Electrochimica Acta xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Electrolyte additive combinations that enhance performance of high-capacity $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$–graphite cells

Ye Zhu [a], Yan Li [a,b], Martin Bettge [a], Daniel P. Abraham [a,*]

[a] *Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, United States*
[b] *Materials Science Program, University of Rochester, Rochester, NY 14627, United States*

ARTICLE INFO

Article history:
Received 16 November 2012
Received in revised form 11 March 2013
Accepted 14 March 2013
Available online xxx

Keywords:
Electrolyte additives
High voltage
Lithium ion
Calendar life
Additive combinations

ABSTRACT

The synergistic effects of $LiB(C_2O_4)_2$ (LiBOB), $LiF_2B(C_2O_4)$ (LiDFOB), triphenylamine (Ph_3N), and 1,4-benzodiozane-6,7-diol (BDOD) as functional electrolyte additives in high-energy electrochemical cells is examined. The influence of these additives, individually, and in different combinations, is evaluated using galvanostatic cycling of cells containing $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ ($0.5Li_2MnO_3\cdot 0.5LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$)-based positive electrodes, graphite-based negative electrodes, and a $LiPF_6$-based electrolyte. Electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), and voltage-hold tests are also used. By itself, LiBOB is a good additive for reducing cell capacity loss, but cell impedance rise is still significant after extended cycling. Similarly, neither Ph_3N nor BDOD alone provide desired improvements in cell performance. However, cells containing LiBOB in combination with LiDFOB, Ph_3N, or BDOD exhibit enhanced capacity retention, rate capability, and cyclability; probable reaction mechanisms are highlighted here. Combining electrolyte additives that act synergestically is a practical and versatile strategy to improve performance and life of lithium-ion cells.

1. Introduction

As part of DOE's Advanced Battery Research (ABR) program, a significant effort is underway at Argonne National Laboratory (Argonne) to develop advanced lithium-ion batteries for transportation applications, including plug-in hybrid (PHEV) and battery electric vehicles (EVs). In order to obtain the required high energy and power densities over many charge and discharge cycles, the effort is focused on the development of high-voltage and high-capacity cathode materials, including $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ ($0.5Li_2MnO_3\cdot 0.5LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$) [1]. However, to take advantage of this new class of materials, new electrolytes systems are needed because the charge voltages approach and exceed 4.5 V vs. Li/Li^+. Most conventional carbonate-based organic solvents start oxidizing at voltages >4.5 V vs. Li/Li^+ [2]. Furthermore, oxide "activation" is accompanied by release of oxygen that causes crystal structural changes and generates surface films on the oxide that impedes Li-ion motion [3,4]. At the negative electrode, cycling, especially at high rates and high temperatures, can induce surface fractures in graphite particles, which increase surface area and enhance electrolyte reduction reactions that consume cyclable Li [5,6].

Recent studies indicate that capacity degradation in $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$–graphite full cells is triggered by the positive electrode but manifests itself at the negative electrode [4,7,8]. The capacity fades that result from lithium-trapping side reactions are enhanced by transition metal elements that dissolve from the oxide-cathode and migrate/electrodeposit on the graphite-anode [9,10]. Electrolyte oxidation at the cathode also produces significant full cell impedance rise after long term cycling at cell voltages ≥4.6 V. Previous studies have demonstrated that lithium difluoro(oxalato)borate (LiDFOB) is an effective bifunctional additive for improving cell performance [7]. The addition of 2 wt.% LiDFOB to EC:EMC (3:7 by wt.) +1.2 M $LiPF_6$ electrolyte improves cell cycling performance by suppressing impedance rise at the positive electrode, and minimizing lithium-consuming reactions at the negative electrode. Sacrificial oxidation of LiDFOB at the positive electrode produces passivation films, which protects the electrode from the electrolyte and reduces transition metal dissolution from the oxide, that ultimately help improve stability of the anode SEI.

Using organic compounds as electrolyte additives is an effective way to suppress electrolyte oxidation at the positive electrode [11–15]. These organic compounds have lower oxidation potentials than the baseline electrolyte and can be sacrificially oxidized to modify the cathode surface during charging. Other reports suggest that some aromatic or heteroaromatic-based additives help protect the carbonate-based electrolytes from decomposition at high cell

---

* Corresponding author. Tel.: +1 630 252 4332; fax: +1 630 972 4406.
E-mail address: abraham@anl.gov (D.P. Abraham).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.03.102

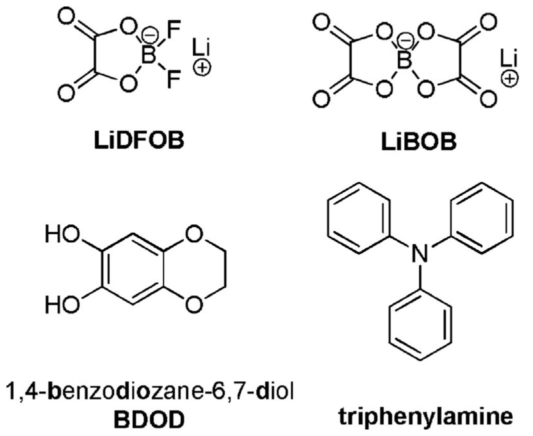

Fig. 1. Chemical structures of additives used in this work.

voltages [16–19]. For example, compounds such as thiophene, 3,4-ethylenedioxy-thiophene (EDT), *N*-methyl pyrole (MPL), are known to form electronically conducting polymers by electrochemically-induced radical polymerization. These types of polymers could be particularly beneficial for positive electrodes with oxides such as $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$, which have relatively low electronic conductivity. Moreover, some organic molecules undergo transition metal catalyzed radical polymerization [20,21]. These additives offer several advantages that include the following: (i) selective passivation of reactive metal ion sites, and (ii) radical-mediated polymerization that does not consume lithium ions. Regardless of the specific mechanism, these types of organic molecules have been shown to be effective in improving cycling efficiency and capacity retention of some high voltage electrodes with minimal effect on the rate capability [18,22,23].

The LiDFOB electrolyte additive slows down cell performance degradation but does not completely stop it. In the quest for additives that further enhance cell life, we expand our investigations to include other compounds. In this article, we examine the performance of lithium bis(oxalate)borate (LiBOB), and aromatic compounds triphenylamine (Ph_3N), and 1,4-benzodiozane-6,7-diol (BDOD), as functional electrolyte additives (Fig. 1). The effect of LiBOB in improving electrochemical performance of graphite-based negative electrodes by forming a more stable SEI is well documented [24–29]. Lucht and coworkers showed that the LiBOB additive also inhibits detrimental reactions of the electrolyte with $LiNi_{0.5}Mn_{1.5}O_4$ cathodes at high voltages [30]. Unlike LiBOB, triphenylamine and BDOD have not been used previously as electrolyte additives in lithium-ion cells. Based on their chemical structures, these two compounds are expected to have relatively low oxidation potentials and, hence, can be sacrificially oxidized at the cathode. In addition, these compounds are expected to form electronically conducting polymers at the cathode, which could reduce degradation in electrode performance. In this article we show that the LiBOB additive improves capacity retention but has a smaller effect on cell impedance rise. Triphenylamine and BDOD additives, used individually, do not provide desired improvements in cell life. However, cells containing LiBOB–triphenylamine or LiBOB–BDOD combinations display superior capacity retention and lower impedance rise. The cells with a LiDFOB–LiBOB combination show the best capacity retention and lowest impedance rise after long-term cycling.

2. Experimental

2.1. Preparation of electrode and electrolyte

Table 1 lists details of the positive and negative electrode materials, separator, and electrolyte used in our cells. The positive electrode contains 86 wt.% $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ and the negative electrode contains 89.8 wt.% graphite, as the active materials. Our baseline electrolyte, 1.2 M $LiPF_6$ solution in EC/EMC (3:7 by wt.) (henceforth referred to as Gen2 electrolyte) is from Tomiyama Chemical Industry (Japan), and the high-purity LiDFOB salt is from Central Glass Co. (Japan). The LiBOB salt is from Chemetall GmbH (Germany); the salt was further purified by recrystallization before electrolyte preparation. The triphenylamine (Ph_3N) was purchased from Aldrich (U.S.) and 1,4-benzodiozane-6,7-diol was obtained from Matrix Lab (U.S.). Extensive screening tests in full cells were conducted to determine the optimal additive concentrations to the baseline electrolyte. The optimal LiBOB additive concentration is 1 wt.%; higher concentrations (e.g. 2 wt.%) result in lower capacity and higher cell impedance [31]. The optimal Ph_3N and BDOD additive concentration is ~0.25 wt.%; higher concentrations lead to more rapid capacity degradation. Therefore, the additive combinations 2 wt.% LiDFOB + 1 wt.% LiBOB, 0.25 wt.% Ph_3N + 1 wt.% LiBOB, and 0.3 wt.% BDOD + 1 wt.% LiBOB, are used in this study.

2.2. Electrochemical characterization

The anodic stability of electrolyte, with and without additives, is examined by linear sweep voltammetry (LSV) tests using a three-electrode setup with platinum as the working electrode and lithium metal as the counter and reference electrodes. The LSV data are obtained at room temperature (~23 °C) with a scan rate of $20\ mV\ s^{-1}$ from an open-circuit voltage of ~3 V to 5.5 V vs. Li/Li^+.

Electrochemical cycling experiments are conducted in 2032-type coin cells ($1.6\ cm^2$ area electrodes). Good reproducibility is achieved for baseline coin cells (no additives) with only a few percent deviation from the average impedance and capacity values; trends observed across multiple samples (e.g. with different additives) are consistent. Therefore, only representative data and trends are reported here. Our coin cells are assembled in an Ar–atmosphere glove box (O_2 < 10 ppm, H_2O < 1 ppm) and galvanostatically cycled within a constant temperature oven held at 30 °C or 55 °C. The positive electrode//Li cells are typically cycled between

Table 1
Cell components and chemistry.

Positive electrode	Negative electrode
86 wt.% $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (Toda HE5050)	89.8 wt.% A12 graphite (ConocoPhillips)
8 wt.% PVDF binder (Solvay 5130)	6 wt.% PVDF binder (KF-9300 Kureha)
4 wt.% SFG-6 graphite (Timcal)	4 wt.% super P (Timcal)
2 wt.% super P (Timcal)	0.17 wt.% oxalic acid
6.6 mg cm^{-2} active-material loading density	5.6 mg cm^{-2} active-material loading density
37.1% electrode porosity	26% electrode porosity
35 μm-thick coating	40 μm-thick coating
15 μm-thick Al current collector	10 μm-thick Cu current collector
Electrolyte	*Separator*
1.2 M LiPF6 in EC/EMC (3:7 by wt.)	25 μm thick, Celgard 2325 (PP/PE/PP)

Please cite this article in press as: Y. Zhu, et al., Electrolyte additive combinations that enhance performance of high-capacity $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$–graphite cells, Electrochim. Acta (2013), http://dx.doi.org/10.1016/j.electacta.2013.03.102