JOURNAL OF
Materials
CHEMISTRY

# Novel electrosynthetic route to calcium phosphate coatings

**G. Helen Annal Therese,[a] P. Vishnu Kamath*[a] and G. N. Subbanna[b]**

[a]*Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India*
[b]*Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India*

Adherent calcium phosphate coatings have been electrosynthesized on stainless steel substrates by cathodic reduction of an aqueous acidified solution of calcium nitrate and diammonium hydrogenphosphate. The as-deposited coating is of the calcium hydrogen phosphate dihydrate which ages in an alkaline buffer to yield adherent coatings of the more useful calcium hydroxyapatite. This simple one step synthesis can be adapted for the fabrication of conformal calcium phosphate coatings on metal endoprostheses and provides an inexpensive alternative to such conventional coating techniques as laser ablation and rf sputtering.

The $Ca(OH)_2$–$H_3PO_4$–$H_2O$ phase diagram is a complex one and consists of over a dozen calcium phosphate compounds with characteristic Ca/P ratios.[1] These materials are structurally and compositionally related to the various calcified tissues of the vertebrates and find application as bone cements,[2] tooth filling materials[3] and as biocompatible coatings for metal endoprostheses.[4] The fabrication of calcium phosphate coatings on metal surfaces is of great technological importance for this last application. Presently such coatings are being fabricated by plasma spraying,[5] rf sputtering,[6] metalorganic CVD,[7] electrophoretic deposition[8] or chemical spraying.[9] In many of these methods, the desired calcium phosphate phase has to be first synthesized in bulk and then processed to obtain an adhesive coating. Some of the processing techniques are energy intensive requiring high power laser or electron beam sources combined with high vacuum chambers. The resulting coating can exhibit significant compositional deviation from the target material and lack of conformity with the substrate. In the course of our continuing work on the electrochemical synthesis of hydroxides,[10] we have developed a simple one step electrochemical method of fabricating adherent calcium phosphate coatings on metal substrates. This technique involves electrogeneration of base by the cathodic reduction of an appropriate solution. By modifying the deposition conditions at least two different calcium phosphate phases could be deposited. In this paper we report the synthesis of adherent coatings of calcium hydrogenphosphate dihydrate [$CaHPO_4 \cdot 2H_2O$] on stainless steel substrates and their subsequent transformation on aging into adherent films of hydroxyapatite [$Ca_5(PO_4)_3(OH)$]. This simple inexpensive technique can be adapted for the fabrication of conformal coatings on metal substrates of different shapes and offers a soft chemical alternative to resource intensive techniques such as laser ablation, plasma etching or rf sputtering.

## Experimental

Diammonium hydrogenphosphate [$(NH_4)_2HPO_4$] crystals dissolved in water (6 g in 50 ml) were added to a standard calcium nitrate solution (1 mol $dm^{-3}$, 62.5 ml). The white precipitate obtained was dissolved in dilute nitric acid and the clear solution made up to 250 ml. This final solution was 0.25 mol $dm^{-3}$ in calcium and has a pH in the range 2.2–2.4. It was then taken in an undivided electrochemical cell. Preweighed stainless steel 316 or Pt foils (6.0 $cm^2$ surface area) were used as cathodes (working electrodes) and a cylindrical platinum mesh (28 $cm^2$ geometric area) was used as the anode (counter electrode). Electrodeposition was carried out galvanostatically at current densities in the range 10–25 mA $cm^{-2}$ for a deposition time 5–60 min. The potential of the working electrode was measured with respect to a saturated calomel electrode as a function of time during deposition, using a high impedance Meco (India) digital multimeter. After deposition the working electrode was rinsed in distilled water and dried to constant mass at 100 °C.

Prior to deposition, the electrodes were washed in detergent and electrochemically cleaned as described elsewhere.[11] The SS 316 (or Pt) flag was polarised anodically for 30 s at 20 mA $cm^{-2}$ in KOH (1 mol $dm^{-3}$) and then cathodically and once again anodically. It was then washed in distilled water and polarised anodically in HCl (1 mol $dm^{-3}$) for 30 s at 20 mA $cm^{-2}$. Stainless steel flags so treated lost $0.13+0.02$ mg $cm^{-2}$ of mass.

Prolonged electrodeposition (2–4 h) resulted in flaking of the coating. Bulk (gram quantities) calcium phosphate could be synthesized by prolonged electrodeposition in a divided cell using potassium nitrate (0.25 mol $dm^{-3}$) as the counter electrolyte. Powders as well as the coatings were aged for one week in buffer solutions of pH 4.0 (0.05 mol $dm^{-3}$ potassium hydrogenphthalate), 7.0 (borate–boric acid) and 9.2 (0.05 mol $dm^{-3}$ borate).

### Characterization

The bulk deposits as well as coatings were characterized by powder X-ray diffractometry (Rigaku-Dmax-1c diffractometer, Cu-K$\alpha$ radiation) and IR spectroscopy (Nicolet Impact 400D FTIR spectrometer, KBr pellets, 4 $cm^{-1}$ resolution). As-prepared and aged coatings were examined by scanning electron microscopy (Cambridge stereoscan S-360, Link AN-10000 EDX analyser) for morphological studies.

## Results

Within 2–3 min of passing current through the electrochemical cell, the growth of a white film on the working electrode could be visually observed. Fig. 1(*a*)–(*d*) shows the coating growth characteristics as a function of different electrodeposition parameters such as deposition time, current density and concentration of the bath solution. From Fig. 1(*a*) and (*b*), it can be seen that the coating growth is linear with time and current density upto a $Q$ (charge passed obtained as a product of current density × time in mA min $cm^{-2}$) value of 750 mA min $cm^{-2}$. On passing further charge, the additional deposits flake off and do not contribute to the coating growth. From Fig. 1(*c*) it is evident that the limiting thickness can be achieved in a reasonable time of 1 h for a 0.1 mol $dm^{-3}$ calcium

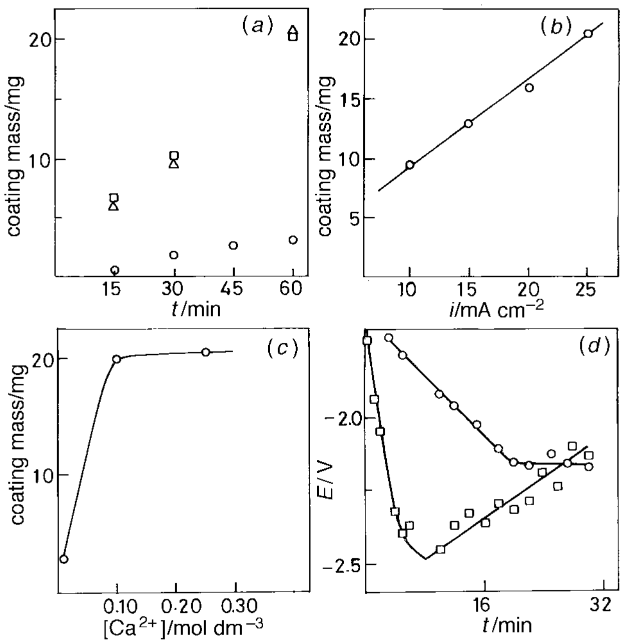

**Fig. 1** (*a*) Coating growth as a function of time at 10 mA cm$^{-2}$ current density from a bath of 0.01 (○), 0.1 (□) and 0.25 (△) mol dm$^{-3}$ respectively in Ca. (*b*) Coating growth as a function of current density from a 0.25 mol dm$^{-3}$ Ca solution; deposition time, *t*, 30 min. (*c*) Coating growth as a function of bath concentration at 10 mA cm$^{-2}$; *t*, 1 h. (*d*) Working electrode potential (*vs.* SCE) as a function of time for 10 mA cm$^{-2}$ (○) and 25 mA cm$^{-2}$ (□); bath concentration 0.25 mol dm$^{-3}$ in Ca.

concentration and the use of a higher concentration does not lead to further growth of the deposit. It is interesting that under a variety of deposition conditions, a limiting coating mass of 20.4 mg (3.4 mg cm$^{-2}$) corresponding to a thickness of 14 µm (estimated from the density of $CaHPO_4 \cdot 2H_2O$, 2.306 g cm$^{-3}$) was obtained reproducibly. Coatings, obtained at a 0.25 mol dm$^{-3}$ calcium concentration at 25 mA cm$^{-2}$, were used for subsequent investigations. A typical plot of the working electrode potential as a function of time during synthesis is shown in Fig. 1(*d*). The potential-time curve shows a sudden change in slope at a *Q* value of 200 mA min cm$^{-2}$ (8 min at 25 mA cm$^{-2}$ or 20 min at 10 mA cm$^{-2}$) indicating a possible change in the reaction leading to the deposit.

Deposits obtained under all the conditions depicted in Fig. 1 were of the same phase. Fig. 2 shows a typical powder X-ray diffraction pattern obtained from an adherent coating and is compared with that of a bulk sample obtained from a prolonged electrodeposition. The prominent *d*-spacings are listed in Table 1 and compared with the powder diffraction pattern assigned in the literature to the phase $CaHPO_4 \cdot 2H_2O$ (PDF: 9–77). It is evident that the coating obtained by us by electrodeposition is of calcium hydrogenphosphate dihydrate. While the relative intensities of the lines in the pattern of the bulk compound match approximately with the standard pattern, the intensities of the lines in the pattern recorded for the coating do not. This disagreement could be due to oriented growth of the deposit in the $22\bar{1}$ and 220 directions.

The IR spectrum of the coating is shown in Fig. 3. The spectrum shows a broad band in the region 3600–3000 cm$^{-1}$ comprising four sharp features, which have been assigned to the OH stretching vibrations of the intercalated water and the hydroxy group of the phosphate ion. The 1400–700 cm$^{-1}$ region shows features characteristic of the $[HPO_4]^{2-}$ ion. Similar spectra with the detailed assignments have been described elsewhere[12] and are considered to be characteristic of the hydrogenphosphate $[HPO_4]^{2-}$ ion. On heating to 250 °C, it is known that the material undergoes dehydration to monetite $[CaHPO_4]$. Accordingly, the major OH vibrations

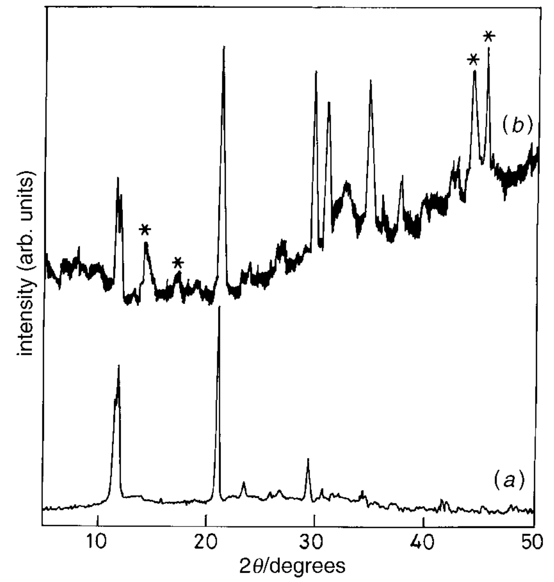

**Fig. 2** X-Ray diffraction pattern of an electrosynthesized powder sample of $CaHPO_4 \cdot 2H_2O$ (*a*) compared with that of the as-deposited coating (*b*). Features marked by asterisks are due to the substrate.

**Table 1** Powder X-ray diffraction data of electrosynthesized (es) calcium phosphate phases compared with the standard pattern of calcium hydrogenphosphate dihydrate phase

| | *d*/Å | | |
|---|---|---|---|
| *hkl* | $CaHPO_4 \cdot 2H_2O$ (PDF:9-77) | es-powder | es-film |
| 020 | 7.570 | 7.513 | 7.692 |
| 021 | 4.240 | 4.237 | 4.248 |
| 040 | 3.800 | 3.792 | 3.789 |
| 041, 111 | 3.050 | 3.050 | 3.051 |
| $22\bar{1}$ | 2.928 | 2.934 | 2.933 |
| $11\bar{2}$ | 2.855 | 2.853 | 2.848 |
| 220, $15\bar{1}$ | 2.623 | 2.623 | 2.624 |
| 060 | 2.532 | 2.539 | 2.538 |
| $24\bar{1}$ | 2.434 | 2.431 | 2.423 |
| 151 | 2.172 | 2.174 | 2.170 |
| $24\bar{2}$ | 2.148 | 2.150 | 2.146 |

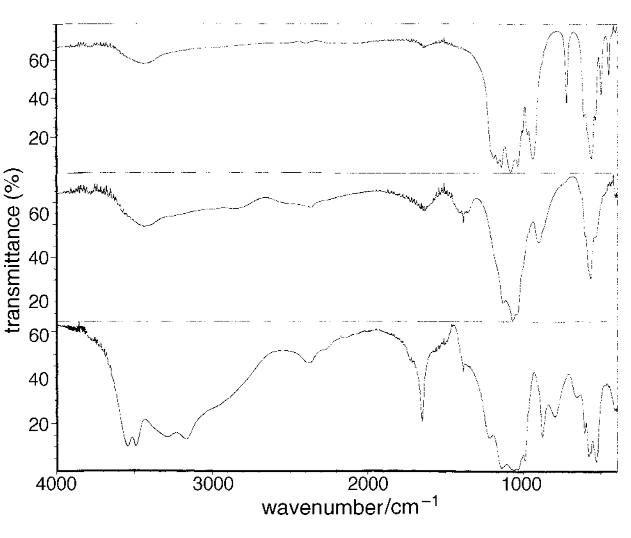

**Fig. 3** IR spectrum of the as-prepared coating (bottom panel) compared with that of the coating after heat treatment at 250 °C (middle panel) and 750 °C (top panel)

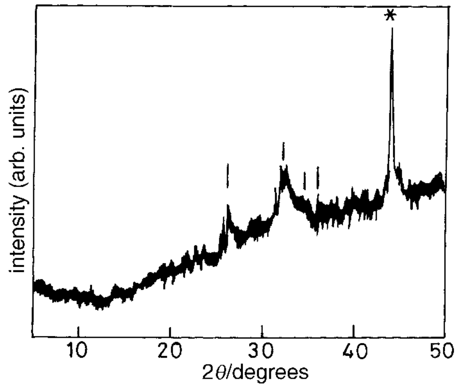

**Fig. 4** X-Ray diffraction pattern of the electrosynthesized $CaHPO_4 \cdot 2H_2O$ coating after ageing for 1 week in a pH 9.2 buffer. Vertical lines show the peak positions expected for calcium hydroxyapatite. Feature marked by an asterisk is due to the substrate.

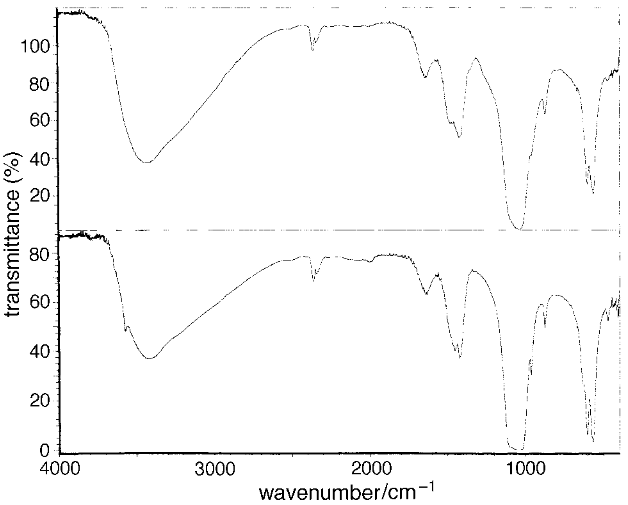

**Fig. 5** IR spectrum of the aged $CaHPO_4 \cdot 2H_2O$ coating (upper panel) compared with that of an authentic sample of calcium hydroxyapatite (lower panel)

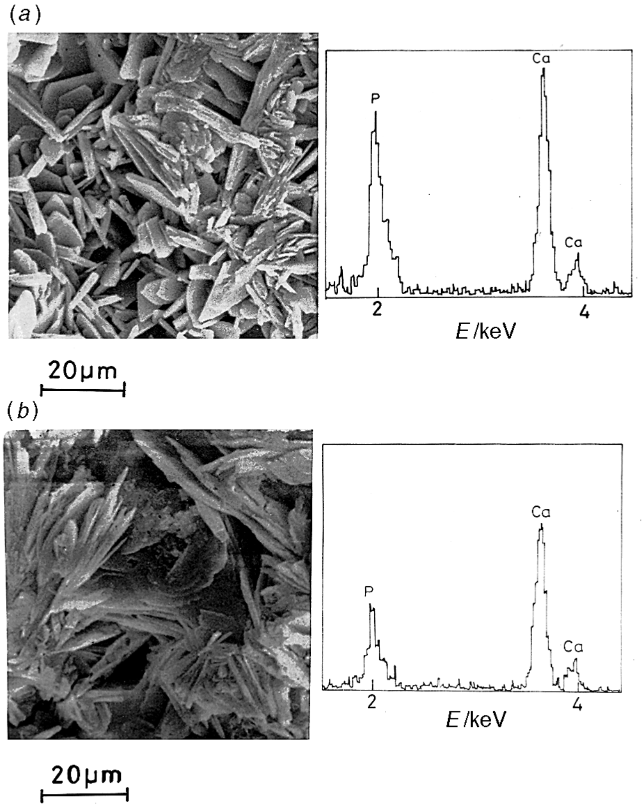

**Fig. 6** Scanning electron micrographs and EDXA data of as-prepared (*a*) and aged (*b*) coatings of $CaHPO_4 \cdot 2H_2O$

are lost in the heat treated sample (Fig. 3) while the characteristic vibrations of the $[HPO_4]^{2-}$ ion are retained. On heating up to 750 °C the sample shows changes in the region 1400–700 $cm^{-1}$, which correspond to the formation of the pyrophosphate group, in keeping with the observations made in the literature.[13] It is therefore clear that both in terms of IR spectra and thermal behaviour the material electrodeposited in the coating behaves as expected of the calcium hydrogenphosphate dihydrate phase. The coatings were aged in buffers of different pH. It was found that they have no chemical stability at pH 4.0 and are completely stripped off the substrate. The coating aged in pH 7.0 undergoes little transformation, while in pH 9.2 the coating transformed into a poorly crystalline apatite-like phase. Fig. 4 and 5 show the X-ray diffraction data and the IR spectra, respectively, for the aged coating and compare it with the data obtained from a standard hydroxyapatite sample. It is evident that the aged coating consists of a apatite-like phase containing some carbonate. Carbonate substitution is typical of self-made apatites obtained from mildly alkaline medium.[14] In fact it is the hydroxyapatite coating that is of value in endoprostheses and the formation of this phase in the adherent coatings is of tremendous technological significance. In Fig. 6 we show the scanning electron micrographs of the as-prepared and aged coatings together with the EDXA data to establish the Ca/P ratio before and after aging. It is evident from the micrographs that the substrate has been completely covered. The morphology of the particles in the as-prepared and aged coatings is acicular. The EDXA data of the as-prepared coating show that the lines due to Ca and P are comparable in intensity as expected of the calcium hydrogenphosphate dihydrate phase. On ageing the Ca/P ratio increases close to 1.6, the value expected for the hydroxyapatite phase. The morphology observed by us can be compared with the angular/nodular morphology of the commercial hydroxyapatite, the glassy surface of plasma sprayed coatings[5] and the cube-like particles observed by MOCVD.[7]

## Discussion

The electrosynthesis of metal hydroxides by the cathodic reduction of nitrates has been practiced for many years especially in the battery industry, for the electrodeposition of nickel hydroxide.[15] We have extended this technique to the synthesis of a wider variety of phases such as the layered double hydroxides.[10] The cathodic reduction reactions of nitrate containing solutions have been discussed by Switzer[16] and by Matsumoto *et al.*[17] The reactions are of two types:

(1) Nitrate reduction

$$NO_3^- + 2e + H_2O \rightarrow NO_2^- + 2OH^- \quad E^\circ = 0.01 \text{ V}$$

(2) Hydrogen evolution

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \quad E^\circ = -0.83 \text{ V}$$

Both these reactions generate hydroxide ions, causing a rise in the pH of the bath solution. This increase in pH is experienced only close to the electrode and not in the bulk leading to the electrodeposition of a hydroxide or an appropriate phase at the electrode. In the present instance, the bath consists of $Ca^{2+}$ and $[HPO_4]^{2-}$ ions and an increase in the pH leads to deposition of the calcium hydrogenphosphate dihydrate phase. The potential of the working electrode varies with time linearly upto a $Q$ value of 200 mA min $cm^{-1}$ showing that a single reaction is taking place. Above this $Q$ value, the potential–time curve discontinuously changes signifying complete coverage of the metal, as verified by SEM data, and further deposition takes place on a calcium phosphate rather than a metal surface.

The preferred coatings on metal endoprostheses are of the hydroxyapatite (HAP). The formation of the hydroxyapatite phase on ageing in mildly alkaline buffer without any deleterious changes in the morphology, or loss of adhesion, enhances the potential of this novel electrodeposition technique for practical applications.

Two of us G.H.A.T. and P.V.K. thank the Department of Science and Technology, Government of India for financial support. The authors thank the Department of Physics, Bangalore University for providing powder X-ray diffraction facilities under the Departmental Research Support programme of the University Grants Commission, India.

## References

1 F. C. M. Drissens, M. G. Boltong, O. Bermudez, J. A. Planell, M. P. Ginebra and E. Fernandez, *J. Mater. Sci. Mater. Med.*, 1994, **5**, 164.
2 B. R. Contantz, B. M. Barr, J. Quiaoit, I. C. Ison, J. T. Baker, L. McKinny, S. B. Goodman, D. R. Summer and S. Gunasekeran, *Fourth World Biomaterial Congress*, Berlin, 1992, Abstract 56.
3 K. Yamashita and T. Kanazawa in *Inorganic Phosphate Materials* ed. T. Kanazawa, Elsevier, Amsterdam, 1989.
4 J. I. Huaxia, C. B. Ponton and P. M. Marquis, *J. Mater. Sci. Mater. Med.*, 1992, **3**, 281.
5 D. M. Liu, H. M. Chou and J. D. Wu, *J. Mater. Sci. Mater. Med.*, 1994, **5**, 147.
6 E. Rukenstein, S. Gourisankar and R. E. Baier, *J. Colloid Interface Sci.*, 1983, **96**, 245.
7 G. Spoto, E. Ciliberto and G. C. Allen, *J. Mater. Chem.*, 1994, **4**, 1849.
8 W. V. Raemdonk, P. Ducheyne and P. D. Meester, *J. Am. Ceram. Soc.*, 1984, **67**, 381.
9 R. Morancho, J. Ghommidh, G. Constant, B. Moyen, J. J. Comtet, R. Santini and B. Buttazzoni, *Mater. Sci. Monogr.*, 1983, **17**, 97.
10 L. Indira and P. V. Kamath, *J. Mater. Chem.*, 1994, **4**, 1487.
11 D. A. Corrigan and R. M. Bendert, *J. Electrochem. Soc.*, 1989, **136**, 723.
12 J. Chen, S. Natarajan, P. A. Wright, R. H. Jones, J. M. Thomas, C. R. A. Catlow and R. P. Townsend, *J. Solid State Chem.*, 1993, **103**, 519.
13 N. W. Beebe and J. S. Kittelberger, *J. Phys. Chem.*, 1975, **79**, 853.
14 E. A. P. DeMaeyer, R. M. H. Verbeeck and D. E. Naessens, *Inorg. Chem.*, 1993, **32**, 5709.
15 E. J. McHenry, *Electrochem. Technol.*, 1967, **5**, 275.
16 J. A. Switzer, *Am. Ceram. Soc. Bull.*, 1987, **66**, 1521.
17 Y. Matsumoto, T. Morikawa, H. Adachi and J. Hombo, *Mater. Res. Bull.*, 1992, **27**, 1319.

*Paper* 7/06079C; *Received* 19*th August*, 1997