Understanding the influence of electrolyte additives on the electrochemical performance and morphology evolution of silicon nanowire based lithium-ion battery anodes

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HIGHLIGHTS

- VC, FEC, LiBOB and VEC all significantly improve the capacity retention of Si NWs.
- Li silicates are a major decomposition product of the Si active material.
- A more stable SEI layer facilitates the formation of a porous morphology of Si.
- The rate capability of Si NWs is considerably affected by SEI layer composition.

GRAPHICAL ABSTRACT
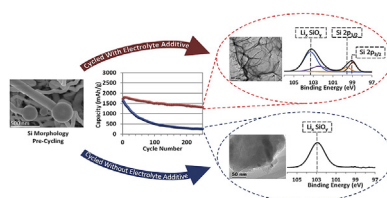
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ABSTRACT

Here we report new insights into the effect various electrolyte additives have on the cycling stability and rate capability of Si nanowire (NW) Li-ion battery anodes. The additives tested were vinylene carbonate, vinyl ethylene carbonate, fluoroethylene carbonate and lithium bis(oxalato)borate. All four significantly improve the capacity retention of the electrodes over 250 cycles compared to the additive-free electrolyte, with vinylene carbonate being the outstanding performer. The results provide a new understanding of the cycling behaviour of Si in the presence of electrolyte additives, revealing that not only is the stability of the SEI layer affected but that this consequently has a profound influence on the morphology evolution and chemical composition of the Si active material. Ex-situ characterisation of the electrodes post-cycling demonstrates that the improvement in cycling stability arises as the additives minimise irreversible decomposition reactions at the surface and facilitate a transformation from a NW morphology into a porous sponge-like network. This transformation process does not occur in the absence of any stable SEI forming additives as instability in the passivating layer leads to the continuous and irreversible consumption of Si to form Li silicates.

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1. Introduction

Lithium-ion batteries (LIB) have emerged as the dominant portable energy storage device on the market today due to their long cycle lives, low propensity for self-discharge and high power and energy densities [1]. A fundamental advantage LIBs possess over other rechargeable battery systems is the high voltages

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obtainable; however this advantage is incurred with a cost as the wide operating potential range is outside the region where commonly used carbonate-based electrolytes are thermodynamically stable. In particular, the low operating potential of Li-ion anodes causes the electrochemical reduction of the electrolyte at the surface of the active material producing a complex mixture of inorganic and organic decomposition products [2]. This is known as the solid electrolyte interphase (SEI) layer and its stability and composition are major factors that contribute to the capacity retention and rate capability of LIB electrodes. In an optimally performing electrode, SEI formation is self-limiting as it forms a passivating layer on the surface of the active material in the initial cycles that prevents further decomposition of the electrolyte.

Si has been intensively studied recently as a Li-ion anode material due to its very high specific capacity (3579 mAh g^{-1}) when compared to graphite (372 mAh g^{-1}); however, its adoption has been hindered by the fact that it undergoes a huge volume expansion (>300%) during cycling that leads to pulverisation of the active material and loss of electrical contact with the current collector [3–6]. The use of Si NWs overcomes this issue although the long-term cycling performance is still limited due to an inherent structural instability in the SEI layer caused by the volume increase during charging [3,7–11]. A simple approach to alleviate this problem is to use film forming electrolyte additives that can improve the electrochemical performance of Li-alloying anodes as they help to form a more stable passivating layer [12,13].

Recent studies in this area have given an insight into the positive influence various electrolyte additives can have on the capacity retention of Li-ion anodes. For instance, it has been shown that carbonate based reduction-type additives produce a more cohesive SEI layer through the formation of polymers [14–16]. These provide a certain flexibility that mitigates against cracking and re-exposure of the active material, thereby prolonging the cycle life. To date, however, there has been little focus on the effect the electrolyte formulation has on the chemical and structural composition of the Si active material after cycling. The composition of the electrolyte has been shown to have a significant impact on the extent of morphological transformation that occurs in Li-alloying materials during repeated lithiation and delithiation [17–19]. In a recent study on Ge NW anodes we showed that the NW morphology is completely transformed as a result of cycling leading to the formation of a porous network structure [18]. It was discovered that this transformation process was facilitated by the presence of the electrolyte additive, vinylene carbonate (VC), in the absence of which the capacity retention was found to be quite poor. Considering their potential as a next-generation Li-ion anode material, a more in-depth knowledge is required on the nature of the morphological transformations that occur in Si electrodes as a result of cycling and the influence the electrolyte formulation has on this.

Herein, we examine the impact electrolyte additives have on the cycling stability and rate capability of Si NW LIB anodes. Unlike most studies to date in the area which mainly focus on the effect additives have on the SEI layer composition, here we reveal for the first time the significant influence they also exert on the morphology and chemistry of the cycled Si active material. Four different stable SEI formers were chosen based on their previously reported success in improving the cycle life of both graphitic and Si based anodes [13–16,20–28]. The additives selected were vinylene carbonate (VC), fluoroethylene carbonate (FEC), vinyl ethylene carbonate (VEC) and lithium bis(oxalato) borate (LiBOB) and their effectiveness were evaluated in a standard 1M LiPF$_6$ in ethylene carbonate/diethyl carbonate (EC/DEC) (1:1 v/v) electrolyte solution. The electrochemical performances of Si NW anodes were directly compared in the presence of each of the electrolyte additives based

on their capacity retention and rate capability. All were found to improve the capacity retention of the Si NWs compared to the standard electrolyte, with VC being the outstanding performer. Through XPS, ex-situ TEM and EIS analysis, we show in all cases that the additives improve the cycling performance of the NWs as they increase the mechanical and chemical stability of the SEI layer, while facilitating the formation of a porous sponge-like network of Si ligaments. This transformation does not occur in the absence of any electrolyte additives as the active material is constantly re-exposed to the electrolyte due to cracking of the SEI layer during charging. This leads to the continuous and irreversible consumption of Si at the surface to form Li silicates. These results offer a fresh perspective on the crucial role electrolyte additives play in the cycling behaviour of Si. The necessity of optimising the electrolyte formulation when designing and testing Li-alloying anodes is revealed herein as we show that additives not only stabilise the SEI layer, but also have a considerable effect on the evolution of the morphology and surface chemistry of the Si active material during cycling.

2. Experimental section

2.1. Si NW electrode fabrication

The Sn seeded Si NWs were synthesised from stainless steel substrates via a previously published method [29]. The stainless steel (SS, 316) foil was purchased from Pi-Kem Ltd. with a thickness of 0.1 mm. Prior to Sn evaporation, the substrates were roughened using P600 grit sandpaper to increase the surface area and improve the contact between the active material and the current collector. Optimal growth was achieved for Sn thicknesses of 20 nm. To synthesise the Si NWs for the long-term cycling experiments, 7 mL of squalane was added to a custom-made Pyrex long-necked round bottom flask. The substrates were placed vertically into the flask using a SS holder so as they were held above the liquid level (i.e. in the vapour phase during synthesis). The flask was attached to a Schlenk line setup via a water condenser. The temperature of the flask was ramped to 125 °C using a three-zone furnace and a vacuum of at least 100 mTorr was applied for 1 h to remove moisture from the system. Following this, the system was purged with Ar. The water condenser was switched on and the temperature of the flask was ramped to 460 °C. To initiate Si NW growth, 0.75 mL of the Si precursor phenylsilane was injected through a septum cap along with 0.05 mL of the reducing agent LiBH$_4$ in a 1:1 v/v mixture with squalane. After 45 min another 0.25 mL of phenylsilane was injected into the reaction mixture. The reaction was allowed to proceed for 1.25 h in total from the initial injection. After synthesis, the substrates were simply rinsed with toluene, to remove excess solvent, and dried using a nitrogen line. No additional cleaning steps were required. By varying the reaction time and the number of sequential injections of phenylsilane, it is possible to achieve mass loadings of up to 0.3 mg cm^{-2} using this method. The specific capacities in the cycling experiments were calculated based on the mass of the Si. This was determined through careful measurement using a Sartorius Ultra-Microbalance SE2 (repeatability ±0.25 μg).

2.2. Electrochemical measurements

The electrochemical performance was evaluated by assembling two electrode Swagelok cells in an Ar filled glovebox. The cells consisted of Sn seeded Si NWs, Li foil as the counter and reference electrode, a porous polyethylene separator, and the standard electrolyte solution of 1M LiPF$_6$ in ethylene carbonate/diethyl carbonate (1:1 v/v). For the additive tests, 3 wt% of each was added to the standard electrolyte. The measurements were carried out