



Highly stable linear carbonate-containing electrolytes with fluoroethylene carbonate for high-performance cathodes in sodium-ion batteries



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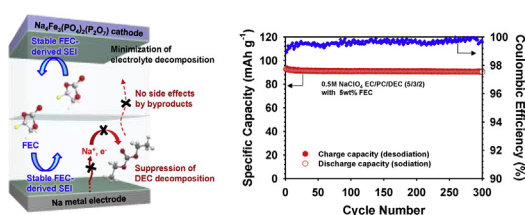
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HIGHLIGHTS

- The FEC additive forms a surface film on the Na metal electrode and the cathode.
- The FEC additive allows the use of linear carbonates in sodium-ion batteries.
- FEC-added electrolytes improve cycling performance of $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ (P_2O_7) cathodes.

GRAPHICAL ABSTRACT



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ABSTRACT

Employing linear carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) as electrolyte solvents provides an opportunity to design appropriate electrolyte systems for high-performance sodium-ion batteries (SIBs). However, in practice, the use of linear carbonate-containing electrolytes is quite challenging because linear carbonates readily decompose at Na metal electrodes or sodiated anodes. One of the promising approaches is using an electrolyte additive to resolve the critical problems related to linear carbonates. Our investigation reveals that remarkable enhancement in electrochemical performance of $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ cathodes with linear carbonate-containing electrolytes is achieved by using a fluoroethylene carbonate (FEC) additive. Importantly, the initial Coulombic efficiency of the Na deposition/stripping on a stainless steel (SS) electrode is drastically improved from 16% to 90% by introducing the FEC additive into ethylene carbonate (EC)/propylene carbonate (PC)/DEC (5/3/2, v/v/v)/0.5 M NaClO_4 . The underlying mechanism of FEC at the electrode-electrolyte interface is clearly demonstrated by ^{13}C nuclear magnetic resonance (NMR). In addition, the $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$ cathode in EC/PC/DEC (5/3/2, v/v/v)/0.5 M sodium perchlorate (NaClO_4) with FEC delivers a discharge capacity of 90.5 mAh g^{-1} at a current rate of C/2 and exhibits excellent capacity retention of 97.5% with high Coulombic efficiency of 99.6% after 300 cycles at 30°C .

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1. Introduction

Sodium-ion batteries (SIBs) have attracted considerable attention as promising next-generation rechargeable batteries, especially for large-scale energy storage systems (ESS), because of the natural abundance of Na and the similarities of these batteries to lithium-ion batteries (LIBs) [1–5]. Much effort has been made to

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improve the electrochemical performances of SIBs through the development of high-performance cathodes [6–8], anodes [9], and electrolytes [10–12]. It should be noted that electrolytes in most studies for SIBs are composed of polar solvents such as ethylene carbonate (EC) and propylene carbonate (PC) [13,14]. Accordingly, instead of commercially available polyethylene (PE) membranes, glass fiber filters (GFFs), which easily uptake polar solvents, have been used as separators for SIBs. However, the too thick, mechanically weak, and highly porous GFF is not suitable as a separator because it can reduce the volumetric energy density and cannot guarantee the safety of batteries. To readily absorb polar solvents with high dielectric constants, their inherent hydrophobic surfaces can be modified by using the surfactants. However, this treatment is temporary because the surfactants are washed away from the separator surface by the electrolyte solution upon the repeated cycling. For the introduction of a conventional PE separator into SIBs, the inclusion of linear carbonate as a cosolvent was attempted, motivated by the fact that this material has been widely used owing to its low viscosity and good compatibility with conventional PE separators. However, the use of linear carbonates such as dimethyl carbonate (DMC) has been limited because of their severe decomposition at the surface of Na metal electrodes and sodiated anodes in SIBs. The Komaba group demonstrated that hard carbon anodes with DMC-containing electrolyte exhibit significant capacity fading [15]. It was proposed that by-products resulting from unwanted reactions between linear carbonates and the Na metal electrode may move to a cathode during cycling and that the migrated by-products can undergo oxidative decomposition at the cathode [16]. Recently, our group reported that the linear carbonate diethyl carbonate (DEC), in EC/DEC/1 M NaClO₄, reacts with the Na metal electrode; the resulting decomposition products, such as active radicals (R-CH₂[•], R=H or CH₃) and sodium alkyl carbonates (R'OCO₂Na), diffuse to the cathode and stimulate electrolyte decomposition at high potentials of around 4.2 V vs. Na/Na⁺ [16]. To properly design electrolyte systems for high-performance SIBs, the high reactivity of linear carbonates toward the Na metal electrode and sodiated anodes should be reduced. Recent studies have reported that fluoroethylene carbonate (FEC) as an additive improved the cycling performance of hard carbon anodes with linear carbonate-containing electrolytes [17]. It was mentioned that FEC readily decomposes on the anode prior to the reductive decomposition of linear carbonates and builds up a protective surface film. Several studies have shown positive effects of FEC on the interfacial stabilization of anodes [12,18–20]. In addition, the FEC additive improved the Coulombic efficiency of NaNi_{1/2}Mn_{1/2}O₂ cathodes through the suppression of the oxidative decomposition of by-products generated by the electrolyte decomposition at the Na metal electrode [21]. Recently, our group demonstrated that the by-products produced from linear carbonate decomposition at the Na metal electrode in Na/Na₄Fe₃(PO₄)₂(P₂O₇) half cells led to the degradation of the electrochemical performance of cathodes [16]. To avoid unwanted electrolyte decomposition on the surfaces of Na metal electrodes in half cells and at sodiated anodes in full cells, electrolyte additives for the formation of protective surface films should be introduced [17,22–25]. To the best of our knowledge, there is no report for detailed failure mechanisms of linear carbonates in SIBs and the unique function of the FEC additive.

Herein, we provide linear carbonate-containing electrolytes with a fluoroethylene carbonate (FEC) additive that could be utilized as a universal electrolyte system for high-performance SIBs to replace lithium-ion batteries. We clearly demonstrate the underlying reaction mechanisms of electrolyte decomposition at the Na metal electrode and the Na₄Fe₃(PO₄)₂(P₂O₇) cathode charged up to high voltage of 4.2 V vs. Na/Na⁺ by means of ¹³C nuclear magnetic resonance (NMR) study. Additionally, we propose a possible

mechanism, which the FEC additive renders linear carbonate-containing electrolytes stable at the Na metal electrode and improves the cycling performance of the cathodes.

2. Experimental

2.1. Electrolytes and electrodes

The electrolytes were 0.5 M sodium perchlorate (NaClO₄, Aldrich, ≥ 98.0%) dissolved in a solvent mixture of ethylene carbonate (EC)/propylene carbonate (PC) (5/5, v/v) or EC/PC/dimethyl carbonate (DMC) (5/3/2, v/v/v) or EC/PC/ethylmethyl carbonate (EMC) (5/3/2, v/v/v) or EC/PC/diethyl carbonate (DEC) (5/3/2, v/v/v). 5 wt% of FEC additive was introduced into each electrolyte. The composition of each electrolyte is listed in Table 1. All solvents (Soulbrain Co., Ltd.) were used as received. The Na₄Fe₃(PO₄)₂(P₂O₇) cathode material was synthesized according to a procedure reported in the literature [8]. For the electrochemical tests, the electrode was prepared by spreading a slurry mixture of 70 wt% Na₄Fe₃(PO₄)₂(P₂O₇) as an active material, 20 wt% super P as a conducting material, and 10 wt% polyvinylidene fluoride (PVDF) binder dissolved in anhydrous *N*-methyl-2-pyrrolidone (NMP, 99.5%, Aldrich) onto an aluminum (Al) foil. The slurry was dried in a convection oven at 110 °C for 1 h. After drying, the electrode was pressed and the thickness was around 50 μm. The electrodes were dried in vacuum at 120 °C for 2 h and at 80 °C for 2 h prior to their assembly into cells.

2.2. Electrochemical measurements

The anodic limits of the electrolytes were determined by means of linear sweep voltammetry (LSV) using an Iviumstat (Ivium Technologies, The Netherlands) at a scan rate of 1 mV/s; we used stainless steel as the working electrode and Na metal as the counter and reference electrodes. A 2032 coin-type half cell with an Na₄Fe₃(PO₄)₂(P₂O₇) cathode, an Na metal electrode, and a glass fiber filter (GFF, Whatman, 260 μm thickness) or a polyethylene separator was assembled in an argon filled glove box with less than 1 ppm of both oxygen and moisture. Galvanostatic charge and discharge cycling (WonATech WBCS 3000) of the Na/Na₄Fe₃(PO₄)₂(P₂O₇) cells was performed in a potential window between 1.7 V and 4.2 V vs. Na/Na⁺. Precycling and cycling tests of the cells were carried out at rates of C/20 and C/2, respectively.

2.3. Characterization

The ionic conductivity and viscosity of the electrolytes were measured using an Oakton CON 11 standard conductivity meter and a BROOKFIELD viscometer (LVDV-II + P), respectively, at room temperature. Contact angle measurements of the electrolytes on a polyethylene (PE, SK innovation Co. Ltd) separator were carried out using a KRUSS DSA100 apparatus within 5 s to minimize any possible contamination. The thickness and porosity of the micro-porous PE film used as a separator were 20 μm and 38%, respectively. To understand the reaction between the linear carbonate and the Na metal electrode, typical experiments were performed as

Table 1
Composition of electrolytes.

Electrolyte	Salt	EC	PC	DMC	EMC	DEC
Ref	0.5 M NaClO ₄	5	5			
DMC-added		5	3	2		
EMC-added		5	3		2	
DEC-added		5	3			2

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