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Original Article

Effect of electrode performance on battery capacity at different temperatures

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ABSTRACT

Based on the literature data on the discharge characteristics of $Li_4Ti_5O_{12}$ (LTO) and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC) electrodes at different temperatures, the discharge curves of batteries composed of LTO and NMC electrodes were calculated. Four models of a battery based on the pristine materials and their modifications (an LTO anode based on a synthesized Cu/Super-P composite and an NMC cathode modified with lithium boron oxide glass (LBO)) are considered. The effect of modification of electrode materials on the temperature dependence of their capacity is estimated. It was found that a battery with a NMC-based cathode modified with LBO coating has good low-temperature properties and that the cathode modification in its effect on the discharge capacity exceeds the effect of the anode modification. It is shown that a battery with two improved electrodes is superior to other options in the entire temperature range from −30 °C to +20 °C.

KEYWORDS: calculation, discharge characteristics, low temperatures, LTO electrode, NMC electrode.

1. INTRODUCTION

An urgent problem for lithium-ion batteries is the capacity decrease in the range of low temperatures. Its solution was sought by variation of the electrodes' materials, as well as the electrolyte composition and concentration. Despite the importance of this problem, it is still poorly understood. Some research results on the effect of electrode materials' modification on the temperature dependence of capacity are presented in works [1-7]. The mentioned problem is aggravated by the fact that the temperature dependence of the capacity of the active material for the positive electrode, in the general case, does not coincide with the temperature dependence of that of the negative electrode. In every battery of a rational design, the amounts of active substances of the positive and negative electrodes are in a stoichiometric (or close to it) ratio. The difference in the temperature dependence of the capacity of opposite electrodes leads to the fact that a battery balanced at one temperature turns out to be unbalanced at other temperatures.

In this work, basing the literature data on the electrodes' discharge characteristics at different temperatures, the discharge characteristics of batteries composed of such electrodes are calculated, and the effect of electrode materials' modification on the temperature dependence of the capacity is estimated. For calculations, the data [1, 2] on the effect of temperature on the electrochemical behavior of electrodes based on lithium titanate $Li_4Ti_5O_{12}$ (LTO) and ternary lithium oxide $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC), as well as their modified versions was used. The modification of the LTO composite with a carbon material consisted in replacing the Super-P

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carbon black with the same carbon black coated with copper nanoparticles (Cu/Super-P). The modification of the NMC was performed by coating it with a lithium boron oxide (LBO) glass. The introduction of metallic copper into the LTO-based composite results in a decrease in the ohmic component of polarization, and the coating of NMC particles with a thin LBO layer helps to reduce the polarization of charge transfer at the interface of the material with the electrolyte. In both cases, the effect of the modification is more pronounced at lower temperatures. The choice of the LTO-NMC electrochemical system is justified by the recyclability, good charge-discharge cycling characteristics and long life of LTO anode, while NMC is considered one of the most attractive cathode materials due to its high capacity, safety and low cost.

2. Calculation of battery characteristics

In this work, for further comparison, the calculated indicators of the following batteries are presented:

1st battery: anode - the pristine LTO, cathode - the pristine NMC;
2nd battery: anode - modified LTO, cathode - modified NMC;
3rd battery: anode - pristine LTO, cathode - modified NMC;
4th battery: anode - modified LTO, cathode - pristine NMC.

To plot the discharge curves of such model (virtual) batteries, their open circuit voltage U was calculated as the difference between cathode and anode potentials for one and the same discharge capacity. According to [1, 2], the specific capacities of the pristine LTO and NMC at a temperature of 20 °C are approximately equal to each other (about 155 mA·h/g); therefore, the calculation for virtual batteries was carried out for a mass ratio of 1:1. For definiteness, it was assumed that in all batteries each electrode contains 1 g of active substance. Under the same conditions both modified materials have a capacity of about 165 mA·h/g. In the calculations, it was assumed that the discharge current is 0.2C. The calculated discharge curves for all four battery options are shown in Figure 1.

It should be emphasized that these calculations give only an “upper estimate”, since when calculating the characteristics of the battery as a whole, only the specific capacities of active materials are taken into account, whereas the weight of the electrolyte and structural materials is ignored. In batteries of a rational design, the proportion of the weight of auxiliary materials can be from 10 to 50%.

When considering the obtained dependences and taking into account the previously made conclusions, one can see that at room temperature the changes are practically insignificant. But they are pronounced at temperatures of −20 °C and −30 °C. And, as expected, the completely modified system has the highest capacities. As a comparison, at a temperature of −30 °C, the capacity of the second battery exceeds the capacities of the others up to amount of 35%, while at +20 °C the advantage is no more than 7%. Good low-temperature properties are more clearly demonstrated in Figure 2, which shows the discharge characteristics of all considered batteries at a constant temperature.

As mentioned earlier, the undisputed leader among the four systems is the fully modified battery, while the pristine one has the worst performance. Therefore, it is much more interesting to understand which modification makes the greatest contribution to the capacity rise. From the above dependences it is clearly seen that at higher temperatures the anode modification has a much greater effect on the discharge capacity than the modification of the cathode. With a decrease in temperature, the difference in the capacities of the 3rd and 4th batteries decreases as follows. At a temperature of −10 °C the difference is insignificant, at a temperature of −20 °C the curves practically coincide, and at −30 °C the order of the curves positioning changes: now a greater contribution to system parameters is made by a cathode with LBO. While cathode considerable contributes into capacity, a copper-based composite is practically useless. Also, it should be noted that the discharge curve of the third battery practically does not change its shape over the entire temperature range. It can be seen much better on the discharge curves in normalized coordinates, where the abscissa represents the ratio of the current Q(t) to the final Q_{fin} capacity $q = Q(t) / Q_{fin}$ [8], shown in Figure 3.

Figure 3 shows that at positive temperatures both batteries behave identically. Further, with a decrease in temperature, the appearance of the discharge

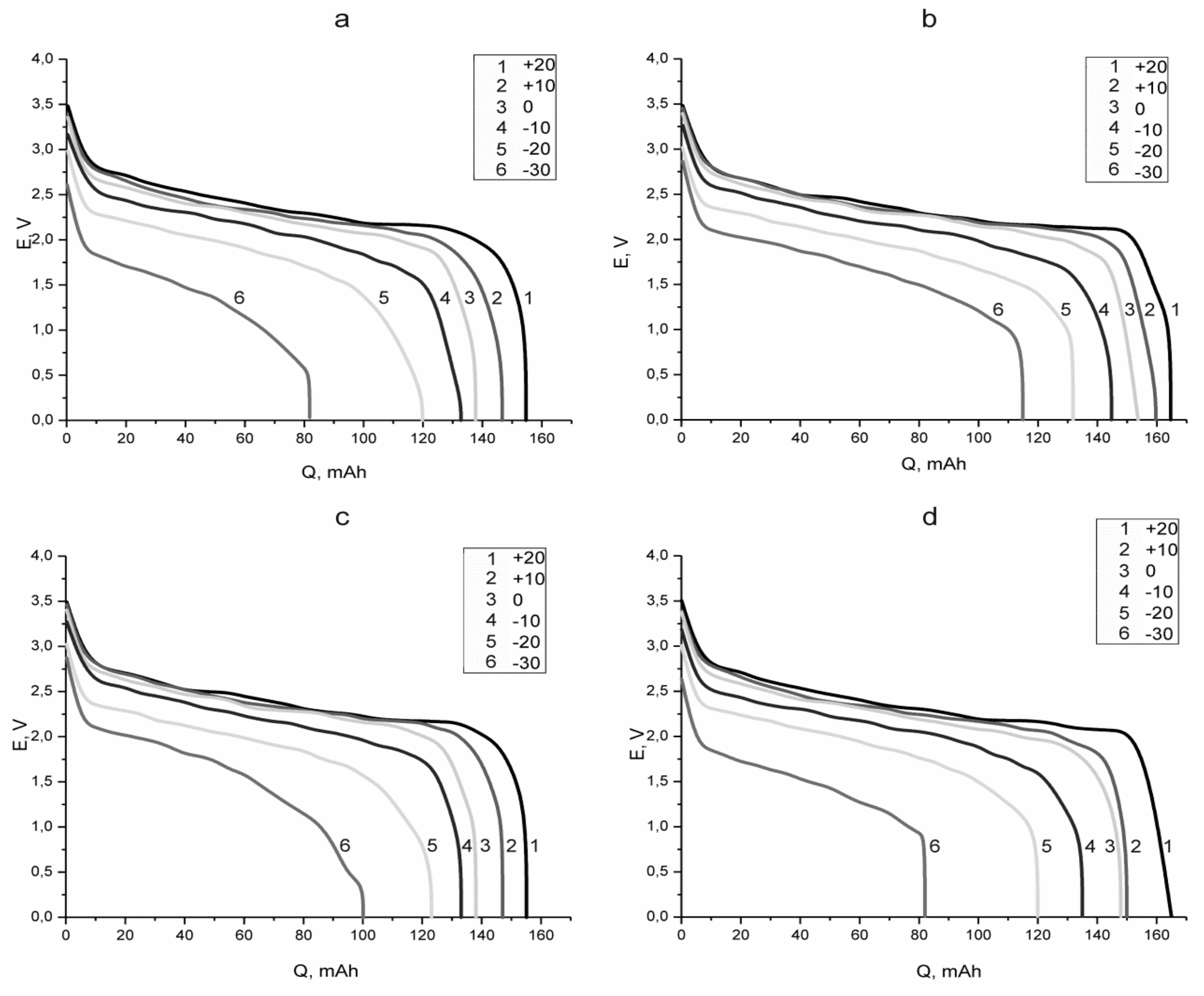

Figure 1. Calculated discharge curves for batteries of the pristine system (a), the modified system (b), the system with the pristine anode and the modified cathode (c), the system with the modified anode and the pristine cathode (d) at temperatures of −30 °C, −20 °C, −10 °C, 0 °C, 10 °C and 20 °C.

curve of the third system changes, but there is still a certain rectilinear section, which is characteristic of all temperatures for both batteries, and a convex region at the end of the discharge. And, it should be noted that the straight sections of the curves of the two systems with temperature changes remains parallel; only the values of the potentials associated with this section suffer the changes. Moreover, the potentials for each temperature in the region of −10 °C to +20 °C are practically equal; however, falling below −10°C, the potential values of the fourth battery fall much more than that of the third. The advantage of the third system is mainly due to the insignificant value of the activation polarization, i.e. the problem of the slowing down of charge transfer during the intercalation or extraction of the lithium ion is solved by the LBO coating of the cathode, reducing the charge transfer resistance. Taking into account the activation nature of the main processes occurring in the battery, it makes sense to consider the dependence of the discharge capacity Q on the temperature T, plotted in the Arrhenius coordinates log Q, 1/T. Such dependences are shown in Figure 4.

The nature of the dependences shown in Figure 4 in general is typical for lithium-ion batteries (see for example [7, 9-12]). In some cases, in limited intervals of 1/T values, straight-line sections can be

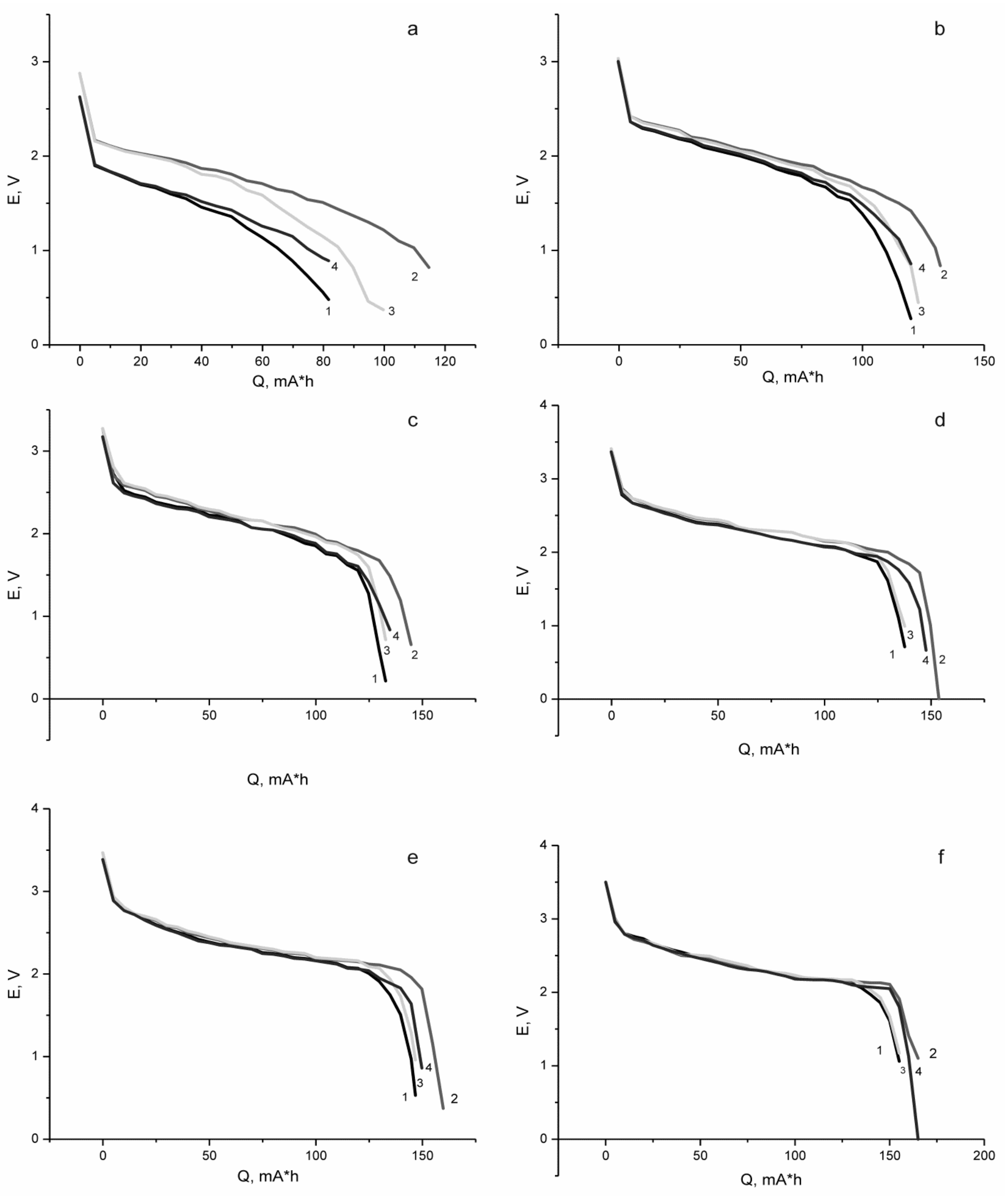

Figure 2. Discharge curves of the 1st-4th batteries at -30 °C (a), -20 °C (b), -10 °C (c), 0 °C (d), 10 °C(e) and 20 °C (f), respectively.

distinguished but in general the dependences log Q, 1/T are nonlinear and their slope d(logQ)/d(1/T) gradually increases with decreasing temperature. This nonlinearity is possibly related to the difference in temperature dependences of the capacities of opposite electrodes.

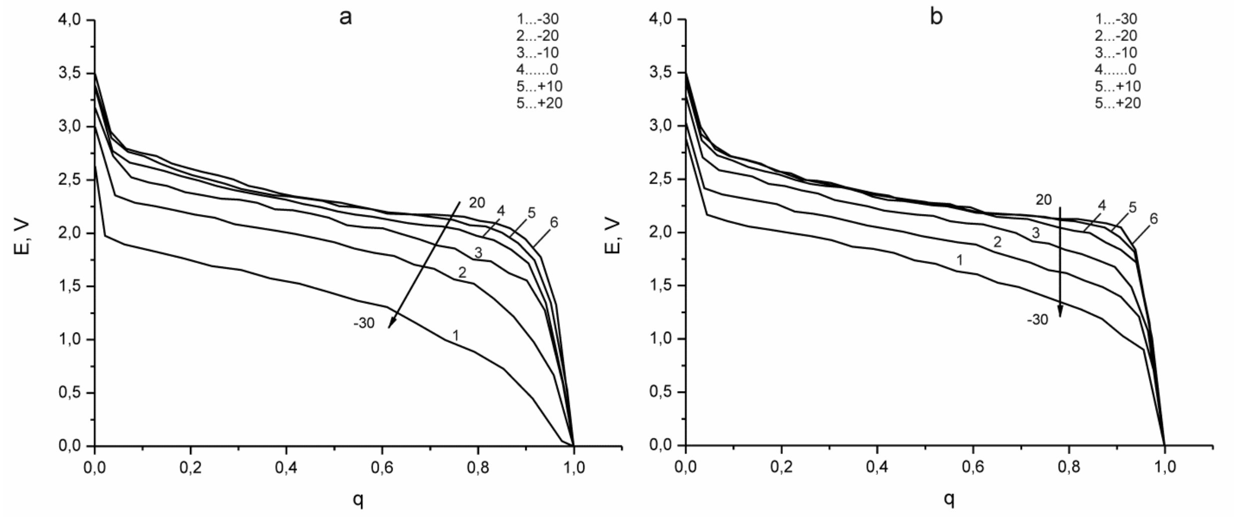

Figure 3. Discharge curves of 3rd and 4th batteries (Figure 1) plotted in normalized coordinates: a – 3rd battery; b – 4th battery.

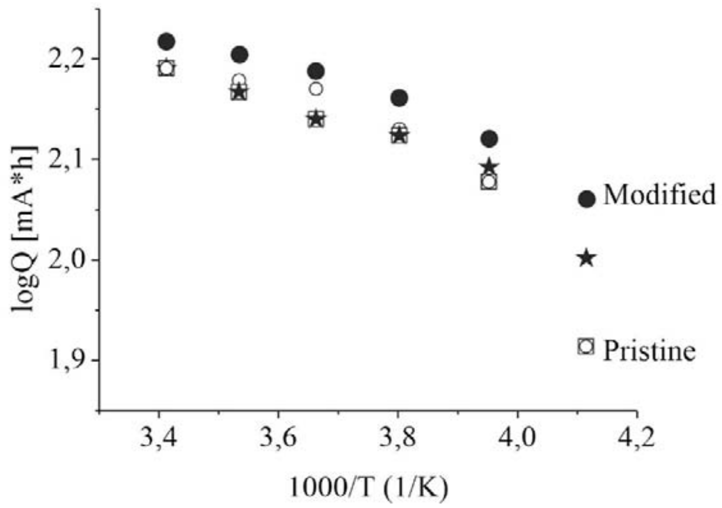

Figure 4. Temperature dependence of the discharge capacity of the 1st-4th batteries. 1st battery - solid squares, 2nd - solid circles, 3rd - stars, 4th - open circles.

3. CONCLUSION

In this work, four virtually simulated batteries based on the $Li_4Ti_5O_{12}/LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ system and their modifications were considered: an LTO anode based on a synthesized Cu/Super-P composite and a $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode modified with lithium boron oxide glass. It was found that the battery with two improved electrodes outperformed the others over the entire temperature range, which indicates self-complementary properties and a good choice of the modified system. The battery, improved only by the LBO coating, met the expectations demonstrating good low-temperature properties, surpassing the properties of the modified anode in its effect on the discharge capacity.

It should be emphasized that the conclusions of this work are valid for a specific electrochemical system. At the same time, the approach used in this work is not related to the nature of electrochemical systems and is fundamentally applicable to any, including completely solid-state batteries.

AUTHOR CONTRIBUTIONS

Conceptualization, AMS and ASR; methodology, AMS; investigation EVR, SAL and YST; resources EVR, SAL and YST; writing-original draft preparation, EVR and SAL; writing-review and editing AMS and ASR; data curation, YST.

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CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflicts of interest.

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