Changes of the lithium battery voltage conditioned by alterations of the lithium electrode's passive film during a battery discharge and recovery

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A lithium electrode together with a porous passive film on its surface / 1 / is a porous electrode, and its passive film undergoes essential changes at discharges of the lithium batteries, even at very weak ones / 2 /. On the other hand, the potential of a porous electrode in an electrolyte solution must depend on the structure of the electrode pores and state of the electrolyte solution in them / 3 /. It means that some portion of change of the battery voltage during a discharge and following recovery can be conditioned by the change of the lithium electrode potential that occurs at passive film alterations. Another possibility of influence of passive film changes on the battery voltage is possibility of influence through alteration of the passive film passivity and resistance during passive film changes. This research was undertaken to study the battery voltage changes originating from alterations of the electrode passive film during the battery recovery.

Here, we present the results of the research of open circuit voltage restoration of lithium batteries after different small-current discharges. The experimental data have been obtained by the intensive research method / 4 /. The VARTA CR 2032, CR 2016 GP, ENERGIZER CR 2025, BR 2020, and BR 2325 lithium batteries were used in the study.

Some of the results of the research which are typical for all of the studied batteries are presented in Fig. 1-3. Fig. 1-3 represent dependencies of the battery remain polarization H_R on recovery time t during recovery after a discharge. The values of H_R in Fig. 1-3 are not averaged.

As we can see in Fig. 1 - 3, the battery remain polarization H_R has a trend to a stepped dependence on the recovery time t at least in the region of relatively great recovery times. In this region, the passive film on the surface of the lithium electrode of the studied batteries is suggested to undergone some changes which can influence on its passivity (/ 5 /). However, a relatively high battery voltage restoration rate in the sections separating the flat areas of the H_R-versus-t dependencies, makes some additional problems in explanation of this trend by an influence of the passivity. We can overcome some of them if we suppose, for instance, that passive film alterations during recovery break temporally the passive film passivity, which was restored in a previous stage of the recovery.

Another possible cause of the mentioned above trend is a dependence of the lithium electrode potential on state of the passive film that undergoes some alterations during battery recovery. In this case, we must suppose that the charge transfer processes are not a limiting factor in the considered time of the battery recovery.

Despite that the last cause seems to be more preferable, to make the final conclusions, we need for additional research, in particular, in the region of very small currents and recovery times.

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References

1. M. Froment, M. Garreau, J. Thevenin, D. Warin, J. Microscop. et Spectroscop. Electron., 1979, vol. 4, p. 111.
2. A.Z.Shekhtman, The 198th Meeting of The Electrochemical Society, Inc., Phoenix 2000.
3. A.Z.Shekhtman, Elektrokhimiya, 32 (1996) 987 (in Russian); The193 Meeting of The Electrochemical Society, Inc., San Diego 1998.
4. A.Z. Shekhtman, The Joint International Meeting of the Electrochemical Societies, Paris 1997; The194th Meeting of The Electrochemical Society, Inc., Boston 1998; The198th Meeting of The Electrochemical Society, Inc., Phoenix 2000.
5. A.Z.Shekhtman, The 199th Meeting of The Electrochemical Society, Inc., Washington 2001.

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Fig. 1 The battery remain polarization H_R versus the recovery time after a discharge of a lithium battery Energizer CR 2025 through the outer resistance R = 40 kOhm and R = 50 kOhm.

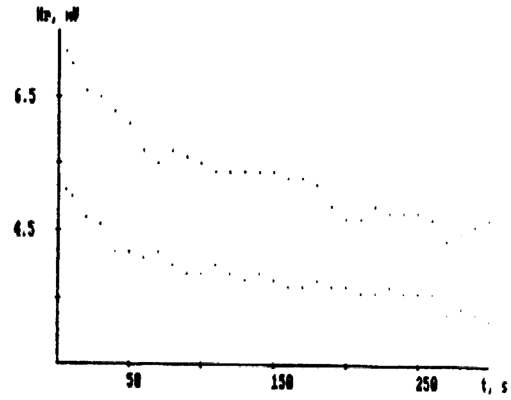

Fig. 2 The battery remain polarization H_R versus the recovery time after a discharge of a lithium battery Energizer BR 2325 through the outer resistance R = 600 kOhm and R = 800 kOhm.

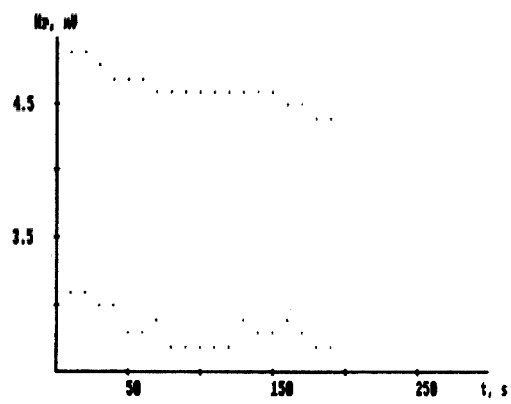

Fig. 3 The battery remain polarization H_R versus the recovery time after a discharge of a lithium battery CR 2016 GP through the outer resistance R = 400 kOhm, R = 600 kOhm and R = 800 kOhm.