



Enabling electrolyte compositions for columnar silicon anodes in high energy secondary batteries



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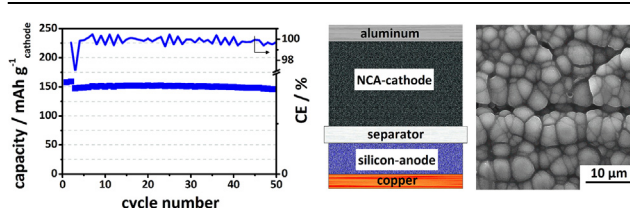
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HIGHLIGHTS

- Electrolyte with low polysulfide solubility to improve cycle life of Li_xSi/S cells.
- Enabling LiTFSI as conduction salt for lithium ion batteries.
- Novel electrolyte system to enhance cycle life of LIB with silicon anodes.
- Pure silicon anodes for high volumetric energy density LIB (980 Wh l⁻¹).

GRAPHICAL ABSTRACT



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ABSTRACT

Columnar silicon structures are proven as high performance anodes for high energy batteries paired with low (sulfur) or high (nickel-cobalt-aluminum oxide, NCA) voltage cathodes. The introduction of a fluorinated ether/sulfolane solvent mixture drastically improves the capacity retention for both battery types due to an improved solid electrolyte interface (SEI) on the surface of the silicon electrode which reduces irreversible reactions normally causing lithium loss and rapid capacity fading. For the lithium silicide/sulfur battery cycling stability is significantly improved as compared to a frequently used reference electrolyte (DME/DOL) reaching a constant coulombic efficiency (CE) as high as 98%. For the silicon/NCA battery with higher voltage, the addition of only small amounts of fluoroethylene carbonate (FEC) to the novel electrolyte leads to a stable capacity over at least 50 cycles and a CE as high as 99.9%. A high volumetric energy density close to 1000 Wh l⁻¹ was achieved with the new electrolyte taking all inactive components of the stack into account for the estimation.

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1. Introduction

The development of rechargeable lithium batteries with high energy density is a critical issue to extend the range of electric vehicles, which is the most urgent customer demand besides price reductions [1]. It is estimated, that state-of-the-art lithium ion batteries (LIB) including a transition metal based cathode and

graphite anode will soon reach their upper energy density limit. Therefore, only incremental progress is expected based on these materials. A good example is the Panasonic high energy cell (NCR18650G, 270 Wh kg⁻¹) with improved energy density achieved by the addition of small portions of silicon to the graphite anode [2].

The substitution of graphite by silicon offers a high potential to increase the cells' energy density, due to its tenfold specific capacity (3579 mAh g⁻¹Si) at room temperature (considering Li_{3.75}Si (1857 mAh g⁻¹Li_{3.75}Si) as fully lithiated state) compared to graphite (372 mAh g⁻¹C), while maintaining a low average voltage of about

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0.5 V vs. Li [3]. Additionally, the volumetric capacity of about 2100 mAh cm^{-3} in the lithiated state (assuming lithium silicide alloy after 300% volume expansion caused by lithium uptake) is outstanding and competitive to pure lithium metal anodes [4,5]. However, the volume expansion also induces active material losses through cracking and pulverization as well as steady reformation of the solid electrolyte interface (SEI), which hindered the application of high quantities of silicon in the anode so far [6,7]. It is well known that tailored nanostructures with high specific surface areas can avoid the pulverization processes, but only at the expense of extensive initial lithium consumption for SEI growth [4]. Therefore, interconnected/encapsulated architectures, microparticles and columnar structures with reduced surface area were developed to combine good capacity retention and low initial losses [8–13]. For practically relevant structures and loadings, the steady reformation of the SEI around cracks caused by the volume change of silicon remains an issue. Commercial LP30 electrolyte (1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) 1:1, by volume) is commonly used for LIB and might, given the introduction of additives such as fluoroethylene carbonate (FEC) and/or vinylene carbonate (VC), also form sufficiently stable SEI films on silicon surfaces [14]. However, a full stabilization of the SEI is not reached until now and thus, the electrolyte decomposition leading to cell drying-out cannot be avoided. Unfortunately, the included LiPF_6 salt also tends to form hydrofluoric acid (HF) in contact with residual water, which can etch silicon and also causes safety risks in case of a cell damage [15]. Hence, a considerable research interest is devoted to alternative electrolyte compositions for LIBs [16,17].

One promising approach is the application of ionic liquids as solvents because of their high thermal stability and non-flammability [18], but so far only a few publications deal with high silicon loadings [19]. Ionic liquids also offer the possibility to substitute LiPF_6 by lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI) [20]. LiTFSI is a promising candidate to replace LiPF_6 , owing to its comparable ionic conductivity, higher chemical and thermal stability and the lack of HF formation when exposed to water residues [16]. However, in the conventional liquid carbonate electrolytes the use of LiTFSI is disadvantageous because of the corrosion of the aluminum current collector above 3.8 V vs. Li/Li^+ [21]. Recently, it was shown that fluorinated carbonates and fumed silica enable the use of LiTFSI salt by passivation of the aluminum current collector [22–24].

An alternative way to increase the energy density of rechargeable lithium batteries is a replacement of the intercalation cathode by a chemical conversion type cathode, for example based on sulfur with its high theoretical energy density of 2570 Wh kg^{-1} [25]. However, the energy density reported recently by Sion Power and Oxis Energy, respectively, for prototype Li/S pouch cells is still far away (up to 400 Wh kg^{-1}) from the theoretical value. Even though high energy densities are already achievable with Li/S prototype cells, their commercialization is still hindered due to the insufficient cycle life. The latter is mainly linked with the lithium metal anode, which forms mossy deposits or dendrites during plating and therefore suffers from continuous active material loss as well as short circuits [26]. In order to overcome these issues, lithiated silicon (lithium silicide) anodes were integrated in Li/S cells to enhance the cycle life and safety and overcome the limitations of lithium dendrite growth by a stabilized SEI [27].

The development of new electrolytes is equally important for both Li/S and LIB, when introducing lithium silicide anodes, in order to stabilize the SEI, avoid safety risks through HF formation or dendrite growth and, at the same time, provide the platform for the development of high energy density batteries with prolonged cycle life. As corrosion of aluminum does not occur at cell voltages below 3.8 V, LiTFSI can be used in Li/S cells typically in combination with

1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) mixtures instead of carbonate solvents (LIB) [28,29]. To hinder the polysulfide shuttle, LiNO_3 is a common additive to form a stable SEI on lithium by reacting with polysulfides [30]. This reference DME/DOL based electrolyte has also been used for the lithium silicide sulfur cell system [31,32]. The typically used electrolyte composition in Li/S cell (1 M LiTFSI + LiNO_3 additive in DME/DOL (1:1, by volume)) reveals a high solvation power for both short- (Li_2S_n , $n \leq 4$) and long-chain (Li_2S_n , $n \geq 6$) polysulfides [33]. Thus, the continuous attack of dissolved, highly mobile polysulfides destabilizes the SEI and results in gradual capacity fading. In turn, reducing the solubility of long-chain polysulfides has the potential to prolong the cycle stability by simply avoiding these side reactions with the lithium anode [34]. In addition, a significant reduction of the required electrolyte amount may be achieved by reducing the polysulfide dissolution, which is a key factor to increase the energy density of Li/S batteries [35].

In the following, we introduce a novel electrolyte system for silicon anodes consisting of 1.5 M LiTFSI in a mixture of sulfolane (TMS) and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) in a ratio of 1:1 by volume (TMS/TTE-electrolyte). The application of this electrolyte system limits the dissolution of long chain polysulfides and, therefore, enhances the cycle life of lithium silicide sulfur cells. The same electrolyte system and silicon anode is also highly stable against a lithium-nickel-cobalt-aluminum oxide (NCA) cathode by adding 5% FEC for SEI formation. The results demonstrate the potential of columnar structured silicon as a future anode material for high energy Li/S and LIB cells.

2. Experimental section

2.1. Preparation of electrodes

The columnar silicon anodes were prepared by roll-to-roll magnetron sputtering at the Fraunhofer FEP, as described before [36]. The loading of was approximately $1.4 \text{ mg}_{\text{Si}} \text{ cm}^{-2}$. The cathode preparation was carried out according to a procedure reported before with slight adjustments [37]. In brief, sulfur (Sigma Aldrich, $\geq 99.5\%$) and carbon black (Printex XE-2B, Orion Engineered Carbons) were mixed in a weight ratio of 12:5, followed by a melt-infiltration step. The slurry was prepared by adding 5% CMC/SBR-binder and 10% (multiwall carbon nanotubes Nanocycl NC 7000, 90%) as conductive additive in deionized water. After coating the slurry on battery-grade aluminum foil (MTI Corp., $>99.9\%$, $15 \mu\text{m}$) using a comma-bar technique, the cathode film was pre-dried using a $70^\circ\text{C}/90^\circ\text{C}$ gradient in air and final-dried for 1 h at 50°C under vacuum. The cathode had a typical density of 0.4 g cm^{-3} and loading of about $2.5 \text{ mg}_{\text{cathode}} \text{ cm}^{-2}$, which corresponds to $1.5 \text{ mg}_{\text{S}} \text{ cm}^{-2}$ (based on the 60% sulfur share in the cathode). The NCA cathodes were purchased from Custom Cells Itzehoe GmbH (Itzehoe, Germany) and had an average loading of 24.5 mg cm^{-2} , a maximum capacity of 162 mAh g^{-1} and $20 \mu\text{m}$ aluminum foil as current collector. Test samples were cut out by punching the electrodes in 12 mm disks.

2.2. Cell assembly and electrochemical testing

For the Li/S cells, the silicon anodes were prelithiated versus pristine lithium. For this purpose, coin cells (MTI Corp., CR2016) were assembled under argon atmosphere (MBraun glovebox, $< 0.1 \text{ ppm O}_2$ and H_2O) using the columnar silicon as working electrode and a lithium chip (MTI Corp., 99.0%, diameter: 15.6 mm, thickness: $250 \mu\text{m}$) as the reference/counter electrode separated by a polypropylene separator (Celgard 2500) and $30 \mu\text{l}$ electrolyte. The electrolyte consisted of 1 M lithium bis(trifluoromethylsulfonyl)

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