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Voltage delay in lithium non-aqueous battery systems

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The voltage delay problem relating to lithium non-aqueous batteries is reviewed on the basis of accessible literature: papers, patents and industrial reports. Most attention is given to the batteries available on the market (e.g. Li/SO_2 and $Li/SOCl_2$). Some problems of film formation on lithium anodes are analysed in an attempt to elucidate the nature of the voltage delay, and different methods of alleviating it are described.

Contents

1. Introduction

Lithium non-aqueous electrolyte batteries are thermodynamically unstable systems and can only exist due to the formation of a protective film on the surface of the lithium anode. The film prevents any chemical interaction between a lithium anode and components of an electrolyte including all impurities and endow the batteries with an extremely long shelf-life.

As soon as a load is applied to a battery the anode film is easily dissipated. However, the electrochemical passivation of an anode, caused by the film, disappears with time giving rise to a phenomenon known as 'voltage delay'. The cell voltage drops initially to a certain value and then recovers gradually as the discharge progresses. The time needed for the cell voltage to recover the predetermined value depends on the nature and pre-history of the battery and the discharge conditions.

Independent of the particular battery system, voltage delay increases with storage life and storage temperature, and with a low discharge temperature and a higher load it can be negligibly small. In certain applications the existence of voltage delay can bar the use of a battery. Alleviating the voltage delay problem is connected with understanding the nature of the chemical and electrochemical processes taking place in a battery and can reduce the stability of lithium non-aqueous systems and shorten their shelf-lives.

Up to now the voltage delay problem in Li batteries has been given rather pragmatic attention. The approach undoubtedly is very useful as has been proven, in the case of $Li/SOCl_2$ cells. However, although these cells have been investigated to a much greater extent than other Li systems, the nature of the problems remains unclear.

The Li film growth in the most commercially successful Li/SO_2 batteries has been given some attention only in one publication [1].

2. Voltage delay in lithium non-aqueous inorganic systems

2.1. *$Li/SOCl_2$ batteries*

The $Li/SOCl_2$ systems have received considerable attention during recent years. A battery of this type comprises a Li anode, a carbon cathode and a $LiAlCl_4$–$SOCl_2$ electrolyte where $SOCl_2$ serves as a solvent and a soluble depolarizer. The spontaneous chemical reaction between the Li

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anode and the depolarizer which remains in physical contact at all times is unavoidable thermodynamically. Bulk reaction does not take place however, due to a protective film on the lithium anode surface that forms as soon as the anode and the depolarizer come in contact.

The protective qualities of the film are very effective and the battery is characterized by a good storage performance. On the other hand the film causes voltage delay which becomes especially severe when discharge is performed at low temperatures or the cells were stored previously at elevated temperatures. Hence the study of voltage delay in this system has been an aim of many investigations.

Several studies on the problem have been carried out by P. R. Mallory and Co. [1–8]. The description of the cells used in the investigations is given in [2, 9, 10]. First an empirical approach [2] was used; it consisted of measuring the voltage delay at −30° C of the fresh and partially discharged cells after storage for up to 6 months at 70° C. The experiments showed the positive role of the previous partial discharge of the stored cells on alleviating the voltage delay.

The further experiments [1, 2, 4–8] consisted of studying the morphology and the growth characteristics of the Li anode film in an effort to establish a relationship between the electrolyte variables (concentration of $LiAlCl_4$, $AlCl_3$ H_2O, SO_2, $SOCl_2$), the Li anode film growth characteristics and voltage delay. This phenomenological approach was carried out with the SEM technique.

In general it was established that voltage delay of the batteries was due to the existence of a protective film on the lithium anode [2, 6] and that the behaviour of the cathode was irrelevant in this respect. The film was found to consist primarily of LiCl crystals. The thickness of the film increased with an increasing storage duration and an increasing storage temperature giving rise to more and more severe voltage delay. It was shown that initially, anodic dissolution of Li was highly localized and occurred at pinholes and other imperfections of the protective film and that the film was dislodged mechanically or fractured when sufficient Li had been dissolved underneath the film. It was proven that the morphology and the thickness of the protective film determines the voltage delay characteristics and that by altering the electrolyte variables it was possible to change significantly the properties of the film and, consequently, the severity of the voltage delay.

It has been found [3] that a relatively small amount of a salt additive having a clovoborate anion structure reduces the passivation of the Li anode, and thus helps to reduce the voltage delay associated with start-up after storage at elevated temperatures.

Important investigations were performed in EIC, Inc. The authors used potentiostatic [11, 12] galvanostatic [11] and cyclic voltammogram [13] techniques and in some cases performed their experiments using special experimental battery configurations, e.g. [12, 14]. It was confirmed that voltage delay in the $Li/SOCl_2$ cells is due only to the lithium anode passivation [15] and that the film growth and hence voltage delay may be altered by modification of the electrolyte composition. It appeared that $SbCl_5$ and $LiSbCl_6$ had a beneficial effect on the initial polarization after storage [14]. The behaviour of construction materials in contact with the Li anode (e.g., support screens, current collectors, and possibly the cell can) was considered as an important practical factor influencing the film growth on Li [11, 12].

An attempt was made to alleviate the voltage delay problem using Li alloys instead of Li as an anode material [14, 16]. Only slight improvement was achieved with Li/Ag (1 at%) and Li/Mg (1 at%) alloys [16]. However, the idea of using Li alloys in order to decrease the voltage delay effect seems to be promising. In [17] it was shown that voltage delay can be alleviated to a significant degree by coating the lithium anode with calcium.

An interesting opinion on the nature of the protective film on Li is held by the authors of [11, 12]. They proposed on the basis of experiments with an electrolyte which should have dissolved LiCl that LiCl may not be the only film and it may not be the protective film at all. This idea differs from the established point of view and will be considered later.

Much significant work has been carried out on Li inorganic systems and especially on the $Li/SOCl_2$ cells in GTE Lab [18–23]. The authors assumed that the protective film on the Li anode in the $Li/SOCl_2$, causing the voltage delay, consisted of LiCl [19, 20]. The many observations made are generally in line with the data given above. One of them describes the positive effect of partial discharge, prior to high temperature storage, on alleviating voltage delay in the cells [22]. This observation confirms the results in [2] and, although it has no clear explanation, might be useful from the practical point of view.

It was found that the composition of the passivating film might have changed at room temperature, after the film had been formed during storage at elevated temperatures [21]. Some other organizations published the results of their investigations of voltage delay in the $Li/SOCl_2$ systems.

In [24] (Honeywell Power Sources Centre) it was confirmed with the use of X-ray diffractometry that the film on the Li anode was LiCl. Trace amounts of S were found in the film. That confirms the similar results [6] and gives some foundation for the hypothesis made in [11] which suggested that elemental sulphur, being a product of a cathode reaction, was soluble in the electrolyte and could diffuse towards the Li anode and react there to form Li_2S. Further it was again shown in [24] that partially discharged cells were subject to a lesser degree of voltage delay. The role of the partial discharge has not found a clear explanation. In [24] it was attributed to the introduction into the $LiAlCl_4$–$SOCl_2$ electrolyte of a new component, SO_2, as a product of discharge. This point of view was further confirmed by the fact that effective control of lithium passivation appeared to be critically dependent on the SO_2 concentration. The voltage delay was significantly alleviated by doping the electrolyte with the optimum concentration of SO_2 around 5 wt%. The influence of SO_2 was not explained. The doping of the electrolyte with SO_2 was attempted in [2, 22] but its significance for alleviating voltage delay was not reported.

The voltage delay, experienced with the hermetically sealed cells which had been stored for a long period of time, was overcome by subjecting the cells either to a physical or thermal (high or very low temperatures) shock. Hydrostatic pressure (~ 60 m depth) also depassivated the cells [25] (Naval Undersea Centre). The voltage delay was observed also in [26] (ECOM).

Although the nature of the film growth characteristics and of voltage delay in the $Li/SOCl_2$ cells has not been fully understood the practical results of eliminating the latter are so impressive that voltage delay was claimed [1, 27] not to be a problem for technical applications of this type of battery. This was confirmed in the recent publication [28]. Honeywell is applying for a patent and the content of the invention is not available.

2.2. *Other lithium inorganic systems*

Other lithium inorganic non-aqueous systems attract much attention at present. However, their development has not apparently reached the point when voltage delay becomes a problem. Hence we failed to find any publications about film growth or the voltage delay, though it is indicated that lithium anodes in such cells do have protective films, e.g. this was underlined in comprehensive reviews on Li/SO_2Cl_2 and $Li/POCl_3$ cells [29, 30].

3. Voltage delay in lithium non-aqueous organic systems

3.1. *Li/SO_2 batteries*

This system is the most advanced and commercially successful of all the Li non-aqueous electrolyte batteries available to date. It consists of a Li anode, a porous carbon cathode, a non-woven polypropylene separator and an electrolyte comprising typically of LiBr in a mixture of acetonitrile (AN), propylene carbonate (PC) and liquid SO_2. The composition of the electrolyte has recently been modified and a new electrolyte contains no PC [31, 32]. It consists of LiBr, SO_2 and AN in approximately the same volume ratio. The construction of the cell and its performance has been described in detail [7, 31–39].

In spite of the fact that the system Li–SO_2 is extremely unstable thermodynamically and the Li anode permanently remains in physical contact with liquid SO_2 chemical reactions between the two are prevented due to the protective film which is formed at the moment when Li is immersed into the electrolyte. On the other hand the existence of the protective film on the anode surface has a negative aspect, causing voltage delay as was discussed in the case of $Li/SOCl_2$ batteries.

The characteristics of the film growth in

Li/SO_2 cells have been investigated only in one paper [1] and there are only a few more publications in which voltage delay was studied as a function of the storage and discharge conditions [7, 34, 37–41]. In general it can be assumed that qualitatively the Li/SO_2 cells behave with respect to the Li film growth and the voltage delay problem in the same way as the $Li/SOCl_2$ systems.

The protective film on the Li anode is proposed to be lithium dithionite [1, 7, 31, 38] which is formed as a result of the cell reaction:

$$2Li + 2SO_2 \rightarrow Li_2S_2O_4$$

and is insoluble in the electrolyte [1, 7]. In the presence of some PC in the electrolyte, the chemistry of the cell becomes more complicated and it is probable that Li_2CO_3 which is a result of the PC decomposition on the Li anode, also becomes a part of the protective film [1, 31]. This conclusion can be confirmed by the fact that the cells with the electrolyte not containing PC demonstrate a significantly decreased voltage delay [1, 31].

During discharge, the film is mechanically ruptured due to the anodic dissolution of Li. Generally, voltage delay in the cells is connected primarily with the anode passivation though in [40] it was shown that the cathode processes can substantially contribute to voltage delay aggravation at a high rate of discharge. The measurements [40] were carried out with the help of a reference electrode.

The morphology of the Li film in the Li/SO_2 system has been examined [1] using the SEM technique. The photographs showed that the film was composed of LiCl crystallites. As in the case with the $Li/SOCl_2$ cells the morphology and the growth rate of the film could have been changed by altering the electrolyte variables and it was claimed to be an effective way of alleviating of the voltage delay problem.

It has been shown [39] that discharge may be interrupted for a few days without voltage delay recurring when the discharge was resumed. A similar observation was made in [37] and used for an activation of the cells in the main depot before delivering them for the practical application.

In general voltage delay for Li/SO_2 batteries is less prominent than for the $Li/SOCl_2$ systems [31].

3.2. *Other lithium organic systems*

There are not many publications dealing with the voltage delay problem in the Li organic systems other than the Li/SO_2 cells.

The Li/polycarbon monofluoride system which is now on the market is characterized by a voltage delay which is noticeable at temperatures even above 0° C. However, the problem as far as we know, has not been discussed in the literature and the voltage delay for the $Li/(CF_x)_n$ batteries was only described very briefly in [1] and was mentioned in the discussion following the delivery of a paper [42]. Voltage delay in the Li/1 M $LiClO_4$ PC/MoO_3 system was reported in [43].

In [44] voltage delay was observed for the Li/PbF_2 system in the $LiClO_4$–methyl formate (MF)/butyrolactone (BL) and $LiAsF_6$–BL electrolytes and it was connected with the passivation of the cathode because in the same solutions with other cathode materials the voltage delay had been absent.

A gel-like massive film on the Li anodes has been described for the systems: Li/V_2O_5 and Li/Ag_2CrO_4 in the 1 M $LiClO_4$–tetrahydrofuran (THF) electrolytes [1]. The appearance of the film was explained by the electrochemical polymerization of THF at the cathodes which are strong oxidizing agents and by subsequent precipitation of the polymer on the anode surface, where it migrated by diffusion. This massive anode film causes significant voltage delay which becomes especially severe in the case of Li/V_2O_5 cells.

4. Some general recommendations on alleviating the voltage delay

In [45] an anode coating for non-aqueous batteries was suggested wherein the anode active material was coated with the insoluble reaction product of the anode metal with an inhibiting reactant such as CO_2, SO_2, O_2, NH_3 and N_2 saturated with respect to water vapour. This coating had a thickness of only several monolayers, and did not passivate the Li anode or any of the other active metal anodes. Under application of a slight overvoltage the coating was rapidly dissolved. On the other hand the protective qualities of the coating against the chemical interaction between the anode and a solvent at high temperatures were excellent. Depassivation of the Li anode immersed into the $LiClO_4$–PC electrolyte was achieved by adding a small amount (0·8 wt%) of a hexamethylphosphoramide to the latter [46].

In many cases it was possible to alleviate significantly the voltage delay in the non-aqueous organic electrolyte cells by amalgamating the light metal anodes (Li, Ca, Mg, Al and Be) [47].

5. The thin film formation in Li non-aqueous systems

It is apparent that there is a gap between the practical achievements in alleviating voltage delay for different types of Li non-aqueous batteries and the degree of understanding of the chemical and electrochemical processes causing this problem. Hence some attempts have been made to contribute new ideas in elucidating the problem of the film formation.

In [48] the role of dissolved oxygen in the systems: Li/$LiAlCl_4$–PC and Li/$LiAlCl_4$–nitromethane (NM) was investigated. The authors suggest that, when the partial pressure of oxygen above the electrolyte is 0·2 atm or higher, chemical adsorption takes place on the Li anode surface:

$$(x + 1)\,\mathrm{Li}^0 + \mathrm{O}_2 \;=\; \mathrm{Li}_x(\mathrm{O}_2^{\mathrm{ad}})\mathrm{Li}$$

and a thin film of lithium/oxygen compounds of variable composition is formed. The film has good protective properties and is able to prevent the chemical interaction between Li and the electrolyte. This conclusion is assumed to apply for the whole range of aprotic solvents.

The popular view is that the Li electrodes are stable in the electrolytes based on PC, owing to the protective film of Li_2CO_3 which is a result of the chemical reaction between Li and PC. However, it might be that in different experiments [1], where the purification of the electrolyte and of the whole system was not carried out to a high degree, the oxygen adsorption played an important role and led to formation of the first thin layer of its products on the Li electrode. The massive and porous Li_2CO_3 film formed the second layer of the complete film.

In experiments e.g. [49] where purification was performed to a very high level and where oxygen was not supposed to be present the protective film was perhaps only Li_2CO_3.

The system Li/0·25–1·5 M $LiAlCl_4$–$SOCl_2$ with a water content of 50 ppm was investigated in [50]. The passivation of the Li electrode was followed by periodic measurements of its capacitance and micropolarization resistance by means of the galvanostatic technique. The passivation of the Li electrode was attributed to the formation of a relatively thin (10–40 nm). non-porous, and electronically insulating, but ionically conducting, LiCl film, which underlies the porous, thick, and coarse-grained LiCl layer.

This conclusion can be compared with the fundamental investigation of the same system by means of SEM which has been described in the most complete form in [1, 2] and it was concluded that the Li film was electronically conductive and porous. The author observed the thin layer of uniformly grown small LiCl crystals and attributed its formation to the chemical reaction between thin protective films on the Li surface formed prior to the immersion of the electrode into the electrolyte, and the electrolyte at the moment of contact. The subsequent growth of the Li film was supposed to be controlled by the electrolyte variables. Depending on the conditions of storage the whole film might have a thickness of up to 384 μm and a porous structure. The author [1, 2] did not investigate the properties of the first thin layer of LiCl crystals and having considered the composite film suggested that it had electronic conductivity due to the presence of defects and that the rate of the film growth was controlled by the surface concentration of pores or by their length.

Perhaps it can be assumed that there is no discrepancy between [50] and [1, 2] if we relate the conclusion in [50] to the thin layer which was observed in both investigations and the conclusions in [1, 2] to the subsequent growth on the first layer which was investigated in the latter work. Moreover in [1, 2] in spite of the assumption of electronic conductivity, the controlling step for the film growth was supposed to be the Li ion transportation through the pores.

In [51, 52] the theory of solid electrolytes was applied to the electrochemical behaviour of alkali and alkaline earth metals in non-aqueous batteries. In more detail the model was described for the Mg/$SOCl_2$ system [52]. The author suggests that in non-aqueous battery systems the alkali and alkaline earth metals are always covered by a surface layer at least 1·5 nm thick. The layer which is formed instantly, consists of some insoluble products of the reaction of the metal with the solution. This layer acts as an interface between the metal and the electrolyte and can be characterized like any solid electrolyte with the following parameters: transference number of electrons and transference numbers, mobilities and concentrations of anionic and cationic defects.

This approach seems to be fruitful and neatly fits the different experimental observations, e.g. it is assumed that this thin film for common non-aqueous cells has no electronic conductivity and the transference number of electrons is zero. However under some extreme conditions a small leakage of electrons can take place and lead to the film growth. Such conditions can be realized at high temperatures for thinner layers. Hence in the experiments [1, 2] electronic conduction, perhaps, did take place to some extent as it was described in their qualitative model. Furthermore this qualitative model assumes the crucial role of the Li^+ ion transportation in film conductivity and the solid electrolyte approach gives a quantitative basis for this assumption suggesting that for the non-aqueous cells the transference number of cations is 1.

In general, it becomes clear that the stability of non-aqueous battery systems and the voltage delay which they demonstrate have different causes though their nature is the same. A very thin and dense protective film on the Li surface is formed instantly and causes no voltage delay though its protective qualities are sufficient to make the battery stable with a very good storage performance. On the other hand, the subsequent film growth on storage does not improve the stability of the system but leads to the voltage delay problems.

From this point of view the conclusion made in [11, 12] and mentioned above that the LiCl film may not be the protective film at all, can be understood assuming that the authors meant by the Li film only the subsequent Li film growth. Perhaps they overlooked the possibility of the existence of the very thin first LiCl layer having completely different properties from the massive and porous film which was observed by them. However even the first part of their conclusion might turn out to be correct. If the existence and actual protective qualities of the instantly formed very thin film on the Li surface in different systems cannot be doubted its nature remains obscure. It may be, after all, a film formed as a result of oxygen adsorption.

Considering the film formation processes and the voltage delay problem it must be borne in mind that they can be influenced to a significant degree by impurities in the electrolyte. The role of dissolved oxygen which is present in any practical battery system was claimed to be very important in [48] reviewed above. Water is another unavoidable contaminant.

However, up to now the role of water and other impurities on the behaviour of cells and electrochemical systems suitable for their production, has not been fully understood. It is clear that industrial production of batteries cannot be consistent with the high level purification which is very complicated and expensive. However the systematic investigation of the role of major contaminants on the performance of any particular battery system is very important.

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