CHRONOVOLTAMMETRY OF ELECTROLYTIC MOLYBDENUM OXIDES AT ELECTROCHEMICAL INTERCALATION/DEINTERCALATION OF LITHIUM IONS

V.P. Tysyachny, E.M. Shembel, R.D .Apostolova, V.M. Nagirny, and K.Ye.Kylyvnyk*

Ukrainian State Chemical Technology University, 49005, Dnepropetrovsk, Ukraine,
E-mail: shembel@onil.dp.ua
**ENER1, Ft. Lauderdale, Fl, 33309, USA E-mail: eshembel@ener1.com*

The aim of the work is the studies of the thermodynamic and mass transport properties of electrolytic (e) molybdenum oxides (e-Mo_4O_{11}). For the production of thin layer molybdenum oxides it has been used the electrolytical method. The wide range of non-stoichiometric compositions of molybdenum oxides promising for application in the electrodes of lithium secondary batteries has been obtained electrolytically [1]. The deposits of e-Mo_4O_{11} oxide cathodically obtained from the aqueous ammonium-molybdenum electrolyte on stainless steel in the quantity of 0.75-2.50 mg/cm^2, and with 1.50-2.50 μm thickness have become the object of the kinetic investigation. All the electrochemical investigations of e-Mo_4O_{11} have been carried out in a sealed 3-electrode cell with Li auxiliary electrode and Li/Li^+ reference electrode in the electrolyte PC, DME, 1 M $LiClO_4$ on test bench with a computer control. e-Mo_4O_{11} electrodes were preliminary galvanostatically cycled (about 20 cycles), until discharge capacity became stable on the level of 225 mAh/g (I_{dch}=20 mA/g). Selection of e-Mo_4O_{11} oxide was determined by the fact that it can be considered as a one-phase material within the wide potential range (1.60-2.50 V). Therefore, the diffusion theory in solid-state material for one-phase processes is usable for e-Mo_4O_{11}.

$\widetilde{D}_{Li}$ in Mo_4O_{11} was determined by using several methods: changing of $\widetilde{D}_{Li}$ in the processes of electrochemical intercalation was observed by (GITT) known as galvanostatic intermittent titration technique [2] and potential relaxation technique (PRT) after current interruption [3], and deintercalation of lithium ions by potential intermittent titration technique (PITT) [2].

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

$$I = \frac{\Delta Q}{L}\sqrt{\frac{\widetilde{D}_{Li}}{\pi t}} \quad . \qquad (1)$$

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

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

where: $\widetilde{D}_{Li}$ - chemical diffusion coefficient of lithium ions in a solid phase, L – thickness of active material, $dl/dt^{-1/2}$ slope of the linear plot on the I-$t^{-1/2}$ coordinates, ΔQ – value of the charge introduced (removed) into electrode at a stepwise potential supply. According to the equation (1) in a time interval corresponding to a half - infinite diffusion (Cottrell region):

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

Provided that $\widetilde{D}_{\mathrm{Li}}$ remains unchanged when a small enough charge supplied, $I \cdot \sqrt{t}$ product in this region should be independent on a time. This conclusion allows to select the Cottrell region on the experimental curves, presenting them on the $I \cdot t^{-1/2} - \lg t$ coordinates. In Fig. 1 such curves, obtained on the $Li_xMo_4O_{11}$ electrode at the different initial potentials during electrochemical deintercalation of lithium ions are shown. All of them have a form of the curves with a maximum, which position and amplitude relative to X-axis depend on the potential. 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 it is shown the influence of the assigned potential on the maximum value 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 (curve 2) has a form of the curve with the maximum similar to the cyclic voltammogram of the electrode (Fig.2, curve 3). According to the equation (2) it is possible in the case if the value of ΔQ charge, introduced in each an impulse ΔE, and (or) diffusion coefficient change depending on the potential on the curves with maxima. Actually, the experimental curves ΔQ-E and $\lg \widetilde{D}_{\mathrm{Li}}$-E shown in Fig. 2, curve 4 and Fig.3, respectively, satisfy this supposition: in the range of voltammogram peaks, ΔQ as well as $\widetilde{D}_{\mathrm{Li}}$ have the maximum values. Dome-like form of the curve is also confirmed by the fact that dependence of the time corresponding to maximum $It^{-1/2}$ (Fig.2, curve 3) on a potential, has a minimum within the peak potential range. If it is taken that $\widetilde{D}_{\mathrm{Li}} \cong L^2/t_{max}$, maximum on $\widetilde{D}_{\mathrm{Li}}$ -E curve has to correspond to this maximum.

The obtained experimental dependence allows to make some suppositions relative to the nature of the transformations in $Li_xMo_4O_{11}$ during intercalation. According to the theory of intercalation/deintercalation of lithium ions in active materials based on Frumkin's adsorption isotherm, character of the transformation in a solid phase is determined by the value and sign of the parameter of interaction 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 *g* growth the width of the half-peaks of cyclic voltammograms increases. Fig.2, curve 3 shows that the width of half-peak $\Delta E_{p/2}$ of e-Mo_4O_{11} voltammogram obtained under quazi-equilibrium conditions (potential scan rate 50μV/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 during Li^+ deintercalation from $Li_xMo_4O_{11}$ $g>0$, and the repulsive forces between intercalated lithium ions are observed. In this case it should be expected that diffusion coefficient $\widetilde{D}_{\mathrm{Li}}$ changes depending on the potential by the curve with the maximum near the maximum of cyclic voltammogram. This is observed in our tests.

PRT method proposed by Q.Wang with coauthors enables determination of 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 finishing charging or discharging process. With the relaxation time $t > L^2/\pi^2 \widetilde{D}_{\mathrm{Li}}$ the value of $\widetilde{D}_{\mathrm{Li}}$ is calculated with

a slope of the linear part of relaxation curve on $\ln\left[\exp\left(\frac{E_\infty - E(L,t)}{RT/F}\right)-1\right]$ coordinates relative to t: $\widetilde{D}_{Li} = -\frac{L^2 \cdot tg\alpha}{\pi^2}$, (4)

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

References

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Figures caption

Fig.1. Dependence of $It^{1/2}$ vs lg t at the initial potentials of e-Mo_4O_{11}, V: 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.2. Effect of the electrode potential of e-$Li_xMo_4O_{11}$ on the values of $(lt^{1/2})_{max}$ and t_{max}: 1.$(lt^{1/2})_{max}$-E, 2. t_{max}-E, 3. voltammogram of electrode charging with the rate 50μV/s, 4. dependence of the quantity of the charge lost by $Li_xMo_4O_{11}$ electrode at the superposition of potential step ΔE= -10mV during charging.

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

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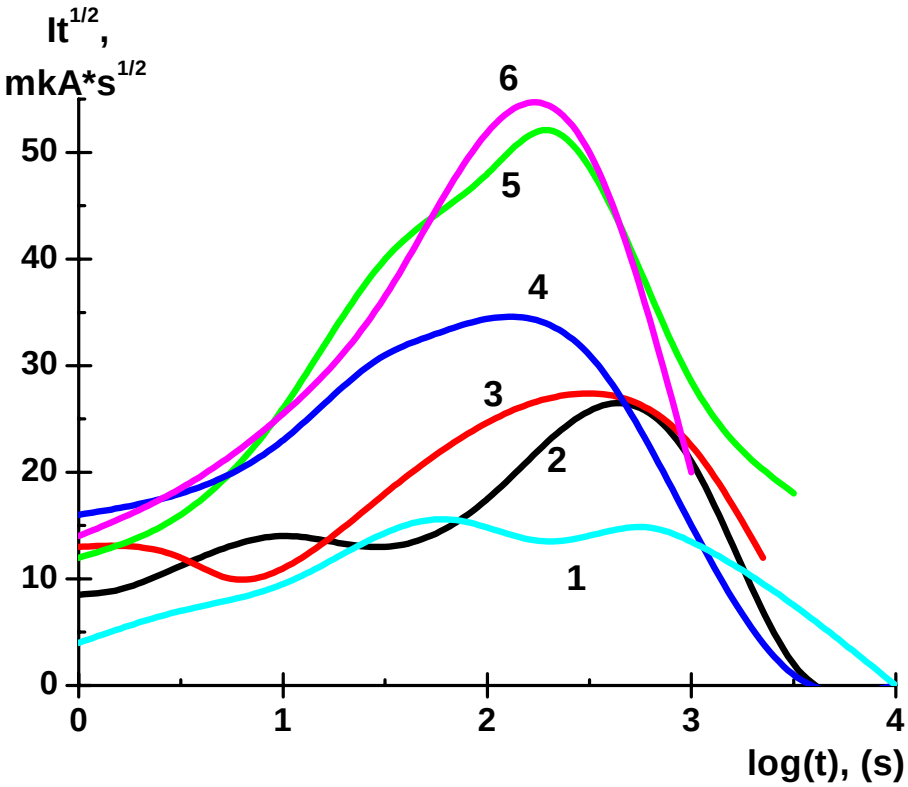
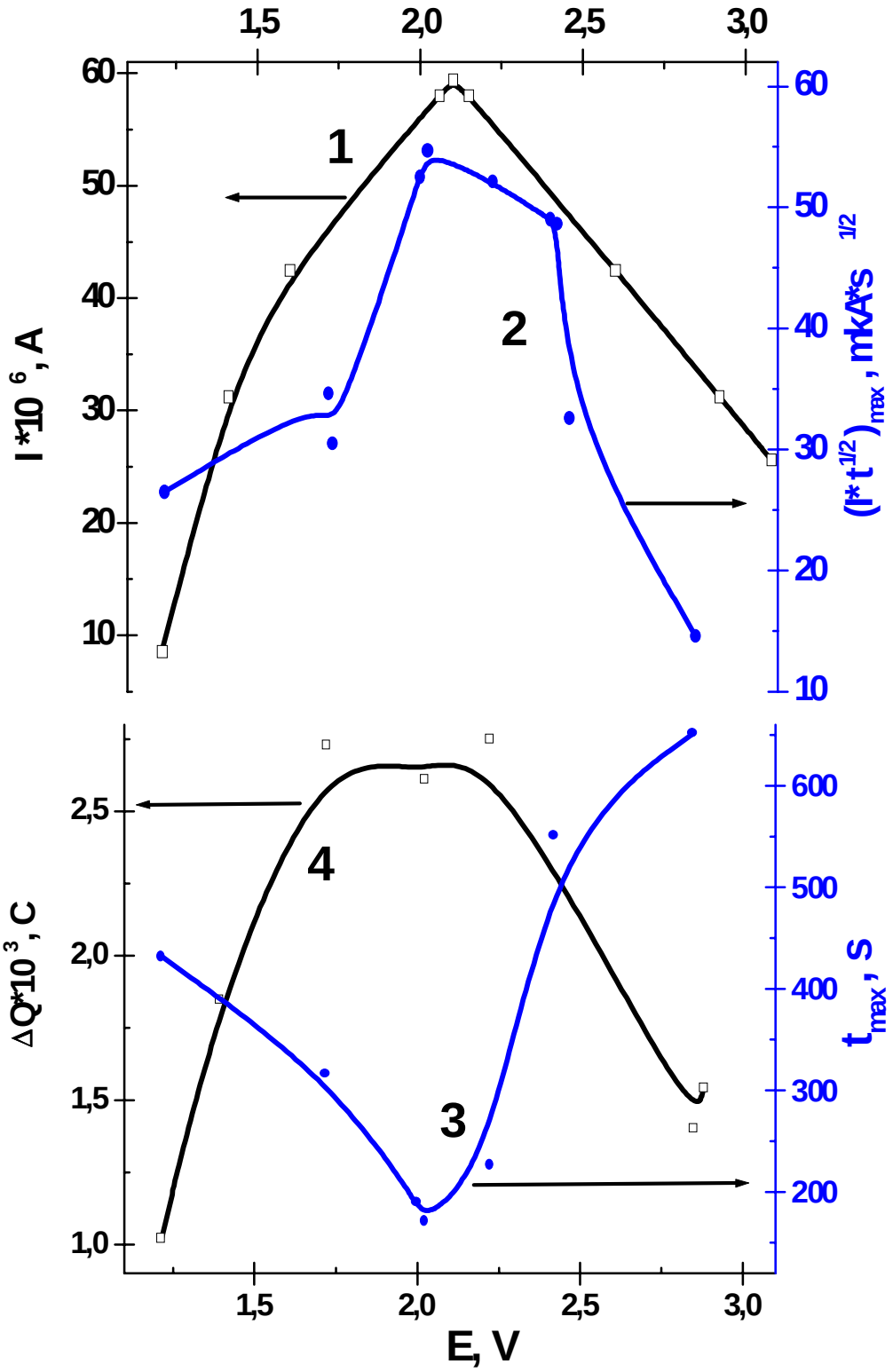


Fig.1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10
1
2
I*10 6, A
(I*t1/2)max, mkA*s 1/2
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4
3
ΔQ*10 3, C
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tmax, s
E, V

Fig.2

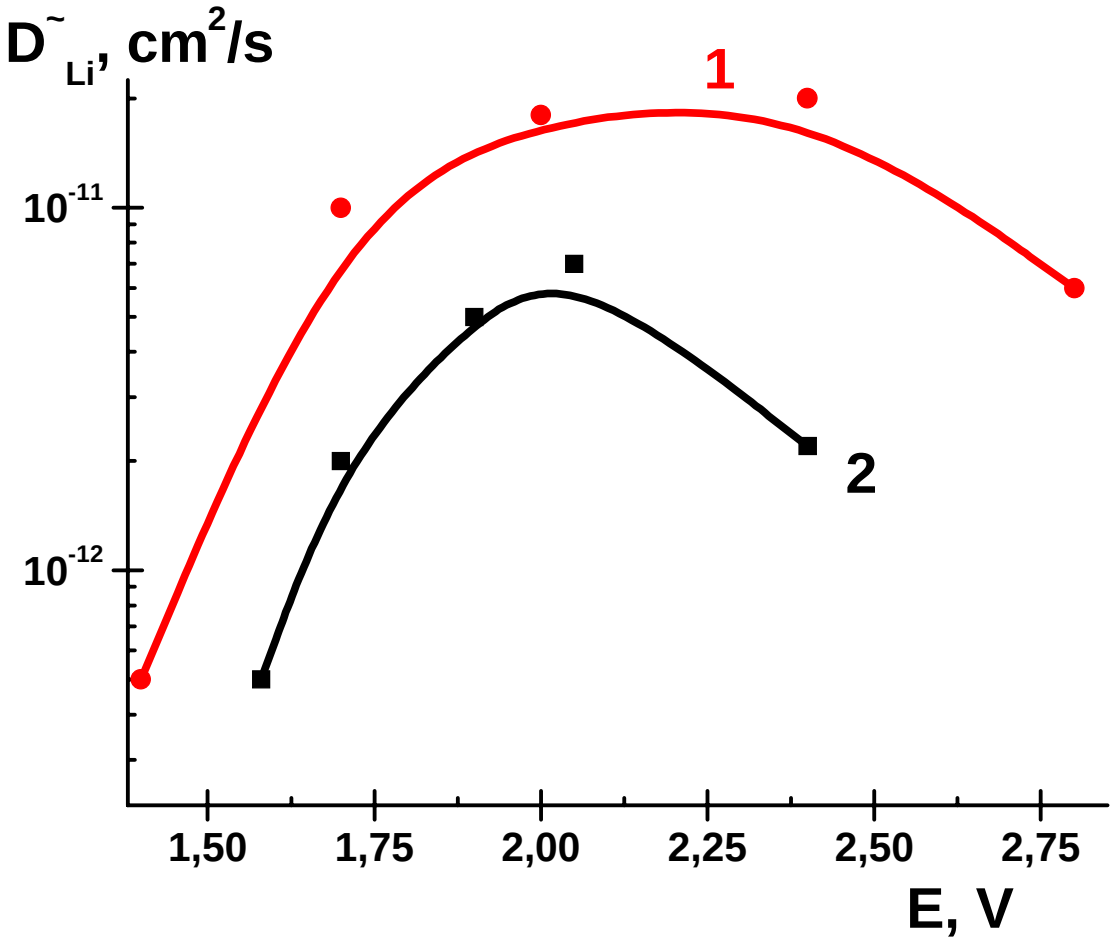

Fig.3.