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# Crystallinity and fluorine substitution effects on the proton conductivity of porous hydroxyapatites

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## Abstract

Porous calcium hydroxyapatite (p-HAp) was prepared by wet chemical methods. The poorly crystalline structure and the high surface specific area ( $235\text{ m}^2/\text{g}$ ) of this hydroxyapatite have effects on the variation of the electrical properties. Good linearity of logarithm of conductivity versus the relative humidity in the range from 19% to 88% (RH) was observed using the complex impedance spectroscopy. The proton conduction was affected by the relative humidity related to  $\text{H}_2\text{O}$  adsorption on the material surfaces. The fluorine substitution in p-HAp also modifies the crystalline and the proton conduction properties.

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**Keywords:** Hydroxyapatites; Fluorine substitution; Crystallization; Electrical properties; Relative humidity

## 1. Introduction

Calcium phosphates  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$  ( $\text{X} = \text{OH}, \text{F}$ ) with the apatite structure possess a large amount of potential applications such as catalysts, sensors, ionic exchangers and biomaterials [1–4]. These properties strongly depend on the crystallinity, the chemical composition and the powder specific surface area (SSA). Apatite biomaterials have a great stability and a good biocompatibility. Therefore, they can be used for composite biomaterials, because of their ability to form a strong chemical bond with natural bones [5,6].

Electrical properties can often be related to physical and structural aspects of the hydroxyapatite [4]. In this study, conductivity measurements were carried out by complex impedance method at room temperature in varying the relative humidity (RH) range, in order to understand the correlation between structural,  $\text{H}_2\text{O}$  molecular adsorption and conduction properties of porous hydroxyapatite material prepared by a modified chemical wet method reported in our previous study [7]. In addition, the fluoride treatment of this material is expected to modify the crystalline structure and the proton conduction of hydroxyapatites.

## 2. Experimental

The porous calcium hydroxyapatite particles (p-HAp) were prepared by a modified chemical wet method reported elsewhere [7]:  $\text{Ca}(\text{OH})_2$  was dissolved in deionized water and mixed with a  $\text{NH}_4\text{H}_2\text{PO}_4$  solution at room temperature in a mixture of ethanol-water (50–50% volume). The reagents were introduced at molar ratio Ca/P 1.67. The suspension was aged for 12 h, filtered and dried at  $100^\circ\text{C}$  overnight.

The fluoridated hydroxyapatite sample (p-FHAp) was prepared as described: 1 g of the p-HAp powder was immersed into a solution containing 0.1 M of  $\text{NH}_4\text{F}$  for 24 h. The particles were filtered and washed with deionized-distilled water and finally dried at  $100^\circ\text{C}$  overnight.

The resulting solids were characterized using X-ray diffraction (Philips PW131 diffractometer) and infrared spectroscopy (Perkin-Elmer 457 spectrometer). The SSA was measured by BET adsorption isotherms using micromeritics ASAP 2001 equipment.  $^{31}\text{P}$ -MAS-NMR spectra were recorded on a Bruker MSL 300 spectrometer equipped with an Adrew type rotor rotating at a frequency of 10 kHz. For chemical titration, the powders were dissolved in HCl 1 M. Calcium and phosphate contents were determined, respectively, by complexometric titration with EDTA and by spectrophotometric

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analysis of molybdenum blue phosphate complexes. The fluoride concentration was determined with an ion-selective electrode connected to a pH/mV meter carefully calibrated.

The electrical conductivity of p-HAp and p-FHAp was measured using the impedance method with a HP4192A impedancemeter at room temperature with the signal frequency ranging from 5 Hz to 13 MHz. Powders were pressed under  $50 \text{ kN/cm}^2$ . Their compactness was around 80% for both the samples. Electrodes were prepared with silver paint on both sides of the pellets. Experiments were performed at room temperature.

### 3. Results and discussions

#### 3.1. Characterization

XRD analysis of p-HAp powders just after precipitation revealed a poorly crystalline apatite structure. The crystallinity increases upon thermal with no secondary phase (Fig. 1). The  $^{31}\text{P}$ -NMR spectrum of p-HAp only shows a single peak at  $-2 \text{ ppm}$  (versus  $\text{H}_3\text{PO}_4$ ). This confirms that one crystallographic site is available of phosphorus in poorly crystalline p-HAp material. The SSA of p-HAp sample as a function of the heating temperature is given in Table 1. The great SSA value observed in p-HAp dried at  $100^\circ\text{C}$  is related to the method of the preparation and to porous texture. We noticed that above  $500^\circ\text{C}$ , no significant temperature effect is observed on the surface specific area. Rapid precipitation between  $\text{Ca}(\text{OH})_2$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  at  $25^\circ\text{C}$  has been demonstrated to form apatites exhibiting high surface areas ( $235 \text{ m}^2/\text{g}$ ), which they can provide for significant adsorption of various elements such as fluoride ions.

The treatment of the p-HAp in fluoride solution ( $0.1 \text{ M NH}_4\text{F}$ ) is accompanied by an improvement of the

crystallinity on the basis of the inverse of the half-peak width of the (300), (211) and (002) reflections (Table 2) although the crystallinity remains low.

Infrared spectra, taken from the various heated products, display the vibration modes of  $\text{PO}_4$  and OH groups. The vibration frequencies characteristic of the  $\text{PO}_4$  groups can be seen at 1090, 1030, 962, 603,  $565 \text{ cm}^{-1}$ . We notice that a spectral bands attributed to apatitic  $\text{OH}^-$  ions at 3560 and  $630 \text{ cm}^{-1}$  for p-HAp sample dried at  $100^\circ\text{C}$  or heated at  $800^\circ\text{C}$ . Other bands with low intensities at 1460, 1430 and  $875 \text{ cm}^{-1}$  characteristics of carbonate vibration modes are observed. About 3.6 wt% of carbonate in the particles has been estimated by the IR measurements. In infrared spectrum of the fluorinated p-FHAp sample, a vibration band appears at  $743 \text{ cm}^{-1}$  and the small shift of OH bands to the low frequency are attributed to hydrogen bonding  $\text{OH}\cdots\text{F}$ . We noticed that the OH bands strongly decreased in intensity in fluoridated hydroxyapatite p-FHAp or entirely disappeared in the pure fluoroapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  (FAp), indicating the formation of the fluorohydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{F}_x$  [8–11]. XRD and IR results p-HAp and p-FHAp products are provided by chemical analyses (Table 3). From these analysis results, the precipitated products are little non-stoichiometry apatites compared to the pure hydroxyapatite HAp or fluoroapatite FAp (Ca/P molar ratio = 1.67). The presence of  $\text{CO}_3$  groups substituting  $\text{PO}_4$  and OH groups is responsible for the

Table 1  
Specific surface area of the p-HAp sample at different temperatures of the calcination

Temperature ( $^\circ\text{C}$ )	100	300	500	800
Specific surface area ( $\text{m}^2/\text{g}$ )	235	159	92	89

Table 2  
Comparison of the crystallinity between the p-HAp and p-FHAp products shown as inverse of the half-peak width of (002), (211) and (300) reflections

Samples	(002)	(211)	(003)
p-HAp	1.477	0.422	0.363
p-FHAp	2.494	1.421	0.706

Table 3  
Chemical composition and structural characteristics of p-HAp and p-FHAp samples

Samples	%Ca	%P	%F	Ca/P ratio	Crystallinity
p-HAp	36.60	17.57	0	1.61	Poorly
p-FHAp	36.99	17.65	2.82	1.62	Medium
HAp	38.84	18.52	0	1.67	High
FAp	38.80	18.08	3.77	1.67	High

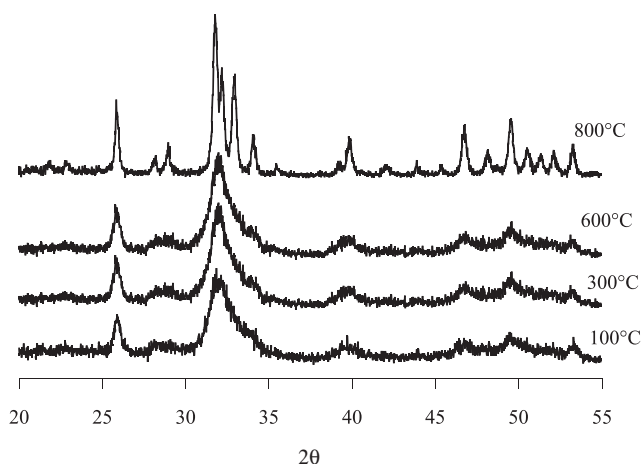


Fig. 1. X-ray patterns of p-HAp product at different temperatures.

Ca/P ratio deviation, not knowing any other phases were detected (Fig. 2).

### 3.2. Electrical properties

Plots of the real  $Z'(\omega)$  and imaginary  $Z''(\omega)$  impedance components are shown in Fig. 3 for different RH (Fig. 3). At high RH, p-HAp dried at 100°C has a high conductivity and its complex impedance diagram exhibits three semi-circles. The bulk resistance was deduced from the high-frequency intersection of the semi-circle with the real axis. Fig. 4 shows the relation between the logarithm of the conductivity and the RH. For humidity in the range from 19% to 88% (RH), a linear relationship between the RH and  $\log(\sigma)$  obtained for p-HAp material. This variation related to the amount of H<sub>2</sub>O molecules adsorbed onto the surface. Therefore, when H<sub>2</sub>O molecules infiltrated into the pores due to the exposure in humidity or containing in apatite structure, protons were generated by dissociation

at material surfaces. So, the water in the interconnecting pores, which increased the defects number in apatite structure, will make significant contributions to the densification process and to the electrical properties. Therefore, lower electrical resistance in increasing of the humidity favored the protons mobility in apatite channels or on the grain surface. We noticed that the proton conductivity of the sintered crystalline hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> (HAp) as a function of the temperature between 200°C and 800°C were reported elsewhere [4]. This conductivity was undefined at 25°C due to the low mobility of the charge carriers at this temperature. Nevertheless, the poorly crystalline structure of p-HAp dried at 100°C was conducting relative to its surface conduction affected by the water in interconnecting pore, which favored the protons mobility between the attracting species (O<sup>2-</sup>).

The electrical resistance of p-FHAp is about one order of magnitude lower than that of p-HAp at 70% RH at room temperature. The impedance response of

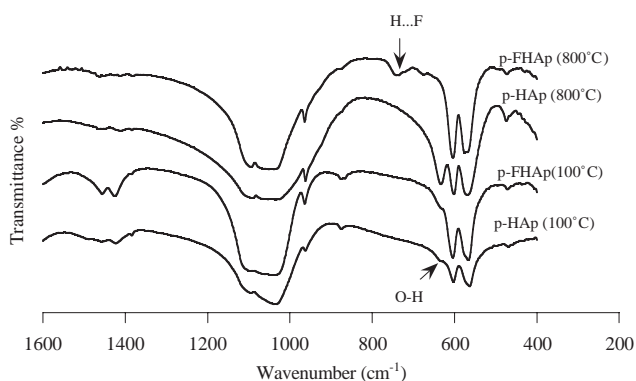


Fig. 2. Infrared spectra of p-FHAp and p-HAp powders.

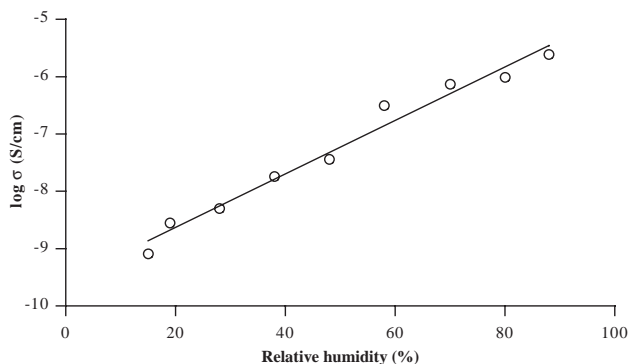


Fig. 4. Relationship between  $\log \sigma$  versus relative humidity for p-HAp at 25°C.

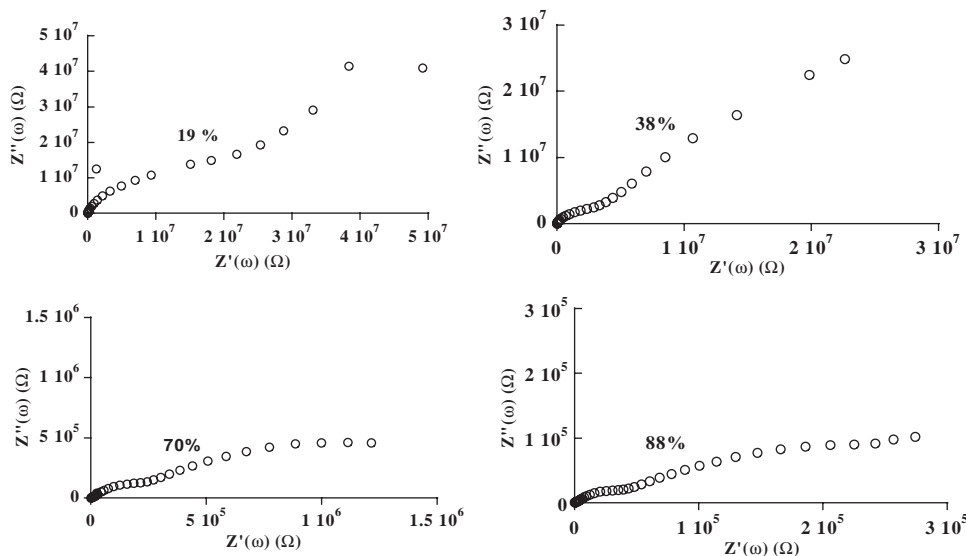


Fig. 3. Complex impedance diagrams for p-HAp material at different relative humidities.

the fluoridated hydroxyapatite exhibits one semicircle at high frequency and a straight line at low frequency probably due to a Warburg impedance associated to the diffusion of the charge carriers (Fig. 5). Moreover, the fluorine-substituted hydroxyapatite shows lower resistance. The change of surface structure by introducing the  $F^-$  ions into  $OH^-$  sites leads to the change of the surface conduction. In addition, the electrical resistance of p-FHAp ceramic measured at room temperature decreases when this material is preheated at  $300^\circ\text{C}$ . This decrease in conductivity value is related to the crystallinity of the preheated material. The conductivity value of the fluoridated p-FHAp at  $25^\circ\text{C}$  is  $5.03 \cdot 10^{-5} \text{ S/cm}$  compared to unfluoridated p-HAp sample ( $\sigma = 7.410^{-7} \text{ S/cm}$ ). Therefore, the increase of the conductivity may be probably associated to a change of the nature of the surface sites from basic OH surface groups to more acidic fluorinated surface [12]. The small change in crystallinity between p-HAp and p-FHAp materials that reflect differences in porosity are not sufficient to explain the marked variation in values for conductivity between species, but the fluoride mobility in (OH,F) chains in apatite structure may be responsible to the difference in conductivity. It is quite possible that, when the proton or fluorine jumps from one  $OH^-$  or  $F^-$  ion to the next, they pass via  $PO_4^{3-}$  ions that line the (OH,F) channels [11,13]. The contribution of fluoride ions to the relative crystalline structure and to the conduction properties can affect the interaction

between  $Ca^{2+}$  and  $PO_4^{3-}$  ions. We noticed that the conductivity measurements of p-FHAp powder preheated at  $800^\circ\text{C}$  were undefined at room temperature due to the very low compactness of sample and to the low ionic conduction at this temperature. In series of crystalline fluorohydroxyapatites  $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$  ( $0 \leq x \leq 2$ ), Maiti et al. [11] have observed the relationship between the proton conductivity and the fluorine quantity incorporated ( $x$ ), which the best conductor has obtained for  $x = 1$  in the range  $250\text{--}500^\circ\text{C}$ . They have proposed a mechanism, where proton can be migrated in a chain of  $-F-OH-F\cdots OH-F$  in apatite structure.

To summarize, the poorly crystalline apatite prepared by rapid precipitation with high surface area shows good proton conductivity at room temperature compared to that of the crystalline apatite. The strong interaction of  $F^-$  ions with the poorly crystalline hydroxyapatite modifies its structural surface, their conduction properties and favored the formation of the more stable F-containing apatites. These results should provide more information for the ionic conduction and the role played by  $F^-$  ions along (OH,F) chains in apatite structure in inhibiting dental caries.

#### 4. Conclusion

Synthetic porous hydroxyapatite has precipitated using a wet chemical method and characterized using both structural and chemical techniques. In this study, we have shown the relationship between the surface changes and the electrical properties of p-HAp material. The increase of humidity in increasing the amount of protons enhances the ionic conductivity at room temperature due to protons mobility in p-HAp structure. Comparing the sharp impedance diagrams of the p-FHAp and of p-HAp minerals, we note that the fluorine substitution in porous hydroxyapatite affects the ionic conductivity related to the hopping of mobile species at the surface of the p-FHAp structure.

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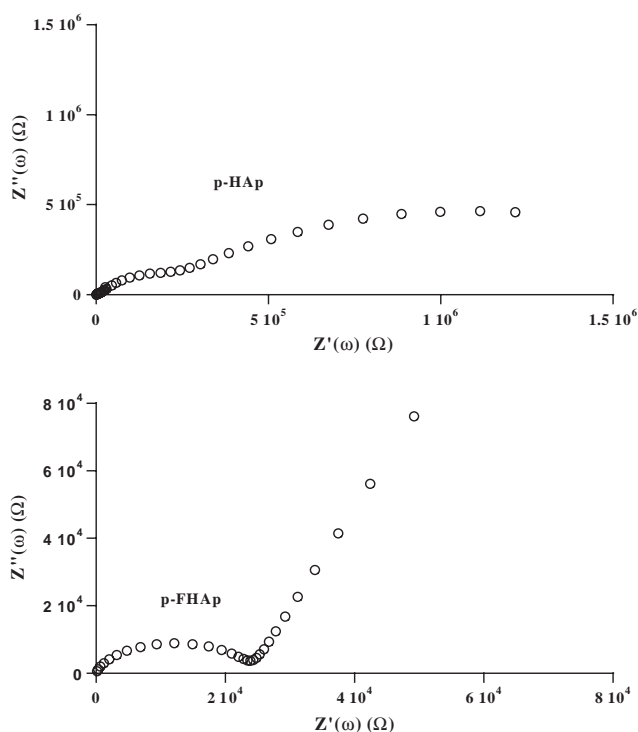


Fig. 5. Comparison of the impedance diagrams between the fluoridated hydroxyapatite p-FHAp and unfluoridated p-HAp materials (70% RH,  $T = 25^\circ\text{C}$ ).

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