Problems of corrosion and other electrochemical side processes in lithium chemical power sources with non-aqueous electrolytes

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Abstract

The following electrochemical side processes were studied: (i) electrochemical corrosion processes in a short-circuited couple of active cathode material (FeS_2)–current-collector material, and (ii) electrochemical and chemical decomposition of non-aqueous electrolytes proceeding in parallel with the base electrochemical reaction in power sources with a working discharge voltage of 1.5 V. The dynamics and direction of corrosion processes in the couple of FeS_2–current collector depend on the potential difference between the active cathode substance and the current-collector material and on the overvoltage value of conjugated electrochemical processes. In the case of a starting unreduced cathode, the reduction process takes place on pyrite and the oxidation process occurs on the current collector. After a partial cathode reduction the process direction changes. The rate of decomposition of the electrolyte in the potential range of 1.5 V is determined by its composition, the conditions of its preparation and purification, and the cathode material used as catalyst in the process of the decomposition of the electrolyte.

Keywords: Lithium batteries; Corrosion; Electrolytes; Electrodes

1. Introduction

Electrochemical side processes in lithium power sources with non-aqueous electrolytes may cause a number of undesirable effects and a decline of the system efficiency. It should be noted that factors such as self-discharge, destruction of current-collector materials, formation of the products of electrolyte decomposition, in particular, gaseous substances, increase the internal pressure in a cell.

The corrosion couple of active anode material–current collector material is of particular concern in side processes proceeding in power sources. Depending on the nature of the active cathode substances, the composition of the non-aqueous electrolytes, the nature of current collector materials, the degree of the cathode reduction, the direction of corrosion processes, their velocity as well as the nature of products formed can change [1].

The dynamics and direction of corrosion processes depend on the potential difference between the active cathode substance and the current collector materials as well as on the overvoltage value of conjugated electrochemical processes. Corrosion processes in short-circuited couples of cathode material–current collector are especially displayed during the storage of power sources and between discharges.

Further to the electrochemical and chemical electrolyte decomposition that can proceed in parallel with the base process, cathode reduction is the second group of side processes [2]. Electrolyte decomposition may proceed both on the surface of solid-phase oxidizer and on the conducting additive introduced into the cathode mass. This process must be taken into account in power sources with working discharge voltages of 1.5 V. This is conditioned by the fact that most of the non-aqueous electrolytes is reduced to this potential range. In this case, the electrode surface may be the catalyst during the electrolyte decomposition. Thus in Refs. [3,4] the catalytic activity of graphite towards the electrochemical decomposition of non-aqueous electrolytes is observed. Different additives, such as zinc [5] and cobalt [6], are also introduced into the cathode mass. However, the properties of these additives are

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not considered in terms of their influence on the side processes.

Investigations and analyses of these side processes in power sources with lithium anodes and non-aqueous electrolytes are necessary for the choice of the materials for the current collector, conducting additive, and electrolyte composition.

In this paper side processes are studied in an electrochemical system with an FeS₂-based cathode.

2. Experimental

Various methods were applied: potentiodynamic and potentiostatic measurements on different materials, investigations of the dynamic characteristics of the FeS₂–current-collector corrosion couple; volumetric determination of electrolyte decomposition rate; chromatographic analyses of gaseous products of the electrolyte decomposition, and atomic adsorptive analyses of the metal content in the electrolyte.

All measurements were carried out in an argon-filled glove box with lithium reference and auxiliary electrodes.

Monocrystalline pyrite and porous electrode on the basis of FeS₂ with various conducting additives were used as the working electrode.

Lead, cadmium, aluminium, nickel, titanium, copper, steel, platinum, graphite and tantalum were used as current-collector materials.

Tests were carried out with real flat cells (diameter = 11.56 mm, height = 4.2 mm).

Solutions based on different aprotic solvents were used as electrolytes. Their water content was less than 0.01%. Some of the electrolytes used were synthesized under the supervision of the Institute of Railway Transport Engineers, Dniepropetrovsk, Russian Federation.

3. Results and discussion

3.1. Corrosion processes in the cathode material–current collector couple

In the initial status, the potential of the unreduced solid-phase oxidizer is considerably higher than that calculated from thermodynamic data. This is due to the oxidized surface state. For FeS₂, this value is about 3.7 V. Table 1 presents the values of stationary potentials of different materials applied as current collectors or conducting additives to the cathode mass. Fig. 1 shows the time dependence of the corrosion current of pyrite–metal couple for unreduced pyrite. When the pyrite reduction process occurs, the oxidation process takes place on the metal. At corrosion couple shortage the initial change of current results from the e.m.f. value. Further change of corrosion current versus time is

Table 1
Stationary potentials of different materials in LiBF₄/propylene carbonate–dimethyl ether of diethyleneglycol electrolyte; reference electrode: lithium

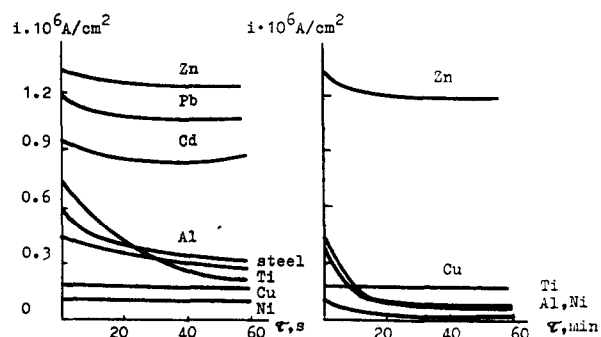| Material	Stationary potential E of metal sample (V)
Lead	2.7
Cadmium	2.6
Zinc	2.5
Aluminium	2.5–2.9
Nickel	2.9–3.1
Titanium	2.9–3.1
Copper	3.3–3.2
Steel 0.6XH28MDT	3.2–3.2
Graphite	3.6
Platinum	3.9

Fig. 1. Time vs. corrosion current in the FeS₂–metal complex. Electrolyte: LiBF₄/propylene carbonate–dimethyl ether of diethyleneglycol; pyrite is unreduced ($E = 3.7$ V); load resistance = 100 Ω.

connected with the accumulation of corrosion products and electrode polarization.

On zinc, copper and lead metals, conjugated electrochemical processes proceed with a small polarization. In these systems a certain value of corrosion current is settled. On nickel, aluminium and titanium the greater polarization value of conjugated process is inherent. The corrosion current decreases with time and tends to zero.

Corrosion processes proceeding in the considered system during the storage of the power source may cause a self-discharge and a destruction of the current collector.

In the second series of corrosion measurements, FeS₂ was preliminary cathodically reduced to a stable value in the potential range from 1.6 to 1.8 V. The rate of corrosion processes is higher than in the case of unreduced pyrite. Thus, in the couple of pyrite–current collector, the oxidation process occurs on pyrite, and reduction takes place on the current collector. Fig. 2 illustrates the current value depending on the material used. From the corrosion diagrams of different electrode couples it is evident that pyrite potential is practically unchanged during the corrosion process (Fig. 3). At
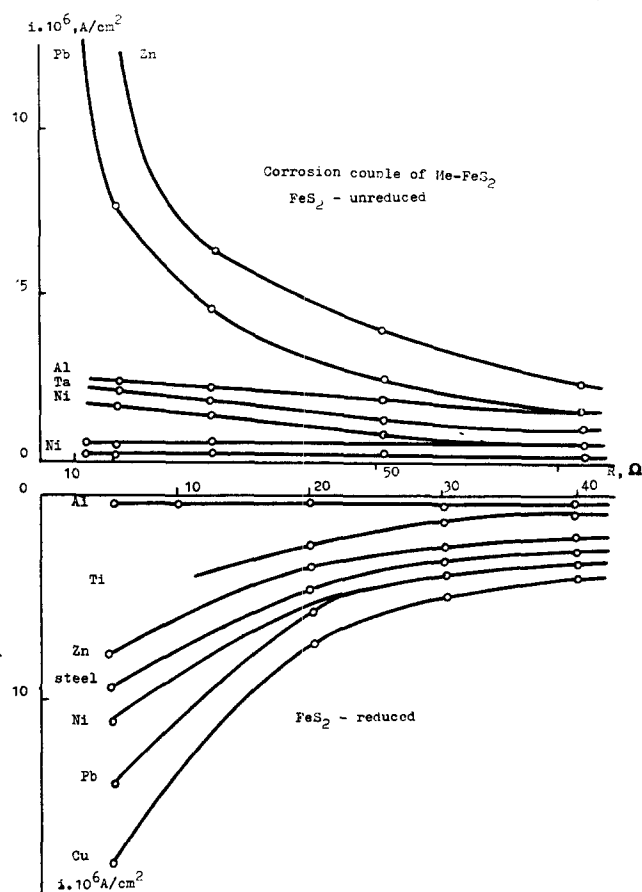
Fig. 2. Corrosion current vs. load resistance of the corrosion couple. Electrolyte: 1 M LiBF₄/propylene carbonate–dimethyl ether of diethylene glycol.

the same time, the current-collector potential changes significantly. Thus, the value of corrosion current is determined by the overvoltage reaction on the current collector. On aluminium, the overpotential value is the biggest, and accordingly, the value of the corrosion current is the smallest.

Studies carried out show that for Li–FeS₂ system aluminium is the best of all investigated materials.

3.2. Electrochemical and chemical stability of non-aqueous electrolytes

Potentiodynamic study of different metals in propylene carbonate (PC), dimethyl ether of diethyleneglycol, LiBF₄: LiClO₄/propylene carbonate–dimethoxyethane electrolytes on different materials showed that in a series of $Al < Ni < Ta < Ti < glassy\ carbon < Zn < Cu < Pb$ the cathode current increases. The decomposition of the non-aqueous electrolyte takes place.

It is evident that the rate of electrolyte decomposition depends on the conditions of electrolyte preparation and purification and is independent of the water content.
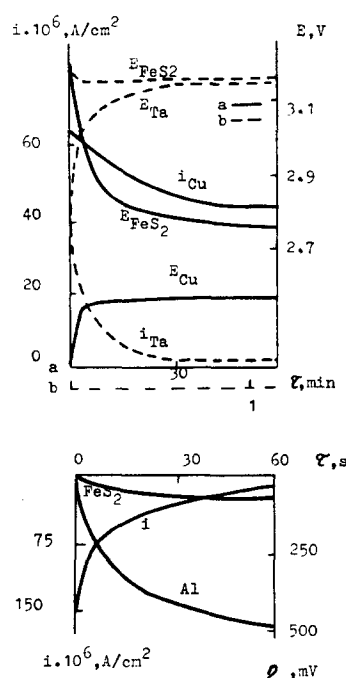

Fig. 3. Change in time of electrode potential, polarization and current in corrosion couples: FeS₂–Ta, FeS₂–Cu, and FeS₂–Al; load resistance = 5000 Ω; electrolytes: 1 M LiBF₄/propylene carbonate–dimethyl ether of diethylene glycol.

Table 2
Decomposition rate of different electrolytes [a] on FeS₂-based cathode

Electrolyte composition	H₂O (%)	Decomposition rate (ml/min)
1 M LiBF₄/γ-BL	0.03	0.3×10^{-3}
1.6 M LiBF₄/SL	0.01	0.2×10^{-3}
1 M LiBF₄/DG	0.05	0.6×10^{-4}
1 M LiBF₄/PC	0.02	0.1×10^{-3}
1 M LiBF₄/γ-BL–THF (1:1)	0.01	0.4×10^{-3}
1 M LiBF₄/PC–DME (1:1)	0.006	0.8×10^{-3}
1 M LiBF₄/PC–DG (1:1)	0.01	0.6×10^{-4}
1 M LiBF₄/PC–DOL (1:1)	0.01	0.2×10^{-4}
1 M LiClO₄/PC–AN (1:1)	0.02	0.4×10^{-3}
1 M LIClO₄/DMSO	0.04	0.4×10^{-3}
1 M LiClO₄/PC	0.02	0.8×10^{-3}

[a] γ-BL = γ-butyrolacetone; SL = sulfolane; DG = dimethyl ether of diethyleneglycol; PC = propylene carbonate; THF = tetrahydrofuran; DME = dimethoxyethane; DOL = dioxalane; AN = acenotrile, and DMSO = dimethyl sulfoxide.

Impurities, like glycols, formed at the high-temperature distillation of PC (it is co-solvent in many non-aqueous electrolytes) play significant roles. At the same time, the nature of solvent and salt determined the electrochemical and chemical stability of non-aqueous electrolytes. The rate of gaseous products evolved at the FeS₂-based cathode depending on the electrolyte composition may change from 8×10^{-3} to 2×10^{-5} ml/min (Table 2). LiBF₄/PC–DG has advantages over the other studied electrolytes.

It should be noted that during the cathodic reduction of the solid-phase oxidizer both electrochemical and chemical electrolyte decomposition take place. The intercalation of lithium cations into the solid-phase cathode during its reduction gives rise to a chemical electrolyte decomposition. Thus, after partial reduction of solid-phase cathode electrolyte, decomposition followed by gaseous products evolution occurs at an electrode currentless holding. This process takes place between the cell discharges.

Conducting additives introduced into the porous cathode are of particular concern during the process of electrolyte decomposition. Graphite and carbon black are usually used as additives. The .potential of the additives is high enough (Table 1), because of their surface oxidation. In the case of unreduced pyrite, the potentials of pyrite and conducting additives are close enough, therefore, the corrosion current value is small. After partial electrode reduction, the particles of the conducting additives become cathode areas. In the electrode body, corrosion microcells are formed. Correspondingly, on the areas of the conducting additives the process of electrolyte decomposition resulting in an evolution of gaseous products is possible.

The evolution of gaseous products during the electrolyte decomposition exerts an internal pressure in a cell resulting in an increased height in the case of flat cells. Table 3 shows the influence of the contact of the solid-phase oxidizer on the working characteristics and the specific gain of height of a cell during discharge.

The data of these investigations show that a good performance of power sources may be obtained due to the special preparation of $LiBF_4/PC–DG$ electrolyte and the cathode based on FeS_2. Traditional power sources on the basis of a $Zn–Ag_2O$ system may be substituted by these cells.

4. Conclusions

1. In the choice of construction materials for the cathode of the current collector in lithium power sources, corrosion processes proceeding during storage and in the interval between discharges should be taken into account. The direction and the rate of corrosion processes depend on the potential difference between the cathode and the current collector, as well as on the overvoltage of conjugated electrochemical process, and may result in a power source self-discharge, current-collector destruction, and formation of side products of the decomposition of the electrolyte.

2. Aluminium is a promising material as cathode in a current collector on FeS_2.

3. In lithium power sources, electrochemical and chemical decomposition of the electrolytes take place in the working potential range of 1.5 V. The rate of these processes depends on electrolyte composition, nature of solid-phase oxidation conducting additives, as well as on the preparation of the electrolyte. Gaseous products evolved may increase the internal pressure in the cell. Electrolytes containing $LiBF_4/PC–DG$ have an advantage over studied ones.

Table 3
Characteristics of lithium cells with different solid-phase cathodes [a]; electrolyte 1 M LiBF₄/propylene carbonate–dimethyl ether of diethyleneglycol

Cathode composition	Discharge capacity (mAh)	Specific gain of height (mm/mAh)
FeS_2:CuO	115	0.002
$Pb_{1.8}Cu_{0.2}Bi_2O_5$	83	
$CuBi_2O_4$	97	0.001
FeS_2 (natural)	134	0.002
CuO	93	0.002
$Pb_2Bi_2O_5$	80	0.002
NiF_2	50	0.004
Fe_xS_y	90	0.003

[a] Diameter = 11.56 mm; height = 4.2 mm.

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