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Electrochemical characterization of lithium–boron composite

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Electrochemical measurements, including a.c. and d.c. techniques, were performed in order to determine the differences between Li–B alloy prepared at 600° C and Li–B composite prepared at 450° C. Li–B composites can be defined as very finely-grained, physically dispersed amorphous boron, entrapped in polycrystalline metallic lithium. SEM analysis of electrode surfaces, corroborating the electrochemical measurements, is given. Some experimental problems arising from passive layer formation on lithium in organic electrolytes which influence the reliability and reproducibility of the results are discussed.

1. Introduction

The preparation of metallic lithium–boron alloys was first described by Wang [1] and consists of two steps: exothermic dissolution of preferably crystalline boron in molten lithium in the temperature range from 350 to 450° C and solidification of the alloy by slow heating to about 550° C. At this point, a vigorous exothermic reaction occurs, leading to the final structure of the alloy, which can be described as a solid porous matrix of Li–B compound containing free metallic lithium in the pores.

The electrochemical characteristics, such as standard potential and gravimetric capacity of the alloy have been found [2] to be comparable to those of pure lithium, although the melting point of the Li–B matrix is considerably higher, and molten lithium is not released from the pores even at 600° C. For this reason metallic lithium–boron alloys have primarily found application in thermal, high-power batteries [2, 3].

These promising characteristics were responsible for extensive studies of lithium–boron alloys [2–14]. However, there are no reports on the characteristics of the intermediate material in the preparation of the alloy, obtained by cooling the solution of boron in a lithium melt, after the first step of alloy preparation. Under these conditions boron does not recrystallize, nor is it contained in the crystal structure of lithium, since the solubility of boron in solid lithium is negligible [9]. Consequently, the intermediate material can be defined as a very fine, physically dispersed, amorphous boron entrapped in polycrystalline metallic lithium. It will be referred to as 'Li–B composite' throughout this article to distinguish it from Li–B alloy described above.

The main purpose of this work was to study the electrochemical characteristics of Li–B composite that have not been previously reported and compare this material to pure lithium and Li–B alloy.

2. Experimental data

All experiments were carried out in a Braun glove box in dry argon with oxygen and water contents lower than 2 and 1 p.p.m., respectively.

Li–B composites and alloys were prepared from battery-grade lithium (Foote Min. Comp.) and crystalline boron (Merck 99.9 w/o pure). All alloy and composite samples contained 20 w/o boron. Electrodes were prepared from 2–3 mm thick foils of the tested materials. The foil was pressed into the electrode holder and an active surface of 0.50 cm^2 was cut with a stainless steel blade in order to clean it prior to exposure to electrolyte. Throughout the experiments, the supporting electrolyte was dry LiCl (Merck p.a.) in dimethylsulfoxide (DMSO, Merck p.a.), dried using molecular sieves. The concentration ranged from 0.5 to 0.05 M. Reference and counter electrodes were made from battery-grade lithium foil.

Measurements were made with a Solartron 1250 frequency analyser, coupled with a Solartron 1286 potentiostat–galvanostat, and were controlled by an HP 9122 microcomputer.

Photographs of electrode surfaces were taken with a Jeol T220 scanning electron microscope and the samples were brought into the vacuum chamber of the microscope in a specially designed vacuum holder [15] in order to prevent the contamination of samples with air.

3. Results and discussion

It is known that lithium is thermodynamically unstable in all organic solvents. Thus the formation of a passive layer at the surface, which kinetically protects lithium from fast degradation, is characteristic of lithium-organic electrolyte systems. The passive layer plays an important role in electrochemical surface processes. It introduces considerable additional resistance into the system and two phase boundaries are formed, i.e. active electrode surface – passive layer and passive layer–electrolyte.

The assumption was that fine particles of boron in Li–B composite change the microstructure of the active electrodes surface in comparison to pure lithium and Li–B alloy and thus cause a different growth of the passive layer. This is likely to result in different electrochemical characteristics although the measured equilibrium potentials of both Li–B materials differed from the equilibrium potential of lithium by less than ±1 mV. This is in agreement with published data [3] and suggests that the active material is free lithium.

3.1. *Impedance response measurements*

Preliminary impedance responses of lithium and both Li–B materials were measured in the range 65 kHz to 10 mHz and compared in order to ascertain if they were similar. The amplitude of the sinusoidal signal was 10 mV, and the electrodes were kept for several hours in the electrolyte prior to measurement. Two depressed semicircles were present in the impedance plot in all cases (Fig. 1(a)). The measured system could be formally described by the equivalent circuit depicted in Fig. 1(b), where the labels assigned to the capacitors and resistors were chosen after the following considerations.

The capacitances of the high and low frequency semicircles were about 1 to 10 μFcm^{-2} and 0.1 to 1 Fcm^{-2}, respectively. According to [16], the high frequency semicircle capacitance may be ascribed to a charge distribution in the passive layer, and the resistance R_t is taken as a sum of the charge transfer resistance R_{ct} and all other contributing resistances in the passive layer R_{pl}. The low frequency semicircle capacitance is too high to be ascribed to the electrostatic storage of energy. In fact, the origin of low frequency phenomena also referred to as low frequency dispersion (LFD) [17], has not been satisfactorily explained until now. These processes have been detected by impedance spectroscopy [16 to 18] but are usually neglected in the interpretation of d.c. measurements. The term R_{el} was assigned to introduce uncompensated resistances, e.g. the resistance of the electrolyte, into the model. According to the equivalent circuit on Fig. 1(b), a comparison of the materials used in this investigation

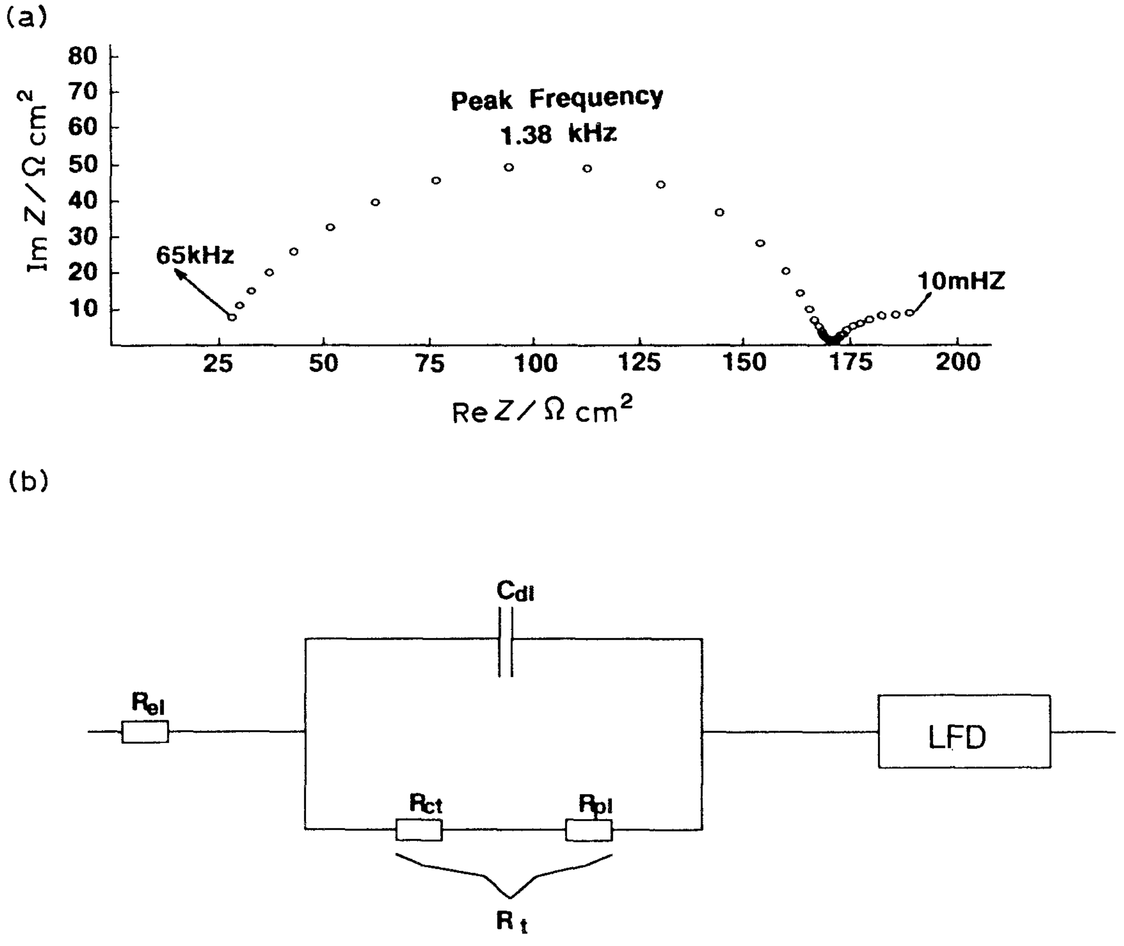

Fig. 1. (a) Typical experimental impedance plot of 1 h old Li–B composite electrode; (b) equivalent circuit.

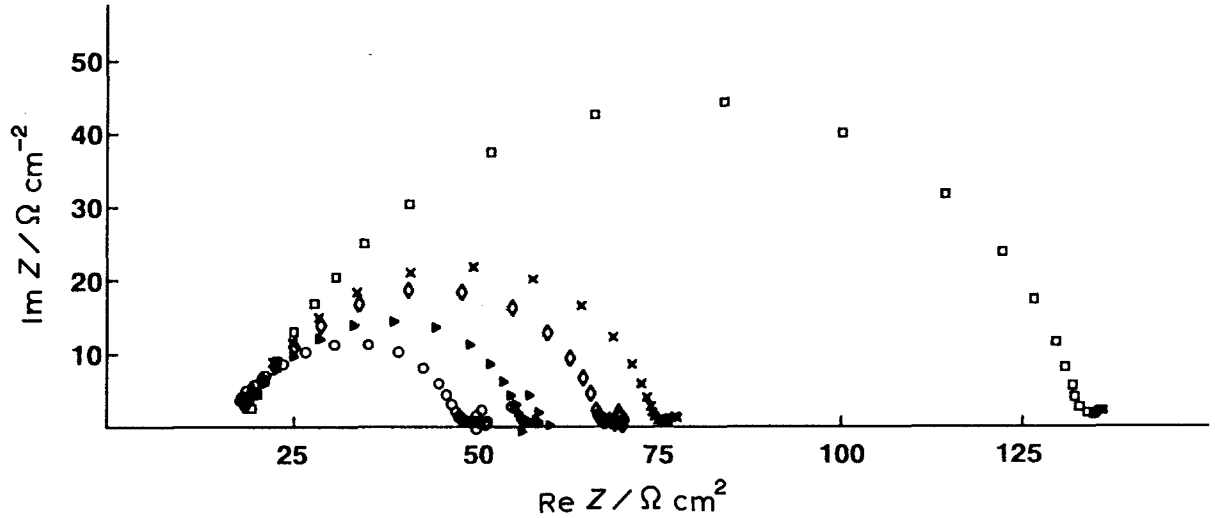

Fig. 2. Typical change in impedance response in time for Li–B composite electrode. After (○) 0.5h, (▶) 1h, (◇) 2h, (×) 4h, and (□) 24h.

was made in terms of absolute values and time dependence of R_t resistances. Further measurements were performed in the frequency range from 65 kHz to 100 mHz with a sinusoidal signal amplitude of 10 mV.

An attempt to measure the impedance response of the electrodes immediately after immersion into the electrolyte failed; the results were inexplicable and irreproducible. It was established that in the investigated case (Li in LiCl/DMSO), at least half an hour was required, after electrode immersion, for the system to stabilize sufficiently in order to obtain reproducible results. Thus, it was not possible to follow the passive layer formation from the beginning by using this method due to rapid change of the measured quantity during the measurement. This is regarded as the feature of the Li–LiCl/DMSO system since in some other cells with lithium anodes an instant measurement was possible [14, 19].

Several series of measurements were performed. Values of resistances and capacities of the equivalent circuit on Fig. 1 were obtained by fitting the theoretical impedance response of the equivalent circuit to the measured data. It was found that after 30 min in the electrolyte. R_t values of lithium electrodes were between 30 and 40 $\Omega\,\mathrm{cm}^{-2}$. Li–B composite and Li–B alloy electrodes had, compared with lithium, 70–80% and 75–85% lower values of R_t, respectively. Measurements were repeated after 1, 2, 4 and 24 h after the immersion of the working electrode into the electrolyte in order to establish the changes of the R_t with time. Fig. 2 shows the characteristic impedance plots obtained. Table 1 gives R_t values normalized with respect to the first measurement in the series in order to present the relative increasing rate of R_t.

Table 1. Relative changes of R_t *values with time*

Material	*0.5 h*	*1 h*	*2 h*	*4 h*	*24 h*
Lithium	1	1.35	1.69	2.00	3.66
Li–B composite	1	1.47	2.16	2.89	7.62
Li–B alloy	1	1.33	1.43	1.85	2.55

According to Table 1, in the case of Li–B composite R_t increases by more than 750% in the first 24 h, while for the Li and Li–B alloy electrodes the increase in R_t is about 350 and 250%, respectively. It was suspected that differences in R_t would be accompanied by differences in the delay effect.

3.2. *Delay effect*

The delay effect is a common phenomenon related to passive layers and is a serious limitation in the use of lithium batteries. It manifests itself as a large drop in the cell voltage as the battery is loaded, after which the voltage rises to a definite constant value. Several models have been proposed to explain this behaviour in different systems. The solid electrolyte interface (SEI) model [20] is generally accepted and potentiostatic measurements are usually used to study the delay effect. Fig. 3 presents a typical time dependence of anodic current density, measured with 24 h old electrodes polarized to 250 mV against a lithium reference electrode. Two aspects of the delay effect can be deduced from Fig. 3: the difference between the starting and stabilized final value of the current density (Δi), and the time needed for the stabilization of the current (t_s). Based on several measurements it was found that both Li–B materials have smaller Δi, the average being about 0.4 $\mathrm{mA\,cm}^{-2}$ in both cases, than lithium where the average Δi is about 0.5 $\mathrm{mA\,cm}^{-2}$. The value of t_s is smallest in the case of the Li–B composite (150 s) and largest in the case of lithium (300 s). Li–B alloy electrodes have t_s about 200 s.

According to [21], the increase in current density with time is due to thermomechanical breakdown of the passive layer. To confirm this, an electrode was held in the electrolyte for about a week to allow the formation of the passive layer. Then the electrode surface was examined by SEM. The photograph (Fig. 4) shows that a sponge-like layer completely covers the electrode surface. The same electrode was then replaced in electrolyte and anodically polarized at 20 $\mathrm{mA\,cm}^{-2}$ for 1 h and subsequently photographed.

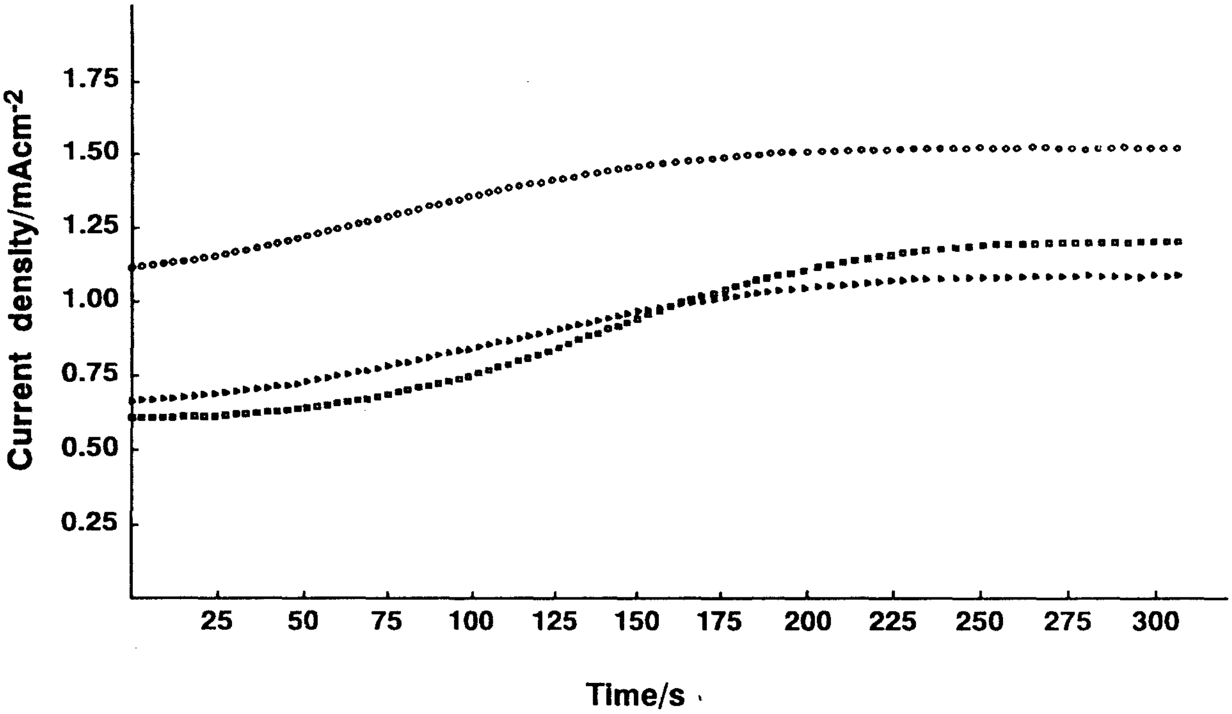

Fig. 3. Delay effect of various electrodes: (○) Li–B composite, (▷) Li–B alloy, and (□) pure lithium.

Figure 5 clearly shows the change in the morphology of the layer. On the basis of additional observations under different conditions, it was concluded that the layer was partially destroyed and the bare electrode surface came in direct contact with the electrolyte, resulting in higher current densities. It was noticed that with higher current density larger parts of the film was destroyed.

It can be concluded that the presence of boron in lithium causes higher resistance of the passive layer and/or the interfaces at current densities below 0.2 mA cm^{-2} (Table 1). On the other hand, at current densities above 0.7 mA cm^{-2} the passive layer on Li–B electrodes is destroyed more easily as in the case of lithium. On comparing Li–B alloy and Li–B composite electrodes, it is evident that the form of the boron is important. When in the form of finely dispersed clusters in the Li–B composite, it raises R_t at low current densities and facilitates the stabilization of the current at higher current densities more than if it is bound in a Li_7B_6 ionic compound in Li–B alloy.

This was also confirmed by comparing the final current densities. In all cases, the depassivated composite electrodes reached higher current densities, the average being 1.5 mA cm^{-2}, than lithium (1.1 mA cm^{-2}) and alloy (1.0 mA cm^{-2}) electrodes. This could be a useful feature for application and it was important to establish the differences between the de-passivated tested materials when lower current densities were applied.

3.3. *Polarization resistance of depassivated electrode*

The measurements were performed according to the following procedure: first a potential of 250 mV against lithium reference electrode was applied anodically to the working electrode in order to depassivate it. After 3 min, a potential sweep was done up to 15 mV cathodically, with a sweep rate of 0.5 mV s^{-1}.

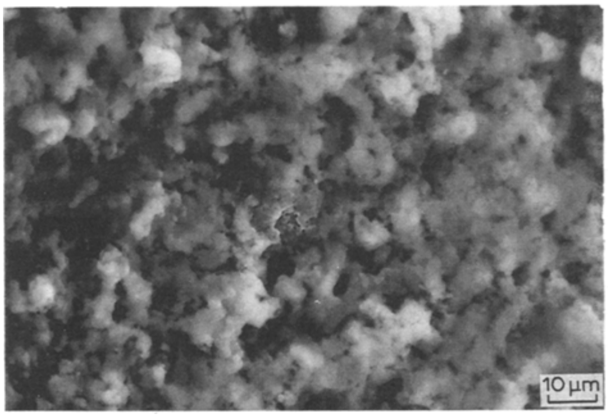

Fig. 4. SEM photograph of a passive layer on lithium electrode: one week old, not polarized.

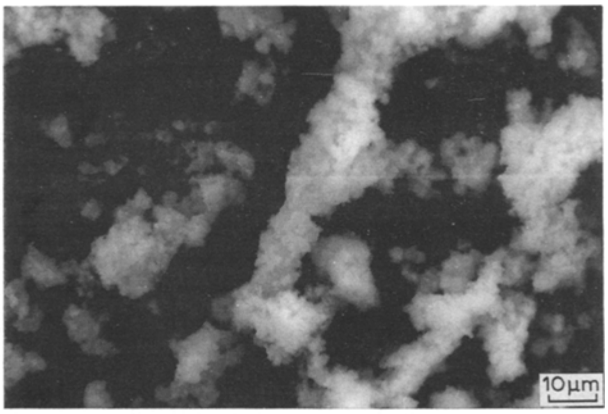

Fig. 5. SEM photograph of the same electode as in Fig. 4: anodically polarized at 20 mA cm^{-2} for 1 h.

Table 2. Polarization resistance of depassivated electrodes

Material	R_p*(dep.)*/$\Omega\,cm^2$
Lithium	578
Li–B composite	428
Li–B alloy	414

The polarization resistance was then calculated in the range ±15 mV against lithium reference electrode. The results are given in Table 2 and show that the polarization resistance of pure lithium depassivated electrodes are considerably higher than that of composite and alloy electrodes. Similar observations have been explained by geometric factors [14], the active surface being larger than the geometric one due to porosity and surface non uniformity of the electrodes containing boron. In the present case this explanation cannot be used since it is in disagreement with experimental data. Note that depassivated Li–B composite and Li–B alloy electrodes had comparable polarization resistances (Table 2), but the former reached higher current densities. This means that the transport of reactants through the pores of inert Li–B compound, which limits the current densities of the Li–B alloy electrodes [14], is not the limiting factor in the case of the Li–B composite. There is no inert porous matrix in the case of Li–B composite as observed with SEM investigation. The lower polarization resistance can therefore not be explained on the basis of porosity, i.e. larger active surface. It is more likely that boron, present in the electrode material, facilitates the thermomechanical breakdown of the film, what was confirmed by SEM observations [Figs 4–8].

A series of electrodes was galvanostatically polarized at 10 mA cm^{-2} for 10 min. The current was applied as soon as the electrolyte was poured into the cell. The electrodes were dried and SEM photographs of electrode surfaces were taken. Some characteristic photographs are shown in Figs 6–8.

It can be seen that the passive layer grows most readily on the pure lithium electrode. It is formed at specific locations, even though the electrode is anodically polarized (Fig. 6) while in the case of Li–B composite there is almost no sponge-like passive layer on the polarized electrode surface (Fig. 7).

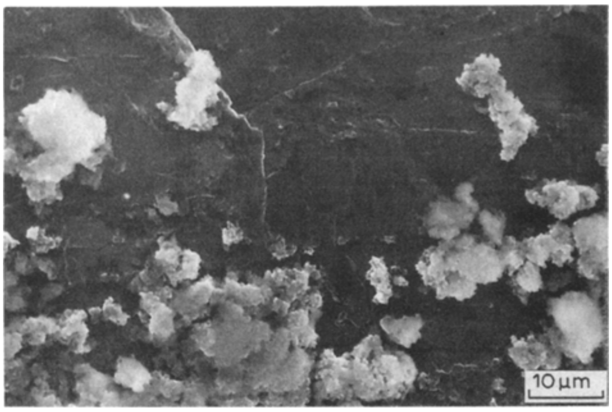

Fig. 6. SEM photograph of lithium electrode surface: anodically polarized at 10 mA cm^{-2} for 10 min.

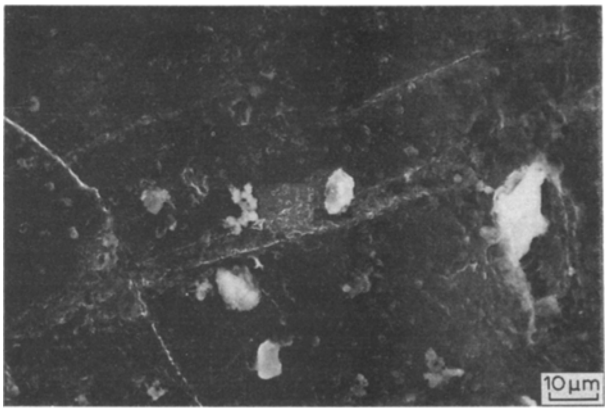

Fig. 7. SEM photograph of Li–B composite electrode surface: anodically polarized at 10 mA cm^{-2} for 10 min.

Fig. 8. SEM photograph of Li–B alloy electrode surface: anodically polarized at 10 mA cm^{-2} for 10 min.

Figure 8 shows that with the anodic polarization of the Li–B alloy electrode, the active lithium near the surface of the electrode is consumed in a relatively short time and the diffusion through pores of the inert Li–B alloy matrix retards the process.

3.4. *Comparison between d.c. and a.c. polarization measurements*

D.c. and a.c. techniques should give comparable values of R_t. However, there is considerable differences between the two quantities as shown in Table 3, which presents some results from a.c. and d.c. measurements. Electrodes made from lithium, Li–B alloy and Li–B composite were held in electrolytes of 0.5 M and 0.05 M LiCl in DMSO for different times and impedance followed by d.c. polarization measurements were performed. All other experimental conditions were kept as constant as possible. The sum $R_{el} + R_t$ was determined from an impedance measurement, while R_p resulted from a d.c. measurement in the range ±10 mV with a sweep rate of 0.1 mV s^{-1}. The difference cannot be ascribed to material, electrolyte or passivation time of the electrodes. The only conclusion following from Table 3 is that the d.c. technique always gives greater value of polarization resistance than the a.c. technique. In our opinion, the difference originates from different time-

Table 3. Comparison of a.c. and d.c. results of resistance measurements

Electrolyte	*Material*	*Time/h*	$(R_{el} + R_t)$ / $\Omega\,cm^2$	$R_p/\Omega\,cm^2$	Δ*/%
0.5 M LiCl in DMSO	Li	0.5	170	194	14
	Li	1	244	278	14
	Li	2	360	386	7
	Li	4	484	496	2
	Li–B composite	1	146	180	23
0.05 M LiCl in DMSO	Li	1	428	512	20
	Li	4	838	896	7
	Li–B composite	1	576	646	12
	Li–B alloy	4	700	800	14

* Δ represents the difference $R_p - (R_{el} + R_t)$ divided by $(R_{el} + R_t)$

frequency characteristics of both methods. If d.c. measurement is considered as constant frequency a.c. technique with the frequency corresponding to the sweep rate, both methods should give equal results. This is confirmed by the data in Table 4 where d.c. and a.c. measurements fulfilling the above condition are compared. Measurements at three sweep rates (frequencies) were performed using a pure lithium electrode, previously held in the electrolyte for 0.5 h. The amplitude of the signal was 10 mV in both cases and the frequency corresponding to a given sweep rate was calculated as the reciprocal of the total time needed to accomplish a sweep from 0 to + 10 to −10 and back to 0 mV around the equilibrium potential. R_p equals $R_{el} + R_t$ if the d.c. sweep rate is set to correspond to the frequency where the impedance semicircle touches the real axis. Therefore, in systems with a passivation lithium anode, d.c. results must be interpreted accordingly and impedance data should be used to detect low frequency processes which might contribute to the R_p value.

4. Conclusions

Li–B composite has been known as an intermediate material in Li–B alloy preparation. In the present work some electrochemical characteristics of this material, as determined by a.c. and d.c. techniques have been reported and compared with properties of pure lithium and Li–B alloy with 20 w/o B.

Establishing proper experimental conditions to obtain reliable data it was found that the passive layer formed on lithium in LiCl/DMSO requires at least 30 min of equilibration. On the other hand, after one week of storage, the passive layer properties are significantly affected even by the small perturbations, including impedance measurements, which can decrease R_t up to 30%. Comparing d.c. and a.c. techniques it was found that the results are similar only if the d.c. sweep rate is set to correspond to the a.c. frequency.

These general observations hold also for the Li–B composite and Li–B alloy. It was, however, found that the passive layer properties are changed if boron is added to lithium. The form of boron addition is important in this aspect. SEM analysis of polarized electrodes indicated that boron in the form of finely-dispersed clusters in Li–B composite facilitates thermomechanical breakdown of the passive layer formed on the electrodes in LiCl/DMSO electrolyte. This decreases the delay effect and increases current densities of depassivated electrodes. Measurements of the delay effect showed that in the case of Li–B composite the time needed for stabilization of the current was shortest (150 s) and the final current density was highest (1.5 mA cm^{-2}) if compared to pure lithium (300 s and 1.1 mA cm^{-2}) and Li–B alloy (150 s and 1.0 mA cm^{-2}). These characteristics of Li–B composite are superior to those of pure lithium. However, additional studies are needed in order to confirm that the advantages are sufficient to recommend the use of Li–B composite in the production of batteries, since the large-scale preparation of Li–B composite is complicated.

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Table 4. Frequency/sweep rate dependence of R_t *measured by d.c. sweep*

Sweep rate/mV s^{-1}	*Corresp. Freq.*/Hz	R_t(d.c.)/Ω cm^2	*R.P.I.**/Ω cm^2
4	0.1	126	126
0.8	0.02	133	133
0.4	0.01	137	139

* R.P.I. is the real part of the impedance at a given frequency.

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