



Performance of electrostatic spray-deposited vanadium pentoxide in lithium secondary cells

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Abstract

A vanadium pentoxide (V_2O_5) thin-film is deposited on to a platinum substrate using an electrostatic spray deposition (ESD) technique and its performance in a secondary lithium cell is reported for the first time. The deposited thin-film is characterized in terms of structure and surface morphology using X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The XRD studies reveals that the structure of the thin V_2O_5 film is amorphous. The crystallinity increases with rise in the annealing temperature from 200 to 275 °C and is composed of orthorhombic V_2O_5 crystals. Scanning electron micrographs indicate the near-porous nature of the annealed thin-film. The electrochemical behavior of the thin-film of vanadate is investigated by means of cyclic voltammetry (CV) and galvanostatic discharge–charge cycling using a lithium metal anode in the voltage range 2.0–4.0 V (versus Li metal) in 1 M $LiClO_4$ /propylene carbonate (PC) as electrolyte. Good cycleability and high capacity (270 mAh g^{-1}) is achieved at a current rate of 0.2C by annealing the thin-film at 275 °C. Furthermore, the capacity remains stable even after 25 cycles; excellent capacity retention is observed even at the 1C rate (260 mAh g^{-1}). It is concluded that ESD is an excellent and cheap technique for fabricating thin-films of vanadate for use as cathodes in secondary lithium cells. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Electrostatic spray deposition; Vanadium pentoxide; Secondary lithium battery; Cycling; Intercalation

1. Introduction

Recently, attention has been focused on the research and development of microbatteries owing to the growing miniaturization of electronic devices [1]. A reduction of the current and the power requirements of electronic devices has resulted in the development of new thin-film materials by means of various deposition techniques [2–5]. Thin-films of materials for positive electrodes (cathodes) in batteries are of special significance as they present a simple geometry without the need for incorporating conductive materials and polymeric binders. This facilitates an easier understanding of the theoretical as well as the practical electrochemical nature of such cathodes [6].

It is well known that a competent cathode material is the foremost criterion for a high-performing and viable lithium battery. Hence, considerable research has been directed to

the development of various types of cathodes, e.g. $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, $Li_xV_2O_5$, $Li_xV_3O_8$, V_2O_5 , V_6O_{13} , and V_3O_8 [7–10]. Among the investigated cathode materials, vanadium oxides are very attractive in view of their large capacity for lithium storage (high specific capacity) and good cycleability [11,12]. Cathode materials based on V_2O_5 have been studied extensively during the past two decades [13]. Crystal V_2O_5 (c- V_2O_5) is the most preferred material. In view of its large capacity fading [14] during cycling, however, improvements such as incorporating metal ions into the structure or tuning the synthesis method, etc. are necessary for meeting the demands of different applications [15–17]. Special attention have thus focused on the chemical methods of preparation, the physical methods for obtaining thin-films, the electrochemical methods for obtaining oxide deposits, and also on the use of molten salt [18–20]. By using either electrochemical or thin-film methods [21,22], the synthesis conditions can be monitored easily and compact and thin oxide deposits can be obtained without using any electroconductive additive or binder. Thin-films of V_2O_5 have received special attention in view of their high lithium intercalating properties. West et al. [23] were the first to report the preparation of a thin-film of V_2O_5 by means of

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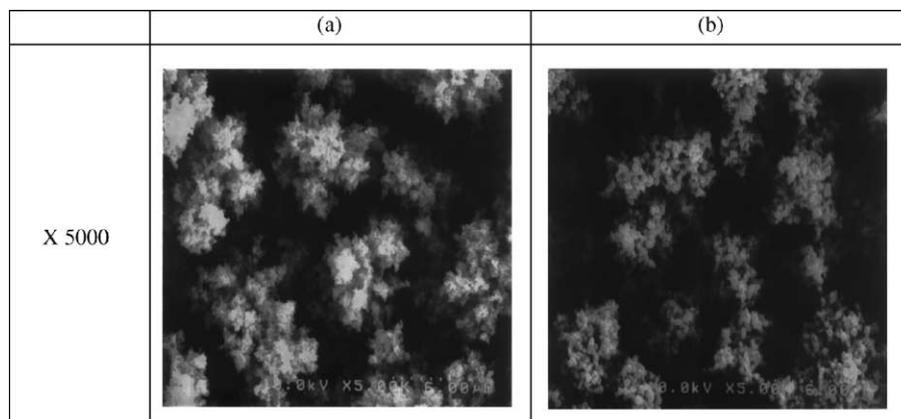


Fig. 1. SEM photographs of V_2O_5 films: (a) as-deposited (200 °C); (b) annealed at 275 °C.

radio frequency (rf) sputtering. Subsequently, Kumagai et al. [24] also investigated rf-sputtered V_2O_5 films, while Levi et al. [6] employed a thermal evaporation method. All authors reported the formation of orthorhombic V_2O_5 crystals with lithium intercalation–de-intercalation capacities between 180 and 200 mAh g^{-1} in the voltage range 2–4 V. Patrissi and Martin [25] prepared thin-films of V_2O_5 via sol–gel template synthesis and compact nanotubes of these oxides could be obtained with capacities around 220 mAh g^{-1} . Thus, encourage by the performance of thin-films of V_2O_5 prepared by these methods, it is considered worthwhile to investigate newer and cheaper methods of obtaining V_2O_5 thin-films.

The present authors have reported several thin-film electrodes of transition metal oxides for lithium secondary batteries and supercapacitors, e.g. LiCoO_2 [26], ruthenium oxide [27], Li-doped nickel oxide [28], NiO_x [29] and LiMn_2O_4 [30,31] prepared by the electrostatic spray deposi-

tion (ESD) technique. In this communication, a novel ESD technique for obtaining V_2O_5 films is reported, together with the electrochemical behavior of the prepared oxide for possible application in secondary lithium batteries.

2. Experimental

2.1. Preparation of solution

Triisopropoxyvandium oxide $[(\text{CH}_3)_2\text{CHO}]_3\text{VO}$, TIVO (Aldrich, USA), was dissolved in ethyl alcohol (99%, Ducksan, Korea) to a concentration of 0.05 M. Two test solutions of precursor were employed. One solution was stirred for 6 h and then stored for 2 weeks for hydrolyzing to a yellow solution in air. The second solution, after initial stirring, was stored for 6 weeks for hydrolyzing to a red solution.

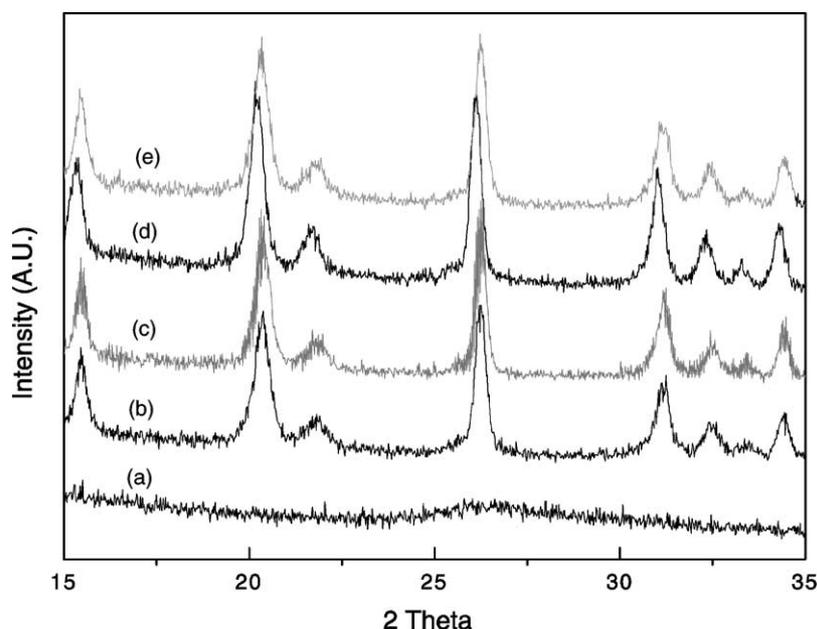


Fig. 2. X-ray diffraction patterns of V_2O_5 films: (a) as-deposited; (b) annealed at 220 °C; (c) annealed at 225 °C; (d) annealed at 250 °C; (e) annealed at 275 °C.

2.2. Preparation of thin-film electrode

Thin-film electrodes were prepared by depositing TIVO solution on to a Pt foil current-collector using an ESD technique [26–28]. The working principle of the ESD method has been described by Chen et al. [2–4]. A high voltage between the nozzle and the substrate atomizes the precursor solution at the orifice of the nozzle and generates a fine aerosol spray. The temperature of the substrate is maintained at 200 °C during deposition. An ethanol precursor solution of 0.05 M TIVO is pumped at a rate of 2 ml h⁻¹ for 1 h through the nozzle which is placed 4 cm above the substrate. The V₂O₅ films were annealed at 225, 250, 275 and 300 °C.

2.3. Characterization

The structures of the deposited and annealed V₂O₅ films were characterized by X-ray diffraction (XRD) with an automated Rigaku X-ray diffractometer using a Cu K α radiation. The diffraction angle (2θ) was measured between 15 and 35° with an increment of 0.04°/min. The morphology of the V₂O₅ films was examined by means of a scanning electron microscopy (SEM).

Electrochemical measurements were carried out with a three-electrode glass cell which used metallic lithium as both the counter and the reference electrodes, and 1 M LiClO₄ in propylene carbonate (PC) as the electrolyte solution. Cyclic voltammetry (CV) measurements were conducted at a sweep rate of 0.10 mV s⁻¹ over the potential range 2–4 V with a EG&G 273A Potentiostat/Galvanostatic. Discharge–charge cycling experiments were performed over the voltage range 2–4 V and recorded with automated battery cycle-life tester (WBCS 3000, Wonatech, Korea). All electrochemical measurements and preparation of the precursor solutions were performed at room temperature in a glove-box filled with purified argon.

3. Results and discussion

Electron micrographs of deposited and heat-treated (275 °C) vanadium oxide films on platinum current-collectors are represented in Fig. 1(a) and (b), respectively. The deposited V₂O₅ film at the substrate temperature of 200 °C has a very porous nature. This is due to the fact that particles arriving at the substrate are wet due to incomplete solvent evaporation and this leads to scattering of the particles and, thereby, dense morphologies. Annealing of the film at 275 °C did not seem to change significantly the morphology of the deposit, Chen et al. [2–4] reported a similar type of morphology for thin-film LiCoO₂ cathode. It is concluded that the deposited V₂O₅ film has poor contact between the particles that leads to less intercalation–de-intercalation of lithium ions.

The X-ray diffraction patterns of the deposited and annealed V₂O₅ thin-films are given in Fig. 2. The pattern

of the deposited V₂O₅ film exhibits an amorphous nature without any V₂O₅ diffraction peaks (Fig. 2(a)). With annealing, diffraction peaks start emerging annealing (Fig. 2(b)). The growth of the diffraction peaks can be ascribed to an increase in crystallinity. Further, this also indicates that the increase in annealing temperature of the deposited films results in an enhancement of the in-plane orientation of the

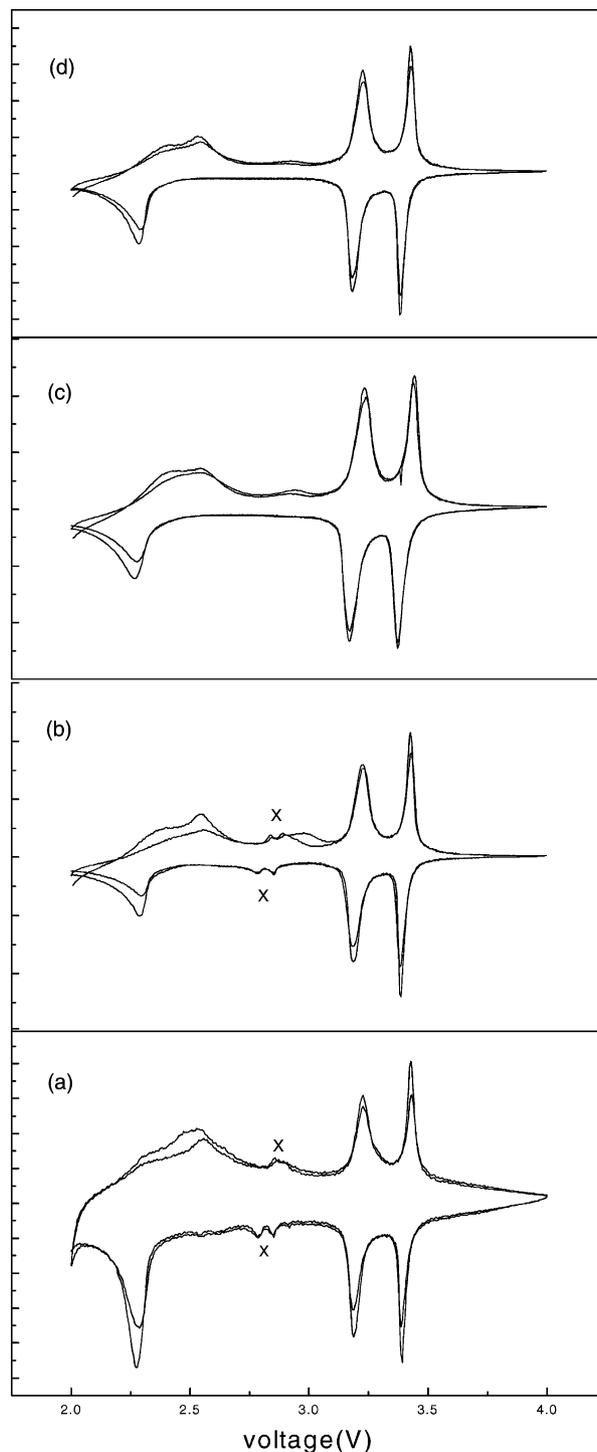


Fig. 3. Cyclic voltammograms of V₂O₅ films: (a) annealed at 200 °C; (b) annealed at 225 °C; (c) annealed at 250 °C; (d) annealed at 275 °C.

V–O–V chains [32]. All the diffraction peaks can be clearly assigned to the well-known hkl values of V_2O_5 , viz. 2 0 0, 0 0 1, 1 0 1, 1 1 0, 3 0 1, 0 1 1, 1 1 1, 3 1 0, and this is in agreement with JCPDS card no. 9-387 [33]. Thus, the post-annealed V_2O_5 can be assigned to an orthorhombic-layered structure. It is to be noted that all the diffraction peaks grow uniformly with increase in annealing temperature from 200 to 275 °C. This indicates that the crystallographic c -axis of the structure is perpendicular to the substrate surface and, thus, highly crystalline V_2O_5 films can be prepared at temperatures below 275 °C using the present ESD technique. A comparison of these results with those in the literature indicates that a thin-film of V_2O_5 prepared by rf-sputtering [23,24], pulsed laser deposition [34] or electron beam evaporation [32] techniques exhibits high crystallinity at temperatures equal and above 300 °C by using an oxygen atmosphere. The films prepared by sputtering techniques tend to grow in the ab -plane perpendicular to the substrate. Indeed, it is to be emphasized here that in the present case, highly crystalline V_2O_5 thin-films have been obtained at temperatures as low as 225 °C. Further, it is worth mentioning that all the prepared V_2O_5 samples in the present case have been annealed in air. The layered structures could be visualized in terms of the edge-sharing of oxygen and vanadium atoms from distorted trigonal bipyramidal coordination polyhedra to form $(V_2O_5)_n$ zigzag double chains along the (0 0 1) directors and are cross-linked along (1 0 0) through shared corners [35]. Thus, it can be concluded that a well-defined network of vanadium and oxygen is obtained in the present ESD technique for the preparation of V_2O_5 films.

Cyclic voltammetry is an excellent, fast, electrochemical technique which gives information on the nature of reactions

taking place at the electrode. As vanadium can exist in different oxidation states, through CV studies were carried out on the electrochemical behavior of the ESD-deposited and annealed V_2O_5 thin-films (Fig. 3). The shapes of the voltammograms are similar to that of pressed V_2O_5 [36] and so the formation of V_2O_5 at temperatures as low as 200 °C using the ESD process is confirmed.

Inspection of the voltammograms indicates that characteristic oxidation and reduction peaks become well-pronounced with increasing annealing temperature of the deposited ESD film. This can be ascribed to an increase in the crystallinity of the deposited films, as supported by the XRD patterns. In spite of the fact that all the representative peaks located at around 2.25, 3.15 and 3.35 V can be easily identified in the cyclic voltammograms of the investigated V_2O_5 films, there exist additional peaks (marked 'x') in case of the deposited film (Fig. 3(a)) and the film annealed at 225 °C (Fig. 3(b)). This observation is interesting in view of the fact that different XRD patterns are obtained even though the films annealed at 225 °C have a crystalline structure which is similar to that of higher annealed samples. The additional peaks could be due the lower oxidation states of vanadium (V^{4+}) coexisting at lower temperatures [24]. The peak at around 2.90 V vanishes in samples annealed above 225 °C, which suggests the formation of pristine α - V_2O_5 . As is well known, the three pairs of oxidation and reduction peaks can be assigned to the successive phase transformation with lithium insertion and extraction, viz. ϵ - $Li_xV_2O_5$, δ - $Li_xV_2O_5$ and γ - $Li_xV_2O_5$ at 2.25, 3.15 and 3.35 V, respectively [37]. It can be further observed that the deposited ESD films exhibit excellent reversibility, and hence increased lithium

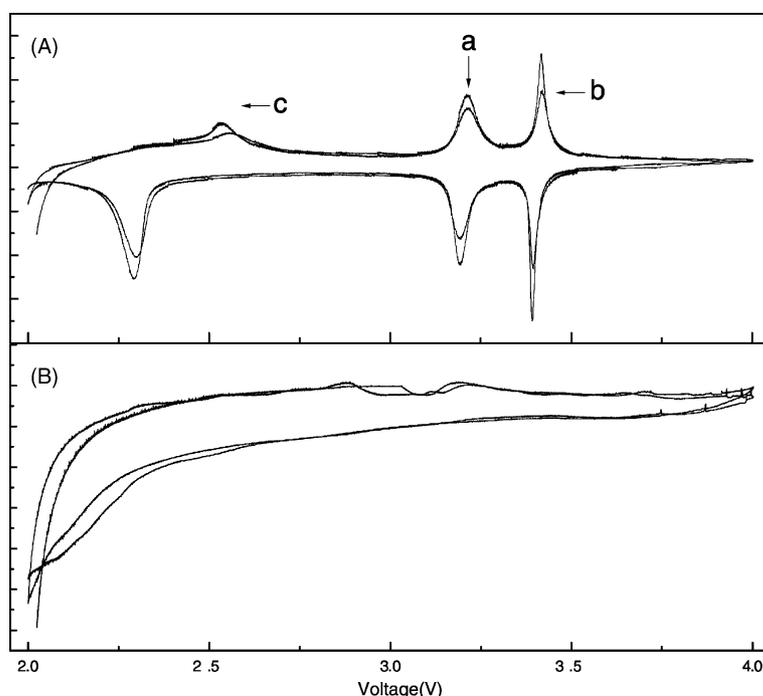


Fig. 4. Cyclic voltammograms of V_2O_5 films annealed for 6 h at 275 °C: (A) 2 weeks storage; (B) 6 weeks storage.

insertion–extraction behavior. The shapes of the CV curves are well developed and sharper than those of pressed powder V_2O_5 electrodes, which indicates enhanced electrochemical properties. This observation in the case of ESD-deposited V_2O_5 films is due to a decrease in the particle size of the V_2O_5 , as demonstrated by SEM studies [26]. Moreover, it is interesting to see from Fig. 4(A) that extending to 6 h the annealing time of the best-performing film, i.e. the sample annealed at 275 °C, leads to a decrease in the intensity of the characteristic V_2O_5 peaks. Further, storing the precursor solution for 6 weeks and then depositing and annealing the ESD film suggests complete hydrolysis of the TIVO solution to give non-identifiable V_2O_5 peaks (Fig. 4(B)). Thus, it can be said that both the storage time of the precursor solution and the annealing temperature are critical factors for achieving a high-performing ESD V_2O_5 film.

Ozer [20] from studies on ϵ - V_2O_5 and α - V_2O_5 reported the absence of intercalation phenomena around voltage below 2.7 V in directly deposited films. They observed the same in the case of a composite electrode and ascribed this to an increase of electronic conductivity by the addition of carbon black. It is interesting to observe from Fig. 4(A) that the present V_2O_5 ESD films exhibit a clear intercalation peak (marked ‘c’) at around 2.60 V. Thus, arguing on similar lines to those of Potiron et al., enhanced electrochemical behavior is expected from the ESD V_2O_5 films. This can be assumed in view of the electrostatic attractive interaction operating in the ESD process that will improve the contact of the particles to form near-porous morphology, as shown by SEM studies [4].

Electrochemical discharge–charge behavior of the V_2O_5 thin-films has been investigated at different conditions using 1 M $LiClO_4/PC$ as an electrolyte. The typical discharge behavior of the deposited and annealed V_2O_5 ESD films in a lithium cell is shown in Fig. 5. The deposited film (Fig. 5(A)) as well as films annealed at 200 °C (Fig. 5(B)) and 225 °C (Fig. 5(C)) exhibit a sloping discharge profile with no characteristic V_2O_5 plateaux. Further, a steep drop in voltage from 4 to 3.25 V indicates reduction of V^{5+} to V^{4+} . It is noteworthy that the maximum contribution towards capacity ($\sim 95\%$) is below 3 V. The observed large decay in capacity above 3 V can be attributed to the presence of large amounts of lower oxidation states of vanadium, viz. V^{4+} , as is evident from the additional peaks around 2.90 V in the CV curves observed for deposited and films annealed at 200 °C (Fig. 3(a) and (b)). Furthermore, the discharge curves for films annealed at 225 °C show improved capacity retention in spite of the fact that the current rate has been enhanced by five times, i.e. from 0.2 to 1C rate. This is easily understandable in view of the fact that the additional peaks of lower oxidation states of vanadium disappear around 2.90 V with increase in annealing temperature.

Kumagai et al. [24] investigated sputtered V_2O_5 films and also observed a sharp reduction in capacity above 3 V and ascribed it to the presence of V^{4+} ions. It is interesting, however, to observe that the films annealed at 250 and

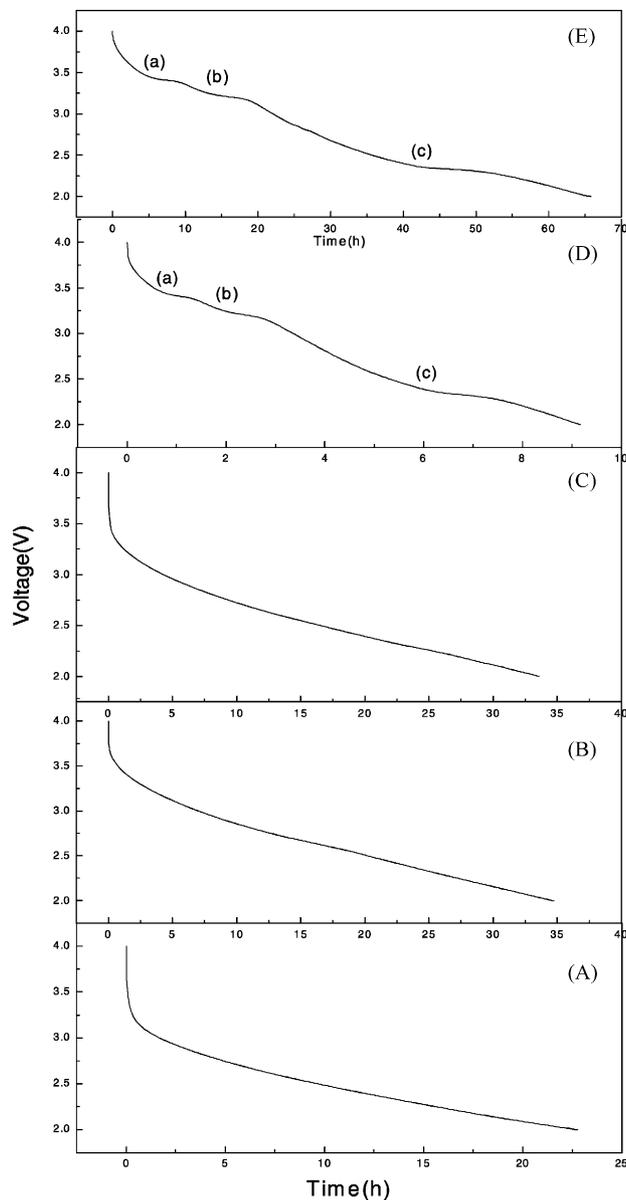


Fig. 5. Discharge curves of V_2O_5 films: (A) deposited; (B) annealed at 200 °C; (C) annealed at 225 °C; (D) annealed at 250 °C; (E) annealed at 275 °C.

275 °C (Fig. 5(D) and (E), respectively) presents altogether a different picture. As is well known, the discharge behavior of pristine V_2O_5 can be divided into three plateaux as described elsewhere [37]. From Fig. 5(D) and (E), it can be seen that the additional peaks centered around 2.90 V completely vanish and three plateaux (a, b, c) emerge which are due to transformation α - V_2O_5 to ϵ - V_2O_5 to γ - V_2O_5 [37], respectively. Further, the capacity above 3 V increases for the samples annealed at 250 and 275 °C, as demonstrated by the ‘a’ and ‘b’ plateaux.

It has to be emphasized here that normally electrochemically active V_2O_5 films are prepared by annealing at temperatures above 300 °C using either sputtering [23,24], PLD [34] or evaporation techniques [32], but in the present ESD

Table 1
Capacity of ESD V_2O_5 films at different conditions

Substrate temperature ($^{\circ}C$)	Annealing temperature ($^{\circ}C$)	Rate	Capacity ($mAh\ g^{-1}$)	Number of cycles
200	–	$C/20$	170	10
200	200	$C/20$	220	10
200	225	$C/5$	225	10
200	250	$C/5$	260	25
200	275	$C/5$	270	25
200	275 (6 h)	$1C$	260	25
200 ^a	275 (6 h)	$1C$	40	25

^a Precursor solution stored for 6 weeks.

technique electrochemically active V_2O_5 films are obtained at temperatures as low as $250\ ^{\circ}C$. Moreover, the sharper peaks observed in cyclic voltammetry curves (Fig. 5(E)) and the disappearance of additional peaks at around $2.90\ V$ indicate a reduction in V^{4+} ions that, thereby, enhances capacity. The capacities obtained for different samples of V_2O_5 film prepared using the ESD technique are listed in Table 1. The values increase with increase in annealing temperature, which suggests the formation of pristine V_2O_5 .

The cycleability of the fabricated Li/V_2O_5 cells was also investigated by galvanostatic discharge–charge cycling in $1\ M\ LiClO_4/PC$ electrolyte. Capacity as a function of cycle number is presented in Fig. 6. The first charge is negligible and this is understandable as the lithium cell and is already in a charged state with an open-circuit voltage (OCV) of 3.12 – $3.57\ V$. The OCV of the deposited sample is lower (i.e. around $3.12\ V$) and, as explained earlier, this is due to the presence of lower oxidation states of vanadium, as suggested by CV and discharge studies. The OCV of annealed films, however, are in the range of 3.57 – $3.58\ V$, which indicates the absence of impurity phases involving V^{4+} due to peaks at around $2.9\ V$ and hence higher electrochemical stability with

enhanced capacity. The cycling behavior of the deposited film exhibits an average capacity of ~ 160 – $175\ mAh\ g^{-1}$ at a $C/20$ cycling rate. By contrast, the capacity of annealed samples is around $300\ mAh\ g^{-1}$ initially but stabilizes at around $270\ mAh\ g^{-1}$ with cycling despite the fact that the current rates are increased by four-fold ($C/5$, Table 1). Further, excellent capacity retention is seen at the $1C$ rate, i.e. $260\ mAh\ g^{-1}$ (Fig. 7(a)). The charging and discharging capacities are identical beyond the second cycle. This suggests that the amount of lithium intercalated is equal to the amount of lithium extracted or, in other words, the synthesized material demonstrates excellent cycleability with no fading.

Comparison of the present results with previously reported work for the films prepared by rf-sputtering [23,24], PLD [34], electrochemical deposition [21], etc., indicates that the present ESD method is more economical and viable. Kumagai et al. [24] obtained thin-films of V_2O_5 by using rf-sputtering techniques. It was found that sputtered V_2O_5 films exhibited capacities of around $200\ mAh\ g^{-1}$ up to a cut-off voltage of $2\ V$. Furthermore, the capacities increased with increase in annealing temperature up to $400\ ^{\circ}C$, but decreased at higher

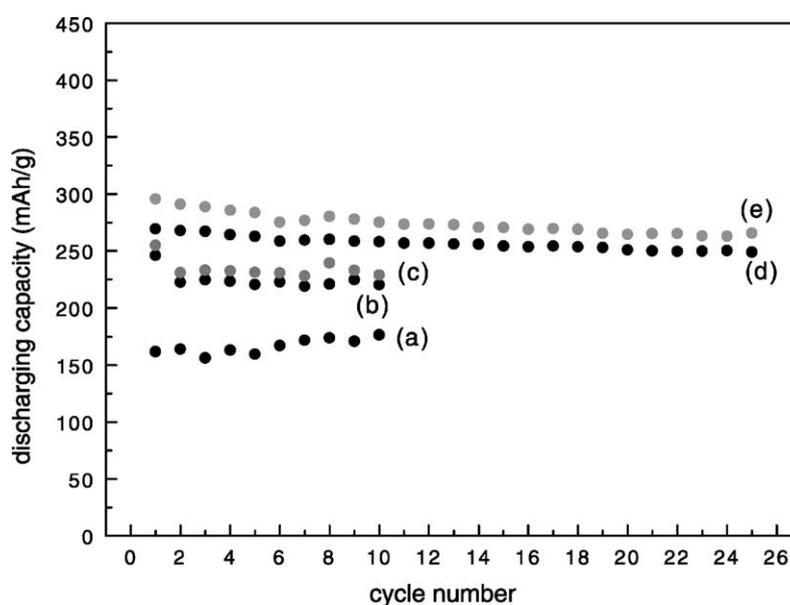


Fig. 6. Capacity ($mAh\ g^{-1}$) vs. cycle number for deposited V_2O_5 films: (a) deposited; (b) annealed at $200\ ^{\circ}C$; (c) annealed at $225\ ^{\circ}C$; (d) annealed at $250\ ^{\circ}C$; (e) annealed at $275\ ^{\circ}C$.

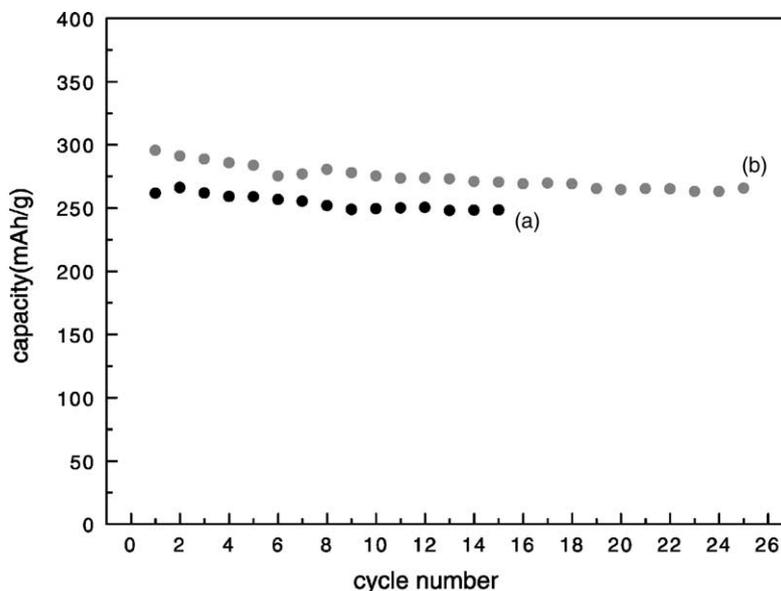


Fig. 7. Galvanostatic cycling of V_2O_5 films annealed at 275°C with current rate of: (a) $C/5$; (b) $1C$.

temperatures. Therefore, it is suggested that thin-films of V_2O_5 prepared by sputtering techniques and annealed at 300°C under oxygen atmosphere deliver an optimum capacity of $\sim 260\text{ mAh g}^{-1}$ (2 V cut-off) during the first discharge, but fade to $\sim 230\text{ mAh g}^{-1}$ in subsequent discharge cycles. Further, the deposited film exhibits large capacity fading above 2 V . Similar behavior is observed in the present case wherein the contribution towards capacity is very low above 3 V in the deposited film, as explained elsewhere in this paper.

Ramana et al. [32] investigated V_2O_5 thin-films prepared by an electron beam evaporation technique by annealing in oxygen at temperatures above 225°C . Julien et al. [34] reported the preparation of V_2O_5 thin-films by means of the PLD technique under oxygen.

The electrochemical deposition technique for the preparation of V_2O_5 thin-films was attempted recently by Potiron et al. [21] and it was shown that $\varepsilon\text{-}V_2O_5$ compounds could intercalate 1.4 mol of lithium per formula weight at a current rate of $C/50$. At higher discharged rates, i.e. $C/5$, the capacities dropped to $110\text{--}120\text{ mAh g}^{-1}$.

Thus, as discussed earlier, electrochemically active V_2O_5 thin-film can be prepared by a variety of techniques. The present work demonstrates, however, that the preparation of V_2O_5 thin-films using ESD techniques not only produces films with excellent electrochemical cycleability but also with no fading in capacity. There are desirable features for a high-performing cathode material for lithium secondary batteries.

4. Conclusions

It has been demonstrated that V_2O_5 films can be synthesized by a novel ESD technique. The films can be prepared in air in lieu of oxygen as in the case of other expensive vacuum techniques such as sputtering, PLD, and electron

beam evaporation. The synthesized vanadium pentoxide exhibits a high stable charge–discharge capacity of $\sim 270\text{ mAh g}^{-1}$ $C/5$, and delivers $\sim 260\text{ mAh g}^{-1}$ even when the current rate is increased to the $1C$ rate. The delivered capacities show no fading even after 25 cycles. The crystalline nature of the synthesized V_2O_5 films has porous morphology, which appears to be beneficial for the lithium intercalation–de-intercalation from the positive electrode. Finally, ESD is an economical and cheap technique for the preparation of V_2O_5 thin-films.

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References

- [1] J.C. Dupin, D. Gonbeau, H.B. Moudren, Ph. Vinatier, A. Lavasseur, *Thin Solid Films* 384 (2001) 23.
- [2] C.H. Chen, E.M. Kelder, P.J.J.M. Van der Put, J. Schoonman, *J. Mater. Chem.* 6 (1996) 765.
- [3] C.H. Chen, E.M. Kelder, P.J.J.M. Van der Put, J. Schoonman, *J. Mater. Sci.* 31 (1996) 5437.
- [4] C.H. Chen, E.M. Kelder, M.J.G. Jack, J. Schoonman, *Solid State Ionics* 86–88 (1996) 1301.
- [5] B. Wang, J.B. Bates, F.X. Hart, B.C. Sales, R.A. Zuhr, J.D. Robertson, *J. Electrochem. Soc.* 143 (1996) 3203.
- [6] M.D. Levi, Z. Lu, D. Aurbach, *J. Power Sources* 97–98 (2001) 482.

- [7] C. Delmas, S. Brethes, M. Menetrier, *J. Power Sources* 34 (1991) 113.
- [8] J.M. Tarascon, *Solid State Ionics* 69 (1994) 1.
- [9] J. Dai, S.F.Y. Li, Z. Gao, K.S. Siow, *J. Electrochem. Soc.* 145 (1998) 3057.
- [10] M. Wakihara, *Mater. Sci. Eng. R* 33 (2001) 109.
- [11] J. Desilvestro, O. Haas, *J. Electrochem. Soc.* 137 (1990) 5C.
- [12] Y.-T. Kim, G. Kumar, K.-B. Kim, B.W. Cho, *J. Power Sources* 112 (2) (2002) 504.
- [13] M.S. Whittingham, *Prog. Solid State Chem.* 12 (1978) 41.
- [14] J.M. Cocciantelli, M. Broussely, J.P. Doumerc, J. Labat, M. Pouchard, *J. Power Sources* 34 (1991) 103.
- [15] J.P. Pereira-Ramos, R. Messina, S. Bach, N. Baffier, *Solid State Ionics* 40–41 (1990) 970.
- [16] J.P. Pereira-Ramos, *J. Power Sources* 54 (1995) 120.
- [17] V. Legagneur, A. Le Gal La Salle, A. Verbaere, Y. Piffard, D. Guyomard, *J. Electrochem. Soc.* 148 (2001) A258.
- [18] J. Livage, *Chem. Mater.* 3 (1991) 578.
- [19] Y. Sato, T. Nomura, H. Tanaka, K. Kobayakawa, *J. Electrochem. Soc.* 138 (1991) L37.
- [20] N. Ozer, *Thin Solid Films* 305 (1997) 80.
- [21] E. Potiron, A. Le Gal La Salle, A. Verbaere, Y. Piffard, D. Guyomard, *Electrochim. Acta* 45 (1999) 197.
- [22] E. Potiron, A. Le Gal La Salle, A. Verbaere, Y. Piffard, D. Guyomard, M. Tournoux, *J. Phys. Chem. Solids* 62 (2001) 1447.
- [23] K. West, B. Zachau-Christiansen, S.V. Skaarup, F.W. Poulsen, *Solid State Ionics* 57 (1992) 41.
- [24] N. Kumagai, H. Kitamoto, M. Baba, S. Durand-Vidal, D. Devilliers, H. Groult, *J. Appl. Electrochem.* 28 (1998) 41.
- [25] C.J. Patrissi, C.R. Martin, *J. Electrochem. Soc.* 146 (1999) 3176.
- [26] W.-S. Yoon, S.-H. Ban, K.-K. Lee, K.-B. Kim, M.G. Kim, J.M. Lee, *J. Power Sources* 97–98 (2001) 282.
- [27] Il-Hwan Kim, K.-B. Kim, *Electrochem. Solid State Lett.* 4 (5) (2001) A62.
- [28] K.-W. Nam, K.-B. Kim, *Electrochemistry* 69 (2001) 467.
- [29] K.-W. Nam, K.-B. Kim, *J. Electrochem. Soc.* 149 (2002) A346.
- [30] K.-Y. Chung, K.-B. Kim, *J. Electrochem. Soc.* 149 (2002) A79.
- [31] D. Shu, K.Y. Chung, K.-B. Kim, *J. Power Sources*, in press.
- [32] C.V. Ramana, O.M. Hussain, B.S. Naidu, *Mater. Chem. Phys.* 50 (1997) 195.
- [33] X-Ray Powder Data File, Card No. 9-387, American Society For Testing and Materials, Philadelphia, PA, 1962.
- [34] C. Julien, E. Haro-Poniatowski, M.A. Camacho-Lopez, L. Escobar-Alarcon, J. Jimenez-Jarquín, *Mater. Sci. Eng. B* 65 (1999) 170.
- [35] C. Julien, J.P. Guesdon, A. Gorenstein, A. Khelifa, I. Ivanov, *J. Mater. Sci. Lett.* 14 (1995) 934.
- [36] H.K. Park, Ph.D. Thesis, University of Minnesota, USA, 1993.
- [37] J.M. Cocciantelli, J.P. Doumerc, M. Pouchard, M. Broussely, J. Labat, *Solid State Ionics* 78 (1995) 143.