

Microstructural and electrochemical properties of rf-sputtered LiMn_2O_4 thin film cathodes

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Abstract Lithium transition metal oxides have received considerable attention in recent years as high voltage positive electrode materials in the fabrication of all solid state microbatteries. Among various lithium-based cathode materials, LiMn_2O_4 is one of the most promising cathode materials as it offers high energy density, high cell voltage, low cost, and low toxicity over the other electrode materials. Thin films of LiMn_2O_4 were prepared by radio frequency magnetron sputtering on gold-coated silicon substrates under various substrate temperatures ranging from 373 to 673 K in a partial pressure of 3×10^{-3} mbar with rf power 100 Watts. In the present investigation, the influence of substrate temperature on the growth and microstructural properties was studied. The films deposited at a substrate temperature less than 473 K was found to be X-ray amorphous. The initial crystallization has been observed at a substrate temperature of 523 K. The X-ray diffraction patterns of the films deposited in the substrate temperature range 523–673 K exhibited predominant (111) orientation representing cubic spinel structure with Fd3m symmetry. The grain size was found to be increased with the increase of substrate temperature as evidenced from SEM studies. However, additional impurity phases like Mn_3O_4 were observed for the films deposited at higher substrate temperatures (>673 K) because of re-evaporation of Li^+ ions in the films. The electrochemical (EC) studies were carried for the films deposited at $T_s = 673$ K in aqueous media in the potential window of 0.0–1.2 V exhibited better electrochemical performance suggesting

that the films are well suited as binder free thin film cathode material for commercially viable Li-ion secondary batteries.

Keywords LiMn_2O_4 thin films · Sputtering · Microstructure · Electrochemical properties

Introduction

In the current nano science and technology era, a great deal of research towards lithium rechargeable batteries is being carried out by the researchers because of the development of miniaturized electronic devices such as cellular phones, notebooks, etc (Komaba et al. 2000). Lithium transition metal oxides (LTMOs), due to their high electrochemical potentials, high reversible lithium insertion/deinsertion and high capacity for lithium storage, are of much interest as a cathode materials for Li batteries. Among numerous transition metal oxides, manganese oxide-based compounds are particularly attractive as cathodes because of their low cost, abundance, and non toxicity. Among them, spinel LiMn_2O_4 has emerged as one of the promising candidates because of its 3D Li^+ diffusion and high theoretical capacity of 148 mAh g^{-1} (Thackery et al. 1983; Thackeray 1997). It crystallizes in normal cubic structure, in which the Li^+ and $\text{Mn}^{3+/4+}$ ions occupy the 8a tetrahedral and 16d octahedral sites, respectively, of cubic close-packed oxygen array to give a cation distribution of $[\text{Li}]_{8a}[\text{Mn}]_{16d}\text{O}_4$. A strong edge shared octahedral $[\text{Mn}_2]\text{O}_4$ array permits reversible extraction of the Li^+ ions from the tetrahedral sites without collapsing the 3D $[\text{Mn}_2]\text{O}_4$ spinel frame work (Thackery 1995; Manjunatha et al. 2011). The $\text{Li}_x\text{Mn}_2\text{O}_4$ provides relatively high voltage (4 V) in the region of $0 < x < 1$ and a plateau at 3 V in the $0 < x < 2$ region. In the high voltage

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region, it exhibits two step reversible de-intercalation and intercalation of lithium mechanism. In the first step, lithium is inserted and de-inserted in a single phase region of spinel ($0.5 < x < 1.0$), while in the second step a phase transformation from spinel to a λ - MnO_2 occurs in the range $0.0 < x < 0.5$ (Amatucci et al. 1999). Nonetheless, the spinel LiMn_2O_4 suffers from capacity fading (Mishra and Ceder 1999; Chiag et al. 2001), which has been a key problem with LiMn_2O_4 for commercialization.

It has been observed that the LiMn_2O_4 in thin film form shown better cycling stability than its powder counter parts and can be effectively used as binder free cathode material in the fabrication of all solid state microbatteries (Fergus 2010). Thin films of LiMn_2O_4 have been prepared by several physical and chemical vapour deposition techniques (Hussain et al. 2007; KalaiVani et al. 2007; Shih and Fung 2006; Shui et al. 2004; Rho et al. 2006a, b). It is well acquaint that the electrochemical properties of the electrode materials strongly depends on microstructural properties which in turn depend upon the type of deposition technique. Among various physical vapour deposition techniques, rf-magnetron sputtering technique is observed to be one of the most favorable and industrially viable techniques since it enables the formation of homogeneous films with definite thickness along with good adhesion. Moreover, the microstructural properties can be altered by properly controlling the deposition parameters. Numerous researchers were extensively studied the LiMn_2O_4 thin films grown by rf-magnetron sputtering technique (Rho et al. 2006a, b; Chen et al. 2009; Xie et al. 2008; Komaba et al. 2000).

Nevertheless, the significance of LiMn_2O_4 in thin film form as positive cathode in advance Li-ion batteries shows impetus scope to carry out the research to investigate microstructural and electrochemical performance in the presence of aqueous electrolyte. The study of electrochemical performance in aqueous electrolyte has several advantages over non-aqueous electrolytes which includes low cost and greater safety (Beck and Ruetschi 2000). In addition, the ionic conductivity of aqueous electrolyte is generally greater than the organic electrolyte allowing higher rates and low voltage drops due to low electrolyte impedance. Dahn and coworkers used synthesized LiMn_2O_4 powders as cathode material to construct aqueous rechargeable coin-type lithium batteries and the electrochemical properties were first reported (Li et al. 1994). Furthermore, most of the investigators studied the electrochemical properties of LiMn_2O_4 thin film electrodes in organic electrolyte cells (non-aqueous electrolyte) (Park et al. 2010), but meager research reports are available with aqueous electrolyte solutions (Eftekhari 2001). Hence in the present investigation, LiMn_2O_4 films are deposited on metallized silicon

substrates using rf-magnetron sputtering technique and studied the microstructural, electrical and electrochemical properties of these LiMn_2O_4 films as a function of substrate temperature.

Experimental details

LiMn_2O_4 thin films of about 0.8 μm thick were deposited from a 3-inch diameter cold pressed and sintered lithium-rich LiMn_2O_4 target using rf-magnetron sputtering technique onto Si/SiO₂ (0.3 μm)/Ti (0.03 μm)/Au (0.3 μm) substrates. The system was evacuated to a base pressure of less than 5×10^{-7} mbar with a turbo-molecular pumping system backed by a rotary pump. The distance between the target and the substrate was maintained constant at 5.0 cm. During the depositions, the substrate temperature was varied from 373 to 673 K and the sputtered gas (O₂/Ar) composition was maintained at 1:6 to minimize the loss of lithium. The rf power applied to the LiMn_2O_4 target during sputtering was 100 W and the pressure inside the chamber while in the process of sputtering was about 3×10^{-3} mbar. A rotary drive mechanism was used to rotate the substrate holder to obtain good uniformity of the films.

The structural properties were studied by the X-ray diffraction technique (Siefert computerized X-ray diffractometer, model 3003 TT) using $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 0.15406$ nm) source filtered by Ni thin film at a scan speed of 0.05°/sec in the 2θ range 10–60°. The peak positions were determined precisely using RAYFLEX-Analyze software. The surface morphological characteristics of the films have been studied by scanning electron microscope (SEM) (Carl Zeiss, EVO MA 15).

The electrochemical measurements like cyclic voltammetry (CV) and chronopotentiometry (CP) were performed by designing a prototype aqueous electrochemical cell to understand the fast transport kinetics of the Li-ions in LiMn_2O_4 thin film positive electrode. The design of the cell (Pt/ LiMn_2O_4) was composed of three electrodes which were electrochemically suffused in saturated (~ 7 M) Li_2SO_4 aqueous electrolyte media. The rf-sputtered LiMn_2O_4 thin film coated on metallized silicon substrate was employed as working electrode (cathode). A platinum counter electrode (anode), which acts as a reversible source and sink of lithium (conducting) ions, and a commercial calomel reference (Hg/Hg⁺) electrode, by which the electrochemical analysis was calibrated in the presence of a saturated Li_2SO_4 aqueous solution as electrolyte, were employed. An electrochemical analyzer (model CHI 608C, CH Instruments Inc., USA) was used for the aqueous cell measurements and is operated in the cut-off voltage between 0.0 and 1.2 V.

Results and discussion

Structural analysis

The X-ray diffraction patterns of rf-sputtered LiMn_2O_4 thin films deposited on metallized silicon substrates at various substrate temperatures ranging from 373 to 673 K are shown in the Fig. 1. It is observed that the substrate temperature during deposition significantly affects the microstructural properties of LiMn_2O_4 thin films. A broad and diffused XRD patterns for the films grown at a substrate temperature less than 473 K exhibited that the films are X-ray amorphous. It is noticed that the onset of crystallization starts for the films deposited at a temperature higher than 473 K. The degree of crystallization in the films gradually increased with the increase of substrate temperature (T_s). The grain size is observed to be increased with the increase in substrate temperature, because as the substrate temperature increases the thermal kinetic energy increases and hence, the mobility of atoms deposited on the substrate increases. That means, the possibility of sputtered atoms settling on a thermodynamically stable position on the substrate increases by suppressing the nucleation. The XRD pattern of the film prepared at $T_s = 673$ K, demonstrated all the characteristic peaks with predominant (111) orientation representing cubic spinel structure of Fd3m symmetry in which Li-ions occupy the 8a tetrahedral sites and manganese cations occupy 16d octahedral sites of a cubic close array constituted by the oxygen located in 32e positions. The full width at half maximum (FWHM) value of (111) peak was used to assess the film crystallinity.

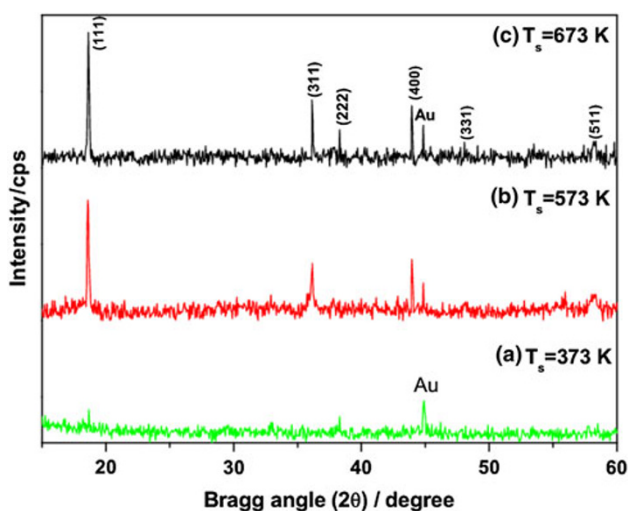


Fig. 1 The X-ray diffraction pattern of LiMn_2O_4 thin films deposited at different substrate temperatures **a** $T_s = 373$ K, **b** $T_s = 573$ K, and **c** $T_s = 673$ K

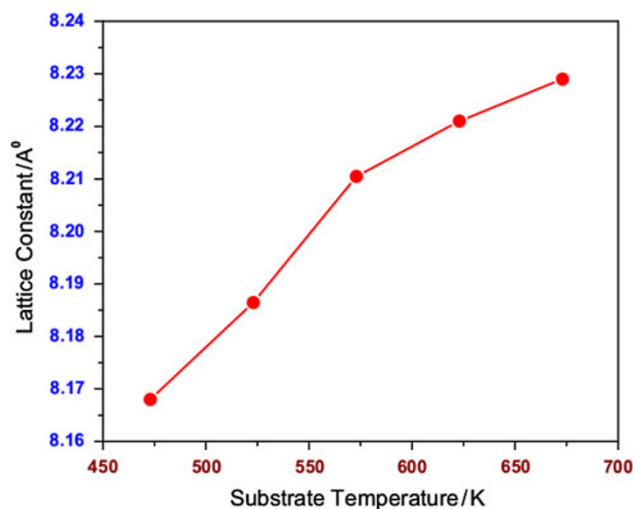


Fig. 2 The lattice constants of LiMn_2O_4 thin films as a function of substrate temperature

With the increase in substrate temperature, the crystallinity of the films was significantly improved.

The lattice parameter for the LiMn_2O_4 films deposited at a substrate temperature of 473 K is found to be 8.168 Å. The lattice parameter is observed to be increased with the increase in substrate temperature as shown in Fig. 2. Higher substrate temperatures generally provide sufficient kinetic energy for the rearrangement of sputtered atoms to grow polycrystalline films with higher grain sizes. As the particle size increases, the lattice of the deposited film expands and the volume of the film increases. Moreover, the higher surface thermal energy changes the valence state of transition element. This may be the reason for the increase in lattice parameter. The observed variation in lattice parameter calculated from the resulted predominant (111) peak deposited at different substrate temperatures is an important indication in determining the nature of spinel phase in the film, i.e. whether the film has a perfect spinel formation or defective spinel formation. At $T_s = 673$ K, the evaluated lattice parameter was found to be 8.229 Å. The reported lattice parameter of the LiMn_2O_4 spinel structure is 8.24 Å. The lattice parameter calculated for the films deposited at lower temperature was much deviated from the ideal value because of the presence of compressional stresses in the films. The observed stress components are noticed to be decreased with the increase of substrate temperature. The Mn–Mn and Mn–O interatomic distances are also calculated by considering oxygen parameter (u) as 0.265 (Ohzuku et al. 1990). The Mn–Mn and Mn–O interatomic distances were also observed to be increased from 2.871 and 1.90 to 2.908 and 1.925 Å, respectively, with the increase of substrate temperature from 473 to 673 K as

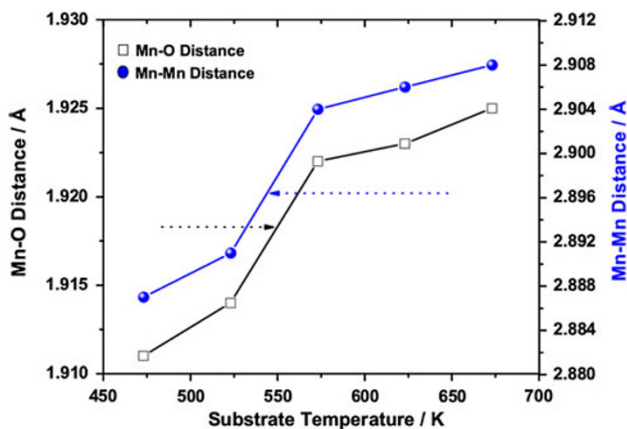


Fig. 3 The variation of Mn–O and Mn–Mn distances with substrate temperature

shown in Fig. 3. The increase in Mn–Mn and Mn–O distance in the cubic lattice structure of the films with the increase of substrate temperature may provide enough channels for the lithium ions to have fast intercalation and de-intercalation. The films deposited at a $T_s = 673$ K are observed to be nearly stress free state with reference to the calculated lattice parameter and Mn–Mn and Mn–O interatomic distances which are nearly equal to the observed value (Shinshu et al. 1997). Additional impurity phases like Mn_3O_4 were observed for the films deposited at higher substrate temperatures i.e., $T_s > 673$ K which may be due to re-evaporation of Li^+ ions in the films.

Surface morphology

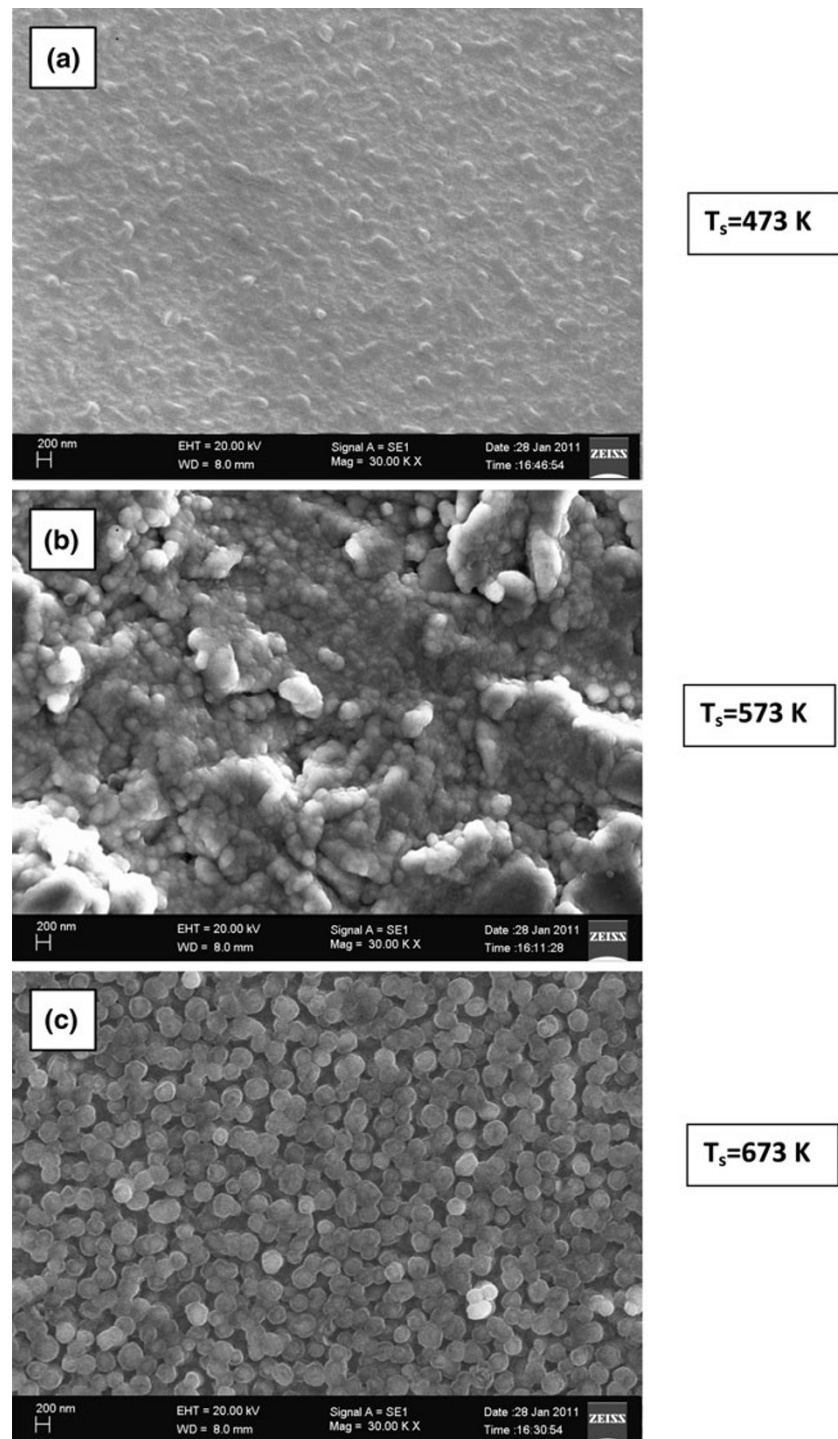
The surface morphology of $LiMn_2O_4$ thin films was studied by SEM measurements. Figure 4 displays the SEM images of $LiMn_2O_4$ thin films deposited at different substrate temperatures. It is observed that the surface morphology of the deposited films at a substrate temperature less than 473 K consists of flat surface with amorphous nature. The surface morphological features are noticed to be predominant at $T_s > 523$ K. A marked improvement in the grain size is observed with the increase of substrate temperature. The $LiMn_2O_4$ films prepared at $T_s = 673$ K exhibited vertically elongated grains which are seen to be in good contact with each other. The grain size of the films was increased with the increase of substrate temperature and found to be around 250 nm for the films deposited at $T_s = 673$ K. At a higher substrate temperature, the mobility of adatoms enhances on the surface, which leads to overcome the potential energy of the nucleation sites on the substrate with net increase in the diffusion distance. In addition to this, the collision process initiates the nucleation and favors the island formation in order to grow

continuous film with larger grain size. The porosity is also found to be increased with the increase of substrate temperature which is one of the major properties influencing the electrochemical property. The electrochemical active surface area is greater for the films with higher porosity i.e., the area of contact between the electrode and the electrolyte is greater hence improved electrochemical performance can be achieved.

Electrochemical properties

The films grown at lower substrate temperatures $T_s < 523$ K showed no obvious redox process, which is the characteristic of amorphous nature of $LiMn_2O_4$ thin films. Figure 5 shows the cyclic voltammogram recorded at a scan rate of 0.5 mVs^{-1} for $LiMn_2O_4$ thin film deposited at a substrate temperature of 673 K. The peaks located at 0.62 and 0.93 V during cathodic scan corresponding to the Li ion de-intercalation from $LiMn_2O_4$ host matrix to form λ - MnO_2 , while the peaks located at 0.60 and 0.79 V during anodic scan correspond to Li ion intercalation into λ - MnO_2 to form $LiMn_2O_4$. This two step de-inserted and inserted kinetics of Li ion during oxidation and reduction reactions indicates the characteristic property of spinel $LiMn_2O_4$ (Li and Dahn 1995). In the spinel $LiMn_2O_4$, lithium ions occupy tetrahedral (8a) sites, Mn ions occupy (Mn^{3+}/Mn^{4+}) octahedral (16d) sites and O^{2-} ions occupy (32e) sites. The oxygen ions form a cubic close-packed array, tetrahedral (8a) sites share face with vacant octahedral sites (16c), so that they form a 3D vacant channels. Lithium ions can intercalate/de-intercalate through these channels during the electrochemical reaction (Okubu et al. 2010). The first oxidation peak (O_1) at 0.62 V is attributed to the removal of lithium ions from half of the tetrahedral sites, whereas the second oxidation peak (O_2) at 0.93 V is due to the removal of lithium ions from the remaining tetrahedral sites. The Fig. 6 shows the first discharge curve of $LiMn_2O_4$ thin film. It can be seen that the discharge curve for the film have two distinct potential plateaus, which is in agreement with the reduction potentials observed from the cyclic voltammogram. The upper plateau region of the discharge curve represents a two-phase equilibrium between λ - MnO_2 and $Li_{0.5}Mn_2O_4$, whereas the second plateau represents phase equilibrium between $Li_{0.5}Mn_2O_4$ and $LiMn_2O_4$. For the first cycle, it is found that the discharge capacity for the films was $44 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$, and for the 10th cycle the discharge capacity was $36.7 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$ as shown in the inset of Fig. 6. Hee-Soo Moon et al. deposited $LiMn_2O_4$ thin films on stainless steel substrates using rf-magnetron sputtering and reported a discharge capacity of $24 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$ (Moon and Park 2002) and Singh et al. (2002) deposited $LiMn_2O_4$ thin films using PLD and reported a

Fig. 4 The SEM images of the LiMn_2O_4 thin films deposited at **a** $T_s = 473$ K and **b** $T_s = 573$ K and **c** $T_s = 673$ K



discharge capacity of about 115 mAh/g for the first cycle. Platinum can act as an excellent current collector/conductor during intercalation and de-intercalation reactions. But it is not an ideal source/sink to be used as an anode in the electrochemical cell and it may be one of the reason for the low cyclic retention of the Pt// LiMn_2O_4 cells (Jeevan Kumar et al. 2010).

Conclusion

LiMn_2O_4 thin films with good adhesion have been fabricated on metallized silicon substrate by rf-magnetron sputtering technique. The influence of substrate temperature on the microstructural and electrochemical properties of LiMn_2O_4 thin films was studied. The degree of

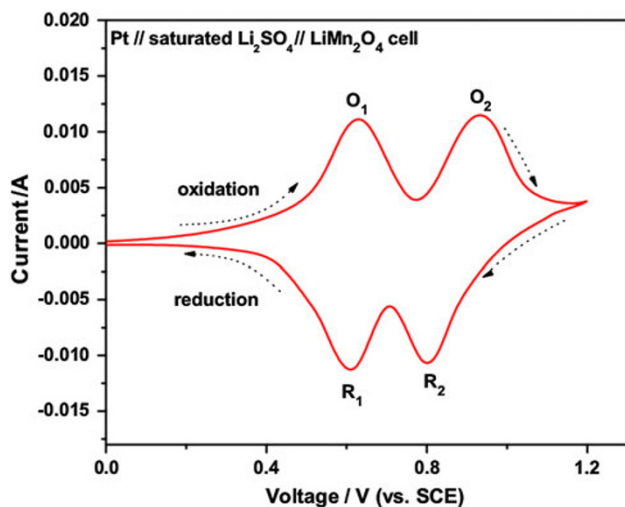


Fig. 5 The Cyclic voltammogram of the LiMn_2O_4 film deposited at 673 K

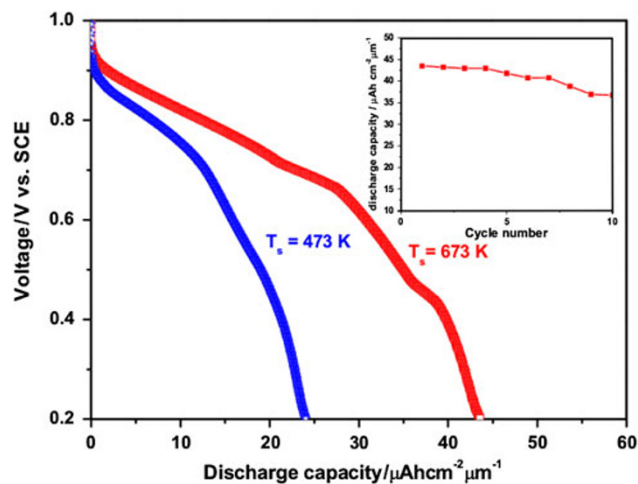


Fig. 6 The first discharge capacity curve of the LiMn_2O_4 thin film deposited at 473 and 673 K. In *inset*, the cycling performance of the LiMn_2O_4 thin film deposited at 673 K for ten cycles

crystallization of the films gradually increased with the increase of substrate temperature. The films deposited at a substrate temperature of 673 K exhibited characteristic peaks corresponding to (111), (311), (222) and (400) orientations of the spinel structure with the cubic $Fd\bar{3}m$ symmetry. The lattice parameter increased from 8.123 to 8.229 Å and the Mn–Mn and Mn–O interatomic distances were also observed to be increased from 2.871 and 1.90 to 2.908 and 1.925 Å, respectively. Typical changes in surface morphology of the films were observed by SEM with the increase of substrate temperature. The slow sweep cyclic voltammetry and chronopotentiometry measurements were carried out by designing Pt/ LiMn_2O_4 aqueous cell. The

electrochemical features show two well-active redox peaks that are characteristic of the extraction-insertion of Li^+ ions from/into the spinel framework of LiMn_2O_4 . The Pt/ LiMn_2O_4 electrochemical cell with LiMn_2O_4 films deposited at a substrate temperature of 673 K exhibited an initial discharge capacity of about $44 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$.

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