitro* bioactovity.

Wet-chemically synthesized HA powders were uniaxially pressed into pellets with a thickness=1mm and a diameter=1cm, then sintered at 1523K for 2h under a water vapor stream. The densities of the sintered pellets were 95% of the theoretical value. The HA structures of specimens were confirmed using crushed powders of the sintered specimens by X-ray diffraction (XRD) and infrared (IR) analyses.

Polarization of HA was carried out with dc 1kVcm^{-1} at 573K using Pt plates as electrodes. As vector effects were dependent upon the electric signs of surface charges, the polarized surfaces were named as N- and P-surfaces. Non-polarized surface was designated as 0-surface for reference. To confirm polarization and evaluate the stored charges in HA, a thermally stimulated current technique was employed, in which thermally dissipated current was measured at temperatures of room temperature to 1073K.

Although slow crystallization took place dispersedly on non-polarized HA, large crystals of 1-4μm in diameter covered the N-surface of polarized HA after an immersion in 1.5SBF for only 12h. Higher field strength gave rise to faster crystal growth; sizable agglomerated crystals of 10mm in diameter were observed in some spots on polarized HA under 1kVcm^{-1}. The accelerated crystal growth mentioned above was observed on the N-surface, whereas no crystal growth ever took place on the P-surface even after 3-day immersion in 1.5SBF. Although the polarization at 573K was effective for the acceleration of crystal growth, we also identified the acceleration effect by the polarization at 473K. The crystal growth was dependent upon the dc field strength, temperature and time for polarization.

Some experiments confirmed 1h-polarization enough for the optimum acceleration of crystal growth; under this condition the surfaces of HA were already coated with thick bone-like layers within 6-12h. Under an optimum polarization condition (actually 1.5SBF), the growth rate was estimated as 6μm/day, almost 3 times of the result obtained by the biomimetic method (1.7μm/day). The growth rate was increased to 10μm/day, as large as several times of that of non-polarized HA . At the early stage of the crystal growth, the grown crystals were spherical and their sizes were dependent on the field strength and time for polarization. The polarization is therefore considered to effect the nucleation as well as the crystal growth.

5. Conclusion

The electroceramic properties of biomedical materials have recently gained an increasing attention for nano-interface engineering, in which polarized bioceramics and bioglasses are centered. Based on the excellent biological performance of the polarized biomedical materials, the new concept of vector materials has been developed for nano-interface engineering.

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