Journal of Power Sources 273 (2015) 954–958

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

A highly safe battery with a non-flammable triethyl-phosphate-based electrolyte

Kazuaki Matsumoto, Kazuhiko Inoue*, Koji Utsugi

Smart Energy Research Laboratories, NEC Corporation, 1120 Shimokuzawa, Chuo-ku, Sagamihara 252-5298, Japan

HIGHLIGHTS

- TEP:FEC-based electrolyte enables the charge–discharge in a battery with a SiO anode.
- The electrolyte suppresses the exothermic reaction around 130 °C in a battery with a charged anode.
- The electrolyte enhances the safety of a lithium-ion battery.

ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form
8 September 2014
Accepted 11 September 2014
Available online 2 October 2014

Keywords:
Non-flammable
Electrolyte
Phosphate
Fluoroethylene carbonate
Safety

ABSTRACT

Applied in a battery with a silicon-oxide (SiO) anode, a non-flammable triethyl-phosphate (TEP)-based electrolyte with fluoroethylene carbonate (FEC) improved the safety and energy density of the battery. This TEP:FEC-based battery demonstrated almost the same performance, namely, capacity retention of 78% after 250 cycles, as that of a flammable electrolyte such as an ethylene carbonate (EC)/diethyle carbonate (DEC)-mixed electrolyte (79%). Moreover, this non-flammable electrolyte significantly enhanced the safety of the battery. This improved performance and safety is attributed to the disappearance of the exothermic peak around 120–160 °C derived from the reaction between the electrolyte and charged anode. Accordingly, this non-flammable (TEP)-based electrolyte can enhance the safety of lithium-ion batteries.

1. Introduction

Lithium-ion batteries with high energy density and capacity for powering electric vehicles and for large-scale energy storage have been widely developed [1]. Especially, silicon as an anode and nickel oxide or cobalt oxide as a cathode are attractive materials because batteries with these materials have high capacity [2–4]. However, these batteries present safety concerns in abnormal use. For that reason, special safety technology to safeguard such high-capacity lithium-ion batteries must be developed and implemented.

To make a battery safer, non-flammable solvents have been applied as electrolytes [5]. Among those solvents, phosphate is a promising candidate owing to its non-flammability [5–12]. However, a phosphate-based electrolyte decomposes reductively on the anode, where its decomposition product deposits [13,14]. This product disturbs the reaction between lithium ions and the anode, especially when graphite is used as an active material. Some solutions to resolve this problem, such as additives to form a film to suppress the phosphate decomposition, have been suggested [15–17]. Effective additives, however, have not yet been found.

Under the above-described circumstances, in the present study, TEP was selected as a phosphate because it has low viscosity and high solubility of lithium salt—which are desirable properties for a lithium-ion battery. Fluoroethylene carbonate (FEC) was found to be the most available additive for a TEP-based electrolyte in a cell with a SiO anode, even if TEP solvent was used as an electrolyte at high concentration. Moreover, to compare this TEP-based electrolyte with a conventional electrolyte, both were evaluated in safety tests on lithium-ion batteries.

2. Experimental

Performances of batteries with the TEP-based electrolyte and a conventional electrolyte were evaluated by using a pouch cell. All electrolytes (TEP/1-M $LiPF_6$, EC:DEC (3:7 by volume)/1-M $LiPF_6$) were purchased from Ube Industries, Ltd. FEC was purchased from

* Corresponding author. Tel.: +81 50 3757; fax: +81 42 1407.
E-mail address: k-inoue@dv.jp.nc.com (K. Inoue).

http://dx.doi.org/10.1016/j.jpowsour.2014.09.086
0378-7753/

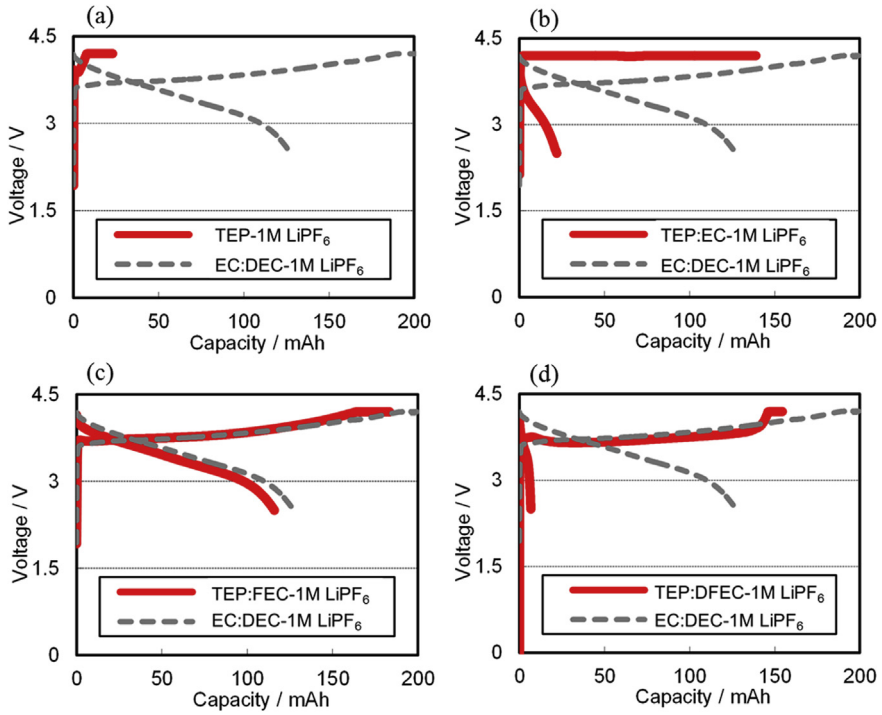

Fig. 1. First charge–discharge in TEP based electrolyte ((a)without additive and with (b) EC, (c) FEC, (d) DFEC) and EC:DEC based electrolyte.

Kishida Chemical Co., Ltd. Carbon-coated SiO powder (C–SiO) was prepared by CVD and used as an anode. C–SiO (85 wt%) and polyimide (15 wt%) were mixed in 1-methly-2-pyrrolidione (NMP). The slurry was coated on a copper foil. The cyclo-dehydration was converted to polyimide by heating at 350 °C under nitrogen atmosphere [3]. $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ was prepared as a cathode. $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (91 wt%) powder, carbon powder (5 wt%), and polyvinylidene fluoride (PVDF) (4 wt%) were mixed in NMP and coated on aluminum foil. The anode and cathode were cut into 8.4 cm^2 square sheets, which were separated by a polypropylene separator and covered by laminated sheets. The pouch cells were charged at constant current (30 mA) and constant voltage (4.2 V) for a total of 12 h. They were discharged at constant current (1.8 mA (0.1C)) up to 3.0 V. The cells were evaluated by cycle tests were at 18 mA (1C rate) (total charge time: 2.5 h) instead of 0.1C. First charge–discharge and cycle test were conducted at 25 °C.

To evaluate the safety of a battery with the TEP-based electrolyte and a conventional electrolyte, the battery was subjected to an

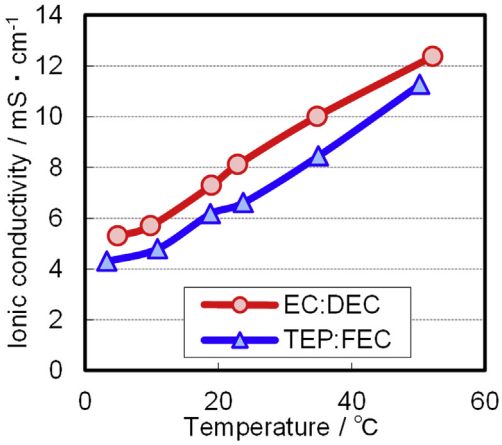

Fig. 3. Ionic conductivity in EC:DEC-based electrolyte and TEP-based electrolyte.

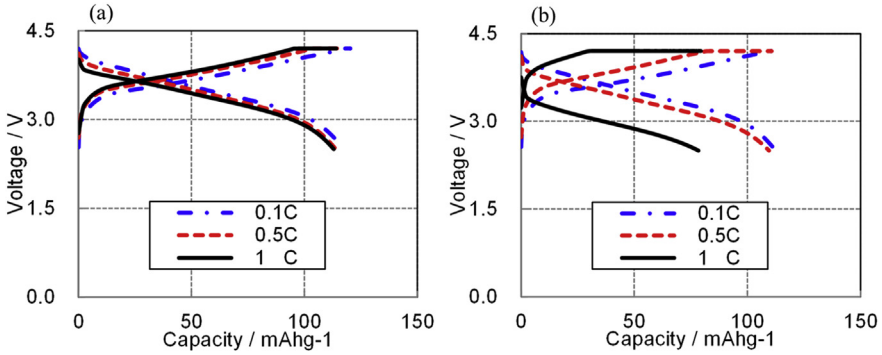

Fig. 2. First charge–discharge curve at different rate (0.1, 0.5 1C) in (a) EC:DEC-based electrolyte and (b)TEP-based electrolyte.