Journal of Power Sources 328 (2016) 433–442

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Some Lewis acid-base adducts involving boron trifluoride as electrolyte additives for lithium ion cells

Mengyun Nie, L. Madec, J. Xia, D.S. Hall, J.R. Dahn*

Dept. of Physics and Atmospheric Science, Dalhousie University, Halifax, B3H4R2 Nova Scotia, Canada

HIGHLIGHTS

- Describes several Lewis acid-base adducts as electrolyte additives.
- Pyridine boron trifluoride is the best adduct studied here.
- Pyridine boron trifluoride improved storage, impedance and long-term cycling.

ARTICLE INFO

Article history:
Received 27 April 2016
Received in revised form
23 July 2016
Accepted 9 August 2016

Keywords:
Lithium ion cells
Electrolyte additives
Lewis acid-base complexes
NMC/graphite pouch cells

ABSTRACT

Three complexes with boron trifluoride (BF_3) as the Lewis acid and different Lewis bases were synthesized and used as electrolyte additives in $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$/graphite and $Li[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_2$/graphite pouch cells. Lewis acid-base adducts with a boron-oxygen (B—O) bond were trimethyl phosphate boron trifluoride (TMP-BF) and triphenyl phosphine oxide boron trifluoride (TPPO-BF). These were compared to pyridine boron trifluoride (PBF) which has a boron-nitrogen (B—N) bond. The experimental results showed that cells with PBF had the least voltage drop during storage at 4.2 V, 4.4 V and 4.7 V at 40 °C and the best capacity retention during long-term cycling at 55 °C compared to cells with the other additives. Charge-hold-discharge cycling combined with simultaneous electrochemical impedance spectroscopy measurements showed that impedance growth in TMP-BF and TPPO-BF containing cells was faster than cells containing 2%PBF, suggesting that PBF is useful for impedance control at high voltages (>4.4 V). XPS analysis of the SEI films highlighted a specific reactivity of the PBF-derived SEI species that apparently hinders the degradation of both $LiPF_6$ and solvent during formation and charge-hold-discharge cycling. The modified SEI films may explain the improved impedance, the smaller voltage drop during storage and the improved capacity retention during cycling of cells containing the PBF additive.

1. Introduction

Incorporating electrolyte additives into the electrolyte of Li-ion batteries (LIBs) is one effective method for extending their lifetime [1–3]. Pyridine boron trifluoride (PBF) and other aromatic amine:boron trifluoride complexes have been proposed and tested as electrolyte additives for NMC-based LiBs [4–8]. Several of these additives have been demonstrated to improve LIB performance during cycling and storage at high temperatures. Recently, possible chemical pathways for solid-electrolyte interphase (SEI) formation on the negative electrode surface in PBF-containing cells were investigated using density functional theory (DFT) and a variety of experimental techniques [9]. However, the actual mechanisms by which the BF_3 and/or the aromatic amine groups in PBF-type additives improve cell performance are not yet understood. Thus far, untested hypotheses about the roles of the different functional groups are based on statements found in Refs. [10–13]. BF_3, as a boron-based anion receptor, might react with insoluble LiF from the SEI layers on the positive and/or negative electrodes to form the soluble electrolyte salt $LiBF_4$ [10,11]. This would rationalize the observation that PBF limits impedance growth during cycling [6,7]. Aromatic amines are widely used as corrosion inhibitors for metals including iron, steel and copper in acidic environments [12,13], so those Lewis base amines might help prevent transition metal dissolution from NMC positive electrodes by neutralizing acidic impurities in the electrolyte. All the aromatic amine: BF_3 Lewis

---

* Corresponding author.
E-mail address: jeff.dahn@dal.ca (J.R. Dahn).

http://dx.doi.org/10.1016/j.jpowsour.2016.08.048
0378-7753/© 2016 Elsevier B.V. All rights reserved.

adducts were synthesized by mixing the amine with $BF_3.Et_2O$ to obtain solid products with a boron-nitrogen bond [14,15].

Moreover, electrolyte additives are not limited to aromatic amine: BF_3 adducts. Researchers at E-one Moli Energy Canada [16] and at Toyota [17] patented carbonate:BF_3 adducts that contain one boron atom bonded to one oxygen atom. Matsui et al. [17] studied asymmetric BF_3 adducts, which can be used as electrolyte solvents due to their wide potential window and excellent oxidation resistance. In this work, trimethyl phosphate boron trifluoride (TMP-BF) and triphenyl phosphine oxide boron trifluoride (TPPO-BF), each of which has a boron-oxygen bond, were synthesized. These were tested as electrolyte additives in $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$/graphite and $Li[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_2$/graphite pouch cells and compared to PBF. The motivation of this work is to test the effect of retaining the Lewis acid (BF_3) from PBF and modifying the nature of the Lewis base (pyridine). This work is complementary to recent studies that utilized pyridine phosphorus pentafluoride (PPF), in which the Lewis base (pyridine) was retained and it was the Lewis acid (PF_5) that was modified [8,9]. The behavior of PBF- and PPF-containing cells are generally similar, although some differences have been noted. It is heretofore unknown whether this indicates that it is the pyridine species that is responsible for the performance of PBF-containing cells, or whether the two Lewis acids (BF_3 and PF_5) are simply so chemically similar that they may play the same role in a Li-ion cell.

2. Experimental

2.1. Synthesis of the Lewis acid-base adducts

The synthesis procedure for the Lewis acid-base adducts is shown in Scheme 1.

Trimethyl phosphate boron trifluoride (TMP-BF): To a 50 ml round bottom flask, 2.5 g of boron trifluoride etherate ($BF_3.Et_2O$, > 46.5% BF_3, Sigma-Aldrich) was dissolved in 10.0 mL hexane, then 2.0 g of trimethyl phosphate (Sigma-Aldrich, > 99%) was added to the solution dropwise, and transparent crystals of the TMP-BF complex formed gradually at the bottom of the flask and were collected by removing the solvent. The solid samples were further rinsed with hexane and dried in vacuum (40 °C) overnight.

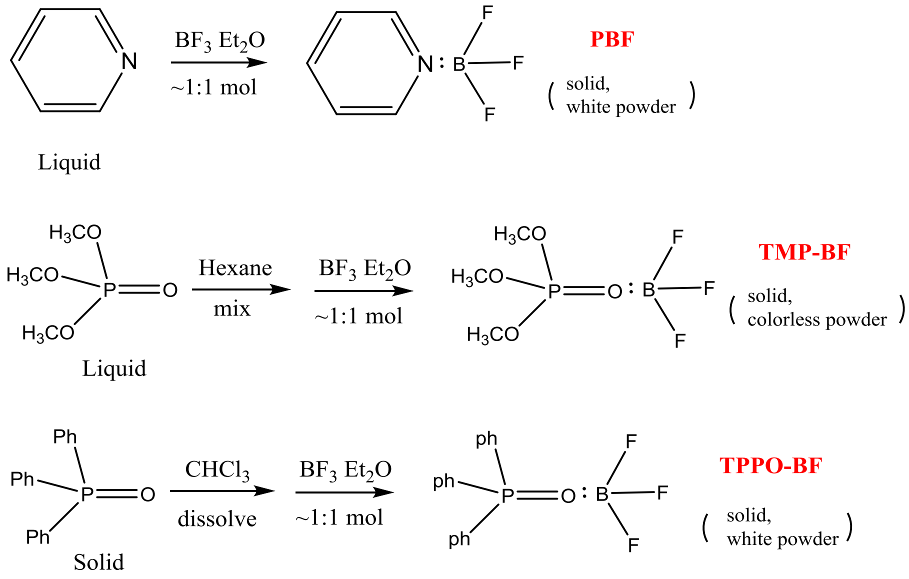
Triphyenyl phosphine oxide boron trifluoride (TPPO-BF): The synthesis of TPPO-BF was similar to the synthesis of pyrazine diboron trifluoride reported earlier [5,6]. **1.0** g (0.0036 mol) triphyenyl phosphine oxide (Sigma-Aldrich, >98%) in **2** mL chloroform was added slowly into 1.0 ml $BF_3.Et_2O$. The reaction was highly exothermic so the reaction bottle was kept near room temperature by the slow addition of the reagents. White or colorless crystals normally precipitated out immediately, but if no precipitate was observed then the reaction mixture was transferred to a −20 °C freezer and crystals then formed. The solid products were then rinsed by chloroform twice and collected by filtration. The wet product was transferred to a vacuum oven and vacuum dried overnight at 45–50 °C.

Pyridine boron trifluoride (PBF) was synthesized as previously described [4]. Table 1 lists the affinity constants of several Lewis acid-base adducts involving BF_3 [14]. The affinity constants are an indicator of the Lewis acid-base bond strength. Larger affinity constants correspond to stronger bonds. In this work, Lewis acid-base adducts showing higher affinity constants than $BF_3.Et_2O$ were targeted so that the exchange with Et_2O is spontaneous. The purity of the synthesized TMP-BF and TPPO-BF after vacuum drying was checked by NMR (^1H, ^{19}F, ^{11}B) and no peaks of the initial reactants were observed in the NMR spectra in Figs. S1 and S2. The NMR spectra of PBF can be found in the supporting information of reference 4.

Table 1
Affinity constants of various Lewis acid-base Complexes.

Lewis base	Abbre.	BF_3 affinity (*KJ mol^{-1}*)
Pyridine	Pyr	128.08 ± 0.50^{14}
Diethyl ether	Et_2O	78.77 ± 0.36^{14}
Trimethyl phosphate	TMP	84.75 ± 0.22^{14}
Triphenyl phosphine oxide	TPPO	103.30 ± 1.50^{14}
Ethylene carbonate	EC	66.40 ± 1.10^{14}

BF_3 affinities (kJ mol^{-1}) of Lewis bases in dichloromethane at 298 K and 1 atm.



Scheme 1. Synthesis procedure and structure of pyridine boron trifluoride (PBF), trimethyl phosphate boron trifluoride (TMP-BF), and triphyenyl phosphine oxide boron trifluoride (TPPO-BF).