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

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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

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 LiPF$_6$ in

EC:DEC:FEC at a weight ratio of 45:45:10, 1 M $LiPF_6$ in EC:FEC at a weight ratio of 1:1, and 1 M $LiPF_6$ 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 0.1–10^6 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.

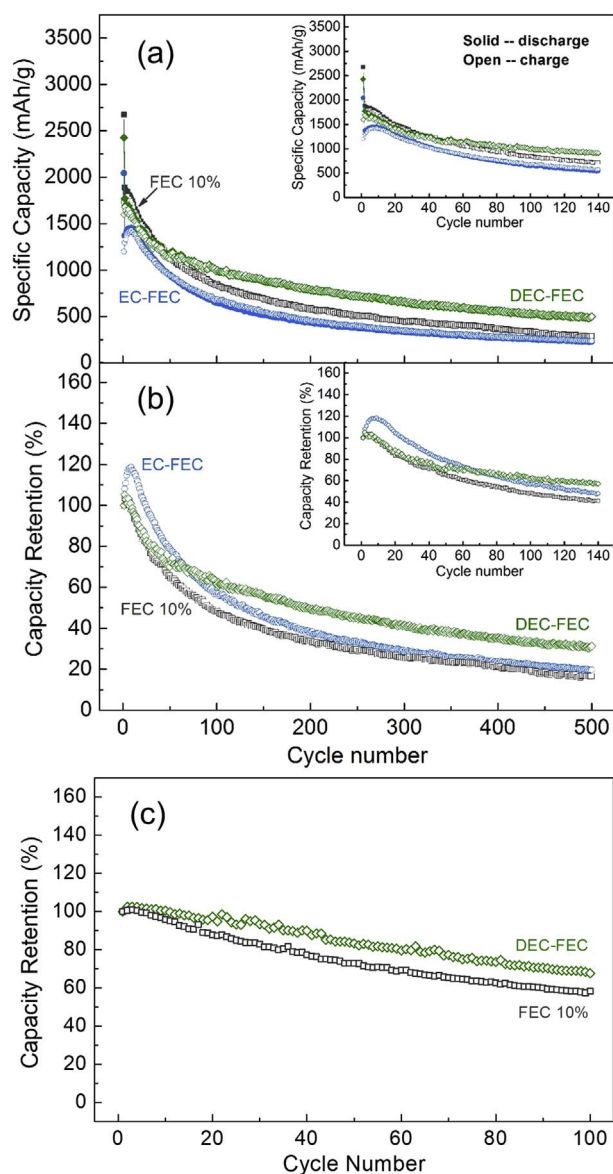| Electrolyte	Discharge capacity (mAh g^{-1})	Charge capacity (mAh g^{-1})	Coulombic efficiency (%)
FEC 10%	2673	1736	65
EC-FEC	2043	1199	59
DEC-FEC	2429	1598	66

Fig. 1. (a) Specific capacities and (b) charge capacity retention vs. cycle number of Si-MW cells using FEC 10%, EC-FEC, and DEC-FEC at 280 mA g^{-1}. Insets show first 140 cycles. (c) Capacity retention of Si-MW cells using FEC 10% and DEC-FEC at 100 mA g^{-1}.

Fig. 2. Nyquist plots of Si-MW cells using FEC 10%, EC-FEC, and DEC-FEC electrolytes (a) before and (b) after 500 cycles.

accessible is low; but meanwhile, the amount of Si available to become activated upon the following cycles can be higher. This can explain why the capacity increase for the EC-FEC cell at the beginning of cycling is more pronounced and lasts longer (Fig. 1a). As a result, the cell has a higher capacity retention. But after around 65 cycles, the capacity retention of the cell with DEC-FEC exceeds those of the other two and remains the highest for the remainder of the cycles. After 500 cycles, the capacity retentions are 17%, 20%, and 32% for the cells using FEC 10%, EC-FEC, and DEC-FEC, respectively. Although the capacity retention is still low, it is improved by 88% for the cell with DEC-FEC compared to the cell with FEC 10%. Etacheri et al. [3] investigated the performance and surface chemistry of Si nanowire (SiNW) electrodes in EC-DMC (1:1 w/w), EC-DMC (1:1) containing 10% of FEC, and DMC containing 10% of FEC. The cell with DMC-FEC was found to have higher capacity, better cycle life, and lower polarization and impedance. However, they seemed to focus on comparing FEC-containing and FEC-free electrolyte solutions, but did not explain why between the two FEC-containing solutions, EC-DMC-FEC and DMC-FEC, the SiNW electrode performed better in DMC-FEC. Our findings that during the
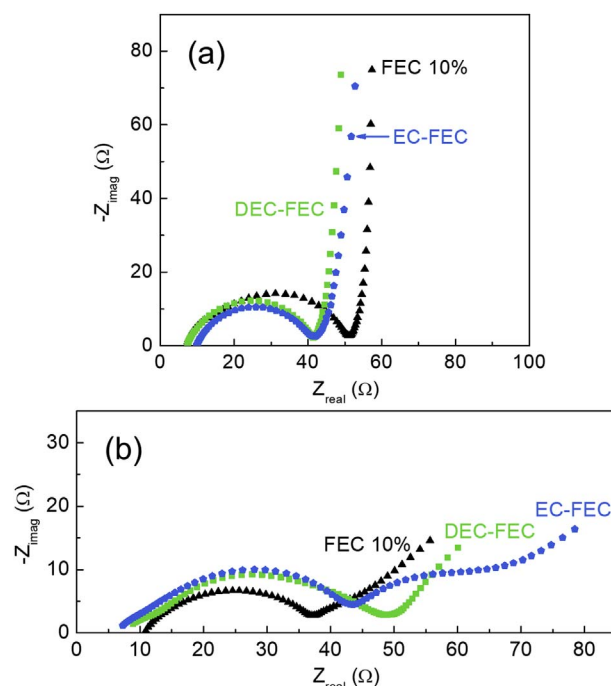
long-term cycling, the cell using DEC-FEC, which is the only electrolyte free of EC under investigation, exhibits higher capacity and better cyclability agree with their observations.

Fig. 1c shows the reversible capacity retention of Si-MW cells using FEC 10% and DEC-FEC electrolytes when cycled in a voltage range of 1–0.005 V vs. Li/Li$^+$ at a lower current rate of 100 mA g^{-1}. Better cyclability is achieved at lower current rate. The cell using DEC-FEC is able to deliver a reversible capacity of around 1300 mAh g^{-1} (70% retention) after 100 cycles and shows a higher capacity retention than that using FEC 10% for the entire testing period.

EIS on the fresh and cycled cells using different electrolytes was conducted in a frequency range of 0.1–10^6 Hz. Fig. 2 shows the resulting Nyquist plots. Overall, the EIS spectra before and after cycling display features including high to medium frequency semicircles associated with SEI layer and charge transfer resistance and low frequency slope lines associated with Warburg diffusion resistance. For the fresh cells, after increasing the FEC concentration from 10% to 50%, the total resistances decrease, but the difference is not large. After 500 cycles, the total resistances from the semicircles do not change appreciably and are still in the same value range. The cell with EC-FEC has a slightly longer tail compared to the other two, indicative of higher Li$^+$ diffusion resistance and slower Li$^+$ movement, which may have contributed to the lower capacity. It is noticed that the diameter of the semicircle of the cycled FEC 10% cell is the smallest, but its capacity retention is inferior to that of the DEC-FEC cell. This can be explained as follows. First, the total resistances developed are of the same order of magnitude and the difference is not large. The higher long-term capacity of the DEC-FEC cell corresponds to longer cycling time, which may contribute to the slightly higher resistance. In this case, it is therefore hard to directly associate higher resistance with poorer capacity retention. Second, there are other factors affecting the capacity retention, especially the composition and thickness of the SEI layer, which will be discussed in detail later.

3.2. SEM-EDX and XPS on electrodes cycled in different electrolytes

Because the chemistry of surface films developed during cycling is vital to understanding the different electrochemical behaviors, the
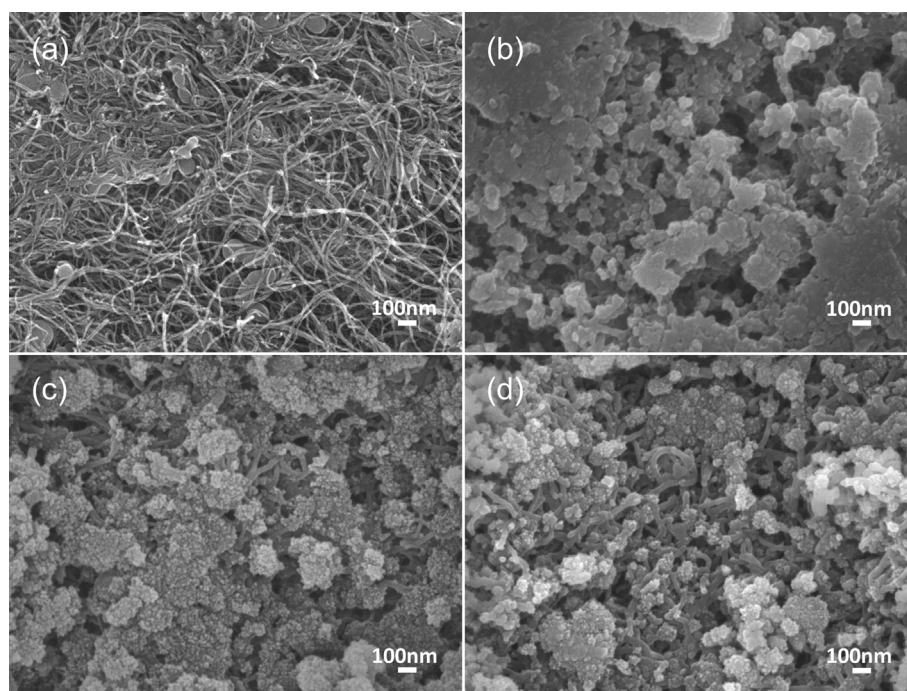
Fig. 3. SEM images of Si-MW electrodes (a) in pristine state and after 500 cycles in different electrolytes: (b) FEC 10%, (c) EC-FEC, and (d) DEC-FEC.
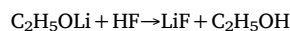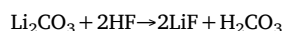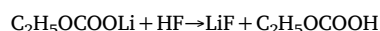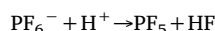
surface morphology and elemental composition of the Si-MW electrodes after cycling tests were examined by SEM-EDX and XPS.

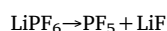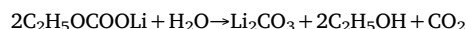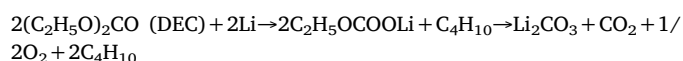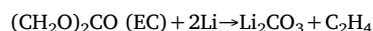Fig. 3 shows SEM images of Si-MW electrodes in a pristine state and after 500 cycles in different electrolytes: FEC 10%, EC-FEC, and DEC-FEC. As expected, formed SEI layer can be seen from all the cycled electrodes, since long-term cycling leads to the growth of large amount of SEI. After cycling, expansion of SiNPs and thickening of CNTs can be clearly observed compared to the pristine electrode. However, while the electrode cycled in FEC 10% (Fig. 3b) is heavily covered with blocks of deposited substance and the CNTs are buried and can hardly be seen, those cycled in EC-FEC (Fig. 3c) and DEC-FEC (Fig. 3d) display more of an amorphous flower-like structure with CNTs clearly visible. In particular, the DEC-FEC electrode shows the least severe SEI formation among the three, which agrees with its best electrochemical cycling performance.

In EDX analysis, peaks ascribed to carbon (C), oxygen (O), fluorine (F), silicon (Si), and phosphorus (P) species are detected. Table 3 lists the obtained elemental compositions at the surface of Si-MW electrodes after 500 cycles in FEC 10%, EC-FEC, and DEC-FEC electrolyte solutions. After increasing the FEC concentration from 10% to 50%, a clear decrease in the O species concentration and a slight increase in the Si species concentration occur. Since O species are often attributed to lithium carbonate (Li_2CO_3) and lithium alkyl carbonate (semicarbonate, ROCOOLi) compounds contained in the SEI layer, we may anticipate the surface films derived from FEC-based electrolytes would include a lower quantity of carbonates. This will be discussed later in more detail in the XPS analysis. On the other hand, since the content of Si at the electrode surface reflects the thickness of SEI [12], the EDX results are indicative of thinner SEI from FEC-based electrolytes. It can be

concluded that the different results of the cycling performance should have been influenced by the various SEI layer properties.

Many studies have been devoted to investigating the SEI formation on Si electrodes with FEC electrolyte additive by XPS [1–3,5,7,9,12]. Other than species unique to Si-containing electrodes, such as silicon oxide and silicate [3], fluorinated silicon [2,7], and lithium silicon oxide (Li_xSiO_y) [7], it is generally agreed that there are species commonly known to the SEI of graphite electrodes. For the traditional $LiPF_6$/EC-DEC electrolyte, the solvents and salt undergo the following reactions [3,15,16]:

$(CH_2O)_2CO$ (EC) $+ 2Li \rightarrow Li_2CO_3 + C_2H_4$

$2(CH_2O)_2CO$ (EC) $+ 2Li \rightarrow (CH_2OCOOLi)_2 + C_2H_4 \rightarrow Li_2CO_3 + CO_2 + 1/2O_2 + 2C_2H_4$

$(C_2H_5O)_2CO$ (DEC) $+ Li \rightarrow C_2H_5OCOOLi + C_2H_5^{\bullet}$ and $C_2H_5OLi + C_2H_5COO^{\bullet}$

$2(C_2H_5O)_2CO$ (DEC) $+ 2Li \rightarrow 2C_2H_5OCOOLi + C_4H_{10} \rightarrow Li_2CO_3 + CO_2 + 1/2O_2 + 2C_4H_{10}$

$2C_2H_5OCOOLi + H_2O \rightarrow Li_2CO_3 + 2C_2H_5OH + CO_2$

$LiPF_6 \rightarrow PF_5 + LiF$

$PF_5 + H_2O \rightarrow PF_3O + 2HF$

$PF_6^- + H^+ \rightarrow PF_5 + HF$

$C_2H_5OCOOLi + HF \rightarrow LiF + C_2H_5OCOOH$

$Li_2CO_3 + 2HF \rightarrow 2LiF + H_2CO_3$

$C_2H_5OLi + HF \rightarrow LiF + C_2H_5OH$

For EC solvent, the formation of polyolefins $(CH_2)_n$ via anionic polymerization of $CH_2 = CH_2$ was also suggested [15,17], although not mentioned in the published XPS studies discussed above. On the other hand, the fundamental mechanisms behind FEC's effectiveness in improving the electrochemical performance of Si electrodes remain controversial in the literature. Etacheri et al. [3] suggested a possible reaction pattern where FEC undergoes elimination of HF and the resultant VC polymerizes to form polycarbonate species. Nakai et al. [12] concluded that FEC-derived SEI consists of LiF and a polyene-compound,

Table 3
Chemical compositions at the surface of Si-MW electrodes after 500 cycles in FEC 10%, EC-FEC, and DEC-FEC electrolyte solutions by EDX.

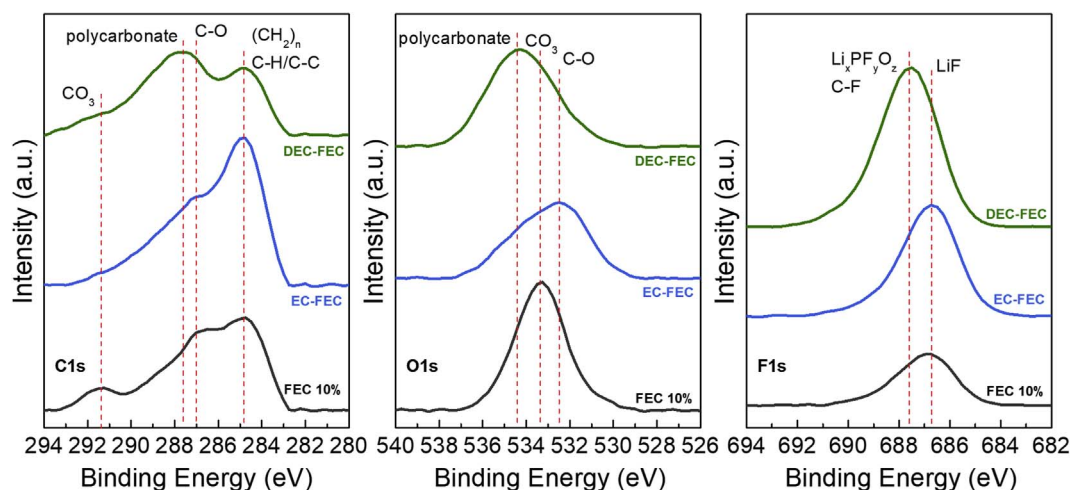| Electrolyte	C (wt%)	O (wt%)	F (wt%)	Si (wt%)	P (wt%)
FEC10%	28.29	31.06	22.25	14.10	4.30
EC-FEC	37.17	24.28	19.69	16.13	2.72
DEC-FEC	30.15	25.79	22.86	14.62	6.58

Fig. 4. C 1s, O 1s, and F 1s XPS spectra of surface films formed on Si-MW electrodes after 500 cycles in FEC 10%, EC-FEC, and DEC-FEC electrolyte solutions.

which are originated from free fluoride and acetylene units due to the preferential reaction of FEC. Nguyen et al. [5] proposed that the reduction of electrolyte containing FEC forms a stable SEI consisting of poly(FEC), LiF, Li_2CO_3, and ROCOOLi. Wang et al. [8] speculated that FEC is reduced through breaking up of its five-membered ring to form a $(CH_2CHFOCOOLi)_2$ dimer. Chen et al. [1] proposed an alternative decomposition mechanism where FEC is reduced through the opening of the five-membered ring leading to the formation of lithium poly(vinyl carbonate), LiF, and some dimers and the lithium poly(vinyl carbonate) enhances the stability of the SEI film. Xu et al. [9] presented a similar FEC decomposition mechanism involving defluorination and ring opening to form products of mainly LiF and $-CHF-OCO_2$-type compounds [9].

In our case, the C 1s, O 1s, and F 1s XPS spectra and chemical compositions at the surface of Si-MW electrodes after 500 cycles in FEC 10%, EC-FEC, and DEC-FEC electrolyte solutions are given in Fig. 4 and Table 4, respectively. The C 1s spectrum of the electrode cycled in FEC 10% contains a broad peak around 291 eV, which corresponds to carbonate groups in Li_2CO_3 and organic carbonates [3,5]. This peak is not pronounced for the electrode cycled in EC-FEC and is hardly noticeable for that cycled in DEC-FEC, which suggests the different compositions of SEI formed from FEC-based electrolytes. It also agrees with our previous assumption based on the EDX results that the FEC-derived SEI may contain less carbonates. The C 1s spectrum for FEC 10% exhibits another two peaks around 287 eV typical of $C-O$ bonds (lithium alkoxide, ether and alkoxy carbon) and 285 eV corresponding to polyolefins and hydrocarbon groups [3,5,15]. These two peaks are also observed in the C 1s spectra for EC-FEC and DEC-FEC. However, the weights of the peaks differ in the three spectra. The FEC 10% spectrum indicates a slightly higher quantity of polyolefins and alkyl carbon (285 eV) than the $C-O$ carbon in semicarbonates and alkoxides (287 eV). The EC-DEC spectrum shows a much stronger peak at 285 eV than that at 287 eV. In contrast, the DEC-DEC spectrum displays a stronger peak at the higher binding energy with the center shifted to around 287.7 eV, which can be assigned to polycarbonate compounds [3,10] produced by the following reactions (Scheme 1), where FEC

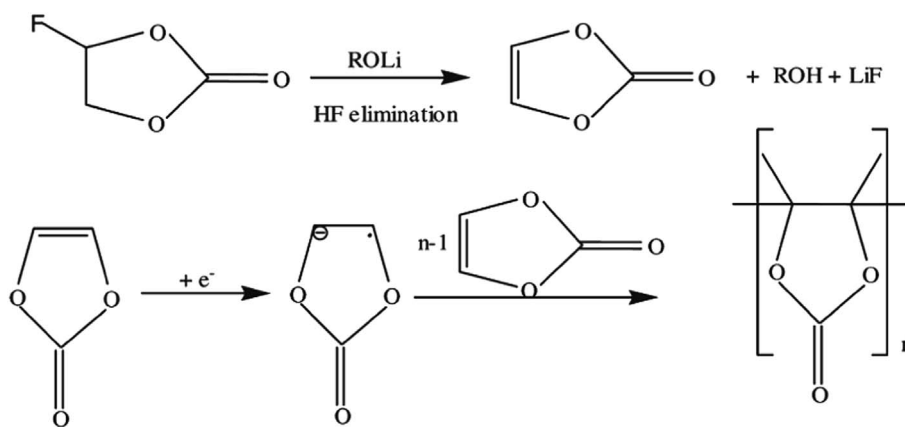undergoes the elimination of HF which forms VC that polymerizes via its double bond:

The O 1s spectra related to FEC 10%, EC-FEC, and DEC-FEC solutions differ from each other and show peaks centered around 533.3, 532.5, and 534.4 eV, respectively. These peaks can be attributed to carbonate groups, $C-O$ bonds, and polycarbonates, respectively [3,5,10], which are in agreement with our discussions from the C 1s spectra. The features of the F 1s spectra all include notable LiF peak at around 687 eV [1–3,5,12]. The center of the peak related to DEC-FEC electrolyte shifts slightly up to 687.6 eV, which may stem from a combination of LiF and $Li_xPF_yO_z$ [5]. This can be attributed to a more pronounced reduction of PF_6^- species in the absence of the highly reactive EC component [3]. The intensities of the peaks in the F 1s spectra suggest that F-rich surface films are developed in the FEC-based electrolytes with DEC-FEC-related SEI having the highest F concentration and the surface film derived from the FEC 10% solution contains less F species. This is reflected in the elemental compositions shown in Table 4. The XPS analysis in Table 4 shows that the surface films of the FEC-based electrolytes contain higher concentrations of F but lower concentrations of O, in contrast to the SEI of the FEC 10% electrolyte. These results are consistent with the EDX analysis in that the FEC 10%-derived SEI has a higher O species concentration, as shown in Table 3. However, for the FEC-based electrolytes, the EDX data in Table 3 does not show increased F species concentration, nor does the XPS data in Table 4 show increased Si concentration. This is because XPS is exceedingly surface sensitive – to less than a few nm, while such technique as EDX commonly yields signals averaging over depths of 1–2 μm. It is likely that the F species are more concentrated on the top surface, while the Si species are buried underneath.

According to the previously discussed electrolyte reactions, the main SEI products of EC comprise Li_2CO_3, $(CH_2OCOOLi)_2$, LiF, and polyolefins, while the main SEI products of DEC are composed of Li_2CO_3, $C_2H_5OCOOLi$, C_2H_5OLi, and LiF. The major difference between the two is the polymer species generated by EC. Therefore, considering the distinctly different C 1s spectra, it is reasonable to assign the peak at 285 eV to polyolefins, even though none of the referenced FEC studies mentioned this possibility. The combined C 1s and O 1s spectra indicate that the surface film from the electrolyte with FEC as additive (10 wt%) mainly consists of carbonates, semicarbonates, alkoxides, polyolefins, and hydrocarbon species, whereas in the FEC-based solutions the surface films feature less of the carbonate species. This is because FEC has a higher reduction potential than other carbonate solvents and is reduced prior to EC and DEC [1]. In the electrolytes with 50 wt% of FEC, its suppression effect is more pronounced. Moreover, the different relative quantities of the peaks at 285 and 287 eV in the C 1s spectra imply that the presence of FEC suppresses the reactions of DEC more
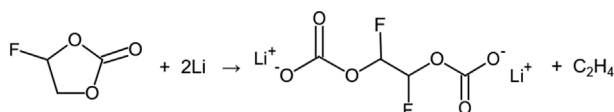
Table 4
Chemical compositions at the surface of Si-MW electrodes after 500 cycles in FEC 10%, EC-FEC, and DEC-FEC electrolyte solutions by XPS.

Electrolyte	C (at%)	O (at%)	F (at%)	Si (at%)	P (at%)
FEC10%	46.40	35.82	16.72	0.50	0.56
EC-FEC	48.28	22.71	27.08	1.29	0.65
DEC-FEC	34.10	24.07	39.90	0.36	1.58

Scheme 1. Possible reaction pattern of FEC suggested by Aurbach group [3].

Scheme 2. A new possible route of reaction for FEC.

than those of EC. The surface film from EC-FEC is rich in polyolefins and alkoxy species, whereas that from DEC-FEC also contains polyolefins but with a higher quantity of polycarbonates. Since the DEC-FEC solution is free of EC, the polyolefins should have been formed from FEC having a similar cyclic structure to EC. Therefore, besides the polymerization reaction which forms polycarbonate, we propose another possible route of reaction for FEC as follows: where the active CH_2 radicals undergo polymerization reaction to generate polyolefins (Scheme 2). The formation of the fluorinated semicarbonate is supported by the F 1s spectrum in the case of DEC-FEC, since its peak center at a higher binding energy compared to FEC 10% and EC-DEC can be associated with a $C-F$ environment [1,3,9].

In FEC 10% with a lower FEC concentration, the reactions of the traditional solvents are inhibited by FEC only to a certain extent, thus

products related to the decomposition of EC and DEC are detected, and the SEI is found to be of an O-rich type. In the FEC-based electrolytes, the large amount of FEC suppresses the EC and DEC reduction, which is revealed by the absence of obvious carbonate peaks in the C 1s spectra for EC-FEC and DEC-FEC, and the SEIs are found to be of a F-rich type. However, in EC-FEC the two solvents are likely to compete, whereas in DEC-FEC the FEC-generated products are more dominant. The FEC solvent demonstrates two possible reaction routes: the Scheme 1 as suggested in literature [3] which produces LiF plus polycarbonate, and the newly proposed Scheme 2 which produces $(CHFOCOOLi)_2$ plus polyolefins.

3.3. CV curves from cells using different electrolytes

The above conclusions are supported by CV results of the cells using FEC 10%, EC-FEC, and DEC-FEC electrolyte solutions as shown in Fig. 5. The CV plots of the cell using FEC-free 1M $LiPF_6$/EC-DEC (1:1 w/w) electrolyte are also provided for discussions. All the CV curves in the first cycle show peaks due to irreversible SEI formation in the cathodic branches, which disappear in the following cycles. Comparing the first cathodic reactions from CV of FEC-free and FEC 10% solutions, it is
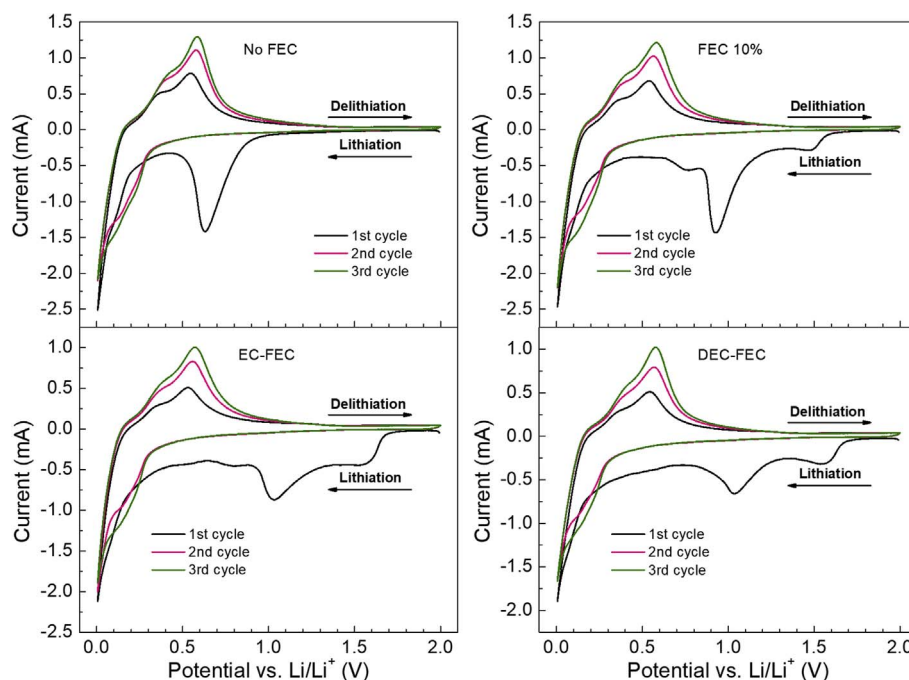

Fig. 5. Initial three cyclic voltammograms at 0.1 mV s^{-1} of Si-MW electrodes in FEC-free, FEC 10%, EC-FEC, and DEC-FEC electrolyte solutions.

clear to see that with higher reduction potentials, FEC degrades prior to EC/DEC, since EC/DEC reduction starts at a lower potential, ~ 0.8 V vs. Li/Li$^+$, as shown in the case of FEC-free electrolyte. The two higher-potential peaks (~ 1.5 and ~ 1.0 V vs. Li/Li$^+$, respectively) support our proposition that FEC has two different reaction mechanisms. In addition, the peak corresponding to EC/DEC reduction is still visible for FEC 10%, but is weakened for EC-FEC, while is barely discernible for DEC-FEC. This confirms that FEC suppresses DEC more than EC.

The SEI layers from the two EC-containing electrolyte solutions (FEC 10% and EC-FEC) contain more polyolefin components. Polyolefins are not conductors of ions and their content in the SEI is a matter of importance. As Peled and Golodnitsky discussed in Chapter 1 of the book *Lithium-Ion Batteries: Solid-Electrolyte Interphase* [15], polyolefins can add flexibility to the SEI and fill voids due to their softness, but excessive polymers can block Li migration in the SEI. Therefore, the higher content of polyolefins in the surface films derived from EC-containing electrolytes can be detrimental to the cell cycle performance and may explain the better cyclability of the cell using the EC-free DEC-FEC electrolyte.

4. Conclusions

In summary, FEC-based electrolytes using FEC as the co-solvent (50 wt%) are investigated and compared with the one using FEC as the additive (10 wt%) for binder-free freestanding Si-MW composite paper anodes for Li-ion batteries. The 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 at 280 mA g^{-1}, 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. After 100 cycles at 100 mA g^{-1}, the cell using DEC-FEC retains a reversible capacity of around 1300 mAh g^{-1} (70% retention). 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 possibly attributed to the formation of more polyolefins, which do not favor Li ion migration. This work sheds new light on FEC reaction mechanism for optimizing the electrolyte composition for the development of high capacity and high energy Li-ion batteries and can be applied to other forms of Si electrodes as well.

Acknowledgments

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