Full paper

Grain boundary transport in sputter-deposited nanometric thin films of lithium manganese oxide

Juliane Mürter, Susann Nowak, Efi Hadjixenophontos, Yug Joshi, Guido Schmitz*

Institute of Materials Science, University of Stuttgart, Heisenbergstr. 3, 70563 Stuttgart, Germany

ABSTRACT

The lithium intercalation into ion-beam sputter-deposited films of lithium manganese oxide is studied as a function of the film thickness (50–500 nm). The kinetics of the intercalation is quantified in cyclic voltammetry under variation of the scanning rate over five orders of magnitude (0.005–768 mV/s). With an increasing rate, the intercalation currents reveal a transition from a finite length diffusion to a semi-infinite diffusion behavior, as it is expected from continuum transport equations. But surprisingly, the peak current in the Randles-Sevcik regime scales with the square root of film thickness. Consequently, the diffusion coefficient apparently increases with the layer thickness. Combining the parameters of the actual microstructure of the thin films with an appropriate kinetic modeling that includes the effects of grain boundaries, it is shown that the observed acceleration is quantitatively understood by outstandingly fast short-circuit transport in a type B kinetic regime of grain boundary diffusion.

1. Introduction

1.1. Lithium manganese oxide as a cathode material

The demand for high energy densities in lithium-ion batteries attracted research efforts in high voltage cathode materials. One of the most frequently discussed materials in this context is lithium manganese oxide (LMO, $Li_xMn_2O_4$, $x = 0...1$), revealing a good cycling stability and an intercalation / deintercalation potential of lithium in the range of 3.9–4.3 V versus lithium metal. The material was first reported as a de-/intercalation host over 30 years ago by Thackeray et al. [1,2], initiating major interest in the battery research community. LMO offers an enhanced cycling stability compared to materials with a layer-like structure such as V_2O_5. Furthermore, it is less toxic than the commercially available lithium cobalt oxide (LCO) and less expensive due to the abundance of manganese.

Intercalation of Li in LMO appears as a two-step process [3]. In the first step, only half of the tetrahedral sites are occupied, due to repulsive interaction between next neighbor sites. The second half of the sites are then filled in a second step at a slightly higher chemical potential. Accordingly, cyclic voltammetry (CV) shows a peak splitting with a potential difference of 0.1–0.15 V, while in chrono-potentiometry (CP), two plateaus are observed during charge and discharge.

Still not many studies dealt with the kinetics and the Li diffusion in the pristine material, even though this basic information is key in

understanding the behavior of the compound electrodes or full battery stacks. Geometrically well-defined thin films produced without binder or conductive additives offer the opportunity to determine the generic materials properties. Thin films of LMO have already been produced by various methods, such as electron beam evaporation [4], magnetron sputtering [5–14] and pulsed laser deposition (PLD) [15–20]. Other nanoscale geometries such as powders [21,22], as well as individual particles [23,24] and single crystals [25] have also been produced and characterized. However, for the various production and electrochemical characterization methods, the reported diffusion coefficients at room temperature vary over some orders of magnitude.

1.2. Diffusion studies in LMO

Previous investigations of the intercalation kinetics in thin films of pure LMO shall be briefly summarized. Julien et al. [15] grew films by PLD and used CV for characterization. The evaluation was based on the critical sweep rate from which the kinetics controls the capacity. The estimated diffusion coefficient was of the order of 10^{-12} cm^2/s but depended on the substrate temperature during deposition. To be more accurate, the diffusion coefficient was also determined by galvanostatic intermittent titration technique (GITT) at a potential of 4 V in samples produced at two different substrate temperatures (1.5×10^{-12} cm^2/s^{-1} and 8×10^{-12} cm^2/s for deposition at 100 °C and 300 °C, respectively).

Morcette *et al.* [26] produced LMO films of different stoichiometry

by laser ablation in various oxygen atmospheres. The diffusivities ranged from 3×10^{-12} cm²/s to 2×10^{-10} cm²/s. The authors attributed the observed variation in diffusivity to the deviation in film stoichiometry and possible impurity phases formed during deposition.

Quan et al. [27] used electrodeposition combined with sintering to produce LMO layers that consisted of nanoparticles. The observed cycling stability varied significantly with the layer thickness. The diffusion coefficient was determined from CV at different scanning rates (ranging from 0.5 mV/s to 20 mV/s) based on the Randles-Sevcik (R.-S.) relation [29] to be 2.516×10^{-9} cm²/s for 115.90 nm thick films, which was two orders of magnitude faster than the value the same authors obtained through impedance spectroscopy (1.49×10^{-11} cm²/s) at identical samples. They claimed that the increased diffusion coefficient of the R.-S. analysis was due to short circuit transport along the sinter boundaries.

Xie et al. [14] produced thin films by PLD. They used GITT (1.1×10^{-11} cm²/s), potentiostatic intermittent titration (PITT) (2.5×10^{-13} cm²/s), electrical impedance spectroscopy (EIS) (3.2×10^{-12} cm²/s) and CV (7×10^{-13} cm²/s) to determine the diffusion coefficient at 3.9 V. Again, the derived values ranged over two orders of magnitude. For comparison, they also investigated slightly over-lithiated thin films produced by r.f. magnetron sputtering. The measurements of PITT (4.6×10^{-11} cm²/s) and EIS (1.6×10^{-9} cm²/s) at 3.9 V demonstrated again a significant difference between the respective electrochemical methods. But more importantly in the present context, a significant variation was demonstrated among pristine materials that were produced using different deposition methods.

Vassiliev et al. [28] analyzed the intercalation kinetics of powder composite electrodes of LMO. They modeled CV spectra by a combination of Fick's laws for volume transport and a Butler-Vollmer concept for surface transport. The composite electrodes differed significantly from thin-film electrodes in the peak height ratio of the first and second peak [23]. This seemed to be not only an effect of the additives but also of the particle size distribution of the studied powders.

1.3. Goal of this work

In summary, the mentioned examples of kinetic studies strongly suggest a significant effect of the respective microstructure on the intercalation in LMO. This makes the easy interpretation of the kinetic coefficients as generic coefficients of bulk diffusion questionable. By quantitative analysis of pristine thin film LMO, this work aims to clarify the role of the GBs in the intercalation transport. Although thin films may be seen primarily as a model structure, the studied grain boundary effect is nevertheless quite relevant to conventional battery electrodes comprising powders of LMO in slurries. With sizes ranging from about 500 nm to several micrometers, commercial powder particles usually represent polycrystalline agglomerates (see e.g. figs. in [22]). Thus, even if these particles are surrounded by electrolyte or conductivity additives as it is usually the case, the diffusion into the particle interior probably appears through the GBs. Thus, clarifying the particular role of grain boundary transport is essential for the understanding of the battery kinetics.

Under suitable conditions, thin films can be produced with well-defined geometry, constant composition and reproducible microstructure. The present study aims at clarifying the transport paths by a systematic variation of the thickness of the produced films. The thin films are produced by ion-beam sputter deposition, a method that has, to the best of our knowledge, not been reported yet for deposition of LMO films. Owing to rather slow growth and controlled kinetic energy of the primary particles, the method tends to produce compact and smooth layers of reproducible quality.

2. Cyclic voltammetry and diffusion in thin film electrodes

The performance of battery electrode materials is conveniently

characterized by cyclic voltammetry. Based on the variation of the scanning rate, information about the kinetics of Li transport is derived. According to Randles [29], the peak current increases in proportion to the square root of the rate, and so the slope in the respective plot represents a direct measure of the diffusion coefficient. However, the underlying diffusion equations are only valid for a semi-infinite diffusion space, which in thin film geometry is only achieved if the diffusivity is low, the layers are still quite thick, or very fast scanning rates are applied.

If, in contrast, the finite thickness of the film becomes effective, the error function-shaped solution of the second Fick´s law (see e.g. [30]) must be extended by suitable reflection terms to fulfill the boundary condition of vanishing flux at the backside counter electrode [31]. A solution for a concentration step Δc_s at time zero at the surface can be expressed by the infinite series

$$\frac{\Delta c(x, t)}{\Delta c_s} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) - \sum_{k=1}^{\infty} (-1)^k \left[\mathrm{erf}\left(\frac{x - 2kh}{2\sqrt{Dt}}\right) + \mathrm{erf}\left(\frac{x + 2kh}{2\sqrt{Dt}}\right)\right]$$

(1)

in which h, D, and t denote the layer thickness, the bulk diffusion coefficient and the time, respectively. In comparison to the perhaps better-known solution by a series of trigonometric functions (see e.g. [30]), Eq. (1) has the advantage of fast convergence, especially with short diffusion times. So, the sum may be interrupted after a few terms without introducing unacceptable errors. The Li flux into the film is consequently:

$$
\begin{aligned}
j(t) &= -D\frac{\partial c}{\partial x}\bigg|_{x=0} \\
&= \Delta c_s \sqrt{\frac{D}{\pi t}} \left(1 - 2e^{-h^2/Dt} + 2e^{-4h^2/Dt} - 2e^{-9h^2/Dt} + \ldots \right)
\end{aligned}
$$

(2)

($x = 0$ indicates the position of the surface.) In cyclic voltammetry, the concentration at the surface boundary varies with the applied voltage. Assuming an ideal interstitial solution of Li, we express this concentration by the applied voltage V

$$c_s(t) = c_{\max} \cdot \frac{\exp(e\,(V(t) - V_0)/k_B T)}{1 + \exp(e\,(V(t) - V_0)/k_B T)}$$

(3)

in which $c_{\max}$ and V_0 denote the volume density of available interstitial sites and the open circuit potential at half filling, respectively. At a given time, the actual flux contains contributions of all earlier concentration changes at the surface. So, the intercalation flux measured in CV is obtained by integration over time

$$j_{\mathrm{tot}}(t) = \int_{-\infty}^{t} \frac{\partial c_s}{\partial t}\bigg|_{\tau} \cdot j(t - \tau)\; d\tau$$

(4)

The numerical result of Eq. (4) in combination with Eqs. (3) and (2) has been calculated by Aoki et al. [32], even though they derived their integral equations by multiple Laplace transformations. In agreement to experimental CV spectra, the calculated flux reveals a clear maximum. Aoki et al. suggested for the peak current density the simplified approximation

$$j_p = 0.446 \cdot e \cdot c_{\max} \frac{D}{h} \sqrt{\tilde{v}}\; \tanh(0.56\sqrt{\tilde{v}} + 0.05\; \tilde{v})$$

(5)

to the exact numerical result. Here, the variable $\tilde{v}$ represents a dimensionless scanning rate

$$\tilde{v} := \frac{e\; h^2}{D\, k_B T} v$$

(6)

while e, D, h and v denote the elementary charge, the (composition-independent) diffusion coefficient, the maximum diffusion depth (here thickness of the film), and the experimental scanning rate (dV/dt), respectively. Eqs. (5) and (6) comprise two important limiting cases. As $\tanh(x)$ approaches unity for large arguments, we can derive the classic