Retention of fluoride ions from aqueous solution using porous hydroxyapatite Structure and conduction properties

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Abstract

Synthetic porous calcium hydroxyapatite (noted p-HAp) treated with different fluoride concentrations at room temperature in the presence of carbonate, sodium chloride and phosphate-rich media was investigated. The fluoridation rate of the porous calcium hydroxyapatite was 89% using 1 mol/L [F$^-$] solution compared with 30% for crystalline hydroxyapatite (c-HAp). The high specific surface area of p-HAp (235 m^2 g^{-1}) compared with c-HAp sample (47 m^2 g^{-1}) has an important effect on the removal of fluoride ions from aqueous solution, when p-HAp was treated with high fluoride concentration to produce calcium fluorohydroxyapatite materials. Fluoride adsorption on porous hydroxyapatites (p-HAp) modified their structural and conduction properties.
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1. Introduction

Fluoridated calcium hydroxyapatites have been studied in relation to their physicochemical properties [1–6]. It is well known that fluoride is one of the elements contained in biological apatites as trace amounts, which strongly modifies their crystallinity and their solubility. Porous hydroxyapatite biomaterials have a great stability and a good biocompatibility. They can be used as composite biomaterials for their ability to form a strong chemical bond with natural bones. Incorporation of fluorine into hydroxyapatite or into tooth enamel increases the proportion of fluoroapatite and induces better biological properties such as promoting a new mineralization of incipient lesions and increasing the resistance to acid demineralization [1–3]. However, too high concentration of fluorine may lead to enamel fluorosis, intoxication or destruction of the gastric mucosa [3]. The present study is devoted to en-

hancing the fluoride adsorption capacity onto hydroxyapatite prepared in a highly porous form using a modified chemical wet method. We also analyzed the effect of the F$^-$ ions on the crystallinity and electrical properties of hydroxyapatite biomaterials. The fluoride retention properties of the poorly and the well-crystalline hydroxyapatites are compared.

2. Materials and methods

Starting powders were prepared and characterized as described in our previous papers [7,8]. Porous calcium hydroxyapatite particles (p-HAp) were prepared by a modified chemical wet: Ca(OH)$_2$ was dissolved in deionized, distilled water and mixed with NH$_4$H$_2$PO$_4$ solution at room temperature in a mixture of ethanol–water (50 vol.%– vol.50%). The suspension was aged for 12 h, filtered and dried at 100 °C overnight. Crystalline calcium hydroxyapatite Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ (c-HAp) was prepared by a diluted decomposition method between (NH$_4$)$_2$HPO$_4$ and Ca(NO$_3$)$_2$ at

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80 °C. The pH value was adjusted to 10 with ammonium hydroxide. The powders were filtered and washed with distilled water and dried overnight at room temperature. The specific surface area was measured by BET adsorption isotherms using micromeritics ASAP 2001 equipment.

One gram of each HAp powder was immersed in 100 ml solutions containing, 10^{-2} M Na_2CO_3, 10^{-2} M Na_2HPO_4 solutions during 24 h with various NaF concentrations ranging from 10^{-3} to 1 M. The ionic strength of solutions was controlled by the addition of 10^{-3} M NaCl solution. The pH of the slurries was measured and remained roughly constant at 7.4. The particles were filtered and washed with deionized, distilled water and finally dried in air at 100 °C. The resulting solids were characterized using X-ray diffraction (Philips PW131diffractometer) and infrared spectroscopy (Perkin-Elmer 457 spectrometer). For chemical titration, the powders were dissolved in 1 M HCl solution. The calcium content was determined in dissolved sample by complexometric titration with EDTA. The phosphate amount was determined in the dissolved sample by spectrophotometric analysis of molybdenum blue phosphate complexes. The fluoride concentration was determined with an ion-selective electrode connected to a pH/mV meter (Orion Research) carefully calibrated and the test solution was buffered at pH 6 by addition of a trisodium citrate solution.

The electrical conductivity of porous hydroxyapatite (p-HAp) and fluoridated hydroxyapatite (p-FHAp) was measured at room temperature (relative humidity around 70%) using the impedance method with an impedance meter (Hewlett-Packard HP4192A) at room temperature with the signal frequency ranging from 5 Hz to 13 MHz. Powders were pressed under 50 kN/cm^{-2}. Their compactness was around 80% for all samples. Electrodes were prepared with silver paint on both sides of the pellets.

3. Results and discussions

After soaking for 1 day in the solutions with various NaF concentrations, the hydroxyapatite shows a large retention of fluoride. The calcium/phosphorus ratio is unaffected by the fluoridation experiments related to the apatite structure and to phosphorus and carbonate excess in initial solution. After exposure to these solutions, which contain carbonate ions, the total amount of CO_3^{2-} ions has slightly increased from 3.6 to 4.5 wt.%. Negligible sodium amount (0.3 wt.%) has been incorporated in the poorly crystalline hydroxyapatite, which indicates only a very little Ca-deficiency apatite.
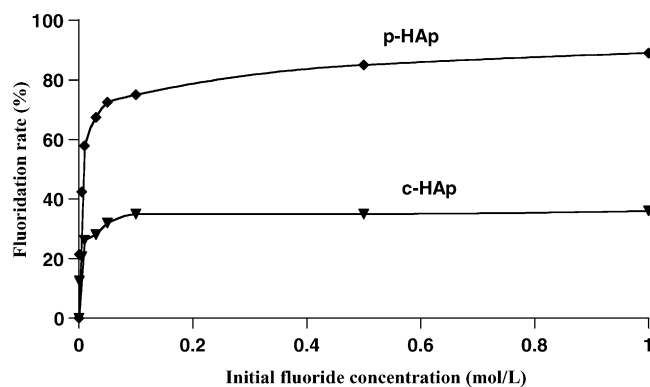

Fig. 1. variation of the fluoridation rate (%) as a function of the initial fluoride concentration in the solution after reacting the powders p-HAp and c-HAp.

The amount of fluorine introduced in the apatite powders shown as the fluoridation rate has been plotted as a function of the initial concentration of fluorine in Fig. 1. The fluoridation rate = the removed fluoride amount/initial fluoride amount in solution. The amount of F^- ions removed by p-HAp from aqueous solution is larger than that by c-HAp sample. The fluoridation rate of p-HAp has increased again to 89% using 1 M [F^-] solution after 4 days of contact time. This is related to the non-stoichiometry that favors the ionic mobility and to the higher specific surface area of p-HAp as compared to that of c-HAp material (Table 1).

Using low fluoride concentration (<0.1 M [F^-]), the X-ray diffraction patterns correspond to an apatite structure with no secondary phases. XRD analysis of the p-HAp powders after immersion in the fluoride solutions clearly shows that the degree of crystallinity has been improved on the basis on the widths at half peak height of the (0 0 2), (2 1 1) and (3 0 0) reflections (Fig. 2). But, the diffraction peaks are still broad as compared to the sharp reflections of well-crystallized apatite obtained after heating the fluoridated samples at 900 °C.

However, for 0.1 and 1 M [F^-] solutions, some additional peaks can be observed in the XRD pattern after calcinations at 900 °C. They correspond to the like-CaF_2. Therefore, the presence of high fluoride concentrations in the solution probably favors the dissolution and precipitation reactions leading to the thermodynamically stable phase CaF_2 formed at the solid interface of the apatite and also leads to a phase separation between p-HAp and CaF_2 in heating the fluoridated products at high temperature.

Table 1
Chemical composition and structural characteristics of starting hydroxyapatites

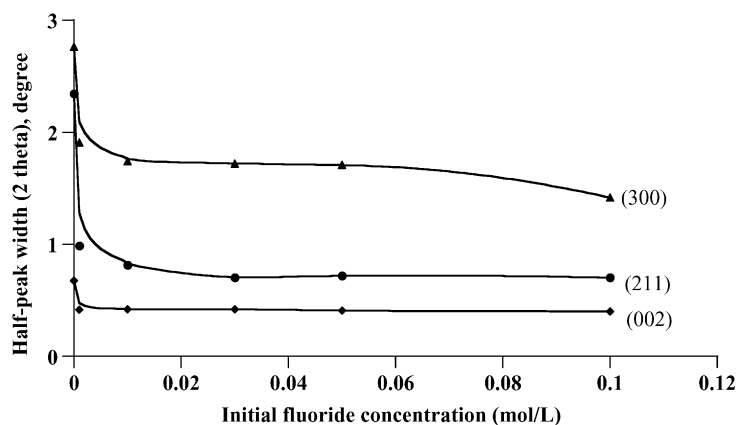| Samples	% Ca ± 0.02%	% P ± 0.03%	% F ± 0.02%	Ca/P molar ratio	SSA (m^2/g)	Crystallinity
p-HAp	36.60	17.57	0	1.61	235	Poor
c-HAp	38.84	18.52	0	1.67	47	High
Pure FAp	38.80	18.08	3.77	1.67	25	High

Fig. 2. Crystallinity of fluoridated p-HAp sample shown as the half-height width of the (0 0 2), (2 1 1) and (3 0 0) reflections.

Infrared spectra of p-HAp and the fluoridated products only show the characteristic bands attributed to PO$_4$ and OH groups (Fig. 3). But, a vibration band appears at 743 cm^{-1} after fluoride adsorption. This band is attributed to hydrogen bonding specific of fluorohydroxyapatite samples as reported in various works [2,9,10]. After soaking in concentrated fluoride solutions (0.1 and 1 M [F$^-$]), the IR spectra of the powders show that the specific vibrations of OH bands at 3560 and 630 cm^{-1} have strongly decreased in intensity or even disappeared to produce the fluoroapatite Ca$_{10}$(PO$_4$)$_6$F$_2$ structure.

The treatment of p-HAp in 0.1 M [F$^-$] solution strongly modifies the electrical transport properties of hydroxyapatite at room temperature (and 70% relative humidity). So, such conductivity measurements could be useful to obtain the degree of fluoridation in the apatite structure. The conductivity value of the fluoridated hydroxyapatite using 0.1 M [F$^-$] (p-FHAp) at 25 °C is $\sigma = 5.10^{-5}$ S/cm much higher than for the unfluoridated p-HAp sample ($\sigma = 7 10^{-7}$ S/cm). This change the shape of the complex impedance diagram at 70% RH compared to that of p-HAp reference (Fig. 4). The frequency dependence of the real part of the complex impedance is also shown in Fig. 5. Although, the interpretation of the high-frequency part of impedance spectra could be doubtful, we see that the samples strongly differ by their low-frequency contribution. Considering the relatively high conductivities measured for apatite at room temperature, we must consider that these conductivity values are related to a contribution of surface conduction at the grain boundaries, associated to surface diffusion of water and protons. This conductivity is associated to the ionic mobility of surface-ionized species as commonly observed in powdered hydrates. It is also increased in the p-HAp by the large specific surface area of the powder. Therefore, the increase of conductivity may be probably associated to a change of the nature of the surface sites from basic OH surface groups to more acidic fluoridated surface. The small change in crystallinity between the fluoridated apatites and the starting hydroxyapatite that reflects the variation in porosity are not sufficient to explain the market change in conductivity values between the last materials, but the fluorine mobility in apatite structure may be responsible to this difference. In series of well-crystallized fluorohydroxyapatites Ca$_{10}$(PO$_4$)$_6$(OH)$_{2-x}$F$_x$ ($0 \leq x \leq 2$), Maiti and Freud [11] have demonstrated that the F$^-$ ions
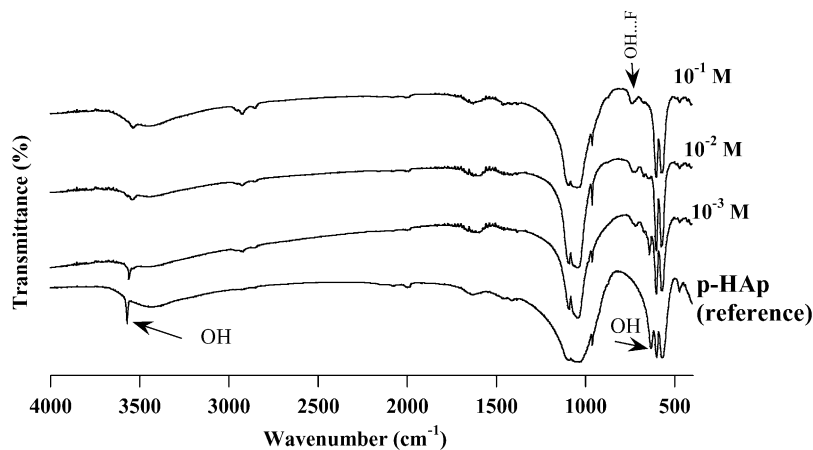

Fig. 3. Infrared spectra of p-HAp sample and its fluoridated samples at different fluoride concentrations.
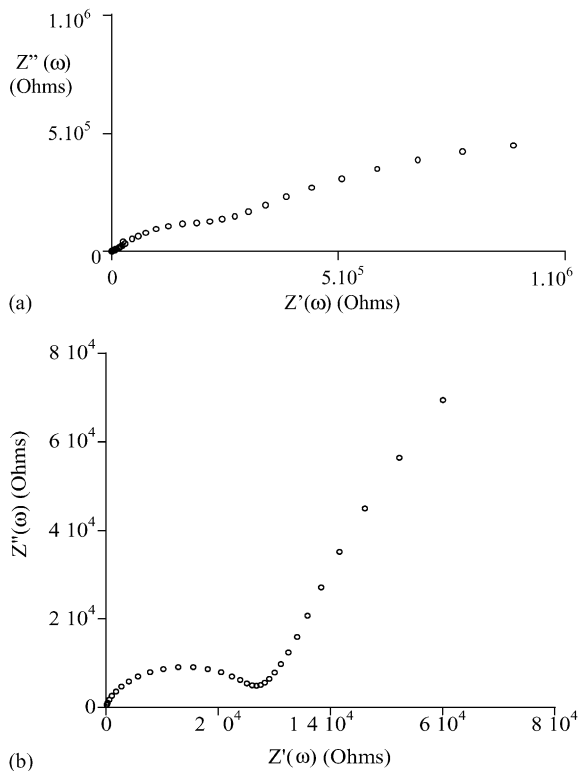
Fig. 4. Complex impedance diagrams of p-HAp before (a) and after (b) chemical fluoride treatment in solution containing [F⁻] = 0.1 mol/L (20 °C, RH = 70%).
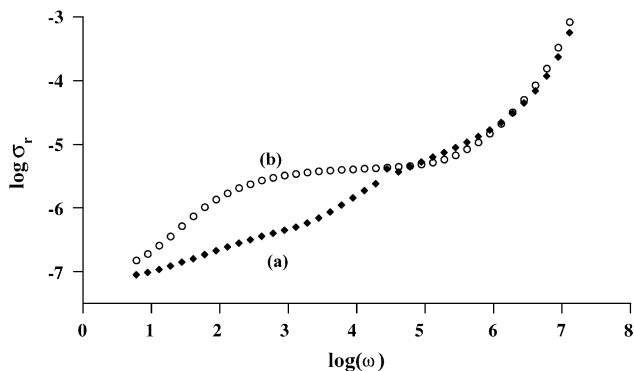

Fig. 5. Frequency-dependent ionic conductivity (20 °C, RH = 70%) of fluoridated sample p-FHAp (a) for starting p-HAp reference and (b) after fluoridation in ([F⁻]$_0$ = 0.1 mol/L).

incorporated in apatite structure have an important effect on the conductivity and the best conductor has obtained for x = 1 in the range of the temperature 250–500 °C. Nevertheless, these materials have not conducing at room temperature, which due to its porosity and its structure surface.

The improved understanding of the ionic conductivity in fluoridated hydroxyapatite may be helpful for aspects of caries research. More details on the fluorine and protonic conductivities in the crystallized fluorapatites have been described in our previous study [12].

4. Conclusion

Porous hydroxyapatite (p-HAp) has prepared using a wet chemical method and characterized using both structural and chemical techniques. The strong interaction of F⁻ ions with the poorly crystalline hydroxyapatite modifies its structural surface, their conduction properties and favored the stable fluoridated apatites. The high retention of F⁻ ions by p-HAp compared to the crystalline sample c-HAp is due to the high specific surface area of p-HAp material and to its crystallinity at room temperature compared to the crystalline hydroxyapatite c-HAp material.

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