J Mater Sci: Mater Med (2008) 19:1787–1791
DOI 10.1007/s10856-007-3337-6

Sonoelectrochemical deposition of calcium phosphates on carbon materials: effect of current density

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Received: 21 February 2007 / Accepted: 21 November 2007 / Published online: 23 December 2007

Abstract Calcium phosphate (CaP) coatings on carbon fabric substrate were produced by sonoelectrodeposition at different current densities (5, 8, 13, 20 and 34 mA/cm^2). The surface morphology and chemical composition of the coatings were characterized by SEM, Raman and FTIR spectra. The results showed that at 5 mA/cm^2 current density, the coating exhibits plate-like morphology, indicating an octacalcium phosphate (OCP) phase was pre-formed in the deposits and then converted into hydroxyapatite (HA). When the current density was increased to 8 mA/cm^2 and higher, the coatings exhibited needle-like morphology corresponding to a HA phase. Furthermore, the sonoelectrodeposited CaP coating exhibited denser and more uniform structures with smaller crystal sizes as the current density increased. Cathodic reaction mechanisms of CaP coatings on carbon in the sonoelectrochemical processes are proposed to explain the different kinds of calcium phosphate obtained.

1 Introduction

Fibrous carbon has previously been considered for use in hard and soft tissue implants due to its exceptional mechanical properties such as flexural and fatigue strength and high strength-to-weight ratio. However, its poor biological activity restricts its use in medical applications and needs to be enhanced [1, 2]. Calcium phosphate (CaP) ceramics, especially hydroxyapatite (HA), have received much attention in the biomedical materials field and have been clinically applied in orthopaedics and dentistry due to their excellent cytocompatibility, bioactivity and osteoconductivity [3]. Carbon fibre-reinforced HA composites, in which the highly cyto-compatible but mechanically weak hydroxyapatite or CaP matrix is reinforced with carbon fibres, is one of the most promising bio-ceramic materials [4], and would therefore be particularly useful in bone re-construction.

The techniques to produce CaP coatings onto implant surfaces have attracted considerable attention in the past decade [3, 5]. Among these methods, electrochemical deposition is especially useful for the production of calcium phosphate coatings on substrates having complicated shapes such as dental implants and orthopaedic fixation devices. A recent and useful approach has been the combination of ultrasound with electrochemistry, i.e. sonoelectrochemistry, which provides various benefits over conventional silent electrodeposition. These are claimed to include increased deposit hardness, enlarged film thickness, improved deposition rates and efficiencies, and greater adhesion of the deposit to the electrode [6–10].

We have previously demonstrated that uniform, bioactive calcium phosphate coatings are produced on carbon fabric surfaces using a sonoelectrochemical method [11]. It is apparent that the sonoelectrodeposition of CaP is sensitive to many factors, including composition of electrolyte, temperature of electrolyte, current loading duration, current density, ultrasound intensity and ultrasound frequency. Preliminary studies indicated that the ionic concentrations

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and temperatures required for HA formation are 10 mM calcium and 6 mM phosphor ions, and 50 °C respectively [12]. These conditions were used for the studies outlined in this paper. The objective of the present study was to investigate the effect of the current density on the morphologies and structures of the calcium phosphate coatings generated using sonoelectrochemical deposition.

2 Experimental methods

An electrochemical cell placed in a Fisher Brand 11002 ultrasonic bath was configured to use carbon fabric as the working electrode and a platinum plate (Advent Research Materials Ltd, UK) as the counter electrode. The carbon fabric (Fig. 1) is the C-Tex product of MAST Carbon Advanced Products Ltd. UK., It has the surface area of 900 m^2/g and surface density 90–140 g/m^2 and its typical applications include wound dressing and medical filters (information provided by MAST company). The schematic of the sonoelectrochemical cell is shown in Fig. 2. The electrolyte used for the fabrication of phosphate coatings was produced by dissolving reagent grade 10 mM $Ca(NO_3)_2 \cdot 4H_2O$ and 6 mM $NH_4H_2PO_4$ in deionised water, using NH_4OH to adjust its pH value to 5.5.

Calcium phosphate deposition was carried out for 45 min at 50 °C and at different current densities, viz. 5, 8, 13, 20 and 34 mA/cm^2. A PGSTAT12 potentiostat was used to maintain constant current density during the process. The intensity and frequency of the ultrasound were set at 2.16 W/cm^2 and 40 KHz respectively.

Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were applied as the main tools for the characterisation of precipitates on the carbon substrate. The phosphate morphology was observed under a JEOL JSM-6310 scanning electron microscope. The FTIR spectra were recorded in the 500–4000 cm^{-1} range, with resolution 4 cm^{-1}, using an AVATAR 320 FTIR Nicolet Golden Gate ZnSe spectrometer. The Raman scattering measurements were performed using a HORIBA Jobin Yvon LabRAM HR dispersive Raman microscope. Excitation was provided by an integrated 633-nm helium-neon laser providing 10 mW at the sample. Spectra were collected through LabSpec software, using an air cooled CCD detector.

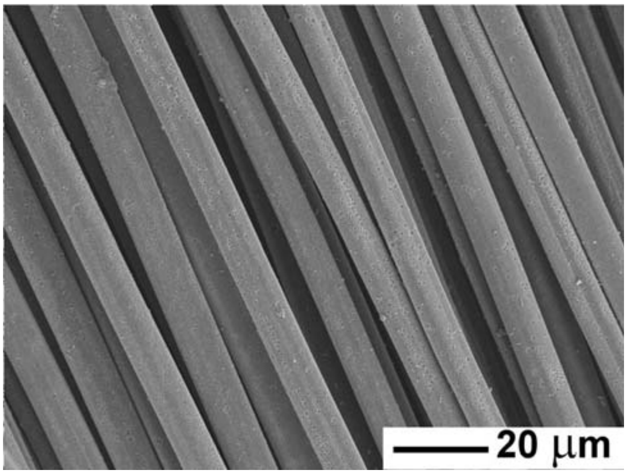


Fig. 1 SEM graph of the as-received carbon fabrics

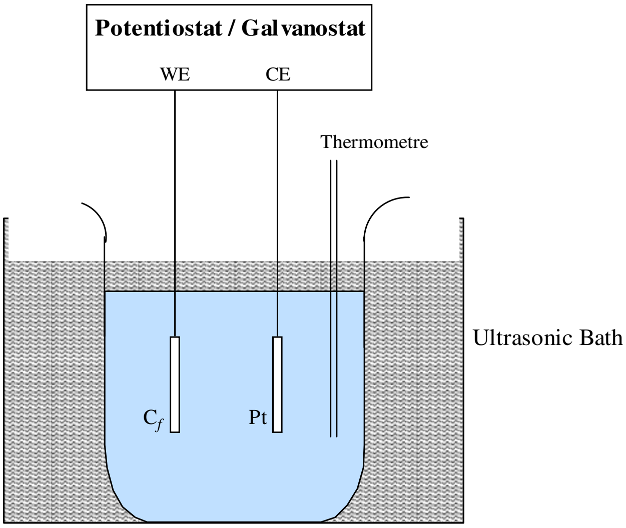


Fig. 2 Schematic diagram of the sonoelectrochemical cell. WE—working electrode, CE—counter electrode, C_f—carbon fabric

3 Results

Figure 3 shows the microstructure morphologies of the CaP formed under different current densities during sonoelectrodeposition. Clearly, the structure of deposited CaP changes with an increase in current density, in terms of both crystal size and crystal shape. When the current density is increased from 5 mA/cm^2 to 8 mA/cm^2, the morphology exhibits a dramatic variation from a plate-like to a mixture of spherical and needle structures. As the current density increases further, beyond 8 mA/cm^2, the coating displays a similar needle-like morphology but with a smaller crystal size. Furthermore, the coatings appear denser and more uniform in the samples subjected to an increased current density.

From the FTIR spectra shown in Fig. 4, the absorption bands at 1026, 962, 602 and 561 cm^{-1} are assigned to vibrations of the phosphate group, PO_4^{3-}. The band at 1026 cm^{-1} emanates from a triply degenerated asymmetric stretching mode vibration, v_3, of PO_4^{3-}. The band at 962 cm^{-1} is assigned to a non-degenerated symmetric stretching mode, v_1, of the PO_4^{3-}, which is typical of HA. The bands at 602 and 561 cm^{-1} contribute to a triply degenerated

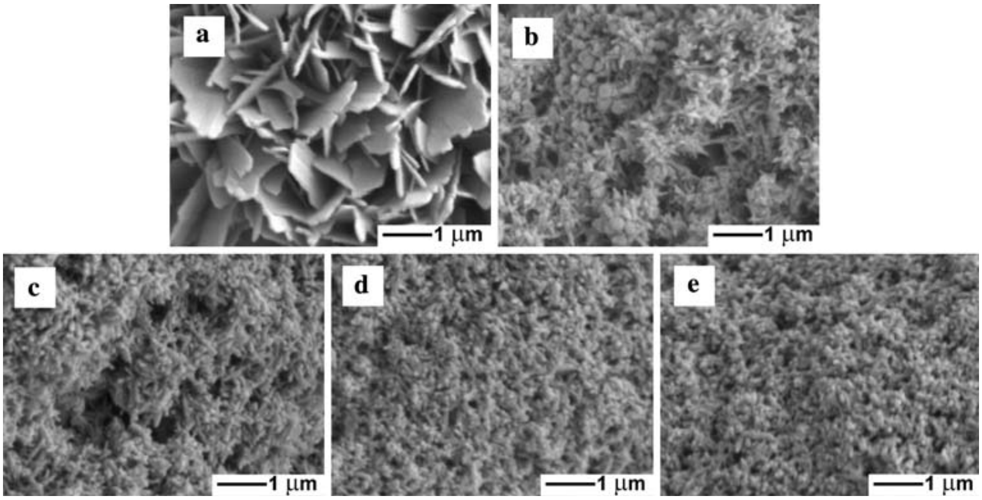


Fig. 3 SEM micrographs of the samples prepared by sonoelectrodeposition under different current densities. (**a**) 5 mA/cm^2; (**b**) 8 mA/cm^2; (**c**) 13 mA/cm^2; (**d**) 20 mA/cm2; and (**e**) 34 mA/cm^2

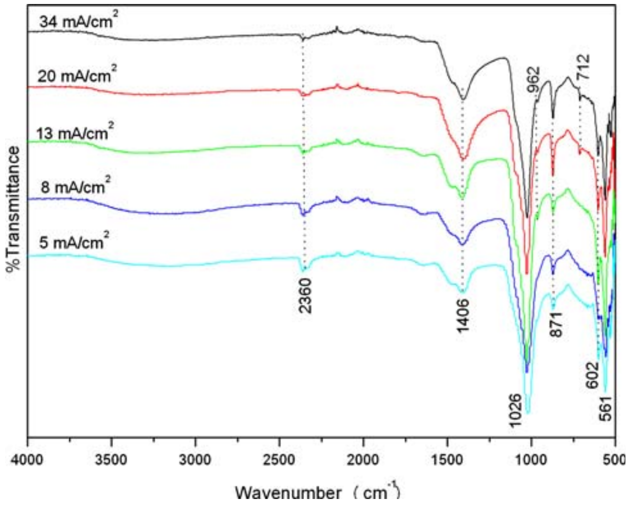


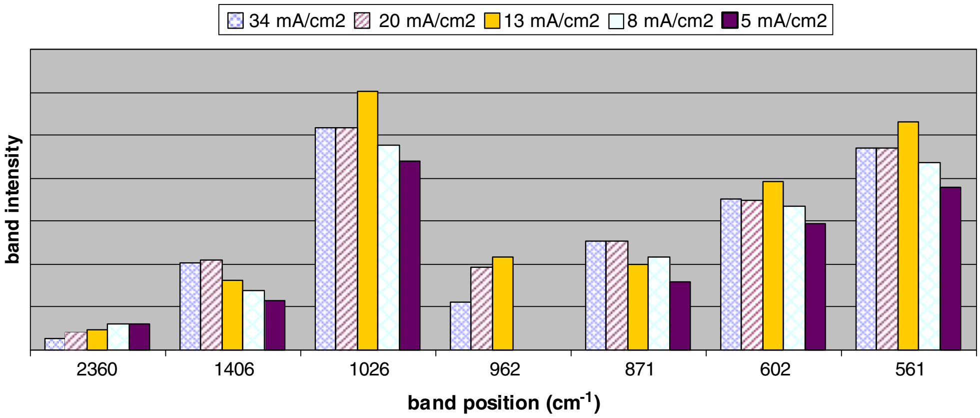
Fig. 4 FTIR spectra of the samples prepared by the sonoelectrodeposition at different current densities

bending mode, v_4, of the PO$_4^{3-}$. Bands around 1406 cm^{-1} are assigned to CO$_3^{2-}$. Bands at 871 cm^{-1} are assigned to HPO$_4^{2-}$ or CO$_3^{2-}$. The band at 2360 cm^{-1} are due to the HPO$_4^{2-}$ in the brushite DCPD. Weak peaks at 712 cm^{-1} have been interpreted as the presence of CaCO$_3$ [13–16].

Whatever is the current density applied, the band intensities relating to PO$_4^{3-}$ (1026, 602 and 561 cm^{-1}) are always stronger than those corresponding to other functional groups. Furthermore, the trend in the band intensities change is the same at all these positions, with the largest values for the samples produced at 13 mA/cm^2 (Fig. 5). As for the band at 962 cm^{-1}, peaks become clearly detectable when the current density is higher than 13 mA/cm^2, inferring the presence of a HA phase in the coatings. In addition, because the band intensity is proportional to the phosphate content [17], it is conceivable that the amount of phosphate in the coatings increases with the current density.

Bands around 1406 cm^{-1} tend to narrow and increase in intensity as the current density is raised, indicating a slightly increased amount of carbonate in the coatings. It is suggested, therefore, that the CaP coatings obtained at a current density higher than 13 mA/cm^2 are carbonate-containing hydroxyapatite, resembling the biological apatite in which CO$_3^{2-}$ replaces PO$_4^{3-}$ in the crystal lattice [13, 14].

Fig. 5 Peak intensities at some particular wavenumbers in FTIR spectra of the samples prepared by the sonoelectrodeposition with different current densities



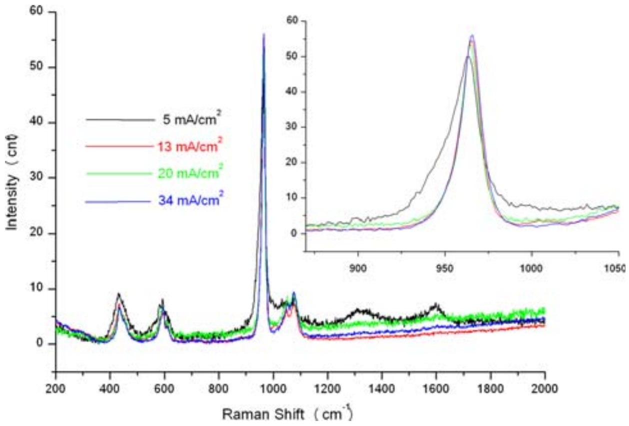


Fig. 6 Raman shifts of the samples prepared by the sonoelectrodeposition with different current densities

Figure 6 exhibits the Raman shifts of the deposited CaP under different current densities in the sonoelectrochemical processes. The bands at 431, 588, 961, and 1074 cm^{-1} correspond to HA [13]. Although the main phase of the formed CaP does not change with the current density (Fig. 6), the 961 cm^{-1} band clearly illustrates the differences in band width, indicating changes in phase/crystallinity [14]. As the current density increases from 5 mA/cm^2 to 13 mA/cm^2, the 961 cm^{-1} band reduces the full width half maximum by a factor of 1/3 and strengthens the intensity slightly. The 961 cm^{-1} band however remains unchanged at the current density greater than 13 mA/cm^2.

4 Discussion

It has been reported that deposits with a plate-like morphology indicate the presence of pre-formed octacalcium phosphate (OCP). However, needle-like structures suggest that apatites are the only formed CaP phases in electrochemical deposition [6, 18]. It is conceivable, therefore, that the lower current density produces pre-formed OCP in the deposits while the greater current density results in apatite deposition. This variation of phase is supposed to introduce the change in bands of Raman spectra as shown in Fig. 6.

The ultrasound used in the present study, 40 KHz in frequency and 2.16 W/cm^2 in intensity, was assumed to induce identical effects considering that the samples and electric cell were located same as possibly during the processes. Therefore the basic mechanisms similar to non-sonicated (silent) electrodeposition remain applicable in the sonoelectrodeposition of CaP coatings. These involve three reaction steps: electrochemical reaction, acid-base reaction and precipitation reaction [3, 5, 14]. The first step is the hydroxyl ion (OH$^-$) generation via the reduction of water at the cathode:

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{1}$$

Meanwhile, reduction of phosphate groups also takes place at the cathode:

$$2H_2PO_4^- + 2e \rightarrow 2HPO_4^{2-} + H_2 \tag{2}$$

$$HPO_4^{2-} + 2e \rightarrow 2PO_4^{3-} + H_2 \tag{3}$$

On the other hand, OH$^-$ generation at the cathode induces acid-base reactions to form PO_4^{3-} and HPO_4^{2-}:

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O \tag{4}$$

$$HPO_4^{2-} + OH^- \rightarrow PO_4^{3-} + H_2O \tag{5}$$

Positive Ca^{2+} ions migrate to the cathodic substrate and react with HPO_4^{2-}, PO_4^{3-} and OH$^-$ ions formed on the carbon surface to synthesise several kinds of CaP phases through precipitation reactions.

It is known that in electrochemical deposition current density controls the rate of OH$^-$ formation and consequently the pH value of the electrolyte at the cathode/solution interface. The formation rates of PO_4^{3-} and HPO_4^{2-} are also controlled by the current density [18, 19].

At lower current density, 5 mA/cm^2, the concentration of OH$^-$ was insufficient to convert all HPO_4^{2-} into PO_4^{3-} by the reaction (5). Only at greater current densities (>10 mA/cm^2), was the concentration of OH$^-$ high enough to convert HPO_4^{2-} into PO_4^{3-}. As a result, the CaP phases formed in the deposits are different at different current densities.

The current density has previously been reported to affect the crystal growth kinetics [5, 20]. Our results support these findings, and suggest that at higher current density, the higher electrostatic force may increase the rate of ion deposition and the amount of ions deposited on the electrode. This infers denser ion distribution per unit area on the electrode surface. Considering that each ion tends to fix into the lattice position, the more fierce crystal growth competition may exist under higher current density, leading to the slower crystal growth. On the basis of the crystallisation theory, the slower crystal growth results in the smaller crystal lattice space indicating the formation of a more compact crystal structure.

5 Conclusions

CaP coatings were prepared by sonoelectrodeposition at different current densities in this study. A plate-like morphology was obtained at a current density of 5 mA/cm^2, indicating that OCP was pre-formed in the deposits and then converted into HA. When the current density was increased to 8 mA/cm^2 and higher, the coatings were present as needle-like morphologies corresponding to a HA phase. The sonoelectrodeposited CaP coating exhibits denser and more uniform structures with smaller crystal sizes as the current density increases. Cathodic reaction mechanisms of CaP coatings on carbon in the sono-electrochemical processes are proposed to explain the different kinds of calcium phosphate obtained.

Acknowledgments The authors gratefully acknowledge the financial support for this project provided through a Marie Curie International Incoming Fellowship (EC Contract MIF1-CT-2004-002913). Donation of carbon fabric by MAST Carbon Advanced Products Ltd (courtesy of Mr A. Blackburn) is also acknowledged.

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