Analysis of factors affecting the capacity of LI-ION rechargeable batteries at low temperatures

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Abstract. This work analyses the factors affecting the capacity of rechargeable chemical electrical power sources. Primarily, it is focused on the classification of these factors and the development of recommendations for increasing the capacity of batteries. We propose an original approach to the Li-ion rechargeable batteries operation, that is mandatory input control and several charge/discharge cycles before placing Li-ion accumulator battery into the operating device. We propose a method for periodic control of Li-ion accumulator batteries in particularly important devices and for the concept of predictive repair. The charge volume loss during operation of a Li-ion rechargeable battery at sub-zero temperatures was assessed quantitatively. The engineered method and the created device can be used when operating a Li-ion accumulator battery at sub-zero temperatures, in the far north, or in the case of increased reliability requirements for devices running on Li-ion rechargeable batteries. Further research will be aimed at the automated monitoring of the state of Li-ion accumulator battery, as well as the possibility of integrating this development into devices using Li-ion accumulator battery in advanced smart systems.

1. Introduction

Among all the possible methods of accumulating electricity, the most widespread are rechargeable chemical electrical power sources. Among the rechargeable chemical electrical power sources, Li-ion rechargeable batteries are widely used and intensively developing at the moment [1].

Li-ion rechargeable batteries are currently actively replacing the previous generation of lead-acid rechargeable batteries. Li-ion rechargeable batteries are widely used because of their large range. They are used wherever it is necessary to separate the processes of generation and use of electricity by time and/or place [2, 3]. Small-sized Li-ion accumulator battery are used in mobile phone, tablets, flashlights, radio stations and other wearable technical devices [3]. Assembled Li-ion accumulating stations, consisting of hundreds of Li-ion energy cells (accumulator batteries) and occupying entire buildings, ensure the operation of complexes for generating electricity from renewable energy sources (RES) for tens and hundreds of megawatts [4] or provide electric energy reserve for small enterprises, settlements and special-purpose facilities (medical, military, etc.), where it is necessary [1,4,5]. Li-ion rechargeable batteries are distinguished by a high volume (kWh) of accumulating electric energy per unit mass, ease of operation, lack of battery memory, long service life, high discharge currents, and, recently, low cost because of significantly increased volumes of their production [6,7].
The popularity of use and the significant contribution of Li-ion accumulator battery technology to the development of mankind is confirmed by the Nobel Prize in Chemistry, awarded in 2019 to scientists who made a great contribution to its development – John Goodenough (American physicist), Stanley Whittingham (British chemist) and Akira Yoshino (Japanese chemist) [6,7].

Thanks to the Li-ion accumulator battery technology, the development of electricity generation from RES was significantly stimulated, since their use enables to accumulate considerable amount of energy, thereby eliminating the mismatch between the time of its production and consumption [3,4,8,9].

Unfortunately, despite all their advantages, Li-ion accumulator batteries have disadvantages and difficulties in organising their operation [10,11,12]. The operating principle and the basic technology of Li-ion accumulator batteries were described 40 years ago [13,14]. Some operating problems of Li-ion rechargeable batteries were the part of its technology and have not been completely resolved until now [9,14,15].

The main difficulty is their exactingness to charging modes, as well as the necessity of avoiding overcharging. In order to control the operation of a Li-ion accumulator battery, monitoring controllers are used that control the charging and discharging (operation) of a Li-ion accumulator battery. Li-ion accumulator battery has a certain charge capacity, which it is able to accumulate and subsequently release. But their actual charge capacity differs from the charge capacity declared by the manufacturer up to 15%, which is normal and corresponds to the error set by the manufacturer [10,15]. When operating several Li-ion rechargeable batteries in an integrated bundle, they require initial calibration and subsequent balancing during operation. These measures are necessary to assemble the entire bundle of elements with the same capacity and individual charging of each cell (a separate Li-ion accumulator battery). This is done to ensure the maximum normalised charge of each cell and to eliminate the influence of cells with a lower capacity on cells with a higher capacity. Different cell capacities can appear both when assembling an integrated bundle of various Li-ion rechargeable batteries, and in operation when battery cells deteriorate. Deterioration percentage is individual for each Li-ion cell in the assembly [12,13].

If several cells in one battery operate with the same initial parameters, and the same operating conditions, the drop in capacity due to degradation can vary up to 7%. Another disadvantage of Li-ion rechargeable batteries is the tendency to self-discharge in the idle state. Self-discharge per day can reach 1% of the remaining charge. Self-discharge of Li-ion rechargeable batteries is especially dangerous in case of long-term idle storage. In this case, the Li-ion rechargeable battery can be discharged entirely, become immune to charge currents, and completely lose its performance [12,13].

One of the most negative features of a Li-ion rechargeable battery, in our opinion, is the negative effect of ambient temperature on its properties. With a decrease in temperature, the battery capacity and the output currents decrease, and the output voltage parameter becomes unstable. In order to improve the efficiency and operational reliability of Li-ion rechargeable batteries, it is necessary to study the dependence of their capacity on the operating temperature and solve the problem of incoming control of new Li-ion rechargeable batteries [2,12,13,14].

In order to determine the dependence of the Li-ion accumulator battery capacity on the ambient temperature and to carry out an input control of the actual capacity of a Li-ion accumulator battery and its change during the first discharge/charge cycles, it is necessary to design and create a device that could charge Li-ion accumulator battery to the required voltage and discharge with certain currents, as well as fix the necessary operating parameters of a Li-ion rechargeable battery for their analysis and further processing. After the experiment is carried out, it is necessary, on the basis of its results, to develop guidelines to ensure effective trouble-free operation of Li-ion accumulator batteries. This article is concerned with generalising the existing experience and solving these problems.

2. Analysis of methods for using Li-ion accumulator batteries and monitoring their condition

Methods used in this work: analysis of the existing experience in using Li-ion rechargeable battery; experiment, formalisation of its results and synthesis of the obtained experimental results with the conditions of the experiment.
As noted above, Li-ion rechargeable batteries are widely used in electricity generation units based on RES [15, 16]. The problem of mismatch in time between the energy supply and the electric energy consumption was solved by energy accumulation and storage in Li-ion accumulator batteries integrated into high-capacity batteries integrated into high-capacity batteries [16, 17]. The intensity of development of units for electricity generation from RES is currently caused by the emergence of Li-ion accumulator batteries. Therefore, the emerging RES power generation market created a high demand for Li-ion accumulator batteries. The increase in the production of Li-ion accumulator batteries led to the improvement of production technology, economies of scale and a decrease in their market cost [18-20]. The affordable cost of Li-ion accumulator batteries gave another impulse to their development and distribution. Li-ion accumulator batteries became more affordable, and the number of devices with their use was increased. We can say that the peak of the modern development of Li-ion accumulator batteries is their use in electric cars, the creation of which became possible largely thanks to them. A large storage volume of electricity, a short charge time, a large number of charge/discharge cycles without significant loss of capacity — all of this enabled using Li-ion accumulator batteries as a source of electric energy for an electric car engine and associated systems.

Electric cars are not yet widespread at the moment, and the experience of their operation still concerns only countries with a warm temperate climate. The countries, in which they have spread, are the countries of Europe, Japan, the United Arab Emirates and the southern states of the United States. This geography can be explained by the place of the technology's origin and the economic well-being of these regions, as well as by a temperate, warm climate. The first experience of operating electric cars in Russia and in other countries with cold climate revealed great problems associated with the effect of low temperatures on Li-ion rechargeable batteries. Under the low temperatures, the electrolyte in Li-ion rechargeable battery loses its properties, its internal resistance increases, and, as a result, the current output decreases, and the capacity of such batteries decreases significantly. In particularly extreme operating conditions, the voltage at the outputs of even charged Li-ion rechargeable batteries may be decreased below the permissible level, which causes the deactivation of the powered device. An example of this case is a self-deactivation of a mobile phone with a Li-ion rechargeable battery is it is operated at low temperatures (-5...-20 °C), followed by a regular (trouble-free) switch-on in a warm room.

An unsuccessful experience of using Li-ion accumulator batteries with solar panels was in Yekaterinburg. For lighting and indication of pedestrian crossings, LED illumination complexes were installed with autonomous power supply from solar panels with Li-ion accumulator batteries as energy storage devices. Unfortunately, the short daylight hours and the extremely low temperatures of the Russian winter did not allow this complex to generate and store enough electricity for the LED illumination to operate for the required time. Due to the cold and lack of light, solar batteries and Li-ion accumulator batteries were unable to maintain the operation of LED pedestrian crossing lights. This equipment proved to be ineffective and was dismantled due to frequent failures [18].

Another example of operating Li-ion accumulator batteries in ground transport is the launch of trolleybuses with an electric engine in Moscow. They were able to follow routes without power lines throughout their entire length. To be able to follow the route without power lines, the trolleybuses were equipped with additional Li-ion accumulator batteries, which were charged on the route with power lines and power the electric motors in the route segments without them. This type of transport had to be additionally equipped with liquid fuel heater for heating the passenger compartment and equipment. This decision was made due to the ineffectiveness of using a Li-ion rechargeable battery to heat the trolleybus passenger compartment. Also, when operating electric vehicles on Li-ion accumulator batteries in Russia in the cold season, it is necessary to especially carefully calculate the route duration outside the coverage of power lines and (or) the runtime on one charge of the Li-ion accumulator battery. In case of deterioration of Li-ion accumulator battery (deterioration of its characteristics, primarily capacity) due to exhaustion and (or) decrease in reliability of current output due to low temperatures, the Li-ion accumulator battery charge may not be enough for the vehicle to reach the final destination of the planned route. Given the vast geography and low temperatures prevailing in some areas of our homeland, Russia, this situation can cause very unpleasant consequences.
3. Methods and means for checking and monitoring the state of li-ion accumulator batteries

In order to prevent this or similar situations, the authors set up an experiment using equipment of their own design. The purpose of the experiment was to determine the actual capacity of a Li-ion accumulator battery, compare it with the capacity declared by the manufacturer, study the change in the capacity of a Li-ion accumulator battery during operation, as well as the effect of low operating temperatures on reducing them.

The created device enables to determine the actual capacity of a Li-ion accumulator battery with a sufficient degree of measurement resolution during the entire discharge period for drawing up graphs of the dependence of the discharge time on the applied load. The schematic structure of the device proposed by the authors and its photograph as an assembly are shown in figure 1.

**Figure 1.** Device schematic structure for analysing the Li-ion rechargeable battery characteristics.

The device is based on the Atmega328P microcontroller. The microcontroller is connected via the I2C line to the display, which shows the actual voltage in real time, the elapsed experiment time and the power already consumed. If it is necessary to collect statistics, the device should be connected to a personal computer via a virtual COM port or equipped with a module for writing to an SSD card via an SPI bus, to which data is written with a certain frequency (about 2 s).

In the case of connection to a computer, the device is powered from it. In the case of autonomous operation of the device, an additional, independent power module should be used. In addition to the display, a speaker is also provided at the output as an interface for communication with the user to notify the beginning and the end of the experiment. The experiment starts when the button is pressed. The experiment ends when the voltage at the output of the target Li-ion rechargeable battery drops to the lower threshold value (2.5 V). The lower threshold is set individually for different types of Li-ion rechargeable batteries. The tested Li-ion rechargeable battery is connected to the load stand via a relay controlled by a microcontroller (MC). The load stand is selected individually, depending on the required discharge current. The discharge current depends on the characteristic of the Li-ion rechargeable battery. In our case, the manufacturer specified a discharge current of no more than 0.5 A to ensure the specified capacity of the Li-ion rechargeable battery. If the actual discharge current specified by the manufacturer is exceeded, the capacity of the Li-ion rechargeable battery drops drastically. The battery deteriorates, overheats, and may begin to burn. In order to ensure the measurement accuracy and prevent over-discharging the Li-ion rechargeable battery below the minimum voltage, the device uses an MC-controlled relay between the battery and the load. The relay is closed by the MC at the beginning of the experiment and is opened when the voltage at the outputs of the target Li-ion rechargeable battery reaches a low threshold value. The voltage at the outputs of the tested Li-ion rechargeable battery is measured through the MC analogue input.

For the experiment, we used 10 Li-ion rechargeable batteries 18650 with a declared capacity of 3200mA.

The test device was connected to a personal computer to record measurement data in real time. The total number of Li-ion rechargeable batteries was 10 in order to reduce the influence of the individual characteristics of each battery on the overall result. The presented results are average values for all Li-ion rechargeable batteries.
The used Li-ion rechargeable batteries had incomplete charge and capacity. An incomplete charge was produced at the manufacturing factory. An incomplete charge (about 70%) is optimal to transport a Li-ion rechargeable battery, since, with such a charge, the self-discharge is minimal, there is no possibility of an overcharge state if the ambient temperature is increased. An over-discharge state is not allowed for long-term transportation and storage in a warehouse.

4. Analysis of the experimental results on input control and change in the capacity of Li-ion rechargeable battery due to external factors
At the beginning of the experiment, the Li-ion rechargeable batteries were completely discharged and immediately charged after that to 4.2 Volts. This operation was carried out four times. The obtained results on the change in capacity are shown in figure 2. The capacity increased after the first three cycles, after which it remained stable and was about 3120 mA.

![Figure 2. Change in capacity of the Li-ion rechargeable batteries during the first charge/discharge cycles.](image)

The average charge capacity of the Li-ion rechargeable batteries was approximately 98% of the capacity declared by the manufacturer, which is a good value and indicates the high quality of the experimental samples.

At the next stage, Li-ion rechargeable batteries were fully charged at room temperature of +19 °C. Charged Li-ion rechargeable batteries were one-by-one connected to the developed device with a load of 6.5 ohms. The load is made by 6 resistors with a nominal value of 10 Ohm and a power dissipation of 10 W each. The resistors are connected in series combination in two bundles of 3 parallel resistors each (figure 2). This decision is caused by the need to eliminate the influence of changes in the resistor characteristics when it is heated. During the experiment, the temperature of the resistors slightly differed from room temperature.

Li-ion rechargeable batteries were placed in a freezing chamber; in which they were discharged. The freezing chamber temperature was set at -18 °C. This temperature simulates operation during the cold season in our country. The obtained data on the discharge of Li-ion rechargeable batteries at a temperature of -18 °C are shown in figure 3.
Figure 3. The process of Li-ion rechargeable batteries discharge at low temperatures (-18 °C).

At the second stage, Li-ion rechargeable batteries were fully recharged and then discharged at room temperature of +17 °C. Obtained results are shown in figure 4.

Figure 4. Li-ion rechargeable batteries discharge process at moderate temperatures (17 °C).

From the graphs presented in figures 3 and 4, it can be seen that the discharge of the Li-ion rechargeable batteries produced at room temperature showed an expected capacity of about 3131 mA/h. The time for a complete discharge was about 6 hours and the total power obtained was 10.83 W*h. The characteristic of a Li-ion rechargeable battery, obtained during discharge at sub-zero temperatures, differs from the characteristics obtained at room temperatures. When the Li-ion rechargeable battery is discharged at sub-zero temperatures, its capacity decreases significantly. At a discharge temperature of -18 °C, the capacity averaged 2807 mA/h with a total power of 9.31 W*h. Thus, the capacity decreased by 300 mA/h compared to the capacity demonstrated by the Li-ion rechargeable battery at moderate temperatures, which amounted to a drop of more than 10%, that is, 89% of the maximum capacity, the power also decreased.
Based on the results of the work performed, the experiment set, and the data obtained, the following conclusions can be drawn. Li-ion rechargeable batteries have significant differences in characteristics, primarily in capacity and maximum discharge current. Therefore, these parameters determine the necessary modes of not only discharge, but also charge, to which Li-ion rechargeable batteries are very sensitive, and if it is violated, Li-ion rechargeable batteries deteriorate and can completely fail. Also, during the operation of a Li-ion rechargeable battery, it is necessary to prevent over-discharge, that is a decrease in their voltage below the minimum threshold value determined by the manufacturer. This may cause a Li-ion rechargeable battery to lose its performance. On the other hand, it is critical not to exceed the maximum charging voltage for the Li-ion rechargeable battery. To prevent the situations described above, Li-ion rechargeable batteries are equipped with charge/discharge controllers individually, or a device, in which Li-ion rechargeable batteries are used, should be supplied with a controller.

It is worth noting the specificity of using several Li-ion rechargeable battery cells in one common assembly. These assemblies are made if it is necessary to increase the output voltage and (or) the total capacity of the powering battery. In order to increase the total voltage, Li-ion rechargeable batteries are connected in series combination and operate at the total voltage. In such cases, additional balancing modules are used, which allow obtaining the total voltage from all Li-ion rechargeable batteries during discharge. But during charging, they control the voltage on each Li-ion rechargeable battery to ensure the maximum allowable charge of all cells. Individual charging is carried out to reduce the difference of the cell capacity during charging, and to prevent overcharging of cells with a small capacity and undercharging of cells with a large capacity. As mentioned above, even new Li-ion rechargeable batteries can differ in capacity by 15%. Li-ion rechargeable batteries purchased from one seller and of one batch most commonly have practically the same parameters. However, during operation, their deterioration can occur in different ways, and after a while, the capacity of Li-ion rechargeable batteries of one assembly may differ significantly.

It is also worth noting that the error in the capacity, even by 7-9% of each Li-ion rechargeable battery, which are within the tolerance limits, in the total value of the entire powering device may cause a lack of very significant amount of electric energy. That can be critical in some cases.

The experiment showed a decrease in the volume of supplied electric energy – about 11-13% in the case of operation at sub-zero temperatures. This phenomenon must be taken into account when organising power supply from a Li-ion rechargeable battery in the cold season at sub-zero temperatures. It should be noted that it is unacceptable for a Li-ion rechargeable battery, fully charged at sub-zero temperatures, to be operated at temperatures that are much higher (10-15 °C) than the charging temperature. In this case, the charge increases and the Li-ion rechargeable battery can become overcharged, that can lead to its damage.

It can be concluded that violation of the operating rules for a Li-ion rechargeable battery can lead to its deterioration, reduction in its service life and deterioration degree; in parity with the process of reducing the capacity during operation and sub-zero temperatures, they can supply from 15 to 30% less power than the declared value.

In order to prevent and reduce the negative impact of this phenomenon when operating a Li-ion rechargeable battery, it is necessary:

- to provide input control of operated Li-ion rechargeable batteries with their "warm-up" by several discharge/charge cycles and measurement of the actual final capacity before operation;
- to provide the necessary operating modes for current and charge/discharge. to consider the decrease in the capacity of the Li-ion rechargeable batteries depending on the power supply modes of the consumer, operating temperature and deterioration degree;
- to provide a capacity margin to reduce the unforeseen operating conditions.

In order to ensure the effective operation of Li-ion rechargeable batteries, it is necessary to consider the operating conditions and to correctly select a Li-ion rechargeable battery with the required
5. Conclusion

The work proposes a new approach to the Li-ion rechargeable batteries operation, that is mandatory input control and several charge/discharge cycles before placing Li-ion rechargeable batteries into the operating device. It also suggests periodic control of a Li-ion rechargeable battery in particularly important devices. The author also specifies the quantitative value of the charge volume loss during operation of a Li-ion rechargeable battery under sub-zero temperatures. The developed method and the created device can be used when operating a Li-ion rechargeable battery under sub-zero temperatures, in the far north, or in the case of increased reliability requirements for devices running on Li-ion rechargeable batteries. Further research will be aimed at the automated monitoring of the state of Li-ion rechargeable batteries, as well as the possibility of integrating this development into devices using Li-ion rechargeable batteries.

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