

CHARACTERIZATION OF LITHIUM THIN FILM BATTERY COMPONENTS PREPARED BY DIRECT CURRENT SPUTTERING

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ABSTRACT

CHARACTERIZATION OF LITHIUM THIN FILM BATTERY COMPONENTS PREPARED BY DIRECT CURRENT SPUTTERING. New electrolyte materials allow the design of flat lithium primary or secondary batteries for miniaturised devices from smart cards to CMOS back up. In this paper, the preparation of LiPON thin film component and an all solid-state thin film batteries consisting of an LiPON solid electrolyte, layered rocksalt LiCoO_2 electrode, Pt and ITO current collectors, and amorphous SnO anode manufactured using sputtering and vacuum evaporation techniques is presented and discussed. The crystal structure of the LiPON thin film deposited on different substrates such as glass, Si wafer and Pt surface was characterized by X-Ray Diffractometer (XRD) method. The as-deposited cathode films are amorphous or partially crystallized. The amorphous intensity pattern appear with diffuse peaks situated at angular positions of $2\theta \sim 14^\circ$, 22° and 48° . The thin-film battery was characterized by complex impedance- and Scanning Electron Microscope (SEM) method. Cracks, which are dependent upon deposition times, are observed for the as-deposited cathode films. The impedance and conductivity characteristics of the sample, do not reflect the standard characteristics of a battery. This type of behaviour could possibly be caused by the existence of a short circuit in the system configuration, so that the sample fails to generate the battery characteristics. In conclusion it could be safely assumed that the final result so far is just a multi-component system with a resistance value of 6 ohm, frequency-dependent capacitance, and a quasi Direct Current conductivity of 1.6×10^{-1} (S).

Keywords: Lithium ion battery, Thin film battery, DC and RF Sputtering, LiCoO_2 , Li_3PO_4 , LiPON

ABSTRAK

KARAKTERISASI KOMPONEN BATERAI LAPISAN TIPIS LITHIUM HASIL PREPARASI DENGAN MENGGUNAKAN METODE *DIRECT CURRENT*. Bahan elektrolit baru telah memungkinkan terciptanya desain sebuah baterai lithium datar primer atau sekunder untuk digunakan pada berbagai perangkat miniatur mulai dari kartu cerdas hingga asesori pendukung CMOS. Dalam tulisan ini dibahas pembuatan komponen lapisan tipis LiPON dan baterai lapisan tipis yang keseluruhannya terdiri dari bahan padatan (*solid-state*), yaitu elektrolit padat LiPON, elektroda *rocksalt* berlapis LiCoO_2 , kolektor Pt dan pengumpul arus ITO, dan anoda amorf SnO. Komponen baterai telah disintesis dengan menggunakan teknik penguapan *sputtering* dan teknik vakum. Struktur kristal lapisan tipis LiPON yang telah dideposisi pada substrat yang berbeda seperti kaca, Si *wafer* dan permukaan Pt dikarakterisasi dengan metode *X-Ray Diffractometer (XRD)*. Katoda lapisan tipis yang terdisposisi berbentuk amorf atau terkristalisasi sebagian. Pola intensitas amorf tampil dengan puncak-puncak difusi yang terletak di posisi sudut-sudut refleksi $2\theta \sim 14^\circ$, 22° dan 48° . Baterai lapisan tipis dikarakterisasi dengan metode impedansi kompleks dan metode *Scanning Electron Microscope (SEM)*. Diamati bahwa pada lapisan katoda terdisposisi terdapat retak (*cracks*), yang ukurannya tergantung pada waktu deposisi. Karakteristik Impedansi dan konduktivitas sampel tidak mencerminkan karakteristik standar untuk baterai. Perilaku sedemikian ini dapat disebabkan oleh adanya hubungan arus pendek dalam konfigurasi sistem, sehingga sampel gagal untuk menghasilkan karakteristik sebuah baterai. Sebagai kesimpulan akhir dapat diasumsikan secara pasti bahwa sejauh ini hasil akhir percobaan menunjukkan sistem belum merupakan baterai sempurna melainkan masih merupakan suatu sistem multi komponen dengan nilai resistansi 6 ohm, kapasitansi tergantung pada frekuensi dan konduktivitas kuasi *Direct Current* sebesar $1,6 \times 10^{-1}$ (S).

Kata kunci: Lithium ion, Baterai lapisan tipis, DC dan RF Sputtering, LiCoO_2 , Li_3PO_4 , LiPON

INTRODUCTION

Portable power applications continue to drive research and development of advanced battery systems. Since lithium ion batteries have superior characteristics such as high energy density, high voltage and long cycle life, they are widely used in portable data terminal equipment starting with cellular telephones and laptop computers as well as in industrial equipment [1]. Often, the extra energy content and considerations of portability have outweighed economics when a system is considered. This has been true of lithium battery technologies for the past thirty years and for lithium ion battery systems, which evolved from the early lithium battery development. In recent years, the need for portable power has accelerated due to the miniaturization of electronic appliances where in some cases the battery system is as much as half the weight and volume of the powered device. Lithium element has been found to have the highest voltage, lightest weight, and greatest energy density of all metals. The first published interest in lithium batteries began with the work of Harris in 1958 [2].

The work eventually led to the development and commercialization of a variety of primary lithium cells during the 1970s. Full-scale use of large lithium batteries is predicted to cover such wide areas such as defence, aerospace, medical equipments, automobiles, transportation equipment, stationary energy storage, industrial machines and construction equipment in the not so distant future.

The configuration of a lithium ion battery that is already in practical use, is one in which the cathode, the anode and the separator that isolates the two electrodes are immersed in an electrolyte; lithium ions move between the cathode and the anode and charging and discharging are carried out by oxidation-reduction reactions that occur at each of these two electrodes [3].

Lithium cobalt dioxide (LiCoO_2) is widely used for the cathode material. Because cobalt is a scarce element, problems related to the high cost arise, despite the fact that LiCoO_2 has outstanding properties. In recent years, batteries that use phosphates (for which there are an abundance of reserves worldwide) in the electrolyte materials, such as Li_3PO_4 have been developed with the primary goal of reducing costs [4,5]. Also in partial fulfilment of this goal, nickel based batteries, which is less expensive than cobalt, and iron phosphate based batteries have been developed in recent times. These cathode materials take the form of composite metal oxides of lithium and transition metals, and they are used as crystals with structures suitable for lithium intercalation and de-intercalation. For example, materials with layered crystal.

In order to construct a thin film battery, all the components of anode, solid electrolyte, cathode and suitable current collectors should be fabricated into a

multilayered thin film. Several techniques have been used for this purpose such as vacuum thermal deposition, RF magnetron sputtering, electrostatic spray deposition, electron beam deposition, and pulsed laser deposition. In this paper, the preparation of LiPON (Li_3PO_4 doped with N) thin film component and an all solid-state thin film batteries consisting of an LiPON solid electrolyte, layered rocksalt LiCoO_2 electrode, Pt and ITO current collectors, and amorphous SnO anode manufactured using sputtering and vacuum evaporation techniques is presented and the results discussed.

EXPERIMENTAL METHODS

All thin film batteries were fabricated by using sputtering and vacuum evaporation techniques [6]. All battery components were deposited onto glass and Si-wafer substrates where the Mn layer acts as a good adhesive layer between glass and SiO_2 . Films were prepared in a flowing Argon atmosphere at a pressure of 2×10^{-1} Pa. The solid electrolyte targets and thin-films were prepared following the literature [7]. The schematic diagram of the thin film experimental plan is shown in Figure 1.

During the sputtering process, it is important that the separated layer must be laid without any possibility of short circuit due to inaccurate sputtering. Hence, the design as related to the sputtering process must also consider the precision limit of the sputtering device. The available Direct Current sputtering device at PTBIN (BATAN) facility was originally a vacuum evaporator

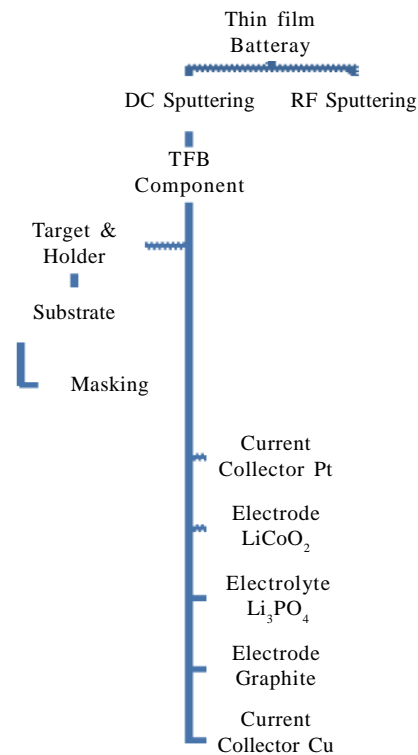


Figure 1. Schematic Diagram of the Thin Film Experimental Plan Conducted in this study



Figure 2. DC Sputtering device in operation at 800 Volt, 30 mA using Argon as sputtering gas with colored glowing plasma showing in the picture

device usually used thin film for coating of materials. The modification included the insertion of electrode for the DC voltage. The sputtering device is typically working at 800 Volt (can be up to 1 kVolt) while the current is at 30 mA. The figure of the Device before and after the modification is shown below in Figure 2.

The targets for sputtering used consisted of the components of the battery. Solid electrolytes (LiPO_3 , LiPON which is a spinel phase Li_3PO_4 doped with N), layered rocksalt LiCoO_2 electrode, Pt-, Cu- and Al current collectors, and amorphous SnO anode are then sputtered and deposited on the silicon wafer substrate [8]. The Pt-, Cu- and Al current collectors (good electron conductors) are coated on the wafer. Once the sputtering is completed the thin layers are then subjected to various measurements including but not limited to X-Ray diffraction (XRD), Scanning Electron Microscope (SEM)-Energy Dispersive X-Ray Spectroscopy (EDS), Optical Microscope, Differential Scanning Calorimetry (DSC) and LCR methods. It is also noted here that for LiCO_2 and LiMnO_2 (both are cathode material), the pellets also include a binding material i.e. the polymer PolyVinylidene Fluoride (PVDF) at 3 %w/w because there is a lack of cohesion among granules of the layered-rocksalt type LiCoO_2 and LiMnO_2 cathode materials. All the layers were fabricated by the same DC Sputtering/RF Sputtering system by changing the targets and hard masks.

RESULTS AND DISCUSSIONS

Characterization by X-Ray Diffractometer

In Figure 3 the intensity pattern of X-Ray diffraction for the LiPON sample sputtered on the glass substrate (each respectively for 30 minutes and 50 minutes deposition times) and the blank glass substrate itself are presented for comparison. It seems that the diffuse peak of the amorphous intensity pattern at $2\theta \sim 14^\circ$ is more prominent in the 50 minutes' sample than in the 30 minutes sample.

In Figure 4 the pattern of X-Ray Diffraction intensity for the sputtered results of LiPON electrolytes

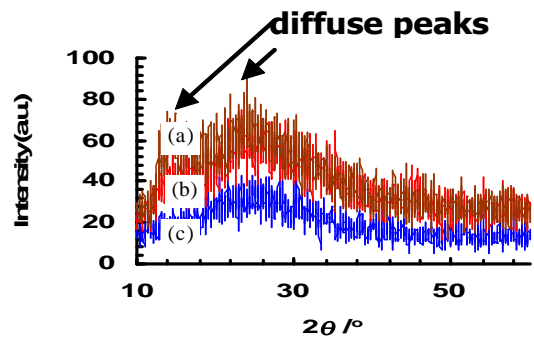


Figure 3. Comparison of the intensity of X-ray diffraction for the sample above substrate LiPON glass each for (a). 50 minutes, (b). 30 minutes deposition duration and (c). the blank glass substrate itself

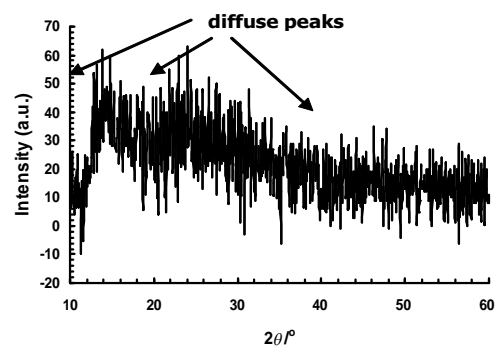


Figure 4. The LiPON X-Ray Diffraction intensity pattern after 50 minutes of deposition on a glass substrate

after 50 minutes deposition time on a glass substrate and after subtraction from the glass intensity patterns is presented. An amorphous nature of the as-deposited film is confirmed because there is no sharp peak appeared. The amorphous intensity pattern appear with diffuse peaks situated at angular positions of $2\theta \sim 14^\circ$, 24° and 48° . It seems that the first diffuse peak of the amorphous intensity pattern appearing at the angular position $2\theta \sim 14^\circ$ has a sharper profile form compared to the second diffuse peak which is centered at $2\theta \sim 24^\circ$ with a slightly wider profile.

In Figure 5 patterns of X-Ray diffraction intensity for the sample substrate Si-wafer/Pt/LiPON are presented. The diffraction pattern is a mixture of

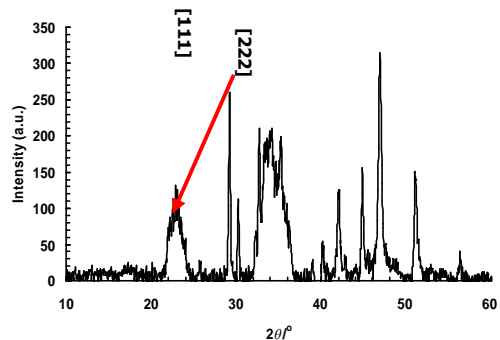


Figure 5. The pattern of X-Ray Diffraction intensity for the Si-wafer substrate /Pt/LiPON configuration

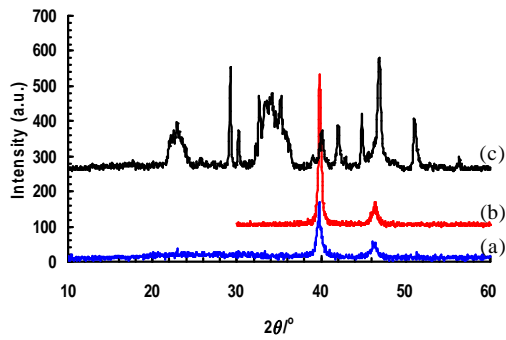


Figure 6. Comparison of the intensity pattern of X-Ray Diffraction for the (a). Si-wafer substrate, (b). Pt and (c). Si-wafer/Pt/LiPON

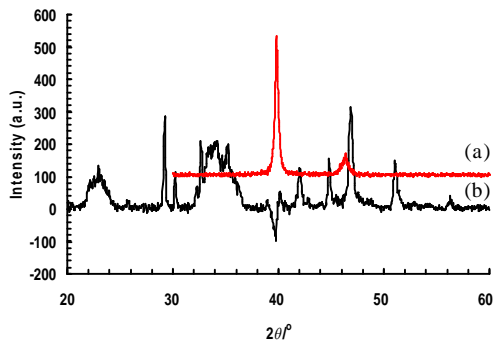


Figure 7. Comparison of the intensity of X-Ray Diffraction patterns for (a). Pt and (b). Si-wafer substrate/Pt/LiPON after subtraction from the intensity of the blank Si-wafer pattern

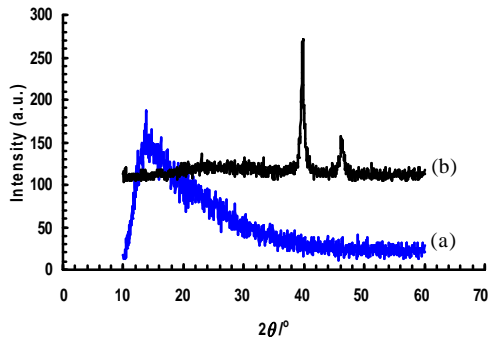


Figure 8. Comparison of the intensity of X-ray diffraction pattern of (a). Si-wafer substrate /LiPON and (b). the blank Si-wafer diffraction pattern

amorphous and crystalline patterns. The observed (111) and (222) reflection peaks in the film after annealing are either of the spinel phase LiPON or Pt and Si substrates.

Comparison of the intensity pattern of X-Ray Diffraction for the Si-wafer substrate, Pt and Si-wafer/Pt/LiPON is presented in Figure 6.

Comparison of the intensity of X-Ray Diffraction patterns for Pt and Si-wafer substrate/Pt/LiPON after subtracted from the intensity of the blank Si-wafer pattern is presented in Figure 7.

Intensity of the measured diffraction pattern of the [Si-wafer substrate/Pt/LiPON] after subtraction from the blank Si-wafer intensity pattern turns out to be negative in the 2θ diffraction angle range $\sim 39^\circ$ - 40.5° .

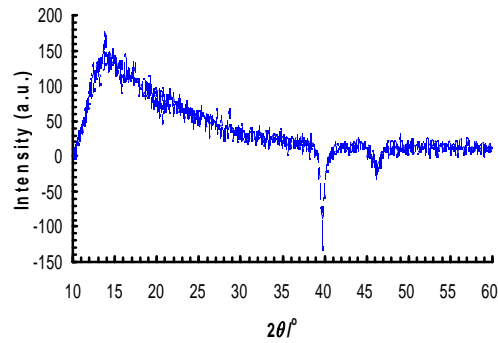


Figure 9. The intensity of Si-wafer/LiPON X-Ray diffraction pattern after subtraction from the diffraction pattern intensity of blank Si-wafer

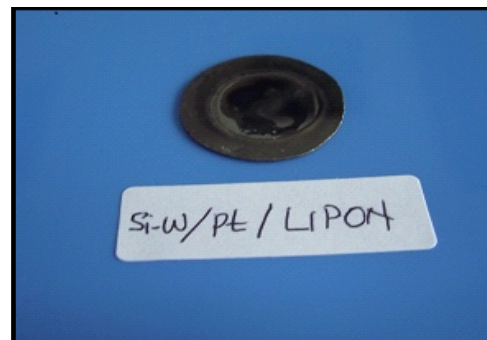


Figure 10. A thin layer of electrolyte LiPON on Pt on Si-wafer substrates obtained by by RF Sputtering. also looks uneven, but it is being optimized to obtain a more homogeneous layer

Here it is obvious that the diffraction pattern of the LiPON sample shows a more crystalline type diffraction pattern.

In Figure 8 the comparison of the intensity of X-Ray Diffraction pattern of Si-wafer substrate /LiPON and the blank Si-wafer diffraction pattern is presented. It is clear that the diffraction pattern of the amorphous substrate Si-wafer/LiPON tends to converge into a diffuse peak centered on the diffraction angle $2\theta \sim 14^\circ$.

In Figure 9 the intensity of Si-wafer/LiPON X-Ray Diffraction pattern after subtraction from the diffraction pattern intensity of blank Si-wafer is shown. As might be expected here the intensity pattern of the amorphous LiPON samples tend to form a single diffuse peak centered at diffraction angle $2\theta \sim 14^\circ$, and it appears that no other diffuse peaks are present in the pattern. On the other hand, negative intensity centered on the diffraction angle $2\theta \sim 40^\circ$ and $2\theta \sim 46.5^\circ$ was also observed.

In Figure 10, a thin layer of electrolyte LiPON on Pt on Si-wafer substrates obtained by by RF Sputtering is shown. It appears that the film has an uneven thickness distribution, but it is being optimized to obtain a more homogeneous layer.

In Figure 11 a complete set of a thin-film rechargeable battery prepared by RF Sputtering method with Pt current collectors, LiCoO₂ electrode, LiPON



Figure 11. A set of a thin film rechargeable battery prepared by RF Sputtering method

electrolyte, tin oxide (SNO) positive electrode and the ITO currents collector (collector) is shown. From the XRD measurements results presented above, it could be concluded that the main components of the lithium based thin-film battery have a mainly amorphous structure and attain the thin film morphology as expected. Next the thin film battery is characterized to further check the performance characteristics.

Characterization of Thin Film Electrolyte LiPON

Impedance characterization of thin film was utilized using LCR meter. All of the sample samples were measured using frequency characteristics in the frequency range of 45 Hz to 1MHz, in a voltage of 1V. The objective of measurement was to find the impedance characteristics and the conductivity of thin film samples.

LiPON Based Thin Film Battery

The sample of the thin-film battery consists of 4 electrode points. Every point was characterized with the same parameters and all produces very similar result. Consequently, only the measurement result of a single point is needed to be shown here since those are representative for all the others. The impedance characteristics and conductivity of LiPON based thin-film battery sample is shown in the next figures.

The impedance and conductivity characteristics of the sample shown in Figure 12 do not reflect the standard characteristics of a battery. The impedance plot consists of just a straight line parallel to the imaginary Z'' -axis which intersects the real Z' -axis at the value of 6 ohms. This straight line pattern normally represents the characteristics of an electronic circuit consisting of a resistor and a capacitor in series. The conductivity of this sample also does not depend on the frequency. The value of conductivity was 1.6×10^{-1} (S) which remains constant along the frequency range. This type of behaviour could possibly be caused by the existence of a short circuit in the system

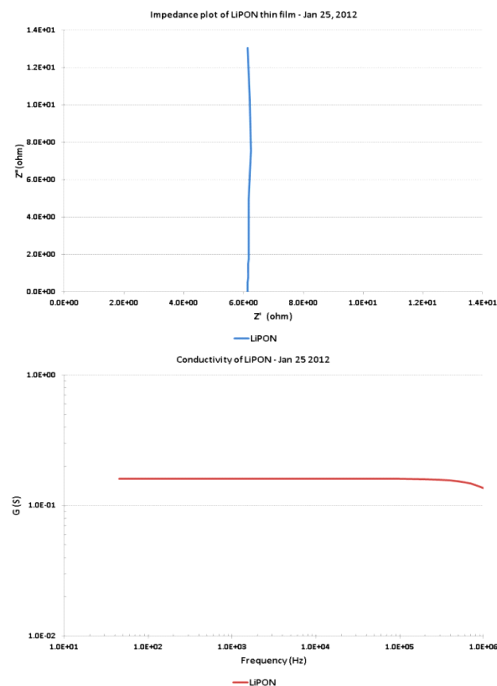


Figure 12. The impedance and conductivity characteristics of the thin film battery

configuration, so that the sample fails to generate the battery characteristics. In conclusion it could be safely assumed that the final result so far is just a multi-component system with a resistance value of 6 ohm, frequency-dependent capacitance, and a quasi DC conductivity of 1.6×10^{-1} (S).

Characterization by Scanning Electron Microscope

The SEM micrograms of the Pt thin film microstructure on a glass substrate and on a Si wafer substrate (FigureS 13 and 14) show the presence of cracks (fracture) even though the grains in the Si wafers are smaller. Cracking is believed to occur due to a prolonged coating duration (30 minutes), which causes the upsurge of excessive heat. When the coating is repeated (for Pt coating on a glass substrate) but with a shorter duration (20 minutes) no cracks were observed.

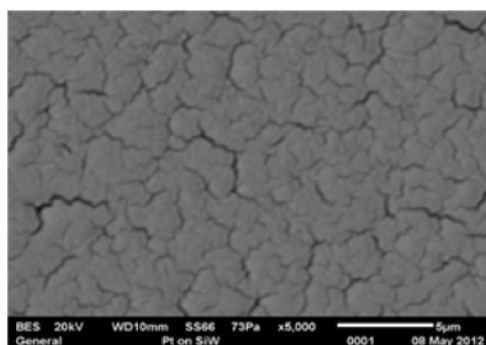


Figure 13. SEM microgram of Pt thin film layer deposited on glassy substrate

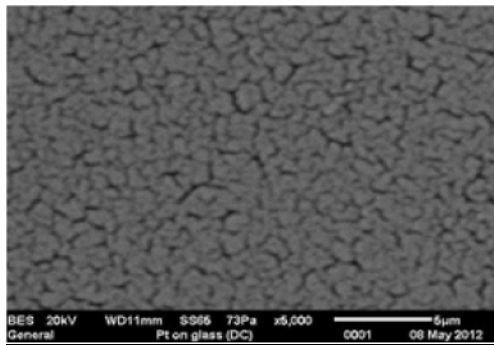


Figure 14. SEM microgram of Pt thin film layer deposited on Si wafer substrate

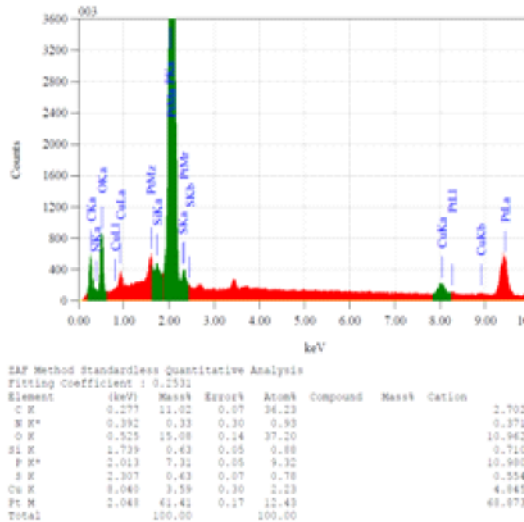


Figure 15. EDS analysis of Pt thin film on glass substrate

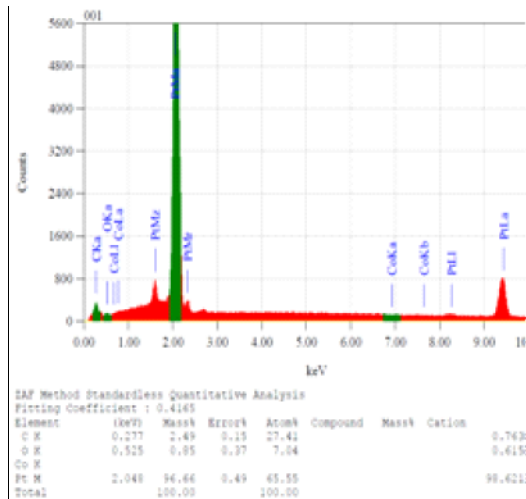


Figure 16. EDS analysis of LiPON thin film on glass substrate

The chemical composition of the surface of a Pt thin film (Figure 15) on a glass substrate shows the presence of 7.04% of elemental oxygen atoms or 0.85% by weight percentage, it is likely to originate from the glass substrate or occurs during the coating process or is caused by the impurity of the applied gas. EDS analysis for chemical composition (Figure 16)

on the surface of a Pt/LiPON/ glass substrate thin-film, signifies the presence of 0.93% nitrogen atoms in the sample, and this proves that LiPON layers have been formed during the coating process. LiPON layer has a somewhat forceful nature, which can be used to enclose Li_3PO_4 layer which is rather soft so that it can diminish the risk of leakage in the system.

CONCLUSION

Thin film battery using LiCoO_2 and LiPON based cathodes deposited on Si-wafer substrates has been fabricated by employing DC and RF sputtering techniques. However the thin film battery's impedance and conductivity characteristics do not reflect the standard characteristics of a battery. This type of behaviour could possibly be caused by the existence of a short circuit in the system configuration, so that the sample fails to generate the battery characteristics. Therefore the future research activity should be focused primarily on improvement of the deposition equipment and techniques, and also the handling of the targets and masks during the deposition should be improved considerably to produce a working standard micro battery.

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REFERENCES

- [1]. N. KUWATA, R. KUMAR, K. TORIBAMI, T. SUZUKI, T. HATTORI, J. KAWAMURA, *Solid State Ionics*, **177** (2006) 2827-2832
- [2]. J. B. BATES, N.J. DUDNEY*, B. NEUDECKER, A. UEDA, C.D. EVANS, *Solid State Ionics*, **135** (2000) 33-45
- [3]. S. L. ZHAO and Q. Z. QIN, *Journal of Power Sources*, **122** (2003) 174-180
- [4]. B. K. MONEY and K. HARIHARAN, *Appl. Phys.*, **A 88** (2007) 647-652
- [5]. J-L SOUQUET and M. DUCLOT, *Solid State Ionics*, **148** (2002) 375- 379
- [6]. E. KARTINI, Laporan Kemajuan (*Progress Report*) Program Insentif, No:1.02/SEK/IRS/PPK/I/2012, 16 Januari 2012
- [7]. H. OHTSUKA and J. YAMAKI, *Jpn. J. Appl. Phys.*, **28** (1989) 2264
- [8]. W. A. VAN SCHALKWIJK and B. SCROSATI eds, *Advances in Lithium-Ion Batteries*, Kluwer Academic/Plenum Publishers, New York, (2002)