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DEVELOPMENT OF THIN FILM OF $LiCoO_2$ FOR MICRO BATTERY ELECTRODE BY USING DC SPUTTERING TECHNIQUE

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ABSTRACT

DEVELOPMENT OF THIN FILM OF $LiCoO_2$ FOR MICRO BATTERY ELECTRODE BY USING DC SPUTTERING TECHNIQUE. In this study, the development of thin film for electrode utilizing the crystalline $LiCoO_2$ by using DC sputtering technique has been done. The goal was to understand the characteristics of $LiCoO_2$ as a candidate material to be used as cathode for a thin film lithium based micro battery. During the sputtering process, a pelletized $LiCoO_2$ that contained approximately 5 %w/w Poly Vinyledene Fluoride (PVDF) binder was used. The $LiCoO_2$ was deposited on silicone as target substrate. The sputtering result was characterized first by an optical microscope, followed by more detail analysis by using Scanning Electron Microscope coupled with EDS (SEM/EDS), X-Ray Diffraction (XRD) and Atomic Force Microscope (AFM) techniques. The results showed that the thin film of $LiCoO_2$ was deposited on the silicon substrate at 4 μm thickness when the sputtering was carried out at 0.225 Torr pressure, 20 mA current for 6 hours. Based on the AFM studies, however, the thin film was not deposited evenly on the surface. The contour of the surface still contained substantial presence of hills and valleys. Improvement on this matter is still required to optimize the outcome.

Key words : Sputtering, Thin film, Micro battery, Lithium battery, $LiCoO_2$

ABSTRAK

PENGEMBANGAN LAPISAN TIPIS $LiCoO_2$ UNTUK ELEKTRODA BATERAI MIKRO MENGGUNAKAN TEKNIK *DC-SPUTTERING*. Dalam penelitian ini, pengembangan lapisan tipis untuk elektroda yang terbuat dari kristal $LiCoO_2$ dengan teknik *DC sputtering* telah dilakukan. Tujuan penelitian ini adalah untuk memahami karakteristik dari $LiCoO_2$ sebagai material yang berfungsi sebagai katoda dalam sebuah baterai mikro lapisan tipis. Proses *sputtering* ini mempergunakan pelet $LiCoO_2$ yang mengandung 5 %w/w *Poly Vinyledene Fluoride* (*PVDF*) sebagai material pengikat. $LiCoO_2$ ini dideposisikan pada permukaan silikon sebagai substrat. Hasil dari *sputtering* dikarakterisasi mempergunakan mikroskop optik, yang diikuti dengan analisis dengan *SEM/EDS*, *XRD* dan *AFM*. Hasilnya menunjukkan bahwa $LiCoO_2$ telah terdeposisi pada permukaan silikon dengan ketebalan 4 μm ketika *sputtering* dilakukan pada tekanan 0,225 torr, arus 20 mA dengan lama *sputtering* 6 jam. Meskipun demikian, dari data *AFM*, lapisan tipis yang dihasilkan masih belum terdeposisi secara merata. Kontur dari permukaan masih menunjukkan keberadaan bukit dan lembah yang signifikan. Pengembangan lebih jauh untuk meningkatkan kualitas dari lapisan tipis masih perlu dilakukan.

Kata kunci : *Sputtering*, Lapisan tipis, Baterai mikro, Baterai litium, $LiCoO_2$

INTRODUCTION

Thin film rechargeable battery is a small energy source that can be ideal for various electronic equipments including micro electrochemical system such as MEMS equipments, smart card, biomedical equipments, RFID (Radio Frequency Identification) and Tag. For these applications, thin film battery will function as the on-board battery, i.e. a portable power source that is integrated with the complete electronic circuit. Moreover, the micro battery has an additional advantage that it can be efficiently recharged, which make it an ideal choice for various applications being developed currently [1]. The studies that support the progress of this technology centers on various findings within the area of solid state ionic that focused on the development of new materials for electrode to be used on the solid state battery [2].

The research of lithium battery as portable energy sources also focuses on the effort to increase the energy density, to create light weight materials with multiple cycles of charge/recharge, with inherent safety characteristics. The work that is reported here was aimed to develop thin film electrode based on the crystalline $LiCoO_2$ that would serve as cathode in the all solid state lithium rechargeable micro batteries [3-5].

EXPERIMENTAL METHOD

To create a pelletized tablet of $LiCoO_2$ with a diameter of 2.54 cm (1 inch) that is suitable to be used as the target in the available DC sputtering device, the $LiCoO_2$ must be added by 3-5 %w/w of binder material. Poly Vinyledene fluoride (PVDF) was used as the binder material in this work. In the process, the PVDF was dissolved in Dimethylsulfoxide (DMSO) as organic solvent at a temperature of 80°C at concentrations between 5-10 %w/v. A known volume of PVDF solution was then mixed with the $LiCoO_2$ such that the final concentration of PVDF in $LiCoO_2$ was between 3-5 %w/w after the solvent was evaporated.

The $LiCoO_2$ and PVDF mixture was then pressed at a pressure of 2000 kg/m^2 for 5 seconds into a tablet with a diameter of 2.54 cm. This pellet was then used as the target during the DC sputtering process for its final deposition onto silicon substrate. The sputtering was carried out at 0.225 Torr pressure, 20 mA current, for 6 hours long duration. The $LiCoO_2$ thin film electrode that was obtained was then characterized by using an optical microscope for visual inspection, followed by SEM-EDX analysis and X-Ray Diffraction (XRD), as well as Atomic Force Microscopy (AFM).

RESULTS AND DISCUSION

The pellet of $LiCoO_2$ with 5% PVDF binder as the compaction result was characterized by SEM/EDS and the results are shown in Figure 1. The figure shows the existence of PVDF being deposited either as nano size cluster of particles or, in the more concentrated region, as fiber looking material that is located between the $LiCoO_2$ granule. This PVDF had been shown to be

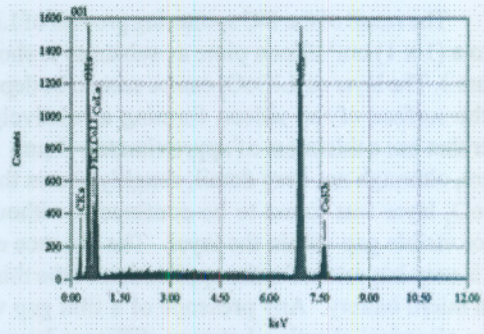

Figure 2. EDS Pattern of $LiCoO_2$/PVDF Mixture

Table 1. Composition of $LiCoO_2$/PVDF mixture from EDS

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2495

Element	(keV)	Mass %	Error %	Atom %
C K	0.277	9.27	0.10	20.59
O K	0.525	27.48	0.11	45.81
F K*	0.677	5.23	0.15	7.34
Co K	6.924	58.02	0.33	26.26
Total		100.00		100.00

capable of binding the $LiCoO_2$ granules and gave the pellet sufficient cohesion for its use as a sputtering target. It is, however, noted, that the distribution of PVDF was not good enough indicating not sufficient level of mixing during the drying process.

The results of the quantitative analysis as shown on Figure 2, also confirmed PVDF existence in $LiCoO_2$ powder, as shown by the peak at 0-1.5 keV. PVDF exist on this area at 5.23 %at. This PVDF functions as binder for granule of electrode and because position PVDF is located between granules, it will also assist to eliminate the gap between $LiCoO_2$ granules.

In terms of shapes, some of granules appeared to approach an ellipsoidal shape to near rectangular shape. However, the average diameters were all effectively falling within the number mentioned above. It is also noted that some of the granules appeared to have agglomerated with their neighbour particles, while some appeared to remain separated on their own. Based on this result, it is seen that the size are relatively uniform and it is already in the lower range of µm, though the shape are quite varied.

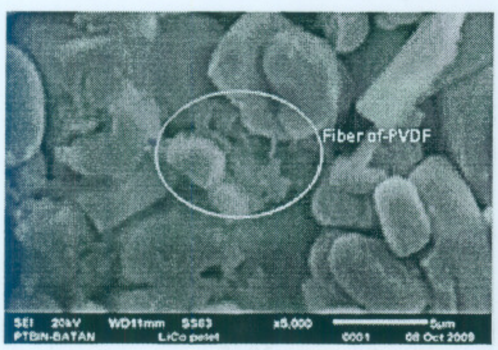

Figure 1. Microstructure of $LiCoO_2$/PVDF

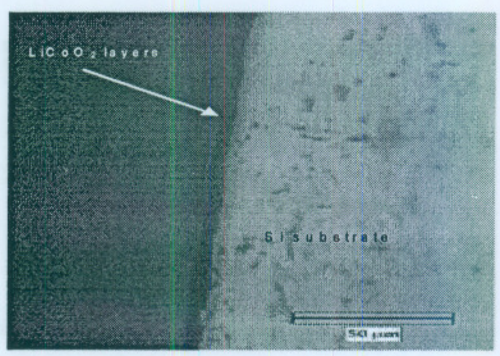

Figure 3. Cross section of thin film $LiCoO_2$.

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The result of the DC sputtering process of $LiCoO_2$ on to a (1 x 1) cm^2 silicon plate as substrate is shown in Figure 3. The layer of $LiCoO_2$ can be seen to be deposited on the surface of the silicon forming a relatively thin layer that has a thickness of approximately 4 μm. In the figure, although not very detail, roughly shows that the $LiCoO_2$ layer was found to be continuous without any major visible gap within the layer. The absence of this gap is very important for the application of the thin film for a micro battery. Any presence of a film gap would cause electrical shorting between different layers that form the battery as they are being stacked on top of the next layer.

The topographical analysis of the $LiCoO_2$ thin film from SEM and AFM analysis is shown in Figure 4 and Figure 5. It shows less than uniform distribution of $LiCoO_2$ on the surface of silicon substrate. It is however noted that the presence of PVDF dots or fibres were not observed. It is likely that the PVDF was not seen here because it had been evaporated during the sputtering process under vacuum. However, it is also possible that the PVDF had been mixed more thoroughly as a result of the sputtering process such that PVDF presence could not be seen physically. Semi quantitative analysis such as EDS could confirm the presence or absence of PVDF on the surface. This analysis should be done in any future experiment.

Moreover, the figures also show the formation of thin film of $LiCoO_2$ on silicon substrate that is very rich with different contour. The presence of hills and valleys are clearly present. This phenomenon is particularly obvious based on the results of the AFM (Figure 5). At the selected area for analysis, that is (5 x 5) μm^2, the surface is shown to possess ranges of thickness contour between -500nm to +500 nm.

Diffraction pattern from XRD analysis for $LiCoO_2$ thin film on silicon substrate can be seen in Figure 6. For comparison, the XRD pattern of the silicon substrate used in this study is also included (Figure 7). Additionally, XRD pattern of $LiCoO_2$ granules are also shown in Figure 8. Upon comparison diffraction pattern of silicon appeared to dominate the pattern of $LiCoO_2$. Likely, during the running of the XRD, the outer edge of the substrate (bare silicon) were also targeted and contributed to the diffraction results. In spite of this, it can still be seen that the pattern on Figure 6 still possess the signature peaks of $LiCoO_2$ at 2θ angles of near 45° and near 23°. The substantial peaks at near 70° and 34° are mainly due to the presence of silicon substrate. It

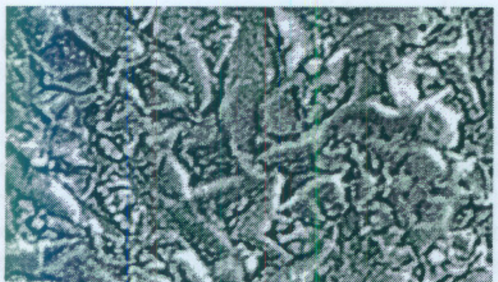

Figure 4. Surface appearance of the thin film based on SEM results

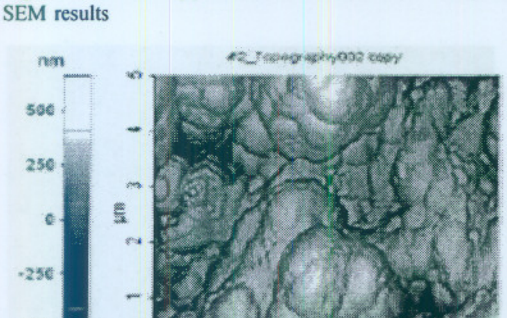

Figure 5. Topographic appearance of $LiCoO_2$ thin film from AFM result

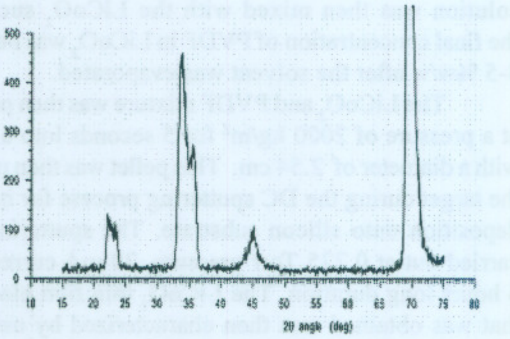

Figure 6. Diffraction pattern of $LiCoO_2$ thin film

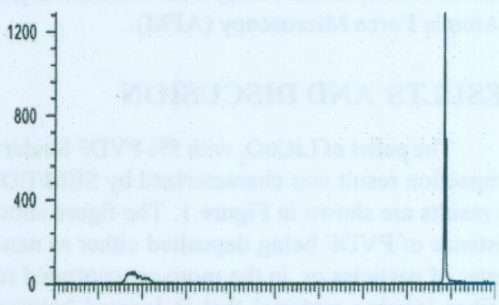

Figure 7. Diffraction pattern of Si wafer

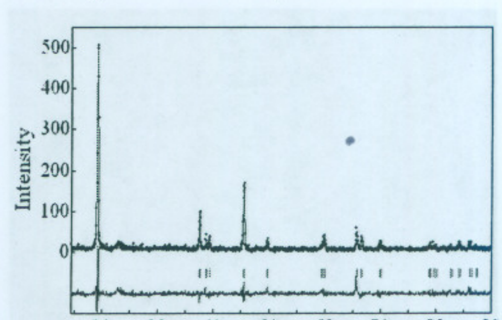

Figure 8. XRD spectra of $LiCoO_2$ crystal granules

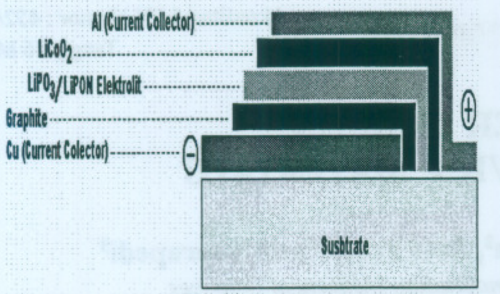

Figure 9. Layer of thin film components for a micro battery

should be noted however, that broadening of $LiCoO_2$ peak is clearly seen. A shift from high degree of crystallinity to the more amorphous forms might have taken place. To reacquired the crystalline form, possibly an annealing process would be needed since the $LiCoO_2$ if it is expected to function as cathode for a battery, it should been crystalline form. The annealing process might need to be done at temperature as high as 700 ºC [4].

The application of Rietveld structural refinement for X-Ray diffraction patterns for $LiCoO_2$, aiming at the determination of the structure of $LiCoO_2$, the authors considered that the $LiCoO_2$ was available as a layered structure (space group R-3m) [5]. Hence, it is possible that the crystalline $LiCoO_2$ that has been purchased commercially is dominated by the layered structure $LiCoO_2$ which is more suitable in terms of its electrochemical properties to be used as chatode materials. The high temperature annealing process of $LiCoO_2$ is expected to alter the more amorphous form of $LiCoO_2$ to attain a structure that is similar to this commercially available $LiCoO_2$.

In the effort to construct the thin film battery, the different layers of current collectors on each end, the electrodes and electrolyte must be carefully designed. It is important to ensure that two distinctive layers that are separated by a layer located in between must not have any physical contact. Any such contact would result in short cutting of the battery internal circuit, causing the battery to become unable to store any electric power.

A design of the multiple layer of current collectors, electrodes and Electrolyte has been made (Figure 9). This design would be used in future experiment to construct the prototype of an all solid state thin film battery. The study of the layers of thin film of electrolyte and current collectors have been reported elsewhere which are also integrated parts of this study [6,7].

CONCLUSIONS

Pellet of $LiCoO_2$ that include 5% PVDF binder suitable to be used for sputtering target has been constructed. The pellet was found to possess sufficient cohesion that gave it good structural integrity to be used for the target.

The layer of $LiCoO_2$ thin film on silicon substrate was analyzed by using optical microscope. It was observed that the thickness of $LiCoO_2$ layer was about 4 µm as result of the DC-sputtering process using the following sputtering condition : 0.225 torr pressure, 20 mA electric current, 6 hours. The topographic properties of this thin film were analyzed by SEM and by AFM. It was observed that the microstructure of the thin film $LiCoO_2$ still exhibit substantial presence of varied contour in the appearance of hills and valleys that ranged in thickness between -500 nm to +500nm. A more even and flattened distribution of the thin film is needed to produce good quality of thin film for a battery component.

The XRD results showed that the deposited $LiCoO_2$ has substantial shift toward a more amorphous form from its originally crystalline nature after it is being deposited onto the silicone surface by DC sputtering. Hence, annealing process may be needed to return the structure to a more crystalline format.

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