

## ***In-situ* pH Measurement at the Electrode/Solution Interface**

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**Abstract:** In this paper a pH microprobe technique was developed to measure *in-situ* the pH value at the electrode/solution interface. Iridium oxide was used as a pH sensitive material with good response behavior in the measured solutions. The experimental results indicated that the interfacial pH increased with the applied potential, first jumped to a maximum, then slowly decreased at the controlled potential during the electrodeposition process of functional ceramics.

**Keywords:** *In-situ* measurement, pH microprobe, electrode/solution interface.

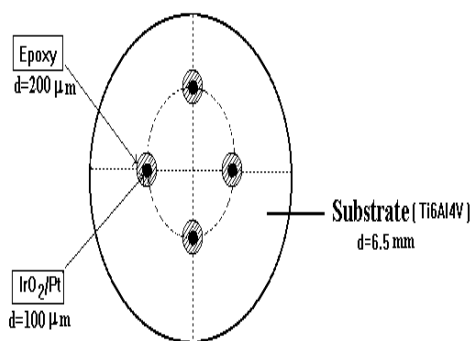
Electrochemical deposition of functional ceramic coatings has recently attracted considerable attention<sup>1-3</sup> because of a variety of advantages of the method of the coating fabrication, such as a low process temperature, the ability to deposit on porous or complex shapes of substrate, the simple control of deposit thickness. The mechanism of electrodeposition for functional ceramics onto the substrate has not been fully clarified at present. It was generally guessed<sup>4,5</sup> that the electrochemical reactions on the electrode surface may cause a pH change at the cathode/solution interface, and functional ceramic coatings were formed in an appropriate chemical environment. At the same time, the complexity of interfacial chemistry may further increase because of chemical precipitation of functional ceramics on the substrate. This thought has not been verified by experiment since the interfacial pH value is usually hard to be measured using a common pH meter. In this work, a novel pH-microsensor system was designed, and the pH change at the substrate/solution interface during the electrodeposition process of bioceramic coatings of calcium phosphates, as a example, was *in-situ* measured.

### **Experimental**

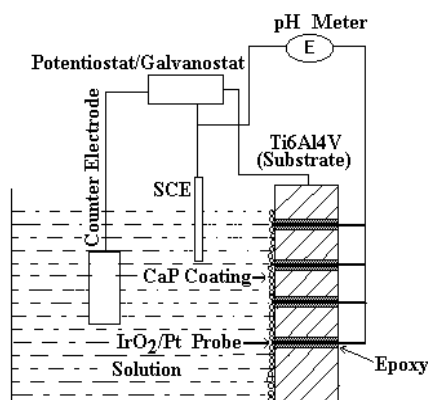
The electrode, on which surface the pH change would be *in-situ* measured, was a round sample of Ti6Al4V surgical alloy (diameter 6.5 mm) onto which four holes with 200  $\mu\text{m}$  in diameter were fairly well-distributed (**Figure 1**). A platinum wire measuring 100  $\mu\text{m}$  in diameter was fixed in each hole by a thermal curing epoxy. Four platinum wires were welded together in the background of the substrate. Iridium oxide, the sensing material for the pH microprobe, was deposited on platinum wire by electrochemical method<sup>6</sup>. The pH microsensor was calibrated by measuring the potential of the iridium oxide microprobe referred to a saturated calomel electrode (SCE) in a set of buffer solutions

pH 1-12.

**Figure 1** Schematic arrangement of pH microprobe of IrO<sub>2</sub> fixed into Ti6Al4V substrate.



**Figure 2** Schematic diagram of the *in-situ* pH measurement system.



The experimental apparatus of *in-situ* interfacial measurement system is shown in **Figure 2**. The electrolyte for electrodeposition of bioceramics contained 0.042 mol/L Ca(NO<sub>3</sub>)<sub>2</sub> and 0.025 mol/L NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The pH of the electrodeposition solution was adjusted to 4.50 by adding ammonia solution at room temperature. The electrochemical deposition of calcium phosphate bioceramics was carried out in potentiostat mode at 60 °C. The round sample of Ti6Al4V alloy with the pH-microsensor of iridium oxide was used as the cathode (substrate) and a platinum foil as a counter electrode. The cathode potential was maintained at a predetermined value ranging -1.300V to -1.900V. During the electrodeposition process, the pH value at the cathode/solution interface was measured *in-situ* by the IrO<sub>2</sub> pH-microsensor, using a saturated calomel reference electrode.

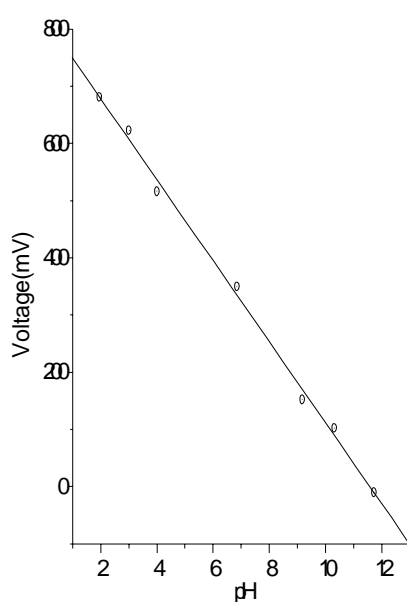
## Results and Discussion

The calibration experiments showed that the microsensor responded well to pH changes in the buffer solutions. The potential decreased linearly with increasing of pH over the entire range by a slope of 70.2 mV/pH unit at 60 °C (**Figure 3**). When the pH microsensor was transferred repeatedly from acid to base, it was of good repeatability to pH response. The response behavior was not affected when the IrO<sub>2</sub> microsensor was stored for about 4 weeks in de-ionized water, acid or base solution.

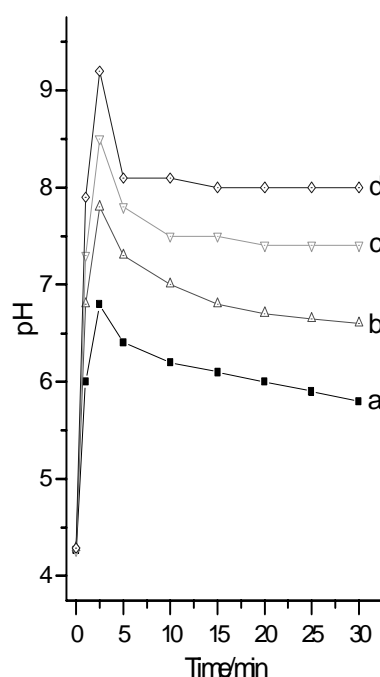
When a potential is applied to an electrode, the related electrochemical reactions take place and lead to the chemical environment near the cathode/solution interface being different from that in the bulk solution. The change of pH in the vicinity of cathode resulted in the precipitation of calcium phosphates and the formation of bioceramic coatings from the electrolyte containing Ca<sup>2+</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. **Figure 4** shows the changes of the pH value in the vicinity of the cathode with the time of electrodeposition for different cathode potentials at 60 °C. For all applied potentials, the pH value at the

cathode/solution interface rapidly increased at beginning, and then slowly decreased with the increasing electrodeposition time. When the electrodeposition time approached 2.5 min, the interfacial pH rose to the maximum of 6.8, 7.8, 8.5, and 9.2 at the applied potentials of -1.300, -1.500, -1.700, and -1.900 V (vs. SCE), respectively.

**Figure 3** The corresponding potential variation with pH for IrO<sub>2</sub> microsensor at 60°C (with respect to saturated calomel)



**Figure 4** Variation of pH at the cathode/solution interface with the electro-deposition time at different applied potentials:



(a) -1.300V, (b) -1.500V, (c) -1.700V  
(d) -1.900V

In our experimental apparatus, the IrO<sub>2</sub>-coated microprobes were embedded into the substrate (cathode). The design ensures that the measurement was able to accurately determine the pH change at the substrate/solution interface, that is said, it is possible to monitor pH value *in-situ* at the cathode/solution interface without interference of the electrodeposition process of functional ceramics. When the current passing between the working electrode and counter electrode was interrupted, the potential instantly detected between the pH sensor and reference electrode changed little. It meant that the influence of the working current on the pH measurement could be negligible in our experiment. The pH value at the substrate/solution interface could influence and even determine the structure and composition of electrodeposition products, so a direct measurement of the interfacial pH would be very important to study the mechanism of electrochemical deposition of functional ceramic coatings and the relationship between electrodeposition products and the pH at the cathode/solution interface during the electrodeposition process of functional ceramic coatings.

**References**

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