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Bioactivated Nano-Space in the Vicinity of Polarized Hydroxyapatite Surface in SBF

Kimihiro Yamashita, Satoshi Nakamura,
Masashi Tanaka,* Toshinori Okura,* Hideki Monma*
Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University
2-3-10 Kanda-Surugadai, Chiyoda, Tokyo 101-0062, Tokyo, Japan
Fax: 81-35280-8016, e-mail: yama-k.bcr@tmd.ac.jp
*Department of Materials Science and Technology, Kogakuin University
2665 Nakanocyo, Hachioji, Tokyo 192-0015, Japan
*Fax: 81-42628-4626, e-mail: monma@cc.kogakuin.ac.jp

Abstract. An electret is a solid in which ions are displaced or dipole moments are aligned in a direction for a considerable period due to an external electric force. An electret can independently irradiate an electrostatic force to the surrounding constituents. Resultantly, a chemically and biologically active space formed in the vicinity of an electret. We have experimentally proved that hydroxyapatite (HA), the most biocompatible material, is an excellent electret. HA electrets are prepared by electrical polarization of ceramics. Using HA electrets, we have observed that crystal growth from a simulated body fluid can be accelerated or decelerated, and microorganism can be manipulated on the surfaces of HA, depending upon the electric signs.

Keywords: hydroxyapatite, bioactive nano-space, electrical poling, electret

I. INTRODUCTION

In addition to the excellent biocompatibility, hydroxyapatite ($Ca_5(PO4)_3OH$; HA) has valuable electric properties [1-3] in relation to biomedical applications: HA can be polarized under a dc field at an elevated temperature [4,5]. We have reported that electrically polarized HA enhanced bone conductivity [5-7]. This paper reports the chemical, physical and biological effects of the electrically polarized HA.

For the preliminary understanding, let us consider a quasi-closed system such as body, consisting of water, typical electrolytic substance, and lots of ionic groups including proteins and cells. Under such biological system, the application of external fields such as magnetic, sonic, or electric ones is limited because of side effects, hence local electrostatic influence is sometimes desirable for biomedical purpose (Fig. 1).

Electrostatic force compares to magnetic one with respect to a physical force, independently irradiated from a material to its surroundings without externally continuous power supply.

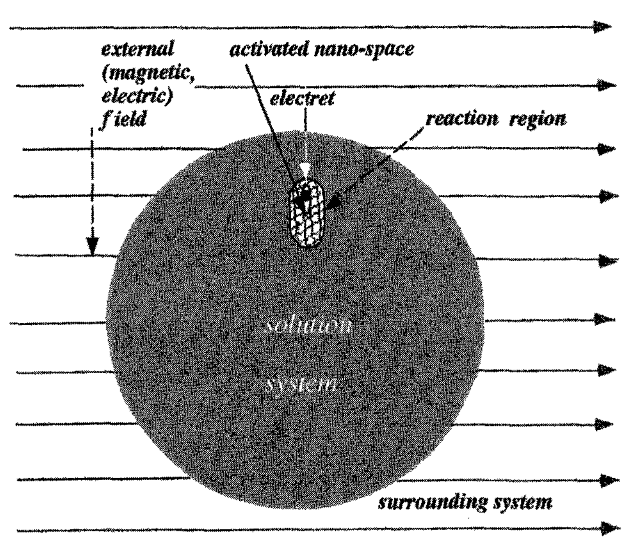

Fig. 1 Schematic living body system, where an electret and activated nano-space are shown in comparison with external fields.

Electrets also have isolated working force, 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 indicated that an important application of electrets has not yet been invented. Considering the effectiveness of HA electrets, we referred to such effects as electrovectorial effects. An HA electret activates a nano-space via electrostatic interactions in the vicinity of its surface (Fig. 2). Electrovectorial effects are considered to arise from an activated space (Fig. 1). It is briefly stressed here that a finding of electrovector materials is expected to a new way for the development of biomedical ametrials.

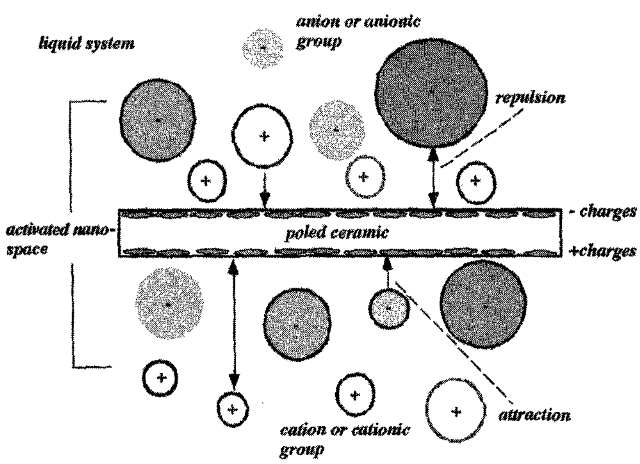

Fig. 2 Activated nano-space in the vicinity of and interactions of a poled electret with surrounding ions and ionic groups.

2. EXPERIMENTS

2.1 Electrical Polarization of HA

Protons can be transported with a dc electric force at an elevated temperature. As a result, polarization takes place in HA due to the proton movement [1,5]. Actual polarization of dense HA was carried out with dc 1kV/cm at several temperatures using Pt plates as electrodes. To confirm polarization and evaluate the accumulated charges in HA, a thermally stimulated current technique was employed, in which thermally dissipated current was measured at temperatures of room temperature to 800 ℃.

As surface characteristics of a polarized solid are expected to depend upon the electric signs of surface charges, the polarized surfaces are named as N- and P-surfaces (Fig. 3) for clarification. Non-polarized or usual surface is also designated as 0-surface for reference for convenience.

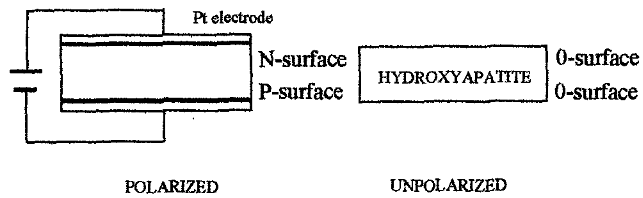

Fig. 3 Names of poled (N and P) and un-poled (0) surfaces.

2.2 SBF assessment of electrovectrial effect

According to our previous works, poled and unpoled HA ceramics were immersed in 1.5SBF for observation of bonelike crystal growth. For comparison, polarizationof HA ceramics was carried out under various conditions . Growth rate was evaluated on SEM micrographs which were taken on completely washed surface after immersion.

3. RESULTS AND DISCUSSION

3.1 Thermally stimulated current

Electric polarization treatment and thermally stimulated depolarization current (TSDC) measurement were carried out on sintered disks with 10 mm in diameter and 0.7 mm in thickness. These specimens were coated with Pt-Pd on both sides, and then sandwiched between platinum plates. Electrical polarization was undertaken on dense HA specimens by heating up to a given temperature (T_{pol}) of 400 to 873K in air, then subjected to the application of dc field of 1 or 5 $kV \cdot cm^{-1}$ for 1h, thereafter cooled to room temperature. There was no current observed during polarization. No change of surfaces was also observed in color during polarization.

TSDC measurements were done by monitoring dissipated current density during heating polarized specimens with an increasing rate (β) of $5K \cdot min^{-1}$ up to 1000K. Results of TSDC were analyzed for evaluation of stored charge (Q) by polarization and activation energy for depolarization.

Our purpose is to store high Q in HA specimens to build high surface charges for biomedical use. The previous result suggested that the polarization took place due to ionic process, possibly proton migration in HA. Based on the presumed mechanism, first of all, we examined whether ultra high Q can be stored or not. The TSDC measurements suggested the dependence of TSDC on polarization temperature (T_{pol}) and applied electric field strength. Figure 4 shows a TSDC curve against heating temperature, indicating that depolarization takes place at the temperatures of 500-1000K. For higher T_{pol}, the temperature (T_{max}) to give the maximum current density (J_{max}) tends to have shifted to higher temperature, and J_{max} increased exponentially with T_{pol}. These results support the mechanism in which the depolarization takes place due to ionic process.

In considering the fact that polarization is instantly relaxed in most solids, the crystal structure of HA is reasonably expected to have some meaning for biocompatibility. This inference will be further studied using polarized HA ceramics.

Although the piezoelectricity of bones have long been reported to be important for bone formation, we are not yet confirmed that the correlation of our polarization with bone piezoelectricity at present.

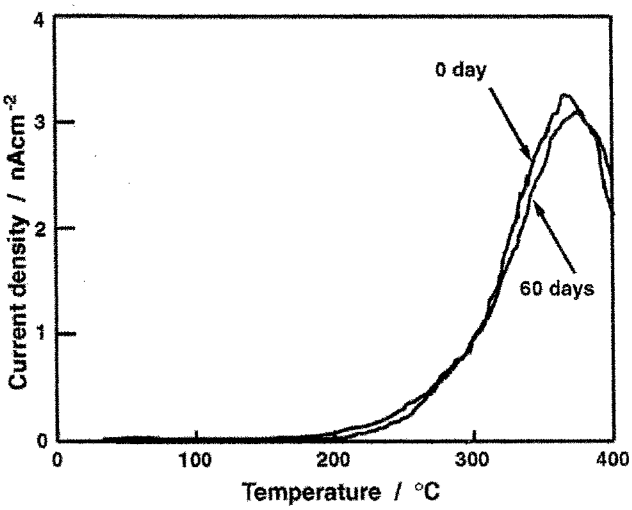

Fig. 4 TSC of polaried HA electret.
The figures inserted show the ageing time (0 and 60d) after polarization.

The stored charge Q is calculated from the integration of TSDC current against T_{pol} as shown in eq. (1).

$$Q=\beta \int I(T)dT \qquad (1)$$

Figure 5 shows the dependence of the calculated Q on T_{pol}; poling at higher T_{pol} gave rise to larger values of Q. The value of Q was enhanced from $10nC\cdot cm^{-2}$ to $1mC\cdot cm^{-2}$. The maximum value of Q further exceeded the previously reported maximum value. It is seen that a surface of a polarized HA has a considerably high energy at body temperature. It is also understood that the polarized state can be maintained for long time at body temperature because the relaxation takes place only temperatures higher than 200℃. The quantitative analysis on the effects of Q is under study.

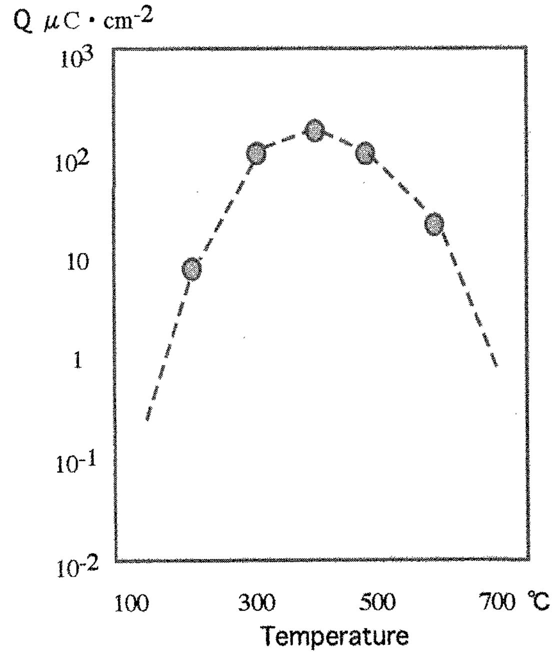

Fig. 5 Dependence of Q on poling temperature.

3.2 Electrovectrial effect n SBF

It was confirmed by SBF tests that HA surfaces are activated by surface charges; although slow crystallization took place on un-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 (Fig. 6). 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. Higher field strength gave rise to faster crystal growth; sizable agglomerated crystals of 10μm in diameter were observed in some spots on polarized HA under 1kV/cm, and the acceleration effect was confirmed even by the polarization as weak as 12V/cm. The accelerated crystal growth mentioned above was observed on N-surface, whereas quite slow crystal growth took place on P-surface even after 3-day immersion in 1.5SBF (Fig. 6). Although the polarization at 300°C was effective for the acceleration of crystal growth, we also confirmed the acceleration effect by the polarization at 200°C.

The crystal growth was dependent upon the dc field strength, temperature and time for polarization. As mentioned above, the surrounding space around the interface between HA and SBF is activated for solidification by a stored energy in a solid such as ceramic HA. As easily expected, the size of the activated space must be on a nano –scale. We refer to this activation effect as electrovectorial effects. Such effects are expected to be of great importance for not merely biomedical but also environmental applications.

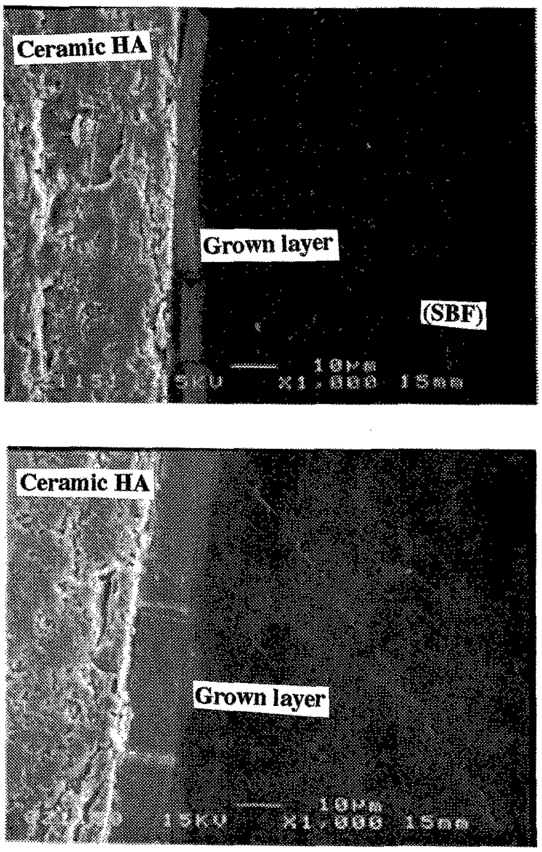

Fig. 6 SEM observation of the un-poled (upper) and N-surfaces of ceramic HA (lower) after immersion in 1.5SBF for 3d.

Summary

Polarized HA has important effects in the biomedical applications, which is called electrovectorial effects. The electrovectorial effects of HA arise from the electrostatic interactions between the poled surfaces and the surrounding media.

Acknowledgements

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