

Short communication

Film formation in LiBOB-containing electrolytes

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Abstract

Lithium bis(oxalato)borate (LiBOB), a new electrolyte salt for lithium batteries, is actively involved in the formation of the solid electrolyte interphase (SEI) at the anode. Part of this formation is an irreversible reductive reaction taking place at potentials of around 1.75 V versus Li/Li⁺ and contributing to the irreversible capacity of anode materials in the first cycle.

Cyclic voltammetry has been performed on several carbon materials as well as on Li₄Ti₅O₁₂ and pre-treated glassy carbon electrodes in order to achieve a better understanding of the underlying processes. It is found that the intensity of the 1.75 V peak depends on the BET specific surface area and the surface chemistry of the active material and increases with the amount of oxygen-containing surface functionalities. It is not specific to carbonaceous materials but is also observed on carbon-free anodes like Li₄Ti₅O₁₂.

In addition, the effect of several potential impurities and of film-forming additives on the filming behaviour of LiBOB-containing electrolytes has been investigated.

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1. Introduction

Recently, the groups of oxalato borates and oxalato phosphates have been proposed as new electrolyte salts for lithium batteries, as fluorine-free, non-toxic and low-cost alternatives to LiPF₆ [1–5]. Among these, especially lithium bis(oxalato)borate (LiBOB) is attracting much interest due to a number of favourable characteristics: as pure salt LiBOB has a higher thermal stability than LiPF₆ [6]. The conductivities of LiBOB-based electrolytes are between those of LiPF₆- and LiBF₄-based systems [6]. It has been demonstrated for full cells with commercial electrodes (carbonaceous anode and layered Ni-based mixed oxide cathode) that galvanostatic cycling is possible over more than 250 cycles without loss in capacity at room temperature. During cycling at 60–70 °C strongly improved capacity retention was observed as compared to LiPF₆ [7]. Soaking tests of unstabilised and stabilised lithium manganese spinels have

revealed that in LiBOB-based electrolytes Mn dissolution is largely suppressed [8,9], resulting in better cycling performance in full cells with graphitic anodes. Accelerating rate calorimetry (ARC) studies have indicated increased safety for LiBOB-based electrolytes in combination with charged meso-carbon micro-bead (MCMB) and LiFePO₄ electrodes, but decreased safety in combination with LiCoO₂ and Li(Ni_{0.1}Co_{0.8}Mn_{0.1})O₂ (compared to LiPF₆-based electrolytes) [10,11].

A basic difference between LiBOB and other electrolyte salts such as LiPF₆ or LiBF₄ is that at the anode side the BOB anion itself is reductively decomposed (starting at voltages of around 1.8 V versus Li/Li⁺) and takes actively part in the formation of the solid electrolyte interphase (SEI). It even allows the use of propylene carbonate (PC) as electrolyte solvent in combination with graphitic carbons, without the occurrence of solvent co-intercalation and graphite exfoliation [12]. Recent investigations by X-ray photo-electron spectroscopy (XPS) [13] and infrared spectroscopy (IR) [14] suggest that the SEI formed is rich in orthoborate, oxalate, and carboxylate functionalities, which are thought responsi-

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ble for the good stability both against solvent co-intercalation and chemical corrosion at elevated temperatures.

For the present contribution, carbonaceous anode materials as well as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and pre-treated glassy carbon electrodes have been studied in LiBOB-based electrolytes in order to achieve a better understanding of the filming-behaviour in general and of the process at ~ 1.75 V versus Li/Li^+ in particular, as a first step towards the final aim of minimising the related irreversible capacity.

2. Experimental

The anode materials under investigation were three meso-carbon micro-bead samples (MCMB 6–28, MCMB 10–28, and MCMB 25–28, from Osaka Gas), two synthetic graphites (SFG 6 and SFG 44, from TimCal), and a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel (from Süd-Chemie).

Two types of composite electrodes were used: “plastic” electrodes were prepared in a solvent-free procedure by mixing 85 wt.% MCMB, 10 wt.% SFG 6, and 5 wt.% poly(tetrafluoroethylene) (PTFE) (Hostafion TFM 2025, from Dyneon), followed by pounding and rolling. “Film” electrodes were prepared in a conventional casting process, by mixing 92 wt.% MCMB or SFG and 8 wt.% poly(vinylidene fluoride) (PVdF) (Solef 6020, from Solvay Solexis) dissolved in 1-methyl-2-pyrrolidone (NMP), casting onto Cu foil, and pre-drying to remove the solvent. In the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite electrodes the composition was 72 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$, 20 wt.% Ni (Inco, Ni 255), and 8 wt.% PVdF.

All composite electrodes were dried under dynamic vacuum at 110°C . The electrodes had diameters of 12 mm and typical loadings of active material of 10.0 – 12.0 mg cm^{-2} for the “plastic” electrodes and 4.9 – 6.0 mg cm^{-2} for the “film” electrodes. Electrochemical tests were performed in T-type cells using metallic Li as counter and reference electrodes and glass-fibre sheets (Whatman) as separators.

The experiments on glassy carbon electrodes were performed in glass cells with an excess of electrolyte. The glassy carbon electrodes were cleaned by abrasion with a suspension of alumina in deionized water and subsequent careful rinsing with deionized water prior to their use.

Unless stated otherwise the electrolyte was a saturated solution (<0.6 mol kg^{-1}) of LiBOB (from Chemetall) in ethylene carbonate (EC)–ethyl methyl carbonate (EMC) (1:1, w/w, from Ube or Tomiyama). As the LiBOB salt was used in the form of its solvate with dimethyl carbonate (DMC) the electrolyte solution contained also a small amount of DMC beside EC and EMC. The preparation consisted of dissolving the LiBOB salt in the solvent mixture, filtering through a micro-filter (Whatman, 0.1 μm) to remove a small amount of an insoluble fraction, drying over Al_2O_3 (from ICN), and decanting or filtering to remove the Al_2O_3 .

Several impurities and additives were tested: diethyl oxalate (Merck, used as received), anhydrous oxalic acid

(prepared by drying of oxalic acid dihydrate at 90°C under vacuum), trimethoxy borate (Merck, used as received), vinylene carbonate (VC, from Bayer, used as received), ethylene sulfite (ES, from Aldrich, distilled and dried over molecular sieve). *n*-Butyllithium used for the pre-treatment of the glassy carbon electrode was produced by Chemetall.

The galvanostatic cycling test was carried out with a current of 74.4 mA g^{-1} within a potential range of 20 – 2000 mV versus Li/Li^+ . Cyclic voltammetry (CV) was performed with a scan rate of 0.1 mV s^{-1} within 0 – 2000 mV versus Li/Li^+ for the carbon materials and within 500 – 2500 mV versus Li/Li^+ for $\text{Li}_4\text{Ti}_5\text{O}_{12}$. For CV tests carried out against glassy carbon working electrodes, scan rates of 10 mV s^{-1} were used.

All specific currents and capacities (specific charges) given in this paper are referred to the mass of active material (and in the case of the “plastic” electrodes to the sum of the masses of MCMB and SFG). The terms “charge” and “discharge” refer to the working electrode being used as anode, i.e. to lithiation and delithiation, respectively. All potentials in this paper are given versus Li/Li^+ .

3. Results and discussion

The reduction of BOB takes place over a wide voltage range, beginning with a short plateau (in galvanostatic experiments) or a well-defined peak (in cyclic voltammetry) at around 1.75 V (Figs. 1 and 2). At lower voltages, the current does not return to 0, but a spurious residual current is observed down to the voltages where reversible Li insertion into carbon (graphite) occurs. Reduction of BOB and electrode filming are limited to the first cycle (see Fig. 2). Nonetheless, these processes contribute significantly to the irreversible capacity of the anode. For instance, for a MCMB 10–28 electrode cycled galvanostatically at a C/5 rate (Fig. 1), the reaction at ~ 1.75 V alone amounts to $\sim 3\%$ of the reversible capac-

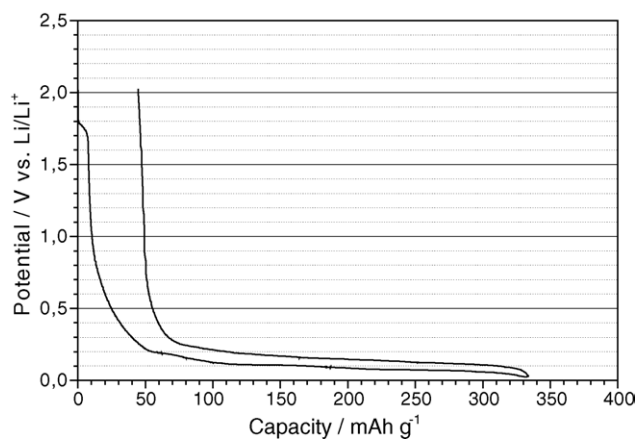


Fig. 1. Galvanostatic charge–discharge curve for the first cycle of MCMB 10–28 “film” composite electrode in LiBOB/EC–EMC (C/5 rate, 20 – 2000 mV).

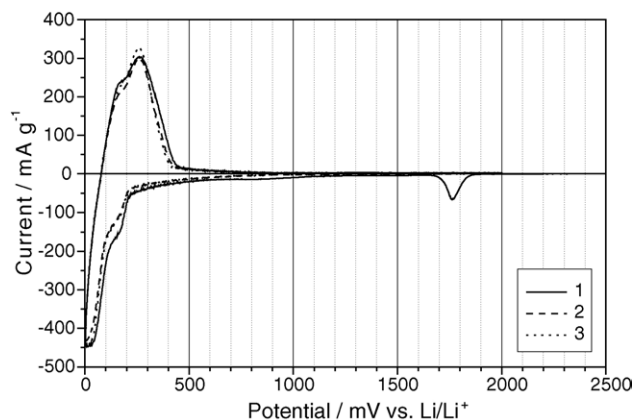


Fig. 2. Cyclic voltammogram (first three cycles) of MCMB 10–28 “film” composite electrode in LiBOB/EC–EMC (scan rate: 0.1 mV s^{-1} and 0–2000 mV).

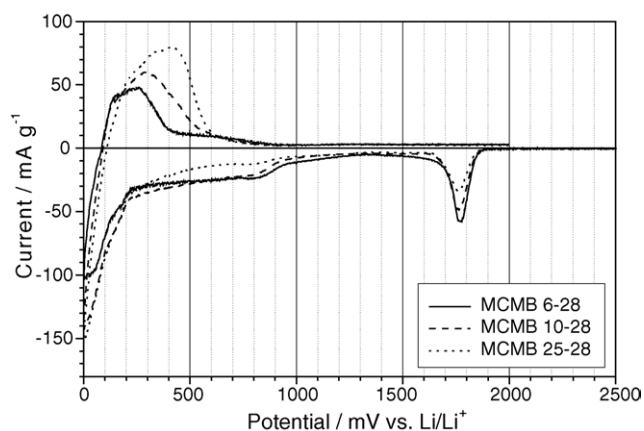
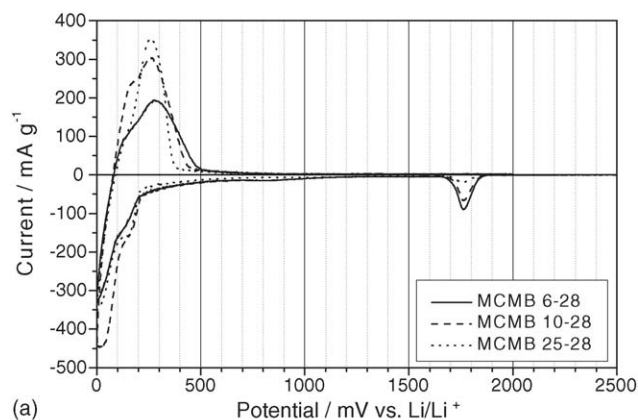


Fig. 3. Cyclic voltammograms (first cycles) of “plastic” composite electrodes made from different MCMBs (scan rate: 0.1 mV s^{-1} and 0–2000 mV).

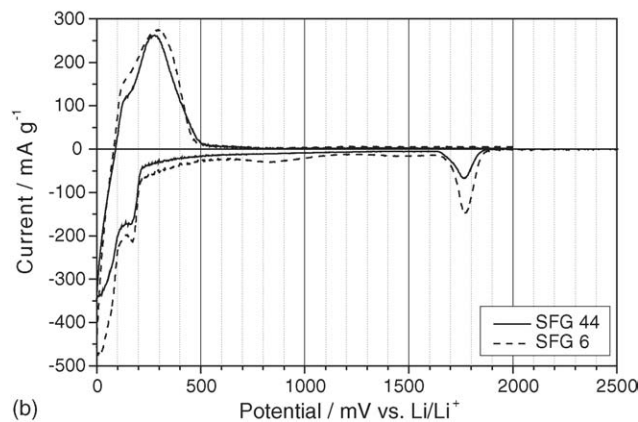
ity, and $\sim 17\%$ of the irreversible capacity of the first cycle.¹ Additional irreversible capacity is accumulated at lower voltages. As a consequence, it has to be regarded for full Li-ion cells that this extra irreversible capacity at the anode side shifts the cell balance (the required relative amounts of anode and cathode materials) and that therefore a simple exchange of a LiPF₆-containing electrolyte with a LiBOB-containing one is not possible without prior readjustment of the cell balance. In the following, the attention will be focussed on the 1.75 V peak as important contributor to the irreversible capacity.

Figs. 3 and 4a show the first CV cycles for MCMB samples with different particle sizes and BET specific surface areas (MCMB 6–28: $3.91 \text{ m}^2 \text{ g}^{-1}$, MCMB 10–28: $2.23 \text{ m}^2 \text{ g}^{-1}$, and MCMB 25–28: $0.78 \text{ m}^2 \text{ g}^{-1}$) in “plastic” and “film” composite electrodes, respectively. Fig. 4b shows those for SFG “film” composite electrodes (SFG 6: $17 \text{ m}^2 \text{ g}^{-1}$ and SFG 44:

¹ These values have been obtained by relating the capacity consumed between the open circuit voltage (OCV) and $\sim 1.6 \text{ V}$ to the reversible capacity (discharge capacity) and the overall irreversible capacity (the difference between charge and discharge capacity), respectively.



(a)



(b)

Fig. 4. Cyclic voltammograms (first cycles) of “film” composite electrodes made from different: (a) MCMBs and (b) synthetic graphites (scan rate: 0.1 mV s^{-1} and 0–2000 mV).

$5 \text{ m}^2 \text{ g}^{-1}$). For both types of composite electrolytes and both sets of materials the intensity of the 1.75 V peak and the overall irreversible capacity increase with the surface area.

To get quantitative data the CV curves from Fig. 4 were integrated in four sections: area *A* from the open circuit voltage (OCV) to $\sim 1.6 \text{ V}$ (comprising the 1.75 V peak), area *B* from $\sim 1.6 \text{ V}$ to 0 V, area *C* from 0 V to the zero-crossing voltage, and area *D* from the zero-crossing voltage to 2.0 V. Hence, the sum (*A* + *B* + *C*) describes the total charge capacity and *D* describes the total discharge capacity.

When plotted as a function of the BET specific surface area of the active material, both the absolute capacities for the 1.75 V peak (Fig. 5a) as well as its ratios to the total charge or discharge capacities (Fig. 5b) give a continuous trend within the series of MCMB samples. However, when different types of carbonaceous materials such as MCMBs and synthetic graphites (SFGs) are compared, whose synthesis processes differ and which may therefore carry different functional groups on the surface, such a clear trend is no longer present. Obviously, the peak intensity does not solely depend upon the surface area but also on the surface chemistry of the active material. Filming in LiBOB-based electrolytes does not differ from filming in other electrolytes (e.g. [15–18]) in this respect.

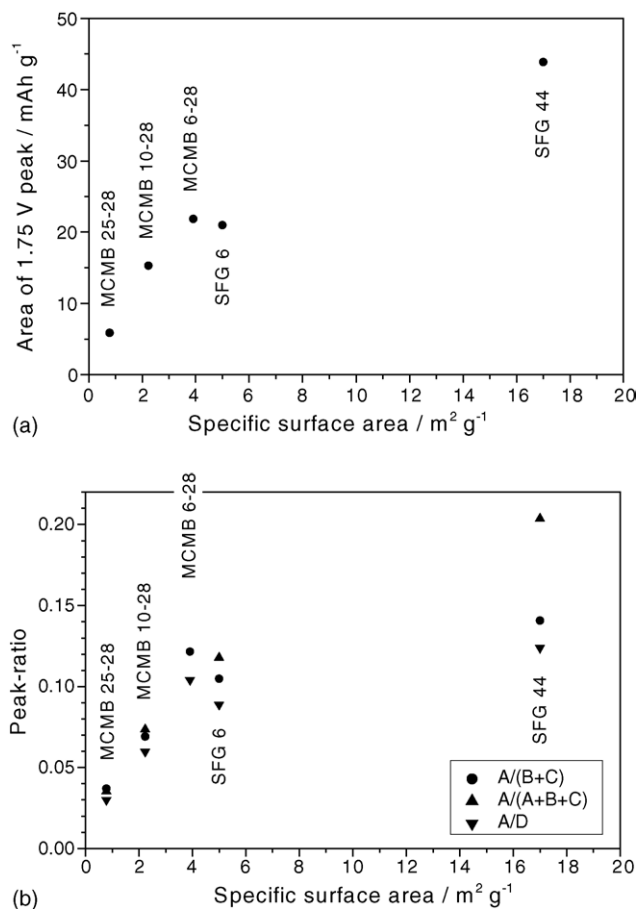


Fig. 5. Intensity of the 1.75 V peak against the BET specific surface area for different carbon materials (integrated values for the data from Fig. 4). (a) Absolute capacities and (b) ratio of the 1.75 V peak to the charge capacity excluding the 1.75 V peak $[A/(B+C)]$, to the overall charge capacity $[A/(A+B+C)]$, and to the discharge capacity $[A/D]$.

The appearance of the 1.75 V peak is not restricted to carbon-based materials, but it is also observed in carbon-free anodes like $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel, as shown in Fig. 6. (The composite electrode has been prepared with Ni powder as

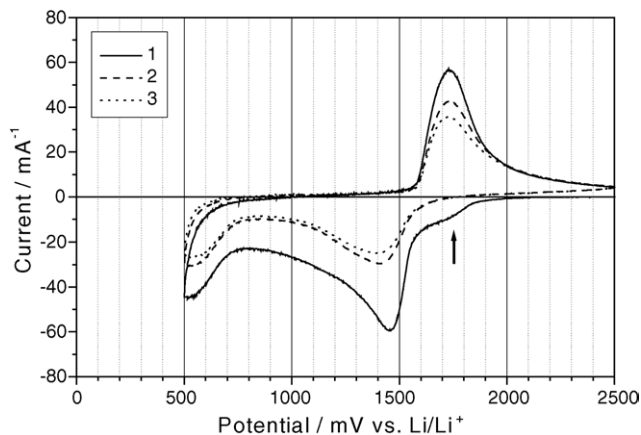


Fig. 6. Cyclic voltammogram (first three cycles) of a carbon-free $\text{Li}_4\text{Ti}_5\text{O}_{12}$ "film" composite electrode (scan rate: 0.1 mV s^{-1} and 500–2500 mV).

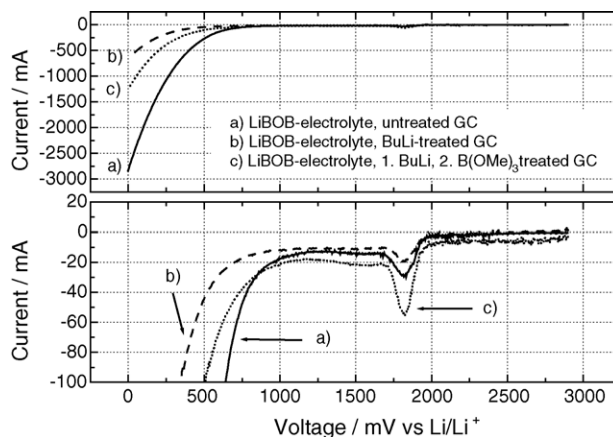


Fig. 7. Cyclic voltammograms of untreated and pre-treated glassy carbon electrodes in LiBOB/EC-EMC. Top graph: overall spectra; bottom graph: detail (scan rate: 10 mV s^{-1}).

conductive additive and is hence totally carbon-free. Compared to conventional carbon black, the Ni powder has a larger particle size and is not well distributed within the composite electrode, which explains the lower conductivity and the resulting broader peaks in the CV.) It can be concluded that the peak is most likely related to oxygen-containing surface groups, which react with BOB and/or its decomposition products [4]. As shown in Fig. 7, this is corroborated by the observation that a pre-treatment of a glassy carbon electrode with *n*-butyllithium (dashed line), which leads to a chemical reduction of these surface groups, resulted in a decrease in the peak intensity, whereas a pre-treatment with $\text{B}(\text{OMe})_3$ (dotted line) resulted in an increase. A glassy carbon electrode (solid line), which received no pre-treatment served as a reference.

To shed some light on the origin of the 1.75 V peak several compounds which are structurally related to LiBOB and which might be present as impurities in LiBOB-based electrolytes have been tested. For this purpose, small amounts of $\text{B}(\text{OMe})_3$, H_2O , diethyl oxalate, and anhydrous oxalic acid have been added to a $\text{LiClO}_4/\text{EC-EMC}$ electrolyte, which by itself does not show any signal in the voltage range of interest. As can be seen in Fig. 8a, $\text{B}(\text{OMe})_3$ (dashed lined) and H_2O (dash-dotted line) can be ruled out as impurities, since they give no signal at around 1.75 V. Instead, a peak appears when LiBOB is added (solid line), or when small amounts of compounds containing the oxalate group are added, such as diethyl oxalate and anhydrous oxalic acid (Fig. 8b). Also, for other borate- or phosphate-based electrolyte salts containing the oxalate group, such as lithium salicylato(oxalato)borate or lithium tris(oxalato)phosphate (LiTOP), signals are observed at around 1.7 and 2.1 V, respectively [4]. In comparison, lithium bis(salicylato)borate (LiBSB), which can be conceived as an oxalate-free analogue to LiBOB, is decomposed only below 1.2 V [4]. It appears that the oxalate group is 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, and that it is most likely the oxalate

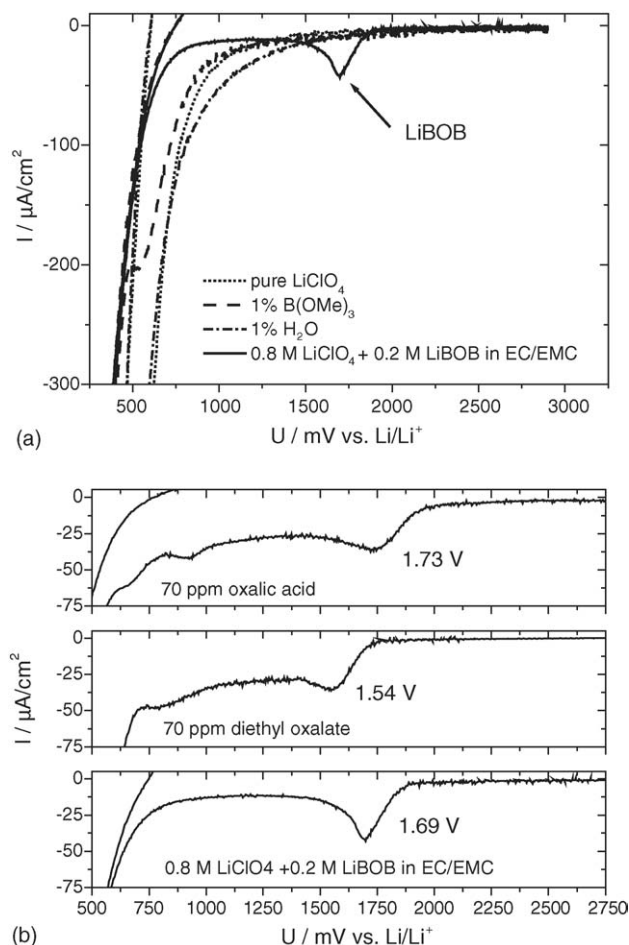


Fig. 8. (a and b) Cyclic voltammograms (first cycles) of glassy carbon electrodes in different electrolytes without and with impurities: 1 M $\text{LiClO}_4/\text{EC-EMC}$, 1 M $\text{LiClO}_4/\text{EC-EMC} + 1\% \text{ B(OMe)}_3$, 1 M $\text{LiClO}_4/\text{EC-EMC} + 1\% \text{ H}_2\text{O}$, 0.8 M $\text{LiClO}_4 + 0.2 \text{ M LiBOB}/\text{EC-EMC}$, 1 M $\text{LiClO}_4/\text{EC-EMC} + 70 \text{ ppm diethyl oxalate}$, and 1 M $\text{LiClO}_4/\text{EC-EMC} + 70 \text{ ppm anhydrous oxalic acid}$ (scan rate: 10 mV s^{-1}).

group or a moiety with similar structure that is responsible for the 1.75 V peak.

Finally, the influence of film-forming additives on the film-forming behaviour of LiBOB-based electrolytes was investigated. Both vinylene carbonate and ethylene sulfite have been shown to be effective film-forming agents, allowing the operation of graphites in propylene carbonate-based electrolytes with LiPF_6 as the conductive salt without solvent-co-intercalation and graphite exfoliation (cf. [19,20] and Fig. 9a). In the case of LiBOB/EC-EMC, neither VC nor ES resulted in a significant change of the CV signature, such as changes in the intensity of the 1.75 V peak or in the lithiation and delithiation profile of the MCMB electrode (Fig. 9b). Assuming that the reductive process, which is responsible for the 1.75 V peak leaves a first film on the electrode surface, the apparent inactivity of VC is not surprising, as VC is reduced below 1.7 V, i.e. at potentials where the electrode surface would be already covered with reduction products from BOB. Interestingly also ES seems to have no significant effect (visible with

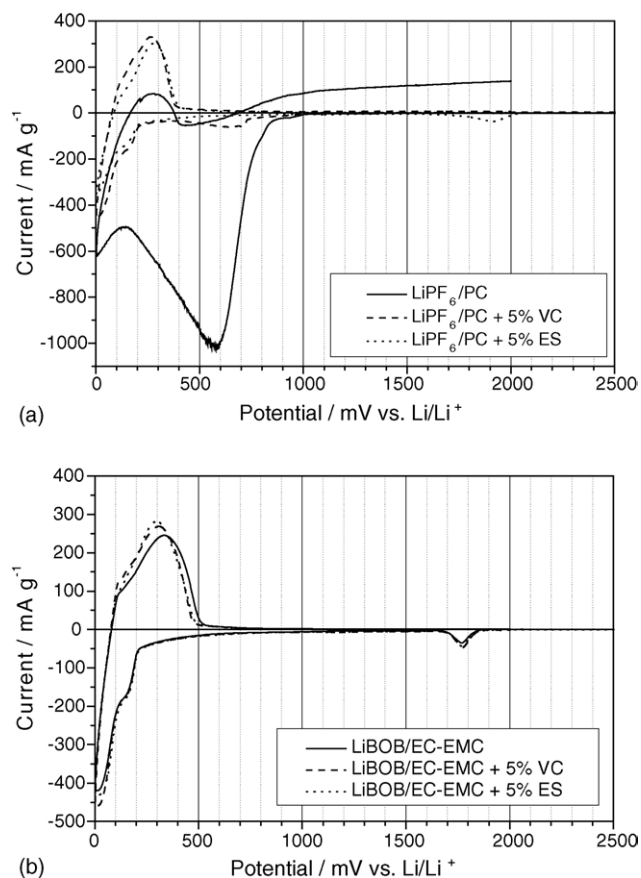


Fig. 9. Cyclic voltammograms (first cycles) of MCMB 10–28 “film” composite electrodes in (a) 1 M LiPF_6/PC and (b) $\text{LiBOB}/\text{EC-EMC}$ with and without 5 vol.% vinylene carbonate (VC) or ethylene sulfite (ES) as film-forming additives (scan rate: 0.1 mV s^{-1} and 0–2000 mV).

CV) in LiBOB/EC-EMC, though the reduction of ES starts at slightly higher voltage than that of LiBOB. It may be that the reduction of ES and BOB are competing reactions, and that BOB is more effective in covering the electrode surface. On the other hand, preliminary results show that ES does have some effect in LiBOB/PC (in preparation). Further experiments are in progress.

4. Conclusions

The BOB anion is actively involved in the formation of the SEI on the anode. The underlying reductive processes, and especially the part at around 1.75 V, give rise to a considerable amount of irreversible capacity. It is found that the intensity of the 1.75 V peak (in CV) is related with the presence of oxygen-containing surface groups of the active material, and is both a function of the BET specific surface area and its surface chemistry. It is not restricted to carbonaceous materials but is also observed on $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Tests with different potential impurities and electrolyte salts, which are structurally related to LiBOB indicate

that compounds containing the oxalate group are generally reduced in the range between 2.2 and 1.5 V. The 1.75 V peak observed in LiBOB-based electrolytes is therefore ascribed to the reduction of oxalate or a moiety with similar structure.

The film-forming electrolyte additives VC and ES apparently show no effect (which would be visible in CV) on the 1.75 V peak.

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