KINETIC PARAMETERS OF Li^+ INTERCALATION IN ELECTROLYTIC MOLYBDENUM OXYSULFIDES

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Introduction

Molybdenum oxysulfide compounds with the mass 1-3 mg/cm^2 have been produced on a conducting substrate by the cathodic reduction of molybdate water electrolytes comprising thiosulfate ions. In investigations of physical and chemical, structural and electrochemical properties of electrolytic molybdenum oxysulfides (e-Mo, S) it is shown the prospects of the synthesized film compounds use in the electrodes of thin layer lithium battery models [2, 3]. Investigation of the mechanism of electrochemical reaction, determination of the factors limiting its efficiency at the individual stages help a purposeful optimization of the process at a technological level, to search the ways of chemical power source serviceability improvement. In electrochemical energy generator with a solid-phase cathode material diffusion component is mostly the limiting stage of a total electrode reaction. In the cathodes of lithium chemical power sources (CPS), it is the stage determining lithium ion transport in a solid state. In the work, the authors' efforts are directed to investigation of the electrode kinetics of (e-Mo, S)/electrolyte system aimed at understanding the cause of lithium battery degradation on its base.

Experimental

Modification of the molybdenum oxysulfide synthesis technology [4] is realized by substitution of stabilizing nickel ion in deposition electrolyte by cobalt ion. In this case thin-layer deposits of molybdenum oxysulfides were obtained on the 10 μm thickness aluminum foil subjected by special preliminary treatment. Active material mass was 3-20 mg/cm^2.

Charge-discharge cycling of electrolytic molybdenum oxysulfides in the model of lithium chemical power sources with polymer electrolyte based on the co-polymer of vinylidene fluoride PVdF-CTFE (314508/1001 Solvay), (EC-ethylene carbonate, DMC-dimethyl carbonate, Merck), 0.5M $LiClO_4$ and with liquid electrolyte (EC, DMC, 1M $LiClO_4$) was carried out under the galvanostatic and potentiodynamic conditions, using the test stand with computing programming. Impedance spectra (IS) of the quasi-stationary systems (e-

Mo, S)/electrolyte/Li and (e-Mo, S)/electrolyte/e-Mo, were taken with the help of radiometer VoltaLab PJZ 301 by method [2].

Results and Discussion

From the cycling voltammograms, the values of the most important parameter of electrode kinetic–lithium ion chemical diffusion coefficient ($\tilde{D}_{\mathrm{Li}}$) for the processes of intercalation and deintercalation in molybdenum oxysulfide for liquid-phase electrolyte CPS [3] have been obtained. At the potentials of peak currents on voltam-mograms the $\tilde{D}_{\mathrm{Li}}$ coefficient values are equal to $2.07.10^{-11}$.and $1.07.10^{-11}$ cm^2/s for discharge and charge, respectively. Estimation of the kinetic of lithium ion transference in cathode-anode process (e-Mo, S)/electrolyte, carried out in the work on the values $\tilde{D}_{\mathrm{Li}}$ by the method of potential relaxation [5] and impedance spectroscopy, is presented below:

***Table 1** Dependence of Li on the potential of e-Mo, S-electrode for liquid electrolyte, obtained by the method of potential relaxation after current switchig off.*

$E_{\mathrm{switch \cdot off}}$, V	1.790	1.595	1.389	1.200	1.095
$\tilde{D}_{\mathrm{Li}}*10^{11}$, $cm^2.s^{-1}$	1.44	0.58	6.17	5.83	4.46

Within the potential range 1.790 - 1.095 V change of Li occurs nonlinearly. The least Li value coincides with the potential of horizontal plateau of galvanostatic curves - near 1.600 V. The Li values, established by the relaxation method of open circuit voltage coincide in the order of magnitude with those determined by the method of cycling voltammetry, but differing from the values determined by the method of impedance spectroscopy. Thus, the Li value for the system (e-Mo, S)/electrolyte with the potential 1.30 B in accordance with the impedance method are equal to $3.9.10^{-12}$, cm^2/s – in liquid, and 6.2.10-13 cm^2/s – in gel polymer electrolytes, respectively.

At comparison of the kinetic parameters of electrolytic molybdenum oxides [6] and their difference is also noticeable depending on the investigation method. Thus, Li values obtained by the method of cycling voltammetry for electrolytic oxysulfides are less than for the electrolytic molybdenum oxides, whereas, the data obtained by the method of potential relaxation at switched off current have opposite regularity.

Values of the kinetic parameter i_0 (exchange current of the process of charge transference through the e-Mo, S electrode /electrolyte interface) is the function of temperature (Fig.1) and electrolyte composition in lithium CPS. The preferred electrochemical reaction, in this case, in lithium CPS (1):

$$Mo_2S_3 + x\bar{e} + xLi \rightarrow Li_x\,Mo_2S_3 \qquad (1)$$

Since, the exchange current of intercalation systems is the function of intercalation degree, in the work on the basis of impedance spectra it has been carried out the calculation of standard rate constant of the heterogeneous reaction Ks, which was determined at a standard potential (x=0.5). Ks is 6.2.10^{-9} and 3.0.10^{-8} cm/s in polymer and liquid-phase electrolytes, respectively, for $LixMo_4O_{11}$ and 0.9.10^{-7} cm/s for molybdenum oxysulfide in liquid-phase electrolyte.

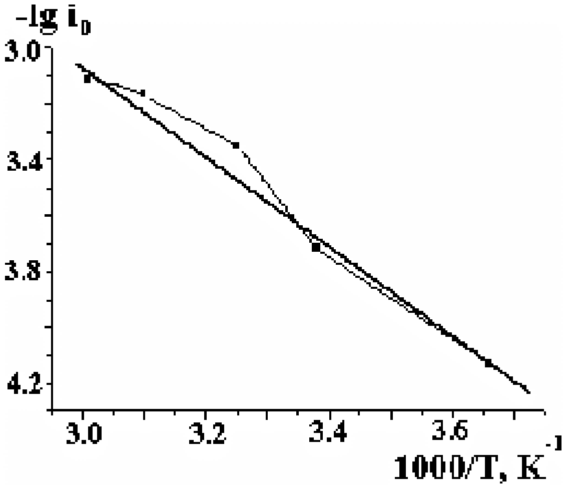

Fig. 1 *Influence of temperature on i_0 of Li^+ transference through the interface e-Mo,S/EC, DMC, 1M $LiClO_4$.E_0 = 1.32 V.*

Activation energy of charge transference through the interface e-Mo, S/liquid electrolyte is 38.8 kJ/mol, activation energy of ion electromigration in liquid-phase electrolyte is 13.76 kJ/mol.

At investigation of discharge-charge cycling of lithium electrode in the system e-Mo, S/EC, DMC, 1M LiClO4/Li it is shown that it does not complicate obtaining satisfactory discharge characteristics of electrochemical system. Electrochemical properties of the system are determined by the properties of e-Mo, S-electrode. Besides, after cycling the system e-Mo, S/gel polymer electrolyte/Li in the model of film battery, by the data of impedance spectroscopy during more than 50 cycles electrolyte resistance increased from 12 Ώ.cm^2 up to 260 Ώ.cm^2.

Conclusion

The Li values of (e-Mo, S)/electrolyte interface change with potential changing in a series of 10^{-11}–10^{-13} cm^2/s and depend on the used investigation method. Difference in Li values determined by the different methods can be connected with both the nature of investigated objects differing in non-identified characteristics and with the imperfection effect of investigation methods and models. Decreasing discharge capacity at cycling the system e-Mo,S/gel polymer electrolyte /Li is determined by the cathode material properties, and to a considerable degree, depends on the electrochemical instability of the polymer electrolyte based on PVdF-CTFE.

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