Investigation of the stability of chlorinated PVC-based polymer electrolytes for lithium batteries

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Abstract

By thermogravimetric analysis, impedance spectroscopy and potentiodynamic cycling, the thermal and electrochemical stability of polymer electrolytes based on PVC and its chlorinated derivatives have been studied. The methods used to modify the properties of these polymeric electrolytes and to provide them with electrochemical stability when used in lithium batteries where the cathode is based on natural, nanostructured, and thermally-sprayed pyrite have been demonstrated. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Electrolyte systems such as polymer–aprotic solvent–lithium salt have a high conductivity at room temperature ($\sim 10^{-3}$ to $10^{-4}\,\Omega^{-1}\,cm^{-1}$) [1,2]. Due to the simplicity of preparation and the use of accessible reagents in the systems described, such gel-polymer electrolytes (GPE) are promising for rechargeable lithium batteries.

Investigation of the conductivity of these systems and understanding of its mechanism are of great importance. GPE conductivity depends on lithium ion mobility in the intermolecular space of the polymer matrix of the electrolyte. It is due to a high mobility of the high-molecular compound segments. The mobility is determined both by the character of its chemical structure and the availability of a low-boiling aprotic solvent in GPE. In this case, the solvent also serves as a plasticizing additive. At the same time, one can find the data in some references, concerning a specific interaction between lithium salt and the functional groups of the polymer matrix, e.g. C–O–C in polyethylene oxide, and its structural analogues [3], –CN in polyacrylonitrile [4]

which also makes its contribution to the conductivity of the electrolyte.

An amorphous polymer structure [5] is preferable for good conductivity. This creates an increased interest in the application of amorphous polyacrylonitrile [4], polymethyl-metacrylate [6] or low-crystalline polymers, e.g. polyvinylchloride [7,8].

In spite of the literature data concerning the application of PVC-based GPE [9] in lithium batteries, investigators are interested in thermal and electrochemical stability of the base system [10].

The comparatively low stability of GPE based upon PVC and many other polymers is due to a variety of reasons.

In the process of battery fabrication, chemical and electrochemical reactions are possible within the polymer electrolyte, resulting in the degradation of the electrolyte components. A high chemical activity of metallic lithium [11] and oxidizer (cathode material) [12], favours these reactions.

Salts and various metal compounds occurring accidentally or as specially introduced additives in polymers or in the base materials can have basically different influences on the decomposition process of the polymer materials. Li^+, Fe^{3+}, Fe^{2+} ions are known [13,14] to be active dechlorination agents for PVC and its derivatives.

Besides the cation influence, in some cases F^-, Cl^-, Br^-, I^-, ClO_4^-, SO_4^- anions and others [14] can accelerate the

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thermal decomposition of PVC. Destruction by anions and cations depends significantly on the state of the plastic. In aprotic solvents, e.g. DMF, chlorides of alkali metals dissociate with the formation of strongly basic Cl^- ions, catalyzing the decomposition process of PVC [15].

Rate of chemical reactions increase with rising temperature. The effect of high temperatures on GPE is possible if an elevated temperature technological process is used for its fabrication, e.g. in drying, when polymer electrolyte is produced from solutions [2], as well as in the case of GPE production by the extrusion method [16], or during battery operation.

In this work, we investigated the influence of lithium salts on the thermal and electrochemical stability of GPE based on chlorinated polyvinylchloride for the Li–FeS$_2$ battery. The method of PVC chlorination has been developed at our laboratory. Earlier [17] we have shown that PVC chlorination results in amorphization of its structure and increased conductivity of the polymer.

2. Experimental

2.1. Preparation of polymer electrolytes

Chlorinated polyvinylchloride (Cl-PVC) was obtained under laboratory conditions by heterogeneous chlorination of a PVC suspension in CCl_4.

Polymer films were formed on a glass sheet from a solution of the components (polymer, aprotic solvents, lithium salts and additives) in tetrahydrofuran. The films were dried for 24 h at room temperature and then at 48 h in vacuum at 45°C.

$LiClO_4$ (Iodobrom, Saki, Ukraine), $LiBF_4$, $LiPF_6$ (Advance Research Chemicals, Inc., USA), $LiCF_3SO_3$ (Aldrich), were used as electrolyte salts. PC was obtained from Angarsk Chemical Reagents Plant, Angarsk, Russia.

2.2. Thermogravimetric analysis (TGA)

Thermal stability of polymer electrolytes has been investigated on a thermogravimetric analyzer Q-1500 (Hungary), at 5 K min^{-1} heating rate with a 200 mg sample. Polymer compositions formed as films from THF by the method described in Section 2.1, were investigated.

2.3. IR spectroscopy

IR spectra of the polymer blends were recorded by a spectrophotometer SPECORD 75IR. The investigations were carried out within the wavelength range from 400 to 3800 μm.

2.4. Measurements of conductivity

The measurements of the conductivity of GPE films were performed by impedance spectroscopy on the symmetrical system: Ni–GPE–Ni over the frequency range of 0.08–200 kHz. This was done in an atmosphere of dry argon within a Teflon cell. Ionic conductivity of GPE was calculated from the data for the total resistance R_e of the electrolyte, measured from the intersection of the high frequency part of the hodograph with the abscissa.

2.5. Impedance measurements

Impedance measurements of symmetrical Li–Li cells (in the atmosphere of dry argon in a Teflon cell) or asymmetrical Li–FeS$_2$ (in 2525 button cells) were carried out with the help of ac bridge P5021 over the frequency range 0.08–200 kHz using a series circuit of the measured values R_s and C_s. The hodographs $1/\omega C_s - R_s$ have the shape of slightly depressed semicircles.

2.6. Potentiodynamic measurements

Potentiodynamic cycling was performed in a Teflon cell with three electrodes in the atmosphere of argon. Reference and auxiliary electrodes were made of lithium. For the investigation of the background potentiodynamic characteristics of the polymer electrolyte, a platinum plate served as a working electrode. The electrodes, made from the different samples of pyrite, were used in studying the kinetics of the cathodic reduction of FeS$_2$.

Electrode potential sweeps were performed with a potentiostat PI-50-1,1 and programmer PR-8. Scan rate ranged from 1×10^{-3} to 1×10^{-4} V s^{-1}. The curves were registered on a two-coordinate recorder PDA-1 within the potential range 0.8–4.8 V in the case of platinum electrode and 1.1–2.8 V with pyrite electrodes.

2.7. Preparation of cathode materials

Natural, nanostructured, and thermal-sprayed pyrites (pyrite) were used as cathode materials. Nanostructured and thermally-sprayed pyrite was produced by the unique technology of US Nanocorporation®, USA.

Natural pyrite was ball-milled, then sieved. The fraction with a particle size less than 40 μm was used as the active cathode material. Before cathode preparation in mass, the pyrite was washed with boiling water up to neutrality of the washing water, then it was dried at 250°C for 4 h. Natural pyrite, carbon black and graphite in the required mass ratio were thoroughly stirred in a ceramic mortar.

Thirty-three percent by weight of fluoroplastic binder F4D mixed with 1.1 ethanol (96%): distilled water was added to the above composition and mixed in a mortar, then dried at 100°C for 6 h. The cathode mass so prepared was then ready for use. Cathodes based on nanostructured pyrite were prepared similarly.

Thermally-sprayed pyrite was produced by US Nanocorp., USA, using a dc plasma arc gun. Samples of thermally-sprayed pyrite were obtained by plasma spraying of

pyrite onto a stainless steel substrate. The thickness of these electrode films ranged from 83.7–212 μm. The porosity of the films was 50%.

2.8. Preparation of a prototype battery

The cathode mass was wetted with heptane and then deposited by a putty knife onto a degreased stainless steel grid-current collector that had been welded to the bottom of the case of a 2525 cell. The assembly was then dried at 100°C for 1 h.

Cell assembly was performed in an atmosphere of dry argon by placing in layers: a cathode, GPE film and metal lithium. The cell was then sealed.

3. Results and discussion

3.1. Thermal stability

The influence of PC and $LiClO_4$ on the thermal stability of chlorinated polyvinylchloride is shown in Fig. 1.

Mass loss in chlorinated polyvinylchloride and in the composition Cl-PVC:PC begins at 105°C. At this temperature, the quantity of the volatile components lost is ∼1%.

The following substances can serve as the volatile components:

- Residues of a solvent in the GPE, which is known from the previous work [4] to be partially removed from gelatinous GPE during drying.
- Chemically bound water.

We have carried out a comparative analysis of IR spectra of Cl-PVC films obtained under the normal conditions, given in Section 2.1, and after preliminary thermal treatment at 90°C for 5 h.
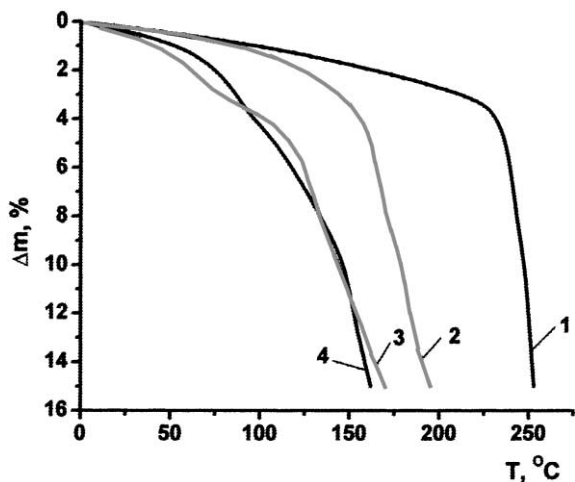

Fig. 1. Mass loss of polymer material samples during thermal oxidation: (1) Cl-PVC; (2) Cl-PVC:PC (1:5); (3) Cl-PVC:PC:LiClO$_4$ (1:5:0.42); (4) Cl-PVC:PC:LiClO$_4$:FeS$_2$ (1:5:0.42:0.3). Mass ratio of the components are given in brackets.
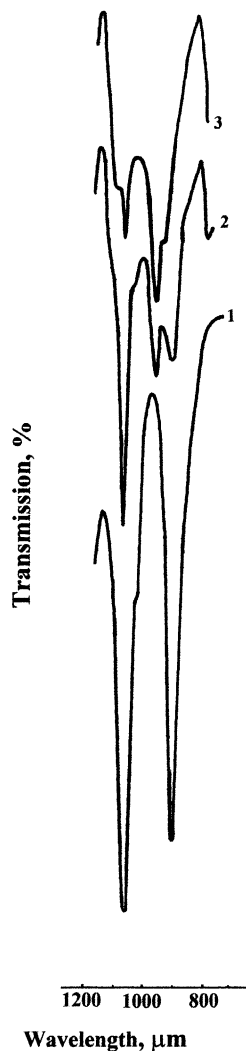

Fig. 2. IR-spectra of THF (1) and Cl-PVC films (2 and 3) obtained from solutions in tetrahydrofuran. Films dried for 24 h at room temperature and 48 h in vacuum at 45°C; (2) for 24 h at room temperature, 48 h in vacuum at 45°C, finally (3) for 5 h at 90°C.

For the thermally treated films, a decrease in the intensity of absorption bands is observed at 1075 and 905 μm These bands correspond to the asymmetric oscillations of a tetrahydrofuran ring and the oscillations of C–O–C group (Fig. 2). According to the thermogravimetric investigation data, the thermal oxidative destruction of Cl-PVC begins at a temperature higher than 220°C. Therefore, the changes in IR spectra after thermal treatment can correspond only to the process of the forced removal of solvent residue from the Cl-PVC films when heated above the boiling temperature of THF.

In accordance with a weight analysis, we have determined that GPE films dried under the standard conditions contain 7–8% of THF.

The IR spectra of the polymer materials Cl-PVC, Cl-PVC:PC and Cl-PVC:PC:LiClO$_4$ the presence of a wide maximum at 3400–3450 μm, being a characteristic feature, confirmed the presence of water in the samples.
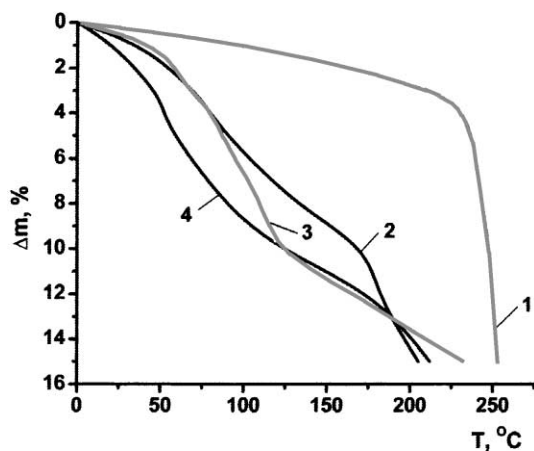
Fig. 3. Effect of the type of lithium salt on the thermal stability of chlorinated polyvinylchloride: (1) Cl-PVC; (2) Cl-PVC:LiClO$_4$ (1:0.42); (3) Cl-PVC:LiCF$_3$SO$_3$ (1:0.6); (4) Cl-PVC:LiBF$_4$ (1:0.38). Mass ratio of the components are given in brackets.

Table 1
Conductivity at 25°C of GPE films based on chlorinated polyvinylchloride

Sample	Electrolyte	Mass ratio	Conductivity[a] q (S cm^{-2})		
			0 days	1 day	5 days
1	Cl-PVC:PC:LiClO$_4$	1:5:0.42	0.045	0.050	0.060
2	Cl-PVC:PC:LiBF$_4$	1:5:0.38	0.065	0.065	0.056
3	Cl-PVC:PC:LiCF$_3$SO$_3$	1:5:0.6	0.032	0.032	0.030

[a] Thickness of GPE films is 0.5 mm.

cing stabilizing additives in the polymer electrolyte is very important. The effect of stabilizing additives is discussed later.

3.2. Conductivity of polymer electrolytes

In Table 1 the results of the measurements of the conductivity of GPE films at 25°C are presented. Except for the LiClO$_4$-based electrolyte where a certain increase in conductivity is observed, it is clear that, after storage for 5 days, conductivity is practically unchanged.

It should be noted that the conductivity of GPE based on chlorinated polyvinylchloride is the same as for the traditional liquid systems [10] and depends on the nature of lithium salts used as solutes. For these electrolytes, conductivity rises in the sequence: LiCF$_3$SO$_3$ ≈ LiClO$_4$ < LiBF$_4$.

3.3. Impedance measurements

Analysis of the impedance curves of the symmetrical system Li/GPE/Li shows that for the GPE based on PVC and Cl-PVC, hodographs take the forms typical of those from traditional liquid systems (Fig. 4). The Cl-PVC-based GPE is characterized by a lower resistance of passivating films on lithium surfaces as compared with PVC. It is evidence of the higher PVC reactivity relative to lithium
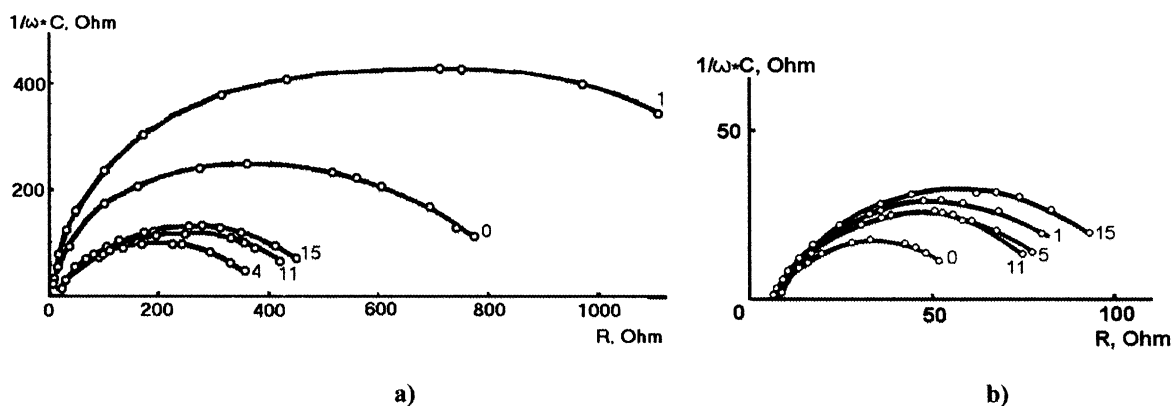
With increasing temperature, the above samples show different behaviour. With the initial polymer, a 3% mass loss occurs at 220°C, but for its plasticized product it occurs at 145°C. Such behaviour of the plasticized system can be explained by the start of PC decomposition and the evaporation of its decomposition products [18].

Introduction of LiClO$_4$ into the system, sharply decreases the stability of the polymer composition (Fig. 1, curve 3). This confirms the catalytic effect of this salt on the thermal destruction of Cl-PVC.

The presence of natural pyrite in gel-electrolyte does not significantly affect the behaviour of the polymer electrolyte, comprising Cl-PVC:PC:LiClO$_4$, at temperatures up to 50°C.

In Fig. 3 the influence of the nature of the lithium salt on the thermal stability of Cl-PVC is shown. All of them act as a catalyst for the decomposition of Cl-PVC. Their effect on Cl-PVC decomposition increases in a series of LiCF$_3$SO$_3$ ≈ LiClO$_4$ < LiBF$_4$. In this connection, introdu-

a)

b)

Fig. 4. Impedance characteristics of Li–Li system with GPE: (a) PVC:PC:LiClO$_4$ (1:5:0.42); (b) Cl-PVC:PC:LiClO$_4$ (1:5:0.42). Numbers by curves indicate ageing time in days.

anodes, than when its chlorinated derivative is used as a polymer matrix.

The results obtained correlate well with the supposition stated earlier [10] about possible lithium passivation by polyvinylchloride in the electrolyte comprising PVC:EC/PC:LiClO$_4$.

In [10] the authors consider that the interaction between PVC and lithium in GPE compositions results in the formation of an inorganic surface layer, comprising LiCl. In this case, the resistance of the lithium anode was noted to depend significantly on the nature of the lithium salt nature GPE. GPEs containing LiPF$_6$ and LiBF$_4$ showed higher reactivity relative to lithium than ones containing LiClO$_4$. The authors explained this fact by the higher reactivity of LiPF$_6$ and LiBF$_4$ than LiClO$_4$ against lithium.

In our opinion, such a significant rise of lithium hydride (LiH) formation can be promoted by the catalytic effect of LiPF$_6$ and LiBF$_4$ on the process of PVC dehydrochlorination and, correspondingly, on the formation of LiH. Evidently, presence of the latter gives rise to a high resistance for the system. Note that such an effect is not observed during investigations of liquid systems.

It can be also supposed that halide ions in the Cl-PVC system activate the passivating film on a lithium surface. The effect of halide ions on the properties of the lithium/nonaqueous electrolyte interface has been reported. For example, when PC:LiBr solutions were compared with PC:LiClO$_4$ ones [19]. Nevertheless, in the case of polymer systems, the influence cannot be so evident and requires additional investigations, in as much as halide derivative-based polymers are widely used in lithium nonaqueous systems.Impedance of the asymmetrical system Li/GPE/FeS$_2$ is complicated by a possible interaction between the polymer system and the oxidizer — FeS$_2$. In [12] we have

shown how the impedance of the nonaqueous system comprising the polymer based on the organosilicone derivatives of polyvinylpyridine changes in of the presence of the different cathode materials MnO$_2$ and FeS$_2$.

In Fig. 5, the impedance of the system Li/GPE/FeS$_2$, using as an active substance, the highly reactive nanostructured pyrite from US Nanocorp., is shown. Earlier we mentioned that in the presence of pyrite, data on the thermal decomposition of the polymer system (Fig. 1) was unavailable. However, comparing Figs. 4 and 5, one can see that with pyrite, as compared with the system comprising only Li/GPE/Li, the impedance becomes distorted, and the system resistance increases.

Impedance degradation can have at least two causes. The properties of the film formed on a cathode surface at its interaction with the components of polymer electrolyte change. These result in an increase in the parameters of impedance "semicircles". The resistance itself also changes with interelectrode spacing, i.e. the specific resistance of the electrolyte changes. This change is reflected by an increase in the length cut-off by the hodograph on an abscissa axis within the high frequency range. The degradation effect is stronger in the PVC-based system (Fig. 5a). When Cl-PVC is used in the asymmetrical system, the resistance value of passivating films on electrode materials and that of GPE in interelectrode spacing are lower as compared with PVC-based system (Fig. 5b).

3.4. Potentiodynamic investigations

In Fig. 6 the ground potentiodynamic curve of polymer electrolyte on platinum electrode is shown. The polymer electrolyte based on Cl-PVC is stable enough within the potential range of 0.8–4.5 V.
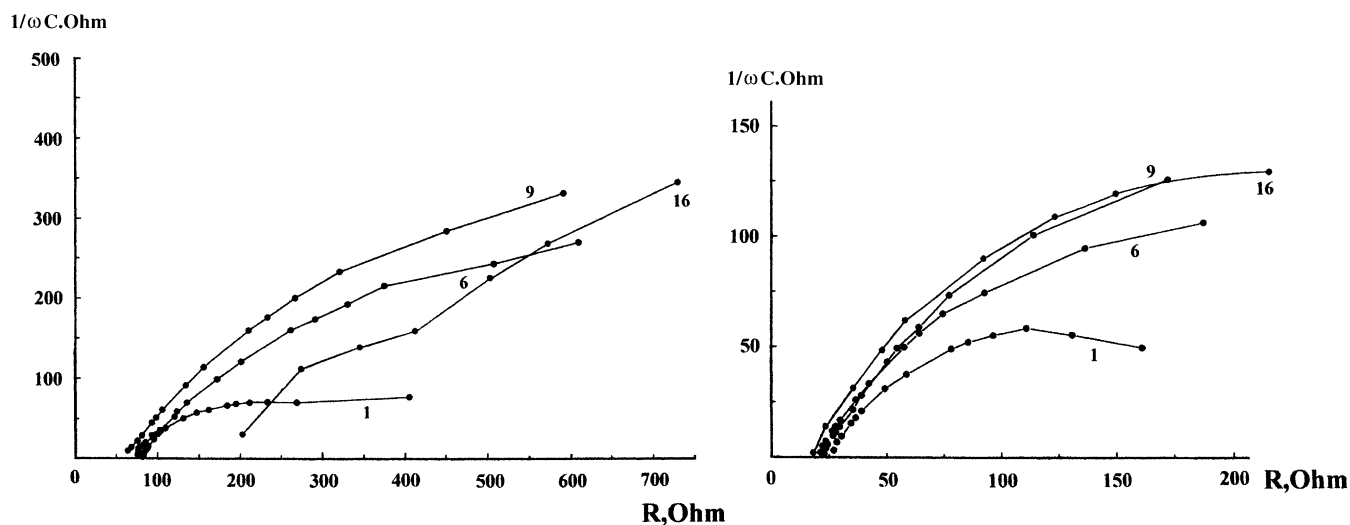

Fig. 5. Impedance hodographs of Li–FeS$_2$ (US Nanocorp.) system with GPE: (a) PVC:PC:LiClO$_4$ (1:5:0.42); (b) Cl-PVC:PC:LiClO$_4$ (1:5:0.42). FeS$_2$ content in cathode is 70%. Electrode area = 1.45 cm^2. Numbers by curves indicate ageing time in days.
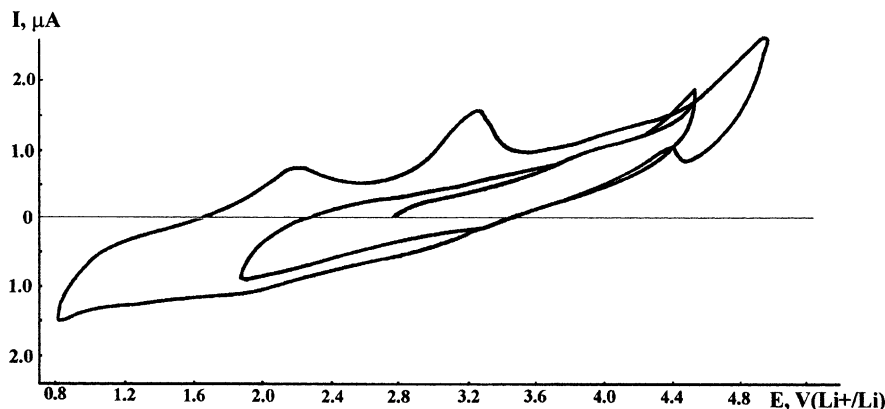
Fig. 6. Background potentiodynamic curve on Pt electrode in polymer electrolyte Cl-PVC:PC:LiClO$_4$ (1:5:0.42). Electrode area = 7.8 × 10^{-3} cm^2.

Thus, the electrolytes developed appear to be promising for rechargeable power sources, with the different operating voltage of: 4.0 V (LiMn$_2$O$_4$), 3.0 V (MnO$_4$), 1.5 V (FeS$_2$). As noted above, this work is devoted to Li–FeS$_2$ system with the operating voltage of 1.5 V.

In Figs. 7–9 the results of the potentiodynamic investigations carried out on the film of thermally sprayed pyrite are presented. Characteristics obtained in liquid and polymer electrolytes have been compared. In Fig. 7 it is seen that in liquid electrolyte, FeS$_2$ films are irreversibly reduced cathodically.
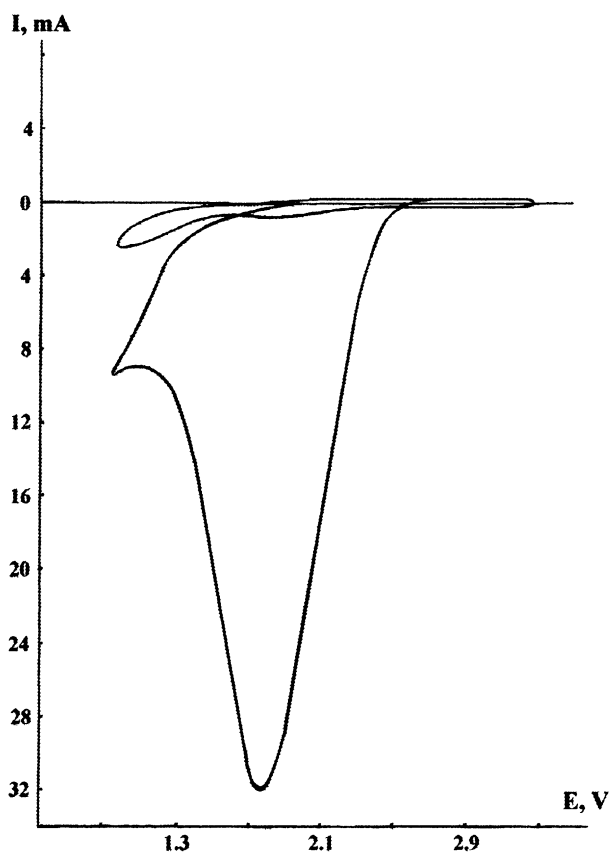
The second potentiodynamic curve practically reduces to the background curve observed with inert platinum electrodes.

With a polymer electrolyte, the thermally-sprayed pyrite cycled reversibly (Fig. 8). In the electrolyte containing LiBF$_4$, during the first cycles the peak value decreases slightly, and then becomes stable. In the LiPF$_6$ electrolyte, the current value is less; however, stabilization occurs during the first few cycles.

In the LiCF$_3$SO$_3$-based electrolyte (Fig. 9), the character of the potentiodynamic curves is different — in the cathodic region, the area occupied by the curve is larger than in anodic one. This could be evidence of the participation of the polymer electrolyte components in the electrochemical process. At the same time, cathode peaks increasing from cycle-to-cycle can be caused by the gradual change in volume of an active cathode. Thus, the potentiodynamic investigations have shown the prospects for application of a new electrochemical system based on the polymer electrolyte and the films of thermal sprayed pyrite as these latter are reversibly cycleable at room temperature.

3.5. Prototype batteries

Here are presented the results of galvanostatic cycling of cells with a polymer electrolyte and the cathode based on natural pyrite. We have suggested above the possibility of PVC dechlorination resulting from its interaction with metal lithium. To increase PVC stability we used additives capable of inhibiting its dehydrochlorination.

The cycling results of a system without modifying additive in the electrolyte (Fig. 10) and the electrolyte comprising this additive (Figs. 11 and 12) have been compared.

In the absence of modifying additive, significant capacity loss occurs during the first five cycles (Fig. 10).
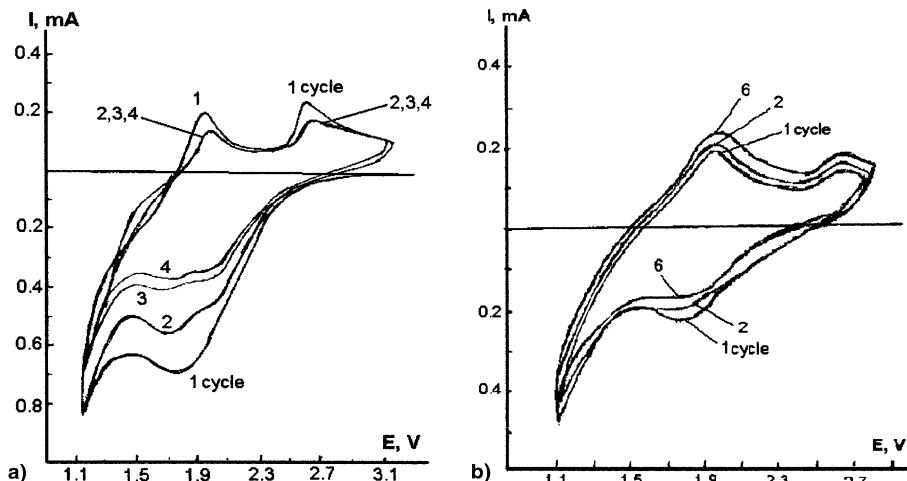

Fig. 7. Cyclic voltammogram of thermally sprayed FeS$_2$ in a liquid electrolyte: PC:DME (3:1): 1 M LiClO$_4$. Scan rate: 5 × 10^{-5} V s^{-1}. FeS$_2$ area = 8 cm^2. Thickness of FeS$_2$ film is 146.7 μm.

Fig. 8. Cyclic voltammograms of thermally sprayed FeS_2 in polymer electrolytes: (a) Cl-PVC:PC:$LiBF_4$ (1:5:0.38); (b) Cl-PVC:PC:$LiPF_6$ (1:5:0.61). FeS_2 area is 8 cm^2. Scan rate: 5×10^{-4} V s^{-1}. Thickness of FeS_2 film is 150 μm (a) and 212 μm (b).
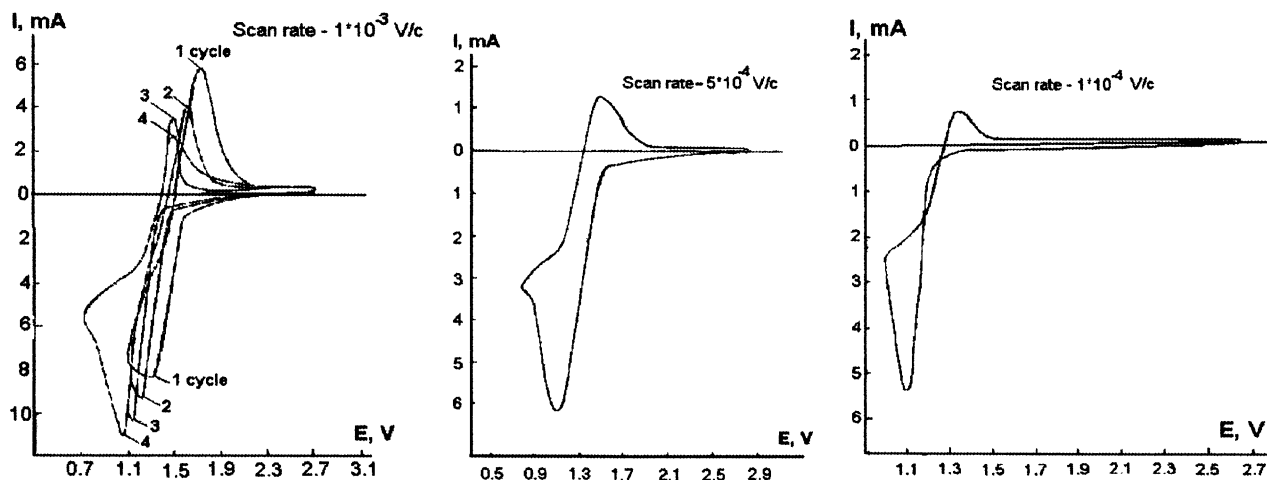

Fig. 9. Cyclic voltammograms of thermally sprayed FeS_2 in polymer electrolyte Cl-PVC:PC:$LiCF_3SO_3$ (1:5:0.6). FeS_2 area = 8 cm^2. Thickness of FeS_2 film is 83.7 μm.

A quite different situation is observed whilst testing GPE with the same composition (Figs. 11 and 12) but with a modifying additive. After the 50th cycle, the discharge capacity of the system becomes stable at a rather high level.

In the case of a polymer electrolyte based on Cl-PVC, the system is stable enough during cycling even without stabilizing additive (Fig. 13).

The nature of the lithium salt influences the discharge characteristics of the Li–FeS_2 system. The maximum capacity value has been obtained with GPE containing $LiCF_3SO_3$. At the 80th cycle, the discharge capacity was about 400 mAh g^{-1}. When $LiClO_4$ or $LiBF_4$ was used in the GPE, by the 50th cycle, the discharge capacity was only 180–200 mAh g^{-1}.

The comparatively fast decrease in capacity and the low values for the system comprising GPE with $LiBF_4$ can be explained by the high reactivity of the salt with lithium [10] and its catalytic ability to decompose polyvinylchloride during the charge/discharge process.
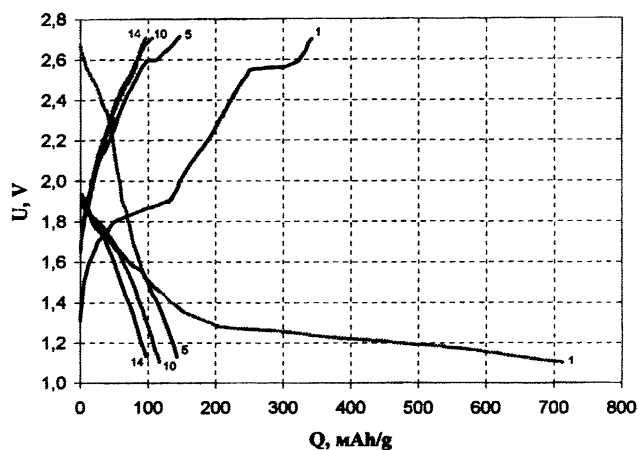

Fig. 10. Change of charge/discharge characteristics of the system Li–FeS_2 with a nonmodified GPE comprising PVC:PC:$LiCF_3SO_3$ (1:5:0.3). Content of natural FeS_2 in cathode is 10% (carbon black, graphite and binding are the remaining components). $I_{discharge}$ = 0.1 mA, I_{charge} = 0.02 mA. Labels on curves correspond to cycle numbers.
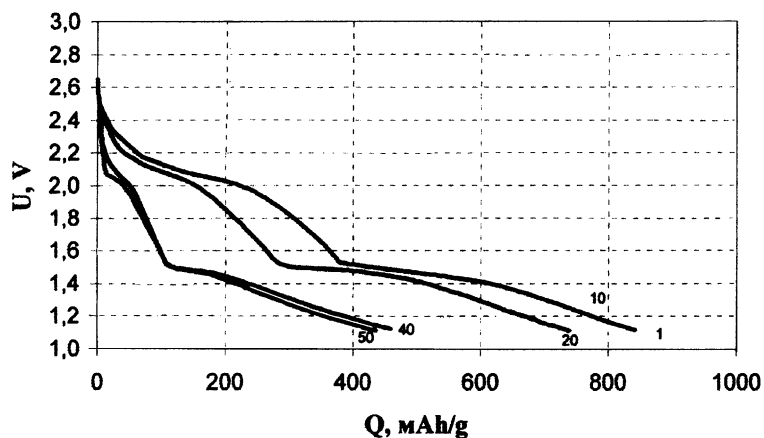
Fig. 11. Discharge characteristics of the system Li–FeS$_2$ with a GPE comprising PVC:PC:LiCF$_3$SO$_3$ (1:5:0.3) and modifying additive. Content of natural FeS$_2$ in cathode is 10%. $I_{discharge} = 0.1$ mA, $I_{charge} = 0.02$ mA. Labels on curves correspond to cycle numbers.

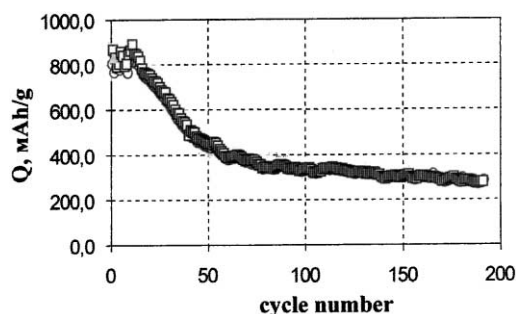Fig. 12. Change of specific capacity during cycling for the Li–FeS$_2$ system with a GPE comprising PVC:PC:LiCF$_3$SO$_3$ (1:5:0.3) and modifying additive. Content of natural FeS$_2$ in cathode is 10%. $I_{discharge} = 0.1$ mA, $I_{charge} = 0.02$ mA.

In the case of LiClO$_4$, such an analogy cannot be drawn. To obtain the data concerning the probable degradation mechanism of GPE based on Cl-PVC and containing LiClO$_4$ additional investigations are needed.
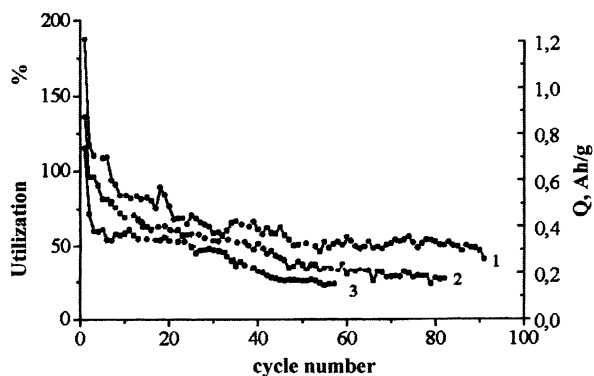

Fig. 13. Influence of the type of salt in the Cl-PVC polymer electrolyte on the discharge characteristics of Li–FeS$_2$ cells (size 2325): (1) Cl-PVC:PC:LiCF$_3$SO$_3$ (1:5:0.3); (2) Cl-PVC:PC:LiBF$_4$ (1:5:0.19); (3) Cl-PVC:PC:LiClO$_4$ (1:5:0.21). Content of natural FeS$_2$ in cathode is 10%. $I_{discharge} = 0.1$ mA, $I_{charge} = 0.02$ mA.

4. Conclusions

A gel polymer electrolyte based on chlorinated PVC for use with Li and FeS$_2$ in secondary cells operating at room temperature has been developed and investigated.

The characteristic feature of this GPE is higher electrochemical stability as compared with polyvinylchloride.

Successful application of polymer electrolytes based on PVC is possible by applying stabilizing additives to increase the electrochemical stability of the electrolyte.

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