LI-ION ACCUMULATORS – COMPARISON OF CATHODE MATERIALS

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Abstract: The issue of energy storage becomes increasingly important with the growing need for safe and clean energy that could be used in portable electronics and electric vehicles. This paper shortly introduces the topic of lithium-ion accumulators, compares currently used cathode materials and discusses promising future materials.

Keywords: Accumulator, Li-ion accumulator, cathode, electric vehicle, high-voltage cells, Li-S

1 INTRODUCTION

The options of energy storage have evolved considerably since the very first electrochemical cell was invented by Alessandro Volta at the end of the eighteenth century. And yet this technology still has a potential of development. Energy, or the lack of it, is one of the greatest issues of our time. Batteries and accumulators play an essential role in everyday life; they provide a wide variety of applications, from small accumulators running pacemakers and most of the applications in our mobile phones, to accumulators that power electric vehicles. Therefore, lithium-ion accumulators are of growing importance. This paper, through the analysis of literature, presents a brief comparison of the currently used and future positive electrode materials for Li-ion accumulators, their benefits and applications.

2 ACCUMULATORS

Accumulators are electrochemical sources of current that transfer chemical energy into electrical energy. The basic unit of an accumulator is an electrochemical cell, which is formed by positive and negative electrode and an electrolyte. Electrochemical sources of current can be further divided into primary and secondary sources, or batteries and accumulators. As opposed to battery, accumulator is electrically rechargeable. [1][2]

The year 1859 is an important milestone in the matter of energy storage. In 1859, the first rechargeable lead-acid accumulator has been invented. More than one hundred years later, lead-acid accumulators are still used in large numbers. This scientific breakthrough was followed by the invention of nickel-cadmium accumulator. Another turning point came in 1991 as the first lithium based accumulator was released by Sony. Thenceforth, lithium based accumulators have become the most frequently used option for electrical energy storage. [3]

2.1 WORKING PRINCIPLE

The working principle (see figure 1) of Li-ion accumulators is based on the interchange of lithium ions between the positive and negative electrodes through electrolyte. These lithium ions carry electric charge. This movement of ions is similar to that of a rocking chair and hence the term *rocking chair battery* is sometimes used. The lithium ions are reversibly removed or inserted into the active material of the electrodes. The electrode materials are so called intercalation compounds.

The negative electrode material is usually a graphitic carbon, whereas the positive electrode materials are lithium oxide compounds. Regarding cathode materials, there is no practical use of pure lithium oxide; at present, $LiCoO_2$, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, $LiMn_2O_4$ and $LiFePO_4$ belong to the most frequently used cathode materials. [1][2]

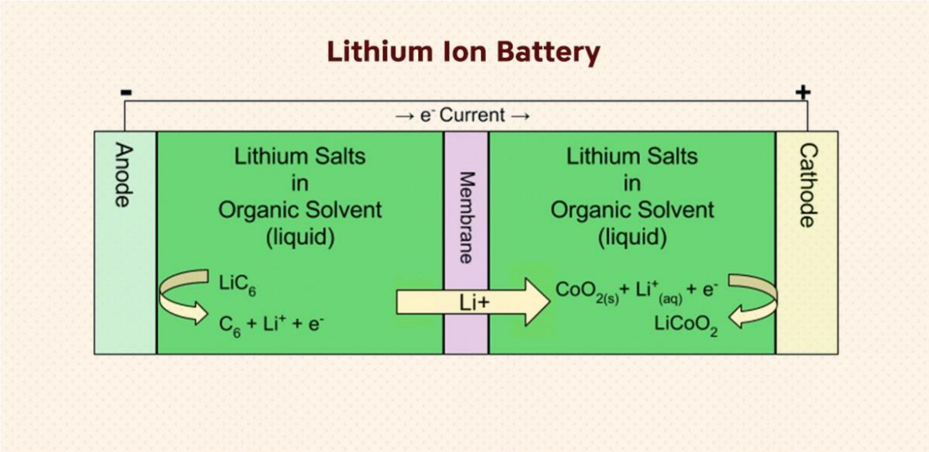

Figure 1: Working principle of a Li-ion cell [7]

2.2 Currently used materials

The latest cathode material is $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$, which was created from $LiNi_{0.5}Mn_{0.5}O_2$ by adding cobalt and therefore improving the stability of the material structure. This compound offers the voltage of approximately 3.8 V and the capacity of 160 mAh/g. However, the use of cobalt might be considered a disadvantage of this compound due to its high price. As far as future is concerned, the electrochemical properties of this material could be enhanced, for instance by coating the electrode with a thin layer of graphite. $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ undoubtedly has the potential to replace $LiCoO_2$, which is the most widely used cathode material nowadays. [4]

Compared to the previous material, $LiCoO_2$ reaches the voltage of 3.88 V, but at the same time it has lower capacity, approximately 140 mAh/g. Even though its theoretical capacity is 274 mAh/g (nearly double the achievable capacity), the structure of the material may collapse during de-intercalation as the lithium ions are removed from the structure. Further disadvantages of this material are thermal instability at temperatures higher than 180 °C and high price of cobalt. [4]

High price of cobalt is the reason for research into new convenient compounds. For instance, $LiFePO_4$ with the voltage of approximately 3.4 V and capacity about 170 mAh/g. $LiFePO_4$ is a perspective material, particularly for its lower cost and nontoxicity. Lithium iron phosphate also exhibits great stability during cycling. Nevertheless, this material has low conductivity at room temperatures. [5]

Another frequently used material is $LiMn_2O_4$. As well as $LiFePO_4$, $LiMn_2O_4$ is characterized by low productional cost and environmental friendliness. Although it offers higher voltage (4.0 V), its capacity is lower (120 mAh/g) compared to the previous compounds. However, the capacity of this material decreases radically during cycling and also during storage in both charged and discharged state, which is a serious drawback. [4]

The development of new materials focuses on developing materials that would reach the voltage of 5.0 V. High-voltage cathode materials might find its utilization in the field of electromobility.

2.3 HIGH-VOLTAGE MATERIALS

$LiNi_{0.5}Mn_{1.5}O_4$ is one of the high-voltage materials derived from $LiMn_2O_4$. The voltage of 4.7 V and high theoretical capacity 148 mAh/g make this material suitable for use in electric vehicles. Energy density of this compound is 20 % higher than that of $LiCoO_2$ and even 30 % higher than that of $LiFePO_4$. [4]

$LiCoPO_4$ offers voltage of about 4.8 V and high energy density of nearly 800 Wh/kg. However, this value is only theoretical. This material is not used in practice due to its low electric conductivity. Its electrochemical properties could be improved by conductive carbon coating. [4]

As for the future, sulphur seems to be very attractive and promising element. The positive electrode of a Li-S accumulator consists of sulphur and a conductive additive, which is carbon, and the negative electrode is made of metallic lithium. [6] Very high theoretical capacity of 1675 mAh/g makes this system attractive especially for automotive industry. In addition, sulphur is naturally abundant and cheap material. On the other hand, sulphur is an insulant, which results in poor electric conductivity of the material. What is more, sulphur is subject to volume expansion during cycling, which might seriously damage the entire cell. [4][6]

3 CONCLUSION

It seems that not only water is crucial for life today. Electrical energy has become nearly as important as water. Even though the most widely used accumulators employ $LiCoO_2$ as the cathode material, there are growing efforts in high-voltage materials research. The long-term trend for vehicle electrification enhances the efforts to find a high-voltage, high-capacity accumulator that would be applicable in power electronics and might serve as an option of electrical energy storage. Despite the fact that the systems Li-S are still in the stage of technological development, they belong to the most promising and perspective accumulators. In addition, a new breakthrough has been announced recently by one of the co-inventors of lithium-ion battery, John Goodenough, giving the accumulators a new direction.

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