The Use of Lithium-Ion Batteries as the Most Promising Traction Current Sources

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Abstract: The article describes the advantages and disadvantages of using lithium-ion batteries as the most promising traction current sources. The greatest number of cycles is typical for lithium titan ate batteries. This is primarily due to the use of heavy metal as an anode material. This structure provides a long service life, high charge-discharge currents, as well as a wide range of operating temperatures. The main disadvantage of this type of battery is its low specific energy intensity compared to other materials. This is primarily due to the low battery voltage level. The use of modified lithium nano-titanate makes it possible to increase the specific energy intensity by 2 times, but this improvement significantly increases the cost of batteries.

1 INTRODUCTION

In most modern Li-Ion batteries, the negative electrode is made of carbon materials. In such batteries, not lithium metal or its alloys with other metals are used as a negative electrode, but an intercalation compound of carbon with lithium. Carbon turned out to be a very convenient matrix for intercalation (introduction) of lithium. The specific volume of many carbons graphitized materials changes by no more than 10% when a sufficiently large amount of lithium is introduced. Carbon electrodes containing not too much intercalated lithium have a potential 0.5–0.8V higher than the potential of the lithium electrode (Daminov et al., 2022a). In order for the battery voltage to be high enough, lithium cobalt oxides (lithium-cobalt), manganese spinel, lithium iron phosphate, and so–called multi-oxides (mixed oxides) were used as the active material of the positive electrode. The potential is approximately 4 V relative to the lithium electrode, so that the operating voltage of the battery has a characteristic value of 3.5−3.8 V. When the battery is discharged, lithium is deintercalated from carbon material (on the negative electrode) and lithium is intercalated into oxide (on the positive electrode). When charging, the processes go in the opposite direction. Thus, there is no metallic lithium in the entire system, and the discharge and charge processes are reduced to the transfer of lithium ions from one electrode to another. That is why the authors of such a battery introduced the term — lithium-ion battery. At the same time, the name "rocking chair type battery" (rocking chair cell) (Wei et al., 2024) or "swing" batteries became stronger for this type of batteries.

In the vast majority of lithium-ion batteries brought to the stage of commercialization, the negative electrode is made of carbon materials.

2 MATERIALS AND METHODS

The current-forming process on a negative electrode is described by the equation $6C + xLi^+ + xe^- \leftrightarrow Li_xC_6$. The forward process corresponds to the charge, and the reverse process corresponds to the discharge of the battery.

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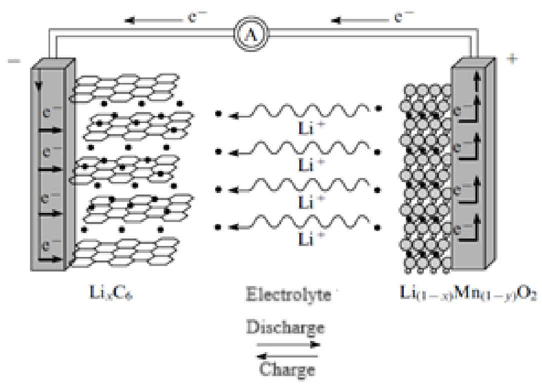

Figure 1: Schematic diagram of the operation of a lithium-ion battery

A schematic diagram of the operation of a lithium-ion battery is shown in Figure 1. On the left is a negative graphite electrode. Its structure is characterized by the presence of layers between which lithium ions can be embedded (black dots). On the right is a positive electrode made of lithium-manganese spinel, in the structure of which lithium ions can also be embedded. Solutions of lithium salts in non-aqueous solvents are used as an electrolyte.

Lithium-ion batteries obey the laws common to all types of batteries. An ideal battery should be completely reversible: all electricity should be spent only on current-generating charge and discharge reactions (in other words, the current output of these processes should be 100%). In a real battery, there are always some processes (electrochemical and chemical) in addition to current-forming reactions. A certain amount of electricity is consumed for these extraneous processes (usually irreversible). As a result, at each cycle, the discharge capacity is less than the amount of electricity consumed at the previous stage of the charge. In addition, as cycling goes on, the capacity decreases from cycle to cycle. The nature of irreversible processes in batteries of different electrochemical systems is different.

Processes on the positive electrode of a Li-ion battery.

If a variety of active materials for the positive electrode are used in primary lithium cells (meaning non-rechargeable cells), then in lithium batteries the choice of positive electrode material is limited. Lithiated cobalt or nickel oxides, as well as lithium-manganese spinels are used here. Currently, materials based on mixed oxides or phosphates are increasingly used as cathode materials. It is shown that the best characteristics of the battery are achieved with cathodes of mixed oxides. Technologies of cathode surface coatings with finely dispersed oxides are also being mastered. The problems of synthesis of these compounds associated with the difference in the structures of nickelate (layered hexagonal) and lithium manganate (layered rhombohedral) were overcome by using nickel and manganese double hydroxide systems for synthesis, after which work towards the synthesis of mixed oxides began to be intensively carried out in different countries (USA, CANADA, South Korea, China) (Matmurodov et al., 2024, Wang et al., 2004, Shlyakhtin et al., 2004, Kovtun et al., 2024, Musabekov et al., 2023).

High rated voltage, a gentle discharge curve, high efficiency of the charging-discharge process, good capacity and cyclability, acceptable self-discharge, ease of production in industrial conditions explain the most widespread use of lithium cobalt in commercially developed LIAS, which provides a reversible capacity of positive electrodes of 135-150 mAh/ g when cycling LIAS in the voltage range of 2.5-4.3 V. Smaller particle size, more uniform distribution and the formation of small-sized agglomerates of small spherical particles contribute to improving the electrochemical characteristics of the cathode material.

Modification of lithium – metal–oxide compounds by doping them, including multidoping with various elements. The introduction of the latter improves the stability of the electrochemical characteristics of the cathode material during cycling by stabilizing its structure and reducing the tendency to phase transitions.

Table 1: The main manufacturers of cathode materials.

Chemical formula of the cathode material	Country of origin	Manufacturing company
LiCoO2	Japan	Nippon Chemical industry Co.; Simimoto Co.
USA		OMG
Germany		Merck KGA
South Korea		Umicore
China		Shanghai Shanshan Science & Technology Co.
LiNi1-yCoyO2	Japan	Simimoto Co.; Seimi Chemical Co
Germany		Merk KGA
LiMn2O4	Japan	Mitsui Mining & Smelting Co. Ltd
USA		FMC Corp
Germany		Merk KGA

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The search for other compounds with stable structures led to the creation of a cathode material with the formula LiNi0.33MN0.33Co0.33O2.The discharge capacity of the resulting compound, which has good cyclability, at a final voltage of 4.3-4.6 V was 159-200 mAh /g, respectively. Doping of this compound with silicon leads to an increase in the parameters of the crystal lattice, which is accompanied by an increase in specific capacitance, speed capabilities and cyclability, as well as a decrease in impedance.

3 RESULTS AND DISCUSSION

During operation (cycling and storage) LIA the most significant changes occur on electrodes made of lithium-manganese spinals.

During table cycling at room temperature, the relatively unstable two-phase structure of LiMn2O4 turns into a stable single-phase one with the loss of Mn3+ and the formation of MnO2, which transforms during lithium intercalation into inactive LiMnO2 with a layered structure. When a positive electrode based on lithium-manganese spinel is recharged to potentials below 3.5 V, a distortion of the crystal structure according to Jan-Teller (Bazarov et al., 2024, Chen et al., 2024, Yehorov et al., 2024, Sessa et al., 2018, Uddin et al., 2016) appears, leading to the dissolution of spinel and slow degradation of the capacity during cycling.

Negative electrodes. Carbon materials

In the initial period of development of lithium-ion batteries, many carbon materials with the ability to reversibly intercalate lithium were investigated. The earliest studies concerned the intercalation of lithium into graphite. Graphitized materials include natural and synthetic graphite, highly oriented pyrolytic graphite, modified graphite materials, including MCMB (from the English "mesocarbon microbeads"), carbon powders. Only some types of carbon materials are widely used commercially, which can be divided into two groups: materials with a highly ordered crystal structure and with a disordered structure (Casals et al., 2017, Kandasamy et al., 2017, El Ghossein et al., 2019, Müller et al., 2019, Zhang et al., 2018, Burzy´nski et al., 2019a, Dudley et al., 2017).

Every six carbon atoms form graphene sheets, similar to honeycombs. These graphene sheets under the action of Vandervaals forces form graphite layers, the latter, located parallel to each other, form a graphite structure. From the point of view of crystallography, the term "graphite" is applicable only to carbon forms having a linear spatial structure with an ideal ordered arrangement of graphene layers. There are two types of graphite phases – hexagonal (α-phase) and rhombohedral (β-phase). The rhombohedral phase is stable at lower temperatures and therefore shows better stability during cycling.

To date, many different carbon materials have been studied and the industry has mastered the production of some special materials for the negative electrodes of lithium-ion batteries. Examples of such materials can be the MCMB material. However, research on carbon materials for lithium-ion batteries is still ongoing, with special attention being paid to various nanofiber materials, nanotubes, nanocomposites, graphene nanoparticles, etc. (Casals et al., 2018, Jinlei et al., 2019, Lai et al., 2018, Zhang et al., 2016).

Reversible processes on carbon materials

The maximum amount of lithium that can be embedded in carbon is 1 lithium atom per 6 carbon atoms (equation (1), $0<x<1$). Lithium is embedded through a prismatic surface. Insertion through the basal surface is also possible, but only if there are defects on this surface.

The mechanism of lithium intercalation into graphite is the sequential filling of the space between graphene layers with lithium. This process can be described by a step index, which is equal to the number of graphene layers between the two closest lithium layers. At maximum filling, there will be only one graphene layer between the lithium layers, and this state will correspond to stage No. 1. Each stage is characterized by a reversible potential and corresponds to a certain concentration of lithium in the graphite matrix. The transition through the steps looks like this:

1. LiC72 + Li ↔ 2 LiC36
(Stage 8) (stage 4)
2. 3 LiC36 + Li ↔ 4 LiC27
(4 Stage) (3 Stage)
3. 2LiC27 + Li ↔ 3LiC18
(3 Stage) (2 Stage)
4. 2LiC18 + Li ↔ 3LiC12
(2 Stage) (2 Stage)
5. 2LiC12 + Li ↔ LiC6
(2 Stage) (1 Stage)

The mechanism of the introduction of lithium into non-graphite carbon materials has not yet been fully elucidated. But, at least, three types of interaction of lithium and carbon material are assumed: interaction with graphene layers, with the surface of polynuclear aromatic planes and the introduction of lithium into micro-voids on the frontal surface of the carbon material. When lithium is intercalated into non-

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graphite materials, lithium is filled simultaneously throughout the entire volume of the carbon material, so the charge-discharge curve has a smoothed appearance, and there are no clear steps on the charge-discharge curve (Nájera et al., 2017, Barcellona et al., 2017, Umerov et al., 2024, DeHoog et al., 2018, Chin et al., 2018, Daminov et al., 2022, DeSutter et al., 2018, Fang et al., 2019, Xia et al., 2021).

Table 4 shows a list of operational indicators of LIA with different chemical composition of the cathode and anode.

Table 4: Comparative characteristics of electrochemical systems used for the production of lithium-ion batteries

Type (formula) of electrochemical system, cathode/anode materials	Specific energy intensity (Wh/kg)	Resource, (the number of charge discharge cycles of 1C discharge depth 80 %	Permissible charge/discharge rates in units that are multiples of the nominal capacity With – (hourly discharge current)	Operating temperature range without the use of passive or active thermal compensation systems
1	2	3	4	5
$LiCoO_2$/C	150-190	≤ 200	0,5C/1C	-15-+50
$LiMn_2O_4$/C	135	≤1500	2C/5C	-30-+50

4 CONCLUSIONS

Lithium-ion batteries have emerged as the most promising source of traction current for modern electric vehicles (EVs), primarily due to their superior energy density, long cycle life, and relatively low self-discharge rates. These batteries represent a significant advancement over traditional lead-acid and nickel-metal hydride batteries, offering a more efficient and sustainable solution to meet the growing demands of electric mobility.

One of the key advantages of lithium-ion batteries is their high energy density, which allows for longer driving ranges on a single charge. This makes them ideal for EVs, where maximizing range is crucial for consumer acceptance and widespread adoption. Additionally, lithium-ion batteries are known for their longevity, maintaining their capacity over many charge-discharge cycles, which translates to a longer operational lifespan for EVs.

Moreover, lithium-ion technology is characterized by a relatively low self-discharge rate, meaning that the batteries retain their charge for extended periods when not in use. This feature is particularly beneficial for EV owners who may not use their vehicles daily, as it ensures that the battery will still have a substantial charge even after being idle for some time (Noh et al., 2019, Somakettarin et al., 2019, Burzy´nski et al., 2019b, Venugopal et al., 2019, Worwood et al., 2018, Fan et al., 2019, Han et al., 2019, Harting et al., 2019, Hildebrand et al., 2018, Osara et al., 2019, Kuo et al., 2019, Wu et al., 2018, Daminov et al., 2022).

Another significant benefit of lithium-ion batteries is their efficiency in energy conversion, which reduces the overall energy loss during charging and discharging. This efficiency contributes to lower energy costs and supports the economic viability of EVs in the long term.

However, challenges such as safety concerns, particularly regarding thermal runaway, and the environmental impact of battery production and disposal, must be addressed to fully realize the potential of lithium-ion batteries. Ongoing research and development are focused on improving battery safety, enhancing recycling processes, and exploring alternative materials that could further reduce environmental impact.

In conclusion, lithium-ion batteries stand out as the most promising traction current sources for electric vehicles, offering a combination of high energy density, long cycle life, and efficiency. With continued innovation and improvements, these batteries are poised to play a pivotal role in the future of sustainable transportation.

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