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Calcium and titanium release in simulated body fluid from plasma electrolytically oxidized titanium

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Abstract The release of titanium and calcium species to a simulated body fluid (SBF) at 37°C has been investigated for titanium treated by dc plasma electrolytic oxidation (PEO) in three different electrolytes, namely phosphate, silicate and calcium- and phosphorus-containing. The average rate of release of titanium over a 30 day period in immersion tests, determined by solution analysis, was in the range $\sim$1.5–2.0 pg cm^{-2} s^{-1}. Calcium was released at an average rate of $\sim$11 pg cm^{-2} s^{-1}. The passive current densities, determined from potentiodynamic polarization measurements, suggested titanium losses of a similar order to those determined from immersion tests. However, the possibility of film formation does not allow for discrimination between the metal releases due to electrochemical oxidation of titanium and chemical dissolution of the coating.

1 Introduction

Titanium is an important biofunctional material, with its durability [1, 2], low material dissipation [3–5] and anti-bacterial properties [6–10] enabling load-bearing applications in dental implants and orthopaedic prostheses. With a large, expanding market and use of implants in younger patients, increasing longevity of implants is a paramount demand. A major factor affecting longevity is the corrosion resistance of the implant material and related metal release to surrounding tissues. Consequently, there has been much interest in the electrochemical behaviour of titanium and titanium alloys in biological media, such as simulated body fluids (SBFs), artificial saline and phosphate buffer solutions. Investigations have also included the influences of coatings, which can accelerate healing and cell integration, as well as improve tribological properties.

Recently, ceramic-like coatings on titanium, produced by plasma electrolytic oxidation (PEO), have been developed with calcium- and phosphorus-enriched surfaces [11–15]. PEO is an electrolytic process, occurring on the anode above the dielectric breakdown voltage and accompanied by gas microdischarges on the coating surface. It usually results in coatings of the order 10 μm thickness containing anatase, rutile and amorphous phase, with significant quantities of incorporated species derived from the electrolyte solute. The anion and cation species of the electrolyte can influence the local compositions of the coatings and the proportions of amorphous and crystalline phases [16], as well in vitro cell responses and metal release to SBF [17]. The present study compares titanium and calcium release in SBF, determined using immersion tests and solution analyses by inductive coupled plasma optical emission spectroscopy (ICP-OES), from PEO coatings produced in three electrolytes. The findings are compared with results of potentiodynamic polarization measurements.

2 Materials and methods

Specimens of dimensions 3 × 2 cm were cut from 250 μm-thick, 99.6% titanium foil (3000 Fe, 750 O, 55 N and <800 C (ppm)), degreased in ethanol and acetone and then rinsed in de-ionized water. Following subsequent chemically polishing for $\sim$25 s in a 1:3 by volume mixture

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Table 1 Sparking voltage (U_{sp}), final voltage (U_f) and coating thickness (t) for PEO of titanium at 20 mA cm^{-2} for 20 min in electrolyte I, II or III at 20°C

Electrolyte	U_{sp} (V)	U_f (V)	*t* (µm)
I—0.026 M Na_3PO_4	285	440	5.7
II—0.01 M KOH + 0.005 M Na_2SiO_3	220	370	5.4
III—0.01 M $CaHPO_4$ + 0.01 M $Na_6P_6O_{18}$	320	490	18.2

of hydrofluoric acid (40–48%) and nitric acid (70%) at room temperature, the specimens were rinsed in de-ionized water, dried and masked with lacquer to produce a working area of 3 cm^2. PEO was later carried out galvanostatically for 1,200 s at 20 mA cm^{-2} in one of the three electrolytes listed in Table 1 using a regulated DC power supply Good Will 0.6A/1,200 V and double-walled cell with re-circulating cooling system that maintained the temperature of the electrolyte at 20°C. The cathode was made of type 430 stainless steel. After PEO, the specimens were rinsed in de-ionized water and dried in warm air. The voltage-time responses were recorded during anodizing: Table 1 lists the voltages when sparking was first visible and the voltages at the termination of PEO. Coating thicknesses were measured by the eddy current method, using a Fischerscope Permascope instrument. The average of 10 measurements on each coating is given in Table 1; the standard deviation was ~0.5 µm.

Coated substrates were exposed to a conventional simulated body fluid (SBF) (Table 2) for times up to 30 days. The SBF was calcium-free due to interest in measuring calcium release from coatings. Each specimen was immersed in 30 cm^3 of SBF, in a tightly-sealed container, at 37°C. Following exposures to SBF, specimens were rinsed in de-ionized water and dried in warm air. The test solutions were acidified with 2 cm^3 of hydrochloric acid to dissolve any precipitated titanium hydroxide then analysed by ICP-OES. Calcium content in the certified AR grade hydrochloric acid was 0.035 ppm, titanium impurity was not present.

Table 2 Reagents per 1,000 cm^3 for simulated body fluid

Reagent	Purity, %	Amount
NaCl	>99.5	8.036 g
$NaHCO_3$	>99.5	0.352 g
KCl	>99.5	0.225 g
$K_2HPO_4 \cdot 3H_2O$	>99.0	0.230 g
$MgCl_2 \cdot 6H_2O$	>98.0	0.311 g
1.0 M HCl	–	40 cm^3
Na_2SO_4	>99.0	0.072 g
TRIS[a]	>99.9	6.063 g
1.0 M HCl[b]	–	~0.2 ml

[a] Tris(hydroxylmethyl)aminoethane

[b] To adjust pH to 7.40 at 36.5°C

Analyses were carried out using a VARIAN Vista MPX instrument operated at a power of 1.2 kW, with a plasma flow of 15 l min^{-1}, replica time of 20 s, sample flow rate of 0.8 ml min^{-1} and argon carrier gas. Calibrations were made using de-ionized water and 2.5 and 5 mg l^{-1} standard solutions of titanium. Three emission wavelengths were employed for measurements, 334.188, 334.941 and 336.122 nm. Calcium concentrations were also determined for electrolyte III (Table 1), with calibrations using deionized water and 10 and 20 mg l^{-1} standard solutions of calcium and analyses at emission wavelengths of 393.366, 396.847 and 422.673 nm. Blank solution (deionised water) was included into the batch measurements as a reference.

Potentiodynamic polarization measurements in naturally aerated SBF at 37°C were made on chemically-polished titanium and PEO-coated titanium, for the latter both before and after immersion tests in SBF. Potentials were measured with respect to a saturated calomel electrode (SCE), kept at 20°C and connected to the cell by a salt bridge. A platinum mesh was used as the auxiliary electrode. The open-circuit potential (OCP) was stabilized firstly for 20 h immersion in the SBF, then the specimen was polarized at a rate of 0.2 mV s^{-1} from −400 to 1,500 mV relative to the OCP.

Plan views and cross-sections of coatings were examined by scanning electron microscopy (SEM), using an Amray 1810 instrument operated at 20 kV, with energy-dispersive X-ray (EDX) analysis facilities. Cross-sections were prepared by grinding through successive grades of silicon carbide paper, with final polishing to a 1 µm diamond finish. Coatings were also examined by X-ray diffraction (XRD) using a Philips X'Pert-APD (PW 3710) diffractometer, at a scanning speed of 0.01 s^{-1} for a scan range of 2θ from 5° to 70°. The X-ray generator was set to 50 kV and 40 mA, with XRD patterns recorded using Cu K_α radiation.

3 Results

3.1 PEO treatment

The voltage-time responses for PEO treatment of the titanium in the three electrolytes are compared in Fig. 1. For electrolyte III, containing calcium and phosphorus species, the voltage rises approximately linearly followed by a progressively reducing slope, particularly above the sparking voltage (labelled U_{sp}), to a final region of slow voltage rise. Oscillations in voltage accompany the development of the coating. Similar trends were found for

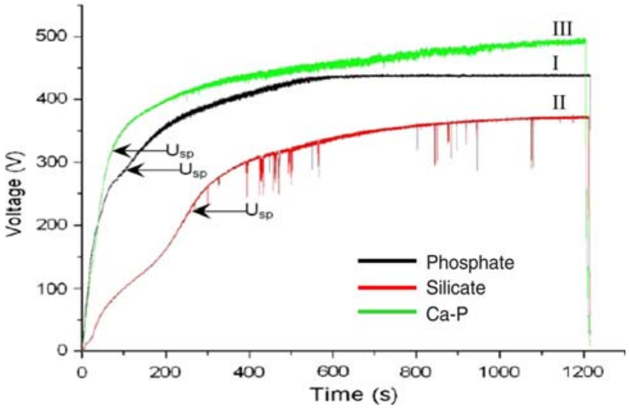

Fig. 1 Voltage-time responses for PEO treatment of titanium at 20 mA cm^{-2} in electrolytes I (phosphate), II (silicate) and III (calcium- and phosphorus-containing) at 37°C

electrolytes I and II, containing phosphate and silicate respectively but with inflections, near the sparking voltage and in the initial voltage rise respectively, which result in a reduced time of sparking.

3.2 Morphologies and compositions of coatings

Figure 2a and d show scanning electron micrographs of the initial coating formed in phosphate-containing electrolyte I and after immersion in the SBF for 30 days. The pore-covered coating surfaces that are typical of PEO, with pores in the micron-size range, were not affected significantly by the SBF at the resolution of the images; any differences in porosity reflect the inherent variability of PEO coatings. EDX area analyses disclosed atomic ratios of P:Ti in the range 0.18–0.21 and of O:Ti ~2.1 (Table 3). All the coatings were ~4–5 μm-thick, independent of exposure to SBF. Thirteen EDX spot analyses carried out in the outer, middle and inner part of cross-sections of coatings immersed for 10, 20 and 30 days in c-SBF indicated P:Ti atomic ratios in the range 0.11–0.24; with no significant dependence on position or immersion time the average ratio was 0.20. Three other analyses yielded reduced ratios in the range 0.03–0.08. Chlorine, derived from SBF, was detected in all parts of the coating at a concentration of ~1.0 at.%.

The surface of the coating formed in silicate-containing electrolyte II revealed numerous nodules in addition to pores, with negligible influence of SBF (Fig. 2b, e). EDX area analyses indicated Si:Ti atomic ratios in the range 0.63–0.95 (Table 3), with average O:(Si + Ti) ratios of ~2.1. In cross-sections, the coatings were 4–5 μm thick, with EDX spot analyses disclosing enrichment of silicon toward the surface. The average ratio of Si:Ti near the surface was ~0.98, compared with ~0.75 in the middle region of the coating. Potassium was detected independent of exposure to SBF at a concentration of ~0.2 at.%. Chlorine was also present for the immersed coatings at a concentration of ~1.2 at.%.

The coatings produced in calcium- and phosphorus-containing electrolyte III revealed a coarser surface morphology than the ones produced using the previous electrolytes (Fig. 2c, f). Although the morphology was not noticeably affected by SBF, EDX area analyses indicated that the Ca:Ti atomic ratios decreased from an initial value of 0.36–0.19 after 30 days immersion, with a corresponding decrease in the Ca:P ratio from 0.31 to 0.23 (Table 3). The P:Ti ratio was in the range 0.83–1.19, which is higher than that of coatings produced in electrolyte I. The coatings were between 10 and 20 μm thick (Fig. 3), with EDX spot analyses confirming major depletion of calcium. XRD indicated a mainly anatase and amorphous material in coating I, while coating II also rutile. Coating III was almost entirely amorphous, with a small peak of anatase (Fig. 4).

3.3 Immersion and potentiodynamic polarization tests

Titanium release from coated titanium during immersion in SBF revealed similar trends for all electrolytes, with titanium release of 0.3–0.4 μg cm^{-2} after 10 and 20 days of immersion, followed by an increase to 4–5 μg cm^{-2} after 30 days (Fig. 5). Calcium release from the coating produced in electrolyte III was 5–10 times higher than titanium release at corresponding times, increasing from 6 to 25 μg cm^{-2} between 10 and 30 days. The average rates of titanium release over the 30 day period were 1.52, 1.69 and 1.99 pg cm^{-2} s^{-1} for coatings produced in electrolytes I, II and II, respectively.

Potentiodynamic polarization curves revealed an OCP of ~−0.270 mV (SCE) for chemically polished titanium in naturally aerated SBF, with passive current densities of ~1 μA cm^{-2} above ~500 mV(SCE), reducing to ~10 nA cm^{-2} near the OCP (Fig. 6a). The decreasing current density is possibly related to changes in the valence state of titanium or the morphology of the passive film. Following PEO, the passive current densities were also about 10 nA cm^{-2} near the OCP, but at the region above 500 mV (SCE) they were significantly reduced by factors of about 10 for coatings I and II, and by a factor of ~100 for coating III, compared with chemically polished titanium. The OCPs of −192, −140 and −90 mV (SCE) for electrolytes I, II and III respectively, further increased to ~15, 45 and 4 mV after 30 days exposure to SBF, i.e. ~300 mV above that of uncoated titanium (Fig. 6b–d). Correspondingly, the passive current densities decreased by up to a factor of ~3. The rise in passive current densities above ~1,000 mV (SCE) was possibly due to oxygen evolution and rupture of the coating. The equilibrium potentials for the reactions

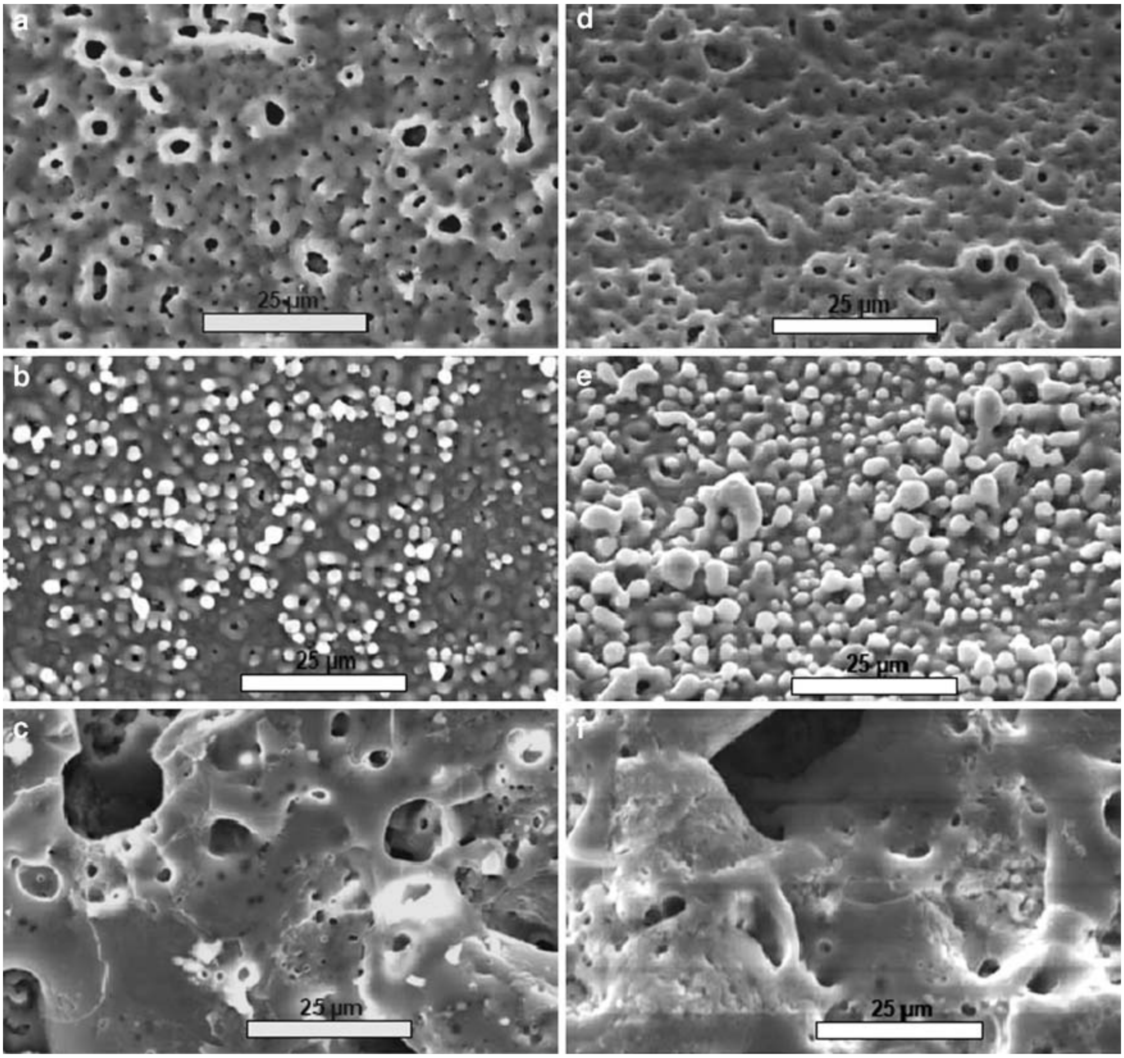

Fig. 2 Scanning electron micrographs of plan views of the coatings formed on titanium for 1,200 s at 20 mA cm^{-2} in electrolytes I (phosphate), II (silicate) and III (calcium- and phosphorus-containing) respectively at 37°C: **a**, **b**, **c** before immersion in SBF, **d**, **e**, **f** after immersion for 30 days in SBF at 37°C

Table 3 EDX area analysis of the coatings formed at 20 mA cm^{-2} for 20 min, before and after immersion in SBF

Electrolyte	Immersion time, days	P:Ti ratio	Si:Ti ratio	Ca:Ti ratio	Ca:P ratio	O:Ti
I	0	0.20	–	–	–	1.97
	10	0.20	–	–	–	2.27
	20	0.18	–	–	–	2.44
	30	0.21	–	–	–	2.27
II	0	–	0.81	–	–	2.80
	10	–	0.63	–	–	2.92
	20	–	0.64	–	–	3.13
	30	–	0.95	–	–	3.95
III	0	1.19	–	0.36	0.31	5.10
	10	0.79	–	0.20	0.26	4.18
	20	0.85	–	0.23	0.28	4.20
	30	0.83	–	0.19	0.23	4.50

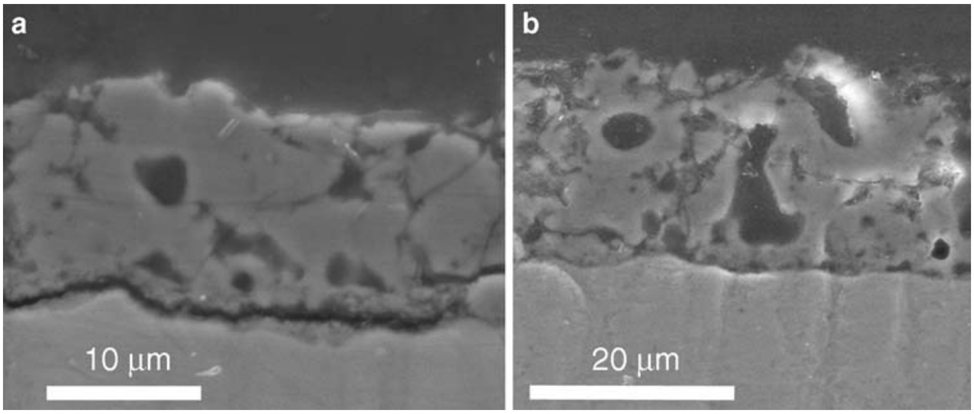

Fig. 3 Scanning electron micrographs of the cross-section views of the coating formed on titanium for 1,200 s at 20 mA cm^{-2} in electrolyte III (calcium- and phosphorus-containing) at 37°C: **a** before immersion in SBF, **b** after immersion for 30 days in SBF at 37°C

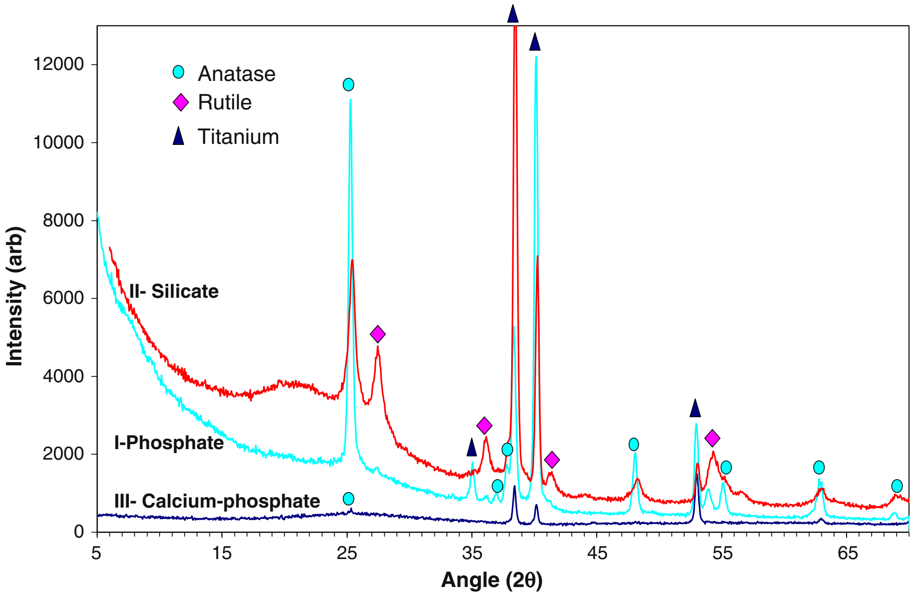

Fig. 4 X-ray diffraction pattern of the coating formed on titanium for 1,200 s at 20 mA cm^{-2} in electrolyte I–III

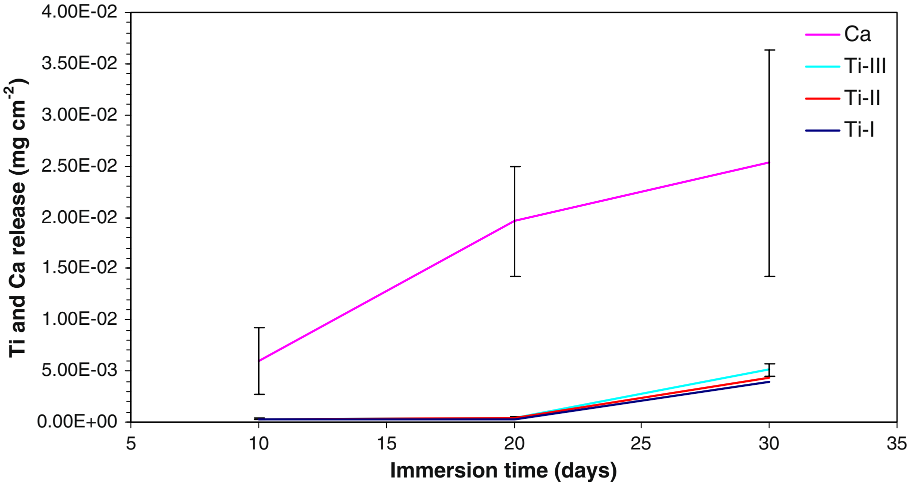

Fig. 5 Titanium and calcium release from coatings formed in electrolytes I (phosphate), II (silicate) and III (calcium- and phosphorus-containing) at 37°C during immersion in SBF at 37°C

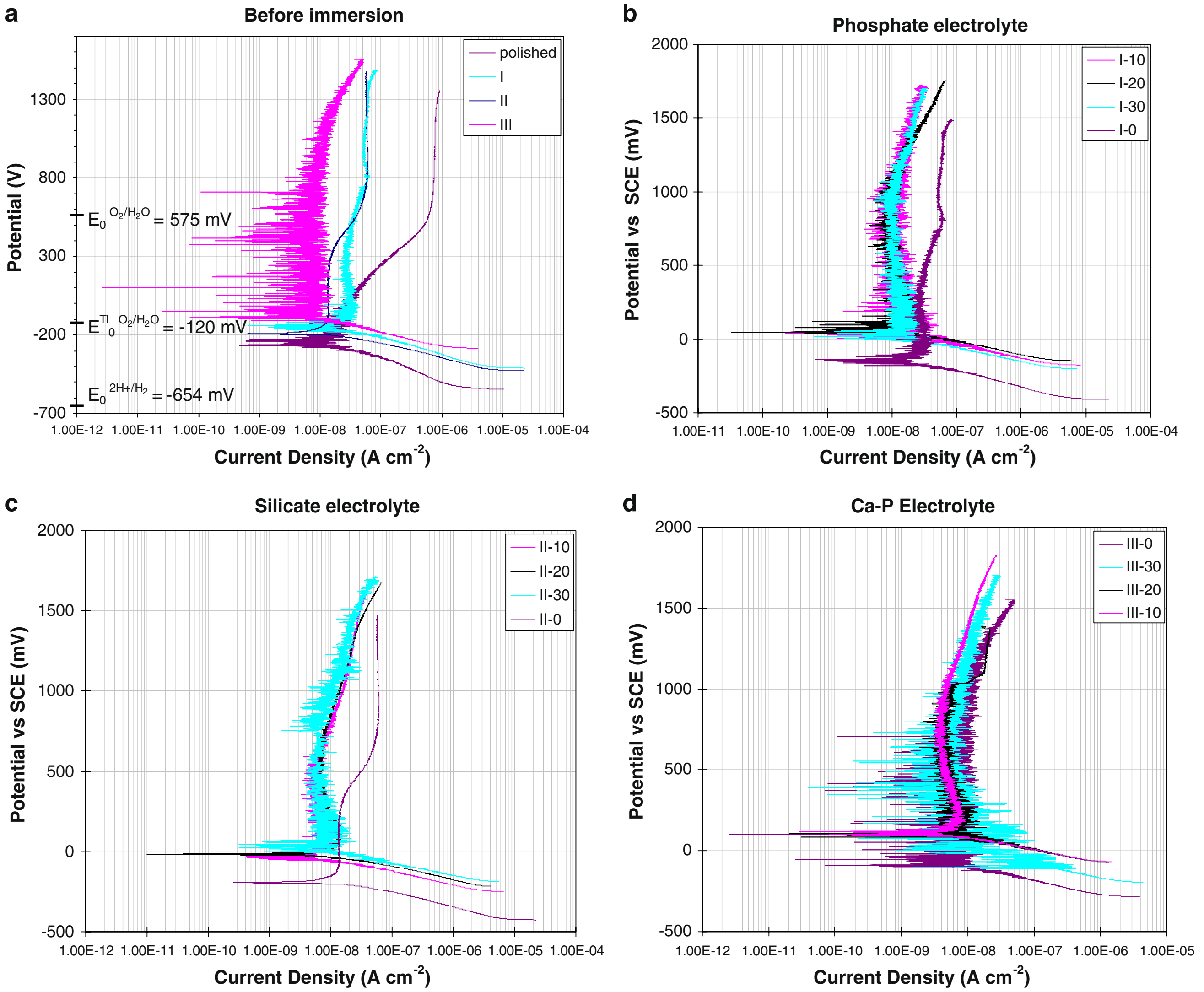

Fig. 6 Potentiodynamic polarization curves in c-SBF solution at 37°C for **a** chemically polished titanium and coatings formed in electrolytes I–III before immersion test; **b–d** coatings formed in electrolytes I–III respectively after immersion for 10, 20 and 30 days

$$O_2 + 4H^+\left(10^{-7}\ \mathrm{M}\right) + 4e \rightarrow 2H_2O \quad E^o = 0.815\ \mathrm{V}(0.575\ \mathrm{V\ vs.\ SCE}) \tag{1}$$

$$2H^+\left(10^{-7}\ \mathrm{M}\right) + 2e \rightarrow H_2 \quad E^o = -0.414\ \mathrm{V}\ (-0.654\ \mathrm{V\ vs.\ SCE}) \tag{2}$$

are marked in Fig. 6a, indicating that oxygen reduction is the cathodic process at the OCPs. It has been shown that in neutral solutions the oxygen reduction reactions on titanium occur at about 0.12 V (SHE) [18], i.e. −0.12 V (SCE). The oxygen reduction reaction may occur under diffusion control, due to the low solubility of oxygen in aqueous media (6.5 mg/l at 37°C). The current densities increased relatively rapidly from the OCP in the cathodic branches of the curves, more steep increase being observed for the coated titanium, possibly because the oxygen reduction is facilitated by the coatings.

4 Discussion

PEO treatment of titanium resulted in relatively thick coatings based on TiO_2. Small amounts of rutile and anatase are detected in the mainly amorphous coating material. In case of the coating produced in silicate electrolyte the main contribution into the amorphous peak possibly comes from silica surface deposit. Further, the coatings contain phosphorus, silicon and calcium species originating from the electrolyte. The P:Ti, Si:Ti and Ca:Ti ratios are ~0.2, 0.8 and 0.4, respectively according to analysis by EDX of the outer regions of the coating. Crystalline phases containing these species have not been detected by XRD, suggesting their predominance in amorphous phase. From previous work, the coatings are permeated by channels and pores [16, 19]. In general, the pores and channels do not reach the metal, due to the presence of ~1 µm thick barrier layer next to the metal.

The selected PEO coatings generally reduced the passive current density of titanium in SBF at 37°C, determined at potentials significantly above the OCP, with exposure to SBF for 30 days resulting in further, though smaller, reductions. The behaviour is probably due to protection by the relatively compact barrier layer at the base of the coatings. The OCP was shifted to potentials up to ~300 mV higher than that of chemically-polished titanium. The passive current density close to the OCP was less influenced by the PEO treatment, being ~10 nA cm^{-2} prior to and following coating. A corrosion current density of this magnitude would release 1.27 pg cm^{-2} s^{-1} of titanium. However, the passive current density probably includes contributions from film growth [19] and healing of flaws, which do not contribute to titanium release. The barrier layer at the base of the coating should prevent general film thickening. Flaws may be generated dynamically in the barrier layer by local dissolution or cracking due to residual stress. Thus, the passive current density will tend to overestimate the titanium release associated with the electrochemical oxidation of titanium. The average rates of titanium release after immersion for 30 days in SBF, determined by ICP-OES, were 1.52, 1.69 and 1.99 pg cm^{-2} s^{-1} with coatings produced in phosphate, silicate and calcium-phosphorus containing electrolytes respectively. Although the rates are relatively similar to the estimate from the passive current density, it is possible that a significant fraction of the titanium originates from the coating. Degradation of the coating was not resolved by SEM. However, the total release of titanium is equivalent to uniform dissolution of only ~10 nm of the titanium substrate.

Three check points during immersion for 30 days in SBF suggest that calcium was leached from the coating formed in electrolyte III at an approximately constant rate of ~11.0 pg cm^{-2} s^{-1}. Constant rate is assumed in this case, since 30 days duration of the immersion test chosen in this work is considered as a short-term assessment of the implant material stability. Such period is approximately comparable with the healing time for the dental implants, but is insufficient for making long-term extrapolation. Release of phosphorus could not be determined from solution analyses due to the presence of phosphate in the SBF. Chemical dissolution of the coating is the source of calcium species, from the external surface and within pores and channels accessible to the solution. The outer regions of the coatings contain the greatest amounts of calcium. The calcium species diffuse from the coating/solution interface to the bulk solution through a boundary layer. The concentration of calcium in the bulk solution is low during the exposure period such that a constant rate of release may be expected, which is consistent with the present result. Other work, in which PEO-coated titanium was immersed in EDTA solution, revealed local degradation of the coating surface due to release of calcium and phosphorus species, with fine crystals of anatase being exposed [11]. At the final immersion time of 336 h, ~142 µg cm^{-2} of calcium were released, corresponding to a rate of 117 pg cm^{-2} s^{-1}, which is about 10 times higher than the present release. The lower rate may be due to the differing calcium contents of the coatings, and the chelating of calcium species by EDTA, which maintains a low concentration of free Ca^{2+} ions. Interactions of the coating surface with the SBF may also affect calcium release. The low release of calcium from the present coatings is consistent with the negligible degradation of the coating surfaces revealed by SEM.

The present polarization curves reveal relatively wide fluctuations of the current density near the zero current potential, which has also been were reported in the anodic behaviour of titanium alloys in Hank's solution [20] and in artificial saliva, containing fluoride ions [21]. This effect has been attributed to competition between film formation and dissolution. It was suggested that current fluctuations may be triggered by dissolution of the passive layer in the presence of fluoride ions [21]. In the present case, residual fluoride ions may remain on the titanium surface following chemical polishing in HF-containing solution. However, the activation of corrosion of titanium and dental alloys by fluoride was reported to occur only at $pH < 3.5$, whereas at $3.5 < pH < 6.15$, formation of an oxide layer occurs, with anodic currents in the range of microamperes [22]. Further, growth of a passive film was reported to be the only electrochemical reaction occurring on c.p. titanium and Ti-6A1-4 V in Ringer's solution (with and without additions of several amino acids) at 37°C in [23].

5 Conclusions

1. PEO treatment of titanium in phosphate, silicate and calcium- and phosphorus containing electrolytes reduces its anodic current density in SBF at 37°C, determined from potentiodynamic polarization measurements, by up to ~2 orders of magnitude.
2. The passive current densities of coated titanium are further reduced by up to a factor of ~3 following their exposure to SBF at the open-circuit potential for up to 30 days.
3. During exposure of PEO-treated titanium to SBF for 30 days, titanium is released to the solution, with an average rate in the range ~1.5–2.0 pg cm^{-2} s^{-1} according to measurements by ICP-OES.
4. Release rates similar to those of immersion tests are suggested by passive current densities.

5. During 30 days of exposure calcium is released to the SBF from the coating produced in calcium-containing electrolyte at an average rate of $\sim$11 pg cm^{-2} s^{-1}.

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