Ionic Conductivity of Poorly Crystalline Apatite: Effect of Maturation

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This study deals with the effect of maturation on the ionic conduction of poorly crystalline synthetic apatite. The tendency of this materials to crystallise during maturation is accompanied by an improvement of its ionic conductivity σ. At room temperature, σ increased by a factor of 300 after 50 days of maturation. The frequency dependence of the ionic conductivity was attenuated gradually during maturation. These results are explained by the short-range organisation of sites with time, and by the fact that the translational movement of the mobile ions becomes less hindered as the material matures.

Key words: Apatite; Maturation; Ionic Conductivity; Crystallinity.

1. Introduction

Mineral parts of calcified tissues contain generally poorly crystalline apatites [1] which become with time nearly stoechiometric apatite by ageing [2]. One of their properties is their ability to incorporate or adsorb foreign ions such as acid phosphates HPO_4^{2-} [3]. The changes in the concentration of these ions during ageing of apatites was reported to have an important effect on their physico-chemical properties [4, 5]. Actually, maturational changes in such materials have been widely studied using different techniques such as Fourier Transformed Infra-Red spectroscopy [FTIR] [6], X-Ray Diffraction [XRD] [7], Electron Diffraction [ED] [8], Nuclear Magnetic Resonance [NMR] [9], Electron Microscopy [EM] [10], and others. The aim of the present work was to investigate the electrical properties of poorly crystalline apatite analogous to the mineral part of bodies in order to more accurately characterise the mechanism of its maturation using impedance spectroscopy.

Actually, previous electrochemical studies using impedance spectroscopy showed that HPO_4^{2-} groups contributed to the ionic conductivity of poorly crystallized apatite involving the transfer of protons along H-bonded networks and a combination of H^+ transferring between adjacent phosphate groups along the chains $PO_4^{3-} \ldots HPO_4^{2-} \ldots PO_4^{3-} \ldots HPO_4^{2-}$ [11]. F^- treatment of these materials improved promptly the conductivity owing to an increase in the apatitic crystallinity [12]. The ability of this material to conduct by protons has been used in environmental devices for the removal of hazardous pesticides and heavy metals from waters [13 - 15]. Moreover, pure and mixed well crystallised apatites have been investigated by the same method and showed a diffusion of anions and cations within apatitic channels [16 - 18]. All of the mentioned works investigated effects of temperature, ionic substitution and chemical treatment on the ionic conductivity of apatites in order to give information on the charge carriers or to improve the conductivity. In the present work, the effect of maturation on the electrical properties of poorly crystallized apatite is studied. This survey provides additional information concerning the relationship between the activity of such biomaterials during ageing and its ionic mobility and shows the potential of the electrical method to study the maturation progress.

2. Material and Methods

Poorly crystallised carbonated-apatites (AC) were prepared by co-precipitation of two solutions at room temperature and slightly neutral pH. The first solution was prepared by dissolving 40 g of diammonium hydrogenophosphate ($(NH_4)_2HPO_4$) in 500 ml of deionised water. 20 g of monosodium carbonate

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($NaHCO_3$) was added to this solution after adjusting its pH to 8.34 by adding a concentrated basic solution (NH_4OH, $d = 0.92$). The second solution was prepared by dissolving 17.7 g of calcium nitrate ($Ca(NO_3)_2.4H_2O$) in 250 ml of deionised water. After co-precipitation, the pH reached 7.35. At the end of different maturation times at room temperature, AC precipitates were filtered, washed with deionised water and finally lyophilised.

Structural changes in maturing apatites were investigated by powder XRD, Specific Surface Area (SSA) and Electrical measurements.

X-ray diffraction patterns of powder samples were recorded on a CPS 120 INEL X-ray diffractometer using Co Kα1 monochromatic radiation. Diffraction data were collected in steps of 0.02 degree between 25 and 70 (2θ).

The specific surface areas of maturing apatites were calculated by applying the conventional BET nitrogen adsorption method.

The Complex impedance method with the Maxwell bridge was used to perform electrical measurements at room temperature with an alternating current mode over a frequency range 10 Hz to 2 MHz. Homogeneous pellets were obtained by pressing the powder at 3 tons/cm^2. The contact between the outside circuit and the pellet was maintained by a platinum gel deposit on the surface.

3. Testing Results

X-ray diffraction showed that maturing apatites were poorly crystallised (Figure 1). However, the crystallinity of these materials improves gradually with time.

It is possible to determine the average crystallite size and preferential growth occurring during maturation along the c or a-axis by determining the dimension of the crystallised domains (L in Å) using the Debye-Scherrer formula [19]. The results showed that the growth occurred in both directions (Figure 2). The increase of the L_{310}:L_{002} ratio (Fig. 3) during maturation indicated that the development of crystals occurred preferably along the (a, b) direction.

Specific surface areas (SSA) of maturing apatites are given in Table 1. It can be observed that, as the apatites mature, their specific surfaces decrease.

Complex impedance diagrams of AC apatites conducted at room temperature were formed by arcs characteristic to intrinsic participation of the bulk, followed by linear plots at low frequencies characteristic to the polarisation of blocking electrodes (Figure 4). Since the participation of grain boundaries could not be seen accurately in these diagrams, it was assumed that the arc presented the total electrical response of the solid including grains and grain boundaries. The corresponding values of the ionic conductivity for different times of maturation are illustrated in Table 2. It can be seen that the conductivity increases with maturation.

Table 1. Specific surface area of some matured AC apatites.

Time of maturation	6 h	1 d	3 d	10 d	50 d
SSA (m^2/g)	289	261	243	189	121

Table 2. Ionic conductivity σ (Ω^{-1} cm^{-1}) of AC apatites at different times of maturation.

Time (days)	0	1	4	10	30	50
10^7 σ (Ω^{-1} cm^{-1})	1.33	1.55	5.14	15.9	126	413

4. Discussion

X-ray diffraction showed an improvement of the crystallinity of poorly crystallised apatites during maturation. The preferential growth of crystallites along the (a, b) direction indicates that a planar growth is favoured by maturation predicting platy crystals similar to apatites of bone and dentine [1]. *A fortiori*, this would have been favoured by the incorporation of $HPO_4{}^{2-}$ ions within the apatitic structure since these ions are reported to cause an expansion in the (a, b) plane of apatites [20]. Also, the high values of SSA did indicate that this material is nanocrystalline. Its decrease during maturation did indicate an increase in grain size of this material or crystal proliferation.

This material is not homogeneous but contains a large boundary area. Moreover, a considerable fraction of its volume has to be attributed to voids between crystallites. Poorly crystalline apatite and matured apatite differ in conductivity mainly because the translational movement of the mobile ions is less and less hindered (e. g., by voids between crystallites) as the material matures.

Furthermore, the crystallinity progression indicated that a progressive short-range organisation of sites occurred, improving the ionic conductivity. It is plausible to imagine that the low values of σ during the first period of maturation is not only due to the resistance of grain boundaries, but also to non-

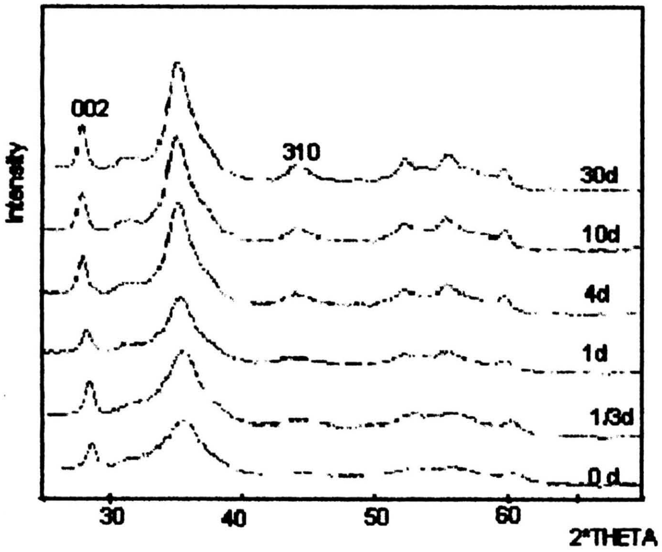

Fig. 1. X-ray diagrams of poorly crystalline apatites having different degrees of maturation.

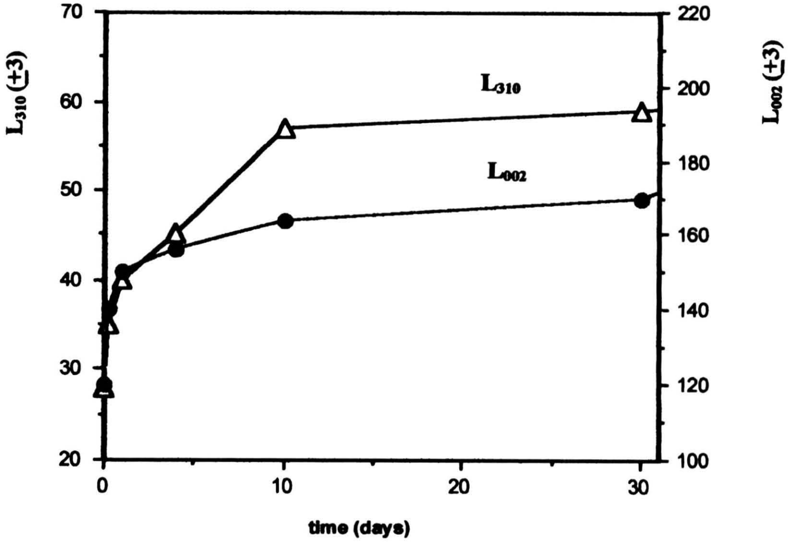

Fig. 2. Variation of apparent dimensions L_{310} and L_{002} (in Å) of apatitic crystallites against time of maturation.

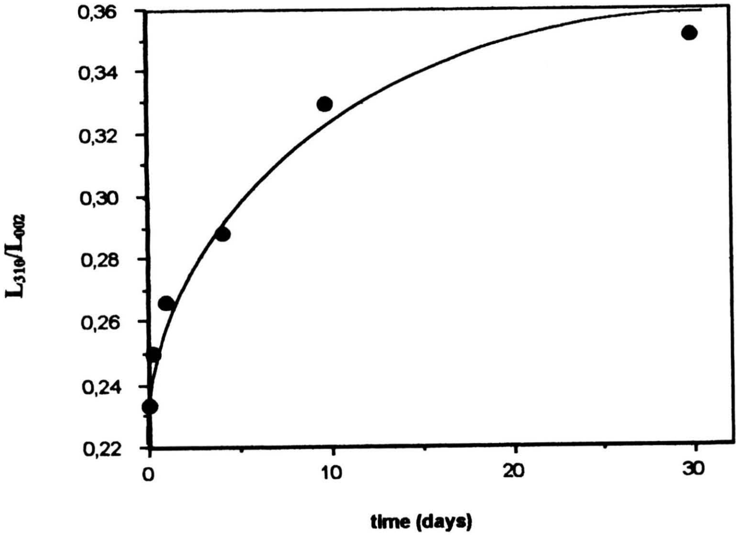

Fig. 3. Variation of L_{310}:L_{002} ratio versus the time of maturation.

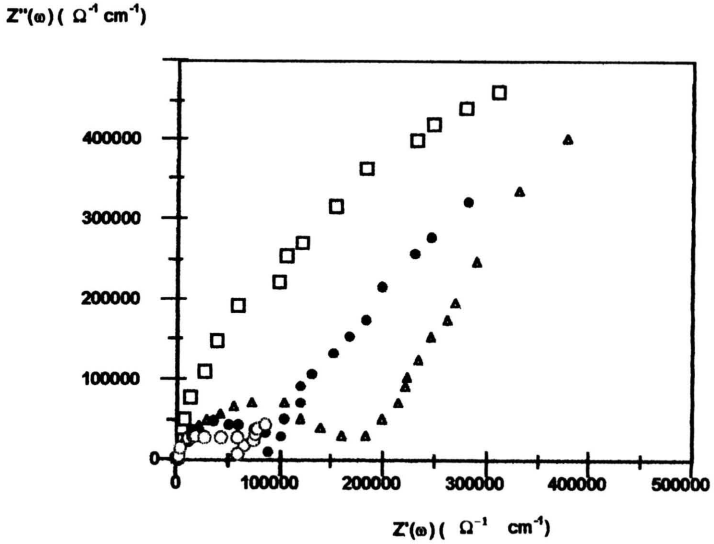

Fig. 4. Impedance Diagrams of matured AC apatites at 25°C. □: 7 h; Δ: 10 d; •: 50 d; ○: 90 d.

ordered sites in such nanocristalline material. Alike, improvement of the ionic conductivity during maturation could be due to the crystal proliferation. Thus, there exists a correlation between degree of crystallisation and maturation and between crystallisation and conductivity.

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