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Chronovoltammetry of electrolytic molybdenum oxides at the electrochemical intercalation/deintercalation of lithium ions

Abstract Chemical diffusion coefficients of lithium ions in processes of electrochemical intercalation/deintercalation in electrolytic molybdenum oxides and the parameter of interaction between the intercalated particles (g) have been obtained by the following methods: the galvanostatic intermittent titration technique (GITT), the potential relaxation technique after current interruption (PRT), and the potential intermittent titration technique (PITT). In the potential range 2.40–1.40 V the values of $\tilde{D}_{Li}$ of the order of 10^{-11}–10^{-13} cm^2/s have been obtained for Mo$_4$O$_{11}$ oxide. Intercalation/deintercalation was realized in one phase when $g > 4$.

Keywords Chemical diffusion coefficient · Molybdenum oxide · Thermodynamic properties

Introduction

The aim of the work is the study of the thermodynamic and mass transport properties of electrolytic (e) molybdenum oxides (e-Mo$_4$O$_{11}$). For the production of thin layer molybdenum oxides we used an electrolytic method. A wide range of non-stoichiometric compositions of molybdenum oxides, with promise for applications as the electrodes of lithium secondary batteries, has been obtained [1]. The deposits of e-Mo$_4$O$_{11}$ cathodically obtained from the aqueous ammonium-molybdenum electrolyte on stainless steel in quantities of

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0.75–2.50 mg/cm^2, and with 1.50–2.50 μm thickness, were the object of the kinetic investigation. All the electrochemical investigations of e-Mo$_4$O$_{11}$ have been carried out in a sealed three-electrode cell with a Li auxiliary electrode and a Li/Li$^+$ reference electrode in the electrolyte PC/DME/1 M LiClO$_4$ on a test bench with computer control. The e-Mo$_4$O$_{11}$ electrodes were initially galvanostatically cycled (about 20 cycles), until the discharge capacity became stable at the level of 225 mAh/g ($I_{dch} = 20$ mA/g). The selection of e-Mo$_4$O$_{11}$ was determined by the fact that it can be considered as a one-phase material within a wide potential range (1.60–2.50 V). Therefore, the diffusion theory for solid-state materials for a one-phase process is usable for e-Mo$_4$O$_{11}$.

The diffusion coefficient $\tilde{D}_{Li}$ in Mo$_4$O$_{11}$ was determined by using several methods: changing of $\tilde{D}_{Li}$ in the process of electrochemical intercalation was observed by the galvanostatic intermittent titration technique (GITT) [2] and the potential relaxation technique (PRT) after current interruption [3], and deintercalation of lithium ions by the potential intermittent titration technique (PITT) [2].

In PITT, if the condition $\tilde{D}_{Li}t/L^2 \ll 1$ is satisfied, the current changes with time according to the following equation:

$$I = \frac{\Delta Q}{L}\sqrt{\frac{\tilde{D}_{Li}}{\pi t}} \tag{1}$$

where the diffusion coefficient $\tilde{D}_{Li}$ is usually evaluated from the slope of a linear relaxation plot on the l–$t^{-1/2}$ coordinates:

$$\tilde{D}_{Li} = \pi \left(\frac{L \frac{dI}{dt^{-1/2}}}{\Delta Q} \right) \tag{2}$$

where $\tilde{D}_{Li}$ is the chemical diffusion coefficient of lithium ions in the solid phase, L is the thickness of the active material, $dl/dt^{-1/2}$ is the slope of the linear plot on the I–$t^{-1/2}$ coordinates, and ΔQ is the value of the charge introduced (removed) into the electrode at a stepwise

potential supply. According to Eq. 1, in a time interval corresponding to a half-infinite diffusion (Cottrell region):

$$I\sqrt{t} = \frac{\Delta Q}{L}\sqrt{\frac{\tilde{D}_{Li}}{\pi}} \qquad (3)$$

Provided that $\tilde{D}_{Li}$ remains unchanged when a small enough charge is supplied, the $I\sqrt{t}$ product in this region should be independent of time. This conclusion allows us to select the Cottrell region on the experimental curves, presenting them on the $It^{-1/2}$–$\log t$ coordinates. In Fig. 1 are shown such curves, obtained on the Li_x-Mo_4O_{11} electrode at different initial potentials during the electrochemical deintercalation of lithium ions. All of them have the form of curves with a maximum, whose position and amplitude relative to the x-axis depend on the potential. The Cottrell region corresponds to the vicinity of the maximum; the other time regions on these curves characterize the processes unconnected with the half-infinite diffusion of the active particles [4].

In Fig. 2 is shown the influence of the assigned potential on the maximum values of $It^{-1/2}$–E (curve 1) and on the time corresponding to these values of $It^{-1/2}$ (curve2). It is clear that the dependence of $It^{-1/2}$–E (curve2) has the form of a curve with the maximum similar to the cyclic voltammogram of the electrode (Fig. 2, curve 3). According to Eq. 2 it is possible in this case if the value of the ΔQ charge, introduced in an impulse ΔE, and (or) diffusion coefficient change depending on the potential on the curves with maxima. Actually, the experimental curves ΔQ–E and $\log \tilde{D}_{Li} - E$ shown in Fig. 2 (curve 4) and Fig. 3, respectively, satisfy this supposition: in the range of voltammogram peaks, ΔQ as well as $\tilde{D}_{Li}$ have their maximum values. The dome-like form of the curve is also confirmed by the fact that the dependence of the time corresponding to the maximum $It^{-1/2}$ (Fig. 2, curve 3) on a potential, has a minimum within the peak potential range. If it is taken
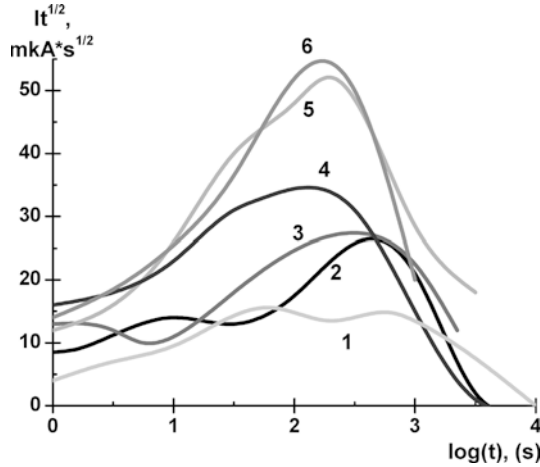

Fig. 2 Effect of the electrode potential of e-$Li_xMo_4O_{11}$ on the values of $(It^{1/2})_{max}$ and t_{max}: *curve 1*, $(It^{1/2})_{max}$ vs. E; *curve 2*, t_{max} vs. E; *curve 3*, voltammogram of electrode charging with the rate 50 μV/s; *curve 4*, dependence of the quantity of the charge lost by the $Li_xMo_4O_{11}$ electrode at the superposition of a potential step $\Delta E = -10$ mV during charging

that $\tilde{D}_{Li} \approx L^2/t_{max}$, the maximum on the $\tilde{D}_{Li} - E$ curve has to correspond to this maximum.

The obtained experimental dependence allows us to make some suppositions relative to the nature of the transformations in $Li_xMo_4O_{11}$ during intercalation.

Fig. 1 Dependence of $It^{1/2}$ vs. $\log t$ at the initial potentials of e-Mo_4O_{11} (in V) of: *curve 1*, 2.85; *curve 2*, 1.21; *curve 3*, 1.72; *curve 4*, 2.46; *curve 5*, 2.22; *curve 6*, 2.00
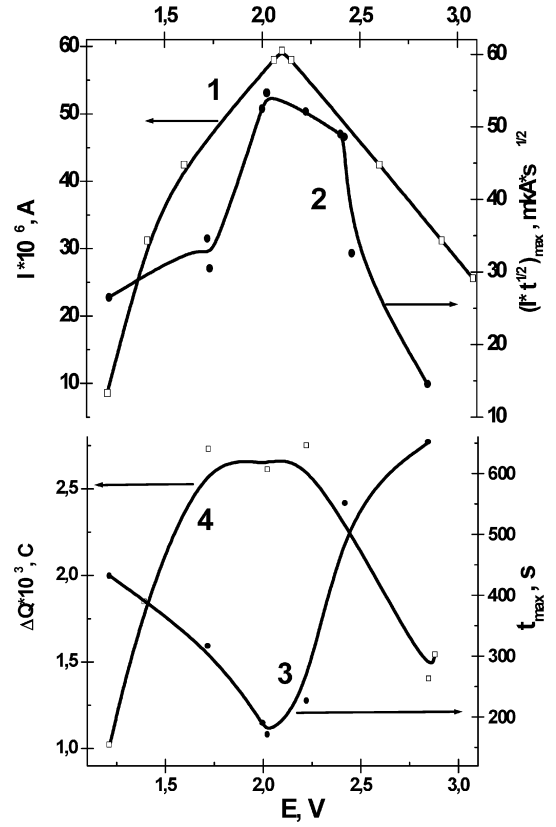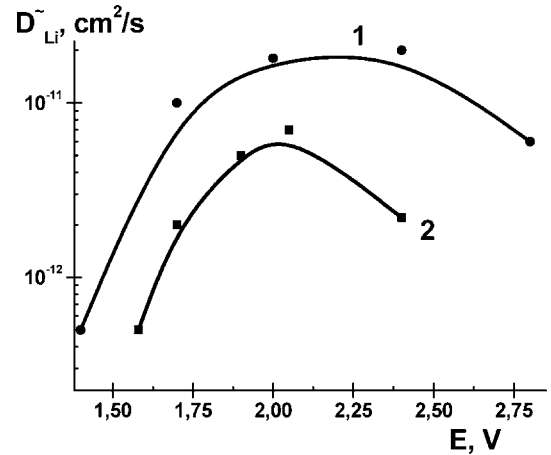

Fig. 3 Dependence of $\tilde{D}_{Li}$ on the potential in $Li_xMo_4O_{11}$: *curve 1*, the PITT method; *curve 2*, the GITT method

According to the theory of intercalation/deintercalation of lithium ions in active materials based on Frumkin's adsorption isotherm, the character of the transformation in a solid phase is determined by the value and sign of the interaction parameter between the intercalated particles, denoted by g [5]. When $g > -4$ the processes proceed without phase transitions; at $g > 0$ the repulsive forces between the intercalated particles predominate; at $g = 0$ interaction between particles is absent. Theoretically it has been shown that with the growth of g the width of the half-peaks of the cyclic voltammograms increases. Figure 2 (curve 3) shows that the width of the half-peak $\Delta E_{p/2}$ of the e-Mo_4O_{11} voltammogram obtained under quasi-equilibrium conditions (potential scan rate 50 μV/s) is 1600 mV, whereas for the reversible one-electron process without interaction ($g = 0$) between the particles, $\Delta E_{p/2} = 90$ mV. If the possible effect of Li^+ transfer through the interface (active mass/electrolyte) is neglected, these data denote that $g > 0$ during Li^+ deintercalation from $Li_xMo_4O_{11}$, and repulsive forces between intercalated lithium ions are observed. In this case it should be expected that the diffusion coefficient $\tilde{D}_{Li}$ changes, depending on the potential of the curve, with the maximum near the maximum of the cyclic voltammogram. This was observed in our tests.

The PRT method proposed by Wang et al. [3] enables determination of the lithium ion diffusion coefficient at the different stages of oxide intercalation, based on the diffusion model describing the behavior of a flat intercalation electrode after the end of the charging or discharging process. With the relaxation time $t > L^2/\pi^2\tilde{D}_{Li}$ the value of $\tilde{D}_{Li}$ is calculated from the slope of the linear part of the relaxation curve on $\ln\left[\exp\left(\frac{E_\infty - E(L,t)}{RT/F}\right) - 1\right]$ coordinates relative to t:

$$\tilde{D}_{Li} = -\frac{L^2 tg\alpha}{\pi^2} \tag{4}$$

where E_∞ is the electrode potential, established after current cut-off when the time $t \to \infty$ and $E(L,t)$ is the electrode potential at the moment of time t after circuit interruption. E_∞ was considered to be equal to the potential established at least 48 h after current cut-off. Using the PRT method in the potential range 2.40–1.40 V, the values of $\tilde{D}_{Li}$ of the order of 10^{-12}–10^{-13} cm^2/s were obtained. The same order for the $\tilde{D}_{Li}$ coefficient has been determined for $Li_xMo_4O_{11}$ by the GITT method. The change of $\tilde{D}_{Li}$ with the potential (by GITT) is shown in Fig. 3 (curve 2). It is typical that the dependence of $\tilde{D}_{Li}$ on the potential both during intercalation and deintercalation (Fig. 3, curve 1) is the curve with the diffused maximum.

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