



Review

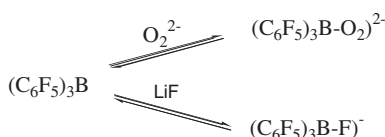
Boron-based anion receptors in lithium-ion and metal-air batteries

V. Prakash Reddy ^{a,*}, Mario Blanco ^b, Ratnakumar Bugga ^c^a Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409, USA^b Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125, USA^c Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

HIGHLIGHTS

- Anion receptors increase lithium ion cell cycle performance and ionic conductivity.
- The boron-based anion receptors also facilitate formation of stable SEI at the electrode surfaces.
- The energetics of the reversible anion binding is modeled by DFT calculations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 July 2013

Received in revised form

29 August 2013

Accepted 6 September 2013

Keywords:

Anion receptors

Boroxines

Solid electrolyte interface

Borate esters

Triarylboranes

Lithium ion transference numbers

ABSTRACT

Boron-based anion receptors, widely used as biosensors, are currently being explored as electrolyte-additives in lithium ion batteries and metal-air batteries, towards the goal of realizing high voltage, high energy density batteries. The potential advantage of the boron-based anion receptors as electrolyte-additives is to improve the lithium ion or metal-air battery cell cycle performance, and increase lithium ion transference numbers and ionic conductivity. These anion receptors also have unique characteristics that facilitate in maintaining a stable solid electrolyte interface (SEI) at the electrode surface. In this comprehensive review, we have outlined the synthesis, computational studies, and applications of various classes of boron-based anion receptors in lithium ion and metal-air batteries.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Anion receptors that selectively bind to the specific anions, have numerous biological and environmental applications [1,2]. The anion-recognition and binding of these receptors may be due to hydrogen-bonding interactions [3], covalent binding of anions to the substrate [4], or through Lewis acid–base interactions [5,6]. Binding of various anions to the widely used bio- and chemosensors generally results in the change of color or fluorescence

properties of the analytes at millimolar to nanomolar concentrations [6].

Although most of the research in this area is focused on the development of bio- or chemosensors, recent interest in the high voltage, high energy density lithium ion batteries prompted developing novel anion receptors that play a major role in the enhanced dissociation of lithium salts such as LiF, leading to their enhanced ionic conductivity and increased lithium- and fluoride ion transference numbers. Further, the anion receptors, when used as additives in the electrolyte solvents such as dimethyl carbonate (DMC) or propylene carbonate (PC), dramatically increase the solubility of lithium fluoride (LiF) or lithium oxides (Li₂O and Li₂O₂), and help maintain stable solid electrolyte interface (SEI) at the

* Corresponding author. Tel.: +1 (573) 341 4768.

E-mail address: preddy@mst.edu (V. Prakash Reddy).

electrode surfaces [7,8]. Tris(pentafluorophenyl)borane (TPFPB), a boron based anion receptor, improves the thermal stability of the SEI formed on a graphite anode [8]. SEI layers are formed normally by the decomposition of the electrolyte materials such as ethylene carbonate (EC) at the electrode surfaces. It was shown that during initial galvanostatic cycling of lithium ion cells, consisting of carbonaceous mesocarbon microbead (MCMB) anode, anion receptors such as TPFPB increase the extent of SEI formation and their thermal stability [9].

Whereas SEI, a protective layer formed on the surfaces of the electrodes during the first charge–discharge cycle, is advantageous in increasing the cell cycle-life, presence of large amounts of insoluble inorganic materials, LiF, Li₂O₂ and Li₂CO₃ in the SEI layers results in increased impedance and capacity loss; anion receptors of appropriate binding affinity can solvate these F⁻, HO⁻, O₂²⁻ and O₂⁻ anions that are present in the protective SEI layers at the anode and cathode surfaces, and facilitate their removal.

Although the mechanisms of the formation of the above lithium salts in SEI is still an active area of research, the following processes are generally believed to be involved: LiF may be formed by the bimolecular nucleophilic substitution reaction (S_N2) of PF₅ a byproduct of PF₆⁻ anion decomposition—with alkoxide anion (OR⁻), a highly reactive nucleophilic species. Lithium alkoxide (e.g., LiOMe), in turn, is formed in trace amounts by the electrolytic reduction of the carbonate electrolyte solvents [10,11]. This process has been recently investigated using high level DFT quantum mechanical methods [12].

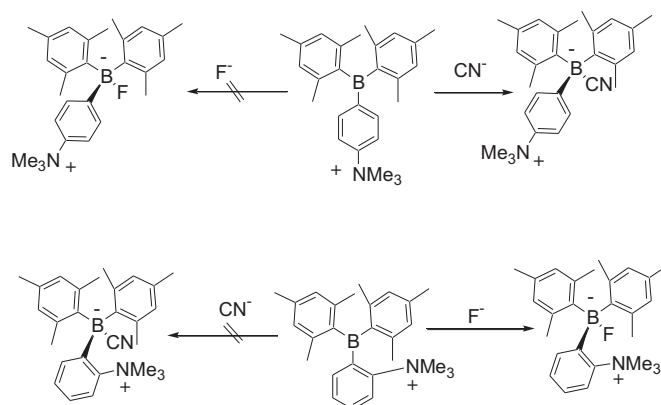
Anion receptors have high importance in the formation of the electrode-protective SEI layers at the anode and cathode surfaces. The efficiency of these anion receptors may be measured by the host-guest stoichiometry and their binding constants [13]. In this comprehensive review, we address the various anion receptors used in the lithium ion batteries, and their synthesis and mode of action. The main focus of the review will be on the boron-based anion receptors as they are readily synthesized and convenient to use as additives in the nonaqueous electrolytes that are commonly used in the lithium ion batteries. Amine-based anion receptors [14–16], which bind anions due to hydrogen bonding interactions, are not discussed here in detail, as they have relatively poor electrolytic stability.

2. Fluoride anion receptors in aqueous solutions

2.1. Fluoride or cyanide specific anion receptors

Boron based anion receptors can be fine-tuned for their selectivity towards fluoride or cyanide anions by adjusting the stereo-electronic effects of the substituents. In particular, it has been elegantly demonstrated that the highly hindered triarylboranes selectively bind to fluoride anion when the electron withdrawing trimethylammonium group is *ortho*- to the boron moiety whereas they are selective to cyanide anion when the cationic substituent is *para*- to the boron moiety [17] (Scheme 1).

Interestingly, this differential selectivity is not found in organic solvents. In aqueous solutions, the fluoride anions are strongly coordinated to water molecules as compared to cyanide anion, and thus relatively more electrophilic boron center (e.g., the *ortho*-trimethylammonium substituted triarylborane) is required for its binding to the receptor. On the other hand, the cyanide anion, being relatively more sterically crowded, would not bind to the latter highly crowded triarylborane. Thus, the electrophilicity of the boranes can be fine-tuned by the appropriate choice of the substituents on the aryl groups so that they can selectively bind to specific anions.



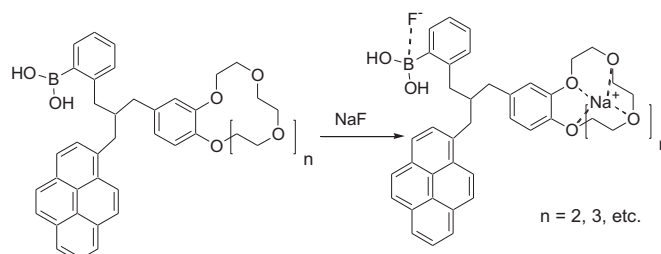
Scheme 1. Triarylboranes as selective anion receptors for fluoride and cyanide anions in aqueous media.

2.2. Ditopic receptors

Ditopic receptors that are selective towards both cations and anions are interesting chimerical compounds as they may help in increased dissociation of the lithium salts, resulting in high anion and cation transference numbers. This concept has not been applied for lithium ion batteries to date. However, ditopic fluorescent sensors having crown ether with appended boronic acid groups have been reported [18] (Scheme 2). The hard boron center would bind to fluoride anions, while the crown ether moiety binds to the cations. In order to be effective receptors for lithium ion batteries, the binding of the cation and anion should be reversible, so that they can be transported from SEI and released into the bulk electrolytes at the appropriate externally applied potential.

3. Effect of anion receptors on ionic conductivity

McBreen and coworkers have prepared a series of trialkyl and triaryl-borates and boranes such as trimethylborate (1), tris(trifluoromethyl)borate (2), tris(heptafluorobutyl)borate (3), tris(hexafluoroisopropyl)borate (4), tris(perfluoro-*tert*-butyl)borate (5), tris(triphenyl)borate (6), tris(hexafluorocumyl)borate (7), tris(pentafluorophenyl)borate (8), and tris(pentafluorophenyl)borane (TPFPB; 9) (Fig. 1) [19]. These anion receptors were found to complex fluoride anions, and as a consequence, increase the solubility of LiF in nonaqueous electrolyte solvents. In dimethyl ether, for example, the solubility of LiF in the absence of some of these anion receptors is about 10⁻⁵ M. Upon addition of the boron based anion receptors, the solubility of LiF increased to about 1.2 M, which is about six orders of magnitude higher than that in the absence of the anion receptors. These anion receptors have high electrochemical stability, up to 5.1 V vs Li⁺/Li. The conductivities of their solutions are also significantly higher. When present in equimolar



Scheme 2. Representative example for a ditopic receptor.

Download English Version:

<https://daneshyari.com/en/article/7738065>

Download Persian Version:

<https://daneshyari.com/article/7738065>

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