

# Preparation and formation mechanism of microporous spheric zinc phosphate

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**Abstract** In this paper, we investigate the formation of microporous spheric zinc phosphate by anodization method. Zinc phosphate microporous spheres with diameters of 5–23  $\mu\text{m}$  were prepared in  $\text{H}_3\text{PO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  aqueous electrolyte when the applied voltage was 1 V. Microstructure was characterized by scanning electron microscopy. Composition and crystal structure were confirmed through energy dispersive spectrum and X-ray diffraction analysis. The formation mechanism of this special structure was also discussed in this paper.

**Keywords** Zinc phosphate · Anodization · Microporous sphere

## Introduction

Zinc phosphate, one of the important metal phosphates, has so many excellent properties that it is widely used as anticorrosion pigment [1, 2], dental cement [3, 4], ceramics [5], fire-retardant [6], protective film on the metal surface [7, 8], and luminescent materials [9–12], etc.

Since Gier TE and Stucky GD prepared zinc phosphate which has the structure of zeolite in 1991 [13], series of microporous zinc phosphate with one-dimensional chain-

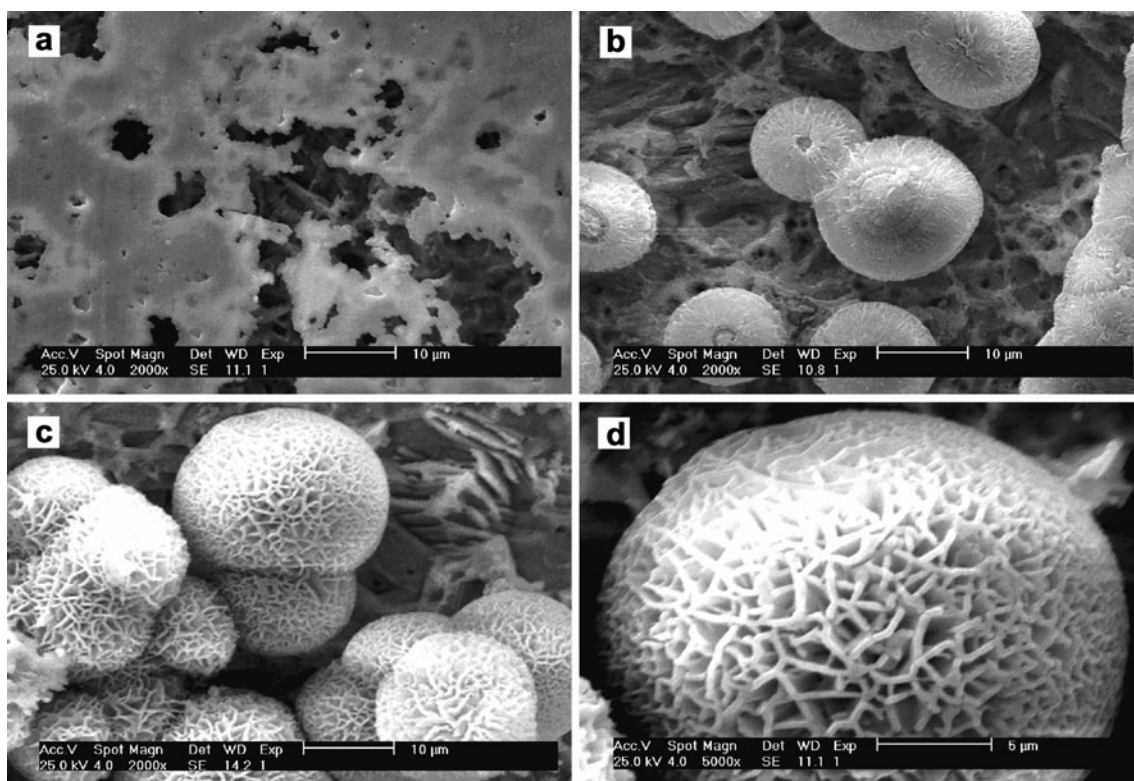
like, two-dimensional layered, and three-dimensional open framework structures has been synthesized by different approaches such as hydrothermal and solvothermal methods [14–21]. Microporous zinc phosphate has found widespread applications in catalyst, absorbent and ion-exchanger, etc. It also has broad prospects and potential applications in such fields as substance isolation, assembly of functional materials, medicine insertion, molecular recognition, and magnetic field [22–25]. In this paper, microporous spheric zinc phosphate was prepared by anodization method; the formation mechanism of this special structure was also discussed. To our knowledge, very few cases of preparation of microporous zinc phosphate by anodization method are documented in references. In comparison with other methods, anodization has obvious advantages such as simple process, low cost, and easily controlled.

## Materials and methods

The zinc foils (purity, 99.99%,  $10 \times 10 \times 0.5 \text{ mm}^3$ ) used in this study was obtained from General Research Institute for Nonferrous Metals (Beijing, China). They were washed in twice-distilled water and acetone by ultrasonic washing before use. Electrochemical experiments were carried out using a program-controlled DC source (Dahua Coop., Beijing, China). Zinc foils were used as anodic electrode while platinum ( $20 \times 20 \times 0.1 \text{ mm}^3$ ) was used as cathodic electrode. The distance between anodic and cathodic electrodes was 20 mm. Electrolytes in this process was 0.2 mol/L  $\text{H}_3\text{PO}_4$ , or 0.2 mol/L  $\text{NH}_4\text{H}_2\text{PO}_4$ . All solutions were prepared from analytical grade chemicals and deionized water. The anodization was conducted through constant voltage operation. The applied voltage was 1 V

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**Fig. 1** SEM images after anodization in 0.2 mol/L  $\text{H}_3\text{PO}_4$  at 1 V (a) 10 min, (b) 20 min, (c) and (d) 30 min

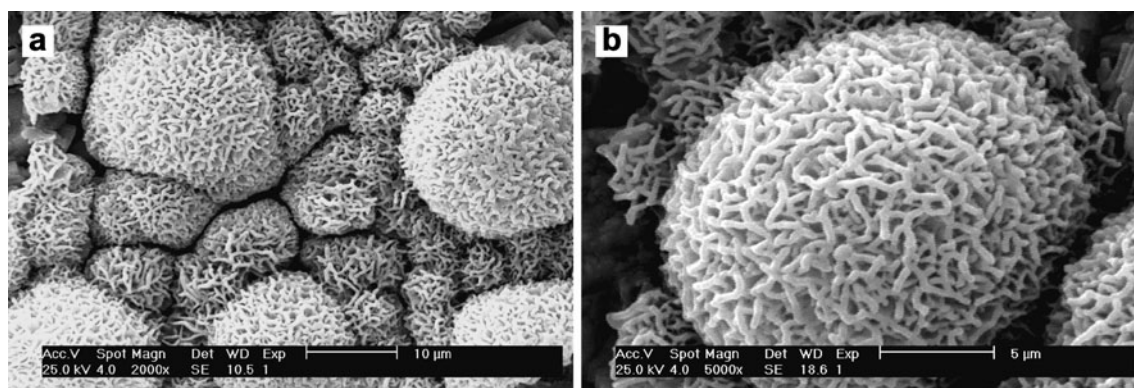
during the anodization process. All anodization experiments were carried out at room temperature. During the experiments, the solutions were stirred using a magnetic stirrer. After the anodization, the samples were rinsed in deionized water, dried, and characterized.

Electrochemical measurements were conducted using LK2005 electrochemical analyzer (Lanlika Instruments Inc., Tianjin, China). X-ray diffraction measurements were performed on D/max-RB diffractometer (Rigaku, Rotafles) using  $\text{Cu K}\alpha$  radiation (0.15416 nm). The scan rate of  $4^\circ\text{min}^{-1}$  was applied to record the patterns in the  $2\theta$  range of  $5\text{--}70^\circ$ . The microstructures were observed on the scanning electron microscopy (XL-30, Philips,

Netherlands) operating at accelerating voltage of 25 kV. Composition analysis were performed on the energy dispersive spectroscopy (EDS) equipped with the scanning electron microscopy.

## Results and discussion

Figure 1 gives the surface microstructure of zinc after anodization at 1 V in 0.2 mol/L  $\text{H}_3\text{PO}_4$  for different time. When the anodization took place for 10 min, the surface of zinc was partially covered with dense film (Fig. 1a). As anodization time was extended to 20 min, microporous



**Fig. 2** SEM images after anodization in 0.2 mol/L  $\text{NH}_4\text{H}_2\text{PO}_4$  at 1 V for 30 min

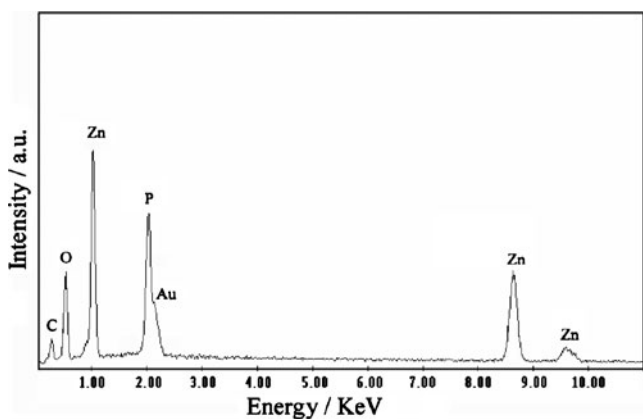


Fig. 3 EDS diagram of the microporous sphere

round disks were formed on the zinc surface, in which a big hole existed (Fig. 1b). Anodization for 30 min resulted in the appearance of microporous spheric objects in different sizes with diameters ranging from 10 to 23  $\mu\text{m}$  (Fig. 1c, d). In addition, it can be noted from Fig. 1c that the exposed part of zinc foil was irregular with local layered structure.

SEM images after anodization in 0.2 mol/L  $\text{NH}_4\text{H}_2\text{PO}_4$  at 1 V for 30 min were given in Fig. 2 which confirmed the formation of microporous spheric objects in different sizes in  $\text{NH}_4\text{H}_2\text{PO}_4$ , the diameters of microspheres were between 5 and 22  $\mu\text{m}$ .

As illustrated in Figs. 1 and 2, the microporous spheres prepared in 0.2 mol/L  $\text{H}_3\text{PO}_4$  solution are smooth with regular shape and bigger pore size, while in 0.2 mol/L  $\text{NH}_4\text{H}_2\text{PO}_4$  solution the microporous spheres are rough with smaller pore size. This might be due to the different pH values of 0.2 mol/L  $\text{H}_3\text{PO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ , which is 1.4 and

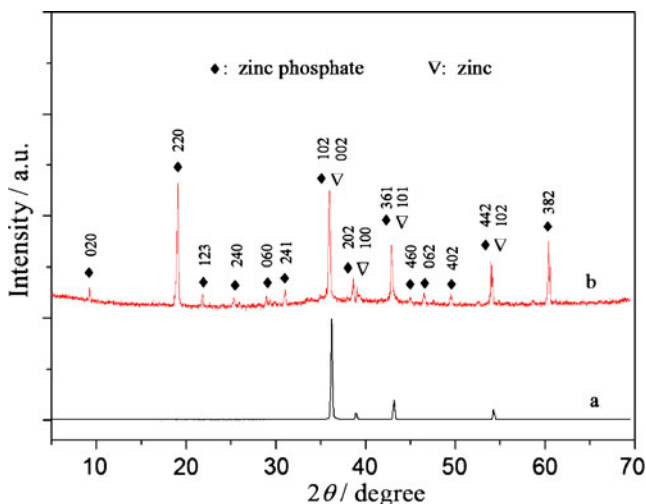


Fig. 4 X-ray diffraction pattern of the microporous sphere. a Zn foil, b microporous sphere

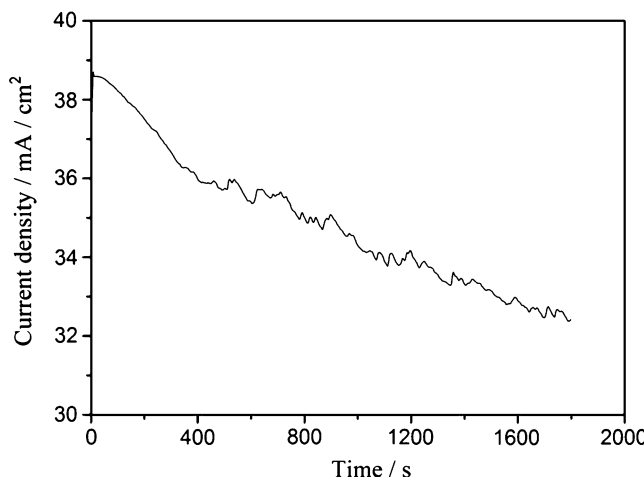


Fig. 5  $I-t$  curves at 1 V during the anodizing process for 30 min

4.2, respectively. Compared with  $\text{NH}_4\text{H}_2\text{PO}_4$  solution,  $\text{H}_3\text{PO}_4$  solution has stronger dissolving action to the product.

Figure 3 shows the EDS diagram of the microporous sphere. EDS analysis revealed the presence of elements of Zn, O, P, and C. Impurity of C was caused by contamination in the reaction, treatment, and measurement process. Au was sputtered on the sample to improve its electrical conductivity during SEM observation. Hence Au is present in the EDS spectrum. X-ray diffraction pattern of the microporous sphere is given in Fig. 4. All the diffraction peaks can be indexed to orthorhombic phase of  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (JCPDS Card No. 74-2275) and the raw material Zn (JCPDS Card No.4-831). The average crystal size is about 50 nm according to Scherrer equation.

Figure 5 presents the current transient ( $I-t$ ) curve recorded during holding the sample at 1 V for 30 min.

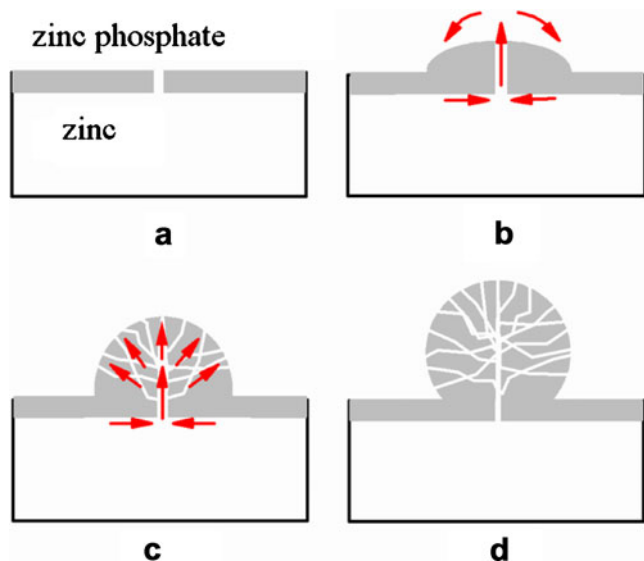
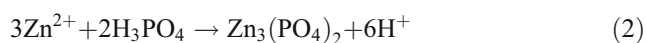


Fig. 6 Schematic diagram of formation of microporous spheric zinc phosphate

The current density tends to decrease slowly during the anodization process. The curve is smooth between 0 and 400 s and periodical fluctuation of the current density after 400 s is illustrated in Fig. 5.

Upon exposure to air, zinc would react with O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O to form the protective layer of zinc hydroxycarbonates (ZnCO<sub>3</sub>·3Zn(OH)<sub>2</sub>), which prevents zinc from further oxidization [26]. When zinc foil was put into phosphorous acid, the basic zinc carbonate would dissolve due to reaction with phosphorous acid. The remnant membranoid substance in Fig. 1a might be the undissolved basic zinc carbonate.

During the anodization process, the following reactions took place:



Formation of zinc phosphate by anodization resulted in the increase of resistance, while dissolving of basic zinc carbonate at the zinc surface induced the decrease of electric resistance. The former applied more influence than the latter, consequently, as anodization extended, the current density decreased gradually.

Upon the transition from zinc-to-zinc phosphate, inner stress appeared in the layer of zinc phosphate due to volume expansion. When the inner stress was high enough, the layer of zinc phosphate would break and form pores, which caused the increase of current density within a narrow range. Then, the subsequently formed zinc phosphate would block the pores and cause the decrease of current density. The repetition of the two above-mentioned process resulted in the periodical fluctuation of the current density.

When there existed pores in the layer of zinc phosphate (Fig. 6a), mass transfer was faster at the position of pores and the reaction product including Zn<sup>2+</sup> would be carried out of the pores by solution medium. The rate of mass transfer outside of the pores reduced promptly and Zn<sup>2+</sup> reacted and deposited at the pore mouth, which resulted in the formation and enlargement of zinc phosphate with round bale shape (Fig. 6b). The process is like the formation of volcano to some extent.

The substance in bale shape might consist of many fine crystallites of zinc phosphate. During the reaction process, the crystallites grew up gradually and micropores appeared among these crystallites. Mass transfer would also conduct through these micropores and the round bale grew along various directions (Fig. 6c).

The initially formed round bales of zinc phosphate might be irregular with incurvate and convex parts. The distance of mass transfer at the incurvate parts was shorter than that at the

convex parts. More Zn<sup>2+</sup> was brought out and formation rate of zinc phosphate was larger at the incurvate parts than that at the convex parts. The unbalanced formation rates induced the shape of zinc phosphate to be more regular along with the growth of round bale and turn to spheric shape ultimately (Fig. 6d).

## Conclusion

The present work investigates the formation of microporous spheric zinc phosphate by anodization method. The results reveal a simple way to fabricate porous phosphate, which may have potential use in adsorption and catalytic field. Keeping the applied voltage to be 1 V, we prepared zinc phosphate microporous spheres with diameters of 5–23 μm. The key factor to achieve this spheric porous phosphate lies in the different rates of mass transfer and deposition.

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