



Optical measurement of lithium diffusivity in cathode materials: amorphous MoO₃ films

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Abstract

We have developed an optical system for measuring diffusion rates of intercalants in transparent cathode materials and have used it to measure the diffusivity of lithium in amorphous molybdenum oxide thin films.

Keywords: Lithium diffusivity; Molybdenum oxide; Cathode materials

1. Introduction

Diffusivities for neutral and ionic species in solids span a range from 10^{-18} to 10^{-3} cm²/s due to the great variety in short- and long-range structure of solids. The diffusion of Li in optically transparent materials can be studied by both electrochemical and optical measurements. The optical methods relies on the application of the Beer–Lambert law, $I(x) = I(0) \exp(-A)$, with

$$A = \int_0^x \alpha(\xi)c(\xi)d\xi \quad (1)$$

the optical absorptivity, c the concentration of the optically active species, α the molar absorptivity and x the film thickness.

2. Experimental

Films (350, 780 and 5500 Å thick) were flash-evaporated from MoO₃ powder with an electron beam onto a glass substrate coated with a 500 Å thick conductive indium–tin oxide (ITO). X-ray diffraction and Raman light scattering indicated that the films were amorphous. Electron microprobe analysis yielded an oxygen-to-molybdenum ratio O:Mo = $(2.75 \pm 0.2):1$.

The experimental apparatus (Fig. 1) consists of a photo-electrochemical cell, a potentiostat (PAR Model 173) and an optical system, which measures both the transmission and reflection of a HeNe laser beam ($\lambda = 632.8$ nm). The cell contains the electrolyte (1.3 M LiClO₄/propylene carbonate), the anode (Li_xAl

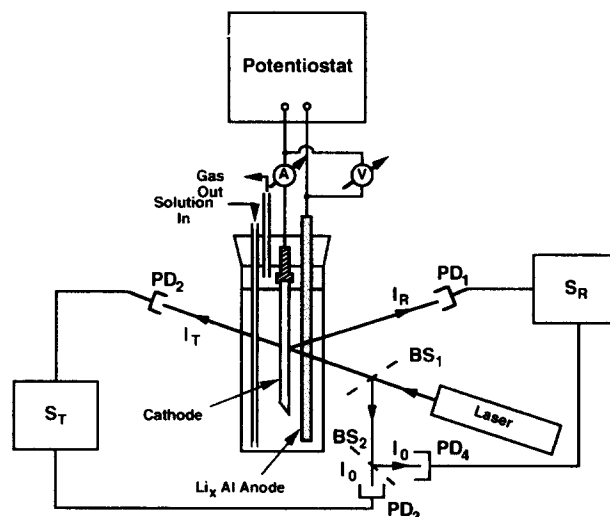


Fig. 1. Experimental setup. PD = photodiode, BS = beamsplitter. I_0 = incident intensity; I_R = reflected intensity; I_T = transmitted intensity; S_R = signal from reflected intensity, and S_T = signal from transmitted intensity.

alloy, $x \approx 0.25$, serving also as reference electrode) and the sample cathode material. Two nickel tubes, connected via plastic tubing to two gastight syringes, allow the introduction of the electrolyte solution into the cell and the removal of excess gas, while keeping the cell airtight. The cell is assembled inside a glove box under an argon atmosphere. Prior to assembly, the cell, syringes and tubing were kept under vacuum, and the cathode sample was baked in a vacuum oven at 140 °C for at least 18 h, in order to remove adsorbed water.

The reflected and the transmitted laser light are monitored by two photodiodes (PD₁ and PD₂). At the

same time two reference beams, split off the incident beam with beamsplitters BS₁ and BS₂, are monitored by photodiodes PD₃ and PD₄. The detection electronics uses the voltages from the photodiodes to calculate two output signals:

$$S = -\ln\left[\frac{I_0 - I_s}{I_s}\right] \quad (2)$$

where I_0 and I_s stand respectively for reference (incident) and signal (reflected or transmitted) light intensity. This detection scheme cancels out noise from electrical pick-up and fluctuations in light source intensity.

The MoO₃ films were doped and undoped with Li under potentiostatic conditions (potential step sizes 0.10, 0.25, 0.50 and 0.75 V), while monitoring the cell current. Data were collected for 600 s at 0.1 s intervals.

3. Model

The insertion of Li into MoO₃ modifies the valence state of Mo by addition of an electron into a normally empty conduction band, causing a change in the optical absorption coefficient due to the lowering of the empty d-band. The electron transfer rate and the electron diffusion in MoO₃ are very fast ($D_e = 7.5 \times 10^{-4}$ cm²/s in amorphous MoO₃ [1]). Hence, Li diffusion will determine the rate of change in the absorptivity of the host material. Li_xMoO₃ is a perfectly non-stoichiometric (type I) intercalation compound [2], so that one need not consider the moving boundary problem associated with the Li insertion into hosts forming two-phase materials. The layered nature of transition metal oxides (and thus possible anisotropy) can also be ignored, since the samples at hand were amorphous. The intercalation of Li into amorphous MoO₃ should then be adequately described by the one-dimensional diffusion equation with appropriate boundary and initial conditions:

$$D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \quad (3)$$

where $D = 2D_{Li}D_e/(D_{Li} + D_e) \approx 2D_{Li}$ is the ambipolar diffusion coefficient for Li, x the direction perpendicular to the film surface, and c the Li concentration in the cathode material.

A constant concentration profile represents the initial condition: $c(x, t=0) = c_0$, achieved by waiting after doping/undoping runs for concentration gradients to subside (~ 20 min). In addition, we assume that Li cannot diffuse into the ITO substrate: $\partial c(x=0, t)/\partial x = 0$. (Measurements on an ITO blank indicated that the Li diffusivity in ITO is at least an order of magnitude smaller than in MoO₃. Moreover, our cell operating range was above the ITO:Li potential (~ 1.6 V), so there was no driving force for Li insertion from Li_xMoO₃

into the ITO substrate.) The second boundary condition is $c(x=L, t) = c_s \pm \Delta c [1 - \exp(-t/\tau_B)]$, taking into account that the steady-state Li⁺ concentration at the cathode/electrolyte interface ($c_i = c_s \pm \Delta c$) is different from the concentration in the bulk solution (c_s) and that it is set up in a finite time τ_B upon application of an electric field [3].

One can use a general series solution of Eq. (3) for a slab of finite thickness L [4] to perform the integral of Eq. (1) and obtain the time dependence of the differential absorptivity, $\Delta A = A(t) - A(0)$:

$$\begin{aligned} \Delta A = & \frac{2\alpha}{L} \sum_{n=0}^{\infty} \left\{ \frac{\Delta c \tau_c}{(2n+1)^2} \left[1 - \exp\left[-(2n+1)^2 \frac{t}{\tau_c}\right] \right] \right. \\ & - \frac{\Delta c}{\frac{(2n+1)^2}{\tau_c} + \frac{1}{\tau_B}} \\ & \left. \times \left[\exp\left(-\frac{t}{\tau_B}\right) - \exp\left[-(2n+1)^2 \frac{t}{\tau_c}\right] \right] \right\} \quad (4) \end{aligned}$$

The times τ_B and τ_c are related to diffusivities through the relation $\tau = (4L^2)/(\pi D)$.

4. Results and discussion

Our model assumes that the molar absorptivity of the host as well as the diffusion constant do not depend on the dopant concentration. From a plot of the differential absorptivity versus charge, it is clear that the assumption $\Delta A \propto Q$ is approximately valid (Fig. 2). The small curvature indicates that the optical properties of the host depend weakly on the intercalant concentration. The linearity assumption $\Delta A \propto c_{Li}$ can also be checked through a comparison of the time dependence for the absorptivity change with that of the deposited charge.

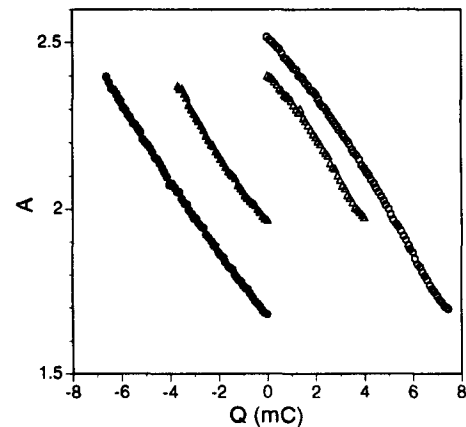


Fig. 2. Absorbance in a 5500 Å thick MoO₃ film as function of charge for potential steps of ± 0.3 and ± 0.5 V and initial cell voltages V_i between 2.0 and 2.5 V, on lithium doping and undoping. (O) $V_i = 2.0$, $\Delta V = +0.5$ V; (Δ) $V_i = 2.0$, $\Delta V = +0.3$ V; (\bullet) $V_i = 2.5$, $\Delta V = -0.5$ V, and (\square) $V_i = 2.3$, $\Delta V = -0.3$ V.

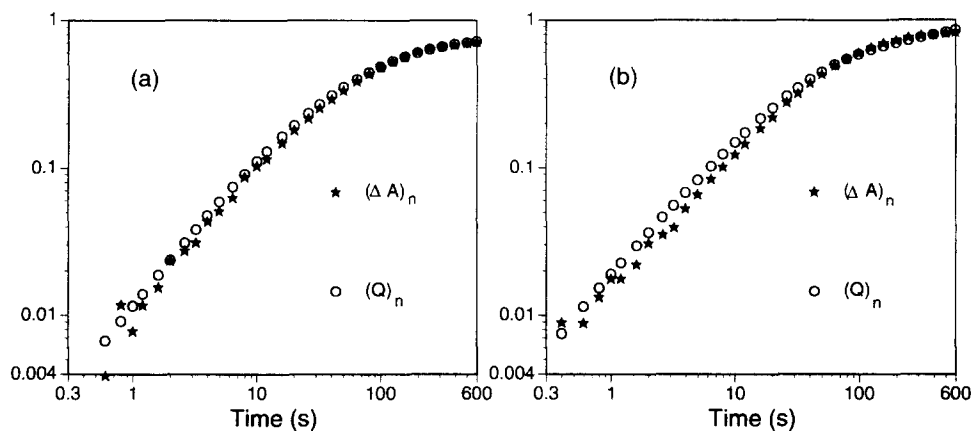


Fig. 3. Differential absorbance $(\Delta A)_n$ and integrated cell current $(Q)_n$ as function of time: (a) lithium doping, and (b) lithium undoping. A normalization factor has been used in order to compare the time dependence of physical quantities with different units.

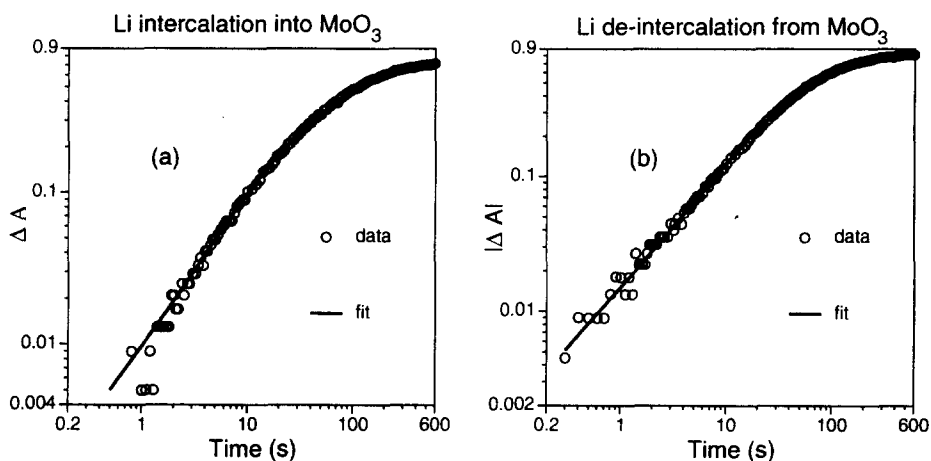


Fig. 4. Differential absorbance for the conditions in Fig. 2, as a function of time on application of a potential step: (a) lithium doping, and (b) lithium undoping. Symbols represent data points, lines represent fits to the model.

Fig. 3 shows that this assumption is fairly well satisfied. (ΔA and Q have been normalized by dividing them through their maximum values.)

In order to avoid the influence of the substrate on the measurements [5], only films with a 5500 Å thickness have been used for the determination of the Li diffusivity. Absorbance differences were calculated from the reflected and transmitted signals. These were then spline interpolated and 10 points per decade determined the data set for further analysis. The 'synthetic' data sets for $\Delta A(t)$ were then fit to Eq. (4) using a nonlinear least-squares Levenberg–Marquardt algorithm. This yielded $70 < \tau_c < 90$ s, which corresponds to Li diffusivities of $(1.2\text{--}2.3) \times 10^{-11}$ cm²/s on doping and $(1.9\text{--}3.2) \times 10^{-11}$ cm²/s on undoping, in agreement with those derived from electrochemical measurements [6]. Typical data for the differential absorptivity as a function of time during potential step experiments and fits to Eq. (4) are displayed in Fig. 4(a) and (b). The boundary

condition 'switch-on' time τ_B had values of 6 to 9 s. Considering Li diffusivities of 10^{-6} to 10^{-5} cm²/s for the 1.3 M LiClO₄/propylene carbonate solution, one obtains a diffusion boundary layer thickness in the range from 80 to 180 μm.

References

- [1] O. Zelaya-Angel, C. Menezes, F. Sanchez-Sinencio and G.F. Leal Ferreira, *J. Appl. Phys.*, 51 (1980) 6022.
- [2] M.B. Armand, in D.W. Murphy, J. Broadhead and B.C.H. Steele (eds.), *Materials for Advanced Batteries*, Plenum, New York, 1980, p. 145.
- [3] C. Barbero, M.C. Miras and R. Kötz, *Electrochim. Acta*, 37 (1992) 429.
- [4] H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids*, Clarendon Press, Oxford, 2nd edn., 1959, Ch. 3.
- [5] R.B. Goldner, G. Foley, E.L. Goldner, P. Norton, K. Wong, T. Haas, G. Seward and R. Chapman, *Appl. Opt.*, 24 (1985) 2283.
- [6] C. Julien and G.A. Nazri, *Solid State Ionics*, 68 (1994) 111.