Amorphous MnO_2 thin film cathode for rechargeable lithium batteries

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MnO_2 thin films have been deposited electrochemically from a MnSO_4 solution. The deposition conditions have been optimized. The open circuit voltage versus lithium content of the Li_xMnO_2 cathode shows a linear relation with a break in the slope at $x=0.5$. The specific energy density is 580 Wh/kg and the volume energy density 2916 Wh/l. The chemical diffusion coefficient of lithium in the MnO_2 film is 4.27 to $4.85 \times 10^{-13} \text{ cm}^2/\text{s}$ for $0 \leq x \leq 0.2$ and $1.1 \times 10^{-11} \text{ cm}^2/\text{s}$ for $x=0.9$. The good reversibility of lithium insertion and extraction has been shown by voltammetry and shallow charge–discharge cycling.

1. Introduction

Due to the rapid development of solid state electronics, the electric power that modern electronic devices require has been sharply reduced. In order to meet the requirements for further minimization of these devices, micro-batteries are now widely studied.

MnO_2 is a promising cathode material with a high and flat discharge voltage. In most cases MnO_2 has been modified with LiOH or Li_2CO_3 to form a spinel phase LiMn_2O_4 . Though MnO_2 has been investigated extensively [1], only a few publications mention its use in a thin-film form [2]. Chen Liquan and his co-workers [3] have studied an ultra-thin MnO_2 film in an electrochromic device. In that case lithium could be inserted and extracted reversibly.

Up to date thin-film amorphous oxide cathodes have been made by gas phase deposition techniques [4,5]. In this paper a simple electrodeposition technique is described for the deposition of manganese dioxide cathodes. It is shown how thin film cells can be assembled from these cathodes, electrochemically deposited lithium anodes and a polymer electrolyte

film. The electrochemical characteristics of both manganese oxide cathodes and the thin film cells will be described.

2. Preparation of manganese oxide thin films

The manganese dioxide thin films were deposited anodically under constant current from a MnSO_4 solution on stainless steel or nickel substrates. The substrates were mechanically polished, cathodically etched in 0.1 M HCl ($7.5 \text{ mA}/\text{cm}^2$, 5 min) and rinsed with distilled water. Reagent grade MnSO_4 was dissolved in distilled water. A constant current was applied over the substrate and platinum counter electrode by a manually controlled potentiostat while the electrolyte was stirred.

The average deposition rate is proportional to the current density, as is shown in fig. 1. However, the current cannot be increased indefinitely because the film adhesion decreases with increasing current density.

The deposition rate increases with the MnSO_4 concentration of the electrolyte. This indicates that a side reaction takes place, which becomes less significant as the manganese concentration increases. There can also be a change in reaction mechanism with increasing concentration. At concentrations higher than 0.1 M brown films appeared on the

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Fig. 1. Average deposition rate of MnO_2 as a function of the current density.

Fig. 2. Voltage versus time for MnO_2 deposition at several current densities.

counter electrode, which indicates a reaction with Mn^{2+} .

The voltage change during the galvanostatic deposition is shown in fig. 2. At low current densities the voltage increases steadily with time. At high current densities the voltage rises steeply at the beginning, then becomes constant. This change in voltage is due to the formation of the MnO_2 film.

MnO_2 deposition starts with the formation of isolated islands as shown in fig. 3. As the conductivity of MnO_2 is rather low (0.3 to $2 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ [6–8]) compared to stainless steel or nickel, the formation and growth of MnO_2 nuclei will increase the resistance and thus cause the voltage to rise. As the entire surface of the substrate is covered by MnO_2 , further increase in the thickness of the film cannot cause a substantial increase of the resistance, hence the voltage remains nearly constant. Rapid deposition leads to the formation of porous structures or even peeling off the substrate. The optimal current

Fig. 3. SEM photograph of the substrate surface after 10 min deposition from a 0.1 M MnSO_4 solution at 0.3 mA/cm^2 showing isolated islands of MnO_2 .

density for obtaining dense, flat thin films is 0.2 to 0.3 mA/cm^2 .

The films have been characterized by XRD and DTA. Samples dried by IR irradiation are X-ray amorphous and remain so when heat-treated at 53°C at 10^{-1} Torr vacuum. However, when a sample is heat-treated at 530°C it undergoes a phase transition to $\alpha\text{-Mn}_2\text{O}_3$. The X-ray diffraction spectrum of such a sample is shown in fig. 4. The TG analysis showed a gradual decrease in weight from room temperature to 200°C , indicating water loss of the film. At 530°C a sudden decrease in weight is seen, corresponding to the oxygen loss that accompanies the phase transition to $\alpha\text{-Mn}_2\text{O}_3$. The transition temperature lies very close to that of the $\gamma\text{-MnO}_2$ – $\alpha\text{-Mn}_2\text{O}_3$ transition at 525°C , whereas the transition from $\beta\text{-MnO}_2$ to $\alpha\text{-Mn}_2\text{O}_3$ takes place at 615°C [9,10]. Thus the local structure of the X-ray amorphous material may be similar to $\gamma\text{-MnO}_2$. This is also indicated by its good cathode characteristics since $\beta\text{-MnO}_2$ has no electrochemical activity.

3. Electrochemical studies on MnO_2 thin films

3.1. Open circuit voltage

A test cell was assembled from a lithium sheet anode, 1 M LiClO_4 in PC electrolyte and an electro-

Fig. 4. X-ray diffraction of a MnO_2 sample heat-treated at 530°C .

deposited MnO_2 thin film. The film has been dried after deposition by IR irradiation. Fig. 5 shows the OCV of this cell versus the lithium content of the Li_xMnO_2 film as obtained by galvanostatic titration.

Fig. 5. OCV of a thin-film Li_xMnO_2 cathode versus lithium.

The open circuit voltage was recorded at voltage variations of less than 1 mV/h. The voltage decreases linearly with a break in the slope for $x \approx 0.5$ according to the following equations:

$$E(\text{V}) = 3.68 - 2.7 \cdot x; \quad 0 \leq x \leq 0.5,$$

$$E(\text{V}) = 2.32 - 1.33 \cdot x; \quad 0.5 < x \leq 1.0.$$

Linear titration curves with a break in their slopes have been found earlier for $\text{P}_2\text{O}_5\text{-V}_2\text{O}_5$ or V_2O_5 -based glassy cathodes [11,12]. It could therefore be suggested that this kind of titration curve is a common feature for an amorphous cathode. The absence of a voltage plateau shows that no phase transition occurs. The slight decrease of the voltage shows that no obvious "structure" changes were involved. The change in slope may be the consequence of a difference in composition between the surface and the bulk of the grains, or composition variation between dif-

ferent domains. The slope change may even be caused by change in the fractal dimension which is equivalent to a slight change in the morphology if the particles have a fractal structure.

The specific energy density of the thin-film MnO_2 is 580 Wh/kg and its volume energy density 2916 Wh/l, both a cut-off voltage of 1.66 V.

3.2. Lithium diffusion coefficient

The chemical diffusion coefficient of lithium in thin film Li_xMnO_2 was determined by the galvanostatic titration technique proposed by Weppner and Huggins [13]. The same sample was used for the determination of both OCV and diffusion coefficient.

The average chemical diffusion coefficient for $0 \leq x \leq 0.1$ is $4.85 \times 10^{-13} \text{ cm}^2/\text{s}$ and $4.27 \times 10^{-13} \text{ cm}^2/\text{s}$ for $0.1 \leq x \leq 0.2$, both at 15°C . These values are three orders of magnitude lower than reported for bulk MnO_2 [14]. This is due to the presence of water in the films, some adsorbed and some incorporated in the crystal structure. The adsorbed water can react readily with incorporated lithium to form lithium oxide. The influence of water in the crystal structure is more complex. This crystal water exists as hydroxyl groups surrounding manganese vacancies [15]. These vacancies could act as traps for the lithium ions.

This explanation is confirmed by measurements at higher lithium contents of MnO_2 , where water had been removed by reaction with lithium: for $x=0.9$ $D=1.1 \times 10^{-11} \text{ cm}^2/\text{s}$, which compares well with values from the literature ($3 \times 10^{-11} \text{ cm}^2/\text{s}$ [16], $4 \times 10^{-11} \text{ cm}^2/\text{s}$ [17]).

DTA, TGA and DTG confirmed the presence of water in the films and showed that the film can be dried completely by a thermal treatment at 200°C . Other investigators found that a heat treatment at $350\text{--}420^\circ\text{C}$ can remove about 80% of water, but causes a transformation of $\gamma\text{-MnO}_2$ to $\gamma/\beta\text{-MnO}_2$ [18]. In the present case a prolonged heat-treatment at higher temperatures may cause crystallization of the amorphous film. Instead, the film was treated at 50°C under 10^{-1} Torr overnight. XRD showed that the treated MnO_2 is X-ray amorphous. A cathode that has been pretreated in this way is rechargeable at $x > 0.1$, indicating that 70% of the water remaining

in the IR-dried sample has been removed.

3.3. Reversibility

An electrochemical cell was used as described in section 3.1. For $x \leq 0.2$ no potential relaxation was observed on step variations in charge current. This indicates that lithium was trapped by reaction with water, and is consistent with the low values for the chemical diffusion coefficient that were measured at low lithium concentrations. At $x \geq 0.3$ no more water was left and lithium could be inserted and extracted reversibly. From this limiting value a water content of 6 wt% can be calculated, which agrees well with the 5 wt% reported in the literature [19].

The good reversibility and large capacity may be the result of the amorphous nature of the MnO_2 film. The good reversibility may also be caused by a fractal surface structure, providing an extremely large surface to bulk ratio.

4. Application of MnO_2 films in all solid state batteries

Several solid state thin film batteries have been constructed. Pure lithium films with a thickness of $0.3 \mu\text{m}$ were deposited cathodically from an 0.1 M LiClO_4 in PC solution on stainless steel substrates. The deposition occurred at about -100 mV . Thin films of $(\text{PEO})_8\text{LiClO}_4$ modified with PC were made by spreading an electrolyte-acetonitrile gel on the cathode surface and allowing the acetonitrile to evaporate under vacuum. This was done twice for each cell to prevent the formation of pinholes. The total assembly of electrolyte-covered cathode and thin film anode had a thickness of about $3 \mu\text{m}$ and an area of 1 cm^2 .

Fig. 6 shows the voltammogram of the thin-film battery cycled between 3.0 and 2.0 V at 10 mV/s . The rather good cycling behaviour and reversibility are indicated by the small difference between the first and the 200th cycle.

Fig. 7 gives the relative capacity change on cycling between 2.0 and 3.0 V at 1 mV/s . The capacity remains nearly unchanged within 50 cycles. Further cycling gradually decreases the capacity. 83% of the initial capacity is retained after 100 cycles.

Fig. 6. Cyclic voltammogram of the cell $\text{MnO}_2|(\text{PEO})_8\text{LiClO}_4|\text{Li}$ in the range 2.0–3.0 V at 10 mV/s.

Fig. 7. Cell capacity as a function of cycle life of the cell $\text{MnO}_2|(\text{PEO})_8\text{LiClO}_4|\text{Li}$.

The charge–discharge curve of a thin film battery is presented in fig. 8. This battery has a practical capacity of 44 μAh , corresponding to a volume capacity of 110 Ah/l when discharged to 2.0 V. The good reversibility is indicated by the charge curve.

The internal resistance of the battery was 10 $\text{k}\Omega$, estimated from the IR drop of the discharge curve. This large internal resistance may be caused by an interfacial problem and by formation of a passivating film on the lithium anode. Better performances of this kind of batteries can be expected by improving the manufacture process.

Fig. 8. Charge–discharge behaviour of the all solid state thin film cell $\text{MnO}_2|(\text{PEO})_8\text{LiClO}_4|\text{Li}$.

5. Conclusions

Amorphous MnO_2 films can be deposited anodically from an 0.1 M MnSO_4 solution at a current density of 0.2–0.3 mA/cm^2 . The dry thin films possess a rather good reversibility for lithium insertion and extraction. The chemical diffusion coefficients of lithium at room temperature are $4.27 \sim 4.85 \times 10^{-13} \text{ cm}^2/\text{s}$ for $x < 0.2$ and $1.1 \times 10^{-11} \text{ cm}^2/\text{s}$ for $x = 0.9$. The OCV curve is linear with a change in slope at $x = 0.5$. A specific energy density of 580 Wh/kg and a volume energy density of 2916 Wh/l has been achieved when $x = 1$. The amorphous MnO_2 thin films can find application as cathodes in secondary lithium batteries, as was demonstrated by the good performance of an ultra-thin, all-solid state lithium battery.

It is clear that the irreversibility that sometimes was found at low lithium contents is mainly caused by water in the cathode. The film itself possesses a good reversibility, which will be confirmed by further studies of its utilization in batteries.

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