Journal of Power Sources 274 (2015) 676–684

Contents lists available at ScienceDirect

Journal of Power Sources

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

A new co-solvent for wide temperature lithium ion battery electrolytes: 2,2,2-Trifluoroethyl n-caproate

Wei Lu [a,*], Kai Xie [a], Zhongxue Chen [a,b], Shizhao Xiong [a], Yi Pan [a], Chunman Zheng [a,*]

[a] College of Aerospace Science and Engineering, National University of Defense Technology, Changsha, Hunan 410073, PR China
[b] College of Chemistry and Chemical Engineering, Hunan University, Changsha, Hunan 410082, China

HIGHLIGHTS

- The wide operating temperature performances of these mixed electrolytes.
- The preferential solvation of Li^+ in EMC and TFENH mixed solvents.
- The possible mechanism of the SEI formation in different TFENH contents.

ARTICLE INFO

Article history:
Received 12 September 2014
Received in revised form
15 October 2014
Accepted 17 October 2014
Available online 22 October 2014

Keywords:
Lithium-ion batteries
Electrolyte
Co-solvent
Wide operating temperature

ABSTRACT

We develop a new co-solvent for wide temperature lithium ion battery electrolytes: 2,2,2-Trifluoroethyl N-caproate (TFENH) in this work and particularly investigate the effect of TFENH content on the electrochemical properties of the mixed electrolytes. The results show that the improved low and high temperature performances of $LiCoO_2$/graphite can be achieved if the volume ratio of TFENH co-solvent is kept between 17 and 25 Vol%. Carbon nuclear magnetic resonance spectroscopy (^{13}C NMR) indicate that TFENH co-solvent is prior to distribute in the bulk of electrolyte, which help to reduce the viscosity and enhance the ionic conductivity of the electrolyte at low temperature. Electrochemical impedance spectroscopy (EIS) show that few TFENH co-solvent incorporation is beneficial to decrease the resistance of SEI film. X-ray photoelectron spectroscopy (XPS) demonstrate that a thin and stable $CH_3(CH_2)_4COOLi$ film decomposed by TFENH is formed on the surface of graphite, which plays an crucial role in improving low temperature performance and cycling stability of lithium-ion batteries.

1. Introduction

In recent years, lithium-ion batteries have occupied most of the power supplies market in consumer electronics. To meet the active developments of EV and HEV markets, batteries tend to be required to operate over a wide temperature range (from 243 to 333 K). The requirement for wide temperature characteristics is even stricter for certain military and space applications (from 223 to 353 K) [1,2]. At present, ethylene carbonate (EC) and linear carbonates such as dimethyl, diethyl, and ethyl-methyl carbonates (DMC, DEC, EMC, respectively) are the main solvents of the commercial electrolytes for LIBs, where EC is a key component for the lithium salt dissociation and sufficient negative electrode passivation and linear carbonates could partly enhance the low temperature performances [3,4]. However, cells with carbonate-only electrolytes always show notable capacity fading and voltage decline when they work at extremely low temperatures (below 243 K), due to the poor ionic conductivity of electrolyte and low diffusion coefficient of lithium ions in the SEI layer [5].Furthermore, owing to the surface reaction of electrodes at elevated temperatures, the cell impedance may dramatically increases upon cycling and finally leads to low cycling stability [6,7]. Therefore, the operating temperature range of LIBs is severely restricted by the native property of the commercial electrolytes.

To achieve electrolytes with wide operating temperature, several strategies have been proposed, such as decreasing EC content and adding co-solvents with low melting point and high boiling point [3,8–11]. Linear carboxylates such as methyl propionate, methyl butyrate, ethyl butyrate have been reported as appropriate co-solvents for carbonate-based electrolytes which could obtain a better performance below 243 K and above 333 K [12]. During last few years, Jet Propulsion Laboratory (JPL) has developed a series of novel electrolytes with wide operating

---

* Corresponding authors. Tel.: +86 0731 84573149; fax: +86 0731 84576578.
E-mail addresses: taigold3rd@hotmail.com (W. Lu), zhengchunman@hotmail.com (C. Zheng).

http://dx.doi.org/10.1016/j.jpowsour.2014.10.112
0378-7753/© 2014 Elsevier B.V. All rights reserved.

temperature range for high energy lithium-ion batteries. According to M.C. Smart's report at 2013, low temperature performances of methyl propionate based electrolytes have been demonstrated in large capacity 12 Ah MCMB-$LiNiCoAlO_2$ cells. These cells could provide capacities above 10Ah at 2C rates down to 223 K, in which capacity retention is close to 85%. As another partner of JPL, A123 has developed new Carbon-$LiFePO_4$ cells using methyl butyrate based electrolytes which could be previously demonstrated to endure >11C discharge rates at 233 K, with over 90% of the room temperature capacity being delivered. M.C. Smart, etc. also claimed that fluorinated aliphatic carboxylate is one of the most promising candidates for low temperature co-solvents [13]. They tried to add four different fluorinated esters (trifluoroethyl butyrate, trifluoroethyl acetate, ethyl trifluoroacetate and methyl pentafluoropropionate) to carbonate-based electrolyte respectively. Results suggest that these fluorinated ester co-solvents are also beneficial to improve film forming properties and physical properties of the electrolytes. The MCMB-$LiNi_xCo_{1-x}O_2$ cell containing the electrolyte consisting of 1.0 M $LiPF_6$/EC + EMC + trifluoroethyl butyrate (20:60:20 vol) has the best performance of all the fluorinated ester containing mixtures.

Herein, we report a new co-solvent for wide temperature lithium-ion battery electrolytes: 2,2,2-trifluoroethyl n-caproate (noted as TFENH). The electrochemical properties of the mixed electrolytes with different TFENH contents are studied. Results show that TFENH co-solvent could improve the electrochemical performances of $LiCoO_2$/graphite cells over a wide operating temperature range. This positive effect of co-solvent on the electrochemical performance has also been investigated in detail. It indicates that the improvement is related to the thin and stable film formed on the surface of graphite by the decomposition of TFENH.

2. Experimental

TFENH co-solvent was synthesized as reported in our previous paper [14]. The water content of the co-solvent was measured using Karl-Fisher titration (831 KF Coulometer, Metrohm) and was certified less than 20 ppm. Binary carbonate-based electrolyte 1 mol L^{-1} $LiPF_6$/EC + EMC (volume ratio 1:4) supported by Novolyte Company was selected as the base-line electrolyte. Ternary electrolyte mixtures were prepared by adding TFENH co-solvent to the base-line electrolyte with the volume ratio of 1:10, 1:5, 1:3, 1:1 and 2:1, respectively. By adding $LiPF_6$ salt to the mixtures, the salt concentrations were maintained at 1 mol $L^{-1}$and the composition of these new electrolytes were approximately represented in Table 1.

Ionic conductivity of the electrolytes was measured by conductivity meter (RIDAO, DDS-307). The constant of conductivity electrode is 0.916, which was calibrated by 0.1 mol L^{-1} KCl solution before the experiment. Oxidation/reduction potential was measured by potential linear sweep method from 0 to 6.0 V (vs. Li^+/Li) with a scan speed of 0.1 mV·s^{-1} [15–17]. Glassy carbon (3 mm in diameter) was used as a working electrode, and lithium metal was used as a counter electrode and reference electrode. 1 mol L^{-1} Et_4NPF_6 was used as electrolyte solute. The potential linear sweep test was carried out by Versa STAT MC (Princeton).

Table 1
Short names and approximate composition of the electrolytes.

Electrolyte	TFENH: Base-line (vol)	Approximate composition (vol)
Electrolyte A	0	1 mol L^{-1} $LiPF_6$/EC + EMC (6:24)
Electrolyte B	1:10	1 mol L^{-1} $LiPF_6$/EC + EMC + TFENH (6:24:3)
Electrolyte C	1:5	1 mol L^{-1} $LiPF_6$/EC + EMC + TFENH (6:24:6)
Electrolyte D	1:3	1 mol L^{-1} $LiPF_6$/EC + EMC + TFENH (6:24:10)
Electrolyte E	1:1	1 mol L^{-1} $LiPF_6$/EC + EMC + TFENH (6:24:30)
Electrolyte F	2:1	1 mol L^{-1} $LiPF_6$ EC + EMC + TFENH (6:24:60)
Electrolyte G	∞	1 mol L^{-1} $LiPF_6$/TFENH

The graphite and $LiCoO_2$ electrodes were prepared by milling 80 wt. % active material, 10 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride (Kynar 741, Arkema Inc., USA) in N-methylpyrrolidone for 1 h. Synthetic graphitic flakes (AGP-8) were provided by BTR New Energy materials INC., and $LiCoO_2$ was supported by Jiangsu Cobalt Nickel Metal Co., LTD. Electrodes were dried at 110 °C for 12 h under vacuum conditions. Lithium foil (China Energy Lithium Co., Ltd, China) was used as counter-electrode in graphite/Lithium cells. A separator (Celgard 2320) was placed between the cathode and the anode. The CR2016 coin-type cells were assembled in a high purified argon-filled box. A multi-channel battery testing system (LAND CT2001-A) was used to test the charge/discharge performance at different temperature. Low temperature testing was carried out in cryostat circulation tank (YU HUA, DFY-80). Elevated temperature situation was provided by a thermo tank (KE WEI, 202-00).

EIS was carried out by Versa STAT MC (Princeton), using a three-electrode cell. Lithium metal was used as counter and reference electrode. Each cell was conducted after the formation process (after five cycles). Collecting frequency range was from 10^6 to 0.01 Hz with an applied ac voltage of 10 mV. The analysis of resultant Nyquist plots was performed by Zview software.

X-ray photoelectron spectroscopy was obtained by XPS system (ESCALAB 250Xi, Thermo Scientific, Al-K_α radiation), which operated under a base pressure of 10^{-9} Torr at a power of 72 W (12 kV). The de-lithiated graphite electrodes (1.5 V vs. Li^+/Li) were transferred into the XPS sample chamber by a vessel in argon atmosphere.

^{13}C NMR technique were used to study the preferential solvation of Li^+ in TFENH and EMC mixed solvents. More details about operating method could follow Ref. [18]. ^{13}C NMR spectra were observed by Fourier Transform nuclear magnetic resonance spectrometer (Bruker AVANCE 600).

3. Results and discussion

TFENH performs both lower freezing point (<197 K) and higher boiling point (423 K), which is possibly used as an effective co-solvent for wide operating temperature range [14]. Temperature dependence of the ionic conductivity of the electrolytes with different amounts of TFENH co-solvent is shown in Fig. 1, as we can see that the conductivities of all the seven electrolytes decrease with the temperature decreases. Carbonate-only electrolyte (Electrolyte A) showed the highest ionic conductivity above 233 K. Although modified electrolytes with low TFENH content (Electrolyte B, C and D) have slightly lower ionic conductivity than the carbonate-only electrolyte (Electrolyte A) when the temperature is above 233 K, the decay rate of their conductivities is also lower than that of Electrolyte A, so these three electrolytes show higher conductivities than that of Electrolyte A below 233 K. Moreover, the decay rate gradually decreases as the amount of TFENH in the mixed electrolyte increases, as a result, Electrolyte D displays the best low temperature performance, next is Electrolyte C, and least is Electrolyte B.

When the content of TFENH in the mixed electrolytes (Electrolyte E and F) was further increased, the decay rate of the conductivities greatly increased and phase separation occurred below 253 K, this might be attributed to the decreased TFENH solubility in carbonate solvents. For comparison, we also tested the conductivity of the electrolyte with only TFENH (Electrolyte G). The value is one