The Irreversibility Index of Processes in the Lithium Battery Inner Medium During Small Current Discharges

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The results of the recent study / 1 / show that growth of the lithium battery polarization at the beginning of a small current discharge (for one second after start of a discharge) coincides relatively well with polarization decrease at the beginning of battery recovery for the same small partial time of discharge and recovery. However, the lithium battery inner medium undergoes changes during a discharge, even a very small one / 2 /. Alterations of the battery inner medium lead to the battery remain polarization that decreases very slowly after discharge stopping and makes discharge process essentially irreversible. Taking this into account, it would be interesting to check the mentioned above coincidence for a continuos time interval. For these goals, it is very convenient to research behavior of the quantity $(H_{dis.} - H_{rec.}) / H_{dis.}$, the index of irreversibility of processes in a battery, where $H_{dis.}$ and $H_{rec.}$ are changes of the battery polarization after some small time of battery discharge and recovery.

The experimental data reported here have been obtained by the intensive research method / 3 /. The VARTA CR 2032, CR 2016 GP, ENERGIZER CR 2025, BR 2020, and BR 2325 lithium batteries were used at the study.

Some of the results of the research are presented in Fig. 1-4. Fig. 1-4 give us dependencies of the irreversibility index $K_i = (H_{dis.} - H_{rec.}) / H_{dis.}$ on time of a discharge from the beginning of the discharge for some of the studied lithium batteries. $H_{dis.}$ and $H_{rec.}$ in the index were calculated for the same partial time from the beginning of correspondingly the discharge and recovery after the discharge.

As we can see in the diagrams, the irreversibility index has the clear trend to zero at small times for non-first discharges that follow after several first discharges in the beginning of the series (Fig. 2, 4); for these non-first discharges, it depends mainly on the discharge time and almost doesn't on the current. However, for several first discharges (Fig. 1, 3), the situation is not so clear. The irreversibility index doesn't show expressive trend to zero at small times. Further, for the first discharges, the irreversibility index has often the negative sign at small discharge times.

One of the possible explanations of the mentioned above results is that the beginning of the first discharges is connected with "the break" of the lithium electrode passivity. Battery inner medium alterations lead both to direct changes of the electrode potentials and to changes of ratio of discharge-recovery process rates. The negative sign of the irreversibility index in the first discharges at small discharge times is probably connected with changes of this ratio. The constant growth of the irreversibility index in the non-first discharges can be probably ascribed mainly to piling of electrode potential changes.

We don't see signs of "the break" of the lithium electrode passivity during the non-first discharges. Possibly, by the time of the non-first discharges, the battery inner medium isn't restored from the changes caused by processes in the first discharges. Nevertheless, it is interesting to continue research on this question with measurements at smaller discharge and recovery times. Such research could also elucidate if "the break" of the lithium electrode passivity is a many-staged process with a reversible stage and if it is possible to get reproducible information about quick discharge processes from measurements in the first discharges at small discharge times. However, for this goal, it would be more useful to research the irreversibility index in conditions when the influence "strength" is connected with the influence time, and duration of discharges increases (starting from the small one) for every following discharge in a series of discharges with the same current.

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References

1. A.Z.Shekhtman, The 199th Meeting of the Electrochemical Society, Washington 2001.

2. A.Z.Shekhtman, The 198th Meeting of the Electrochemical Society, Phoenix 2000; Elektrokhimiya, 30 (1994) 690 (in Russian).

3. A.Z.Shekhtman, This Meeting; the Joint International Meeting of the Electrochemical Societies, Paris 1997; the 194th Meeting of the Electrochemical Society, Boston 1998; the 198th Meeting of the Electrochemical Society, Phoenix 2000, abstr. 943; the 199th Meeting of the Electrochemical Society, Washington 2001, abstr. 1028.

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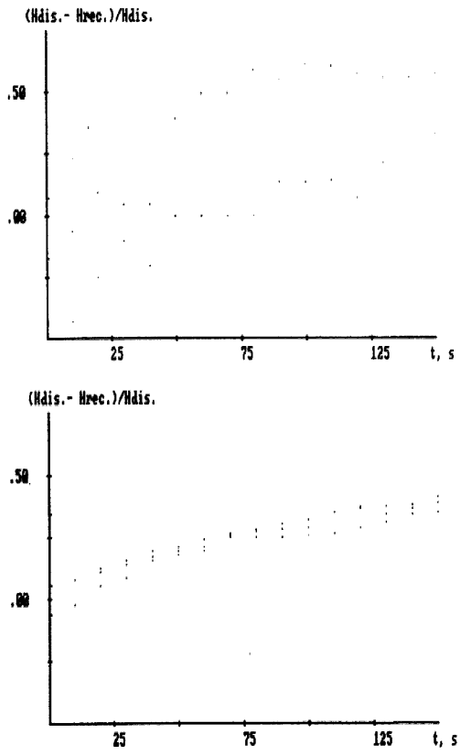

Fig. 1 – 2 The irreversibility index of processes in a lithium battery ENERGIZER CR 2025 versus the discharge time for discharges through 200kΩ and 100kΩ (the upper diagram) and 50kΩ, 40kΩ and 20kΩ (the lower diagram).

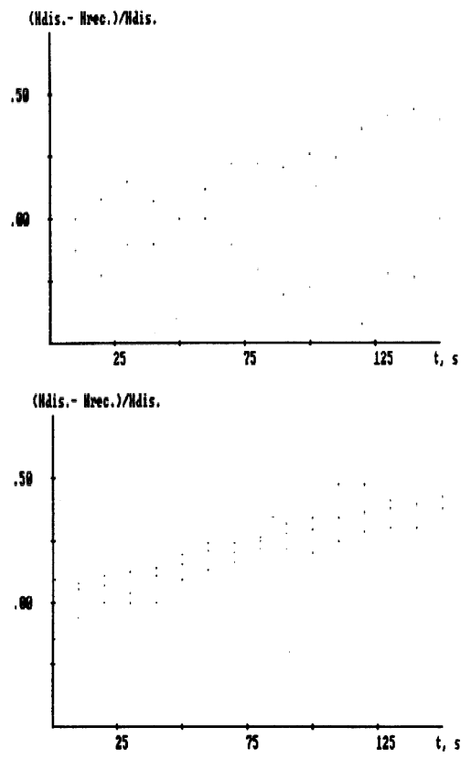

Fig. 3 – 4 The irreversibility index of processes in a lithium battery CR 2016 GP versus the discharge time for discharges through 800kΩ and 600kΩ (the upper diagram) and 400kΩ, 300kΩ and 100kΩ (the lower diagram).