

PAPER • OPEN ACCESS

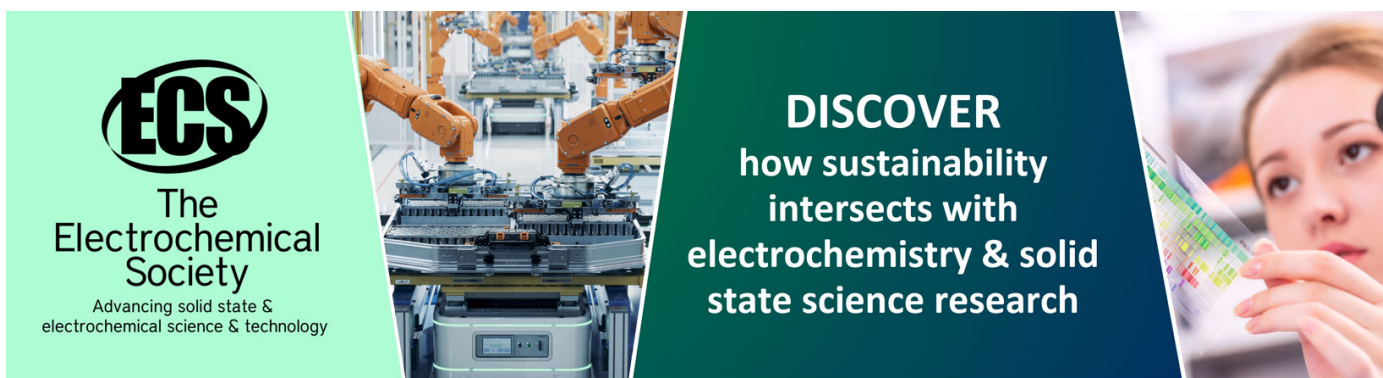
Checkerboard deposition of lithium manganese oxide spinel (LiMn_2O_4) by RF magnetron sputtering on a stainless steel in all-solid-state thin film battery

To cite this article: T H Hsueh *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **324** 012004

View the [article online](#) for updates and enhancements.

You may also like

- [Optimizing spatial properties of a new checkerboard-like visual stimulus for user-friendly SSVEP-based BCIs](#)
Gege Ming, Weihua Pei, Hongda Chen et al.
- [Charge ordering in high-temperature superconductors visualized by scanning tunneling microscopy](#)
Xintong Wang, Yonghao Yuan, Qi-Kun Xue et al.
- [Wideband radar cross-section reduction using plasma-based checkerboard metasurface](#)
Zhiming ZHAO, , Xiaoping LI et al.



Checkerboard deposition of lithium manganese oxide spinel (LiMn_2O_4) by RF magnetron sputtering on a stainless steel in all-solid-state thin film battery

T H Hsueh^{1,2}, Y Q Yu¹, D J Jan¹, C H Su¹ and S M Chang²

1 Physics Division, Institute of Nuclear Energy Research (INER), Longtan District, Taoyuan City, Taiwan

2 Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei, Taiwan

E-mail: tshsueh@iner.gov.tw

Abstract. All-solid-state thin film lithium batteries (TFLBs) are the most competitive low-power sources to be applied in various kinds of micro-electro-mechanical systems and have been draw a lot of attention in academic research. In this paper, the checkerboard deposition of all-solid-state TFLB was composed of thin film lithium metal anode, lithium phosphorus oxynitride (LiPON) solid electrolyte, and checkerboard deposition of lithium manganese oxide spinel (LiMn_2O_4) cathode. The LiPON and LiMn_2O_4 were deposited by a radio frequency magnetron sputtering system, and the lithium metal was deposited by a thermal evaporation coater. The electrochemical characterization of this lithium battery showed the first discharge capacity of 107.8 μAh and the capacity retention was achieved 95.5% after 150 charge-discharge cycles between 4.3V and 3V at a current density of 11 $\mu\text{A}/\text{cm}^2$ (0.5C). Obviously, the checkerboard of thin film increased the charge exchange rate; also this lithium battery exhibited high C-rate performance, with better capacity retention of 82% at 220 $\mu\text{A}/\text{cm}^2$ (10C).

1.Introduction

The thin film lithium battery (TFLB) is likely to be integrated with thin film solar cells and wireless signal network to be an energy harvesting module. Furthermore, the energy harvesting module is an inexhaustible power supply for internet of things (IoTs) applications and wearable devices [1].

According to related study for all-solid-state TFLBs that have significant advantages in high safety, long term storage and high cycle ability than that of the liquid electrolytes in batteries [2-6]. Among these solid electrolytes, lithium phosphorus oxynitride (LiPON) is the most popular and stable in all-solid-state TFLBs [7-9]. However, solid electrolyte has not been widely used in TFLB because of its ionic conductivity is too low to meet the required capacity at high power density. To overcome this drawback, some researchers focus on improving the ionic conductivity of the solid electrolytes, and succeeded in increasing the ionic conductivity, but the stability of these solid electrolytes is not good enough with the cathode or anode electrode [10-14]. Instead of above mentioned research, it was considered changing the morphology could create a larger area of solid electrolyte/solid active material contact, thus increasing the charge exchange rate. Here, we introduced a checkerboard deposition in all-solid-state lithium battery, which was made through radio-frequency magnetron sputtering of an amorphous LiMn_2O_4 thin film, and had changed its subsequent transformation to a crystalline phase by conventional thermal annealing. The checkerboard deposition of TFLB showed a discharge capacity of 107.8 μAh between 4.3V and 3V at a current density of 11 $\mu\text{A}/\text{cm}^2$ (0.5C).



Furthermore, the checkerboard deposition of thin film increased the charge exchange rate; also this lithium battery exhibited high C-rate performance, with better capacity retention of 76% at 220 μ A/cm² (10C).

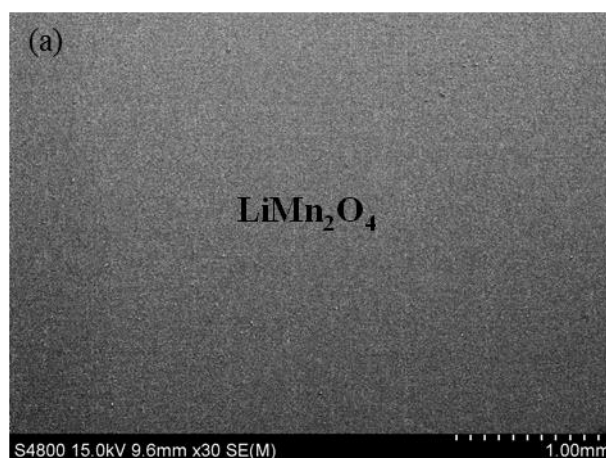
2. Experimental details

All-solid-state TFLBs (on the basis of Li/LiPON/LiMn₂O₄) were fabricated by using a home-made radio frequency (RF) magnetron sputtering system to deposit thin-film LiMn₂O₄ electrodes from a 3 inches crystallized LiMn₂O₄ (99.9 wt.%) target. First, a flexible 100 μ m-thick of stainless steel was used as the substrate and current collector; the target-to-substrate distance was fixed at 70 mm. 1,000nm-thick of LiMn₂O₄ thin film was deposited by introducing an Ar gas into the sputtering chamber at a working pressure of 5×10^{-3} torr and a RF power of 91 W. The spinel-phase LiMn₂O₄ thin film was then subjected to conventional thermal annealing at 600 $^{\circ}$ C for 90min. Next, the solid-state LiPON electrolyte was deposited to a thickness of about 2,000nm by RF magnetron sputtering of a Li₃PO₄ target under nitrogen atmosphere. The ionic conductivity of LiPON was measured as $\sim 1.5 \times 10^{-6}$ S/cm. Finally, a Li metal film with the size of 22 mm $\times$ 22 mm was deposited on the LiPON electrolyte by a thermal evaporation coater, wherein a small evaporator (cylinder type, height 40 cm, and diameter 20 cm) was set up in an argon-filled glove box.

The film structure was characterized by field emission scanning electron microscope (FESEM, model Hitachi-S4800) (Japan) and X-ray Diffractometer (XRD, model Bruker-AXS D8 Advance) (USA); the cyclic voltammograms (CV) test was carried out between 3.6–4.3 V at a scan rate of 0.01mVs⁻¹, the frequency range of AC impedance was investigated from 1×10^{-3} Hz up to 2×10^5 Hz and an AC voltage of 30mV was superimposed on a dc bias that was set at the 4.1V of each cell. The charge-discharge tests were conducted at a constant current of 55 μ A between a voltage range of 3.0–4.3 V at 298K, while the high discharge current density tests were conducted at various discharge current between 5 and 200 μ A on an electrochemical workstation (model VMP3) (USA). All measurements were conducted in an argon-filled glove box.

3. Results and discussion

Figure 1(a) and 1(b) show the top view SEM images of the layer and the checkerboard deposition of LiMn₂O₄ thin films, respectively. The layer deposition of LiMn₂O₄ thin film acting as the compared specimen is 22mm $\times$ 22mm in area and the checkerboard deposition has a deposition of 1mm $\times$ 1mm square with a distance of 0.1mm to each other under 22 $\times$ 22mm area. Both of the LiMn₂O₄ thin films are spinel structure without cracking or peeling after annealing, that indicates strong adhesion to the flexible stainless steel substrate achieved by RF magnetron sputtering. The ratio of active area between layer and checkerboard deposition of LiMn₂O₄ thin film is around 1.21:1.



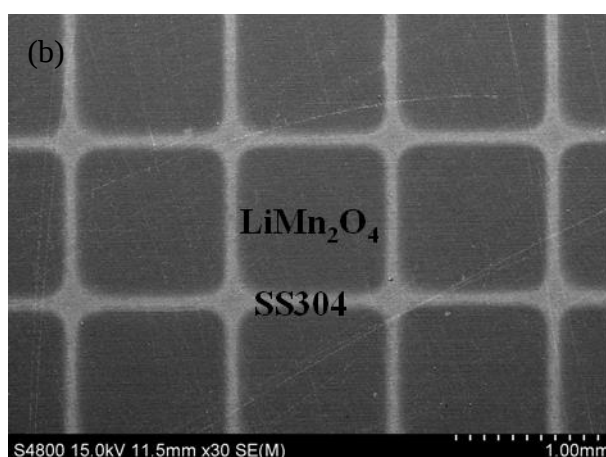


Figure 1. SEM images of top view of (a) layer and (b) checkboard deposition of LiMn_2O_4 thin film.

Figure 2 shows the XRD patterns of LiMn_2O_4 thin films deposited on stainless steel substrates annealed at 650°C for 90min. As, all the XRD measurements were carried out with a scan rate of $1^\circ/\text{min}$ in diffraction angle (2θ) range $10\text{--}70^\circ$. Both of the layer and checkboard films subsequently annealed at 650°C for 90min after deposition, the onset of crystallization was observed. These two samples exhibited similar intensity of characteristic peaks corresponding to (111), (311), (222) and (400) lines.

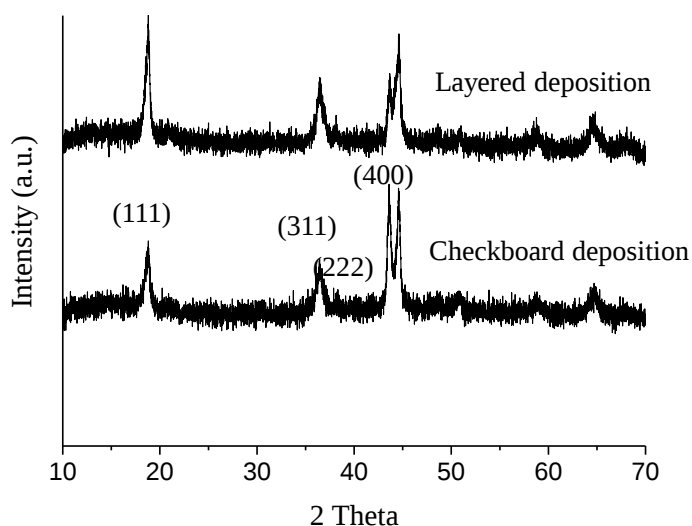


Figure 2. XRD patterns of layer and the checkerboard deposition of annealed LiMn_2O_4 thin films.

Cyclic voltammograms were investigated in this study. Figure 3 shows peak separation in the 4 V regions for the two-step de-/intercalation process of lithium ions into/out of the spinel-crystal lattice. The curves show two couples of redox peaks of the layer deposition of LiMn_2O_4 thin film were 3.97, 4.08 and 4.10, 4.18, respectively, and for the checkerboard deposition of LiMn_2O_4 thin film was 3.98, 4.04 and 4.11, 4.17, respectively. The potential differences of two pairs of redox peaks of the checkerboard deposition of LiMn_2O_4 thin film was smaller than the values of the layer deposition of LiMn_2O_4 thin films. This cyclic voltammograms indicate that the checkerboard deposition of LiMn_2O_4

thin films provide smaller resistance and clearer two couples of redox peaks than the layer deposition thin films.

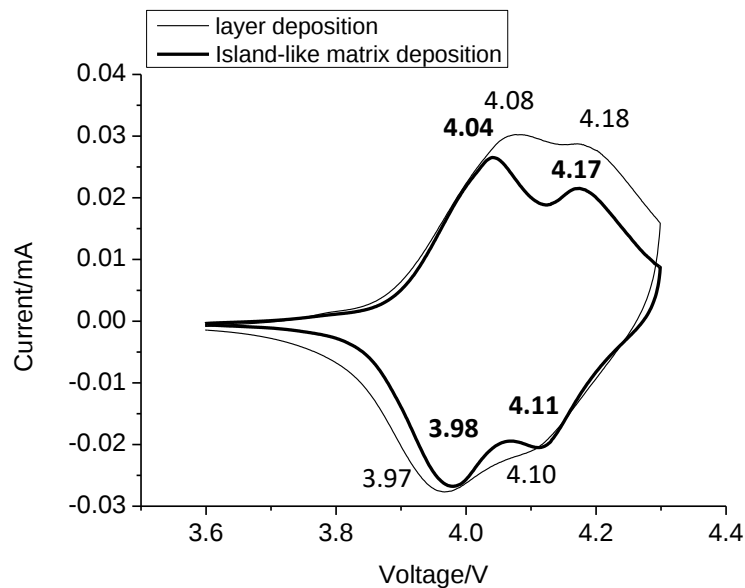


Figure 3. Cyclic voltammograms of the layer and the checkerboard deposition of LiMn_2O_4 thin films.

Figure 4 shows the Nyquist plots of the layer and the checkerboard deposition of LiMn_2O_4 thin films at room temperature. A single cell was tested at various frequencies ranging from 100 Hz to 100 MHz, with frequency decreased gradually; the Nyquist plots show two semicircles and a diagonal line. It is clear that the checkerboard deposition of LiMn_2O_4 electrode possesses low resistance of charge transfer (second semicircle), with resistance of 60 Ohm, but the value of the layer deposition LiMn_2O_4 electrode is up to 130 Ohm. The checkerboard LiMn_2O_4 electrode possesses smaller charge transfer resistance. This result is correspondent with the cyclic voltammograms mentioned above.

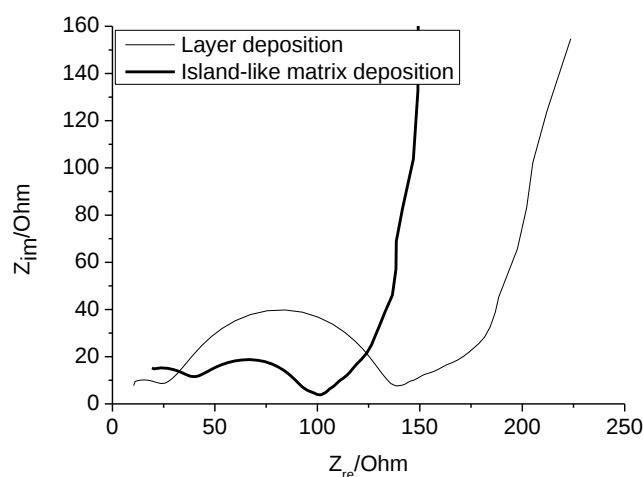


Figure 4. Nyquist plots of layer and checkerboard deposition of LiMn_2O_4 thin film.

Figure 5 displays the charge and discharge curves of the layer and the checkerboard deposition thin films. For the voltage region of 3.0–4.3 V, the characteristic charging and discharging plateaus of the checkerboard deposition of LiMn_2O_4 thin film slightly occur clearly than the layer deposition thin films. A discharge capacity of about $124\mu\text{Ah}$ at a current density of $13\mu\text{A}/\text{cm}^2$ (0.5C) was obtained for the layer deposition thin film and $108\mu\text{Ah}$ at a current density of $11\mu\text{A}/\text{cm}^2$ (0.5C) for the checkerboard deposition thin film. The ratio of discharge capacity between the layer and the checkerboard deposition of LiMn_2O_4 thin film is around 1.15:1. The data is very close to the ratio of active area between two type deposition thin films. Both of all-solid-state thin film batteries with the similar charge/discharge profile from the 1st to 3rd cycle between 4.3V and 3V means that the interfaces between $\text{LiPON}/\text{LiMn}_2\text{O}_4$ and Li/LiPON were stable.

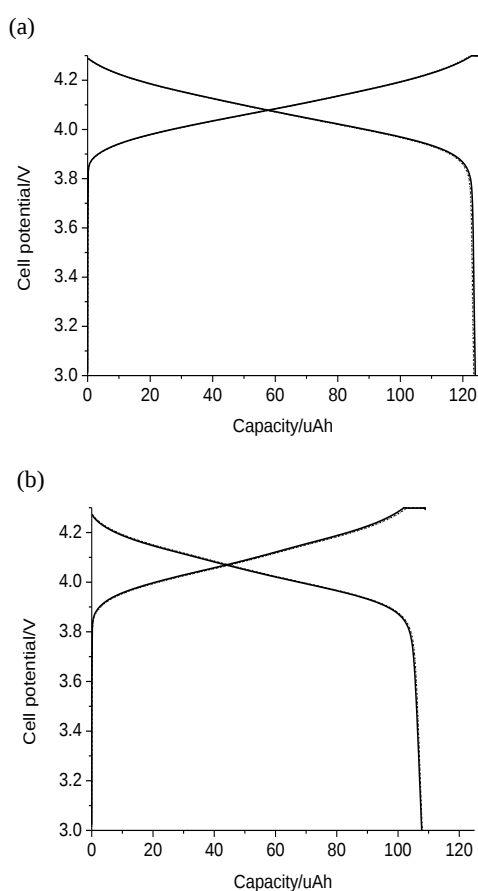


Figure 5. Charge and discharge curves of (a) layer deposition and (b) checkerboard deposition of LiMn_2O_4 thin film.

To confirm the all-solid-state of the layer and the checkerboard deposition of LiMn_2O_4 thin film lithium batteries were stable, the charge and discharge cycle test were investigated by an electrochemical workstation. Figure 6 shows the 1st discharge capacity of the checkerboard deposition of LiMn_2O_4 thin film lithium battery was $107.8\mu\text{Ah}$ between 4.3V and 3V at current density of $11\mu\text{A}/\text{cm}^2$ (0.5C) and discharge capacity of about $\sim 124\mu\text{Ah}$ (0.5C) was obtained for the first cycle of the layer deposition of LiMn_2O_4 thin film lithium battery. Within 3.0–4.3V charge/discharge cycle tests, the 150th discharge capacity was 102.9 and $117.2\mu\text{Ah}$, respectively. The results obtained after 150 cycles revealed that the checkerboard deposition of LiMn_2O_4 thin films retain over 95.5% of its initial discharge capacity and the layer deposition thin film battery was 94.5%. High capacity retention indicates a highly stable structure during long-term charging/discharging.

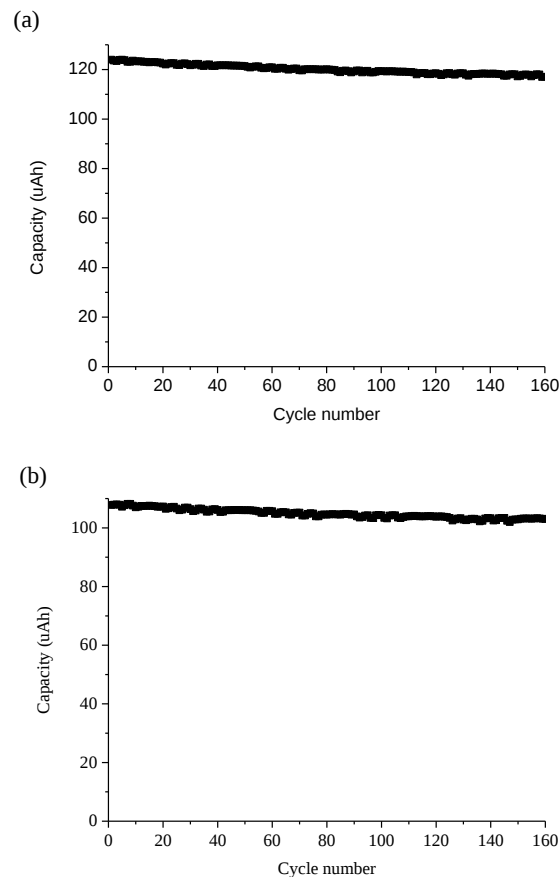


Figure 6. Capacity retention of Li/LiPON/LiMn₂O₄ cells cycled from 3.0 to 4.3 V.

Figure 7 shows the rate capability of the layer and the checkerboard LiMn₂O₄ thin films at room temperature. A single cell was discharged at various current densities ranging from 11 $\mu\text{A}/\text{cm}^2$ to 220 $\mu\text{A}/\text{cm}^2$, i.e., 0.5C to 10C for battery operation, with the gradual increase of discharge rate; the discharge capacity goes down by the restricted Li-ion diffusion. It is clear that the checkerboard LiMn₂O₄ electrode possesses excellent high current density capability, with capacity retention of 82% at 220 $\mu\text{A}/\text{cm}^2$ (10C) better than the capacity retention (70%) of the layer deposition thin film battery. By comparison with the layer sample, the checkerboard LiMn₂O₄ electrode possesses better rate capability because of the following factor - the larger specific surface area ensures a larger interfacial area for electrochemical reaction. The checkerboard LiMn₂O₄ electrode shows a discharge capacity of 84.2 μAh between 4.3V and 3V at a current density of 220 $\mu\text{A}/\text{cm}^2$ (10C). The capacity retention is about 82.5%. However, the discharge capacity of the layer sample is only 75.9 μAh at the same C-rate. The capacity retention is only 69%. Furthermore, the checkerboard sample almost recovers the capacity at a current density of 11 $\mu\text{A}/\text{cm}^2$ (0.5C) but the discharge capacity of the layer sample is slightly decreased when the current density goes down to 0.5C again.

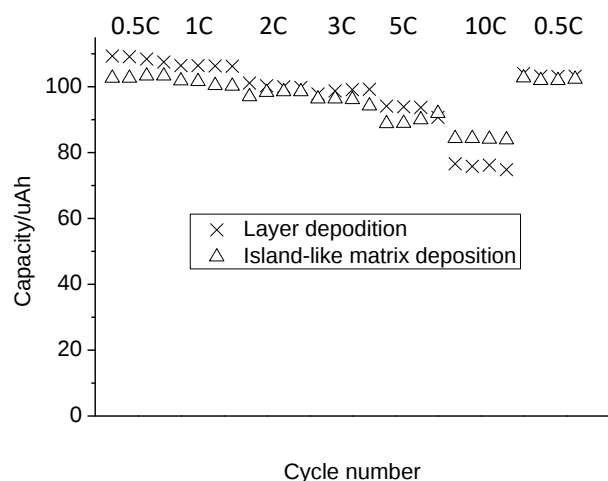


Figure 7. Rate capability of layered and checkerboard LiMn_2O_4 thin film.

From the results obtained above, the kinetics of Li^+ diffusion is normally the major reason for electrode polarization at a high discharge current; we believe that this checkerboard LiMn_2O_4 thin film electrode provides more lithium-transfer pathways as shown in figure 8. This can be attributed to the large surface area provided by the grains of the LiMn_2O_4 thin film, which allows a large number of Li^+ ions to be exchanged during conditions of high discharge current density. This large surface area also contributes to the reduction observed in the cathode polarization.

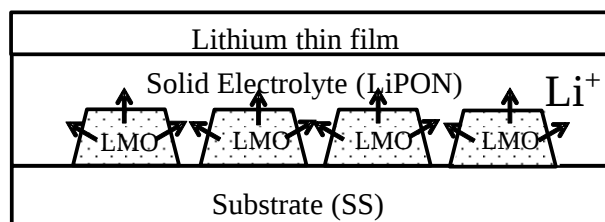


Figure 8. Scheme of the checkerboard deposition of LiMn_2O_4 thin films in all-solid-state lithium battery.

4. Conclusion

This study has demonstrated that checkerboard deposition of LiMn_2O_4 thin films in all-solid-state lithium-ion batteries can be successfully fabricated on a stainless steel substrate through the use of radio-frequency magnetron sputtering method and increase the area of solid electrolyte/solid active material contact, thus increasing the charge exchange rate. A single cell of such a battery demonstrated a discharge capacity of 107.8 μAh between 4.3V and 3V at a current density of 11 $\mu\text{A}/\text{cm}^2$ (0.5C). It also proved to have a very stable cycling performance, retaining over 95 % of its initial capacity after 150 cycles. Similarly promising electrochemical properties were obtained at a high discharging current, with capacity retention of 82.5% at 220 $\mu\text{A}/\text{cm}^2$ (10C). On the basis of these results, we believe that the checkerboard deposition of LiMn_2O_4 thin films in all-solid-state lithium batteries has great potential by some improvements for the future development of flexible lithium batteries capable of functioning equally well in high current density charge and discharge condition.

Acknowledgments

This work was supported by the Ministry of Science and Technology of Taiwan under Grant numbers MOST 106-3111-Y-042A-093 and MOST 106-3114-Y-042A-007.

References

1. Chamanian S, Ulasan H, Zorlu O, Baghaee S, Uysal-Biyikoglu E (2016) Wearable battery-less wireless sensor network with electromagnetic energy harvesting system. *Sens Actuator A* 249 : 77-84
2. Chiu KF, Chen CL (2011) Plasma assisted and manipulated deposition of thin film electrodes for micro batteries. *Thin Solid Films* 519 :4705–4708
3. Haruta M, Shiraki S, Ohsawa S, Suzuki T, Kumatani A, Takagi A, Shimizu R, Hitosugi T (2016) Preparation and in-situ characterization of well-defined solid electrolyte/electrode interfaces in thin-film lithium batteries. *Solid State Ion* 285: 118-121
4. Kato A, Hayashi A, Tatsumisago M (2016) Enhancing utilization of lithium metal electrodes in all-solid-state batteries by interface modification with gold thin films. *J Power Sources* 309 : 27-32
5. Lobe S, Dellen C, Finsterbusch M, Gehrke HG, Sebold D, Tsai CL, Uhlenbruck S, Guillon O (2016) Radio frequency magnetron sputtering of Li₇La₃Zr₂O₁₂ thin films for solid-state batteries. *J Power Sources* 307 : 684-689
6. Li D, Ma Z, Xu J, Li Y, Xie K (2014) High temperature property of all-solid-state thin film lithium battery using LiPON electrolyte. *Mater Lett* 134 : 237-239
7. Chiu KF, Chen CL, Chen BS, Leu HJ (2011) Modification of Electrolyte/Cathode Interfaces by Solid-State Electrolyte Thin Films. *ECS Transactions* 32: 67-75
8. Jouybari YH, Berkemeier F (2016) Enhancing Silicon Performance via LiPON Coating: A Prospective Anode for Lithium Ion Batteries. *Electrochim Acta* 217 : 171-180
9. Oukassi S, Giroud-Garampon C, Dubarry C, Ducros C (2016) All inorganic thin film electrochromic device using LiPON as the ionconductor. *Sol Energy Mater Sol Cells* 145 : 2-7
10. Kali R, Mukhopadhyay A (2014) Spark plasma sintered/synthesized dense and nanostructured materials for solid-state Li-ion batteries: Overview and perspective. *J Power Sources* 247:920–931
11. Takahashi K, Hattori K, Yamazaki T, Takada K, Matsuo M, Orimo S, Maekawa H, Takamura H (2013) All-solid-state lithium battery with LiBH₄ solid electrolyte. *J Power Sources* 226:61–64
12. Yamamoto K, Iriyama Y, Asaka T, Hirayama T, Fujita H, Nonaka K, Miyahara K, Sugita Y, Ogumi Z (2012) Direct observation of lithium-ion movement around an in-situ-formed-negative-electrode/solid-state-electrolyte interface during initial charge–discharge reaction. *Electrochem Commun* 20:113–116
13. Richards WD, Miara LJ, Wang J, Kim JC, Ceder G (2016) Interface stability in solid-state batteries. *Chem Mater* 28:266–273
14. Yamada Y, Nozaki T, Kuriyama K, Kushida K (2013) Three hundred micron squared all-solid-state Li ion secondary battery fabricated by Si very large scale integration technology. *J Alloy Compd* 551:44–47