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Compatibility of Aprotic Electrolytes with Negative Electrode Materials in Lithium-ion Batteries

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This short research presents an introduction to the fire safety of Lithium-ion batteries. Nowadays, as the most weak part of aprotic battery is its aprotic electrolyte. The aprotic electrolyte (commonly the mixture of aprotic solvents) that is used in Lithium-ion batteries have got low flash point with poor thermal stability. This paper describes using sulfolane as an aprotic solvent in Lithium-ion battery. Measurements were focused on performance, cyclability and stability of aprotic electrolyte with relation of graphite material as a negative electrode. Like a possible substitution of graphite, the LTO material was used and tested. Lithium Titanate Oxide (LTO) seems to be promising negative electrode material for Lithium-ion batteries.

Introduction

Litihum-ion batteries are without doubts one of the most promising kind of electrochemical energy sources. Nowadays, the quick development of lithium-ion batteries (hereinafter LiBs) going to get new sorts of LiBs with better capacity characteristics, higher specific voltage, high cyclability, material stability and other parameters. Using of LiBs in electronic applications like small portable devices is well-known, with evolution of electric cars, getting interesting to using the LiBs for electric propulsion. With using of LiBs in electric vehicles, as in high power applications, is coming to the forefront the question of safety of LiBs. In LiB system is most problematic part, by the viewpoint of fire safety, aprotic electrolyte. Aprotic electrolytes use in LiBs, have poor thermal resistance, during thermal stressing occurs to electrolyte decomposition. Product of electrolyte decomposition can take gas or solid state and getting worse battery characteristics and may lead to evolution of hydrogen gas. The evolution of hydrogen and other gasses may cause dangerous mixture in case of contact with oxygen, especially in enclosure space. For high power applications is necessary to find out aprotic electrolyte that can be stable in wide range of temperatures at maintaining of good electric conductivity. Another request on aprotic electrolyte can be set as

electrochemical compatibility with electrode material in the range of working electric potential window. The most widespread material for negative electrode into LiBs is graphite. Graphite is stable and good working active material, its operation is based on intercalation reaction of lithium atoms among grapheme sheets. Negative electrodes made from graphite have discharge potential plateau around 0.25 V vs. Li/Li⁺ and theoretical capacity 372 mAh/g. In LiB's cell arises on negative electrode and electrolyte interface the Solid Electrolyte Interface (SEI) layer. The layer is being formed during first few charge-discharge cycles and is made by the decompositions products of electrolyte. Properties of SEI layer significantly influences LiB characteristics like self-discharge rate, current loading, lifespan and cyclability of LiB etc. This layer is necessary for proper operation of LiB. The composition, constitution and structure of SEI layer depends on the electrolytes which were used, thus on aprotic solvents used in. (1, 2, 3, 4, 5)

Among the new materials for negative electrode, which have been discovered in recent times, belongs Litihum Titanate Oxide, Li₄Ti₅O₁₂ (LTO). LTO has in comparison with graphite different spinel structure, good reversibility and stability. The LTO material has the higher discharge potential plateau approx. 1.55 V vs. Li/Li⁺, theoretical capacity of LTO is 175 mAh/g. The high redox potential of LTO reduces electric power that can be supplied to load, this drawback can be solved by using high voltage positive materials for example LiNi_{0.5}Mn_{1.5}O₄. This high voltage materials give nominal voltage around 4.9 V vs. Li/Li⁺ in comparison with standard cathode materials which provide voltage around 3.7 V vs. Li/Li⁺. On the other hand, as an advantage of high working potential allows to using different kinds of electrolyte solvents without their decomposition at low electrode potential. The high working electrode potential also inhibits the growth of lithium dendrites, which may cause a short circuit of cell. (6, 7, 8, 9)

Results and Discussion

In experiments were used two kinds of negative electrode materials for LiB. Natural graphite, type COND CR5995 (manufacturer Graphite Týn. s.r.o.) and alternative material to conventional graphite the LTO. As an electrolyte was used sulfolane $(C_4H_8O_2S)$ with LiPF₆ salt in 1 mol concentration. First measurement was performed as a set of graphite electrode (as negative electrode) and sulfolane electrolyte. The cell was connected in half-cell arrangement, where the counter electrode was made from metal lithium. Obtained characteristics are depicted in Figure 1 and Figure 2 below.

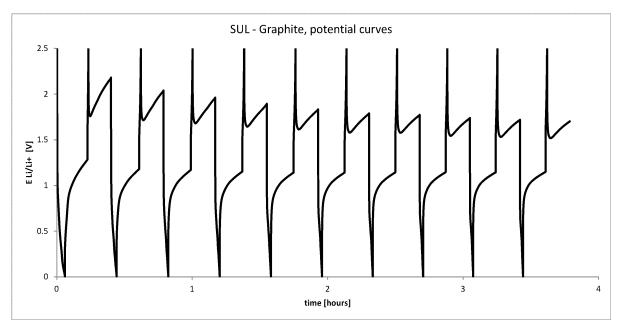


Figure 1. Charge-discharge characteristics of graphite.

As is shown in Figures, the graphite material is decomposed by sulfolane solvent, thus it is losing almost all its potential capacity. The maximum capacity in first cycle is 5 mAh/g. Based on these poor results, has been approached to testing of LTO material that has got spinel intercalation structure.

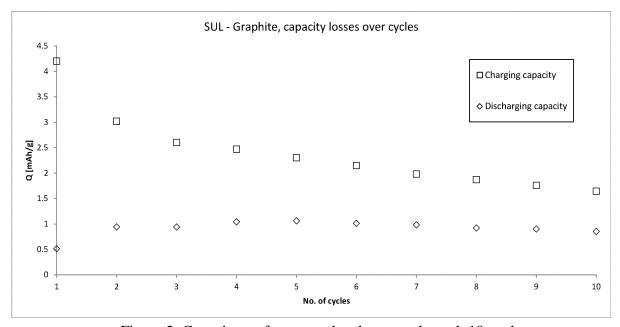


Figure 2. Capacity performance development through 10 cycles.

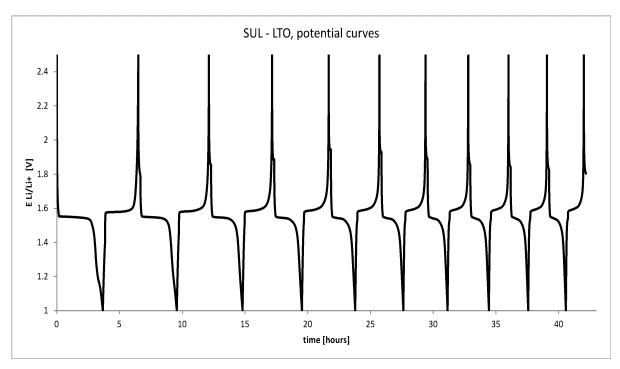


Figure 3. Charge-discharge characteristics of LTO.

As can be seen from Figure 3 above, there is no LTO material decomposition by sulfolane. The capacity performance reach its maximum in first charging cycle where it hit 119mAh/g. This results allow to keep on LTO testing and opening another space for further research of LTO material as one of the most promising material for negative electrode for LiB.

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