



Electrochemical stability of lithium salicylato-borates as electrolyte additives in Li-ion batteries



Serife Kaymaksiz^a, Florian Wilhelm^a, Mario Wachtler^{a,*}, Margret Wohlfahrt-Mehrens^a, Christoph Hartnig^b, Irina Tschernych^b, Ulrich Wietelmann^b

^aZSW, Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Helmholtzstr. 8, 89081 Ulm, Germany

^bRockwood Lithium GmbH, Trakehner Str. 3, 60487 Frankfurt am Main, Germany

HIGHLIGHTS

- ▶ Reduction and oxidation stabilities of bis(salicylato)borates are reported.
- ▶ A combined experimental and theoretical approach has been used.
- ▶ Lithium bis(5-fluorosalicylato)borate is reported for the first time.
- ▶ Salicylato ligands show higher reduction and lower oxidation stability than oxalato ligands.
- ▶ Variations in stability can be explained by substituent-induced electronic effects.

ARTICLE INFO

Article history:

Received 5 November 2012

Received in revised form

21 December 2012

Accepted 29 December 2012

Available online 11 January 2013

Keywords:

Electrolyte component

Reduction stability

Oxidation stability

Oxidation potential

Density functional theory (DFT)

Solvent model

ABSTRACT

A systematic study has been performed for several chelato-borate complexes by combining electrochemical characterization and ab-initio calculations to reveal whether they are appropriate to be used as electrolyte components in Li-ion batteries. The chelato-borates used in this study are lithium bis(oxalato)borate (LiBOB), lithium salicylatooxalato-borate (LiSOB), lithium bis(salicylato)borate (LiBSB), lithium bis(3-methylsalicylato)borate, lithium bis(5-fluorosalicylato)borate, lithium bis(5-chlorosalicylato)borate, lithium bis(5-bromosalicylato)borate, and lithium bis(3,5-dichlorosalicylato)borate. A graphite electrode is chosen to study the cathodic stability, while LiMn₂O₄ is selected to estimate the anodic stability limits of these chelato-borates. Additionally, the oxidation potentials of these compounds are predicted by employing density functional theory (DFT) calculations. The CV studies of graphite electrodes in these electrolyte mixtures indicate that irreversible reduction of the oxalato and salicylato groups occurs at 1.6–1.8 and 0.9–1.3 V vs. Li/Li⁺, respectively. Besides, irreversible oxidation of the bis(salicylato)borate anions between 4.3 and 4.8 V vs. Li/Li⁺ is observed in the CV curves of LiMn₂O₄ electrodes, depending on the respective ligands around the central boron atom. The theoretical calculations are generally in line with the experimental observations. Furthermore, they help to explain the differences between the oxidation potentials of the anions, which are caused by the different groups that donate the electron and the respective substitution pattern.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

During the last decades lithium-ion batteries (LIBs) have penetrated daily life by being used in household electronics and portable electronic devices [1]. The superiority of LIBs over the alternatives is due to their lightness and compactness reaching a specific energy between 100 Wh kg⁻¹ and 150 Wh kg⁻¹ at potentials up to 4.2 V [2].

Beyond being the preeminent energy storage and power sources of the current technology, LIBs are nowadays designed to fulfill the high power and energy needs in areas such as automotive [3] and space applications [4]. In view of the extensive use of LIBs cost and safety have become major issues. Safety is related both to the electrode materials, the electrolyte, and their interactions. Today's state-of-the-art electrolytes use highly flammable solvents and conductive lithium salts which are corrosive. However, it is possible to improve the safety characteristics of these electrolyte systems by using functional additives, which is the easiest and most adequate way of obtaining safer electrolytes [5]. By introducing a new

* Corresponding author. Tel.: +49 731 9530 403; fax: +49 731 9530 666.

E-mail address: mario.wachtler@zsw-bw.de (M. Wachtler).

component to the state-of-the-art electrolytes, enhanced cycling performance and desired safety features can be achieved. An additive can, for instance, play an efficient role in decreasing flammability, increasing overcharge tolerance, improving ion conduction, modifying the solid electrolyte interphase (SEI), and preventing Al corrosion [5].

One interesting class of substances, which has been proposed both as electrolyte salt and electrolyte additive, are lithium chelato-borate salts. The most well-known chelato-borate in the LIB community is lithium bis(oxalato)borate (LiBOB). The electrochemical properties of LiBOB (Fig. 1) and its behavior as an electrolyte salt or as an electrolyte additive for LIBs have been studied previously in detail (e.g. Refs. [6–11]). Thermal stability up to 300 °C, stabilization of the Al current collector up to 5 V vs. Li/Li⁺, and stable SEI formation at the graphite surface even in propylene carbonate (PC) containing electrolytes have been mentioned [12–15]. Additionally, LiBOB is a non-toxic and low-cost alternative to LiPF₆ and has provided high anodic and cathodic stability and increased safety with several electrode materials [6,16,17]. But LiBOB has also some limitations such as lower conductivity [18] and higher interfacial impedance for carbon-based anodes as compared to LiPF₆ [19,20].

Apart from LiBOB, boron-based chelate complex anions with aromatic or aliphatic diols, or carboxylic acids, e.g. lithium bis[1,2-benzenediolato(2-)-O,O']borate, were introduced as a new class of lithium salts by Barthel et al. [21–26]. Their studies indicate that these large and bulky organoborate anions provide better charge delocalization and higher oxidation stability due to the covalent bonds in their structures. Additionally, the effect of an electron-withdrawing substituent such as fluorine on the oxidation stability of those anions was investigated, and a raise by 0.1 V per fluorine and chelate ligand was observed in the electrochemical stability window of benzenediolato borate [24].

Among the organo-borates, especially salicylato-based chelato-borates have attracted the interest of researchers. Aurbach et al. [27] studied the anodic and cathodic stabilities of lithium bis(salicylato)borate (LiBSB) as an electrolyte additive in a graphite/LiMn₂O₄ cell. Their results exhibited the contribution of this additive to the SEI formation on the surface of the graphite electrode by irreversible reduction at around 830 mV vs. Li/Li⁺. Besides, this additive acted electrochemically on the cathode surface by forming a passivation film and thus suppressing further surface reactions. Sasaki et al. [28–31] studied lithium bis[3-methylsalicylato(2-)]borate (LiBMSB), lithium bis[3,5-dichlorosalicylato(2-)]borate (LiBCl₂SB), lithium bis[3,5,6-trichlorosalicylato(2-)]borate (LiBCl₃SB), lithium bis[5-bromosalicylato(2-)]borate (LiBBrSB), and lithium bis[5-chlorosalicylato(2-)]borate (LiBCISB). These investigations have consistently demonstrated the substituent effect on the thermal and electrochemical properties. The oxidation stabilities of these compounds on glassy carbon (GC) electrodes were reported to decrease in the order LiBCl₃SB ~ LiBCl₂SB > LiBCISB > LiBBrSB > LiBSB > LiBMSB [28]. The reduction stability (on GC electrodes) decreased in the opposite order, except for LiBCISB. Furthermore the galvanostatic cycling behavior of these substances used as electrolyte additives at a concentration of 0.01 mol L⁻¹ was studied in Li/V₂O₅ primary and Li/CoO₂ and graphite/LiCoO₂ secondary cells. For Li/V₂O₅ cells the discharge capacity was increased, for Li/LiCoO₂ cells the cycling stability was increased, and for graphite/LiCoO₂ cells the results were ambiguous [28].

The aim of the present work is to broaden the current knowledge of the use of Li chelato-borates as electrolyte components for LIBs. In this context, several chelato-borate complexes with unsubstituted and substituted salicylato ligands, as shown in Fig. 1, have been synthesized and investigated: LiBOB, lithium salicylato-oxalato-borate (LiSOB), lithium bis(salicylato)borate (LiBSB),

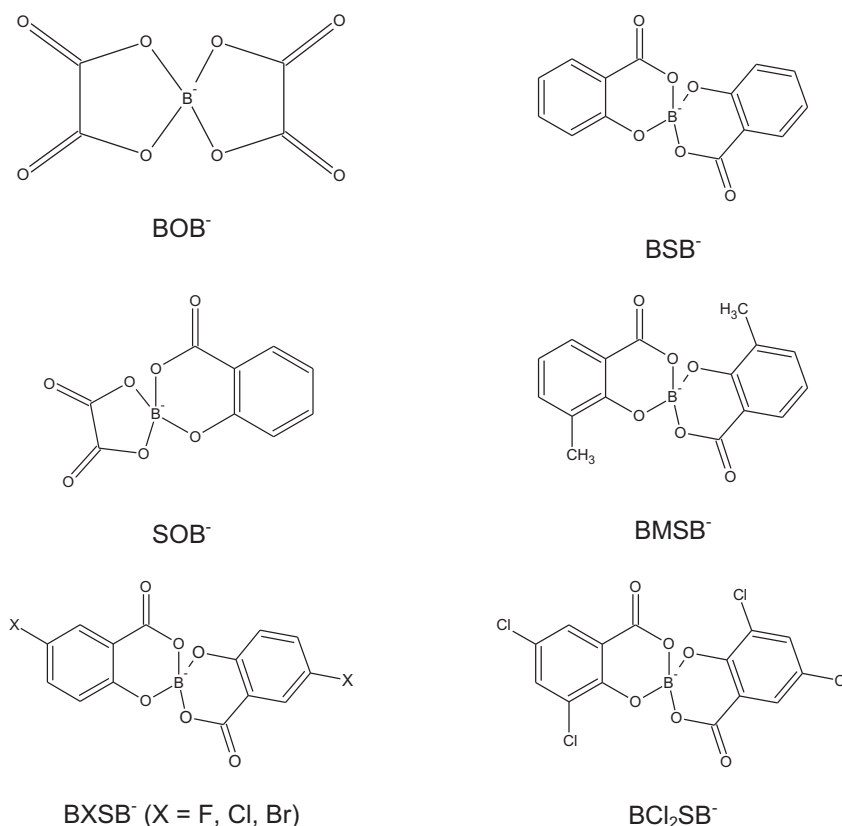


Fig. 1. Structural formulas of lithium chelato-borate anions.

Download English Version:

<https://daneshyari.com/en/article/7740931>

Download Persian Version:

<https://daneshyari.com/article/7740931>

[Daneshyari.com](https://daneshyari.com)