

THIN LAYER ELECTROLYTIC MOLYBDENUM OXYSULFIDES FOR LITHIUM SECONDARY BATTERIES WITH LIQUID AND POLYMER ELECTROLYTES

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Introduction

Films of transient metal oxides and sulfides are widely used in electrochromic equipment and other electronic hardware components. Nanosize film formations are synthesized by the different methods, and the technologically simple method of electrodeposition is among them. Electrolytic (e) synthesis is attractive in terms of the possibility to control easily the properties of final products. For efficient use of electrolytic films in lithium thin layer secondary batteries the mass of active product in a film should be increased up to $\geq 10 \text{ mg.cm}^{-2}$. Usually, with increasing the mass of electrolytic deposit its adhesion to a substrate decreases as, for example, in the case of electrodeposited molybdenum sulfide [1] and oxysulfides [2] which are efficient only in nanolayers. Electrolytic non-stoichiometric molybdenum oxides were synthesized by us in the compact layers with the mass of $1 - 3 \text{ mg.cm}^{-2}$ [3] and the processes of lithium ion transport at electrochemical intercalation / deintercalation have been investigated in them [4]. For realization of the films of e-Mo-oxides in thin layer secondary batteries the further efforts for film thickness optimization are undertaken.

Recently, the authors of the work have synthesized the films of Fe,S-comprising compounds doped by the metals (Me=Ni,Cu.Mo) in electrodeposition process [5]. These films are successfully approbated in the models of thin layer lithium secondary batteries. In the work the investigations of thin layer electrolytic molybdenum oxysulfides doped by nickel [6] were continued as applied to lithium secondary batteries with liquid and polymer electrolytes.

Experimental

Electrolytic deposits were produced on the internal bottom surface of the stainless steel case of the 2325 size cell or the stainless steel plate by the cathodic reduction of mixed water solutions of sodium molybdate and nickel sulfate in the presence of sodium thiosulfate [6]. The synthesis of molybdenum oxysulfides was performed in glass cells with a volume of 0.25 dm^3 at $80 - 85^\circ \text{C}$. For cathode and anode stainless steel plates were used with the area ratio $S_{\text{cathode}} : S_{\text{anode}} = 1 : 5$. It has been used the solution, g.l⁻¹: $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} - 10$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} - 5$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} - 2.5$, $\text{pH} = 5.0 - 6.0$. Cathode current density was $i_{\text{cathode}} = 3.5 - 7.7 \text{ mA.cm}^{-2}$. Deposits of e-Mo-oxysulfides were produced both as a disperse powder and a compact film. They were treated at 180°C (7h).

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Investigations of e-Mo-oxysulfides were carried out by X-ray diffraction analysis, in AFM. Electrochemical characteristics were determined in the coin-type 2325 size batteries with lithium anodes and in 3-electrode sealed cells with an auxiliary lithium electrode and a reference Li/Li⁺ electrode. The electrolyte PC+DME+1M LiClO₄ containing not more than 100 ppm water was used. Polymer electrolyte PVdF-CTFE (31508/1001 Solvay), (EC, DMC, Merk) 1M (LiPF₆, Merk) have been used in the batteries with ballast-free electrodes (mass=1 - 3 mg.cm⁻²). Polymer films were formed on a glass sheet from polymer and DMF (Angarsk Chemical Reagents Plant, Russia) solution and then were activated in the solution comprising EC, DMC, 1M LiPF₆. The charge/discharge characteristics were plotted on a test bench with computer control and registration.

Results and Discussion

Changing the ratio of the electrolyte components (Mo:Ni:S) and intensity of heat effect on the produced deposits in the latter, the compositions providing availability of the components from a series of Mo₄O₁₁, Mo₉O₂₆, Mo₈O₂₃, Mo₁₇O₄₇, MoO₃, NiO, Mo₃S₂, MoS₂, Mo₃S₄ or Ni₃S₂, Ni₃S₂ have been formed. At the increased content of thiosulfate in electrolyte biphasic oxide, sulfide compounds of NiMoO₄, NiMo₂S₄ can be formed. Under optimal conditions the oxide phase of molybdenum (88-95%) is the quantitatively prevailing one in the deposits. Content of molybdenum sulfide MoS₂ can range from 0.5 to 9 mass % in this case.

Mo₄O₁₁, MoS₂ with NiO admixture composition (*K*) has been investigated in the deposits of 3-10 mg.cm⁻² mass using Atomic Force Microscope (AFM) and profilometrically. Black-brown deposit of *K* was uniformly distributed on a substrate surface, degree of deposit surface roughness is 43 nm. Deposit grains have not well defined cut but have a typical form. Apparent density of deposit is 4.17 g.cm⁻³.

Discharge capacity of *K* thin layer in the model of lithium chemical power source in the first cycle is 537 mAh.g⁻¹, the reversible one is 183 mAh.g⁻¹ (the 39th cycle) under the following conditions: active component mass is 2.0 mg.cm⁻², $I_{\text{charge}}=0.03 \text{ mA.cm}^{-2}$, $I_{\text{discharge}} = 0.05 \text{ mA.cm}^{-2}$, the cycling voltage range is 3.5 - 0.9 V, electrolyte composition: PC, DME, 1M LiClO₄. Application of the 5-6 μm film of polymer electrolyte (PE) based on PVdF-HFP Solef[®] 21508 (Solvay), PC, 1M LiClO₄ on the cathode material promotes cycling efficiency. Discharge / charge curves of Mo-oxysulfides / polymer electrolyte / Li system are shown in Fig. 1. Change of discharge capacity during 20 cycles is given in Fig. 2 for Mo-oxysulfide system containing Mo₄O₁₁, Mo₃S₂, Ni₃S₂.

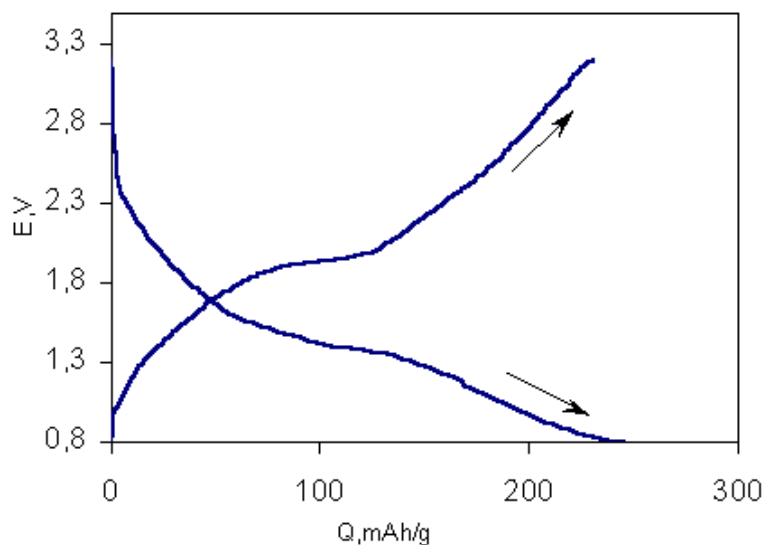


Fig. 1 Discharge/charge profile of Mo-oxysulfide / PE / Li system, $I(\text{discharge}) = 25 \text{ mA.g}^{-1}$, $I(\text{charge}) = 15 \text{ mA.g}^{-1}$, Mo-oxysulfide mass 2 mg.cm^{-2} .

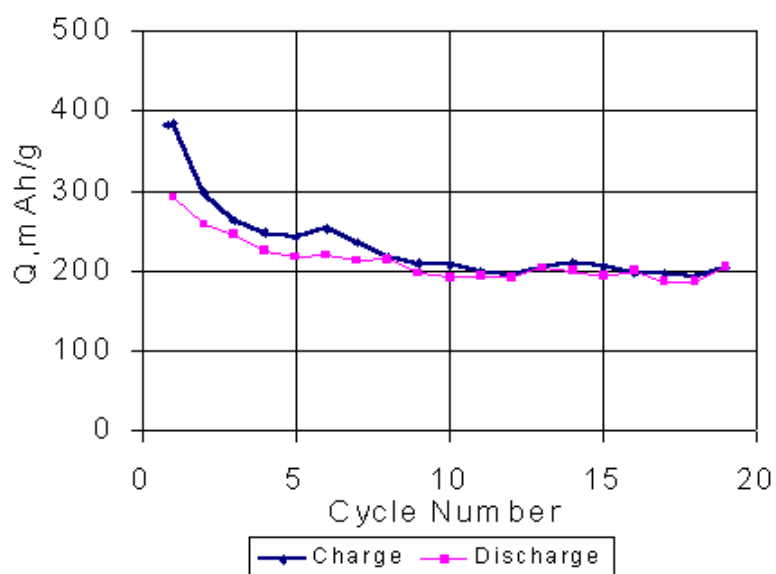


Fig. 2 Charge and discharge capacity of Mo-oxysulfide/PE/Li at cycling

Availability of horizontally sloped plateau on the discharge/charge curves near 1.4 V is the advantage of Mo- oxysulfides, thermal treated at 180 °C as compared with the analogous Mo-oxides. Monotonous voltage change in the range 2.8 - 1.1 V is the characteristic feature of non-stoichiometric molybdenum oxides ($T_{\text{treat.}} = 180^\circ\text{C}$).

Polymer electrolyte in lithium chemical power source promotes adhesion increase of thin-layer Mo-oxysulfide to a substrate, on which it has been deposited. In its turn, this promotes increasing cycling efficiency of Mo-oxysulfide.

Conclusions

In the work it is shown the possibility of the electrolytic production of thin layer ballast-free molybdenum oxysulfide-based electrodes for rechargeable lithium power sources with polymer electrolyte. The synthesized materials are promising for film lithium rechargeable batteries, which are in a great demand.

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