



Thermal and oxidation stability of organo-fluorine compound-mixed electrolyte solutions for lithium ion batteries



Daiki Nishikawa^a, Tsuyoshi Nakajima^{a,*}, Yoshimi Ohzawa^a, Meiten Koh^b, Akiyoshi Yamauchi^b, Michiru Kagawa^b, Hirokazu Aoyama^b

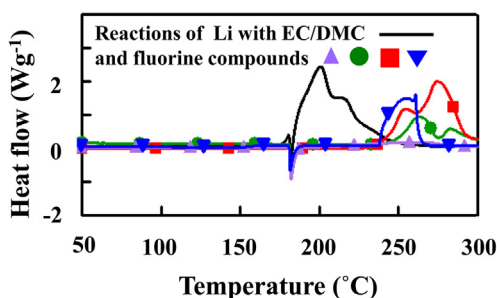
^a Department of Applied Chemistry, Aichi Institute of Technology, Yakusa, Toyota 470-0392, Japan

^b Daikin Industries, Ltd., Settsu 566-8585, Japan

HIGHLIGHTS

- Organo-fluorine compounds have much lower reactivity with Li than EC/DMC.
- Organo-fluorine compounds improve thermal stability of electrolyte solution.
- Fluorine compounds improve electrochemical oxidation stability of electrolyte solution.
- Organo-fluorine compounds increase first coulombic efficiencies in PC-containing solution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 March 2013

Received in revised form

7 May 2013

Accepted 7 June 2013

Available online 15 June 2013

Keywords:

Organo-fluorine compound

Thermal stability

Oxidation stability

Natural graphite electrode

Lithium ion battery

ABSTRACT

Thermal and oxidation stability of fluorine compound-mixed electrolyte solutions have been investigated. Charge/discharge behavior of natural graphite electrode has been also examined in the same electrolyte solutions. Fluorine compounds demonstrate much lower reactivity with metallic Li than ethylene carbonate/dimethyl carbonate. Fluorine compound-mixed electrolyte solutions show the lower reactivity with LiC₆ and the smaller exothermic peaks due to decomposition of electrolyte solutions and surface films than original solutions without fluorine compound. Oxidation currents are also smaller in fluorine compound-mixed electrolyte solutions than in original ones. First coulombic efficiencies in fluorine compound-mixed electrolyte solutions are similar to those in original ethylene carbonate-based solutions except one case. Mixing of fluorine compounds highly increase first coulombic efficiencies of natural graphite electrode in propylene carbonate-containing solution.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Lithium ion batteries with high rate charge and discharge are urgently requested for their application to hybrid cars and electric vehicles. However, lithium ion batteries have a possibility of firing and/or explosion at high temperatures, by short circuit formation,

by overcharging and so on since they use flammable organic solvents. The high safety is now one of the most important issues for the practical use of lithium ion batteries. High oxidation stability of organic solvents is particularly needed for the use of 5 V class cathodes. Several different type compounds have been examined to improve the oxidation stability of electrolyte solutions. Phosphorus compounds such as phosphates usually show good flame retardant properties [1–31]. Mixing of ionic liquids is also useful to increase the oxidation stability of electrolyte solutions [32–36]. In addition to these compounds, organo-fluorine compounds are new

* Corresponding author. Tel.: +81 565 488121; fax: +81 565 480076.

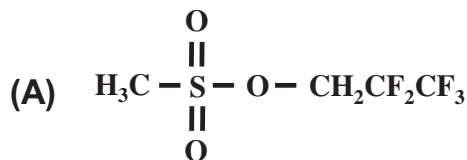
E-mail addresses: nakajima-san@aitech.ac.jp, hako@f5.dion.ne.jp (T. Nakajima).

candidates to improve thermal and oxidation stability of electrolyte solutions [37–47]. Fluorine substitution of organic compounds normally increases the stability against oxidation [41,42]. Partially fluorinated carbonates, ethers and esters have been studied because they are miscible with solvent mixtures consisting of cyclic and linear carbonates such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) [41–44]. Miscibility of highly fluorinated organic compounds with EC and PC having high dielectric constants is low. Furthermore highly fluorinated organic compounds reduce the solubility of inorganic electrolyte such as LiPF_6 . Therefore partially fluorinated carbonates, ethers and esters are preferable as new solvents with high oxidation stability. It was recently shown that fluorine-containing carbonates, ethers and esters improve thermal and oxidation stability of electrolyte solutions [37–47]. However, fluorine substitution of organic compounds simultaneously elevates their reduction potentials, i.e. organo-fluorine compounds are electrochemically reduced at the higher potentials than those for EC, PC, DMC and DEC [41,42,48,49]. It is therefore important to check charge/discharge behavior of graphite in low potential region in organo-fluorine compound-mixed electrolyte solutions. Among the examined fluorine compounds, many fluoro-carbonates and fluoro-ethers facilitate the formation of solid electrolyte interphase (SEI) on graphite electrode [41–44]. Additionally LiPF_6 contributes to the safety of lithium ion battery. LiF formed by the reaction of LiC_6 with PF_6^- deposits on graphite anode to facilitate SEI formation. LiPF_6 dissociates into LiF and PF_5 at around 100 °C, and LiF may deposit on graphite electrodes. Deposition of LiF on graphite would improve the safety of lithium ion battery because exothermic reactions of LiC_6 with SEI and organic solvents are highly suppressed in LiPF_6 -containing electrolyte solutions, compared with LiClO_4 -containing ones [44]. Deposition of both LiF and decomposed products of organo-fluorine compounds on graphite increases coulombic efficiency at 1st cycle [44]. In the present study, the effect of organo-fluorine compounds on the thermal and oxidation stability of electrolyte solutions and charge/discharge behavior of natural graphite electrode have been investigated to develop new nonflammable solvents for lithium ion batteries.

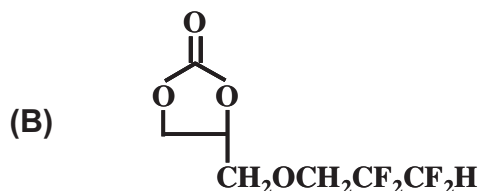
2. Experimental

2.1. Organo-fluorine compounds

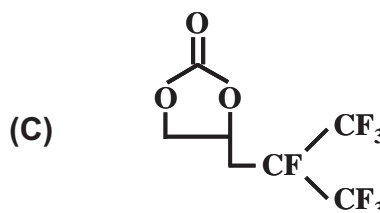
The following organo-fluorine compounds (purity: 99.9%, H_2O : <10 ppm), synthesized in Daikin Industries, Ltd., were used in the present study.



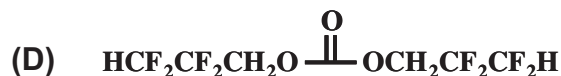
2,2,3,3,3-pentafluoropropyl methanesulfonate



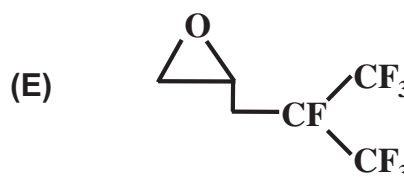
4-[(2,2,3,3,3-tetrafluoropropoxy)methyl]-[1,3]-dioxolan-2-one



4-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl]-[1,3]-dioxolan-2-one



Bis(2,2,3,3,3-tetrafluoropropyl) carbonate



2-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl]-1-oxirane.

Viscosities and specific conductivities of fluorine compounds, **B** and **D** are 4.79 and 0.80 cP at 20 °C, and 5.5×10^{-3} and $8.9 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature, respectively.

2.2. Thermal stability by differential scanning calorimetry (DSC)

Thermal stability of organo-fluorine compound-mixed electrolyte solutions was investigated by DSC (DSC-60, Shimadzu). DSC measurement was carried out using a mixture of electrolyte solution with or without fluorine compound and lithiated or delithiated graphite (NG15 μm) between room temperature and 300 °C at a temperature increasing rate of 5 °C min^{-1} . DSC measurements of only lithiated graphite without electrolyte solution, and reaction of metallic Li with EC/DMC (1:1 vol.) or fluorine compound **A**, **B**, **C** or **E** were also performed in the same manner. Fluorine compound-mixed electrolyte solutions used were 1 mol L^{-1} LiPF_6 -EC/DMC(**A**, **B**, **C** or **E**) (1:1:1 vol.) and 0.67 mol L^{-1} LiPF_6 -EC/DEC(**A**, **B**, **C** or **D**) (1:1:1 vol.). The 1 mol L^{-1} LiPF_6 -EC/DMC(**A**, **B**, **C** or **E**) was prepared by dissolving LiPF_6 into fluorine compound-mixed electrolyte solution. For EC/DEC mixture, 0.67 mol L^{-1} LiPF_6 solutions were used because it is difficult to prepare 1 mol L^{-1} LiPF_6 -EC/DEC(**D**) (1:1:1 vol.). Fully lithiated and delithiated graphite samples were electrochemically prepared by 2.5 and 3 cycles corresponding to Li-intercalated and -deintercalated states, respectively. Composition of Li-intercalated graphite samples was calculated from discharge capacity to be $\text{Li}_{0.88-0.98}\text{C}_6$. Lithiated and delithiated graphite samples used for DSC measurements were 1.4–1.6 mg. Electrolyte solution and metallic Li were 3 μL and 9.0–11.0 mg, respectively. To discuss about the reactivity of fluorine compounds with Li, C–O bond lengths were calculated by semi-empirical AM1 method using Spartan '06.

2.3. Electrochemical oxidation current measurements

Oxidation currents were measured by linear sweep of potential at 0.1 mV s^{-1} between 4 and 10 V vs Li/Li^+ for 1 mol L^{-1} LiPF_6 -EC/

Download English Version:

<https://daneshyari.com/en/article/7740609>

Download Persian Version:

<https://daneshyari.com/article/7740609>

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