

ON THE ELECTROCHEMISTRY OF THE NONAQUEOUS LITHIUM CELL

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Summary

The results and achievements in selected topics in the field of lithium cell electrochemistry, based on investigations performed in the author's laboratory, are presented. The active lithium electrode, passive films on lithium, and several cathode materials are considered. Opinions are given on where our electrochemical knowledge is still inadequate in order to achieve faster progress in the development of the lithium cell.

1. Introduction

The spectacular development of the lithium nonaqueous cell could hardly have been possible without recent progress in the electrochemistry of its active components. Earlier attempts to produce Li cells without sufficient knowledge in this new branch of applied electrochemistry have ended in failure. An unfortunate example in this respect is the now already forgotten Li/NiCl₂ secondary battery, which in the mid-sixties was proclaimed as the future electric car battery. It was realised that real success in the development of the Li cell is unthinkable without systematic research based on sound electrochemical principles. The present status report reviews the author's experience in some selected topics of the electrochemistry of the Li cell, based on experimental work performed in the Central Laboratory of Power Sources in Sofia.

2. The active Li electrode

2.1. The 'film-free' Li surface — a fiction ?

Owing to its extremely negative oxidation potential, Li is thermodynamically unstable, not only in aprotic organic solutions, but also when in contact with organic compounds having no hydrogen atom in their molecule (e.g. Teflon). Fortunately, the expected rapid oxidation of Li is in many cases strongly inhibited by passive films having unique properties. It is generally assumed that the electrochemical reaction



takes place on an Li surface covered by a thin compact film with comparatively good ionic conductivity, if special precautions are not taken to eliminate it before the electrochemical measurements are performed. Recent investigations of the Li surface by sensitive spectroscopic and other physical methods under ultra-high vacuum conditions [1] have clearly demonstrated that the idea of a 'film-free' Li surface is more or less a fiction. This is especially true for the usual electrochemical investigations, where the freshly cut Li surface is exposed for several minutes in a dry box atmosphere, containing at best 5 - 10 p.p.m. of H₂O and O₂. Thus one has always to take into account the native Li₂O film, which after immersion in the test electrolyte solution will undergo slower or faster conversion.

2.2. The effect of the surface pretreatment

Several methods of pretreatment have been employed so far to clean the native films from the Li surface before studying the electrochemical kinetics of reaction [1]:

- mechanical cutting or scraping in the dry box (MCB);
- anodic stripping in the test solution (AS);
- mechanical cutting in the test solution (MCS).

The effects of the different methods of pretreatment on the initial exchange current density, i_0 and the double layer capacitance C_d of the Li electrode are illustrated in Table 1, where available data for electrochemical reaction (1) in the most widely used electrolyte solution, 1 M LiClO₄ in propylene carbonate (PC), are juxtaposed with results obtained in this laboratory [8]. Inasmuch as the electrochemical techniques employed are quite

TABLE 1

Initial kinetic parameters of the Li/Li⁺ reaction in 1 M LiClO₄/PC solutions at 25 °C

Measurement technique	Pretreatment method	i_0 (mA/cm ²)	C_d (μF/cm ²)	Ref.
MP	MCS	10.2	45	[2]
TP	AS*	2.7	5.2	[3]
MP	MCB	0.95	—	[4]
MP	AS	3 - 6	—	[5]
ACI	AS	3.3	5.0	[6]
TP	AS*	0.7	—	[7]
ACI	MCB	2.8	6.2	[8]
ACI	AS	3.3	7.5	[8]
ACI	MCS	1.3	4.0	[8]

MP = micropolarization; TP = Tafel plots; ACI = AC impedance; MCS = mechanical cutting in the solution; MCB = mechanical cutting in the dry box; AS* = anodic stripping under unspecified conditions; AS = anodic stripping at 2.5 mA/cm², 10 C/cm².

reliable, the considerable dispersion of the results is most probably due to the different states of the Li surface at the moment of measurement. The results in Table 1 and our own experience make it possible to draw the following conclusions.

(i) The anodic stripping (AS) method is obviously to be preferred, since it can be easily performed under controlled conditions. Nevertheless, the kinetic parameters obtained in Table 1 after AS vary by almost a whole decade. A systematic evaluation of the AS method has been made by Garreau *et al.* [5]. According to these authors, at potentials exceeding 200 mV vs. Li/Li⁺, the anodic dissolution of Li is accompanied by a film formation process (FF), whereas at lower potentials only dissolution occurs, removing all traces of native films. This assumption is supported by SEM pictures ($\times 1500$), showing a smooth and clean Li surface, obtained by AS at $E < 200$ mV. Two objections can be raised against this presumption: first, the passive film on Li, as on any other metal, is so thin (30 - 300 Å), that it cannot be detected by SEM observation; and second, there are experimental data (see §3) which show that the anodic dissolution of Li is accompanied by FF at potentials lower than 200 mV as well as at the open circuit potential (OCP). Depending on the difference in the rates of the two competing processes, AS and FF, on the time of treatment, and on the thickness of the native film, the AS can yield a lower or higher film coverage which, at present, can only be evaluated by electrochemical methods.

With the progress of film removal by AS one has to take into consideration at least three concomitant processes: the increase of the surface roughness; the formation of active centres on the Li crystallites at kinks, steps, corners and edges; and the increase in the surface Li⁺ concentration. At this stage it is very difficult to decide to what extent each of these factors affects the kinetic parameters.

(ii) The MCB yields, when properly performed, quite reproducible initial kinetic data. The values of i_0 and C_d obtained after MCB are very similar to those measured after a slow AS at $E < 200$ mV, implying that the Li₂O film, formed inevitably in the dry box, is so thin that it cannot affect the kinetic parameters.

(iii) Because exposure of the freshly cut Li surface to the ambient atmosphere is excluded altogether, the MCS was expected to be the most efficient pretreatment method. This seemed to be supported by the high values of i_0 and C_d reported by Butler *et al.* [2] (Table 1). Strangely enough, since then no one else has reported data approaching these high values. Our own numerous measurements using the MCS method with the aid of a guillotine in the test cell always yielded considerably lower values, not only than those of Butler *et al.* [2], but also than those obtained after the other pretreatment methods. The reasons for this discrepancy are not clear. They cannot be associated, however, with experimental errors since, as seen in Table 1, our data obtained after the slow AS are in close agreement with those of Epelboin *et al.* [6].

In our opinion more systematic work is still needed in order to determine the optimum surface pretreatment conditions which could provide the

measurement of the real kinetic parameters of electrochemical reaction (1). This would enable us to understand not only the anodic dissolution reaction and the film formation processes, but also to elucidate the more complicated cathodic deposition reaction.

3. Passive films on Li

3.1. *Experimental techniques*

The detailed study of passive films on Li, as on any other metal, requires the application of a number of electrochemical, physical, spectroscopic, and optical methods. The limited thickness of the primary films on Li, responsible for its passivity, precludes their investigation by SEM or *in situ* ellipsometry. The electrochemical methods are still the most sensitive tools with which to study the primary films *in situ*. Most frequently used are potentiodynamic micropolarization, the galvanostatic pulse technique (both at low and high electric fields), and the AC impedance method. The first two are characterized by their simplicity and rapidity and are especially suitable for studying the initial stages of the passivation process. The AC impedance method employs rather sophisticated instrumentation and interpretation of the impedance data is not always straightforward. In favourable cases, however, this method can yield more ample data for the film properties, the charge transfer reaction, and the ionic diffusion.

3.2. *Passivation in strong inorganic oxidants*

The passivation of Li in SOCl_2 electrolyte solution is quite severe and was the first to be investigated more closely. The SEM photographs by Dey [9] revealed the growth on the Li surface of a thick, porous, and coarse crystalline film. At ambient temperatures this film grows at a constant rate, reaching about $40 \mu\text{m}$ in 150 days. Such a film cannot in principle protect the active Li metal from the strong oxidant, but literature data have shown an exceptionally low corrosion rate of Li in this solution. By the use of the galvanostatic pulse method it was demonstrated in this laboratory [10 - 12] that the passivity of Li in SOCl_2 solutions is not related to the thick, porous, and optically visible film, but only to the underlying, thin, compact film which has excellent insulating properties. The most relevant characteristics of the primary passive film on Li in SOCl_2 solutions, established in our investigations, are outlined below.

(i) The specific conductivity of the film, $3 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$, obtained in LiAlCl_4 solutions, well neutralized by a small excess of LiCl , is close to that of bulk samples of LiCl . The activation energy of the conductance of the film, 0.37 eV, is also in good agreement with that of bulk LiCl , 0.41 eV. These findings imply that the primary film on Li has the compact crystalline structure of LiCl .

(ii) The slope of the Tafel plots obtained at fields around 10^6V/cm is proportional to the film thickness, yielding a field constant of 1.1×10^{-6}

cm/V, which is typical for ionic crystals conducting by the field-assisted migration mechanism. The half-jump distance estimated from this constant, 2.7 Å, is practically equal to the Li-Cl distance in the crystal lattice of LiCl. These results confirm the solid state ionic crystal character of the primary passive film.

(iii) Based on a model for field-assisted growth, coupled with a chemical corrosion process at a constant rate, a kinetic equation was derived for the momentous growth rate of the film:

$$v = A/l - v_c \quad (2)$$

where A is the rate constant, l the film thickness, and v_c the corrosion rate. This equation fits well with the experimental data, showing that the constant A is proportional to the specific conductivity of the film, as expected from theory.

(iv) In contrast to the secondary film, which grows at a constant rate practically throughout the whole useful life of the Li/SOCl₂ cell, the primary film reaches a limiting thickness $l_\infty = A/v_c$ within 10 - 20 h.

(v) The specific conductivity and corrosion rate of the film increase with excess of Lewis acid, AlCl₃, in the solution. It is supposed that the latter is incorporated in the crystal lattice of LiCl, thereby raising the concentration of point defects.

(vi) The corrosion rate determined experimentally, about 10⁻¹⁰ cm/s, is in good agreement with the self-discharge rate of practical Li/SOCl₂ pacemaker cells, stored over 5 years.

(vii) The role of the secondary film in the voltage delay phenomenon is revealed. The latter acts as a porous membrane, increasing the diffusion polarization during the initial stages of discharge.

The properties of the primary film on Li as a solid ionic conductor, its kinetics of growth, and the dual film model studied and developed in this laboratory are already recognised by a number of authors [14 - 18].

3.3. Passivation in weak inorganic oxidants (SO₂)

Judging from the considerable difference in the OCP of the Li/SOCl₂ and Li/SO₂ couples, SO₂ should be thermodynamically a much weaker oxidant than SOCl₂. Our study of the passive film on Li obtained in the electrolyte solution used in practical Li/SO₂ cells (LiBr in CH₃CN + SO₂) confirmed this expectation through the much slower rates of growth of both the primary film (as established by galvanostatic measurements) and the secondary film (as observed by SEM) [19]. The principal results of this study can be summarized as follows.

(i) In CH₃CN solutions of LiBr containing less than 12 wt.% SO₂, a rapid corrosion process is observed, accompanied by gas evolution and the formation of a voluminous jelly-like coating, possessing no protective properties.

(ii) At higher SO₂ concentrations, a thin passive film is formed, growing according to a similar kinetic law to that found for the films in SOCl₂ solu-

tions. The rate of the film growth and its specific conductivity are practically independent of the concentration of SO_2 in the range 15 - 50 wt.%, and of the LiBr concentration from 0.1 to 0.5 M.

(iii) By increasing the water content in the solution from 80 to 1600 p.p.m., the limiting thickness of the film was increased almost seven times.

(iv) Substitution of the Br^- ion by ClO_4^- or AlCl_4^- in the solution did not appreciably affect the film conductivity. The film obtained in the presence of AsF_6^- ions, however, showed a much lower conductivity.

(v) The activation energies of the resistivity of the films formed in solutions of LiBr, LiAlCl_4 , and LiAsF_6 (0.66, 0.53, and 0.50 eV) are characteristic of solid ionic conductors of the alkali salt type and differ substantially from that of the liquid electrolyte solution (~ 0.15 eV). This result strongly suggests that also in these solutions, with a weak inorganic oxidant, the primary passive film is compact and conducts by ionic migration in the solid state.

It was further established that the passivation of the Li anode in practical Li/ SO_2 cells can also be studied reliably by the galvanostatic pulse method [20]. In these measurements the porous carbon electrode served both as a counter and a reference electrode by virtue of its highly developed surface area. Only in cells discharged below 2.0 V was the impedance of the carbon electrode so high as to interfere with the correct measurement of the Li electrode impedance.

A series of twelve commercial D-size cells stored for 2.5 years at room temperature was investigated by the galvanostatic pulse method [20]. It was found that the degree of anodic passivation, as evidenced by its capacitance, varies by a factor of 7. During a discharge of a deeply passivated cell, having a polarization resistance of $3200 \Omega \text{ cm}^2$, at a current density of 0.9 mA/cm^2 and room temperature, the minimum discharge voltage was attained within 1 - 2 s, while the rated discharge voltage of 2.82 V was regained only after 20 - 25 min. This is not a typical voltage delay as observed in Li/ SOCl_2 cells, but one should bear in mind that after the maximum storage period of 5 years and at sub-zero temperatures it could reach unacceptable levels.

Thanks to its simplicity and rapid performance the galvanostatic pulse method can be recommended as a nondestructive control test in the production of Li/ SO_2 and Li/ SOCl_2 cells.

3.4. Passivation in weak organic oxidants

An example of a fruitful combination of electrochemical with *in situ* ellipsometric measurements is the recent study [21 - 23] of the passivity of Li in the most popular electrolytic solution, 1 M LiClO_4 in PC, used both in practical cells and in basic investigations. With the aid of the galvanostatic pulse method and *in situ* ellipsometry it was found that the nature of the film, its growth kinetics, and the dual film model are similar to those observed in inorganic oxidant solutions. The most relevant results from these studies are the following.

(i) The specific conductivity of the primary passive film is practically equal to that of films formed in inorganic oxidant solutions.

(ii) The high field behaviour of the film and the Tafel slope, 1.2×10^{-6} cm/V, are also similar to those found for the films grown in SOCl_2 and SO_2 .

(iii) The film growth follows the same kinetic equation, derived for the case of SOCl_2 solutions.

(iv) The rate constant A in the kinetic equation, and the corrosion rate of the primary passive film in PC solutions are, however, about two orders of magnitude lower than those in SOCl_2 solutions, in agreement with the lower oxidation potential of PC, setting a smaller electric field across the film.

(v) The activation energy of the film obtained in PC solutions, 0.61 eV, is again typical for alkali salt ionic conductors.

This is in agreement with many authors, who consider that the primary film on Li in PC solutions of LiClO_4 is most probably Li_2CO_3 with minor amounts of LiCl .

Ellipsometric measurements of the Li surface *in situ* in the same PC solution [23], on the other hand, revealed that a thicker secondary film is growing on top of the primary one. However, at least in the first 200 hours of growth at the OCP and room temperature, the secondary film is not detectable by the galvanostatic pulse method, implying that its resistance is much lower than that of the primary film. Most probably the secondary film is a porous polymeric substance, well soaked in the electrolyte solution and possessing no protective properties. Thus the dual film model was exhibited in this case as well.

Additional information on the properties and growth of the primary passive film on Li in the same 1 M LiClO_4/PC solution was acquired recently by the AC impedance method [8]. More specifically, the effects of the preliminary surface treatment and of traces of water on the kinetics of the film growth were investigated. The evolution of the impedance parameters after immersion of the Li electrode in the test solution was followed for 150 - 200 h at the OCP, as well as during anodic polarization of fresh and passivated Li electrodes. Under favourable conditions three arcs can be observed on the complex plane diagram: the high frequency arc, reflecting the bulk resistance R_b and the geometric capacitance of the solid passive film; the medium frequency arc related to the charge transfer resistance R_t and the double layer capacitance C_d ; and the low frequency arc associated with the slow diffusion of ions in the compact or the porous film. The following experimental findings obtained from the AC impedance measurements are worth noting.

(i) In solutions containing not more than 20 p.p.m. of water the limiting film thickness is very low and the high frequency arc is not discernible, even after 200 h of storage of the electrode in the test solution. The film growth is, however, indirectly revealed by the growth of the medium frequency arc, reflecting the polarization resistance, which comprises R_b and R_t in an inexplicit way.

(ii) The high frequency arc can be observed more clearly under conditions of higher film resistance, e.g. at sub-zero temperatures, of films grown in solutions containing more than 200 p.p.m. of water, and of films formed in Li^+ free electrolyte solutions (1 M (TBA) ClO_4).

(iii) The double layer capacitance at the film-solution interface after a brief initial decline remains practically constant for at least 200 h, as expected for an intensive magnitude.

(iv) The growth of the polarization resistance R_p , determined from the medium frequency arc, can be described approximately by an empirical equation, $R_p = R_{p,0} + k \log t$. The rate constant k depends on the method of pretreatment and the water content in the solution.

(v) The rate constant k is lowest after anodic stripping and is, in this case, insensitive to changes in water concentration in the range 10 - 50 p.p.m.

(vi) Following mechanical cutting in the box atmosphere the rate constant is much larger. It grows considerably with the water content in the solution.

(vii) From the above results it is inferred that the film obtained after anodic stripping has a higher resistivity and/or a lower chemical corrosion rate.

(viii) The parameters of the low frequency arc remain quite invariable during the Li electrode passivation at the OCP. The arc may be interpreted in terms of retarded diffusion of Li^+ ions either in the compact or in the porous film.

(ix) The specific conductivity of the film estimated from the high frequency arc is about one order of magnitude higher than that measured by the galvanostatic pulse method [21, 22]. The reason for this discrepancy is assigned to the fact that the galvanostatic pulse method measures the polarization resistance R_p , which comprises the film resistance R_b and the charge transfer resistance R_t . When, as in the case of Li in PC solutions, the film is very thin, $R_b < R_t$ and a considerable error is introduced in the calculation of the resistivity. This error is, however, negligible for thicker films where $R_b \cong R_p$, as in SOCl_2 solutions.

(x) The rate of anodic stripping of passivated Li electrodes, assessed by the decay of R_p with increase in the anodic charge passed, grows with increase of the anodic current density. This suggests that the competing film formation process depends less on the anodic overpotential than the anodic dissolution. On the other hand, the results indicate that the film formation rate is not zero, even at the OCP.

Despite the importance of passive films in the performance of all types of Li cells, their investigation is still in its early stages. We have but a limited knowledge of, for example, the exact chemical composition, the mechanism of the film disintegration and stripping under anodic polarization, the mechanism of the rebuilding of the film after its partial removal, the mechanism of the anodic film formation, etc.

4. Cathode materials

Despite the large number of available cathode materials used in practical Li cells or still under exploration, the energy and power characteristics

of the Li anode are so high that it cannot be matched by any cathode. The search for new, and the improvement of existing, high performance cathode materials is a major goal in most laboratories involved in the development of Li cells. The numerous depolarizers suitable for cathodes can be tentatively classified into three main groups:

- liquids and dissolved gases;
- non rechargeable solid materials;
- rechargeable solid materials.

The results and achievements in the study of several cathodic materials performed in this laboratory are outlined below.

4.1. Liquids and dissolved gases

4.1.1. Reduction of thionyl chloride

A preliminary study was carried out on the reduction of SOCl_2 on a smooth Pt electrode in 1 M LiAlCl_4 solutions by linear sweep voltammetry [24]. At a scanning rate of 0.6 V/min two peaks appear on the cathodic branch: a major peak at 3.0 V vs. Li/Li^+ and a secondary one at 2.5 V. Following the cathodic sweep no anodic peaks are observed on the reverse sweep, implying a blocking of the Pt electrode by the reduction product LiCl . The secondary cathodic peak appears only in the presence of small amounts of HCl in the solution, introduced either intentionally or through the hydrolysis of SOCl_2 by traces of atmospheric water vapour. The secondary peak is almost equal in height to the major one, which reflects the main reduction process of SOCl_2 with a concentration of about 14 M. The secondary peak therefore can in no way correspond to the reduction of HCl , having a concentration of not higher than about 0.01 M. It is assumed that this peak is also due to the reduction of SOCl_2 but via another mechanism catalysed by HCl .

4.1.2. Reduction of SO_2

The reduction of SO_2 , which is the cathodic reaction during the discharge of Li/SO_2 cells, has been studied in dilute solutions (10^{-3} M SO_2) in several organic solvents (DMF, DMSO, and PC). In order to approach more closely the conditions of the practical Li/SO_2 cell, we studied the electrochemical reduction of SO_2 in 0.1 - 0.5 M LiBr solutions in CH_3CN containing 1×10^{-3} - 1 M SO_2 on glassy carbon and Pt electrodes with the aid of linear sweep voltammetry [25, 26]. The relevant experimental findings can be summarized as follows:

(i) The overall cathodic process involves fast one-electron charge transfer, followed by irreversible electrochemical adsorption, followed in turn by fast formation of a solid film.

(ii) The parameters of the charge transfer reaction on both carbon and Pt electrodes were determined, leading to the following kinetic equation:

$$i \cong 10^{-6} C_{\text{SO}_2} \exp[(1 - 0.6)F\eta/RT] \quad \text{A/cm}^2$$

(iii) At sweep rates higher than 0.1 V/s the electric charge associated with the adsorption reaction corresponds to that of a monolayer. The dependences of the peak current and the peak potential on the sweep rate obey the expressions derived by Srinivasan and Gileadi [27] for a slow electrochemical adsorption reaction.

(iv) Water has a strong depassivation effect on both electrodes. Upon the addition of 5×10^{-5} M of water to a 0.5 LiBr solution of CH_3CN , containing 5×10^{-3} SO_2 , the dependence of the peak current on the sweep rate follows the Matsuda-Ayabe equation [28] for a diffusion limited reaction, implying that the electrode surface is depassivated.

In a closer approach to the conditions in practical Li/ SO_2 cells we studied [29] the effect of the parameters of the porous carbon electrode on the utilization of the carbon material during the discharge in a D-size cell configuration. The cathode mix of acetylene black and Teflon was applied by pressure to an Al exmet grid. The electrolyte composition was the same as that used in practical Li cells: 1 M LiBr in CH_3CN , containing 70 - 75 wt.% SO_2 . The following results are of practical interest.

(i) The cathodic utilization with respect to SO_2 in the range of current densities studied (0.5 - 4 mA/cm^2) and room temperature was always better than 90%.

(ii) The optimum porosity of the cathode lies between 80% and 82%.

(iii) The cathode utilization with respect to the carbon material grows with decrease in binder content. The lowest limit of this content is 5%, below which the mechanical stability of the electrode becomes unsatisfactory.

(iv) At low current density, $\sim 0.5 \text{ mA}/\text{cm}^2$, the cathode utilization falls exponentially with increase of electrode thickness from 0.025 to 0.15 cm.

(v) In the current density range 1 - 4 mA/cm^2 the relationships utilization versus thickness have a flat maximum at about 0.05 cm.

(vi) An empirical equation has been derived relating the cathode utilization η and the current density i at a constant thickness: $\log \eta = \log \eta_0 - ki$. The constant η_0 represents the limiting utilization at $i \rightarrow 0$, and is determined as the ratio of the specific volume of the solid reduction product, $\text{Li}_2\text{S}_2\text{O}_4$, to the specific pore volume of the cathode.

The above data for the cathode utilization as a function of the electrode dimensions are indispensable in the design of Li/ SO_2 cells for a required discharge rate. On the basis of the material balance in the cell, expressions were derived in this laboratory [30] for calculation of the optimum electrode dimensions, which provide the maximum cell capacity at a given load. Using the cathode utilization data from the previous study [29], the validity of these expressions was confirmed experimentally over a wide range of current drains and electrode dimensions for the D-size cell configuration. The expressions are especially useful in the design of cells which must perform safely under abuse conditions. Their application could be extended also to cells operating at low temperatures, where, however, experimental data on the cathode utilization are still not available.

4.2. Non rechargeable solid materials (MnO_2)

Thanks to the high energy density and the low cost of MnO_2 the Li/ MnO_2 cell has found the widest application among primary Li cells with solid cathodes. The availability of various types of MnO_2 , produced for the needs of the Leclanché cell, presents a wide choice for researchers of the new Li/ MnO_2 cell. Since the patent of Ikeda *et al.* [31], numerous papers have been devoted to the study of the thermal treatment of electrolytic manganese dioxide (EMD) and chemical manganese dioxide (CMD), aimed at improvement of the cathode performance. It was generally assumed that by treating MnO_2 at a temperature between 360 and 400 °C the optimum results would be obtained irrespective of the type of initial material. This assumption was mainly based on the results of TGA measurements, which record the total weight loss (H_2O and O_2) as a function of temperature.

A new apparatus has been designed in this laboratory [32] which can separately and simultaneously record the rate of H_2O and O_2 evolution during heating of the MnO_2 sample at a constant rate. The investigation of several commercial MnO_2 samples with this apparatus yielded valuable information on the optimization of the conditions for thermal treatment of this material before its use as a cathode in Li cells. The following results obtained with two CMD and two EMD samples are worth noting.

(i) It is possible to determine separately the free (adsorbed) and bound water. The three maxima observed in the diagram of evolved water against temperature imply three different types of bound water.

(ii) Most of the water evolves below 300 °C, but some residual water remains up to 400 °C.

(iii) The evolution of O_2 begins at various temperatures in the range 300 - 400 °C for the different samples. Thus it is not recommended that the less stable MnO_2 samples should be heated at or above 400 °C, where they can lose about 7% of O_2 over 24 h, corresponding to an 80% conversion of MnO_2 to Mn_2O_3 .

(iv) No general rule for the thermal treatment of MnO_2 samples before their use in Li cells can be proposed, since the temperatures for their full desiccation and their thermal decomposition may vary from type to type.

4.3. Rechargeable solid materials ($Na_{0.1}CrS_2$)

The last decade is marked by a steeply rising interest in layered compounds, which are suitable for cathode materials in secondary Li cells. Starting with TiS_2 in 1973 [33], practically all transition metal dichalcogenides have been investigated with respect to their ability to intercalate Li reversibly by electrochemical reduction and oxidation. The dichalcogenides of Cr were to a certain extent neglected owing to the fact that CrS_2 cannot be synthesized. By oxidation of $NaCrS_2$, a compound prepared for the first time a century ago [34], the nonstoichiometric compound $Na_{0.1}CrS_2$ was obtained [35 - 37], which is so far the closest approach to CrS_2 . The three-dimensional layered structure of $Na_{0.1}CrS_2$ can intercalate reversibly up to one equivalent of Li by electrochemical reduction and oxidation, proving

to be exceptionally rugged during long cycling tests. The OCP of $\text{Li}_{0.5}\text{-Na}_{0.1}\text{CrS}_2$ of 2.50 V is 0.25 V higher than that of $\text{Li}_{0.5}\text{TiS}_2$. The X-ray diffraction patterns reveal only minor lattice parameter variations with increase of Li in the host structure, implying a single phase over the whole compositional range.

In an attempt to improve the performance of the new cathode material a study was performed on the effect of the conditions of its synthesis on its physical properties and its electrochemical behaviour in an Li nonaqueous cell [38]. By lowering the temperature of synthesis, T_s , of the starting compound NaCrS_2 from 800 to 400 °C, the specific surface area was increased from 1.5 to 20 m^2/g , while the electric conductivity of pellets pressed from the samples increased by two orders of magnitude. The host structure was obtained either by slow electrochemical oxidation in a nonaqueous electrolyte solution or by chemical oxidation by H_2O_2 in an aqueous dispersion. The lowering of T_s from 800 to 500 °C brought about an increase in the initial cathodic efficiency from 20% to 80% (with respect to the theoretical value) in cells discharged at a two hour rate.

The cycling life of thin model cathodes prepared from $\text{Na}_{0.1}\text{CrS}_2$ containing 50% Teflonized acetylene black was studied in a cell discharged and charged at a two hour rate between 1.5 and 3.5 V as a function of the conditions of synthesis. The initial discharge capacity of the optimum sample obtained at 500 °C was 0.15 A h/g and diminished only by 10% after 100 cycles. In a test lasting 1000 cycles at a two hour rate the performance of the $\text{Na}_{0.1}\text{CrS}_2$ cathode was comparable with that recently reported [39] for a stoichiometric TiS_2 cathode tested under not very different conditions. Having in mind also the simple and reproducible preparation technique of $\text{Na}_{0.1}\text{CrS}_2$ and the availability of its raw materials, it appears that it could find practical application in the future secondary Li cell.

5. Conclusion

Not very long ago Professor Bockris described electrochemistry as an underdeveloped science. Without any exaggeration one can freely say that the electrochemistry of the Li cell is still in its cradle. Indeed, in comparison with the centennial Leclanché cell the Li cell is only a teenager which badly needs the support of its own electrochemistry. One should not forget also that for the classic aqueous cell it was necessary to study only one anode, one solvent and 3 - 4 cathode materials and solutes, but for Li cells the number of active materials is enormous and continuously growing. This is really a great challenge to all scientists working in the field of Li cells.

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