

ELECTROCHEMICAL METHOD FOR STUDYING THE REVERSIBILITY OF THE LITHIUM INTERCALATION IN SECONDARY BATTERIES

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Summary

In studies of the rechargeability of intercalation material there is no clear demonstration of performance, mainly because experimental data conditions differ between authors. These data depend on material structure, grain size, preparation mode and also cycling procedure. In this article, we present a theoretical study of intercalation during galvanostatic cycling. Experimental results on the intercalation of lithium in MoO_2 are in good agreement with theory. The chemical diffusion coefficient of Li in MoO_2 has been calculated: $D \approx 4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C.

1. Introduction

In the development of secondary batteries for vehicle propulsion, considerable progress has been made with rechargeable cathode materials [1].

The most extensively studied and promising materials are solid state cathodes which undergo intercalation or topochemical reactions with alkali metals. Of these, only TiS_2 has received a significant development effort. A potentially attractive group of materials are the transition metal oxides.

Preliminary studies of several rutiles have been carried out recently by Murphy and co-workers [2, 3]. Several studies [3, 4] have also indicated that vanadium oxides, particularly stoichiometric V_6O_{13} , are potentially attractive materials as high energy density cathodes for Li cells.

However, in studies of the rechargeability of intercalation material, there is no clear demonstration of performance, mainly because experimental data conditions differ between authors. These data strongly depend on material structure, grain size, preparation mode and also on cycling

procedure. We present in this paper a theoretical study of intercalation during galvanostatic cycling. Starting with the work of Atlung and co-workers [5] we have accepted that the limiting process in the intercalation of alkali metal is the diffusion in the host structure.

The theoretical results of these authors has been represented by the following equation:

$$y = \frac{a^2}{D} \frac{1}{p\tau} \left(p \frac{Dt}{a^2} + \frac{1}{2} \left(\frac{r^2}{a^2} - \frac{p}{p+2} \right) - 2 \sum_i \frac{\exp(-\alpha_i^2 Dt/a^2)}{\alpha_i^2} C \left(\frac{\alpha_i r}{a} \right) \right) \quad (1)$$

where y is the degree of occupancy at a distance r from the grain center or from the collector in a thin film configuration, a the grain radius or film thickness, D the diffusion coefficient (chemical), τ is the time of complete discharge for a given current, and α_i are the non-zero roots of the following equation $J_{p/2}(\alpha) = 0$ (Bessel function of the 1st kind) and

$$C \left(\frac{\alpha r}{a} \right) = J_{(p-2)/2} \left(\frac{\alpha r}{a} \right) / J_{(p-2)/2}(\alpha)$$

2. Cycling method and theoretical results

It was easier for theoretical study to introduce a rest period between charge and discharge than it was to reverse the current immediately (Fig. 1), so that the bulk of the grains come into equilibrium.

In this sequence, at each charge or discharge, eqn. (1) is applicable with the following theoretical capacities, respectively, for the n th discharge or charge.

$$Q_d(n) = Q_{\max} - R_c(n-1) - Q_d(n-1) + Q_c(n-1)$$

and

$$Q_c(n) = R_c(n-1) + Q_d(n)$$

where $R_c(n-1)$ is the residual capacity after $n-1$ cycles. For the n th cycle, eqn. (1) becomes, for $r = a$:

$$y = \frac{a^2}{D} \frac{Q_{\max}}{Q(n)} \frac{1}{p\tau} \left(p \frac{Dt}{a^2} + \frac{1}{p+2} - 2 \sum_i \frac{\exp(-\alpha_i^2 Dt/a^2)}{\alpha_i^2} \right) \quad (2)$$

Figure 2 shows the coulombic efficiency, t/τ , of the n th discharge *vs.* the coulombic efficiency of the first discharge for thin films ($p = 1$). These curves show that the coulombic efficiency levels off very rapidly for a deep first discharge.

Figure 3 shows that in the cases of cylindrical ($p = 2$) and spherical particles ($p = 3$) in a composite cathode no significant variations for the n th

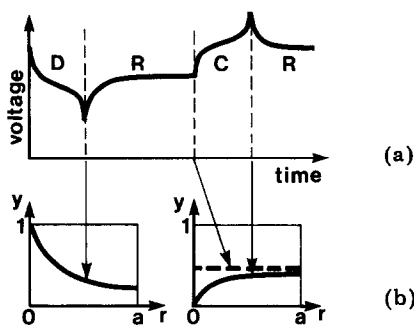


Fig. 1. (a) Voltage vs. time cycling diagram. D = discharge, R = rest, C = charge; (b) degree of occupancy profiles in a host material.

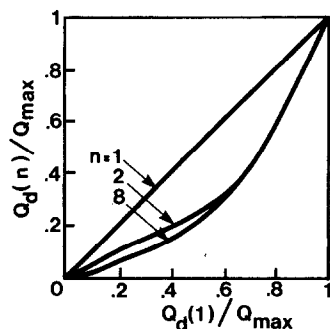


Fig. 2. Coulombic efficiency change as a function of number of cycles for thin film material.

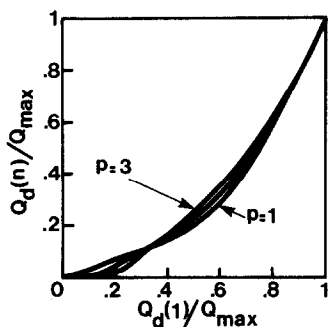


Fig. 3. n th Discharge coulombic efficiency as a function of structure parameters. 1 = thin film, 2 = cylindrical particles, 3 = spherical particles.

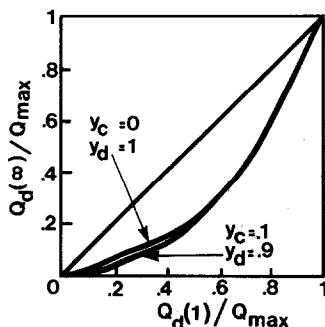


Fig. 4. n th Discharge coulombic efficiency as a function of end of charge or discharge potential. y_c = limit of degree of occupancy for a charge; y_d = limit of degree of occupancy for a discharge.

cycle appear when the coulombic efficiency of the first discharge is large. For these results the diffusion coefficient has been assumed to be constant and the end point of charge or discharge has been in the electroactivity range of the electrolyte. When the end point of charge or discharge potential is limited by the electrolyte destruction (Fig. 4), there are no significant changes in the stationary limit after n cycles.

3. Results and discussion

We have studied the reversibility of intercalation in MoO_2 with the following cell:



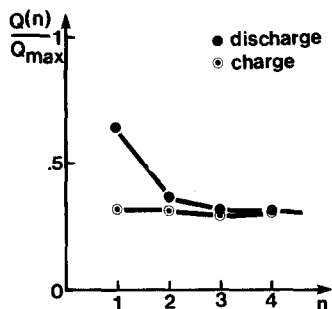


Fig. 5. Experimental coulombic efficiency for lithium intercalation in MoO_2 with PC + LiClO_4 . Mean grain size = $30 \mu\text{m}$ dia., $\tau = 10$ h.

The cell used an MoO_2 powder of $15 \mu\text{m}$ mean grain radius and the current was chosen to obtain a maximum of 10 h discharge (or charge).

Figure 5 shows a stationary limit after 3 cycles with a first discharge coulombic efficiency of 63%. This is in good agreement with the theoretical results. The value of the chemical diffusion coefficient calculated from Atlung's equation is $4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at 25°C .

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