Available online at www.sciencedirect.com
ScienceDirect
Journal of Power Sources 162 (2006) 1379–1394
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

A review on electrolyte additives for lithium-ion batteries

Sheng Shui Zhang *

U.S. Army Research Laboratory, AMSRD-ARL-SE-DC, Adelphi, MD 20783-1197, USA

Received 5 July 2006; received in revised form 21 July 2006; accepted 21 July 2006
Available online 10 October 2006

Abstract

This paper reviews electrolyte additives used in Li-ion batteries. According to their functions, the additives can be divided into these categories: (1) solid electrolyte interface (SEI) forming improver, (2) cathode protection agent, (3) $LiPF_6$ salt stabilizer, (4) safety protection agent, (5) Li deposition improver, and (6) other agents such as solvation enhancer, Al corrosion inhibitor, and wetting agent. The function and mechanism of each category additives are generally described and discussed.
Published by Elsevier B.V.

Keywords: Electrolyte; Additive; Solid electrolyte interface; Overcharge; Li-ion battery

---

Contents

---

1. Introduction

Use of electrolyte additives is one of the most economic and effective methods for the improvement of Li-ion battery performance. Usually, the amount of an additive in the electrolyte is no more than 5% either by weight or by volume while its presence significantly improves the cycleability and cycle life of Li-ion batteries. For better battery performance, the additives are able to: (1) facilitate formation of solid electrolyte interface/interphase (SEI) on the surface of graphite, (2) reduce irreversible capacity and gas generation for the SEI formation and long-term cycling, (3) enhance thermal stability of

---

* Tel.: +1 301 394 0981; fax: +1 301 394 0273.
E-mail address: szhang@arl.army.mil.

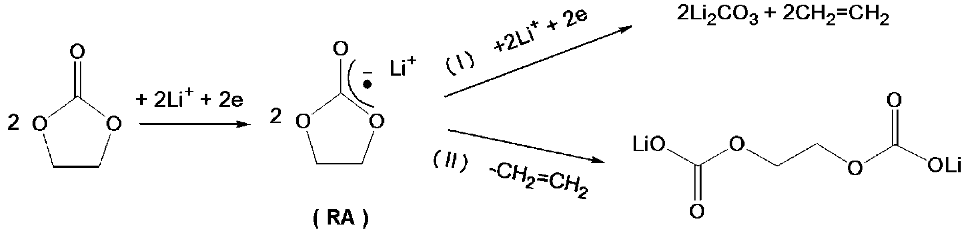
0378-7753/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jpowsour.2006.07.074

$LiPF_6$ against the organic electrolyte solvents, (4) protect cathode material from dissolution and overcharge, and (5) improve physical properties of the electrolyte such as ionic conductivity, viscosity, wettability to the polyolefine separator, and so forth. For better battery safety, the additives are able to: (1) lower flammability of organic electrolytes, (2) provide overcharge protection or increase overcharge tolerance, and (3) terminate battery operation in abuse conditions. This paper reviews these additives and discusses their functions in improving Li-ion battery performance.

2. SEI forming improver

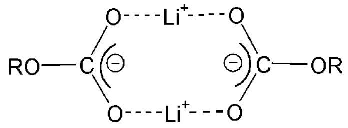
2.1. Understanding of SEI formation

Extensive investigations using various spectroscopic techniques have identified that the main components of SEI are the decomposed products of electrolyte solvents and salts. These components include Li_2CO_3, lithium alkyl carbonate, lithium alkyloxide, and other salt moieties such as LiF for $LiPF_6$-based electrolytes [1,2]. Based on this fact, two mechanisms have been proposed for the electrochemically induced reduction of carbonate-based solvents, for example ethylene carbonate (EC):



where RA is an abbreviation for "radical anion". Both of these two mechanisms are present in the process of SEI formation and compete with each other. When mechanism (I) is predominate, the reduction of solvents generates more gaseous products, and the resulting SEI is Li_2CO_3-abundant and less stable. On contrary, mechanism (II) leads to less gaseous products and the resulting products are substantially insoluble in the electrolyte. As a result, the formed SEI is more compact and stable. Many researches have indicated that these two mechanisms are affected by the morphology and chemistry of graphite surface, and are associated with the catalytic activity of the fresh graphite surface. The catalytic effect has been confirmed by the strong location-dependence of SEI composition [3,4]. That is, the SEI formed in prismatic (edge) areas of a highly oriented pyrolytic graphite is enriched with inorganic compounds, while that in basal planes is enriched with organic compounds [3,4]. The catalytic phenomenon was further supported by the fact that surface modification, such as mild chemical oxidization [5–8] and physical surface coating [9–11], on graphite materials significantly facilitated SEI formation and reduced gas generation in the first intercalation of Li^+ ions into graphite. These modifications are considered to deactivate the catalytic activity of the fresh graphite surface.

On the other hand, a dynamic study using an electrochemical impedance spectroscopy (EIS) reveals that the SEI formation takes places in two major voltage stages [12,13]. The first stage takes place before the intercalation of Li^+ ions into graphite and the SEI formed in this stage is structurally porous, highly resistive, and dimensionally unstable. The second stage occurs simultaneously with the intercalation of Li^+ ions and the resulting SEI is more compact and highly conductive. For a specific electrolyte system of a 1.0 M $LiPF_6$ 3:7 (wt.) EC–ethyl methyl carbonate (EMC), these two stages produce nearly same irreversible capacities. The irreversible capacities suffered in the second stage are associated not only with the reduction of solvent molecules, but also with the electrochemical reduction of surface functional groups, such as carbon–hydrogen bond, carboxyl, carbonyl, and lactone, on the edge sites of graphite [5]. In the view of chemical composition, the SEI formed in the first stage is more enriched with inorganic components, while that formed in the second stage with organic components. Better stability of the latter is attributed to the formation of a network between organic compounds through the coordination of Li^+ ions and organic carbonate anions as below [14]:



As suggested by its chemical composition, the "dried" SEI itself is neither ionic conductive nor electronic conductive. The ionic conduction in the SEI must origin from the migration of solvated Li^+ through the micro-pores of SEI. Therefore, the ionic conductivity of SEI can be taken as the measure to evaluate the compactness and stability of SEI. Generally, high resistance corresponds to a compact and stable SEI [13]. Xu et al. [15] further examined the stability of the SEI formed in an EC-based electrolyte with different voltage range by changing the electrolyte into a fresh propylene carbonate (PC) electrolyte, and found that the SEI formed above 0.5 V versus Li^+/Li, i.e., corresponding to the first stage, was unable to suppress the reduction of PC molecules. The information described above would be very useful to understand and develop a desirable additive.

2.2. Reduction-type additive

As described above, the SEI formed before the intercalation of Li^+ ions is unstable and abundant with inorganic compounds. Furthermore, this period produces more gaseous products, especially for PC-containing electrolytes. In the similar manner as surface modification, the SEI formation can be facilitated by chemically coating an organic film onto the surface of graphite