

Kinetics of the Relaxation Redox Processes on Nano-FeS₂ in Polymer Electrolytes

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The paper is related to a cycle of works, which are developed by the authors and aimed at the design of high-energy secondary lithium battery based on Li-FeS₂ system. The investigations carried out earlier [1-2] have shown that while using non-aqueous polymer electrolyte based on modified polyvinyl chloride the system with FeS₂-based cathode can be efficiently cycled at room temperature. The system is especially promising by using synthesized nano-FeS₂, which is characterized by the increased electrochemical activity. Cathodic reduction of FeS₂ from non-aqueous electrolyte is a multistage process where consecutive-parallel electrochemical and chemical reactions occur.

For optimization of the system characteristics it has been carried out a complex of investigations concerning the reduction process and cycling efficiency effected by the following factors:

- FeS₂ structure (synthesized nano-FeS₂ and natural pyrite)
- Macrostructure of porous electrode
- Composition of polymer electrolyte (nature of polymer matrix, lithium salt LiClO₄, LiPF₆, LiBF₄, LiSO₃CF₃, plasticizer – PC, EC, DMC, DME).

In the investigations there were used: a) 100-130 μm composite cathode, comprising iron disulfide (10, 30 or 80%), conducting additive (black, graphite) and a binder; b) cathodes with a thickness up to 30 μm, comprising only iron disulfide and a binder.

The investigations were carried out by using XRD analysis, ESM, IR spectroscopy, pulse chronoamperometry, impedance spectroscopy, cycling chronovoltammetry, standard porometry. Depending on FeS₂ nature and electrolyte composition the process is limited by the electrochemical stage of a charge transfer at the electrode/electrolyte interface or by the diffusive transfer of lithium cations in a volume of the solid phase of iron disulfide. The constants of electrochemical reaction and diffusion coefficient of lithium in a solid phase of cathode material have been determined at the different stages of discharge/charge processes. Transient process at the electrode/electrolyte interface to a great extent depends on solvation interaction between lithium cations and electrolyte components.

Tests of the actual samples of secondary battery Li-FeS₂ have shown a high serviceability and cycling efficiency of the system at room temperature.

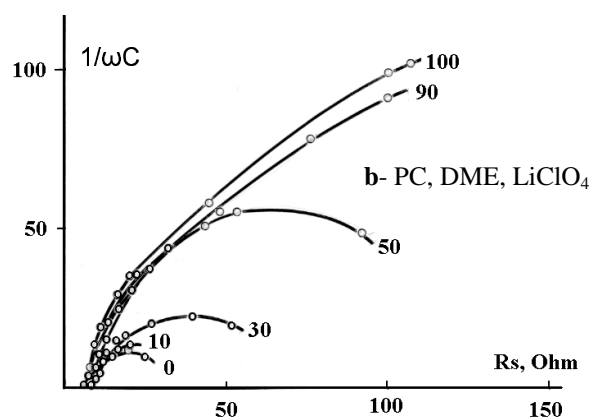
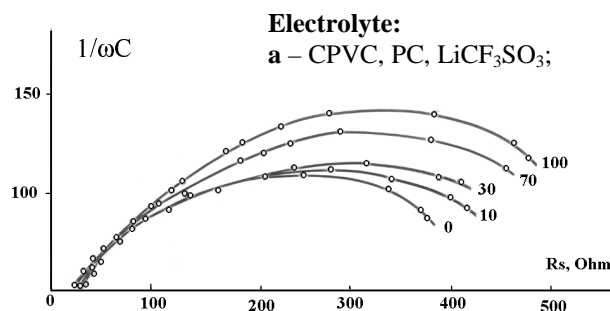
References.

[1] E.Shembel, P.Novak et al. Determination of the Diffusion Lithium Battery Discussion: Electrode Materials, Bordeaux – Arcachon, France, May 27 - June 1, 2001.

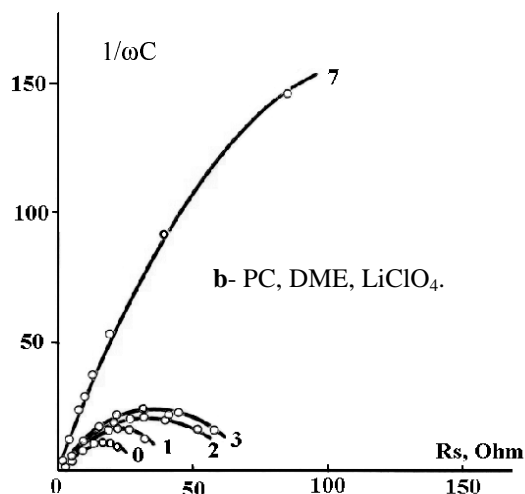
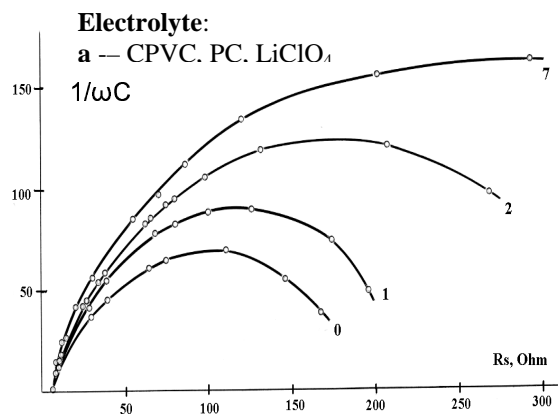
[2] E.Shembel, P.Novak et al. 200th Meeting of The Electrochemical Society, San Francisco, California, USA, September 2-7, 2001.

The impedance hodographs of the cell of Li-FeS₂ system (2325 size)

Cathode comprises 10% pyrite



During a discharge. Discharge current - 100 μA.; Labels on curves correspond to a discharge degree (%) of the cell. Natural pyrite



During a storage. Labels on curves correspond to a storage time of the cell (days). Synthesized pyrite