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Hydrothermally Synthesized Strontium Peroxyapatite

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Abstract

The current research focuses on peroxide ion incorporation in the structure of strontium hydroxyapatite (SrHAp) by exposure to H_2O_2 in a closed hydrothermal vessel under mild conditions at 130 to 170 °C. Peroxide enriched strontium apatite (SrPerAp) was characterized for structure by X-Ray diffraction, for peroxide content- by permanganometric titration and then viewed by SEM. This study continued from previous work that used 30% H_2O_2 and showed a higher included peroxide content after processing with 50% H_2O_2 at 130 °C 70% of the theoretical peroxide content in apatitic channels of strontium apatite. This is the highest peroxide content incorporated to date and employs a lower temperature than heating at 1300 °C.

Introduction

Hydroxyapatite, (HAp), $[Ca_{10}(PO_4)_6(OH)_2]$ is a common biomaterial, that exhibits the characteristics for further improvement. This has direct implications for its use as a catalyst, LC column, lighting material, chemical sensor [1]. But more important is the wide range of clinical applications - both as coated implants in joint prostheses and as bone grafts for bone regeneration. Bone is a very complicated hierarchical material, fulfilling multiple functions (mechanical, biological and chemical), and has a unique ability for self-repair. The similarity with biological apatites provides almost excellent biocompability, although synthetic HAp can be improved to exhibit an antibacterial property [2].

Therefore, to minimize undesirable incidents of infection, it is necessary to improve the antibacterial properties of HAp. The apatite lattice is very tolerant of substitutions and HAp substitution with Sr is assumed favourable to modify apatite features in medicine [3, 4]. Sr as a trace element is present in the mineral phase of bone and as it enhances the bone strength, stimulates its' healing and formation, reduces bone resorption and lowers the risk of osteoporosis [5].

The other useful reagent for substitution is H_2O_2, also is found in the human body where it isgenerated by phagocytes to modulate the inflammatory processes. H_2O_2 is widely regarded as a harmful cytotoxic agent, but in low concentrations it has an important physiological role in the homeostatic maintenance of normal cell function [6].

Almost forty years ago peroxyapatites, containing oxygen in a -1 oxidation state in the lattice, were prepared at 1000 °C requiring heating for two days [7]. Oxygen enriched apatites were also obtained allowing β tricalcium phosphate to react with boiling H_2O_2 for 15h and then apatite was obtained by precipitation [8]. Later on, peroxyapatite was made by heat treatment at 1200 °C in dry oxygen gas followed by annealing was conducted at 800 °C for 2h [9]. In a very recent study, the formation of strontium peroxy-hydroxyapatite solid solution was investigated at 900-1350 °C in oxygen, air and argon atmosphere [10]. Comparing the previously mentioned methods to the hydrothermal process treatment, used in the current study, the latter is less time-consuming and cheaper. But attention should be paid to the several parameters – such as providing high vapour pressure inside the steel pressure vessels and a constant stirring throughout the hydrothermal process is needed to obtain an evenly coloured powder.

Incorporation of Sr and peroxide in the apatite lattice would impart an antibacterial and anti – inflammatory characteristic. Despite the intense research on hydroxyapatites in the last decades, very little research has been conducted on peroxyapatites and the most appropriate synthesis routes have still not been developed.

Experimental

Strontium hydroxyapatite (SrHAp) powder - used as the host for peroxide ions to create strontium peroxyapatite (SrPerAp) - was obtained by wet chemical method using two solutions. Solution A was prepared from 0.02 mol of $Ca(NO_3)_2{\cdot}4H_2O$, 0.06 mol of $Sr(NO_3)_2$, and 0.4 mol of NH_3 water solution, but solution B consisted of 0.03 mol of $(NH_4)_2HPO_4$ and $(NH_4)_2CO_3$ additive. Analytical grade chemicals were dissolved in deionised water and the two solutions mixed, the obtained suspension was stirred for 10 minutes at room temperature, washed, filtered and dried at 100 ^oC for 30 min. According to Rey *et al.*, SrHAp accommodates higher concentrations of oxygen, therefore 75% substituted SrHAp was chosen for peroxide incorporation in the current research [8].

Synthesis of SrPerAp was performed in a closed system - hydrothermal steel pressure vessel (total volume $2.5{\cdot}10^{-5}$ m^3) at temperatures of 130 ^oC to 170 ^oC, contrary to Kazin who has used very high temperatures. 0.05 g of SrHAp powder and concentrated H_2O_2 solution were loaded in the hydrothermal steel pressure vessel and heated for 3 hours at adjusted temperature, then cooled until room temperature under cool air flow with cooling rate 1,5^o per min. At the first set of experiments 30% wt. H_2O_2 was used to confirm the reproducibility of previous results, but the second set of experiments used 50% wt. concentrated peroxide solution (17.6M H_2O_2) to see if more peroxide could be included. Different volumes of H_2O_2 were further investigated as a means to incorporate more peroxide ions.

The classical permanganometric titration was used to determine the amount of H_2O_2 in peroxyapatite. Permanganometric titration involves two steps – the standardization of $KMnO_4$ solution with oxalic acid standard and the titration of analyte. Peroxide titration is based on the reaction involving MnO_4^- (purple) and Mn^{2+} as the redox couple in acidic medium. Powder of SrPerAp was dissolved in concentrated perchloric acid and then diluted with deionised water. The titration was performed using potassium permanganate solution (0.001 M) until the stoichiometric point was reached as evidenced by the characteristic purple colour of permanganate ions.

The physico-chemical characterisation was followed by other complementary techniques. The obtained powder of SrPerAp was investigated by X-ray diffraction on a D8 Advance diffractometer (Bruker), recorded from 5^o till 60 ^{o} using Cu Kα radiation (λ = 1.54180Å generated at 40 mA and 40 kV). A Scanning Electron Microscope (SEM) recorded views of the powder in a Hitachi S-4800 microscope operated at 7 kV.

Results and Discussion

Peroxide quantification. A classical redox titration quantified the peroxide content in strontium peroxyapatite samples, allowing the report of the peroxide content (expressed as a weight fraction against the theoretical 2.35% content, calculated from the chemical formula $Sr_{7.5}Ca_{2.5}(PO_4)_6O_2$) in a range of ~ 0.36 up to 0.70. The degree of incorporation depended on the temperature of the hydrothermal process. These results confirmed the presence of peroxide ions in the composition of strontium apatite samples treated in H_2O_2 medium.

Due to poor peroxyapatite solubility in water, samples were dissolved in concentrated perchloric acid to liberate the peroxide ions for quantification by permanganometric titration. A small but noticeable gaseous release occurred during sample dissolution in perchloric acid. It was assumed that the released gas is molecular oxygen. That could be explained not only by the presence of such oxygenated species as H_2O_2 or peroxide ions O_2^{2-}, but also by superoxide ions O_2^- as it is reported by other researchers [11]. Both O_2^{2-} and O_2^- show different hydrolysis reactions in acidic medium (Eq. 1, 2).

$$O_2^{2-} + 2\ H_3O^+ \rightarrow H_2O_2 + 2\ H_2O \quad (1)$$

$$2\ O_2^- + 2\ H_3O^+ \rightarrow H_2O_2 + 2\ H_2O + O_2 \quad (2)$$

As the permanganometric titration quantifies only peroxide molecules and peroxide ions O_2^{2-},this redox titration method is not suitable for quantification of superoxide. The O_2^- hydrolysis reaction additionally enriches the content of peroxide determined in strontium peroxyapatite, thus not only peroxide incorporates in the apatitic lattice channels but H_2O_2 molecules could possibly be linked to the apatite surface like water molecules.

At the first step of the current investigation, a 30 %wt. peroxide solution was used for peroxide incorporation into OH channels of strontium hydroxyl-apatite. Previous work showed successful incorporation of peroxide by hydrothermal processing at 150 °C [12]. Results of the previous and the current research were comparable – a difference of 0.02 in the peroxide content lies within the experiment error. The use of 50% wt. H_2O_2, instead of 30% wt., increased the incorporated peroxide content by 35 %, Fig 1.

Permanganometric titration results illustrate an optimum powder/H_2O_2 ratio for inclusion of peroxide ions in strontium apatite. A greater powder loading provided a lower incorporation of peroxide [12], Fig. 2. The resulting peroxide content increased and reached a maximum with a 3.5mL H_2O_2 volume, but greater H_2O_2 volumes led to a decrease in peroxide content, Fig. 2.

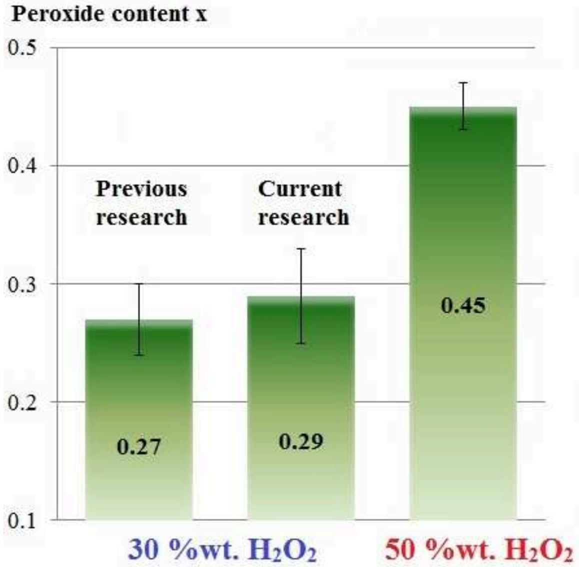

Fig.1. Peroxide content in SrPerAp made at 150 °C depends on H_2O_2 concentration

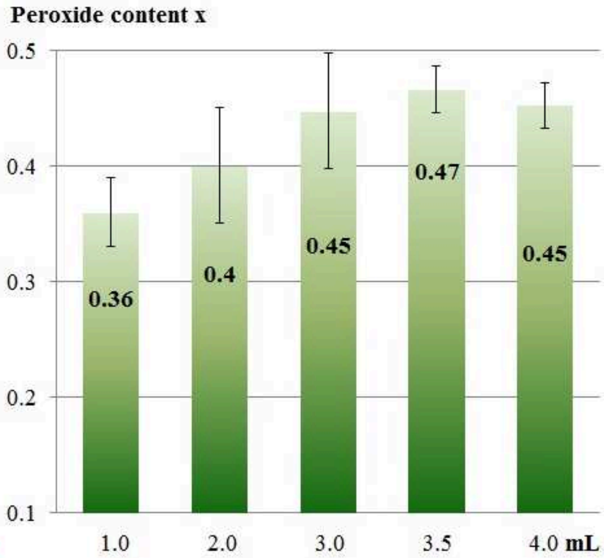

Fig. 2. Peroxide content in SrPerAp (obtained at 150 °C) as a function of H_2O_2 volume

The titrimetric results of peroxide showed greater concentrations at lower processing temperatures; only 36% of the theoretical possible peroxide was included at 170 °C, but twice as much was incorporated at 130 °C, Fig. 3. Processing at 130 °C has included just as much as Kazin [10] was able to include at temperatures in excess of 1200 °C. Other processing methods have only included up to 59% peroxide.

X-Ray Difraction analysis. Starting SrHAp powders showed an amorphous structure in XRD patterns. The XRD pattern (compared with the PDF-2 2012, ICDD) of all powders synthesized at a remarkably lower temperature (150 °C compared to 1200 °C [10]) under vapour pressure displayed diffraction peaks characteristic of well-crystallized peroxyapatite, Fig. 4. This independently confirms that the previously developed method of peroxyapatite synthesis is reproducible at a lower temperature [12].

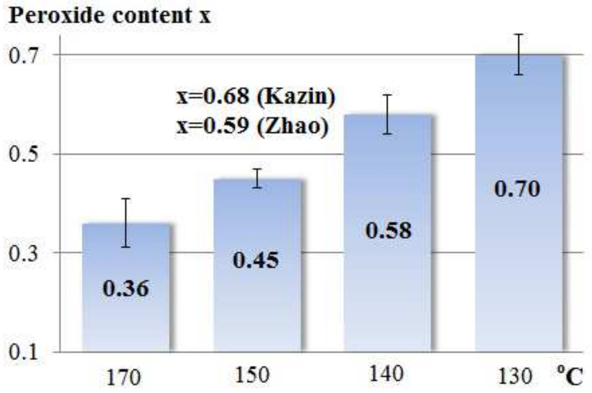

Fig. 3. Peroxide content in SrPerAp as a function of temperature of the hydrothermal process with 50% H_2O_2

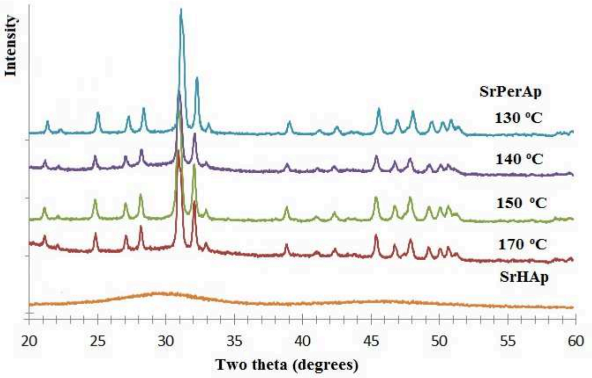

Fig. 4. XRD patterns of SrHAp and SrPerAp

SEM analysis. SEM micrographs of SrPerAp synthesized at 150 °C showed elongated particles formed by joining of individual spherical particles during peroxide inclusion. The average crystal size is 160 nm long and 70 nm wide. The structure of SrHAp before peroxide treatment represented individual spherical particles.

Summary

The use of 50 %wt. H_2O_2 increases the incorporated peroxide content by at least 35 %. The amount of incorporated peroxide ions depends on the amount of H_2O_2 and the treatment temperature. The newly developed synthesis method for making peroxyapatite at lower temperature (even at 130 °C) is suitable, less time consuming and simpler for obtaining well crystallized strontium peroxyapatite, confirmed by X-ray diffraction. In future investigations, more concentrated hydrogen peroxide – 60 %wt. will be explored to see if more peroxide can be included in the lattice.

Acknowledgement

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