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DIFFUSION OF Li^+ IN THIN FILM VANADIUM OXIDES FOR LITHIUM BATTERIES

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The values of the effective diffusion coefficient of the lithium ions (D_{Li}) obtained by PITT, GITT, network thermodynamics measurements and by the method of relaxation of potential upon interruption of current during discharge of electrolytic vanadium oxide ($e\text{-V}_2\text{O}_y$) are presented.

The electrochemical insertion of the Li^+ -ions during discharge in thin films of vanadium oxides V_2O_y is determined by their stoichiometry, thickness, structural and transport properties, the discharge rate and other factors. Among transport properties, the kinetic parameter – the effective diffusion coefficient of the lithium ions (D_{Li}) plays an important role among other factors in the electrochemical insertion of the Li^+ -ions during discharge in thin films of vanadium oxides.

We present the D_{Li} results obtained by PITT and GITT [1,2], network thermodynamics measurements [3] and using the method of relaxation of potential upon interruption of current [4] during discharge of $e\text{-V}_2\text{O}_y$ produced by electrolysis.

Experimental

The optimal conditions of electrolysis providing compact coatings of $e\text{-V}$ -oxides have been determined in [5]. The synthesis of $e\text{-V}_2\text{O}_y$ from vanadyl sulfate solutions (0.25 mol/l L) was performed on the anode of the electrolytic cell. The electrolysis of the aqueous solutions was provided in glass cells with a volume of 0.25 dm³. The parameters of the synthesis were as follows: anodic current density of 7.5–12.5 mA/cm², pH of 1.8 and a temperature of 80–85°C. Stainless steel plates were used as substrates for vanadium oxide precipitates. The deposits were treated at 180–500°C for different periods of time. The active mass of annealed electrodes was 0.8–4.0 mg/cm².

X-ray analysis of $e\text{-V}_2\text{O}_y$ was carried out on the device DRON-2 in Cu K_α -radiation.

$e\text{-V}_2\text{O}_y$ surface was investigated using Digital Instruments Nanoscope IIIa.

Electrochemical characteristics of $e\text{-V}_2\text{O}_y$ were determined in 3-electrode sealed cells with lithium counter electrode and a reference Li/Li^+ electrode on a test bench with computer control and regis-

tration. An electrolyte PC, DME, 1 M LiClO_4 containing not more than 100 ppm of water was used.

The effective diffusion coefficients of the lithium ions (D_{Li}) were obtained using an analytic radiometer VoltaLab PGZ 301.

Results and discussion

Stoichiometry of $e\text{-V}_2\text{O}_y$ is defined by the synthesis conditions and it varied from $y=4.3$ to $y=5.0$. Vanadium oxide deposits electrochemically synthesized and stored in the air exhibits a mixture of dispersed crystalline and amorphous phases of the general formula of $\text{V}_2\text{O}_y \cdot 0.9\text{H}_2\text{O}$ ($y=4.3\text{--}5.0$). A nonstoichiometric composition corresponding to $\text{VO}_{2.2}$ was obtained for V-oxide sample of the thermally treated (300°C, 2.5 h). At the more intensive thermal treatment (350°C, 5.5 h or 450°C, 1–3 h) V-oxide corresponds to the orthorhombic syngonia cell of V_2O_5 .

The morphology of the $e\text{-V}_2\text{O}_y$ deposits depends on their thermal treatment (Fig. 1, 2).

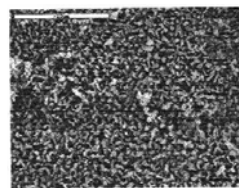


Fig. 1. $e\text{-V}_2\text{O}_y$ was treated at 500°C. (2 h)

Electrochemical characteristics of $e\text{-V}_2\text{O}_y$ depend also on its thermal treatment (Fig. 3).

GITT and PITT measurements of D_{Li}

We used a mathematical model of diffusion that does not include phase transitions in the electrode material in order to describe the discharge processes in $e\text{-V}_2\text{O}_y$ thin films and demonstrated that increasing the $e\text{-V}_2\text{O}_y$ film thickness up to 1.4 μ results

in the discharge capacity of 3.2 C/cm² at the current density of 20 mA/cm². It was found that the steady-state potential (both the theoretical value and that calculated from the experimental results) depends linearly on the Li-intercalation level in the range of 0.3–0.7 x (Li_xV₂O₅).

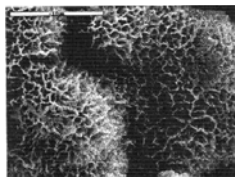


Fig. 2. e-V₂O₅ was not thermally treated

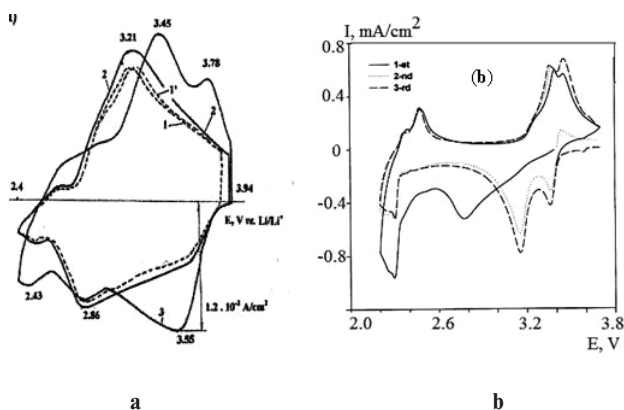


Fig. 3. a – Cyclic voltammograms measured from the cathode based on e-V₂O₅. Thermal treatment: (1) 18°C, 48 h; (2) 300°C, 2.5 h; (3) 300°C, 7.5 h. Electrode active mass 4.0 mg/cm². Electrolyte: PC, DME, LiClO₄; b – cyclic voltammograms obtained in EC, DMC, LiAsF₆ electrolyte solution with e-V₂O₅-cathode. Electrode active mass 1.0 mg/cm². Thermal treatment: 500°C, 2.5 h. Potential scan rate 0.5 mV/s

For the vanadium oxides annealed at 350–450°C, the dependence of D_{Li} vs. electrode potential (E) is non-linear and demonstrates extreme values, which tend to increase with the increasing the annealing temperature. The minimal values of the diffusion coefficient correspond to the peak currents registered from the slow rate cyclic voltammograms of the V₂O₅ electrode that may relate to the phase transitions in the oxide.

Fig. 4 demonstrates log D vs. E functional relationships obtained for vanadium oxide electrodes with a different thermal treatments. The value of D_{Li} remains almost constant (10⁻¹¹ cm²/s) in a 3.7–2.4 V potential range in the case of a thermally nontreated electrode (fig. 4,a). There is a pronounced decrease of the D_{Li} values up to 10⁻¹² cm²/s only at a discharge potential of 2.6 V.

D_{Li}-evolution for crystalline V₂O₅ becomes complex and has extremes (Fig. 4,c,d). D_{Li} values obtained by GITT and PITT measurements correspond well with each other (Fig. 4,b,c).

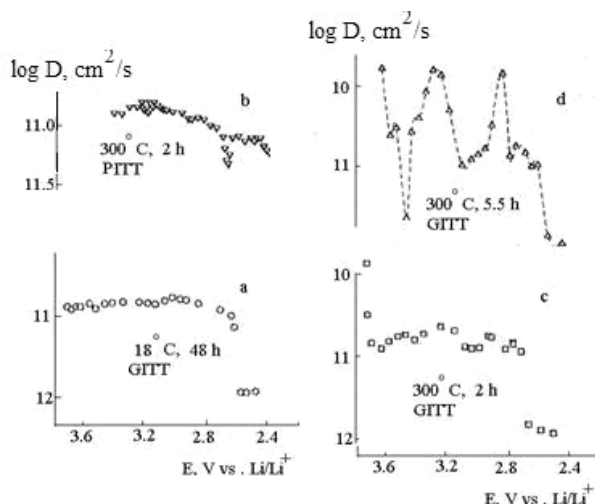


Fig. 4. log D vs. E functional relationships of e-V₂O₅ on dependence of thermal treatment

D_{Li} of the e-V₂O₅ obtained upon Interruption current

A mathematic diffusion model of Partly-Discharged Li_xV₂O₅ thin film electrodes upon Interruption current is put forward. The films were obtained by anodic deposition on 18Kh12N10T steel from 0.1 M vanadyl sulfate solutions with pH of 1.65 [5] and were dried for 2.5 h at 120°C. Fig. 5 shows schematically the sequence in which the experimental curves were measured.

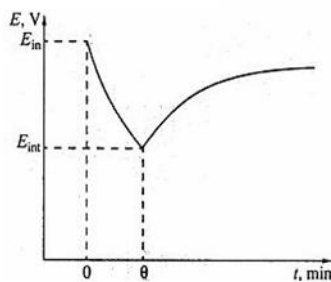


Fig. 5. Scheme of the OCP measurements for Partially-Discharged Li_xV₂O₅ electrodes

The electrode was discharged by applying a current (I) of 20 μA/cm² from the potential E_{in}, which corresponds to an equilibrium state, to a final potential E_{int}. Then the current was switched off and the potential transient was measured for 6 h. The potential growth rate upon interruption of the discharge current is proportional to the discharge current and inversely proportional to the film thickness (l):

$$\ln\left(\frac{dE_{t-\theta}}{dt}\right) = \ln\left(\frac{IV_M(-dE_{eq}/d\delta)}{FL}\right) - \frac{\pi^2 D}{L^2}(1-\theta), \quad (1)$$

V_M – molar volume of V_2O_5 (cm^3/mol), δ – film thickness, F – the Faraday constant, L – diffusion length, D – diffusion coefficient. According to (1), in the dE/dt vs. $(t-\theta)$ coordinates, we have a straight line, the slope of which allows the chemical diffusion coefficient of lithium ions to be calculated, and the intercept on the y-axis allows $dE_{oc}/d\delta$ to be assessed.

The mathematic model for the behavior of partly-discharged electrodes upon interruption of the current was tested on 1.5 μm -thick V_2O_5 films. Fig. 6 shows the dependence of OCP for such a film on the Li intercalation degree x . In the range of x values from 0.3 to 0.74, the potential decreases linearly. Fig. 7 exemplifies the experimental transients of OCP for different current-interruption potentials.

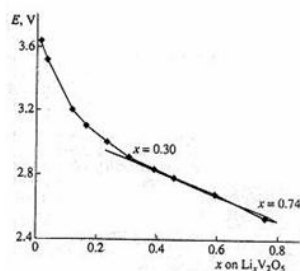


Fig. 6. The dependence of OCP for e- V_2O_5 film on the Li intercalation degree x

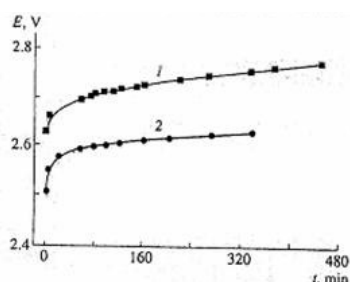
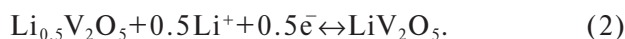


Fig. 7. Variations in OCP for an $Li_xV_2O_5$ electrode at current-interruption potentials (1) 2.63 and (2) 2.50 V

It is worth to note that the dependences of $\lg D_{Li} - E$ obtained for the Li-insertion in thin e- V_2O_5 films by PITT, GITT, and upon Interruption current coincide well with one another and are in agreement with those measured for the sputtered V_2O_5 [6]. We have established that D_{Li} varies from 10^{-10} to 10^{-12} cm^2/s in the potential range of 3.7–2.0 V for vanadium oxide film annealed at 300–450°C.

The method of the network thermodynamics

The method [3,7] was also used in this work to analyze diffusion coefficient of the Li^+ in the intercalation processes corresponding to the following phase transition $\epsilon \leftrightarrow \delta$ in V_2O_5 (2):



The method of the network thermodynamics is based on the mathematical model of diffusion of the Li^+ in electrode material using the diffusion

equation for one-dimensional system:

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

Equation (3), according to principles based on the network thermodynamics, may be transformed to the equation (4) [3]:

$$Z(t) = A1 \cdot \left\{ A0 \cdot t - 2 \cdot \sum_{k=1} \frac{1}{k^2} \exp[k^2 \cdot A0 \cdot t] \right\} + A2, \quad (4)$$

where

$$A0 = \frac{\pi^2 \cdot D_{Li^+}}{\delta^2}, \quad (5)$$

$$A1 = \frac{RT \cdot \delta}{(nF)^2 \cdot c \cdot D_{Li^+} \cdot \pi^2}, \quad (6)$$

$$A2 = R_f + A1 \cdot \frac{\pi^2}{3}, \quad (7)$$

k – quantity of the exponents in the equation (4); t – relaxation time, s; δ – thickness of the electrochemical active layer, cm; D_{Li} – diffusion coefficient of the Li^+ in the electrode structure, (cm^2/s); R – gas constant, 8.31 J/mol·K; T – temperature, K; n – number of electrons in the electrochemical process (2); R_f – resistance of the electrode, $\Omega \cdot cm^2$.

Equation (4) was used for approximation of the relaxation curves.

The description of research methods:

1. Method of current relaxation and transformation of this curve to relaxation of impedance during time.

2. Approximation of the relaxation curves according to the equation obtained on the basis of principles of the network thermodynamics. The goal of this approximation is determination of the variable factors ($A0$, $A1$ and $A2$) in the equation (4). A satisfactory approximation of the results can be obtained for $k=3$.

3. Calculation of the Li^+ diffusion coefficient into V_2O_5 electrode according to the equation (5).

The relaxation of the current in time (curve a) and the relaxation of the impedance of the electrode process (curve b) are shown in Fig. 8. The last curve was obtained as a result of the next following function:

$$Z(t) = \frac{\Delta E}{i(t)}, \quad (8)$$

where ΔE – step of the potential, V; i – current of relaxation, A/ cm^2 .

The example of the approximation result is shown in the Fig. 8, 9.

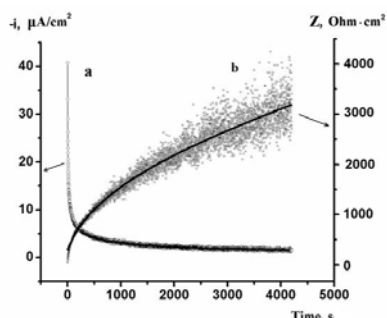


Fig. 8. Change of a current (a) and impedance (b) in time. Amplitude of the potential displacement is 5 mV

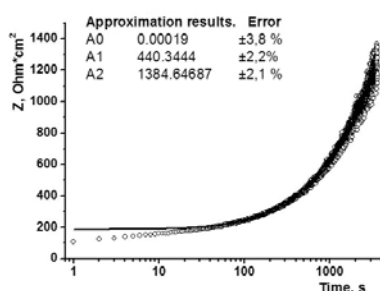


Fig. 9. Change of the impedance in time. Initial potential of V₂O₅-electrode is (curve b) transformed to the semi 3.20 V. logarithmic coordinate. k=3

Using these results for each potential of the e-V₂O₅ electrode with characteristics shown in Fig.10 the diffusion coefficients of the Li⁺ in the electrode material structure were calculated and are shown in the Fig. 11.

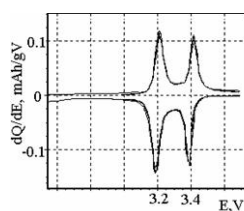


Fig. 10. Dependence of the differential capacity of e-V₂O₅-electrode on the electrode potential

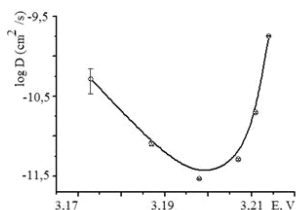


Fig. 11. The Li⁺ diffusion coefficient at various potentials of e-V₂O₅-electrode

Conclusion

It was shown that the effective diffusion coefficient of the lithium ions (D_{Li}) vs. E functional relationships depends on the thermal treatment of

the electrolytic vanadium oxide. The value of D_{Li} remains almost constant (10^{-11} cm²/s) in a 3.7–2.4 V potential range in the case of a thermally nontreated electrode. D_{Li} -evolution for crystalline V₂O₅ becomes complex and has extremes. D_{Li} varies from 10^{-10} to 10^{-12} cm²/s in the potential range of 3.7–2.0 V for vanadium oxide film annealed at 300–450°C. D_{Li} values obtained by GITT and PITT, and also using the network thermodynamics measurements and upon interruption of the current measurements correspond well with each other.

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The results of the effective diffusion coefficient of the lithium ions (D_{Li}) obtained by PITT, GITT, network thermodynamics measurements and relaxation of the potential upon interruption of current during discharge of electrolytic oxide vanadium (e-V₂O₅) are presented. It was shown that the effective diffusion coefficient of the lithium ions (D_{Li}) vs. E (V) functional relationships depends by thermal treatment of electrolytic vanadium oxide. The value of D_{Li} remains almost constant (10^{-11} cm²/s) in a 3.7–2.4 V potential range in the case of a thermally non-treated electrode. D_{Li} -evolution for

crystalline V_2O_5 becomes complex and has extremes. D_{Li} varies from 10^{-10} to 10^{-12} cm^2/s in the potential range of 3.7–2.0 V for vanadium oxide film annealed at 300–450°C. The minimal values of the diffusion coefficient correspond to the peak currents registered from the slow rate cyclic voltammograms of the V_2O_5 electrode that may relate to the phase transitions in the oxide. D_{Li} values obtained by GITT and PITT, network thermodynamics measurements and upon interruption of current measurements correspond well with each other.

Keywords: electrolytic vanadium oxide; diffusion coefficient; PITT; GITT; network thermodynamics methods; current interruption.

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