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The behaviour of graphite, carbon black, and $Li_4Ti_5O_{12}$ in LiBOB-based electrolytes

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Abstract

The film formation behaviour of lithium bis(oxalato)borate (LiBOB), a new electrolyte salt for lithium batteries, on graphite, carbon black and lithium titanate is reported. LiBOB is actively involved in the formation of the solid electrolyte interphase (SEI) at the anode. Part of this formation is an irreversible reductive reaction which takes place at potentials of around 1.75 V vs Li/Li^+ and contributes to the irreversible capacity of anode materials in the first cycle. Carbon black interacts strongly with LiBOB-based electrolytes, which results in strong film formation and loss of electronic conductivity within the composite electrode. In LiBOB-based electrolytes the electrode kinetics increase in the order: carbon black $\ll$ fine particulate graphite $\sim$ metal powder, due to decreased film formation of the conductive additive. The influence of various solvents, surfactant additives, and potential impurities was also studied.

1. Introduction

In the course of the continuous efforts to increase the energy and power of the Li-ion battery, issues such as safety, toxicity, and cost are gaining importance. The safety of a battery system during normal operation and abuse conditions such as overcharge, overdischarge, and high temperature is strongly governed by the interactions between the electrode materials and the electrolyte. $LiPF_6$, which is the prevailing electrolyte salt in commercial batteries today, has many limitations in this respect, and the search for alternatives is in progress.

A potential replacement for $LiPF_6$ could be lithium bis(oxalato)borate (LiBOB). LiBOB shows high thermal, chemical and electrochemical stability. It is non-toxic, non-corrosive and non-mutagenic. The conductivities of LiBOB-based electrolytes are lower than those of $LiPF_6$- but higher than those of $LiBF_4$-based systems [1]. The successful operation both at room temperature and at elevated temperatures has already been demonstrated for various electrode combinations, including graphite | Ni-based mixed layered oxide [2], graphite | stabilised lithium manganese oxide spinel [3], graphite | $LiFePO_4$ [4–6], or $Li_4Ti_5O_{12}$ | $LiFePO_4$ [5]. Accelerated-rate calorimetry (ARC) was performed on various electrode materials to study their thermal stability in the presence of the electrolyte and gives a complex picture: for charged meso-carbon micro-bead (MCMB) electrodes, $Li_4Ti_5O_{12}$, and $LiFePO_4$, LiBOB-based electrolytes are observed to be safer than $LiPF_6$-based ones. They are, however, observed to be less safe for $LiCoO_2$ and $Li(Ni_{0.1}Co_{0.8}Mn_{0.1})O_2$ electrodes [7–9].

LiBOB appears to be especially suited for Li-ion batteries with lithium manganese oxide spinels as the cathode material. Mn dissolution from the spinel lattice, which has been identified as one of the main reasons for the insufficient cycling stability in $LiPF_6$-based electrolytes, is negligible for LiBOB-based electrolytes [6, 10]. Improved capacity retention was observed during cycling at 50 °C (as compared to batteries with $LiPF_6$-based electrolytes) [3]. Only a minor increase of cell impedance occurred during a hot-box test for 24 h at 85–90 °C in the charged state [6]. Furthermore, $LiMn_2O_4$ shows unique overcharge characteristics with LiBOB-based electrolytes, resulting in high safety [6, 11, 12]. This system is therefore especially interesting, for instance, for electric and hybrid electric vehicle applications.

LiBOB also differs fundamentally from other conductive salts on the anode side, because LiBOB actively takes part in the formation of the solid electrolyte interphase (SEI), as first reported by Xu et al. [2]. As a consequence, graphites can be utilised even in pure PC-based electrolytes without exfoliation when LiBOB is present. LiBOB's participation in the SEI formation changes the SEI chemistry so that the SEI contains boric-ester-type compounds and is richer in alkyl carbonates species than the SEI formed in $LiPF_6$-based electrolytes [13, 14]. The LiBOB-SEI appears to have better chemical, electrochemical, and thermal stability than $LiPF_6$-SEI and results in better cycling stabilities and self-discharge characteristics both at room and elevated temperatures. Unfortunately, this higher stability comes at the expense of a slight decrease in the anode kinetics and power capability. It is therefore of utmost importance to understand the interactions between the anode materials and LiBOB-based electrolytes and the process of film formation.

Several studies were performed by Xu and Jow et al. [2, 13–17], concentrating mainly on questions like the composition of the SEI, or the potential at which an effective SEI – i.e. a SEI which can suppress PC cointercalation – is formed. There is less information in the literature about a reductive process at around 1.75 V vs Li/Li^+ (causing a peak in cyclovoltammetry or a plateau during galvanostatic cycling), which is observed in all LiBOB-based electrolytes and which contributes strongly to the irreversible capacity. It is considered to stem from an electrolyte impurity and whether or how it contributes to the formation of an effective SEI has not yet been satisfactorily addressed. Obviously, this phenomenon is worth a closer look.

In a previous study [18] with various graphitic anode materials, we demonstrated that the intensity of the 1.75-V peak is both a function of the surface area and the surface chemistry. Based on tests with hypothetical electrolyte impurities, such as $B(OMe)_3$, H_2O, diethyl oxalate, and anhydrous oxalic acid, we speculated that the 1.75-V peak would have its origin in the oxalate functional group.

The present paper summarises results obtained in our laboratories in the past, which were presented at various conferences [6, 10–12, 19], and which are not contained in [18]. For a more mechanistic point of view of the processes occurring at 1.75 V vs. Li/Li^+ and its practical implications for the anode formation, the reader is referred to a forthcoming publication [20].

2. Experimental

Composite electrodes were prepared via a conventional casting process. $Li_4Ti_5O_{12}$ (Süd-Chemie, Germany), carbon black Super P for lithium batteries (BET area: 65 $m^2\ g^{-1}$, TimCal, Belgium), or a meso-carbon microbead sample (MCMB 10–28, Osaka Gas, Japan) were used as active materials; Ni powder (type 210, BET area: 1.5 – 2.5 $m^2\ g^{-1}$, Inco, USA), carbon black Super P for lithium batteries, or SFG 6 (TimCal, Switzerland) were used as conductive additives; and poly(vinylidene fluoride) (PVdF) (Solef 6020, Solvay Solexis, Belgium) predissolved in 1-methyl-2-pyrrolidone (NMP, Fluka), was used as the binder. The components were mixed and cast onto Cu foil, followed by pre-drying to remove the solvent. Composite electrode discs with diameters of 12 mm and typical loadings of 4.9 – 6.0 mg cm^{-2} active material were cut out from the electrode foil, then dried under dynamic vacuum at 110 °C, and finally stored under dry Ar. The exact electrode compositions were: 82 % $Li_4Ti_5O_{12}$, 10% carbon black/SFG 6, and 8 % PVdF; 72 % $Li_4Ti_5O_{12}$, 20 % Ni, and 8 % PVdF; and 92% carbon black/MCMB 10–28 and 8 % PVdF (all values are given in wt.%).

Lithium bis(oxalato)borate (LiBOB), lithium bis(salicylato)borate (LiBSB), lithium salicylato(oxalato)borate (LiSOB), and lithium tris(oxalato)phosphate (LiTOP) were synthesised by Chemetall as described elsewhere [21–23]. The LiBOB-containing electrolytes were prepared with solvents from UBE Industries (Japan). Unless stated otherwise, the electrolyte was a saturated solution ($\sim$0.6 mol kg^{-1}) of LiBOB in ethylene carbonate (EC) – propylene carbonate (PC) – and dimethyl carbonate (DMC) (1:1:3 by wt.). The electrolyte was dried over Al_2O_3 (from ICN). The LiBSB-, LiSOB-, and LiTOP-containing electrolytes were prepared with solvents from Ferro Chemical (USA).

Several impurities and additives were tested: diethyl oxalate (DEO, from Fluka, 98%, used as received), ethylene sulfite (ES, from Aldrich, destilled and dried over molecular sieve), acetonitrile (AN, Aldrich), ethyl acetate (EA, Aldrich), and hydrogen bis(oxalato)borate (HBOB, synthesised by Chemetall according to Ref. [22]).

Electrochemical tests were performed in T-type cells using metallic Li (Chemetall) for the counter and reference electrodes, and glass-fibre sheets (Whatman) as separators. Cyclic voltammetry was performed with a scan rate of 0.1 mV s^{-1} within 0–2000 mV vs. Li/Li^+ for the carbon materials and within 500–2500 mV vs Li/Li^+ for $Li_4Ti_5O_{12}$. This method was chosed for this work over galvanostatic cycling, since it allows the interactions between the electrode and the electrolyte to be studied in more detail, especially in potential regions where the active material is not yet actively charged. Nonetheless, the slow scan rate assured that the active materials were deeply charged (and discharged).

Throughout this paper the specific currents and capacities are referred to the mass of active material. The terms "charge" and "discharge" refer to the working electrode being used as the anode (against metallic Li as is actually done in half-cells), i.e. to lithiation and delithiation, respectively. All potentials are given vs. Li/Li^+.

3. Results and discussion

3.1. *Anode*

For graphitic materials (of similar surface chemistry) it has been found that the intensity of the 1.75-V peak increases with the surface area [18]. Given this result, it is important to understand the behaviour of high-surface-area carbon blacks which are frequently used as conductive additives for electrodes. Though carbon blacks do not show extensive Li intercalation, they are polarised to the same potentials as the active materials in the composite electrode and hence to potentials where it may react with electrolyte. Furthermore, their surface chemistry is quite similar to that of graphites. Strong film formation can be anticipated.

As an example, the cyclic voltammogram (CV) of the carbon black Super P for lithium batteries (from TimCal) is shown in Figure 1. The huge intensity of the 1.75-V peak is evident. Integration gives a capacity of ~ 260 mAh g^{-1} (under the present experimental conditions, using a scan rate of 0.1 mV s^{-1}). This result should be compared, for instance, with ~ 17 mAh g^{-1} for MCMB 10–28. Further values can be found in Figure 2, where the 1.75-V peak intensities of several carbon materials are plotted as a function of the BET specific surface area. Hence, even when used as conductive additive in amounts of only a few percent, carbon black adds a considerable irreversible capacity to the overall composite electrode. Besides, the film formation of carbon black must affect the electronic conductivity, as shown below.

$Li_4Ti_5O_{12}$ is an ideal electrode material to study potential film formation effects at 1.75 V caused in LiBOB-based electrolytes and their influence on the electrode kinetics, as $Li_4Ti_5O_{12}$ can be fully charged and discharged at potentials well above those of EC and PC decomposition (starting at around 900–800 mV, depending on the exact electrolyte composition). Hence, in $LiPF_6$-based electrolytes, the $Li_4Ti_5O_{12}$ electrode should be totally film-free, whereas in LiBOB-based electrolytes any film formation effects caused by LiBOB or an accompanying impurity should become visible and not be mingled with film formation by EC.

As has been pointed out before [18], the 1.75-V peak is not restricted to carbon materials, but may in principle also be observed on carbon-free anodes such as $Li_4Ti_5O_{12}$ with Ni metal as the conductive additive (Figure 3b), where it gives rise to a small shoulder at ~ 1.75 V. If one compares the composite electrodes with Ni metal (Figure 3a) and carbon black (Super P for lithium batteries) (Figure 4a) as conductive additives cycled in $LiPF_6$/EC-PC-DMC (1:1:3 by wt.), the kinetics appear to be decreased for the electrode with Ni metal, as can be roughly estimated from the reduced sharpness of the insertion and de-insertion peaks, and from their

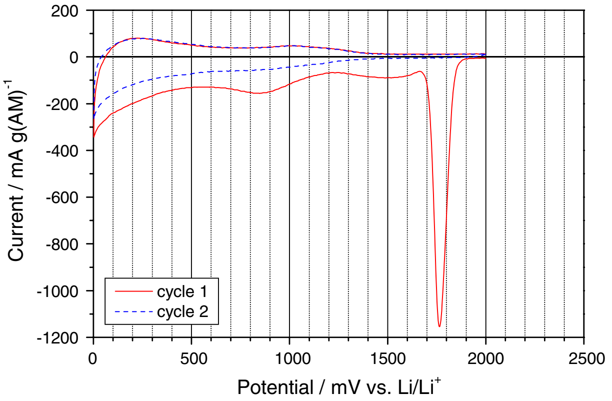

Fig. 1. Cyclic voltammograms (0.1 mV s^{-1}) of carbon black Super P in LiBOB/EC-PC-DMC (1:1:3 by wt.).

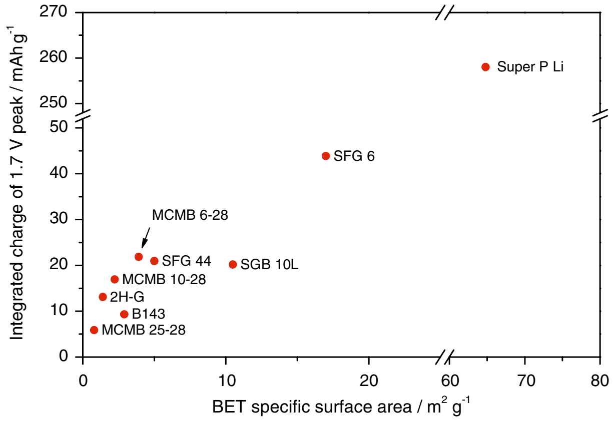

Fig. 2. Charge of the 1.75-V peak (obtained by integrating the respective peak of the CV recorded at 0.1 mV s^{-1}) of various graphites and carbon black Super P for lithium batteries as a function of the BET specific surface area. (Please note the x- and y-axis breaks).

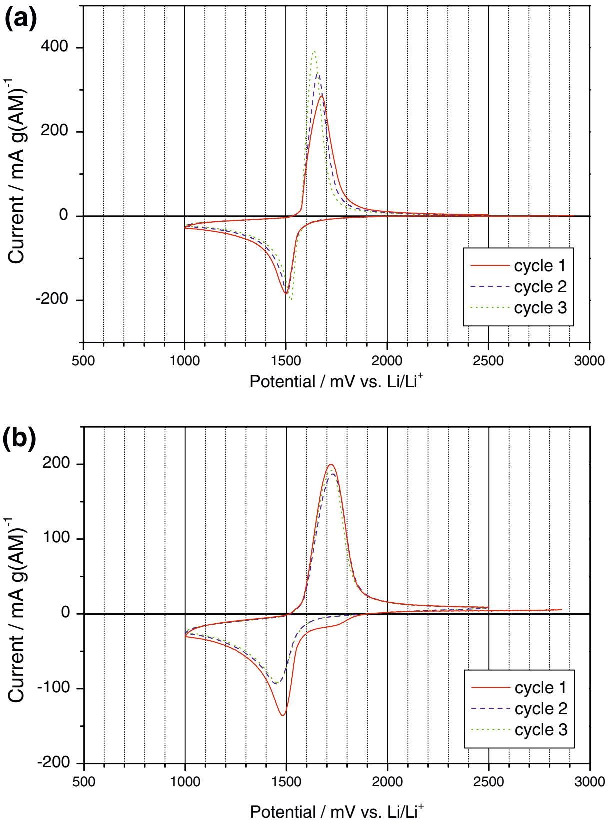

Fig. 3. Cyclic voltammograms (0.1 mV s^{-1}) of $Li_4Ti_5O_{12}$ composite electrodes with 20 wt.% Ni metal powder as a conductive additive in (a) $LiPF_6$/EC-PC-DMC (1:1:3 by wt.) and (b) LiBOB/EC-PC-DMC (1:1:3 by wt.).

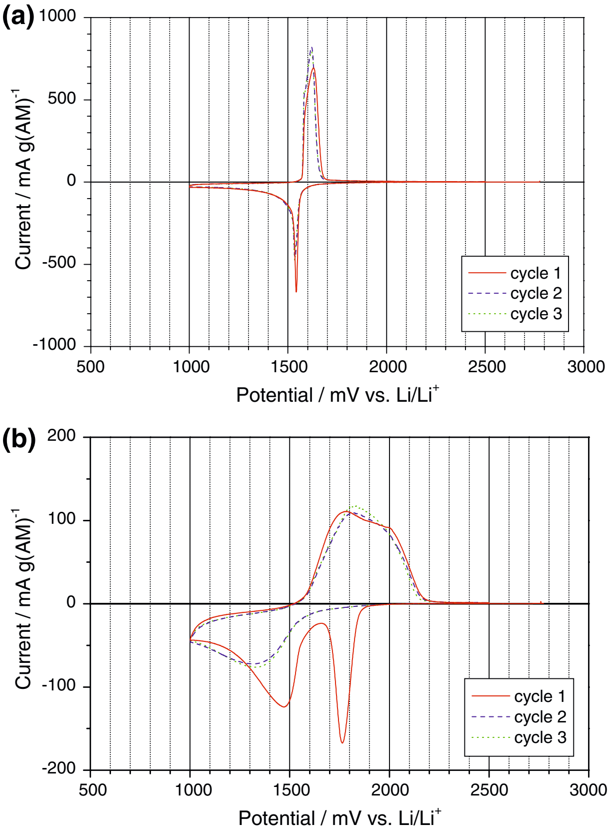

Fig. 4. Cyclic voltammograms (0.1 mV s^{-1}) of $Li_4Ti_5O_{12}$ composite electrodes with 10 wt.% carbon black Super P as a conductive additive in (a) $LiPF_6$/EC-PC-DMC (1:1:3 by wt.) and (b) LiBOB/EC-PC-DMC (1:1:3 by wt.).

shifts to lower and higher potentials, respectively. The reduced kinetics may be explained by the larger primary particle size and particle aggregate size of the Ni metal powder as compared to the carbon black and by the difficulty to obtain a homogeneous dispersion of the Ni metal powder within the oxidic material, which results in a lower electronic conductivity within the composite electrode.

The opposite situation is found when the same composite electrodes with Ni (Figure 3b) and carbon black (Figure 4b) are cycled in LiBOB/EC-PC-DMC (1:1:3 by wt.). Here, the kinetics appear to be better for the composite electrode with Ni. Furthermore, a very strong 1.75-V peak is observed for the carbon-black-containing electrode. Since only the conductive additive differs between the two types of composite electrodes, it is reasonable to assume that the carbon black is responsible for the large 1.75-V peak in the composite electrode from Figure 4b. This assumption is proved by normalising the current observed for the $Li_4Ti_5O_{12}$/carbon black electrode to the amount of carbon black and comparing it with a pure carbon black electrode, as is done in Figure 5. The 1.75-V peak can almost be quantitatively attributed to the carbon black component within the composite electrode. It appears that the film formation of carbon black in LiBOB-based electrolytes is stronger than that of Ni, and that due to this film formation, the higher initial conductivity in the pristine carbon-black-containing electrodes is then reduced below that of the Ni-containing electrode.

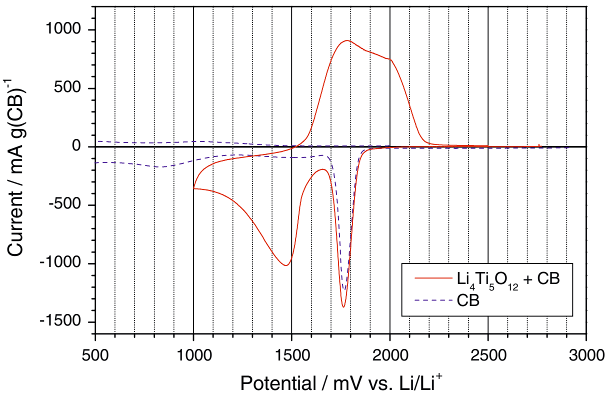

Fig. 5. Cyclic voltammograms (0.1 mV s^{-1}, first cycles) of a $Li_4Ti_5O_{12}$ composite electrode containing 10 wt.% carbon black Super P and a pure carbon black Super P electrode in LiBOB/EC-PC-DMC (1:1:3 by wt.). The currents were normalised to the amount of carbon black.

To corroborate this model, fine-particulate graphite (SFG 6 from TimCal) was tested as a third conductive additive (Figure 6). SFG 6 has a lower BET surface than carbon black, but a larger one than Ni. Due to its smaller particle size and different surface chemistry it should be easier to disperse within the composite electrode and give a better percolation pattern than Ni. For the $LiPF_6$-based electrolyte, the electrochemical response and the kinetics of the composite electrode with SFG 6 lie between those of the electrodes with Ni and carbon black. For the LiBOB-based electrolyte, the kinetics of the electrode with SFG 6 are approximately similar to those of the electrode with Ni and better than those of the electrode with carbon black. This result supports the above interpretation.

These results clearly prove that film formation starts with the 1.75-V peak in LiBOB-based electrolytes. Furthermore, for all three composite electrodes cycled in the LiBOB-based electrolytes, a comparison of the first three cycles shows that the kinetics decrease from the first to the second insertion half-cycle, whereas they remain approximately the same for the second and third insertion half-cycles and for all three de-insertion half-cycles. This finding indicates that the film formation process which starts with the peak at 1.75 V, and hence the electrode formation, continues throughout the first insertion half-cycle down to the lower vertex potential of 1.0 V. Once the lowest potential has been reached, the film remains rather stable. This finding is in good agreement with the fact that, for graphite and glassy carbon electrodes, residual spurious currents are observed between the 1.75-V peak and the region of Li-intercalation into the graphite lattice, which are restricted to the first charge, and which have been ascribed to further electrolyte decomposition and film formation reactions [18].

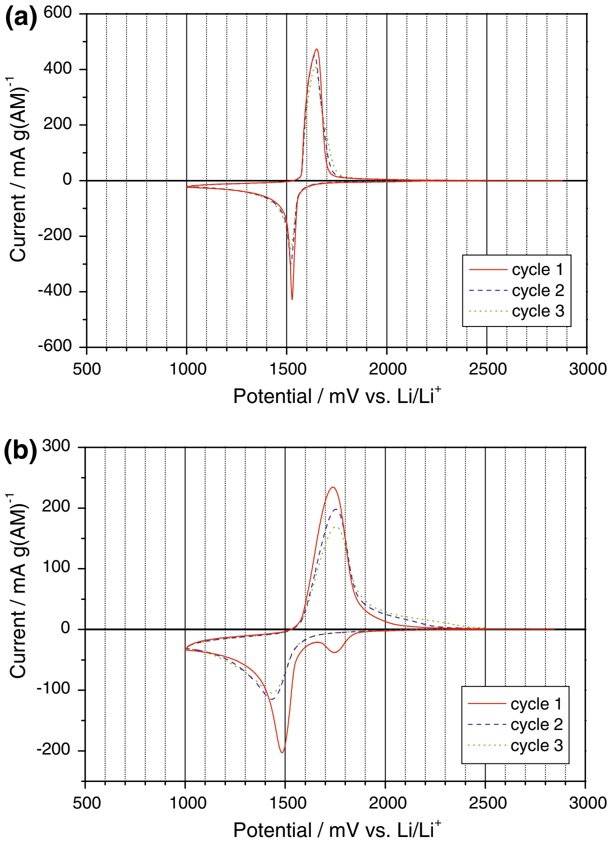

Fig. 6. Cyclic voltammograms (0.1 mV s^{-1}) of $Li_4Ti_5O_{12}$ composite electrodes with 10 wt.% of fine particulate graphite SFG 6 as conductive additive in (a) $LiPF_6$/EC-DMC (1:1 by wt.) and (b) LiBOB/EC-PC-DMC (1:1:3 by wt.).

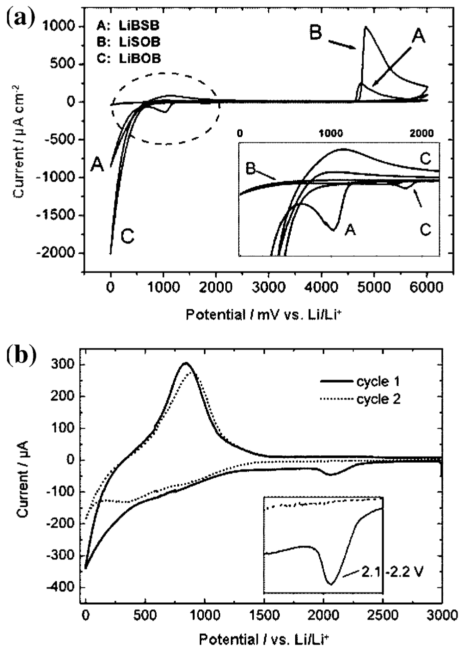

Fig. 7. Cyclic voltammograms of (a) glassy carbon electrodes in LiBOB, LiBSB, and LiSOB/EC-EMC (1:1 by wt.) electrolytes (first cycles, 10 mV s^{-1}) and (b) a commercial graphite electrode in LiTOP/EC-EMC (1:1 by wt.) (first and second cycle, 10 mV s^{-1}).

3.2. *Electrolyte*

To identify the origin of the 1.75-V peak, several potential impurities which might be present in the electrolyte right from the beginning, or substances which might trigger the formation of impurities from LiBOB after dissolution in the electrolyte solvents, were investigated. Preliminary tests on a glassy carbon electrode showed that oxalic acid and diethyl oxalate (DEO) (added to a $LiClO_4$/EC-EMC electrolyte) gave peaks at 1.73 and 1.54 V, respectively, whereas trimethoxy borate did not [18].

Also for other borate- or phosphate-based electrolyte salts containing the oxalate group, such as lithium salicylato(oxalato)borate (LiSOB) or lithium tris(oxalato)phosphate (LiTOP), signals are observed at around 1.7 V and 2.1 V, respectively (Figure 7). Compared to LiBOB with its two oxalato ligands, in LiSOB with only one oxalato ligand, the intensity of the 1.75-V peak is significantly reduced. For lithium bis(salicylato)borate (LiBSB), which can be conceived as an oxalate-free analogue to LiBOB, this peak is totally absent, and the first electrochemical activity is observed only below 1.2 V (Figure 7).

Ethyl acetate, an example of an ester of a monocarboxylic acid and the analogue to the bicarboxylic oxalate, can be excluded as responsible impurity, as its addition to a $LiPF_6$/EC-DMC baseline electrolyte does not provoke the 1.75-V peak (Figure 8).

It appears that compounds containing the oxalate group are generally reduced in the range between 2.2 and 1.5 V, with the exact position depending on the stabilisation of the oxalate ester through its ligands. We therefore speculate that it is most likely the oxalate group that is responsible for the 1.75-V peak.

What could not be clarified so far is whether the exact origin is free oxalate, i.e. the remainder of unreacted oxalate esters or oxalic acid from the synthesis process as proposed [2, 16], or if it is a direct reduction of the oxalate group contained in BOB (involving ring-opening etc.). Experiments relying on the different

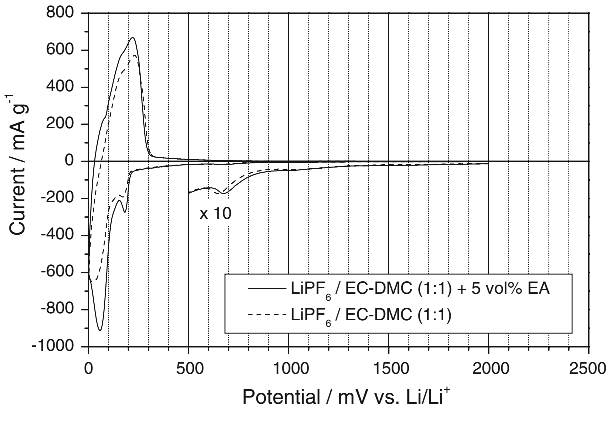

Fig. 8. Effect of adding 5 vol.% of EA to $LiPF_6$/EC-DMC (1:1 by wt.) on the CV response of MCMB 10–28 composite electrodes (first cycles, 0.1 mV s^{-1}).

concentrations with which the potential impurity or the electrolyte salt LiBOB would be present, are inconclusive in this respect, as during this reductive process a primary film is formed on the electrode surface which suppresses further and hence quantitative reduction. Thus, a small amount of impurity may have the same effect as a large amount of electrolyte salt.

If the 1.75-V peak were due to remains of unreacted oxalate esters or oxalic acid from the synthesis procedure, then it should, in principle, be possible to remove it by purification of the LiBOB salt. Figure 9 shows the galvanostatic profiles of full Li-ion cells with graphite as the anode, a lithium manganese oxide spinel as the cathode and two lots of LiBOB salt of different purity. For the purified salt the plateau at ~1.7–1.9 V (which can be translated into the 1.75-V plateau in the Hall-cell) is slightly shortened, but not eliminated. Actually, none of the purification methods which have been tested so far have resulted in the complete elimination of the 1.75-V peak.

One of the solvents which can be used for the synthesis and purification of LiBOB is acetonitrile (AN). As can be seen in Figure 10, the addition of 5 vol.% acetonitril to LiBOB/EC-PC-DMC (1:1:3 by wt.) does not change the CV. Hence, AN is also not responsible for the 1.75-V peak, neither as a direct source, nor as a solvent which promotes the formation of impurities by decomposition of BOB.

Another potential impurity which can be excluded is hydrogen bis(oxalato)borate (HBOB). HBOB is the corresponding acid to LiBOB. Due to its strong dissociation in the present electrolyte solvents, it behaves like a strong acid. Surprisingly, additions of HBOB of up to 100 ppm to LiBOB/EC-PC-DMC (1:1:3 by wt.) do not show significant effects in the CV (Figure 11). And even more surprisingly, the addition of HBOB to LiBOB-based electrolytes had no effect on the dissolution of Mn and Fe from $LiMn_2O_4$ and $LiFePO_4$ during soaking tests at 40 °C for 4 weeks. This result is in strong contrast to the effect of small amounts of HF present in $LiPF_6$-based electrolytes, which is detrimental to the cycling performance of Li-ion cells.

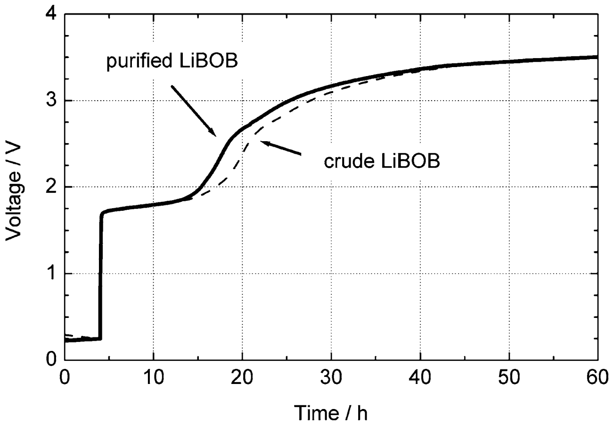

Fig. 9. First charge of graphite | LiBOB/EC-EMC (1:1 by wt.) | $Li(Ni,Co)O_2$ cells with two different LiBOB qualitities (raw and purified).

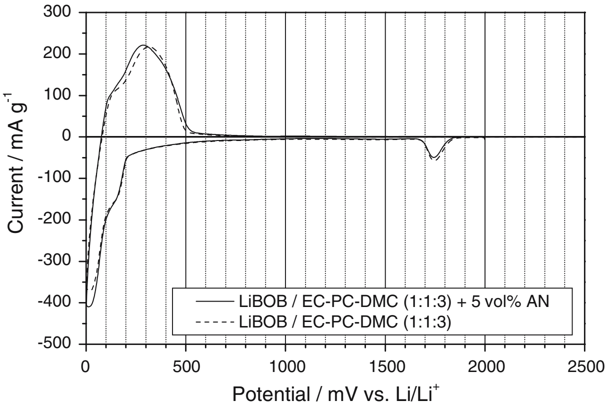

Fig. 10. Effect of adding 5 vol.% of AN to LiBOB/EC-PC-DMC (1:1:3 by wt.) on the CV response of MCMB 10–28 composite electrodes (first cycles, 0.1 mV s^{-1}).

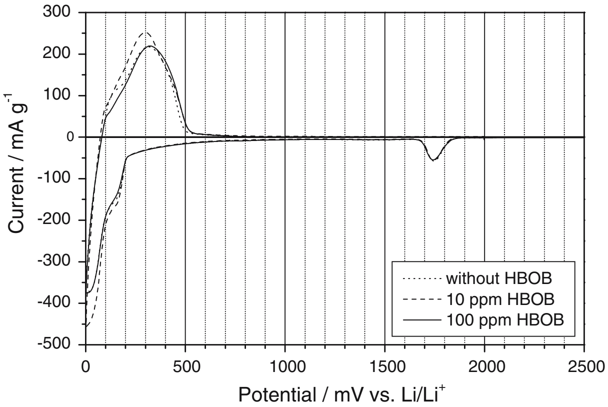

Fig. 11. Effect of adding HBOB to LiBOB/EC-PC-DMC (1:1:3 by wt.) on the CV response of MCMB 10–28 composite electrodes (first cycles, 0.1 mV s^{-1}).

For a given quality of LiBOB, some differences in the 1.75-V peak are observed with changing solvent composition of the electrolyte, as may be seen in Figure 12a. Whereas LiBOB/EC-DMC (1:1 by wt.) and LiBOB/EC-PC-DMC (1:1:3 by wt.) give virtually the same results, in LiBOB/PC the intensity of the 1.75-V peak is decreased, and the peak maximum is shifted to slightly lower potentials. Furthermore, an additional feature is observed beginning below 900 mV which probably indicates a small rest of PC co-intercalation and decomposition. However, this side-reaction is very limited in magnitude as compared to $LiPF_6$/PC and does not result in a full exfoliation and destruction of the graphite matrix as shown in Figure 12b. This finding reproduces previous results which showed that LiBOB takes part in the film formation process and can suppress (extensive) PC co-intercalation [2]. The small amount of PC co-intercalation and decomposition may indicate that LiBOB alone forms less effective films than EC or special film-forming additives do.

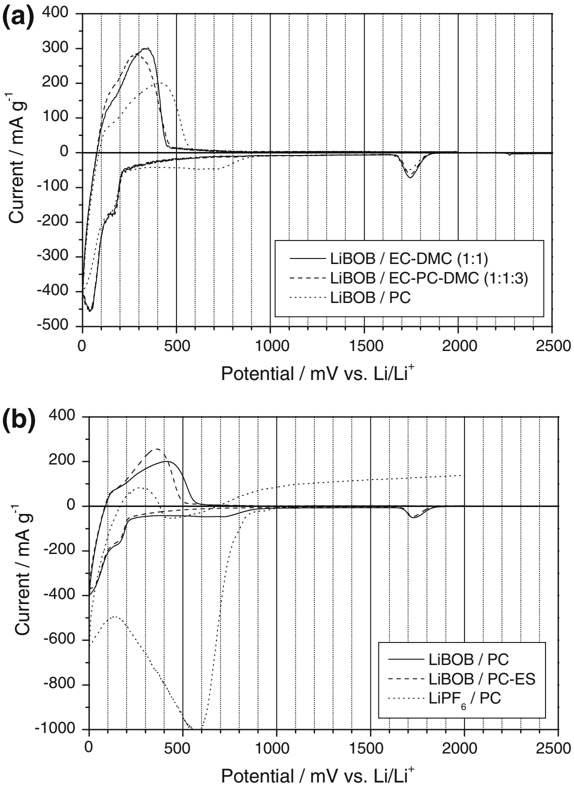

Fig. 12. Comparison of the CV profiles (first cycles) of MCMB 10–28 composite electrodes in different electrolyte formulations. (a) LiBOB/EC-DMC (1:1 by wt.), LiBOB/EC-PC-DMC (1:1:3 by wt.), and LiBOB/PC. (b) LiBOB/PC, LiBOB/PC + 5 vol.% ES, and LiPF$_6$/PC

A total suppression of PC co-intercalation in LiBOB/PC is possible when a film-forming additive, such as ethylene sulfite (ES), is additionally present (Fig. 12b). In the previous study [18] where we investigated the effect of ES in LiBOB/EC-EMC (1:1 by wt.), no difference was observed in the 1.75-V peak for the ES-containing and ES-free electrolytes. This finding was surprising as the electrochemical reduction of ES should occur at slightly higher potentials than that of the LiBOB electrolyte (or more exactly of the intrinsic impurity in the LiBOB electrolyte). It was speculated as to whether film formation by LiBOB and ES could be competing reactions. The present result in LiBOB/PC shows that even in the mixture of LiBOB and ES the latter is active as a film formation additive.

4. Conclusions

Carbon black interacts strongly with LiBOB-based electrolytes, resulting in strong film formation and loss of electronic conductivity within the composite electrode, as demonstrated with $Li_4Ti_5O_{12}$ model composite electrodes. In LiPF$_6$-based electrolytes, the kinetics decrease in the order: carbon black > fine particulate graphite > metal powder as the conductive additive, due to the decreasing electronic conductivity which is achieved within the composite electrode. In LiBOB-based electrolytes, however, the electrode kinetics increase in the order: carbon black $\ll$ fine particulate graphite $\sim$ metal powder, due to decreased film formation of the conductive additive and despite the increased electronic conductivity of the composite electrode before cycling.

Considering conductive additives for anodes in general, these results imply that for LiBOB-based electrolytes carbon black does not appear to be the ideal additive, and carbon materials with low surface area or non-carbonaceous materials such as metal or ceramic powders are better choices. Similar conclusions can be drawn for the active material where again carbon materials with a large surface area should be avoided.

The large set of data obtained with different electrolytes based on different electrolyte salts and solvents, either pure or with the addition of impurities, indicates that the 1.75-V peak is likely related to the oxalate moiety. So far it is not clear whether the oxalate originates from the BOB anion or from an independent oxalate impurity in the LiBOB electrolyte. So far the 1.75-V peak could not be eliminated with any of the LiBOB salt purification methods. Therefore, the 1.75-V peak must be regarded as intrinsic to LiBOB-based electrolytes. As a result, suitable electrochemical formation procedures must be developed to minimise its impact on the cycling performae and the irreversible capacity of anodes [20].

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