

INVESTIGATION OF LITHIUM ION MASS TRANSFER IN A SOLID PHASE OF THE CATHODE MATERIALS OF LITHIUM POWER SOURCES

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Specific energy characteristics and the rate of charge/discharge processes of lithium secondary batteries to a great extent is limited by the diffusion transfer of lithium ions through the volume of the solid phase of electrode during intercalation/deintercalation process. Under the actual operational conditions of solid-phase oxidant lithium diffusion coefficient depends on the chemical composition of solid phase, its structure and can range within $10^{-9} \div 10^{-12} \text{ cm}^2 \text{ c}^{-1}$.

In this work a diffusion transfer was investigated by using the mathematical model describing the diffusion transfer for the case of phase composition effect and at approximation of unavailability of this influence.

Electrochemical characteristics of the system were investigated in a discharge/charge process and during relaxation after current disconnection. Investigations were carried out with the cathode materials based on $\text{Li}_x\text{V}_2\text{O}_5$, FeS_2 , LiCoO_2 and anode materials based on different graphite modifications. Liquid and polymer nonaqueous systems based on aprotic solvents were used.

Different types of electrodes, such as electrochemically synthesized layers without conducting additive and a binder; layers of active material, deposited on a substrate by thermal, vacuum or magnetron spraying; standard porous electrodes based on active substance, conducting additive and a binder.

At the investigation the following electrochemical methods were used: cyclic voltammetry, galvanostatic cycling, electrochemical impedance spectroscopy, and others. Transient technique for the determination of diffusion coefficient (D_{Li^+}) of lithium in cathode materials was also applied. Chronoamperometry, (CV) with the quick step change of potential and the analysis of current response of a system allowed to determine a limiting stage.

As the limiting stage can be:

- surface process of lithium intercalation into thin surface layer of a particle. It depends on the aprotic solvent/cathode material interface. The analysis of this process was carried out on a Cottrell section commonly presented as Q vs. $t^{0.5}$ plot (Anson plot);
- lithium diffusion into the particle depends on the structure, production method of cathode material. The analysis was carried out with the longer periods of the current response in the investigated system.

The determination method of lithium coefficient together with impedance measurements was used for the analysis of cathode materials based on $\text{Li}_x\text{V}_2\text{O}_5$, LiCoO_5 , FeS_2 and graphite depending on the synthesis method of material and the degree of discharge.