Peculiarities of lithium-cation kinetics through passivating film on the surface of lithium electrodes

A.Z. Shekhtman [1]

KVANT State Science Production Enterprise, Moscow, Russian Federation

1. Introduction

Many studies of the passivating films covering the surface of lithium electrodes in aprotic electrolyte solutions have been made. There is no perfect clearness in the understanding of the structure and the conduction mechanism of such films, even in the most studied electrochemical systems.

2. Experimental

This paper presents a new method of cell investigation; some of the results concern the properties of passivating such films [1–3]. The method consists in measuring cell voltages during a number of series of short-time discharges with different currents in each discharge cycle, and with recovery time after each discharge and after each series. Then, on the basis of the data, different discharge characteristics versus current are investigated. The advantages of the method are, in equal conditions for every discharge cycle, simplicity and a relatively small period of time for the investigation of a great number of cells. The method allows statistical processing of current discharges data to be obtained in different cells and the data from repeated discharge series in the same cell.

3. Results

Some of the most typical results obtained from experimental and commercial cells based on different electrochemical systems are represented in Figs. 1 to 3. The following designations are accepted:

[1] Present address: Freedom Street 75, Building 2, Apartment 191, Moscow 123481, Russian Federation.
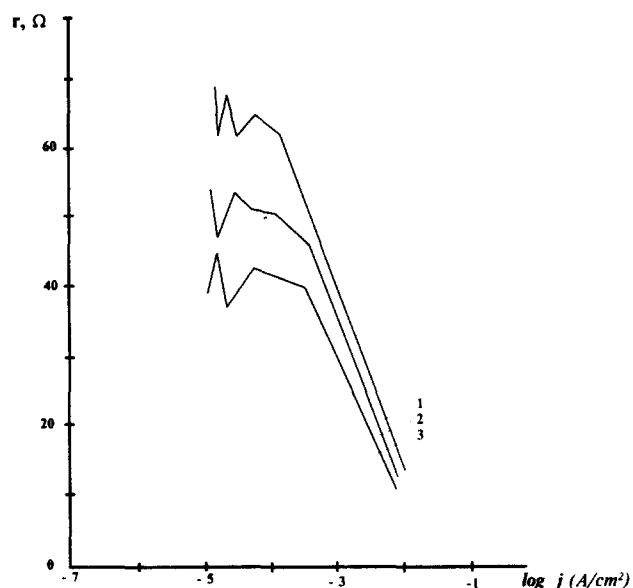
Fig. 1. Typical inner resistance of the lithium cells vs. logarithm of current density at the surface of the lithium electrode for three subsequent series of short-time discharges carried out with the time intervals 1 min and 1 h, respectively.

$$\mathcal{U}_i = U_{oi} - U_i \tag{1}$$

$$I_i = U_i/R_i \tag{2}$$

$$r_i = \mathcal{U}_i/I_i \tag{3}$$

$$\Delta\mathcal{U}_i = \mathcal{U}_i - \mathcal{U}_{i-1} \tag{4}$$

$$\Delta I_i = I_i - I_{i-1} \tag{5}$$

where U_{oi} is the open-circuit voltage of the studied cell before the onset of discharge at resistive load R_i, U_i the cell voltage before the end of discharge at R_i, R_i the ith resistive load, and r the inner resistance.

The resistance of the passivating film which covers the surface of the lithium electrode gives the main contribution to the inner resistance r of the studied lithium cells, at least when the discharge current is not
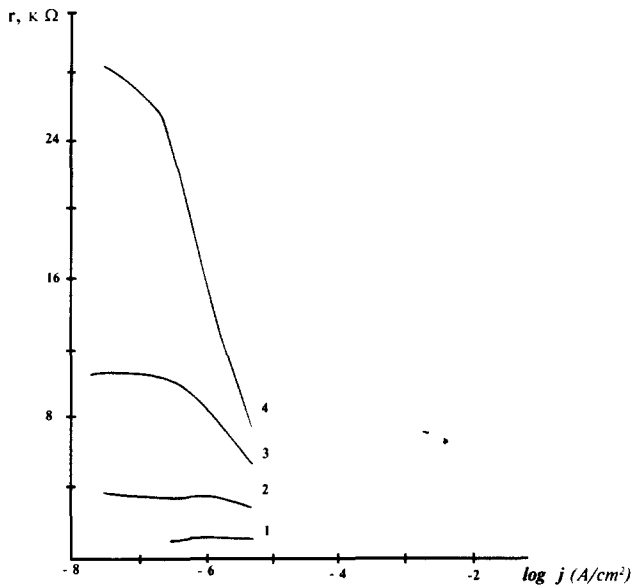
Fig. 2. Typical inner resistance of the lithium cells vs. logarithm of current density at the surface of the lithium electrode at different negative temperatures: (1) −10 °C; (2) −20 °C; (3) −30 °C, and (4) −40 °C.
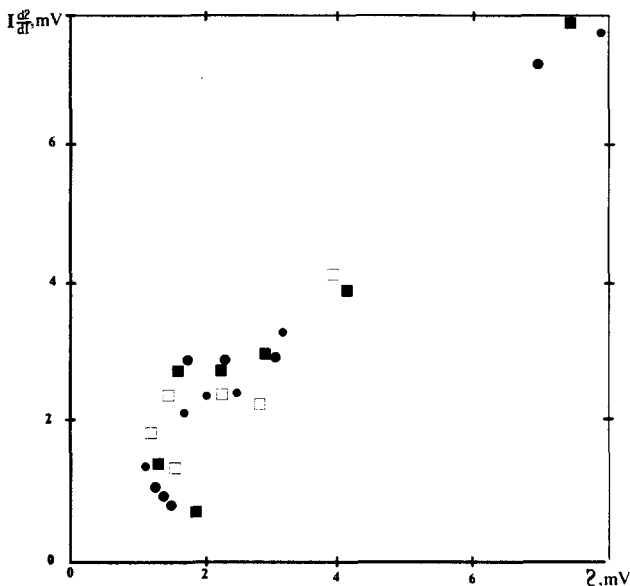

Fig. 3. Typical $I(d\mathscr{E}/dI)$ vs. $\mathscr{E}$ for lithium cells for four subsequent series of short-time discharges marked respectively: (●) 1; (□) 2; (○) 3, and (■) 4. The time intervals between the series are 3 min.

too high [4]. Thus, the results present the properties of the passivating films.

There are two common features for all studied lithium cells. The first one is the well-known one which is usually considered as a result of the disruption of the passivating film. In Figs. 1 and 2, this process is represented by the lower section of function $r(I)$. It can be seen from Fig. 2 that, for the lithium cells using $LiClO_4$ in propylene carbonate as the electrolyte solution, that the values of r before sharp decreasing $r(I)$

are temperature dependent while at higher currents this dependence decreases significantly. This indicates that the 'disruption' of the passivating film in some lithium cells is rather a process of changing the film-pore structure than a process of changing its thickness, at least in the initial stage of the 'disruption' [2].

The second feature is the presence of a number of extremes in function $r(I)$ in the region of weak discharge current [1,3] (Fig. 1). Such a structure in $r(I)$ is absent at temperatures below 0 °C (Fig. 2). If series of short-time discharges comprise only small discharge currents the reproducibility of these peculiarities of $r(I)$ will be better and it may be possible to find some additional details of this phenomenon [3] (Fig. 3). The fact of the presence of non-linearity in volt–ampere characteristics of the passivating film is not a surprising phenomenon. There are many processes that can take place in the passivating film and lead to some peculiarities in the function $r(I)$. The fact that these peculiarities take place for all cells studied, both lithium and non-lithium, confirms the common reason of their origin. They could be, for example, be the reason of a local decrease in the negative electrode volume during discharge. It could lead, in turn, to a deformation of the discharge canals and to the gassing of the electrolyte solution [5]. If the number of the discharge canals, at a weak discharge current, is not big the decrease of the negative electrode volume during discharge can be compared with the typical pore volume of the conducting canals even for a relatively short time of discharge; this may have a noticeable influence on the resistance of the film.

4. Conclusions

Although this method continues to be developed, the results obtained show that it will take a deserving place, due to its simplicity and possibilities, in scientific research and industrial applications.

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