

Rapid thermal annealing effect on surface of $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode film for thin-film microbattery

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Abstract

The effect of rapid thermal annealing (RTA) on the surface of a $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode film is examined by means of scanning electron microscopy (SEM), atomic force microscopy (AFM) and auger electron spectroscopy (AES). It is found that the as-deposited $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film undergoes a surface reaction with oxygen in the air, due to the high activity of lithium in the film. AES spectra indicate that the surface layer consists of lithium and oxygen atoms. The RTA process at 500 °C eliminates the surface layer to some extent. An increase in annealing temperature to 700 °C results in complete elimination of the surface layer. The surface evolution of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film with increasing annealing time at 700 °C is examined by means of AFM examination. It is found that the surface layer, which is initially present in the form of an amorphous like-film, becomes agglomerated and then vaporizes after 5 min of annealing. A thin-film microbattery (TFB), fabricated by using the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film without a surface layer, exhibits more stable cyclability and a higher specific discharge capacity of 60.2 $\mu\text{Ah cm}^{-2} \mu\text{m}$ than a TFB with an unannealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film. Therefore, it is important to completely eliminate the surface layer in order to achieve high performance from all solid-state thin-film microbatteries. © 2002 Published by Elsevier Science B.V.

Keywords: Rapid thermal annealing (RTA); Thin-film microbattery; $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$; Surface layer; Auger electron spectroscopy (AES); Cyclability

1. Introduction

In the last few years, a considerable interest has developed in the thin-film microbattery (TFB) and the thin-film microsupercapacitor (TFSC) for use in microelectronic mechanical systems (MEMSs), smart cards, on-chip power sources and portable electronic devices [1–3]. To fabricate high performance TFB, various LiMO_2 ($M = \text{Co}, \text{Ni}, \text{and Mn}$) types of compound, in the form of a layered structure, such as LiCoO_2 , LiMnNiO_2 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ have attracted great attention as cathode film materials for secondary thin-film microbatteries [4–8]. In particular, it is important to understand the surface phenomena of the cathode film, since TFB performance is affected by the surface conditions of the cathode films. In spite of numerous studies on LiMO_2 type cathode films, there have been no reports on the surface phenomena on LiMO_2 type cathode films. Recently, we observed that as-deposited LiMO_2 type cathode films, such as LiCoO_2 , LiNiO_2 , and $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ films, undergo a

spontaneous reaction with oxygen in air after deposition, due to the low heat of formation energy of a Li-based oxide. For example, the standard heat of formation (ΔH_{298}°) of Li-based oxide such as $\text{Li}_2\text{O}(\text{s})$, $\text{Li}_2\text{O}_2(\text{s})$ and $\text{LiO}_2(\text{s})$ is -596 , -634 , and $-238.6 \text{ J kmol}^{-1}$, respectively [9]. Therefore, it is not surprising that the surface layer on the LiMO_2 type cathode is formed via a rapid reaction of lithium in the surface region with moisture or oxygen in air. If the surface layer, is not removed, it could act as a barrier to the diffusion of the lithium ions and thus, affect the performance of the TFB and influence the characteristics of the subsequent layer (solid electrolyte: LiPON) on the LiMO_2 type cathode film. Therefore, it is imperative to remove the surface layer on the cathode film in order to prepare a TFB of high quality.

In this work, the effect of rapid thermal annealing (RTA) on the surface of a $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode film is investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM), and auger electron spectroscopy (AES) depth profiles. In addition, the possibility of a RTA-treated $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film without a surface layer as a cathode for a TFB is suggested by fabricating an all solid-state TFB, which has a Li/LiPON/ $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ /Pt/MgO/Si multi-layer structure.

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2. Experimental

A 600 nm thick $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film ($\text{Li}_{0.94}\text{Ni}_{0.51}\text{Co}_{0.49}\text{O}_2$) was grown over a platinum current-collector on MgO/Si substrate using a radio frequency (rf) reactive magnetron sputtering system with 4 in. $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ target [10]. The target was fabricated in-house from LiCoO_2 and LiNiO_2 powders (Cerac) by cold pressing and sintering (1100 °C), and was 80–85% of theoretical density. The X-ray diffraction pattern showed that the target has a rhombohedral structure with space group $R\bar{3}m$ which is the same as that for LiCoO_2 or LiNiO_2 [10]. A MgO layer, deposited by rf sputtering, was required in order to assure adhesion and a diffusion barrier to the platinum current-collector. The ambient gas ratio $\text{O}_2/[\text{Ar} + \text{O}_2]$ for growing the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film was 20% and the rf power was maintained at a constant 200 W. The base pressure and working pressure were maintained at 5×10^{-6} and 5×10^{-3} Torr, respectively. After deposition of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film, an abrupt change in its surface was observed. To eliminate the surface layer and to form a layered structure, a vacuum RTA system was employed (Samwon, Vac. Inc. RTP-2001). The $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ films were annealed in oxygen at temperatures of 500 and 700 °C for 10 min at 1×10^{-1} Torr. The rate of temperature increase was kept constantly at 5 °C s^{-1} . To fabricate an all-solid state TFB, a 1.5 μm thick LiPON ($\text{Li}_{2.94}\text{PO}_{2.37}\text{N}_{0.75}$) solid electrolyte film was subsequently deposited on the annealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ films by rf reactive sputtering at a power of 200 W in pure nitrogen for 6 h. The ionic conductivity of the as-deposited LiPON film was $9.43 \times 10^{-7} \text{ S cm}^{-1}$. Subsequently, the lithium anode metal was evaporated on the LiPON film by thermal evaporation at 3×10^{-6} Torr.

In order to observe the change in surface of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ films with increasing annealing temperature, scanning electron microscopy (SEM: HITACHI, S-4100) and atomic force microscopy (AFM: PSIA) were employed. In addition, auger electron spectroscopy (AES: PHI 670) was used to verify the surface layer on the as-deposited $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ films, as well as to examine the subsequent effect of annealing the films. The Auger microscope had an electron beam of 10 keV and 0.0236 μA . The structure of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film was characterized by X-ray diffraction (Rigaku diffractometer: D/MAX-RC). The charge–discharge properties of the films in an all solid-state cell operated at a constant current of $10 \mu\text{A cm}^{-2}$ were determined with cycling equipment (Wonatech com. WBCS300) between 2.2 and 4.2 V.

3. Results and discussion

Scanning electron micrographs of the cross-section of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film ($\text{Li}_{0.94}\text{Ni}_{0.51}\text{Co}_{0.49}\text{O}_2$) as a function of increasing RTA temperature under oxygen are shown in Fig. 1. The as-deposited sample in Fig. 1(a) has a surface

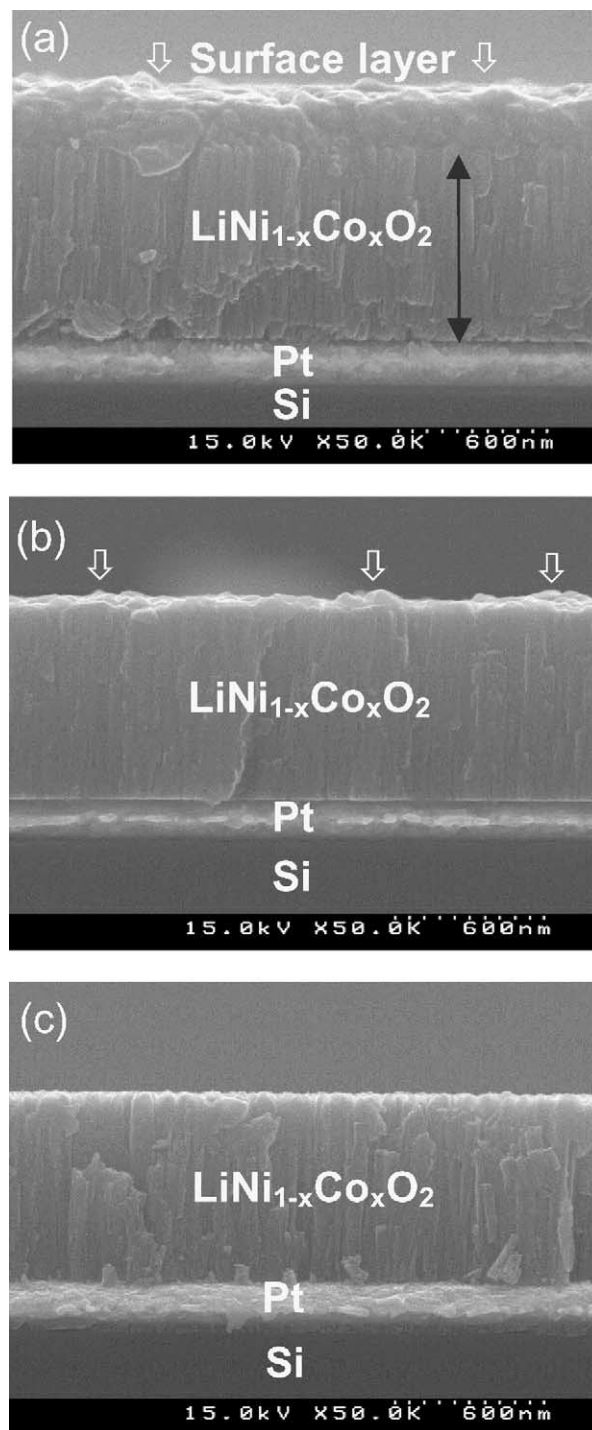


Fig. 1. Cross-sectional electron micrographs of (a) as-deposited, (b) 500 °C, and (c) 700 °C rapid thermally annealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film in oxygen for 10 min. Arrows indicate remaining surface layer after annealing at 500 °C.

layer, which is formed by a surface reaction with moisture or oxygen in the air after deposition. It should be noted that the 500 °C rapid annealing process results in removal of the surface layer, so that the films exist in the as-deposited state, as shown in Fig. 1(b). Some of the top regions of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film continue, however, to contain some of

the surface layer, as indicated by the arrows. The sample annealed at 700 °C, see Fig. 1(c), shows that complete removal of the surface layer can be achieved by means of a RTA process. In addition, the film exhibits a much smoother surface, compared with the as-deposited and 500 °C annealed samples. To examine the surface morphology, SEM examination was also performed. Electron micrographs of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film with increasing temperature of RTA under oxygen are given in Fig. 2.

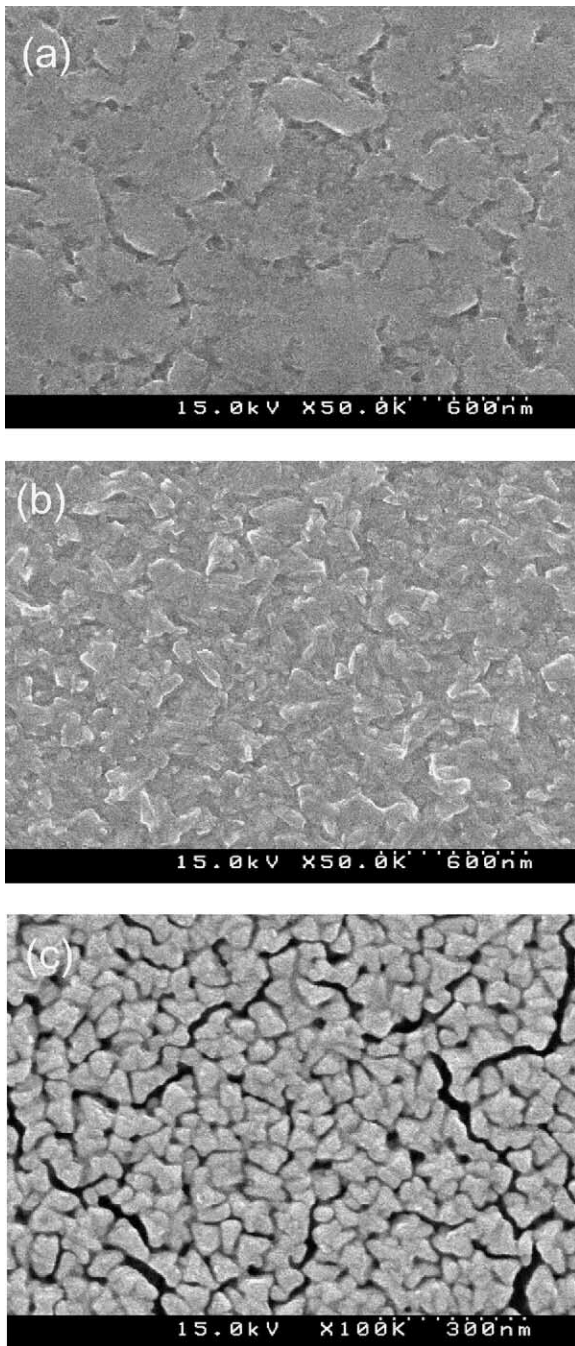


Fig. 2. Electron micrographs of surface of (a) as-deposited, (b) 500 °C and (c) 700 °C rapid thermally annealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film in oxygen for 10 min.

The as-deposited sample (Fig. 2(a)) has a fairly rough surface, with no voids, or cracks. Furthermore, the electron micrographs indicated that the surface layer on the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film has amorphous-like characteristics, such as the absence of grains and grain boundaries. This is consistent with views of the cross-section (Fig. 1(a)). On increasing the annealing temperature to 500 °C, the surface begins to agglomerate and volatize, as shown in Fig. 2(b). The agglomerated region represents the remaining surface layer, that covers the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film. The region indicated by arrows in Fig. 1(b) is consistent with the agglomerated region in Fig. 2(b). After annealing at 700 °C, the complete removal of the surface layer occurs and crystallization of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film is achieved. The surface has a fairly smooth morphology, compared with the sample, which contains a surface layer.

In order to investigate removal of the surface layer at 700 °C in more detail, AFM analysis was calculated for increasing annealing time, as shown in Fig. 3. After 1 min of annealing under oxygen at 700 °C, the AFM image of the surface in Fig. 3(a) shows features similar to those of the as-deposited sample in Fig. 2(a). The existence of a surface layer on the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film induces a rough surface morphology, due to rapid reaction of the lithium atoms in $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film with moisture or oxygen in the air. On increasing the annealing time to 2 min, as shown in Fig. 3(b), the morphology of the surface layer increases, due to the initiation of agglomeration on the surface layer. Furthermore, an increase in the annealing time to 5 min results in an abrupt increase in the morphology of the surface layer, since the surface layer begins to volatize in the oxygen ambient. The random vaporization of the elements in the surface layer causes a much rougher morphology, as shown in Fig. 3(c). After a 10 min of annealing treatment under oxygen, the surface layer disappears completely as shown in Fig. 3(d), and the AFM image displays the pure surface of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film. Although some micro-cracks are present due to the RTA process, it is clear that complete elimination of the surface layer is achieved by using the RTA process. An AFM image for $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ annealed at 700 °C for 7 min is presented in Fig. 4. Because the annealing time is insufficient, there is still an island-like surface layer on the annealed sample. From AFM analysis, it can be observed that the surface layer on the cathode film is evaporated not a layer-by-layer type, but in random clusters.

To identify the elements contained by the surface layer and to investigate the annealing effect on the surface layer, AES depth profiling was employed, as illustrated in Fig. 5. The results for the as-deposited sample show that the surface layer consists of lithium and oxygen atoms. The Auger spectra results after 0.25 min and 1.5 min of sputtering time, as presented in Fig. 5(b), demonstrate the presence of lithium and oxygen peaks, which confirms the existence of lithium and oxygen atoms in the surface layer. In addition, the Auger spectra indicate that the nickel, cobalt, lithium and oxygen atoms are uniformly distributed under surface layer

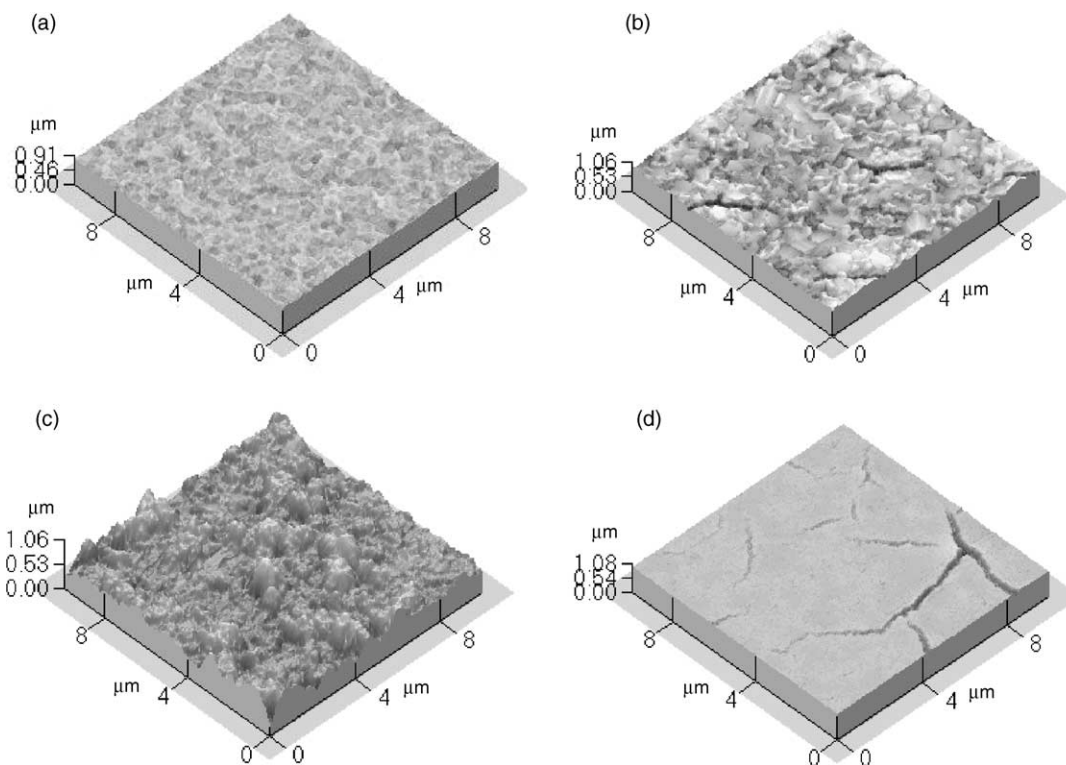


Fig. 3. AFM images of 700 °C annealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film during (a) 1 min, (b) 2 min, (c) 5 min, and (d) 10 min in oxygen.

after 30 min for the as-deposited film (Fig. 5(c)). In contrast, the AES depth profile results (Fig. 6.) for the 700 °C annealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film reveal a uniform distribution of lithium, nickel, cobalt and oxygen atoms, even though the rapid annealing process has been used at high temperature. It is also worth nothing that there is no evidence for the presence of the surface layer on the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film. The Auger spectra after 0.25 min for the surface region and 30 min for the film region contain a similar Auger electron peaks. This indicates that the 700 °C annealed samples have a uniform distributing of elements regardless of location in the films.

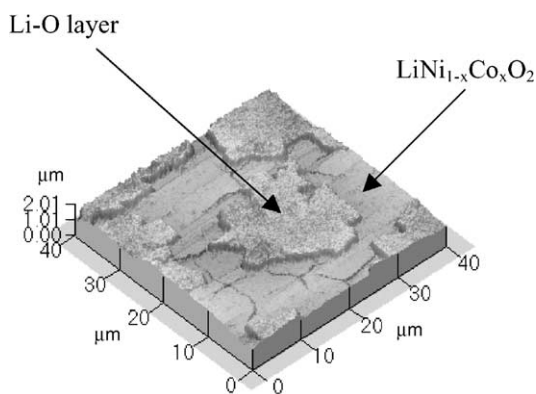


Fig. 4. AFM image of 700 °C RTA treated $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film island which shows a random, island-like, surface layer.

To investigate the structure of the surface layer, XRD analysis was performed on the as-deposited $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film (Fig. 7). The XRD pattern of the as-deposited sample reveals diffraction peaks which are characteristic of crystalline $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($2\theta = 18.9^\circ$, $(0\ 0\ 3)$ $2\theta = 37.0^\circ$ $(1\ 0\ 1)$, $2\theta = 39.1^\circ$ $(1\ 0\ 2)$ and $2\theta = 45.0^\circ$ $(1\ 0\ 4)$) and the Pt substrate. The extra broad peak in the region of $2\theta = 18.9^\circ$ $(0\ 0\ 3)$ indicates that the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ has $(0\ 0\ 3)$ oriented microcrystallinity [11]. There are no peaks in representative of the Li-based oxides such as Li_2O , LiO and LiO_2 . This indicates that the surface layer has an amorphous structure. Although the exact identification of the surface phases is not possible at this time, it is likely that the surface layer consists of a lithium-based oxide, such as Li_2O , LiO , or LiO_2 , since the value of standard heat of formation (ΔH_{298}°) for Li-based oxide is much lower than that for $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$. For example, the standard heat of formation of $\text{Li}_2\text{O}(\text{s})$, $\text{LiO}_2(\text{s})$ and $\text{LiO}_2(\text{s})$ is -596 , -634 , and $-238.6\ \text{J kmol}^{-1}$, respectively [9].

The specific discharge capacity at room temperature for a TFB, including both the as-deposited and the 700 °C annealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film, is given in Fig. 8, as a function of cycle number cycling between 2.2 and 4.2 V. The specific capacity on the first cycle is $60.2\ \mu\text{Ah cm}^{-2}\ \mu\text{m}^{-1}$. Detail electrochemical properties of the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode film will be discussed elsewhere [10,13]. It is clear that a TFB with a 700 °C annealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode film exhibits a stable cycling performance. The as-deposited sample displays very unstable cyclibility with very low

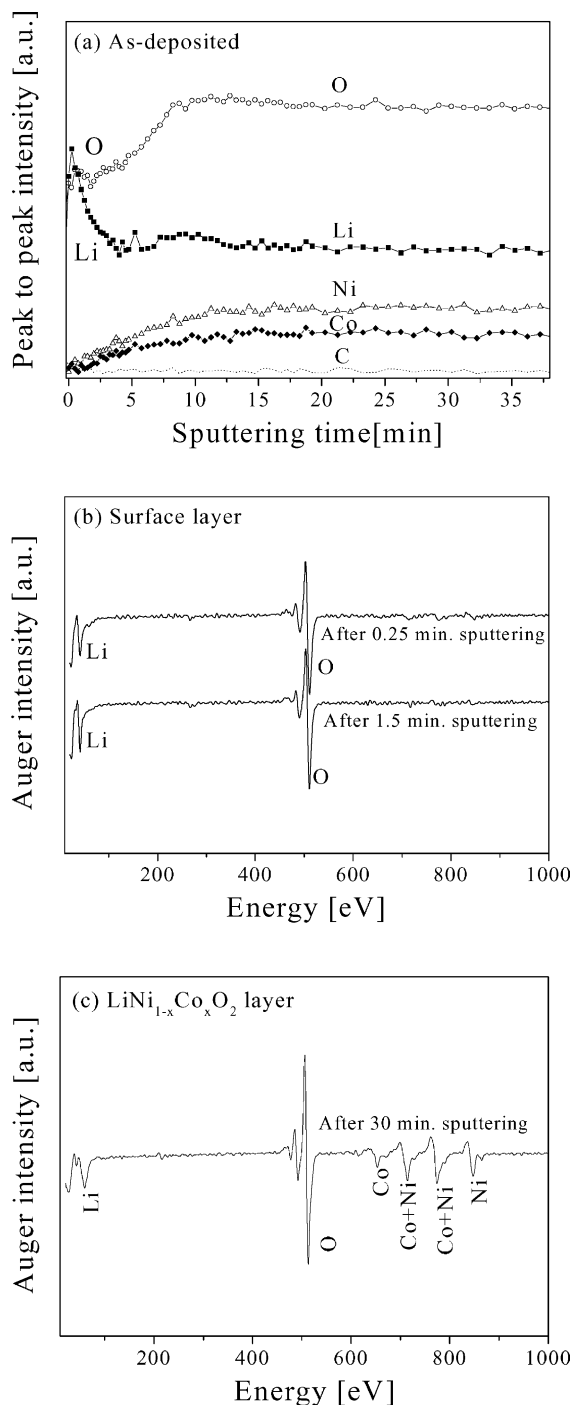


Fig. 5. (a) AES depth profiling of as-deposited $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film with Auger spectra for (b) surface region and (c) film region. Auger spectra results obtained from surface layer after 0.25 and 1.5 min sputtering.

capacity ($1\text{--}5\ \mu\text{Ah cm}^{-2}\ \mu\text{m}^{-1}$) or failure due to the presence of a surface layer, which acts as a barrier to the diffusion of Li ions. We have already reported [12,13] that the presence of an interfacial layer between LiPON and the cathode film can influence the performance of a TFB [12,13].

Based on SEM, AFM, AES and electrochemical results, the effect of the RTA process can be explained as follows.

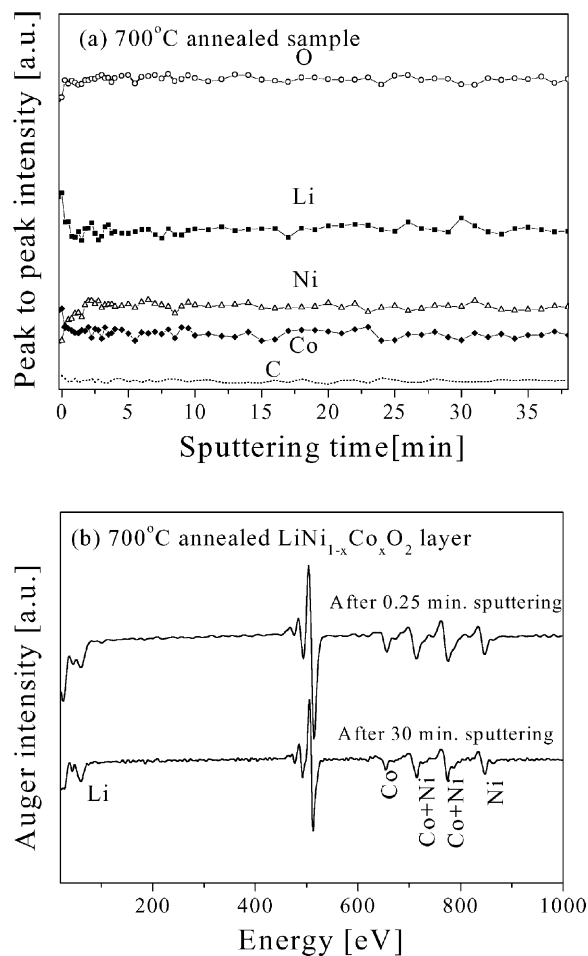


Fig. 6. (a) AES depth profiling of as-deposited $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film with Auger spectra for (b) surface region and film region. It is worth noting that there is no evidence for presence of surface layer on $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film after 700 °C annealing.

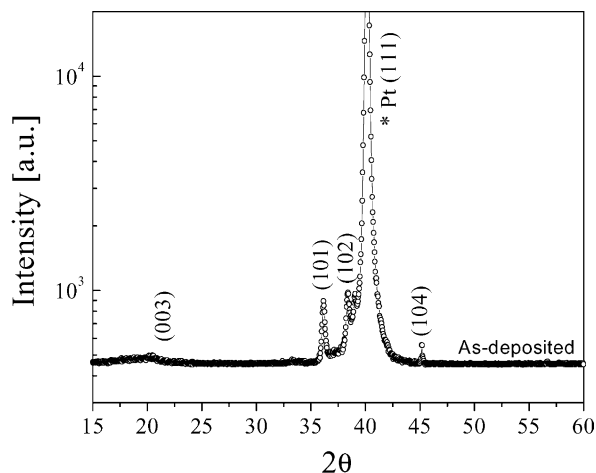


Fig. 7. XRD plot of as-deposited $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ film. There are no peaks for lithium-based oxides, such as Li_2O , LiO , LiO_2 phases, which indicates that the surface layer has amorphous characteristics.

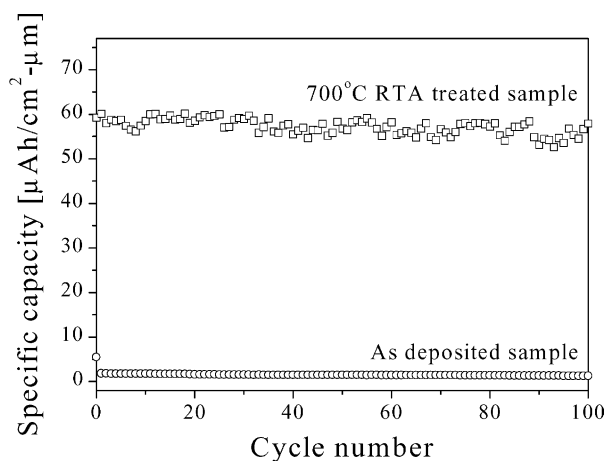


Fig. 8. Discharge specific capacitance for TFB containing as-deposited and 700 °C annealed $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode film, as a function of cycle number, cycle between 2.2 and 4.2 V at constant current density of $10 \mu\text{A cm}^{-2}$.

The SEM, AFM and AES data for samples show that the as-deposited form basically has a surface layer, which is composed of lithium and oxygen atoms. In addition, a surface layer is found on as-deposited LiMO_2 type cathode films, such as LiCoO_2 and LiNiO_2 . This layer might hinder lithium diffusion and degrade the performance of a TFB. After rapid annealing at 700 °C, however, the surface layer is removed completely. The AFM results demonstrate that the surface layer, which shows amorphous-like features, initially agglomerates, with a much higher RMS roughness than the as-deposited sample, and then rapidly disappears with increasing annealing time. This indicates that the lithium based oxide layer, which covers the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode film, is evaporated by rapid annealing. Therefore, a comparison of the surface and electrochemical results indicates that the complete elimination of the surface is crucial for achieving high performance from TFBs.

4. Conclusions

Using SEM, AFM and AES analysis, a surface layer has been observed on an as-deposited $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode

film. AES spectra results indicate that the surface layer consists of lithium and oxygen atoms. A rapid annealing process at 700 °C easily removes the surface layer and improves the performance of the TFB. AES spectra and AFM data after annealing also show that the $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode film has a uniform distribution of elements (Li, Ni, Co, and O) and a smooth surface, even though a high temperature rapid annealing process is used. Therefore, it is important to eliminate completely the surface layer for achieving high performance from all solid-state, thin-film micro-batteries.

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