POLYMER ELECTROLYTES FOR LITHIUM POWER SOURCES BASED ON METAL DISULFIDES

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Selection of electrolyte system is one of the key problems which should be solved by researchers at the development of highly efficient Li-FeS_2 power source. During operation of liquid electrolytes in rechargeable systems the problems caused by destruction of aprotic solvents (PC, EC, etc) in the presence of the products of iron disulfide oxidation-reduction arise [1, 2]. Earlier, we showed the principle possibility to use plasticized polymer electrolytes based on chlorinated PVC in the composition of rechargeable Li-FeS_2 power sources operational at room temperature [3].

In the work the results concerning development of highly efficient rechargeable Li-FeS_2 power source with polymer electrolyte based on the co-polymer vinylidenfluoride and hexafluorpropylene are presented. In this case the main attention was paid to:

- optimization of the composition of plasticizing system;
- selection of lithium salts;
- optimization of the composition of cathode material based on natural pyrite;
- search of highly efficient modifying additive in polymer electrolytes.

To optimize the composition of plasticizing system by the method of potentiodynamic cycling, the charge/discharge characteristics of the cathodes based on natural pyrite in the presence of liquid systems based on lithium salt solutions in the mixtures of aprotic solvents. In Fig. 1 the investigation results are given.

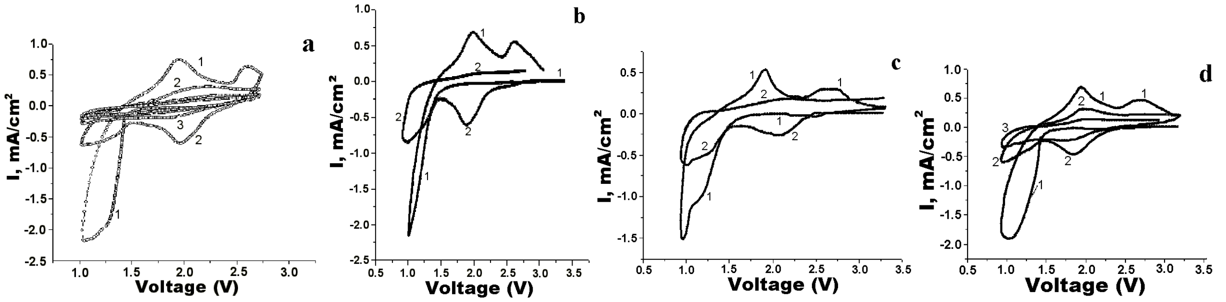


Fig.1 *Potentiodynamic characteristics of cathode based on natural FeS_2 (in cathode mass – 30% FeS_2) in liquid electrolyte:*
a – PC/1,4-Dioxolane/M $LiAsF_6$; *b – PC/Dimethylacetamide/1M $LiAsF_6$;*
c – PC/DME/1M $LiClO_4$; *d – PC/1,4-Dioxolane/0.5M $LiN(SO_2CF_3)_2$.*
Scan rate: 0.2 mV/s.

It should be noted that for the all investigated liquid systems availability of only one discharge peak during the first cycle is a characteristic property. During charging 2 peaks in the potential range 2.0-2.6 V are observed. The ratio and peak value depend on a lithium salt nature and the composition of aprotic solvent. During cycling at 3 and 4 cycles cathode and anode peaks disappear. This can indicate pyrite electrochemical irreversibility in a liquid electrolyte. It has been established that the system based on $LiN(SO_2CF_3)_2$ (Fig.1 d) has the highest stability among the investigated systems. Availability of anode and cathode peaks during 2 and 3 cycles is observed for it. Such composition of solvents as plasticizing systems and application of $LiN(SO_2CF_3)_2$ as a conductive additive are more promising for polymer electrolytes application.

The works concerning optimization of the composition and production technology of polymer electrolytes based on the co-polymers of vinylidene fluoride with hexafluorine propylene (PVdF) were also carried out. Production technology of polymer electrolytes which consists of the stage of microporous material formation and the activation stage of the material produced with lithium salt solution in aprotic solvents has been selected as a basic one. As a result of the carried out investigations it has been established that the specific characteristics of lithium-pyrite system depend both on the technology of microporous material preparation and the composition of electrolyte solution used for its activation. In Figs. 2 the discharge curves of the system lithium-natural pyrite with polymer electrolyte based on microporous film activated by liquid electrolytes of different composition are presented.

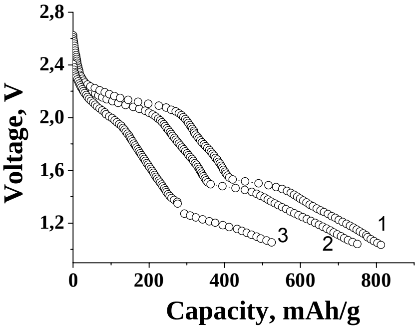


Fig.2. *Discharge characteristics of the system Li-natural pyrite (2nd cycle) with polymer electrolytes based on PVdF:*

1 – EC/DMC/1M $LiClO_4$;

2 – PC/1,4-Dioxolane/0.5M $LiN(SO_2CF_3)_2$;

3 – PC/DME/1M $LiClO_4$.

Pyrite concentration in cathode mass – 30%. $I_{ch} = I_{dch} = 0.1$ mA.

At the 2nd discharge (Fig.2a) the best specific characteristics have been obtained with 1M $LiClO_4$ solution in the mixture of EC/DMC and 0.5 M $LiN(SO_2CF_3)$ solution in the mixture of PC/1,4-dioxolane. The presented dependences show that at the second cycle with all investigated electrolytes a discharge plateau is observed at the voltage 2.2-2.1V. The plateau is conditioned by polysulfide reduction process. On this plateau the maximum capacity value is obtained by using EC, DMC and 1M $LiClO_4$. During cycling the value of the plateau decreases, and prior to the 10th cycle it practically disappears for the electrolytes comprising PC.

The developed polymer electrolytes have been tested in the composition of lithium power sources with the cathode materials comprising the different quantity of natural pyrite (fraction < 40µm): 30%, 50% and 80%.

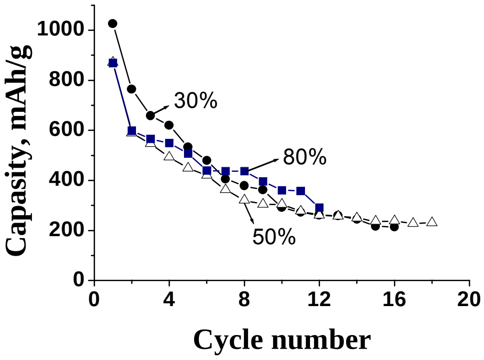


Fig 3. *Change of specific capacity at FeS_2 - based cathode cycling (30%, 50% and 80% pyrite in cathode mass) in polymer electrolyte PVdF/PC/DME/1M$LiClO_4$.*

$I_{ch} = I_{dch} = 0.1$ mA (30% natural pyrite in cathode mass);

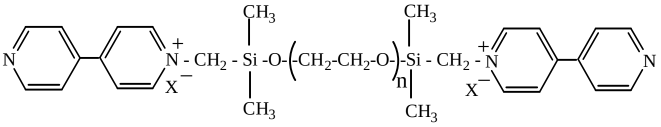
$I_{ch} = I_{dch} = 0.2$ mA (50% natural pyrite in cathode mass);

$I_{ch} = 0.2$ mA, $I_{dch} = 0.35$ mA (80% natural pyrite in cathode

In Fig.3 the change of specific capacity is shown at cycling of the cathodes comprising the different quantity of natural pyrite. The investigations carried out have shown that the specific capacity of lithium-pyrite systems based on the developed microporous polymer electrolytes is practically independent on a natural pyrite concentration in cathode mass.

On the basis of the obtained experimental it has been established that the electrolyte comprising PVdF, EC, dioxolane, $LiN(SO_2CF_3)_2$ is the most promising in terms of the anode and cathode cycling.

As it was noted above, introducing additives into electrolyte is the important method improving the qualities of lithium deposit (and hence, increasing a cyclability degree). The investigations carried out by us earlier have shown that introducing into electrolyte the developed by us additive increases cycling of lithium anode in the cells with the cathode based on manganese dioxide [4]:



were n = 5, X = Cl.

We used the additive to study its effect on the characteristics of lithium-pyrite cells at cycling. In this case the additive was introduced into the composition both of polymer electrolyte and a liquid electrolyte which was used for polymer film impregnation. Investigations carried out in the course of project execution have shown that additive influence is determined by its concentration in electrolyte composition. Introducing the additive in a considerable concentration decreases stability of pyrite cathode at cycling. Insignificant concentration of additive in the composition of polymer electrolyte practically does not effect on the character of charge/discharge curves (till the 17th cycle). (Fig. 4).

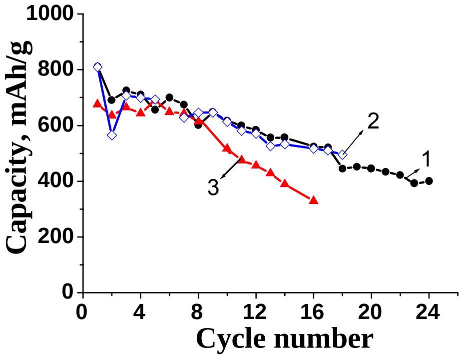


Fig. 4. *Change of the specific capacity of natural FeS_2-based cathode (80% pyrite in cathode mass) at cycling in the polymer electrolyte comprising:*
1 – PVdF/EC/1,4-dioxolane/0.5M $LiN(SO_2CF_3)_2$;
2 – PVdF/EC/1,4-dioxolane/0.5M $LiN(SO_2CF_3)_2$+additive in a plasticizer;
3 – PVdF/EC/1,4-dioxolane/0.5M $LiN(SO_2CF_3)_2$+additive in a polymer matrix.
Cathode mass was deposited on a stainless steel grid.
I_{disch}.– 0.35 mA, I_{ch} – 0.2 mA. Concentration of additives in aprotic solvents mixture is $1{\cdot}10^{-3}$ mol/l.

Cycling of cells is in progress.

Acknowledgements

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