



# Electrochemical performance and interfacial investigation on Si composite anode for lithium ion batteries in full cell



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## HIGHLIGHTS

- Lithium ion secondary batteries using Si composite anode are investigated.
- High rate capability can be achieved with FEC additive electrolyte.
- A stable SEI composed of inorganic species is formed with FEC additive electrolyte.

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## ABSTRACT

Lithium ion batteries (LIBs) containing silicon (Si) as a negative electrode have gained much attention recently because they deliver high energy density. However, the commercialization of LIBs with Si anode is limited due to the unstable electrochemical performance associated with expansion and contraction during electrochemical cycling. This study investigates the electrochemical performance and degradation mechanism of a full cell containing Si composite anode and LiFePO<sub>4</sub> (lithium iron phosphate (LFP)) cathode. Enhanced electrochemical cycling performance is observed when the full cell is cycled with fluoroethylene carbonate (FEC) additive compared to the standard electrolyte. To understand the improvement in the electrochemical performance, x-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM) are used. Based on the electrochemical behavior, FEC improves the reversibility of lithium ion diffusion into the solid electrolyte interphase (SEI) on the Si composite anode. Moreover, XPS analysis demonstrates that the SEI composition generated from the addition of FEC consists of a large amount of LiF and less carbonate species, which leads to better capacity retention over 40 cycles. The effective SEI successively yields more stable capacity retention and enhances the reversibility of lithium ion diffusion through the interphase of the Si anode, even at higher discharge rate. This study contributes to a basic comprehension of electrochemical performance and SEI formation of LIB full cells with a high loading Si composite anode.

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## 1. Introduction

Rechargeable LIBs are widely used for many types of electronic devices because of their high energy density and longevity [1,2]. Many researchers have focused on high capacity materials to further propel the electrochemical performance, creating the next generation LIBs [3–6]. The current market is dominated by carbon

(graphite) anode which offers limited power and energy density (372 mAh g<sup>-1</sup>). In order to make a significant increase in power density, higher capacity anode materials are required given that carbon materials have already reached their full theoretical capacity.

Silicon (Si) is theoretically expected to have almost 10 times higher capacity than the conventional graphite material (Si: 3579 mAh g<sup>-1</sup>) [7]. However, Si as an anode poses several challenges such as serious volume change during electrochemical cycling causing rapid capacity decay and continuous electrolyte side reactions on the surface that prevent its stability during cycling

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[8–10]. Researchers have investigated several types of Si anodes and binders such as nano sized Si particles, Si imbedded in a carbon matrix, and amorphous Si thin film to overcome these issues [11,12]. While these strategies improve the cycling performance, they have not reached a basic resolution. This is partially due to the solid electrolyte interphase (SEI) which forms on the surface of the anode due to instability of the conventional electrolyte at the lower voltage regime and dictates the electrochemical stability of the anode. The SEI formation is also affected by the large volume expansion and contraction during the charge and discharge, which propagates the sequestration of Li ions at each cycle [13,14]. The morphology and composition of the SEI also depends on the electrolyte components, thus it is crucial to produce a stable SEI on the anode surface to achieve long cycle performance. To enhance the electrochemical stability of Si, vinylene carbonate (VC) [15] and fluoroethylene carbonate (FEC) are extensively used as additives for the standard carbonate electrolyte (LiPF<sub>6</sub>, ethylene carbonate (EC): diethyl carbonate (DEC)) [16–18]. FEC has favorably been considered a more effective electrolyte additive because it is more effective at stabilizing the capacity retention and lowering the cell impedance. Schroder, Alvarado et al. demonstrated the effect of FEC additive (10 wt%) to the conventional carbonate electrolyte and found that the SEI derived from FEC can effectively improve the discharge capacity retention and coulombic efficiency (C.E.) [19]. According to Mullins and coworkers, the addition of 3 wt% FEC into a EC-based electrolyte demonstrated that capacity retention of the Si anode can slightly improve, albeit, until 20 cycles [16]. However, Lucht and coworkers showed that 5% FEC is not sufficient to form an effective SEI on the Si interface. On the other hand, increasing the FEC percentage to 25% does not further stabilize the electrochemical cycling and increase cell resistance [20]. Given, the extensive studies on the effect of FEC percentage in conventional electrolytes, the addition of gives the best results for increasing capacity retention and C.E [17,19].

Typically, researchers have focused their efforts in investigating the electrochemical performance of Si anode in a half cell, where lithium (Li) metal is used as a counter electrode which contains a limitless supply of Li in the cell. This inherently hides the true electrochemical properties of the anode. Conversely, in a full cell the supply of Li is governed by the cathode material; hence, making it more difficult to maintain the electrochemical performance of the Si composite anode [21–23]. Given what is known about the SEI, during the charge and discharge process the active Li ions are continuously consumed by the SEI on the negative electrode, which can cause devastating effects in a full cell. Dupre and coworkers demonstrated the electrochemical performance and degradation mechanism of the Si composite anode in a full cell using lithium nickel manganese cobalt oxide (NMC) as the cathode [24]. They suggest that the available Li ions are consumed in the SEI or in the electrolyte causing capacity fade for extended cycles. Their study gave a detailed understanding for the decomposition mechanism of Si composite in a full cell when cycled with FEC. However, previous full cell studies fail to reveal the actual effect of FEC additive to the electrolyte because their work do not compare the results with an electrolyte not containing the additive [24–26]. A systematic comparison of the standard electrolyte and FEC additive electrolyte has yet to be studied. One must fully understand if the effect of FEC is also positive when used in a full cell with Si anode and the cathode to further verify the use of FEC additive in commercial cells.

In this study, we compare the electrochemical performance of the Si composite anode full cell in LiPF<sub>6</sub>/ethylene carbonate (EC)/diethyl carbonate (DEC) and LiPF<sub>6</sub>/EC/DEC/FEC (10 wt%). The detail influence of FEC additive on the electrochemical reaction of the full cell is investigated by means of cyclic voltammetry (CV). Electrochemical impedance spectroscopy (EIS) measurement is used to

determine effect of FEC in the electrolyte on the overall impedance of the cell after electrochemical cycling and XPS is used to characterize the chemical components of the SEI on the Si composite anode. Given the transition metal instabilities of NMC during electrochemical cycling, researchers have focused their efforts on LiFePO<sub>4</sub> (LFP) to enhance the electrochemical performance in both half cells and full cells [27–30]. Until now, LFP has been one of the most versatile, stable, and promising cathode materials. Therefore, to isolate the effects of Si anode and its SEI in a full cell, LFP is utilized in this study. LFP has been extensively studied in a half cell in the literature, the results suggest that the LFP cathode is stable upon prolonged cycling. This is reflected by the negligible iron dissolution and reduced formation of the cathode electrolyte interphase, therefore, the resistance within the cell during electrochemical cycling of the half cell is negligible. Moreover, this has been verified by XPS and electrochemical analyses [27,31,32]. Herein, we discuss the difference between the full cell cycled in LiPF<sub>6</sub>/EC/DEC and LiPF<sub>6</sub>/EC/DEC/FEC. CV measurement gives insight to highly reversible lithium ion diffusion into the Si SEI for electrodes cycled with FEC at high scan rate. Si electrodes cycled with FEC have higher amounts of LiF and less carbonate species compared to electrodes cycled without FEC, contributing to the improvement of the full cell battery performance.

## 2. Experimental methods

### 2.1. Electrode fabrication

Si nanoparticle (Alfa Aesar, average particle size: 50 nm) was used as the active material of negative electrode. The Si composite anode was fabricated as follows: 50 wt% nano-Si powder, 25 wt% Ketjenblack (Akzo Nobe: EC-600JD), and 25 wt% sodium carboxymethyl cellulose (CMC-Na, DS = 0.9, Mw = 250,000, Sigma Aldrich) were mixed in water. The obtained slurry was coated on Cu foil by using a doctor blade and dried at 100 °C for 20 h under a vacuum to completely dry any water on the surface. The electrode sheet was cut into a disk and applied for the battery test. The mass of the Si active material on the electrode was 0.5 mg of Si per cm<sup>2</sup>. The positive electrode was prepared as follows: 80 wt% LiFePO<sub>4</sub> powder (MTI Corporation), 10 wt% carbon black (Timcal, Super-P) and polyvinylidene fluoride (PVDF) were mixed in *N*-methyl-2-pyrrolidone (NMP) as solvent to prepare a slurry. The obtained slurry was coated on Al foil by using a doctor blade and dried at 100 °C for 20 h under a vacuum to completely dry any NMP on the surface. These electrodes were used to assemble the 2032 coin cell using a polymer separator (C480, Celgard Inc., USA). The electrolyte (Battery grade, BASF) was a solution of 1 M LiPF<sub>6</sub> dissolved in EC/DEC 1:1 (wt%): Selectilyte LP 40 and EC/DEC/FEC 45:45:10 (wt%): Selectilyte A6 where LiPF<sub>6</sub>/EC/DEC and FEC stand for ethylene carbonate, diethyl carbonate, and fluoroethylene carbonate, respectively. Coin cells were assembled in a glovebox purged with high purity Ar gas and maintained with water vapor levels at or less than 5 ppm.

### 2.2. Electrochemical test

After the coin cells were assembled, electrochemical performance tests were performed using an Arbin battery cycler in galvanostatic mode. The charge and discharge performance of the full cell was conducted between 2.5 V and 3.5 V. The open circuit voltage of the coin cells was monitored for 10 h and then we started to charge and discharge the cell with the current density of 60 μA cm<sup>-2</sup>, which is approximately corresponding to a C-rate of C/15. The percent capacity retention was calculated with respect to the first discharge capacity. Cyclic voltammetry (CV) measurements

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