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New lithium organic salts for promising polymer electrolytes

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Introduction

In polymer electrolytes, the inorganic lithium salts of LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 types and others are widely used as the traditional ion-conducting additives. Properties of the lithium salt used affect the performance of rechargeable lithium-polymer power sources. Lithium salts should provide:

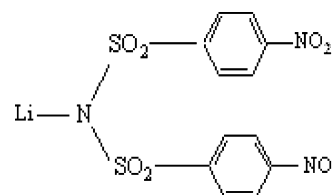
- Transport of lithium ions in polymer electrolyte and at the electrode/electrolyte interface
- Formation of passivating layers at the electrode/polymer electrolyte interface, which are changed during the repeated charge/discharge cycles

In the plasticized and gel-like polymer, electrolytes containing such aprotic solvents as plasticizers, cations and anions of lithium salts are mobile. As a rule the transport number of lithium ions in these systems is far less than 1 (usually ~ 0.5). Such a situation can result from the possibility of cation binding by polymer matrix polar groups (e.g., -O- in polyethylene oxide, -CN in polyacrylonitrile, -NR in polyamide, etc). In this case, an anion can contribute more to the conductivity than a cation can.

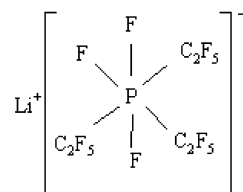
The problems of the undesirable participation of anions in ion transport and decreasing reactivity of polymer electrolytes relative to the electrode materials can be solved by using lithium organic salts with large anions. This is illustrated by the increased interest in the

application of new organic and inorganic lithium salts in the composition of polymer electrolytes:

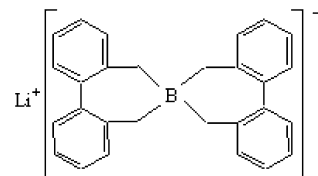
- Such lithium imide salts as monoatomic $\text{LiN}(\text{SO}_3\text{CF}_3)_2$, $[(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)]\text{NLi}$, $(\text{C}_4\text{F}_9\text{SO}_2)_2\text{NLi}$, etc types [1, 2], dilithium [3] and oligomer polyolithium perfluoroalkyl salts [4]
- Lithium bis-(4-nitrophenyl)sulfonilimide [5] of the structure formula:



- Alkylphosphate [5]



and organoborate lithium salts [6]



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Liquid and polymer electrolytes based on such material are characterized by the high conductivity ($\sim 10^{-3}$ S/cm) and electrochemical stability up to 5 V [1]. Besides, on the surface of a lithium anode they provide the formation of solid electrolyte interfaces (SEI) with the optimal morphology, conductivity and stability under the conditions of repeated cycling and high temperature.

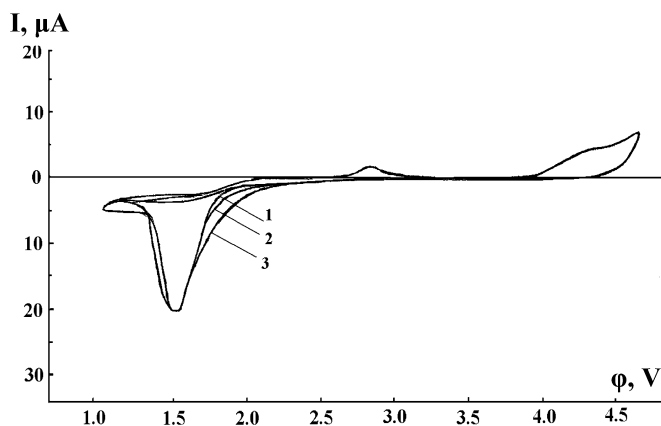


Fig. 1 Investigations of 0.5 M salt solutions in PC have shown that they are stable within the voltage range 1.1–4.6 V under the conditions of repeated cycling

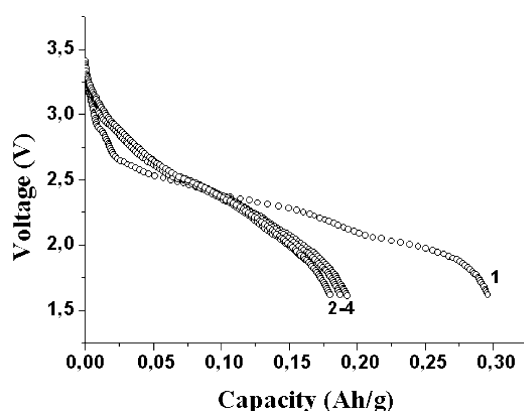


Fig. 2 Discharge characteristics of Li- V_6O_{13} system. Polymer electrolyte based on microporous PVDF modified by lithium salts of N, N'-disubstituted amides of pentane iminosulfonic acid. $I_{\text{charge}} = 120 \mu\text{A}/\text{cm}^2$. $I_{\text{discharge}} = 290 \mu\text{A}/\text{cm}^2$. Labels on curves correspond to cycle numbers

Application of the above salts as ion-conductive additives for solvent-free polymer electrolytes (without plasticizer additives) is of undoubted interest. It is supposed that in such electrolytes an organic anion will be able to play a part of the agent providing an increased mobility of the polymer matrix segments.

Nevertheless, high prices of the initial reagents and their complex production technology are the significant disadvantages of the presented lithium organic salts.

We carried out a series of investigations to develop the synthesis methods for new, previously unknown lithium salts of N,N'-disubstituted amides of alkane iminosulfonic acid.

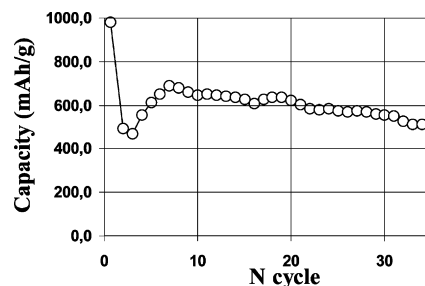
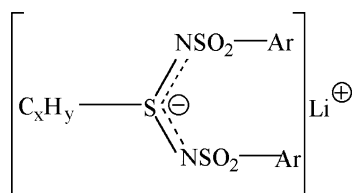


Fig. 3 Discharge characteristics of Li- FeS_2 system. Polymer electrolyte based on plasticized chlorinated PVC modified by lithium salts of N, N'-disubstituted amides of pentane iminosulfonic acid. Content of nanostructured FeS_2 (US Nanocorp., USA) in cathode is 30%. $I_{\text{charge}} = 15 \mu\text{A}/\text{cm}^2$. $I_{\text{discharge}} = 50 \mu\text{A}/\text{cm}^2$

Ar is aromatic group. The hydrocarbon C_xH_y can be methane, ethane, butane, propane, pentane, hexane, heptane, octane, nonane, or other alkanes.

Their synthesis can be accomplished using available raw materials by a method that does not require complex apparatus. They can be manufactured commercially in a short time.

The preliminary research carried out by the authors of the proposal has shown that these salts are thermally and electrochemically stable compounds which are easily-soluble in many aprotic solvents. Conductivities of 0.24 M solution of lithium salts of N,N'-disubstituted amides of pentane iminosulfonic acid in DMFA and 0.5 M solution in propylene carbonate are 4.9×10^{-3} and 5.2×10^{-4} S/cm respectively. Investigations of 0.5 M salt solutions in PC have shown that they are stable within the voltage range 1.1–4.6 V under the conditions of repeated cycling (see Fig. 1). Some representatives of this class of compounds are thermal stabilizers for halogen-containing polymers (PVC, chlorinated PVC, polyvinylidenefluorine).

Lithium salts of N, N'-disubstituted amides of alkane iminosulfonic acid were tested as components of polymer electrolytes based on chlorinated polyvinylchloride and PVdF copolymers.

Figure 2 and Fig. 3 show the discharge characteristics of the rechargeable electrochemical systems Li- V_6O_{13} and Li- FeS_2 with polymer electrolytes based on the PVdF copolymer and chlorinated polyvinylchloride, respectively.

The results show that, using the lithium salts with hyper-large anions, polymer electrolytes operational with 1.5 and 3.0 V lithium power sources can be prepared. It should be noted that the new lithium organic salts provide power sources with good discharge characteristics and stability during cycling.

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