

IMPEDANCE INVESTIGATION OF ELECTROLYTIC IRON OXYSULFIDES FOR LITHIUM SECONDARY BATTERIES WITH POLYMER ELECTROLYTES

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Introduction

Electrolytic iron oxysulfides (e-Fe,S) are promising cathodic materials for film lithium secondary batteries [1]. Being produced on electron-conducting substrate in the thin layers with the mass 1-10 mg/cm² they are the attractive objects for electrode kinetics investigation. Electrochemical impedance spectroscopy [2,3] is the effective instrumental means of kinetic investigations. Determination of correlation between the behavior of actual system and ideal model, search of the analogy between discrete elements of equivalent circuit and electrochemical process is one of the aspects of impedance spectroscopy. Macroscopic parameters of the electrode/electrolyte system promoting search of the ways enhancing efficiency of electrochemical energy conversion in lithium secondary batteries can be determined by the analysis of impedance response parameters of the investigated system and equivalent circuit. Impedance theoretically grounded spectroscopy

is, as a rule, applied for the analysis of stationary or quasi-stationary systems. In dynamic impedance, it is more complicated for analyzing the results, but more rapid for experimentation.

In the work, in the search of the analogy, the data of impedance spectroscopy of quasi-stationary and non-stationary (in discharge/charge processes) system (e-Fe,S)/electrolyte/Li were compared.

Experimental

Electrolytic iron oxysulfides were produced from Fe(II)-sulfate water solutions in the presence of thiosulfate-ion by cathodic reduction on the substrate of aluminum foil or stainless steel grid, as in

[1]. Active material mass was 3-11 mg/cm².

Discharge- charge cycling of electrolytic iron 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 LiClO₄, was carried out under the galvanostatic conditions, using the test stand with computing programming .

Impedance spectra (IS) of the quasi-stationary systems (e-Fe, S)/electrolyte/Li and (e-Fe,S)/electrolyte/ (e-Fe,S) were taken with the help of radiometer VoltaLab PJZ 301.

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Impedance response of the systems with the different dischargeness/chargeness degree of e-Fe, S to the electrical signal with 10 mV amplitude was measured automatically in the frequency range 100 kHz – 4 mHz after 15 - hour interval at current unavailability. The programs Zplot, ZView (Version 2.1 b) were used for registration and fitting the spectra.

To obtain IS of the quasi-stationary system (e-Fe, S) - electrode /gel electrolyte, the 4-electrode

model Li-(e-Fe, S) – (e-Fe,S) -Li was used.

Electrodes are placed in hermetically sealed insulated film bag of laminated aluminum foil. Two similar measuring electrodes e-Fe,S, which alternative geometrical area is 1x1 (cm), are the (e-Fe, S) – material with the mass 1.5-3.0 mg/cm², deposited on a stainless steel grid by cathodic reduction of the water solution of transient metal (Me=Fe) salt with thiosulfate ion admixture [1]. Auxiliary Li-electrodes with the size of 1x1x 0.01 (cm) are on the both side of the investigated working (e-Fe, S) electrodes. They are used for polarization of investigated measuring electrodes aimed at the achievement of a certain lithiation degree. Application of gauze thin-layer working electrodes enables their uniform polarization. In the model of chemical power sources, electrodes are separated by the 100-300 μ m layer of gel polymer electrolyte. After discharge/charge before the impedance measurement there was 15- hour non-current condition, during which the investigated system approaches to equilibrium. During the interval, the electrodes (e-Fe,S) were electrically connected to reach equipotentiality.

Essence of the proposed dynamic impedance pulse method comes to the following. Impedance response of the system (e-Fe,S) /electrolyte/Li was registered in the discharge/charge process. For charge-discharge cycling we used the test stand with a computer control, similar to that described in [4]. The parameters enabling periodic changing of current in the model of chemical power source have been introduced into the program of stand control. Summed current is composed of a direct current (charging/discharging) and alternating current ($\gamma \sim 200$ -250 Hz). During superposition of the alternating current component (duration less than 0.1 s, periodicity is 9 s), the internal resistance of chemical power source was measured. The value of alternative current potential component determined by the potential deviation relative to its level at direct current did not exceed 50 mV. Shape of a pulse current (200-250 Hz) approaches to rectangular one. Alternative current of the half - less value frequency (125 Hz) is similarly imposed. Active impedance component was evaluated by the value of internal resistance, established at two frequencies, with the help of the equivalent circuit from the series connected resistor and capacitor. IS of the model of lithium chemical power source e-Fe, S /(electrolyte)/ Li, obtained by the traditional method of electrochemical ac IS for the equilibrium and quasi-equilibrium systems was compared with the established pulse dynamic method in discharging-charging process.

Results and Discussion

Reversible capacity of “thin” e-Fe, S (1-3 mg/cm²) in lithium secondary batteries is more than 200 mAh /g [1]. By the data of X-ray pattern analysis, electrolytic e-Fe, S is a mixture of preferable disulfide FeS₂ (pyrite) with the admixture of non –stoichiometric iron oxide Fe₂O₃. Change of discharging-charging profile of e-Fe, S in the model of e-Fe, S /(electrolyte)/Li, where the mass of active cathode material is equal to 11.2 mg/cm², is

shown in Fig.1. Discharge capacity of such a model with the comparatively “thick” cathode drops from a cycle to cycle, stabilizing on the 35th – 40th cycle on the level of 220-240 mAh/g. IS were taken at the different values of OCV (V) ranging from 2.8 up to 1.1 V after stabilization of discharge capacity. ac IS of the models e-Fe, S / (electrolyte)/Li is a depressed semi-circular arc at the high-mid-frequencies, and a diffusion tail at low frequencies.

Change of internal resistance and the active component of the resistance of non-equilibrium system e-Mo, S/ electrolyte/Li during discharging/charging is shown in Fig 2,a (the 10th cycle). General tendency in changing the impedance of quasi-stationary and non-stationary system e-Fe, S/ electrolyte/Li depending on a discharge degree is observed. Within the range 1.90-1.55 V the impedance corresponds to the least value, its subsequent non-linear growth occurs from 1.55 up to 1.1 V. Impedance of the discharged system is 3-4 times greater than with charged one. At the small charge/discharge rates ($30-50 \mu\text{A}/\text{cm}^2$), the absolute values of impedance differ slightly on those for quasi-stationary system. At increasing the rate of electrochemical intercalation ($200 \mu\text{A}/\text{cm}^2$), the tendency of impedance change with the potential of quasi-stationary and non-stationary system remains. However, in this case the absolute values of non-stationary impedance exceeds significantly that of quasi-stationary one.

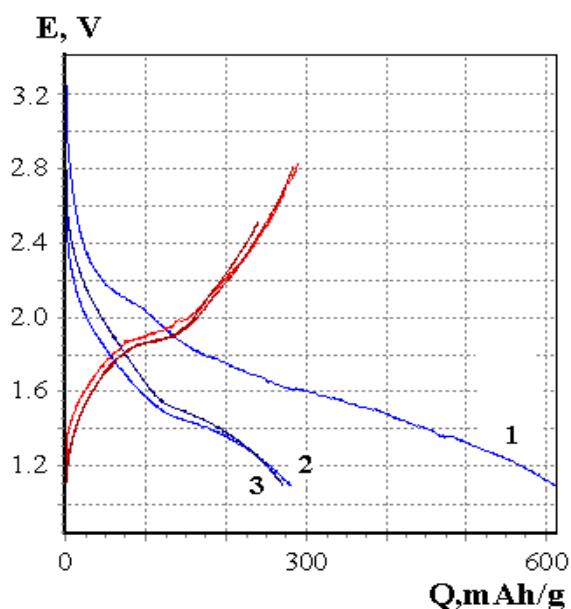


Fig. 1 Discharge/charge profile of Fe-oxysulfide/electrolyte/Li system. $I_{\text{charge}}=0.03 \text{ mA.cm}^{-2}$, $I_{\text{discharge}}=0.05 \text{ mA.cm}^{-2}$, Fe-oxysulfide mass is 11.2 mg.

After long cycling impedance of the model determined by the dynamic method (Fig2,b) as by ac IS method increases so that the impedance of discharged and charged models becomes practically the same.

Impedance of the quasi-equilibrium system e-Fe, S/ electrolyte at the frequency 200 Hz changes depending on the intercalation degree analogously to the model e-Fe, S/ electrolyte /Li, increasing as e-Fe,S lithiation occurs. The process is reversible: impedance decreases during deintercalation process. In Fig. 3 it is shown the impedance spectrum of the quasi-equilibrium system e-Fe, S / electrolyte together with the equivalent system, its

parameters and model impedance spectrum, when e-Fe, S potential against Li/Li⁺ is equal to 1.94 V.

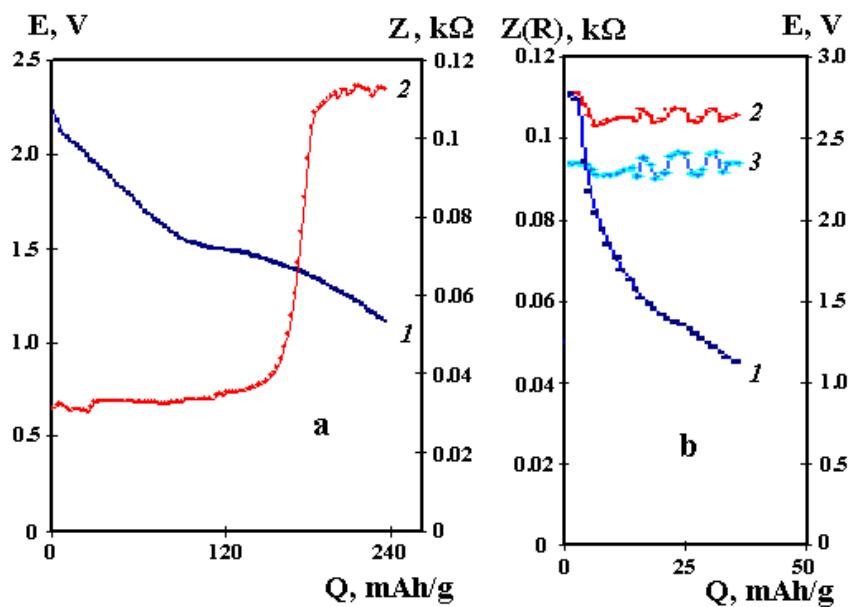
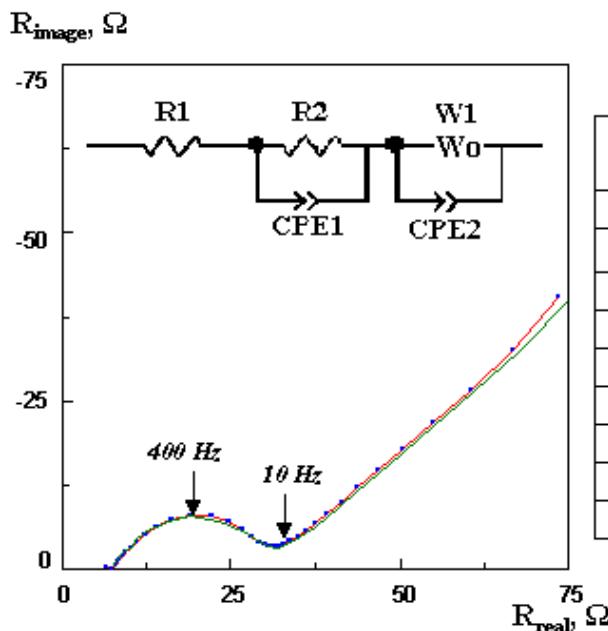


Fig. 2 Discharge profile (1), change of internal resistance Z (2) and the active component R (3) for e-Fe, S/ electrolyte /Li model. a- the 10th cycle, b –the 160th cycle. $I_{\text{disch}}=0.05 \text{ mA/cm}^2$.



Circuit element	Value	Error, %
R_1	7.308	1.41
R_2	23	1.88
CPE_1-T	$1.81 \cdot 10^{-4}$	2.03
CPE_1-P	0.7	1.27
W_1-R	0.08	9.6
W_1-T	0.00012	1.24
W_1-P	1.026	1.08
CPE_2-T	0.057	1.45
CPE_2-P	0.453	1.45

Fig. 3 Impedance spectrum of e-Fe,S (gauze electrode, $S=1.2 \text{ cm}^2$, $m=1.5 \text{ mg}$)/electrolyte/e-Fe,S (gauze electrode, $S=1.2 \text{ cm}^2$, $m=1.45 \text{ mg}$) and analogue spectrum corresponding to the equivalent circuit: $E_0=1.94 \text{ V}$ (frequency range is 100 kHz – 4 mHz). The 10th cycle.

Analysis of the results obtained allows to consider, that at the beginning of cycling the model e-Fe, S/ electrolyte/Li the limitations of the electrochemical energy conversion are determined by the intercalation/deintercalation process of lithium ions in e-Fe, S. At long cycling, increase of gel electrolyte resistance indicating its electrochemical instability, effects on the electrochemical parameters of investigated system. Increase of surface film formation impedance on lithium electrode during storage in a gel electrolyte testifies to lithium incompatibility with the used electrolyte based on PVdF-CTFE (31508/1001 Solvay), EC, DMC, 0.5M LiClO₄.

Satisfactory analogy of the results of IS quasi-stationary and non-stationary (discharge/charge by the small currents 30-50 μ A/cm²) system is the argument in the favor of the further development of the proposed dynamic impedance method for electrochemical investigations in lithium secondary batteries.

Acknowledgements

The authors acknowledge with thanks the financial support provided by the Ministry of Education and Science of Ukraine (Contract 42020290) and by Ener1 CRDF (Contract # USO-1207).

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