

Short communication

Electrolytic Li_3PO_4 coating on Pt

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Available online 5 June 2006

Abstract

Electrolytic Li_3PO_4 coating on Pt as the solid electrolyte has been carried out in the mixture of LiNO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ aqueous solution. The cathodic reactions during the polarization could be divided into three stages: (I) $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{OH}^-$ (+0.49 to -0.33 V); (II) $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (-0.33 to -0.68 V); (III) $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$, $\text{HPO}_4^{2-} + \text{OH}^- \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O}$ and $\text{H}_2\text{PO}_4^- + 2\text{e}^- \rightarrow \text{PO}_4^{3-} + \text{H}_2$ (-0.68 to -2.0 V). The orthorhombic β -phase Li_3PO_4 was found until the transition to orthorhombic γ -phase at 500°C . The lithium ionic conductivity of 100 nm crystalline Li_3PO_4 thin film was about $8.62 \times 10^{-8} \text{ S cm}^{-1}$ at 25°C . Also, the mechanism of electrolytic Li_3PO_4 coating on Pt was discussed in this article. © 2006 Elsevier B.V. All rights reserved.

Keywords: Electrolytic coating; Li_3PO_4 ; Solid electrolyte; Lithium ionic conductivity

1. Introduction

The miniaturization of electronic devices results in low current and power requirements today. Therefore, thin film batteries reveal more potential in this field, such as the potential to make batteries which thickness thinner than $10 \mu\text{m}$, and the possible integration of battery fabrication with the microelectronic devices [1]. This very low thickness allows using poor conductive electrolytes like lithium phosphorus oxy-nitride (LiPON), manufactured by sputtering, vacuum evaporation, etc., which revealed a pure Li^+ conductivity about $2 \times 10^{-6} \text{ S cm}^{-1}$ [2–4]. Also, its redox stability range is very large and allows the use of very oxidizing species as positive electrode. The phosphorus influenced the electronic resistance following the valence state -3 (metal like), $+1$ (semiconducting) and $+5$ (insulating). Consequently coating PO_4^{3-} ion compounds may become the competitive for electrolyte. The Li_3PO_4 specimen was usually used as the CO_2 sensor [5], thermo-luminescence dosimetry (TLD) materials [6], and the coating on positive electrode to prevent the degradation of solid polymer electrolyte [7].

In this study, a novel method of electrolytic Li_3PO_4 coating on Pt was conducted in the mixture of $0.02 \text{ M NH}_4\text{H}_2\text{PO}_4$ and 0.5 M LiNO_3 aqueous solutions as the solid state electrolyte of secondary lithium ion batteries.

2. Experimental

2.1. Cathodic polarization tests

To investigate the effect of solution concentrations on cathodic reaction, the platinum plates were electrochemically polarized in the mixture of $0.02 \text{ M NH}_4\text{H}_2\text{PO}_4$ and 0.5 M LiNO_3 aqueous solution assigned to solution A, by using an EG&G 273A Potentiostat and M352 Software. Furthermore, characterized the effect of O_2 and H^+ concentrations on the cathodic reaction in solution A, 0.01 M HCl was added into solution A to adjust the pH value and deaerated solution A by N_2 purging assigned to B and C, respectively. The potential range was swept from the equilibrium potential of the platinum to a final potential of -2.0 V (versus the potential of saturated Ag/AgCl), with a scanning rate of 0.167 mV s^{-1} .

2.2. Electrolytic deposition and annealing

The electrolytic deposition of $\beta\text{-Li}_3\text{PO}_4$ was carried out in an aerated 0.5 M LiNO_3 and $0.02 \text{ M NH}_4\text{H}_2\text{PO}_4$ mixed aqueous solution A at room temperature and carried out by potentiostatic method at -1.0 V (Ag/AgCl) for 1000 s by using an EG&G M273A Potentiostat and M352 Software. The $1 \text{ cm} \times 1 \text{ cm}$ platinum plates were as working electrode, a long narrow platinum strip as the counter electrode and saturated Ag/AgCl the reference electrode. The coated specimens were then naturally dried and annealed for 3 h in air at 300 , 500 , 600 and 800°C , respectively, for XRD study.

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2.3. XRD, SEM and FE-SEM

The crystal structures of the as-deposited and annealed films were analyzed by X-ray diffraction (XRD) in a MAC MO3X-HF diffractometer, with Cu K α radiation ($\lambda = 1.54185 \text{ \AA}$), 2θ in the range $10\text{--}70^\circ$, at a scanning rate of 1° min^{-1} , a voltage of 40 kV and a current of 30 mA.

The cross-sectional view and surface morphology of the deposited specimens were observed by scanning electron microscopy (JEOL JSM-5400 and JSM-6700F).

2.4. AC-impedance spectroscopy

The $\beta\text{-Li}_3\text{PO}_4$ coated specimen annealed at 300°C for 3 h to remove the extra water for AC-impedance measurements. The coated specimen was used as the working electrode, lithium metals as the counter and reference electrode in 1 M LiPF_6 in 1:1 (v/v) EC-DMC solution as the liquid electrolyte. The assemblages of cells were conducted in an argon glove box (M. Braum Unilab). Using Potentiostat 273A with an EG&G M5210 installment the frequency range from 100 kHz to 0.1 Hz at room temperature. The data were dealt with the Z Plot for Windows Software 2.8.

3. Results and discussion

3.1. Cathodic reactions

There are three distinguishable regions on the polarization curves, as shown in Fig. 1. By way of cathodic simulated in solution A, possible cathodic reactions are suggested as following:

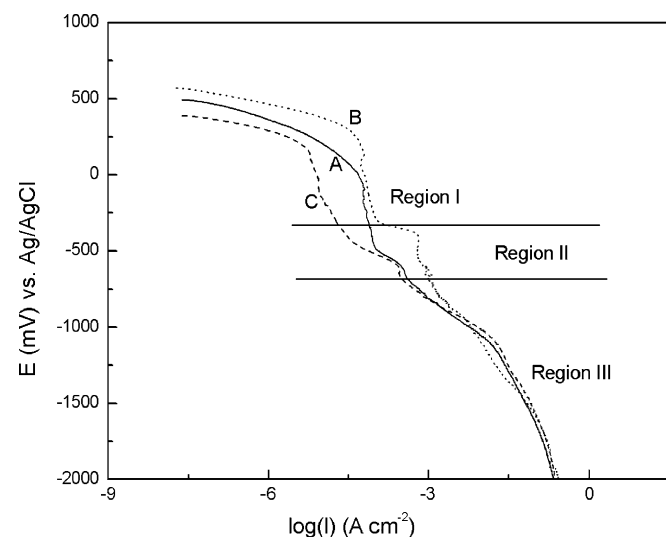
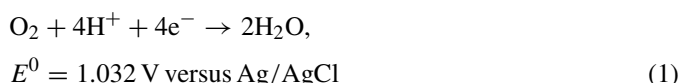
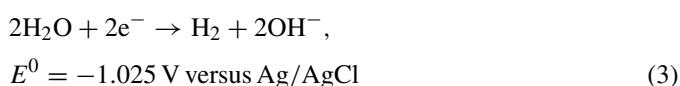
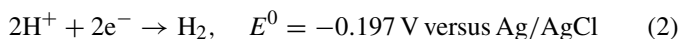


Fig. 1. Cathodic polarization curves of the platinum in 0.5 M LiNO_3 and 0.02 M $\text{NH}_4\text{H}_2\text{PO}_4$ mixed aqueous solutions aerated in air, added HCl and deaerated with N_2 was assigned to curves A–C, respectively.

Table 1

The diffusion limited current densities of polarization curves corresponding to regions I and II in the 0.5 M LiNO_3 and 0.02 M $\text{NH}_4\text{H}_2\text{PO}_4$ mixture aqueous solutions aerated with air, added with 0.01 M HCl and deaerated with N_2 were assigned to A–C, respectively

Solution	pH	O_2 (mg L^{-1})	Limiting current density (mA cm^{-2})	
			Region I	Region II
A	4.23	7.4	0.065	0.336
B	2.25	7.4	0.077	0.669
C	4.22	0.6	0.009	0.306



3.1.1. Region I (+0.49 to -0.33 V)

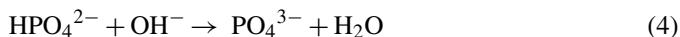
The deaerated treatment by N_2 purging made the first limiting current density from 0.065 down to 0.009 mA cm^{-2} , as shown in Fig. 1, solutions A and C, respectively. This means that O_2 played a major role at this region. Further the similar limiting current density of solutions A (pH 4.23) and B (pH 2.25) means that region I was not controlled by H^+ diffusion.

3.1.2. Region II (-0.33 to -0.68 V)

Once the pH value was modified from 4.23 down to 2.25 as given in Table 1, solutions A and B, the second limiting current density was enhanced from 0.336 up to 0.669 mA cm^{-2} , as shown in Fig. 1, solutions A and B. This means that H^+ played the major role at region II, and the diffusion limited current density was controlled by the diffusion rate of H^+ in reaction (2).

3.1.3. Region III (-0.68 to -2 V)

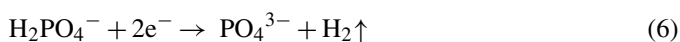
Much more hydrogen bubbles were formed at region III. This means that reaction (3) occurred. On the other hand the XRD diagram of as-coated specimen revealed $\beta\text{-Li}_3\text{PO}_4$ structure peaks, as shown in Fig. 2a, this indicates that some chemical reactions:



and



may occur or some electrochemical reaction



occurred and resulted in chemical reaction (5). The coatings were carried out by potentiostatic method in solution A at -1 V (versus the potential of saturated Ag/AgCl). During deposition, the current density generally followed Cottrell equation [8]. This means the concentration polarization mainly controlled this reaction. In other words, it is diffusion controlled.

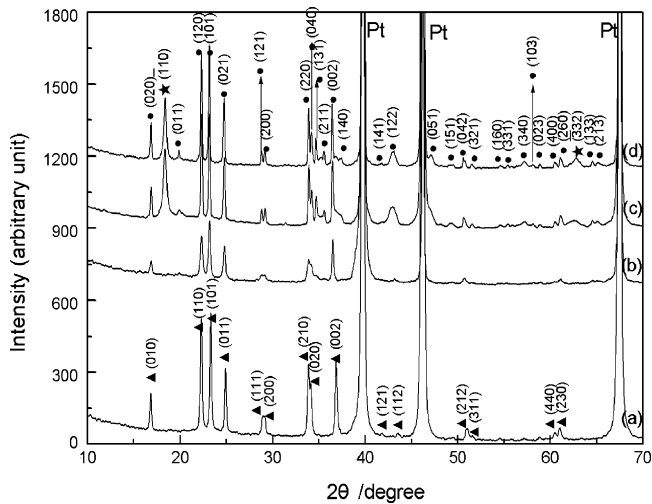


Fig. 2. XRD diagrams of the as-deposited films (a), annealed at 500 °C (b), annealed at 600 °C (c) and annealed at 800 °C (d) for 3 h, respectively. ▲, ● and ★ are the symbols of β - Li_3PO_4 , γ - Li_3PO_4 and P_4O_9 phases, respectively.

3.2. X-ray diffraction

The coated specimen β - Li_3PO_4 as shown in Fig. 2a, was gradually transformed into γ - Li_3PO_4 as shown in Fig. 2b. Though these peaks were not obvious differences between the strong peaks of β -phase (1 1 0), (1 0 1) and (2 1 0) (JCPDS 25-1030) and γ -phase (1 2 0), (1 0 1) and (2 2 0) (JCPDS 15-0760) in Fig. 2. There was a distinguished peak of γ -phase (0 1 1) increased with increasing annealing temperature, as shown in Fig. 2c and d. At the same time different peaks of P_4O_9 were found. After cooling to room temperature, no β -phase was found on the annealed specimen at 500 °C. This means that the irreversibility of phase transformation from β to γ is the same as the results of refs. [9,10].

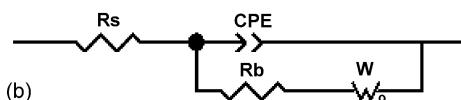
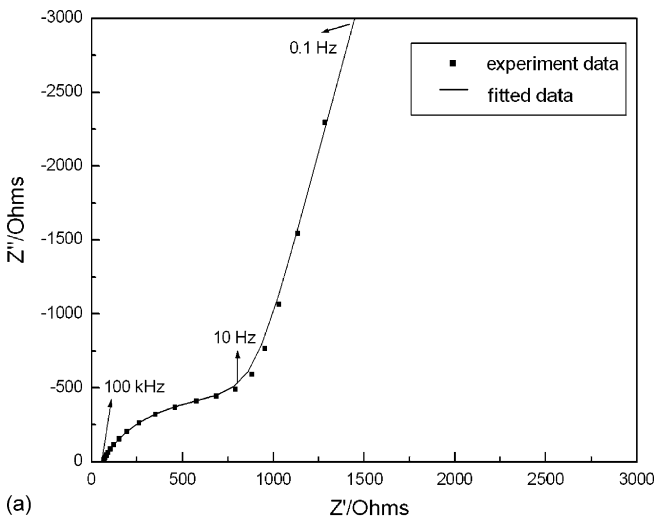


Fig. 3. Nyquist complex impedance diagram for β - Li_3PO_4 at room temperature (a) and equivalent circuit simulated diagram (b).

3.3. AC-impedance and surface morphology

An impedance diagram plotted in the Nyquist complex plane at room temperature is shown in Fig. 3a. At high frequencies, consider solution resistance R_s following a semicircle was present as a result of a parallel combination of bulk resistance (R_b) and constant phase element (CPE). The bulk resistance includes both the grain interior resistance (R_{gi}) and the grain boundary resistance (R_{gb}). These two components are not separated in all samples. At low frequencies, there was inclined line at an approximate 45° angle to the real axis, i.e. the Warburg impedance. This is part of the interfacial impedance and was due to an electrode contribution. The behavior of the impedance plots shows characteristics of a pure ionic conductor composed of bulk and electrode contributions [11,12]. By the equivalents circuits fitted as showed in Fig. 3b. The conductivity is determined using $\sigma = (d/A)/R_b$, where d is the film thickness to obtain from the cross-section view in Fig. 4a, about 1 μm , A the contact area of the sample, about 1 cm^2 and R_b is the film resistance deter-

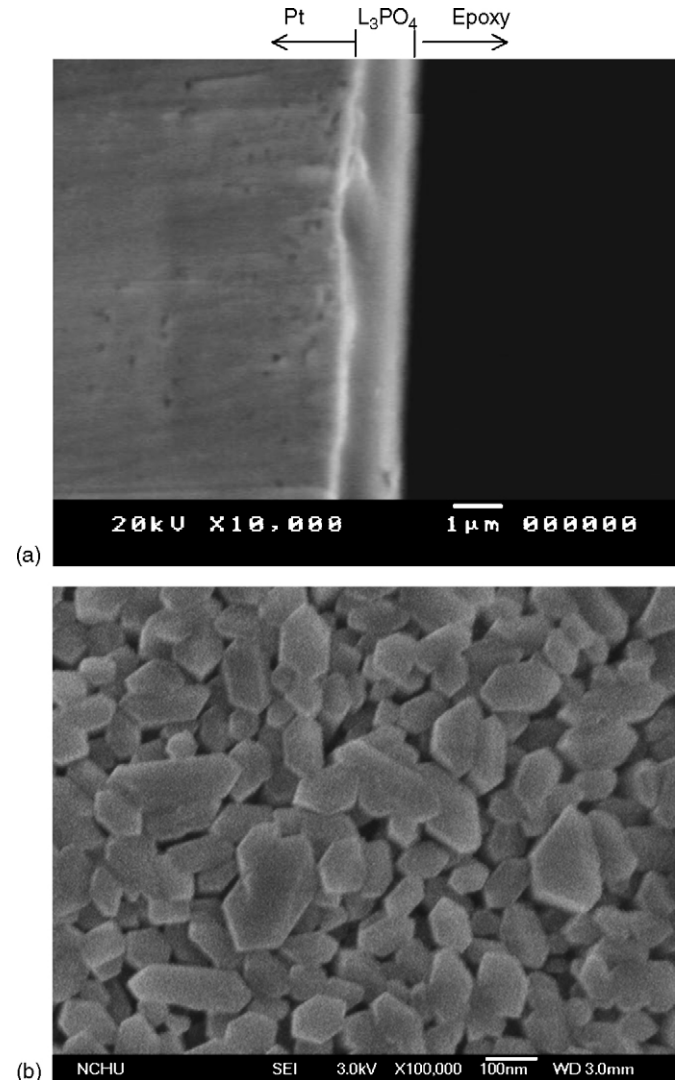


Fig. 4. SEM micrograph of the cross-sectional view (a) and FE-SEM surface morphology (b) of the coated β - Li_3PO_4 film.

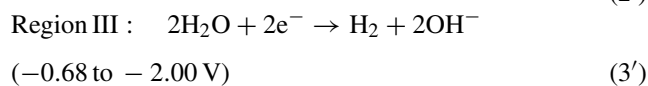
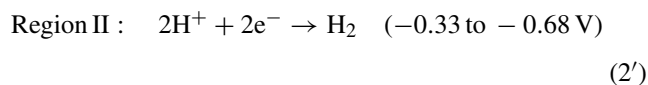
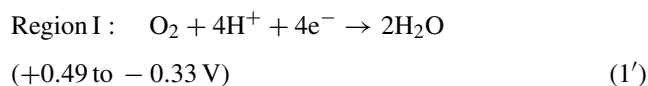
mined from the complex impedance plots about 1106 Ω . The conductivity approaches $8.62 \times 10^{-8} \text{ S cm}^{-1}$ at room temperature to be close to Bates' $7 \times 10^{-8} \text{ S cm}^{-1}$ [2] which deposited by sputtering in Ar + O₂ ambience. In this result reveal the poor ionic conductivity of this compound therefore must add some ions like M⁴⁺ (M = Ge, Ti, Sn and Zr) or M³⁺ (M = Al, Cr, Fe and Sc) [13] to enhance the ion conductivity, but it can provide the characterization for future thin film cell discussions. If a power supply with 10 μA is applied, the voltage drop is 10^{-2} V which is acceptable for a lithium battery with 2–4 V.

Fig. 4b was the field emission SEM observation on the coating film. The loosely packed crystals revealing particle size about 100 nm were due to the deposition accompanied with the formation H₂ bubbles. Furthermore, FE-SEM micrograph also showed the apparent aggregated morphology, hence caused the low ionic conductivity; Jak et al. also reported the total Li⁺ ion conductivity increased with decreasing particle size [14].

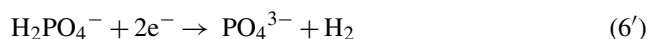
4. Summary and conclusion

A novel method for preparing orthorhombic Li₃PO₄ on Pt was successfully conducted in the mixture of LiNO₃ and NH₄H₂PO₄ aqueous solution by cathodic synthesis. According to polarization tests, XRD and SEM, several conclusions are listed below.

1. Three main cathodic reactions in LiNO₃ and NH₄H₂PO₄ mixed aqueous solution which belongs to various applied voltage ranges (versus Ag/AgCl) were identified, respectively:



and/or



2. Combined cathodic reactions and XRD results indicated that the reactions sequence for the formation of Li₃PO₄ coating was resulted from reaction (5). PO₄³⁻ in reaction (5) was provided by reaction (6) or reaction (4).
3. From XRD diagrams β -Li₃PO₄ coating specimens transformed into γ -phase until annealing 500 °C.
4. From cross-sectional observation the β -Li₃PO₄ coated film with thickness about 1 μm revealed good interface between the coating and substrate. Its resistance was 1160 Ω and its ionic conductivity approached to $8.62 \times 10^{-8} \text{ S cm}^{-1}$ at room temperature.

Acknowledgment

The authors are grateful for the support of this research by the National Sciences Council, Republic of China under contract no. NSC-93-2216-E-005-020.

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