



Ethylene carbonate-free fluoroethylene carbonate-based electrolyte works better for freestanding Si-based composite paper anodes for Li-ion batteries

K. Yao^{a,b,c,*}, J.P. Zheng^{a,b,d,e}, R. Liang^{a,c,f}

^a Materials Science & Engineering, Florida State University, USA

^b Aero-propulsion, Mechatronics and Energy Center (AME), Florida State University, USA

^c High-Performance Materials Institute (HPMI), Florida State University, USA

^d Center for Advanced Power Systems (CAPS), Florida State University, USA

^e Department of Electrical & Computer Engineering, Florida A&M University-Florida State University College of Engineering, Tallahassee, FL 32310, USA

^f Department of Industrial and Manufacturing Engineering, Florida A&M University-Florida State University College of Engineering, Tallahassee, FL 32310, USA

HIGHLIGHTS

- Investigated electrolytes using fluoroethylene carbonate as co-solvent and additive.
- Optimized electrolyte composition capable of higher capacity and better cyclability.
- Proposed a new possible reaction mechanism of fluoroethylene carbonate.

ARTICLE INFO

Keywords:

Li-ion battery

Si anode

Ethylene carbonate-free

Fluoroethylene carbonate electrolyte

ABSTRACT

Fluoroethylene carbonate (FEC)-based electrolytes using FEC as the co-solvent (50 wt%) are investigated and compared with the electrolyte using FEC as the additive (10 wt%) for freestanding Si-carbon nanotubes (CNTs) composite paper anodes for Li-ion batteries. The ethylene carbonate (EC)-free FEC-based electrolyte is found to achieve higher specific capacity and better capacity retention in terms of long-term cycling. After 500 cycles, the capacity retention of the cell using diethyl carbonate (DEC)-FEC (1:1 w/w) is increased by 88% and 60% compared to the cells using EC-DEC-FEC (45:45:10 w/w/w) and EC-FEC (1:1 w/w), respectively. Through SEM-EDX and XPS analyses, a possible reaction route of formation of fluorinated semicarbonates and polyolefins from FEC is proposed. The inferior cell performance related to the EC-containing electrolytes is likely due to the formation of more polyolefins, which do not favor Li ion migration.

1. Introduction

While the role of fluoroethylene carbonate (FEC) as the electrolyte additive at low concentrations (typically 10% or lower) has been intensively investigated [1–10], only a few studies have examined its role as the electrolyte co-solvent where conventional solvent, such as ethylene carbonate (EC), was totally replaced by FEC [11,12]. For example, Nakai et al. [12] investigated the solid-electrolyte interphase (SEI) derived from EC-based (EC:diethyl carbonate (DEC) 1:1, v/v) and FEC-based (FEC:DEC 1:1, v/v) electrolytes on 2 μm thick Si thin film electrodes. Lin et al. [11] compared the performance of Si nanoparticle (SiNP) anodes in three electrolytes: 50% FEC-50% dimethyl carbonate (DMC), 50% EC-50% DMC, and 25% FEC-25% EC-50% DMC. Meanwhile, the optimal concentration of FEC remains a controversy. Lin et al. [11] showed that the SiNP electrode achieved better specific

capacity, capacity retention, and coulombic efficiency in 50% FEC-50% DMC than in 25% FEC-25% EC-50% DMC, and suggested that the more FEC present (up to 50%) in the electrolyte, the better the cycling performance. However, in the study by Nguyen et al. [5] involving different FEC concentrations (5–25 wt%) in the electrolytes, they found that the cells prepared with electrolyte containing 10–15% FEC had the highest specific capacity, best capacity retention, and smallest impedance.

The lack of FEC co-solvent study and the contradictory results regarding the optimal FEC concentration found in literature were the motivations for this study. Herein, we report our work comparing electrolyte containing FEC as the additive (10 wt%) with two other electrolytes using FEC as the co-solvent (50 wt%) for freestanding Si-carbon nanotubes (CNTs) composite paper anodes for Li-ion batteries. The specific electrolyte compositions investigated are: 1 M LiPF₆ in

* Corresponding author. Materials Science & Engineering, Florida State University, USA.
E-mail address: ky12@my.fsu.edu (K. Yao).

EC:DEC:FEC at a weight ratio of 45:45:10, 1 M LiPF₆ in EC:FEC at a weight ratio of 1:1, and 1 M LiPF₆ in DEC:FEC at a weight ratio of 1:1. These three electrolytes are denoted as FEC 10%, EC-FEC, and DEC-FEC, respectively. The EC-free FEC-based electrolyte (DEC-FEC) is found to achieve higher specific capacity and better capacity retention in terms of long-term cycling. After 500 cycles, the capacity retention of the cell using DEC-FEC is increased by 88% and 60% compared to the cells using FEC 10% and EC-FEC, respectively. Post-cycling SEM-EDX and XPS results are discussed, which reveal a possible reaction route of formation of fluorinated semicarbonates and polyolefins from FEC.

2. Experimental

2.1. Electrode and coin cell fabrication

The bind-free freestanding composite electrodes were prepared from commercial SiNPs and multi-walled CNTs (MWCNTs) by ultrasonication and positive pressure filtration. The raw materials and detailed preparation of the SiNPs-MWCNTs (Si-MW) composite paper were reported elsewhere [13]. Briefly, SiNPs and MWCNTs at a mass ratio of 3:2 were dispersed in 1 vol% deionized (DI) water solution of Triton X-100 surfactant through ultrasonic agitation using a probe sonicator. A filtration process under positive pressure on the resultant dispersion was conducted using a 0.4 μm pore size polycarbonate (PC) membrane. During filtration, the MWCNTs and SiNPs were deposited onto the membrane surface to generate a dark green composite thin film. Upon natural drying overnight, the thin film could be peeled off from the PC membrane, creating a freestanding Si-MW composite paper. To remove the residual surfactant, the composite paper was washed with DI water, isopropyl alcohol (IPA) and DI water sequentially, followed by heat treatment at 500 °C in a nitrogen gas atmosphere for 1 h. Prior to cell assembly, the freestanding composite paper was cut into circular electrode sheets using a half-inch punch and dried at 120 °C in vacuum overnight to make a working electrode without any additives or Cu current collector. The obtained half-inch electrode has a thickness of ~40 μm and an areal mass loading of ~3 mg cm⁻² [13,14]. CR2032-type coin cells using the FEC 10%, EC-FEC, and DEC-FEC electrolytes were constructed in a glovebox filled with argon gas for battery performance tests. A Li metal foil was used as the reference and counter electrode, and a glass fiber separator (EL-CELL) was placed in between the electrodes.

2.2. Characterization

The electrolyte conductivities were measured using an Oakton CON 6 + Handheld Conductivity Meter. The microstructural image analysis was conducted with a JEOL JSM-7401F Field Emission Scanning Electron Microscope (FE-SEM). The elemental composition of the prepared composite was examined quantitatively by energy-dispersive X-ray spectroscopy (EDX) integrated with the SEM. X-ray photoelectron spectroscopy (XPS) was carried out using a Physical Electronics (PHI) 5100 series spectrometer with nonmonochromated Mg Kα radiation of 1253.6 eV.

The galvanostatic charge-discharge cycling performance was tested using MTI Battery Analyzer systems. Cyclic Voltammetry (CV) was conducted from 2 to 0.005 V vs. Li/Li⁺ at a scan rate of 0.1 mV s⁻¹ using Gamry Instruments. Electrochemical Impedance Spectroscopy (EIS) was performed at an AC voltage amplitude of 10 mV in a frequency range of 0.1–10⁶ Hz using Gamry Instruments on the cells before (2.8 V vs. Li/Li⁺) and after cycling (0.5 V vs. Li/Li⁺). All the specific capacity values are based on the total weight of SiNPs and MWCNTs in the electrode.

For post-cycling analyses, the cells were opened in the glovebox, where the electrodes were extracted from the cells and carefully rinsed with DMC, and then dried overnight at 70 °C on a hotplate. The electrode samples were transferred from the glovebox to the analytical

Table 1
Conductivities of three electrolytes: FEC 10%, EC-FEC, and DEC-FEC.

Electrolyte	Conductivity (mS cm ⁻¹)
1 M LiPF ₆ in EC:DEC:FEC 45:45:10 by weight (FEC 10%)	7.83
1 M LiPF ₆ in EC:FEC 1:1 by weight (EC-FEC)	6.59
1 M LiPF ₆ in DEC:FEC 1:1 by weight (DEC-FEC)	7.34

instruments using a tightly closed container to avoid exposure to the air.

3. Results and discussion

3.1. Electrical and electrochemical properties

The electrolyte conductivities were measured using an Oakton CON 6 + Handheld Conductivity Meter and the results are listed in Table 1. All three electrolyte solutions show good conductivity values yet with minor differences. The conductivity is the highest for the FEC 10% electrolyte (7.83 mS cm⁻¹), decreases slightly for the DEC-FEC (7.34 mS cm⁻¹), and is the lowest for the EC-FEC (6.59 mS cm⁻¹).

The Si-MW composite electrodes were assembled into CR2032-type coin cells using these different electrolytes and subjected to long-term discharge-charge in a voltage range of 1–0.005 V vs. Li/Li⁺ under a constant current of 1 mA (280 mA g⁻¹) for 500 cycles. Table 2 provides the first cycle specific capacities and coulombic efficiency of the Si-MW cells using different electrolytes. After totally replacing EC with FEC, the discharge (lithiation)/charge (delithiation) capacity decreases from 2673/1736 mAh g⁻¹ for FEC 10% to 2429/1598 mAh g⁻¹ for DEC-FEC and the coulombic efficiency increases slightly from 65% to 66%. However, the cell with EC-FEC shows the lowest discharge/charge capacity (2043/1199 mAh g⁻¹) and efficiency (59%), which indicate it must have undergone more SEI reactions upon initial cycling. Considering that the only difference between EC-FEC and DEC-FEC electrolytes is the solvent, the lower capacity and efficiency may be attributed to the EC solvent. However, one may argue that the EC-containing FEC 10% electrolyte shows the highest initial capacity, which appears to contradict our preliminary hypothesis. This is probably because, unlike EC-FEC, the FEC 10% contains a combination of EC and DEC. These two solvents have different initial reactions and consequently produce different SEI layers, leading to distinct charge-discharge performance of the cells. This will be discussed further in the following sections.

The specific capacities and charge capacity retention vs. cycle number of Si-MW cells using FEC 10%, EC-FEC, and DEC-FEC electrolytes are plotted in Fig. 1a and b. The corresponding insets show close-ups of the first 140 cycles. In Fig. 1a, the cell with EC-FEC shows the lowest capacities throughout the 500 cycles. The specific capacities of the cell with DEC-FEC gradually surpass those of the cell with FEC 10% after around 40 cycles and remain the highest for the remaining cycles. Surprisingly, Fig. 1b shows that at the beginning of the cycles, the cell with EC-FEC has the highest capacity retention, while the other two exhibit lower and comparable capacity retention. Since the EC-FEC cell has the most SEI formation on the first cycle, the amount of Si

Table 2
Specific capacities and coulombic efficiency of Si-MW electrodes in three different electrolytes at first cycle.

Electrolyte	Discharge capacity (mAh g ⁻¹)	Charge capacity (mAh g ⁻¹)	Coulombic efficiency (%)
FEC 10%	2673	1736	65
EC-FEC	2043	1199	59
DEC-FEC	2429	1598	66

Download English Version:

<https://daneshyari.com/en/article/7725552>

Download Persian Version:

<https://daneshyari.com/article/7725552>

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