



Synthesis of Li_2PtO_3 Thin Film Electrode by an Electrostatic Spray Deposition Technique

Heung Min Oh^a, Ji-Young Kim^a, Kyung-Keun Lee^a, Kyung Yoon Chung^{b,†} and Kwang-Bum Kim^{a,†}

^aDepartment of Material Science and Engineering, Yonsei University, Seoul 120-749, South Korea

^bAdvanced Battery Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

ABSTRACTS :

Li_2PtO_3 thin film electrodes, which might be possible candidate for the cathode materials for implantable batteries, were synthesized using an electrostatic spray deposition (ESD) technique onto a platinum foil substrate. Single phase Li_2PtO_3 with a structure similar to layered LiCoO_2 structure were synthesized by spraying a precursor solution of $\text{CH}_3\text{CO}_2\text{Li}_2\text{H}_2\text{O}$ in ethanol onto a Pt substrate at temperatures ranging from 200 to 400°C followed by annealing at above 600°C. Lithium carbonate was the only major phase at temperatures up to 500°C. The X-ray diffraction (XRD) peaks of the Pt foil substrate and lithium carbonate disappeared at temperatures > 600°C. The volumetric capacity of the Li_2PtO_3 thin film synthesized using the ESD technique was approximately 817 mAh/cm³, which exceeded that of LiCoO_2 (711 mAh/cm³).

Keywords : Li_2PtO_3 , Electrostatic spray deposition (ESD) technique, Thin-film electrodes, Lithium secondary batteries, Cathode material.

Received September 7, 2010 : Accepted September 24, 2010

1. Introduction

Lithium secondary batteries are expanding its application from portable electronics to various applications. Currently the most promising applications are large-scale applications such as electric vehicles (EV) or energy storage systems (ESS). However, medical applications will be one of the very important applications because the world is moving towards the aging society. The demands for the implantable medical devices such as artificial heart and artificial cochlea will increase dramatically and the lithium secondary batteries as their power sources as well. The lithium secondary batteries used for the implantable medical devices should be safe and inert in the human body. Thus, the materials used in the batteries

should be inert. Since the platinum is very inert materials, the cathode material made of platinum, i.e. Li_2PtO_3 may be one of the possible candidates for the cathode materials for the lithium batteries for implantable medical devices. Previously used cathode materials were made of Co, Ni, Mn, Fe and others, and those materials are potentially harmful to human body since they are not inert and can be absorbed into human body. In this study, we tried to fabricate thin film type cathode materials that can be used for the implantable medical devices that does not consume too much energy but needs rechargeable characteristics. The examples of this application can be artificial cochlea, implantable hearing aids, etc. LiCoO_2 and LiMn_2O_4 thin films have been studied more intensively than other thin film cathodes due to their simple synthesis routes. However, it is important to integrate a larger quantity of the active material into a limited area/volume and maintain inertness for the implantable medical device application. Therefore, materials with high volumetric capacities and inertness are preferred. One cathode material that meets this demand is Li_2PtO_3 .

[†]Corresponding author. Tel.: +82-2-2123-2839

E-mail address: kbkim@yonsei.ac.kr(K.-B. Kim)

kychung@kist.re.kr(K.Y. Chung)

However the thin film form has not been synthesized.

Previously, K. Asakura et al. reported the synthesis of the powdered form of Li_2PtO_3 using a solid-state method. It was prepared by firing a 1 : 1 molar ratio mixture of reagent grade lithium carbonate and platinum black at 800°C for 24 hours in air. The volumetric capacity of prepared powder was 764 mAh/cm^3 , which exceeded that of LiCoO_2 (711 mAh/cm^3). In addition, they compared its structural and electrochemical characteristics with that of LiCoO_2 .¹⁻³ Li_2PtO_3 is a Li_2MO_3 ($M = \text{Mo, Ru, Ir, Mn, Pt}$) type compound, which has a similar structure to $\alpha\text{-NaFeO}_2$, which is the structure of the rocksalt-type ternary oxide, LiCoO_2 and LiNiO_2 . These compounds can be represented as $(\text{Li}^+)_{3a}(\text{Li}^{1/3}\text{M}^{4+}_{2/3})_{3b}\text{O}_2$.⁴ In addition, these compounds can reversibly deintercalate Li from the initial composition. Although it has a lower gravimetric capacity than LiCoO_2 , it has been reported to have a 7.5% higher volumetric capacity,^{2,3} which makes it a potential candidate for a cathode material in lithium secondary microbatteries.

In our previous studies, various types of thin film electrodes were prepared using an electrostatic spray deposition (ESD) technique, which includes the cathode materials for lithium secondary batteries (LiCoO_2 ,⁵ LiMn_2O_4 ,⁶ LiNiO_2) and electrode materials for supercapacitors (RuO_2 ,⁷ $\text{Li}_x\text{Ni}_{1-x}\text{O}$,⁸ MnO_x). As part of an ongoing study to synthesize cathode materials for lithium secondary microbatteries, this study reports the synthesis of Li_2PtO_3 thin film electrodes using an ESD technique as well as an evaluation of its structural, morphological, and electrochemical characteristics. The thin film type Li_2PtO_3 cathode can be used without any additives such as conducting materials and binders unlike power type cathode materials, which feature may give more bio-compatibility to the electrodes.

2. Experimental

The synthesis of the Li_2PtO_3 thin film electrodes was carried out using an ESD technique. A schematic diagram of the ESD system is reported elsewhere.^{5,9,10} The precursor solution was an ethanolic solution of $0.05 \text{ M CH}_3\text{CO}_2\text{Li}\cdot 2\text{H}_2\text{O}$. The substrate used was Pt foil with the dimensions of $3 \text{ cm}(\text{length}) \times 1 \text{ cm}(\text{width}) \times 0.1 \text{ mm}(\text{thickness})$, which also worked as a source for the platinum in Li_2PtO_3 . During deposition, the needle to substrate distance was set to 3~5 cm. The applied voltage between the needle and the substrate was 10~15 kV and the surface temperature was set at 300°C . The flow rate of the precursor solution was fixed to 2 ml/h and a total of 2 ml was

sprayed over a deposited area of $10 \text{ mm} \times 10 \text{ mm}$. After deposition, the samples were annealed at temperatures ranging from 400 to 800°C for 1 hour with an oxygen stream of not less than 200 ml/min and left to cool in a furnace.

The crystal structure of the Li_2PtO_3 films annealed at the various temperatures was characterized by X-ray diffraction using $\text{Cu K}\alpha$ radiation in a Rigaku diffractometer, which was equipped with a thin film X-ray diffractometer attachment. The surface morphologies of the films were observed using scanning electron microscopy (SEM, Hitachi S-4200, Japan). The mass of the substrate was measured both before and after deposition using an electronic balance (Sartorius UltraMicrobalance S4, Germany) to determine the mass of the Li_2PtO_3 thin film deposited on the substrate, which was calculated assuming that the supplied lithium ions all reacted with platinum leaving no residue.

The electrochemical performance was evaluated using a beaker cell in a glove box under a dry argon atmosphere. The counter and reference electrodes were lithium metal foil and the electrolyte used was $1 \text{ M LiClO}_4/\text{PC}$. The cells were galvanostatically cycled between the voltage limits of 3.0 and 4.5 V at a 1/20 C-rate using a computer-controlled cycler.

3. Results and Discussion

3.1. Structural characterization

The synthesis of Li_2PtO_3 films consisted of two steps. These are the deposition of the precursor solution at $200\text{--}300^\circ\text{C}$ and the subsequent annealing at $400\text{--}800^\circ\text{C}$. Fig. 1 shows the X-ray diffraction (XRD) patterns of the annealed films at the various temperatures. The deposition temperature was fixed to 300°C . The as-deposited films were annealed at the designated temperatures for 1 hour. At 400 and 500°C , the peaks from the Pt substrate and that of Li_2CO_3 were mostly observed. At higher temperatures, these peaks disappeared and the peaks for Li_2PtO_3 could be observed. Due to the preferred orientations of the thin film electrode, the intensities of the peaks other than the (003) directions are much reduced. In addition, as the annealing temperature was increased, the intensities of the (003) peak increased, which indicates that the preferred orientation to the (003) directions becomes more pronounced.¹¹ From these results, Li_2CO_3 was the major phase present on the substrate after depositing the ethanolic precursor solution of Li acetate, and it reacts with the Pt foil to form Li_2PtO_3 at temperatures above 600°C . The diffraction peaks became sharper as the annealing temperature was increased. This indicates an increase in

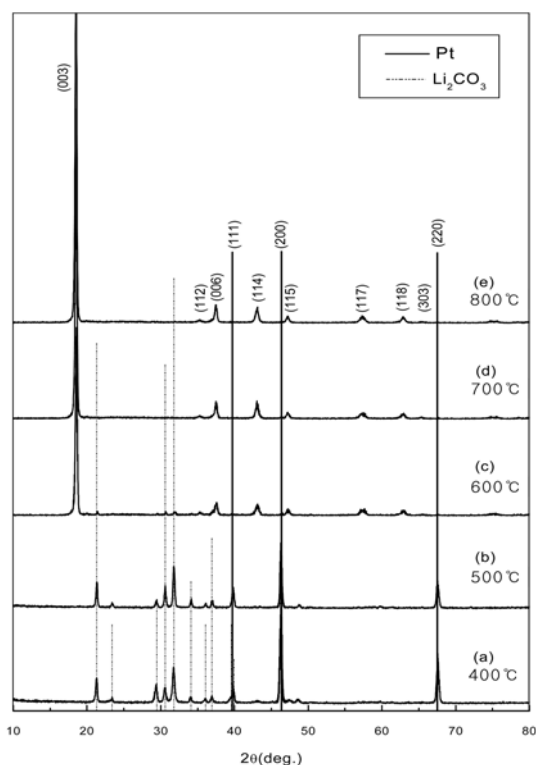


Fig. 1. The XRD patterns of the samples annealed at various temperatures.

crystallinity. From the XRD patterns shown in Fig. 1(e), Li_2PtO_3 could be indexed to a hexagonal unit cell, $P3_1$. Its lattice parameters were calculated to be $a = 5.18 \text{ \AA}$ and $c = 14.42 \text{ \AA}$ using a least-squares method, in which the values were very close to those of powdered Li_2PtO_3 reported previously.¹⁻³⁾ Therefore, the structure of the thin film Li_2PtO_3 is identical to those of powdered Li_2PtO_3 .

3.2. Surface morphologies of Li_2PtO_3 thin film electrodes

Fig. 2 shows the surface morphologies of the annealed films. Each film was deposited at 300°C followed by annealing at the various temperatures. Fig. 2(a) shows the surface morphologies of the as-deposited films. In addition, Fig. 2(b), (c), and (d) show the films annealed at 400°C , 700°C , and 800°C , respectively. During the annealing process, the morphologies of the films undergo severe change. The morphologies of the thin films deposited by an ESD technique were categorized into four different types, which are (I) a dense layer, (II) a dense layer with incorporated particles, (III) a porous top layer with a dense bottom layer, and (IV) a fractal-like porous layer.⁹⁾ Fig. 2(a) and (b) can be categorized into type (III), and Fig. 2(c) and (d) can be characterized into type (I) even though some irregularities at the surface could be observed.

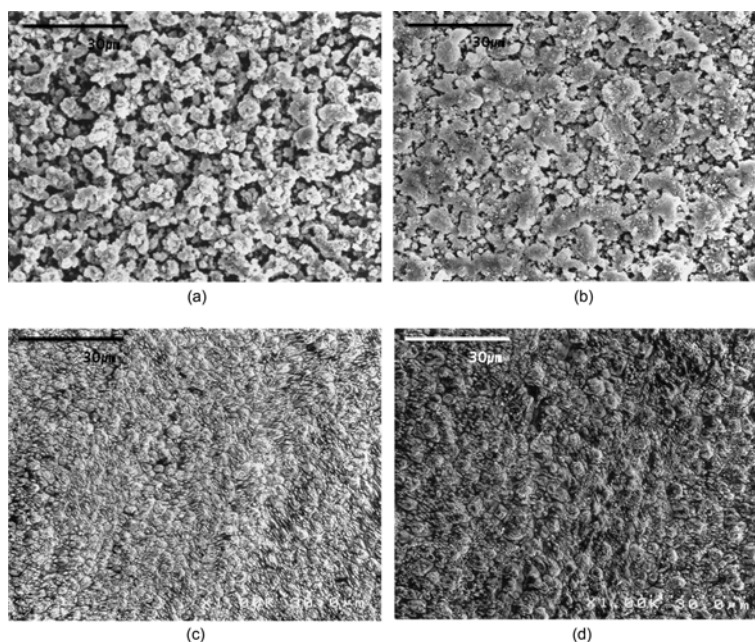
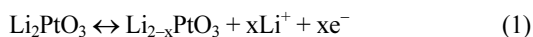


Fig. 2. Surface morphologies of the Li_2PtO_3 thin films deposited at (a) 300°C followed by heat treatment at (b) 400°C , (c) 700°C and (d) 800°C .

Considering the structural characterization in section 3.1, Fig. 2(a) and (b) show the morphologies of Li_2CO_3 and Fig. 2(c) and (d) show those of Li_2PtO_3 . The film has a porous top layer with a dense bottom layer after deposition at 300°C and became dense when Li_2CO_3 reacts with platinum to form Li_2PtO_3 during the annealing process. The SEM images shown in Fig. 2(c) and (d) provided the basis for calculating the volumetric capacities presented in section 3.3. The thickness of dense Li_2PtO_3 thin film prepared at temperatures $> 600^\circ\text{C}$ is calculated to be around $3.5\ \mu\text{m}$.

3.3. Electrochemical properties of Li_2PtO_3 thin film electrode

Li_2PtO_3 has a theoretical capacity of $209\ \text{mAh/g}$ with an assumption that it can accommodate two lithium ions per molecule according to the following reactions;



However, the actual rechargeable capacity of Li_2PtO_3 has been reported to be approximately $100\sim 120\ \text{mAh/g}$ due to structural instability. According to previous reports Li_2PtO_3 can accommodate up to ca. 1.2 lithium ions per molecule.¹⁻³⁾

Fig. 3 shows the charge/discharge curves of Li_2PtO_3 thin films prepared at various temperatures. The cutoff voltages ranged from 3.0 to 4.5 V. The films were galvanostatically cycled at a C-rate of 1/20. The annealing temperatures of each sample are shown at the upper right corner of the graphs. The open circuit potentials of the films were

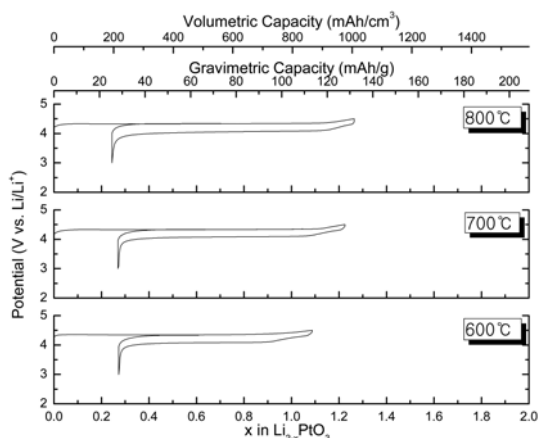


Fig. 3. Charge-discharge curves of Li_2PtO_3 annealed at various temperature. The gravimetric and volumetric capacity scales are indicated at the top.

approximately 3.2 V. The initial charge capacities of the films were $113, 128,$ and $132\ \text{mAh/g}$ for $600, 700,$ and 800°C , respectively. According to equation (1), the x value for each sample was $1.09, 1.22,$ and $1.26,$ respectively. The initial charge capacities increased as the annealing temperature was increased, and that of the sample annealed at 800°C exceeded that of the previously reported value.¹⁻³⁾ The first discharge capacities for each sample were $85, 100,$ and $107\ \text{mAh/g}$, respectively. These values were $28, 28,$ and $25\ \text{mAh/g}$ smaller than the initial charge capacity of each film, which indicates $75\%, 78\%,$ and 81% efficiency (= discharge capacity/charge capacity) in the first cycle, which are the similar to those reported previously.¹⁻³⁾ Overall, the electrochemical performances of the films improve as the crystallinity of the films increase.

The gravimetric capacities of the Li_2PtO_3 thin film electrodes in this study were slightly larger than $100\ \text{mAh/g}$, which are less than that of other layered structured cathode materials, LiMO_2 ($M = \text{Co}, \text{Ni}$). However, its volumetric capacities were greater than that of the other layered cathode materials. The top of Fig. 3 shows the volumetric capacity scale. The volumetric capacity was calculated from the gravimetric capacity and density of the films, with the assumption that the films were dense. The density of Li_2PtO_3 is $7.636\ \text{g/cm}^3$. The volumetric discharge capacity of the film prepared at 800°C was $823\ \text{mAh/cm}^3$. This value is ca. 10% higher than that of LiCoO_2 (ca. $750\ \text{mAh/cm}^3$), and even exceeds that of powdered Li_2PtO_3 ($764\ \text{mAh/cm}^3$).¹⁻³⁾ In microbatteries, it is important to integrate a larger quantity of the active materials into a limited area or volume. Therefore, materials with a high volumetric capacity are preferred. Li_2PtO_3 thin film electrodes meet these demands and are potential candidates for cathode materials in lithium secondary microbatteries that can be implanted into human body.

4. Conclusions

In this study, Li_2PtO_3 thin film electrode was synthesized. Li_2PtO_3 is a unique 4 V class cathode material among 5d metal compounds, which shows a very high volumetric capacity. Its structural change during the annealing process, electrochemical performance and surface morphology changes were investigated. Using an ESD technique, a dense thin film of Li_2PtO_3 was easily prepared by a two-step process involving deposition of the precursor solution onto a heated Pt substrate and the subsequent annealing process in a furnace. After deposition, Li_2CO_3 was the major phase that existed on the substrate.

During annealing process, at temperatures $> 600^{\circ}\text{C}$, Li_2CO_3 reacted with the platinum substrate and formed a dense Li_2PtO_3 thin film. The electrochemical performance of the films annealed at 800°C showed volumetric capacity of 817 mAh/cm^3 , which was approximately 15% larger than that of LiCoO_2 .

Acknowledgement

The work done at Yonsei University was supported by the IT R&D program of MKE/KEIT [KI002177, Pouch/Radial type Lithium Ion Capacitor for Ubiquitous Electronics]. The work done at KIST was supported by the Growth Engine Technology Development Program funded by the Ministry of Commerce, Industry and Energy (MOCIE) of Korea.

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