

Fluorinated Ethylene Carbonate as Electrolyte Additive for Rechargeable Na Batteries

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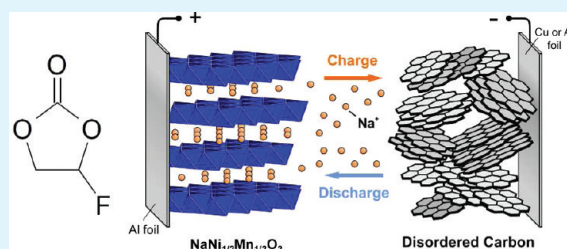
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S Supporting Information

ABSTRACT: Fluoroethylene carbonate is an efficient electrolyte additive to improve the reversibility of electrochemical sodium insertion for hard-carbon and $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ electrodes in aprotic Na cells. The additive is also capable of the electrochemical deposition/dissolution of metallic Na with higher reversibility because of improved passivation and suppression of side reactions between Na metal and propylene carbonate solution containing Na salts.

KEYWORDS: Na-ion battery, sodium insertion, sodium electrodeposition, electrochemistry



Sodium-ion batteries are attracting considerable interest as post lithium-ion batteries because the sodium resources are unlimited everywhere. However, a limited number of successful reports are found in the field of sodium insertion for layered Na_xMeO_2 (Me = transition element) materials compared to Li_xMeO_2 , for example, NaFeO_2 ,¹ Na_xCoO_2 ,² $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2]$,³ and $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$.^{4–6} To the best of our knowledge, there are a few reports on challenges to rechargeable sodium-ion cells.^{7–9} Recently, we demonstrated the rechargeable Na-ion cell consisting of hard-carbon (nongraphitizable carbon) and $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrodes, which are operable at the room temperature, and we fairly succeeded in the passivation of hard-carbon as electrode.⁴ It is generally known that the electrolyte additives are required for the practical Li-ion batteries.^{10–12} In this study, we examine and compare electrochemical performance of Na cells with several additives, such as fluoroethylene carbonate (FEC),^{13–17} *trans*-difluoroethylene carbonate (DFEC),¹⁵ ethylene sulfite (ES),¹⁸ and vinylene carbonate (VC)¹⁹ (their molecular structures are shown in the Supporting Information, Figure S1) which are well-known to be the efficient electrolyte additives for Li-ion batteries. Because there have been no reports on acceptable electrolyte additives for Na or Na-ion cells according to our knowledge, herein we demonstrate for the first time the unique and promising electrolyte additive, FEC, to improve the reversible capacity and its retention for the Na insertion electrodes.

Figure 1 shows initial reduction and oxidation curves for hard-carbon electrodes in the PC electrolyte solution (experimental conditions are found in Supporting Information). The reversible capacity of 200–240 mA h g^{-1} is achieved for the hard-carbon electrodes in the propylene carbonate (PC) electrolyte with the reversible sodium insertion.⁴ When a small amount of FEC is added into the PC solution, an additional voltage plateau at ca. 0.7 V appears during the first reduction due to the decomposition

of FEC, which agrees with the previous report on the decomposition of FEC at ca. 1.1 V vs Li.¹⁴ The capacity and Coulombic efficiency at the first cycle are hardly influenced by the FEC addition because both FEC and PC are decomposable by electroreduction as discussed below. The capacity retention is remarkably improved by the addition of ca. 2 vol % FEC as shown in inset of Figure 1.

As reported previously,⁴ the acceptable capacity retention has been achieved by using the hard-carbon electrodes in the beaker-type cells with flooded electrolyte solution. However, the decrease in capacity is observed by using coin-type cells in which thin glass separator soaked with the minimal amount of electrolyte solution sandwiched between the Na and hard-carbon electrodes (see Figure S2 in the Supporting Information). This capacity degradation is sufficiently avoided by the FEC addition in Figure 1. Besides, the FEC addition is noticeably effective to achieve the comparable reversibility of the Na insertion even in the PC: dimethyl carbonate (DMC) solution, which is easily decomposable in the sodium cells⁴ (see Figure S3 in the Supporting Information).

The film-forming additives into electrolyte solutions are widely known to improve the electrode property for the lithium-ion battery,^{10,14,19,20} When a small quantity of DFEC is added in the PC, any beneficial effects are not found in the Na/hard-carbon cells (see Figure S4 in the Supporting Information), and the ES addition causes the detrimental effect to the Na cells. In the case of VC, which is known to be practically used in Li-ion cells, the reversible capacity decreases (see Figure S5 in the Supporting Information).⁴

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After the first cycle, the coin-type Na cells were disassembled to take out and observe the separators. The PC-based solutions with and without any additives are transparent and colorless liquid prior to electrochemical tests. However, the PC solution clearly became colored in yellow after the first cycle of Na/hard-carbon cells with VC addition compared to that of the VC-free

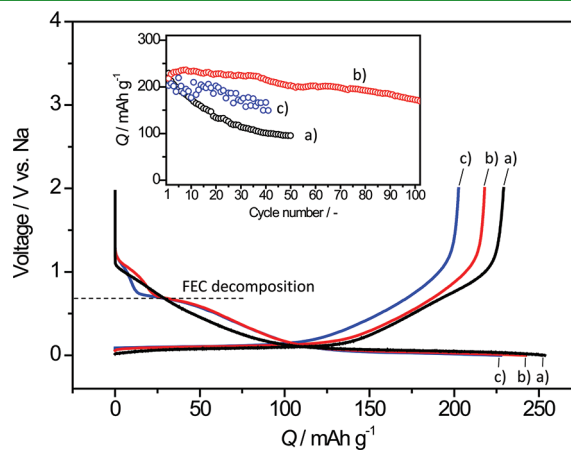


Figure 1. Initial reduction/oxidation curves for hard-carbon electrodes in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ PC solution (a) without and with (b) 2 vol % and (c) 10 vol % FEC at a rate of -25 and $+25 \text{ mA g}^{-1}$ in coin-type Na cells. Inset shows variation in reversible oxidative capacities for hard-carbon during successive cycle test.

electrolyte, and the similar change in color is also observed in a hard-carbon/ $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ full cell (see Figure S6 in the Supporting Information). These results imply that the reductive decomposition of electrolyte solutions is induced not only by Na metal but also by Na-inserted hard-carbon in the VC-added or VC-free cell.

The dependency of the morphology of hard-carbon electrodes on the FEC is shown in Figure 2. Clearly, the deposit is increased with the increase in the amount of FEC addition, supporting the electrochemical decomposition of FEC at the voltage plateau around 0.7 V associated with the deposit. The decomposition of PC results in no apparent deposit by SEM (Figure 2b) because the decomposed product is almost soluble as described later. The XPS measurement reveals that the peak assigned to sodium fluoride is evidently observed in F 1s XPS spectra as increase in the amount of added FEC while there is no remarkable difference in C 1s and O 1s XPS spectra (see Figures S7 and S8 in the Supporting Information). We believe that the improved cycle performance by FEC addition (Figure 1 and Figure S3 in the Supporting Information) originates from the modification of the surface passivation layer including solid electrolyte interphase (SEI).

When the Na insertion/extraction was repeated without the FEC addition, the capacity of the Na/hard-carbon coin-type cells rapidly decreased as already described. After disassembling the tested coin-type cells, we visually observed that the separator soaked with the FEC-free PC solution was colored in pastel yellow after 5 cycles (see Figure S9 in the Supporting Information). On the other hand, the FEC-added electrolyte is

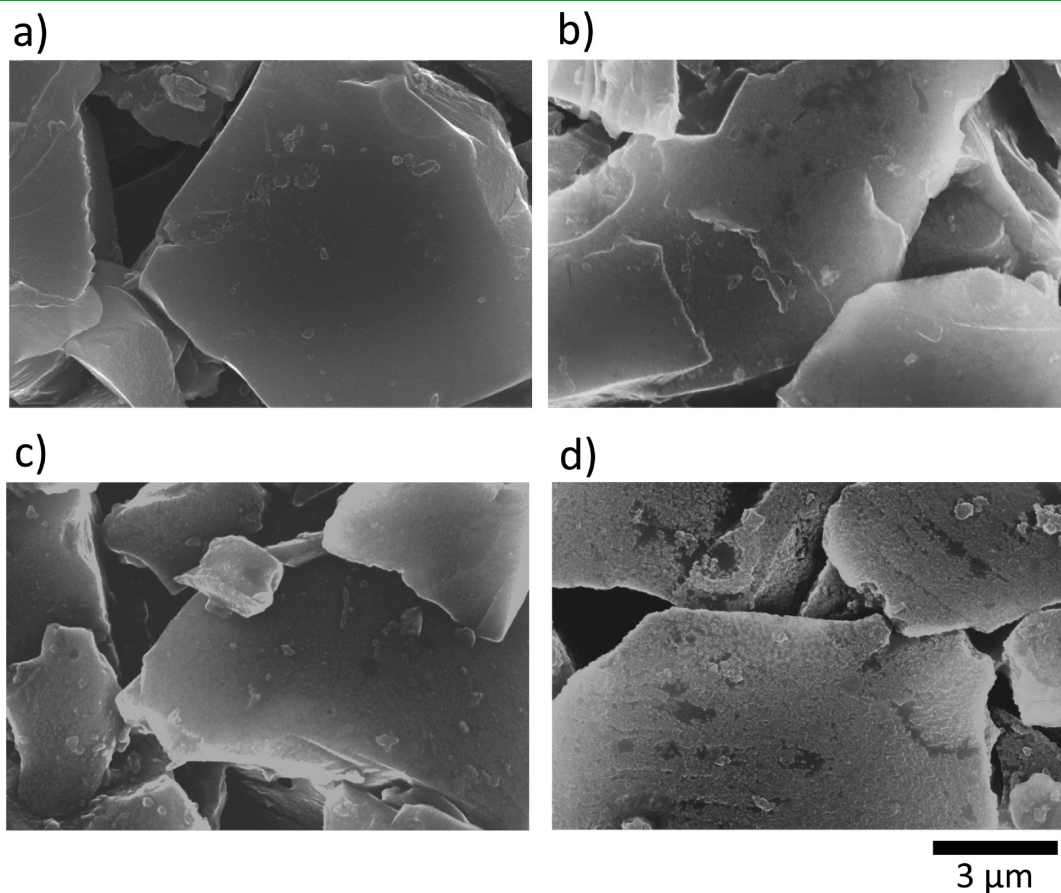


Figure 2. SEM images for hard-carbon electrodes; (a) pristine, and (b–d) after the first reduction–oxidation cycle test in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ PC solutions (b) without and (c, d) with (c) 2 vol % and (d) 10 vol % FEC at a rate of 25 mA g^{-1} in the coin-type Na cells.

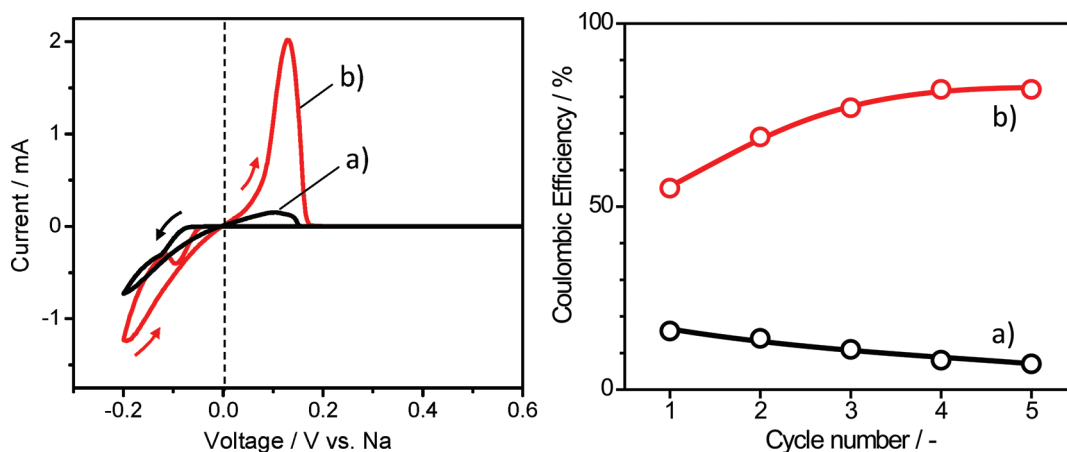


Figure 3. (Left) Second cyclic voltammograms for Al foil electrodes (10 mm in diameter) at a rate of 3 mV min^{-1} and (right) Coulombic efficiency defined as the ratio of (reduction capacity)/(oxidation capacity) during the voltammetry tested in (a) FEC free and (b) 2 vol % FEC added 1 mol dm^{-3} NaClO_4 PC solutions in coin-type Na cells.

not colored in yellow over 100 cycles (see Figure S9 in the Supporting Information), implying that the decomposition of PC is effectively suppressed in the cells. When the yellow-colored electrolyte solutions within the separator were examined by ATR FT-IR, several additional peaks intensively appear in the FT-IR spectra only for the FEC-free solution (see Figure S10 in the Supporting Information). According to previous reports,^{21–23} the infrared absorption is mainly assigned to sodium propyl carbonate (see Figure S11 in the Supporting Information). It is reasonable to speculate that sodium propyl carbonate was formed by the reductive decomposition of propylene carbonate at the Na metal and hard-carbon electrodes. We thought that the degradation of coin-type cells with FEC-free electrolyte (Figure 1) is due to the consumption of the electrolyte solution penetrating the separator by the gradual decomposition. From the above results, it is concluded that FEC is the unique additive showing the positive effect on the suppression of the electrolyte decomposition, resulting in the improved battery performance.

To further examine the influence of FEC on the reversibility of Na (counter) electrode, we performed cyclic voltammetry for bare Al foil electrodes, which are able to be used as current collector as well as Cu foil.⁴ In Figure 3, the FEC additive clearly enhances the electroplating rate and reversibility of Na because the larger redox current flows nearby at the equilibrium potential of Na. The Coulombic efficiency for the sodium deposition and dissolution processes is significantly improved from approximately 10 to 80%. The higher reversibility could prove the passivation of Na deposited in the FEC-added solution which suppresses the unfavorable side reactions between Na and PC solution to form the sodium propyl carbonate. Generally, almost all polar organic solvents including PC are not stable thermodynamically at $\sim 0 \text{ V vs Na}$, however, the FEC additive is found to achieve the highly reversible Na plating and the highly stable Na insertion into hard-carbon despite the thermodynamic restriction.

The influences of both the FEC addition and sodium propyl carbonate contamination on the anodic potential window of the electrolyte solutions are further investigated in the coin-type Na cells (see Figure S12 in the Supporting Information). The irreversible anodic current is apparently observed above 3.2 V in the FEC-free pristine PC, whereas the current is much suppressed at least up to 3.8 V by the FEC addition (see Figure S12 in the Supporting Information). It is noted that the

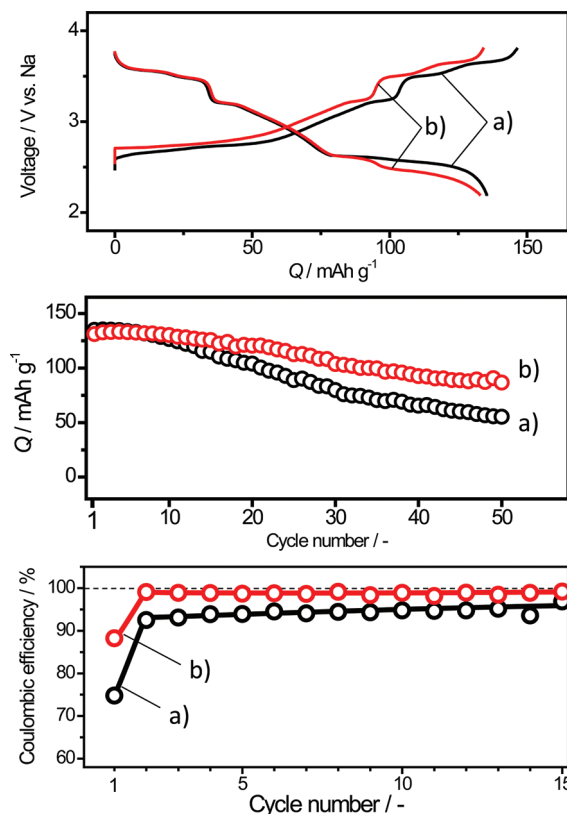


Figure 4. (Upper) Charge–discharge curves at the second cycle, (middle) reversible capacity versus cycle number plots, and (bottom) Coulombic efficiency variation of Na/ $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ cells with (a) FEC-free and (b) 10 vol % FEC added PC electrolyte solutions containing NaClO_4 at a rate of $23.9 \text{ mA (g of oxide)}^{-1}$ in coin-type cells.

irreversible oxidation is observed from 2.8 V in the reused PC electrolyte containing sodium propyl carbonate, which was collected and moved from the ten-cycle tested Na/hard-carbon cell. Therefore, the decomposition product, sodium propyl carbonate, released from the Na and hard-carbon electrodes to the electrolyte is considered to be readily oxidized above 2.8 V vs Na. This indicates that the irreversible reaction is inevitable at the electrode beyond 2.8 V vs Na without the additive.

We recently showed the reversible Na extraction and phase transition process for $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$.^{4,6} The FEC addition also improved the electrochemical reversibility of a Na/ $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ cell because of the suppressed dissolution of sodium propyl carbonate from Na electrode. As shown in Figure 4, the similar trend of the potential variation and discharge capacity at the initial cycle is observed regardless of the FEC addition, and the superior capacity retention is achieved by the FEC addition. Figure 4 further confirms that the FEC additive improves the efficiencies and realizes 98–99% coulomb efficiency for each cycle except the first cycle, resulting from the suppression of the oxidative decomposition of sodium propyl carbonate generated at the opposite Na electrode.

In recent papers, electrochemical Na insertion of Na_xCoO_2 ² and Na_xCrO_2 ⁵ suffers from the oxidative decomposition in Na cells. The anodic decomposition must be due to the byproducts of sodium alkyl carbonate and/or alkoxide,⁴ such as sodium propyl carbonate, generated at Na electrode. We believe that the FEC additive will solve this problem in Na cells. As broadly accepted, the thin passivation layer, so-called SEI, is formed on the negative electrode in the Li-ion cells as first introduced by Peled.²⁴ We have recently demonstrated that the SEI layer allows for the reversible Na insertion of the hard-carbon.⁴ The SEI surface layer modified by the FEC will attain longer cycle life and higher reversibility of Na insertion electrodes. It is believed that the FEC is the promising candidate as an electrolyte additive to realize the rechargeable Na-ion batteries.

CONCLUSIONS

It is found that the FEC is the only efficient electrolyte additive for the Na cells among FEC, DFEC, VC, and ES that are well-known as film-forming organic electrolyte additives in the Li cells. The combination of electrolyte and electrode components including additives, binders, current collector etc. will have to be optimized to realize the advanced Na-ion batteries, which reminds us of the history of lithium-ion batteries over the past 30 years. The Na^+ shuttlecock battery with environmentally and cost friendly materials, which is free from rare metals, has high potential as a possible alternative to lithium-ion batteries in the future.

ASSOCIATED CONTENT

S Supporting Information. Detailed description of the experimental setup, molecular structures of the electrolyte additives, comparison of galvanostatic charge/discharge curves between coin- and beaker-type cells, electrochemical behavior of sodium cells in EC:DMC electrolyte with or without FEC, effect of DFEC and VC as electrolyte additives, photographs of separators after the cycle test in Na cells. X-ray photoelectron spectra of the hard-carbon electrodes. FT-IR spectra of the electrolyte solutions, cyclic voltammograms of the Na cells. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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