LITHIUM BATTERIES WITH SOLID POLYMER ELECTROLYTE

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Abstract

We investigated polymeric electrolyte from amorphous rigid chain polymer - poly(sulfide sulfone) and lithium perchlorate. It have high elasticity, mechanical durability and have sufficient adhesion to a material of electrodes. Tests of initial elements and secondary cells show that they have higher power parameters in comparison with the analogues with liquid electrolyte.

We developed original manufacturing techniques of cathodes for lithium power sources a current, which assumes hashing components of electrode weight (active component, binding, the electrowire additive) during plastic flow on the high pressure equipment. Average value of loss of specific capacity for 1 cycle makes

0,09 %, that is much lower, than at known.

Index Terms — accumulator, lithium, lithium secondary batteries, solid polymer electrolyte, gel-polymer electrolyte, poly-(hetero arilen), poly-(sulfide sulfone), lithium - manganese spinel.

Introduction

Deterioration of ecological conditions is connected to motor transport in the big cities. The vehicles with engines of internal combustion throw out 87% hazardous substances in an atmosphere. The contents of lead which inhabitants in the centre of Moscow and other areas with intensive transport streams in tens times breathe exceeds maximum permissible value. Only the direct material damage from air pollution exceeds 0,8 billion roubles per one year (in the prices of November 1998). In this connection transition to nonconventional vehicles - electric vehicle, electro-bicycle, scooter can become the cardinal decision of an environmental problem. For example, electric vehicle with the accumulators recharged from an industrial network, today on 97% cleanly vehicles with engines of internal combustion. Important value has reduction of noise level, improvement of comfortableness and working conditions of the driver. On the processes of introduction electric vehicle today render the big influence cost factors: cost electric vehicle in 2-5 times more cost similar car.

As autonomous energy sources is the storage batteries which isn't full satisfy to the requirements at cost of power consumption, ecological safety and the traffic safety. Today widely used lead acid, Ni – Cd and Ni - MeH accumulators. This accumulators have low energy density and contain highly toxic materials (lead, cadmium). Therefore now are developed new accumulators, such as lithium accumulators. Lithium accumulators with organic solvents have high specific energy, but have a low resource (100 cycles) because of passivation of lithium and dendrite formation [1]. Recently created the lithium - ionic accumulator with the anode from a carbonaceous material, in which ions of lithium were intercalated. Presence of carbonaceous aterials reduces capacity and voltage of the accumulator. Therefore the lithium - ionic accumulator can be the intermediate stage of creation the new accumulators. Now more perspective accumulators with polymeric electrolyte (PE) [2]. This accumulators are deprived the specified lacks. There also are more compact and convenient in assembly.

Polymer electrolyte based on poly(sulfide sulfone

Now aliphatic polymers is known as potential polymeric components for PE. The maximum quantity of works is devoted polyethylene oxide (PEO). However, serious lack PEO, interfering its practical use, is propensity to crystallization. That is causes low conductivity at room temperature - 10-6¸10-8 S×cm-1.

Conductivity about 10-4 S×cm-1 is increased at 80¸100 °C, however it is obvious, that at such temperature the source of a current can be used in very rare cases. Except for PEO as polymeric component PE investigated поли polypropylene oxide, poly-(ethylene adipate), poly-(alkylene sulphide), poly-(phosphagen). However electrolytes basis of these polymers have rather low conductivity, on exceeding 10-5 S×cm-1 at 35¸90 °C. The next step there was use gel-polymer electrolyte (GPE) which received to plasticize polymers a solution of lithium salts in organic solvent. The conductivity of GPE based on the polyacrylonitrile and polyvinylchloride reaches 2×10-3 S×cm-1 at room temperature. However the subsequent researches have shown, that lithium have been passivated in contact to these electrolytes.

In this work we investigated polymeric making aromatic polymer – poly-(hetero arilen) which exist, as a rule, in an amorphous condition. Poly-(hetero arilen), used as component PE, receive polycondensation at presence specially developed hight selective metallic macrogeterocicling polymeric catalyst. The big influence on conductivity PE is rendered with lithium salt concentration. It is established, that conductivity PE passes through extremum with increase of concentration of lithium salt. Maximal conductivity it is achieved at concentration of salt 1,1-1,2 mol/l [3]. Due to loss of crystals of salt in a deposit the further increase of concentration didn’t give results in deterioration conductivity. For investigated PE uniformity of properties is characteristic: conductivity does not depend on layer thickness. Convertibility of process of the charge - category in system Li-PE-Li was investigated during 350 cycles. The category was carried out on 100% of discharge capacities at density of a current 1,0-2,5 mA/cm2 and cycling depth up to 60 Kl/cm2. It is shown, that polarization all over again sharply grows, and then is slowly reduced if of discharge current was increased. At the charge - category in density of a current of 2,5 mA/cm2 polarization of lithium decreased during the first 100 cycles, and then remained practically a constant. The conductivity PE did not change in cycling process.

The given data testify that PE based on a poly(sulfide sulfone) have high stability of properties and decrease polarization in cycling process [4]. It is possible to believe, that it is connected by that during the charge - category the surface of lithium does not undergo serious changes. For check of this assumption the lithium electrode condition after 100 cycles of the charge - discharge in system Li-PE-Li. We also investigated accumulators of system Li-PE-LiMn2O4 by a method of electronic microscopy. We received micro photos of a lithium surface before and after cycling performance [5]. Studying of them has shown that originally on a lithium electrode surface there are particles of the needle form. During the charge - category alongside with particles of the needle form on a surface of an electrode particles of the scaly form are formed. As a whole the lithium electrode surface an electrode becomes more homogeneous in comparison with an initial condition. That fact is rather important, that the treeing centres on lithium electrode surface are absent. At use both liquid and polymer-gel electrolyte is possible to their interaction with a surface of lithium with passivate film formation. By the given results, at use PE based on a poly(sulfide sulfone) a such interaction is not present. It proves to be true the data received at research of a surface of the lithium anode by a X-ray photoelectronic spectroscopy after cycling during 100 cycles. Thus it is possible to draw a conclusion, that PE does not enter chemical interaction with metal lithium.

The received data, testify that PE based on poly-(sulfide sulfone) conductivity is highest. (Tab. 1.)

Table 1. *Polymer electrolyte conductivity*

Polymer electrolyte	Conductivity, $S \cdot cm^{-1}$
PEO-MC-3-$LiCF_3SO_3$[b]	$5 \cdot 10^{-5}$
PEO-TEG-$LiCF_3SO_3$[b]	$6{,}5 \cdot 10^{-5}$
PEO-Li TFSI	$5 \cdot 10^{-5}$
PEO-Li Tri TFSM	$3 \cdot 10^{-5}$
PEO-$LiSO_3CF_2SF_5$	10^{-5}
PEO-$LiCH(SO_2CF_3)_2$	10^{-4}
PSS- $LiBF_4$	10^{-2}
PSS-$LiClO_4$	10^{-3}
PEO-graft-polyester[d]-$LiClO_4$	10^{-5}

In the present work we carried out comparative tests of accumulators with liquid and solid - polymeric electrolyte [6]. Initiatingly the accumulator with liquid electrolyte has some advantage on a voltage, that electrode - electrolyte can be bound to smaller contact losses on boundary. But already from 5-th charge - discharge cycle, the accumulator with solid - polymeric electrolyte has more high voltage during all discharge. This result were speaks two phenomena. On the one hand there is "running-in" SPE to electrodes and ohm drops on phase boundary drop. On the other hand, it is interlinked to deterioration of the anodic polarization performance at the accumulator with liquid modified electrolyte. The given fact speaks that to 5 cycle on a surface of lithium the specific film who has a fixed ohmic resistor which is preserved in the further process of charge - discharge is formed. Presence of this film provides stable discharge of the accumulator of the given type since it interferes with formation of dendrites on a surface of the lithium anode. Thus, the scoring in a voltage of the accumulator with polymeric electrolyte is connected to smaller anodic polarization.

New cathodes for lithium accumulators

Lithium metals oxides are perspective cathode materials for the lithium accumulators. The most perspective materials in this line are connections of manganese, cobalt and the nickel, which capable is convertible to intercalation lithium ions and having in high electrochemical parameters. Manganese oxides is a most popular cathode materials because of it is much cheaper and more favorable to mass application. The basic materials used for manufacturing of positive electrodes, are lithium - manganese spinel.

One of the effective ways of influence on structure of firm bodies is their processing on the equipment of a high pressure such as Bridgman anvils. During such processing firm substances are exposed to joint influence of pressure in a range (1÷5)×106 Pascal and shift deformations; thus degrees of deformation can make hundreds and thousand times [7]. At the plastic deformation under a high pressure the structure of firm bodies of a various chemical nature - molecular crystals, metals, polymers - is sated with a plenty of structural defects: Dispositions, vacancies, vacancion clusters. Processing under a high pressure of mixes powder-like substances results in essential reduction of the sizes hetero-phase; in structure of separate components a plenty of defects is formed.

Now process of reception lithium - manganese spinel includes two basic stages. At the first stage mixing powder-like components (manganese dioxide with salts or lithium hydrate), and on the second - sintering of the received mixes at temperatures is higher 400 °C during tens hours. Was of interest to investigate structure and electrochemical properties spinels, in that case when mixes of the substances used for synthesis, at a stage of mixture were exposed to plastic deformation under a high pressure. Sample MnO2×LiOH, after processing under pressure and annealin at 400 °C represents fine-dispersed phase having structure badlyordered spinel, that is in an interval of temperatures 300 ÷ 400 °C there was a phase transition and formation of new structure. The sizes of microcrystals make the tenth shares of micron. Parameter of an elementary cell a=b=c » 8,18 ÷ 8,25A°. Thus, preliminary deformation under pressure of mixes MnO2×LiOH has resulted to that already after annealing at 400 °C there was a formation of a spinel monophase which in usual conditions receive at much higher temperatures (about 600 °C). The received phase is badlyordered and consists of ultra disperse particles, that is the conditions necessary for formation of efficient cathodes are satisfied. Comparison with spinels, synthesized in the way solid-phase reactions of interaction manganese oxides with connections of lithium by other authors, shows, that the new material has the smaller sizes of microcrystals and, accordingly, higher dispersiveness. Comparative digit characteristics of cathodes on a basis spinels, received by various ways [8, 9], at i=0,5 mA/cm2 testify that offered cathodes have a prize, both on specific capacity, and on potential of the category.

Concusions

New polymeric electrolyte based on poly-(sulphide sulhone) have highest conductivity. Tests of initial elements and secondary cells with electrolyte based on poly-(sulphide sulhone) show that they have higher power parameters in comparison with the analogues with liquid electrolyte.

Were developed original manufacturing techniques of cathodes for lithium power sources a current, which assumes hashing components of electrode weight (active component, binding, the electrowire additive) during plastic flow on the high pressure equipment. The cycling efficiency of this cathodes was 95 %. Average value of loss of specific capacity for 1 cycle makes 0,09 %, that is much lower, than at known.

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