Advanced Electrolyte/Additive for Lithium-Ion Batteries with Silicon Anode

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Abstract

State-of-the-art lithium-ion batteries (LIBs) are based on a lithium transition metal oxide cathode, a graphite anode and a non-aqueous carbonate electrolyte. To further increase the energy and power density of LIBs, silicon anodes have been intensively explored due to their high theoretical capacity, low operation potential, and low cost. However, the main challenges for Si anode are the large volume change during lithiation/delithiation process and the instability of the solid-electrolyte-interphase associated with this process. Recently, significant progress has been achieved via advanced material fabrication technologies and rational electrolyte design in terms of improving the Coulombic efficiency and capacity retention. In this paper, new developments in advanced electrolyte and additive for LIBs with Si anode were systematically reviewed, and perspectives over future research are suggested at the end of the review.

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Introduction

Commercially available lithium-ion batteries (LIBs) for consumer electronics and electric vehicles are based on a lithium transition metal oxide cathode and a graphite anode with an electrolyte, either a solution of a lithium salt dissolved in an organic solvent or the same solution trapped in a gel.¹ Currently, development of battery technology is rather imperative to accommodate applications demanding even higher energy density and power density, such as electric vehicles²⁻³. For this purpose, great advances have been made in both high-energy cathode materials⁴ and high-energy anode materials⁵. Development of cathode materials progressed dramatically by our colleagues at Argonne National Laboratory⁶. On the anode side, silicon-based materials emerged as a super high-capacity candidate (4008 mAh/g for $\text{Li}_{22}\text{Si}_5$, 3579 mAh/g for $\text{Li}_{13}\text{Si}_4$) (Figure 1) for LIBs.⁷ Other alloys⁸⁻⁹ and metal oxides¹⁰ as new anode materials also witnessed great promise. However, due to their distinctive characteristics from the conventional carbonaceous anode, these anode materials have raised additional challenges for battery electrolytes and additives.¹¹⁻¹²

Figure 1. Phase diagram of the Li-Si binary system. (Reproduced with permission of Springer ³).

Two major issues were identified to be critical to realize the application of Si anode in LIBs: large volume expansion and shrinkage of Si particles during lithiation and delithiation and the instability and high resistance of solid-electrolyte-interphase (SEI) due to the repeated construction and destruction in the presence of the conventional electrolytes and additives, leading to continuous electrolyte decomposition.¹³

The dramatic volume expansion (>300% when completely lithiated) remains a challenge for LIBs with Si anode. Cracking of active material and loss of electrical conduction paths is inevitable due to the large volume change of the active silicon phase during the insertion and extraction of lithium. The reductive reaction of electrolytes and additives with the components of the native layer (SiO_x) and silanol (Si-OH) involves lithium species during the repeated lithiation process, causing active lithium loss and fast capacity fade.

A stable SEI is indispensable for the Si anode to afford extended charge and discharge cycles to protect electrolyte from continuous degradation and subsequent depletion.¹⁴ Despite the complexity of SEI, the relative performance of LIBs is highly dependent on electrolyte composition, impurity concentration, presence of protective additives, charge/discharge conditions etc. Therefore, the insight into the decomposition mechanism of electrolytes and additives is complicated by a number of contributing factors ranging from formulation to operation conditions, and challenged by the sensitivity of varied characterization techniques.¹⁴

A variety of electrolytes/additives have been investigated in the last decade for silicon anode. Carbonate based electrolyte is still the main stream of the research with a couple of emerging systems. Electrolyte additive plays a significant role in passivating the Si/electrolyte interphase during the initial lithiation process. Fluoroethylene carbonate (FEC) is the most effective additive for extended cycle life of Si anode. Other additives including carbonates, silanes, ethers, carboxylic anhydrides, and organoboron compounds have been also developed and reviewed in the paper.

Carbonate electrolytes

Figure 2. (a) Chemical structure of lithium salt and carbonate solvents and (b) ethylene carbonate and (c) dimethyl carbonate reduction reactions on the surface of Si anode (one-electron and two-electron reduction).¹⁴ (Reproduced with permission from American Chemical Society).

The conventional electrolytes for LIBs are liquid solutions of lithium salts in mixtures of aprotic organic solvents, such as lithium hexafluorophosphate (LiPF₆) or lithium

bis(trifluoromethanesulfonyl)imide (LiTFSI) in ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), or mixture of the above (Figure 2 (a)). The electrochemical reactions of EC and DMC solvents during the lithiation process were theoretically calculated by density function theory (DFT) and experimentally revealed by ^1H , ^{19}F , ^7Li , and ^{13}C solid-state nuclear magnetic resonance spectroscopy (ssNMR). The most abundant products were identified to be poly(ethylene oxide)-type species with one plausible reaction releasing carbon dioxide. The proposed mechanisms for the one-electron and two-electron reductive decomposition of EC and DMC were shown in Figure 2(b) and 2(c).¹⁴ These results were consistent with the prior analysis performed with X-ray photoelectron spectroscopy (XPS).¹³ To develop stable electrolyte, non-carbonate based electrolytes are currently sought and actively investigated.¹⁵

Ionic liquid electrolytes

Ionic liquids (ILs) based electrolyte has been reviewed for LIBs with graphite anode and other energy storage systems in prior art.^{1, 16} Ionic liquid electrolyte are room-temperature molten salts and composed mostly of organic ions that may undergo almost unlimited structural variations.¹ Beyond its chemical and electrochemical inertness at the interface of the electrode/electrolyte, ILs is thermally stable and non-flammable which renders the improved safety property, a critical technical challenge especially for the electric vehicle application. Typical cations and anions of the ILs investigated in LIBs with Si anode were summarized in Figure 3.

Figure 3. Chemical structures of typical anions and cations used in ionic liquid electrolytes.

It was demonstrated that ILs electrolyte based on 1-methyl-1-propylpyrrolidinium (PYR₁₃) or 1-methyl-1-butylpyrrolidinium (PYR₁₄) cation and TFSI anion cycled well in cells with lithium metal as an anode, offering a dramatic increase in energy density.¹⁷ The same electrolyte was also investigated with 60 nm Si-Cu film electrode in a three-electrode configuration. A stable SEI layer was formed on the surface of the Si-Cu film evidenced by *ex-situ* attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) and XPS studies.¹⁸ The SEI layer is found to be composed of organic and inorganic compounds that are the decomposition products of PYR₁₃ cation and TFSI anion, and effectively passivate the electrode surface during initial cycling. Formation of a stable SEI layer leads to an excellent capacity retention 98% of the maximum discharge capacity, delivering discharge capacities of >1620 mAhg⁻¹ over 200 cycles. The data contribute to a basic understanding of SEI formation and composition responsible for

the cycling performance of Si-based alloy anodes in ionic liquid electrolyte-based rechargeable lithium batteries.¹⁰

More recently, Piper *et al.*¹⁶ studied the 1.2 M LiFSI in PYR₁₃FSI and 0.6 M LiTFSI in PYR₁₃TFSI ionic liquid electrolytes on the Si-based nanocomposite electrode rather than thin-film electrode. The cycling performances of the Li half cells were directly compared with the commercial EC/DEC (1.0 M LiPF₆) electrolyte, demonstrating the exceptional cycling stability of the nSi-cPAN anodes in FSI anion-based ILs and their unprecedented Coulombic efficiency (CE) of 99.97% in 200 cycles in the PYR13FSI system. The unparalleled CEs of the Si-PYR13FSI system are attributed to the formation of a highly stable SEI by the decomposition product of FSI anion, which mitigates the continuous SEI formation experienced in organic electrolyte.

Superior cycling performance of 1.2 M LiFSI in PYR₁₃FSI was also obtained for LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂/Si full-cells, attributed to the high half-cell CEs, with an average irreversible charge loss of just 0.076% for the first 100 cycles (Figure 4(a)) followed by negligible Li consumption, providing an average full-cell charge capacity of 110.98 mAh g⁻¹ at a rate of C/2. To further investigate the SEI stability of the Si-PYR13FSI system, a full-cell was cycled for longevity with a brief rate study. Figure 4(b) depicts the nSi-cPAN/PYR13FSI (1.2 M LiFSI)/L333 cell run for 1,000 cycles delivering 107.33, 74.70 and 58.26 mAh/g at rates of 1C, 4C and 6C, respectively.

Figure 4. Full-cell electrochemical performance of Si-PAN/L333 with PYR₁₃FSI versus EC/DEC electrolyte systems. (a) Specific charge capacities and coulombic efficiencies of nSi-PAN/L333 full-cells assembled with PYR₁₃FSI (1.2M LiFSI) and conventional EC/DEC (1M LiPF₆) electrolytes. (b) nSi-PAN/PYR₁₃FSI/L333 full-cell rate study and long-term cycling. Cycling was carried out at room temperature in 2032 coin-type half-cells operated between 2.0 and 4.15 V (versus Li/Li⁺).¹⁹ (Reproduced with permission from Nature Publishing Group)

As an analogue of pyrrolidinium, the piperidinium based ionic liquids was also studied in a full cell comprising of LiCoO₂ cathode and Si anode. Preliminary studies on 1-methyl-1-propylpiperidinium (PP₁₃) bis(trifluoromethylsulfonyl)imide (TFSI) yielded 3000 mAh/g in half-cells and only suffered from moderate capacity fading.²⁰ This discovery was followed by a

comparative investigation performed with PP₁₃FSI, PP₁₃TFSI, and imidazolium based ionic liquid EMIFSI and EMITFSI using LaSi₂/Si composite anode.²¹ Despite of the improved performance of LaSi₂/Si composite anode over neat Si anode, PP₁₃FSI was identified as the best among all the ILs, with discharge capacity of 800 mAh/g after 250 cycles. More studies were performed on effects of cation structures on the Si anode by introduction of hydrophilic and hydrophobic substituents onto the nitrogen center, e.g., 1-((2-methoxyethoxy)methyl)-1-methylpiperidinium (PP_{1MEM}) and 1-hexyl-1-methylpiperidinium (PP₁₆), respectively.²² Raman analysis and electrochemical impedance measurements revealed that PP_{1MEM} cation played a role reducing the interaction between Li⁺ and TFSI anions, and that Li-ion transfer at the electrode–electrolyte interface in PP_{1MEM}-TFSI was remarkably improved compared with PP₁₆-TFSI. These results indicate that the excellent performances obtained in PP_{1MEM}-TFSI originate from a smooth Li-insertion into Si electrode. Functionalization of the cation structure is effective approach in improving the electrode performance.

Other ionic liquid electrolytes including imidazolium based and ammonium based were also investigated. The widely studied imidazolium ionic liquids are 1-ethyl-3-methylimidazolium (EMI) bis(fluorosulfonyl)imide (FSI) and EMITFSI in LIBs with Si composite anode.²³ While ILs based on FSI anion offered reversible capacity for a Si composite anode without any solvent, ILs based on TFSI anion showed no reversible capacity at all. Chakrapani *et al.* reported that ILs based on butyltrimethylammonium (BTMA) cation and TFSI anion delivered higher discharge capacity for Si nanowire anode.²⁴ Discharge capacity up to 2000 mAh/g was documented after 50 cycles with CE of 97%. This discovery readdressed the significance of quaternary ammonium (QA) ionic liquids in LIBs with Si anode.

Table 1 summarized and compared the electrochemical properties of all the ionic liquid electrolytes for lithium-ion battery with Si anode reported in the literature.

Other electrolytes

Polymer electrolytes are complexes formed by polymers capable of solvating ions of metal salts. The most representative examples are those involving polyethylene oxide (PEO), and lithium metal salts (LiX with X=PF₆, TFSI, ClO₄).¹⁵ Although widely studied in LIBs with graphite anode, there are only few reports on polymer electrolyte for Si anode. Haruta *et al.* recently reported an oligomeric PEO electrolyte of tetraethylene glycol dimethyl ether complexed with LiTFSI. The complex shows high ionic conductivity and is capable of forming SEI in the presence of FEC on Si anode.²⁵

Due to their low ambient conductivity, PEO based polymer electrolytes have a limited application in LIBs. Alternative, more conductive gel-type polymer electrolytes, GPEs, appear to be a promising choice. Bok *et al.* developed a GPE via thermally initiated free-radical crosslinking reaction of ethoxylated trimethylolpropane triacrylate (ETPTA) in the presence of EC/DEC containing 10 wt% FEC.²⁶ The specific capacity was over 2000 mAh/g with capacity retention up to 92 % after 100 cycles when the cell was fabricated with mesoporous silicon anode. The internal stress induced by volume expansion of silicon was partially alleviated by the presence of GPE and mesoporous structure of silicon. Although intense efforts had been made in

the development of polymer electrolytes for LIBs with Si anode, the overall performance still needs to be improved towards practical application in full cells.

Fluoroethylene carbonate (FEC) additive

Figure 5. Chemical structures of studied electrolyte additives for Si anode.

Fluoroethylene carbonate (FEC) (structure shown in Figure 5) has been found to be the most effective electrolyte additive for silicon anode. A few percentage of FEC in the conventional carbonate electrolyte significantly improves the electrochemical performance of silicon anode. Studies on FEC additive were initiated by Choi and his colleagues in discovering improved performance with 200-nm Si thin-film anode.²⁷ The effectiveness of this additive in promoting half-cell discharge capacity retention and Coulombic efficiency was rationalized by smooth morphology evolution and composition analysis via scanning electron microscopy (SEM) and XPS. In the presence of 3 wt% FEC in EC:DEC (3:7 in volume) containing 1.3 M LiPF₆, the

initial Coulombic efficiency and discharge capacity retention were promoted to 88.7 % and 88.5 % at 80 cycles from 87.8 % and 67.9 %, respectively.

More recently, performance of FEC (20 wt% in DMC containing 1 M LiPF₆) was also demonstrated in LIBs with Si film anode and LiNi_{0.5}Mn_{1.5}O₄ cathode, and compared to that of EC:DMC (1:1 in mass containing 1 M LiPF₆).²⁸ The amorphous Si anodes with thickness of ~ 6 μm were deposited onto current collector via dc magnetron sputtering. While EC and FEC could both contribute to columnar morphology on the thick film, FEC outstood by preventing isolated columns from propagation and subsequent exfoliation. Capacity retention was up to 92.2 % after 200 cycles, 88.5% after 300 cycles and 74.2% after 500 cycles, as shown in Figure 6(a). This improvement was also confirmed by X-ray diffraction (XRD) analysis (Figure 6(b))²⁹ and XPS (Figure 6(c))³⁰. The exact chemical composition of the SEI is not fully understood, however, the improved performance was always associated with the presence of decomposition product of LiF. The effectiveness of FEC at improving the Coulombic efficiency and capacity retention is due to fluoride ion formation from reduction of the electrolyte, which leads to the chemical attack of any silicon-oxide surface passivation layers and the formation of a kinetically stable SEI comprising predominately lithium fluoride and lithium oxide. Therefore, an electrochemical reaction of FEC was proposed following a one-electron lithium-assisted reductive decomposition mechanism as show in Figure 7.³⁰

Figure 6. (a) Typical curves of charge (full dots) and discharge (hollow dots) capacity vs. cycle number obtained upon galvanostatic cycling of Si|LiNi_{0.5}Mn_{1.5}O₄ cells at a current rate of C/8, referred to the cathode;²⁸ (b) XRD profiles of the cycled Si anodes with CMC/SBR depending on FEC addition;²⁹ (c) comparison of relative compositions of SEI on thin-film Si anode during 1st cycles of charge and discharge and after 100 cycles in half-cells.³⁰ (Reproduced with permission from Elsevier, PCCP Owner Societies and American Chemical Society for a, b and c, respectively)

Figure 7. Reaction 1: electroreduction of fluoroethylene carbonate to form lithium fluoride, lithium carbonate, and ethylene; Reaction 2: electroreduction of fluoroethylene carbonate to form lithium fluoride, methylenedioxy ion (or alternately carbon dioxide), and lithium ethoxide.³⁰ (Reproduced with permission from American Chemical Society)

Cell performance improvement was also observed for a LIBs with a pre-lithiated Si film anode (thickness: $\sim 3 \mu\text{m}$) coupled with TiS_2 cathode.³¹ From morphological perspective, typical features of the columnar amorphous structure of the cycled Si electrodes in FEC based solutions can be observed after >1000 cycles, and are similar to the morphology of the pristine electrode while thicker layers were always present on the Si electrodes surface when EC-based electrolyte was used (Figure 8).

Figure 8. Morphology of pristine amorphous Si electrode (a) with cross section view (left inset), and amorphous Si anodes after the (b) 1st, (c) 575th, and (d) 1227th cycles after being cycled in FEC-containing electrolyte, and after the (e) 1st and the (f) 180th cycles, in a standard FEC-free electrolyte.³¹ (Reproduced with permission from Electrochemical Society)

LIBs with Si nanowires³² and Si nanoparticles^{29, 33} fabricated via more advanced techniques were recently analyzed in the presence of FEC and achieved promising results. These results have been further rationalized by varied experimental methods³⁴⁻³⁵ and simulation efforts³⁶⁻³⁷. Numerous studies compared the performance of varied additives to that of FEC and used FEC as a model compound for baseline calibration.^{33, 38-40}

3,4-Difluoroethylene carbonate (DFEC), a derivative compound of FEC, was also evaluated as an electrolyte additive on thin-film Si anode.⁴¹ Although inferior to FEC, DFEC still managed to deliver a limiting capacity of 600 mAh/g for over 1400 cycles at 1C rate.

Silane additives

The surface of silicon consists of silicon oxide ($-\text{Si}-\text{O}-\text{Si}-$) and silanol ($-\text{Si}-\text{OH}$) which can reductively react with lithium ion, giving rise to irreversible capacity loss. Surface modification by a group of alkoxy silane additives (Figure 5) has been studied. Effects of trimethoxy methyl silane additive on SEI formation on nanocrystalline Si thin-film electrode in 1 M LiPF_6 /ethylene carbonate:diethyl carbonate 1:1 electrolyte were studied using ATR-FTIR. It was found that silane effectively protected the Si surface by formation of a stable SEI layer composed of organics with alkyl carbonate and carboxylic acid metal salt functionalities, and PF-containing species, leading to a stable cycling at 0.1–1.5 V vs Li/Li^+ delivering 2400 mAh/g over 200 cycles. The film surface obtained after cycling without silane, however, showed primarily PF-containing species, which is responsible for inefficient passivation of the Si surface, resulting in a rapid capacity fade. Silane additives with multi-alkoxy substitutions were also studied to analyze the effect of substituents.⁴² Alkoxysilane functionalities were confirmed to be effective in construction of stable SEI in LIBs with Si anode.

Other additives

Vinylene carbonate (VC) was inspired by prior reports in LIBs with graphite anode and identified as an effective additive for LIBs with Si thin-film anode.⁴³⁻⁴⁴ In the presence of 1 wt% VC in EC:DMC (1:1 in volume) containing 1 M LiPF_6 , the initial Coulombic efficiency was promoted to 72.5 % from 67.9 %. The reversible capacity in VC-containing electrolyte was stable at ~ 2000 mAh/g even up to 200 cycles, and gradually decayed to more than 500 mAh/g after 500 cycles. The morphology of SEI layer from VC-containing electrolyte was smooth and

uniform as observed via SEM, and the impedance remained invariant with respect to cycle number as evidenced by EIS. The elemental and chemical compositions of SEI layer from VC-containing electrolyte were qualitatively determined by EDX and FTIR, and further quantified by XPS. Oxidation of Si was considered primarily in Li^+ insertion process with EC when SEI layer was broken in the valleys as captured by SEM. Artificial SEI can also be constructed via atomic layer deposition (ALD) of reduced graphene oxide (rGO) and carbon nanotube (CNT) onto Si nanoparticles, and contributed to further improvement in addition to VC.⁴⁵

Exceptional electrochemical performance of 1,3-dioxolane (DOL) was recognized on LIBs with Si nanowire anode, and could be used with solely LiTFSI or in conjunction with LiNO_3 .⁴⁶ Formation of flexible and elastic SEI layers was considered as the polymerization product of DOL, accommodating the volume change of anode during cycling. The discharge capacity with DOL containing 1 M LiTFSI and 0.1M LiNO_3 was 1200 mAh/g even after 1000 cycles. Comparative studies confirmed that DOL/ LiNO_3 delivered the best cycling performance in LIBs with porous Si/C nanocomposite anode.⁴⁷

Succinic anhydride (SA) was discovered by recognition of its superior electrochemical performance over amorphous Si film anode.⁴⁸ The discharge capacity was ~ 1800 mAh/g after 100 cycles, which was attributed to suppressed decomposition of LiPF_6 on Si surface.

Later studies of SA on LIBs with Si/C nanowire anode fabricated via electrospin confirmed its effectiveness in EC:DEC:DMC (1:1:1 in volume) containing 1 M LiPF_6 .⁴⁹ In addition, by careful control over state-of-charge condition at 70 % in the presence of a polymer binder, capacity fading rate could be reduced significantly, and discharge capacity could be maintained over 600 mAh/g after 150 cycles.

Similar to FEC, research of lithium bis(oxalato)borate (LiBOB) in LIBs with Si anode was initiated by transplanting from its application in LIBs with graphite anode.⁵⁰ Performance of ED/DEC (3:7 in volume) containing 0.7 M LiBOB was evaluated in LIBs with Si thin-film anode, and compared to that containing 1.3 M LiPF₆. LiBOB was confirmed to be effective in reducing lithium consumption by trapping lithium in the Si anode and constructing an SEI layer. It was proposed that the reductive decomposition of LiBOB proceeded relatively fast with respect to LiPF₆ and thus suppressed the electrochemical reactions of lithiated Si with electrolyte and the consequent formation of cracks on Si anode. Isolated (inactive) Si particles could therefore be limited by maintaining the integrity of thin-film anode. The initial Coulombic efficiency and discharge capacity retention in the presence of 0.7 M LiBOB were promoted to 88.1 % and 83.5 % at 100 cycles, compared to 87.8 % and 50.8 %, respectively for 1.3 M LiPF₆ electrolyte.

Lithium difluoro(oxalato)borate (LiDFOB) was also examined, and delivered slightly better performance in half-cell LIBs with Si film anode compared to its analog LiBOB.³⁸

Tris(pentafluorophenyl) borane (TPFPB) (Figure 5) was later demonstrated as an effective additive for LIBs with Si thin-film anode (thickness: ~ 40 nm).⁵¹ The performance of LIBs in the presence of TPFPB was very much dependent on additive concentration, and comparable to FEC and SA but slightly superior to VC. In the presence of 5 wt% TPFPB in EC:DEC (1:1 in volume) containing 1 M LiClO₄, the discharge capacity was 1808.6 mAh/g with capacity retention of 87.2 % after 100 cycles. Perfluoroglutaric acid diethyl ester (PF₅M₂) was evaluated against LIBs with Si film anode, although the conductivity was low compared to conventional electrolytes.⁵²

Future direction

In the present review article, the most recent advances in the electrolyte and electrolyte additive for LIBs with Si anode were reviewed systematically. Despite the advantages of the silicon materials, a number of challenges impede its commercialization. While the commercialized graphite electrode expands 10–13% during lithium intercalation, silicon expansion amounts to nearly 300%, generating structural degradation and instability of the all-important SEI. Such instabilities ultimately shorten the battery life to inadequate levels. Degradation of the active material can be mitigated by incorporating materials with dimensions of less than 150 nm; however, research has not yet developed a practical solution to expansion-induced breaking of conductive channels, active material isolation and continuous SEI reformation. Building a robust SEI on the silicon anode electrochemically or through a surface modification is pivotal for the improved performance of Si anode. Ultimately, a combinatorial approach involving a mechanically resilient electrode architecture coupled with an electrolyte/additive capable of forming a stable SEI, is the most promising strategy to integrate structural integrity with stable interfacial chemistry.

Furthermore, the current understanding of the lithium reaction mechanisms on the surface of Si anodes employs assumptions about mechanisms and material properties that are not fully validated. Therefore, it is critically important to quantitatively explore the lithiation and delithiation processes in operando mode (*in-situ* SEM, transmission electron microscopy (TEM) and XRD) to provide invaluable information for designing functional electrolyte and additives for Si anode. A reverse-engineered approach to fabricate stable SEI via *ex-situ* formation (polymerization, encapsulation, etc.) and rational design of binder materials are envisioned to deliver better performance of LIBs with Si anode.

Table 1. Cell Performance of LIBs with Si anode with ionic liquid electrolytes

Cell architecture	Anode fabrication	Anode Form	Binder	Electrolyte	Initial Capacity, mAh/g	Initial Coulombic Efficiency	Coulombic Efficiency, (Cycle #)	Capacity (mAh/g) or Capacity Retention (Cycle #)	Cutoff voltage (V)	Rate (C)	Ref.
Si Li	DC magnetron sputtering	Thin film, 100 nm		1 M LiTFSI in PP ₁₃ TFSI				3000 (38)		0.0625	²⁰
Si LiCoO ₂	DC magnetron sputtering	Thin film, 100 nm		1 M LiTFSI in PP ₁₃ TFSI				1000 (32)	3-4.3	0.1	²⁰
(Si/Cu) Li	Pulsed laser deposition	Thin film, 60 nm		1 M LiTFSI in PYR ₁₃ TFSI				1500 (200)	0.1-1.5		¹⁸
(Si/Ni/C) Li	Mechanical milling	Fine powder	PVDF	0.3 mol/kg LiTFSI in EMIFSI			100 (20)	900 (20)	0.005-1.5		²³
Si Li	Chemical vapor deposition	Fiber, 80-100 nm		1 M LiTFSI in BTMATFSI with 10 wt% PC	1800	91	93 (50)	1000 (50)	0.001-2.0	0.05	²⁴
(Si/Cu) Li	Pulsed laser deposition	Thin film, 60 nm		1 M LiTFSI in PYR ₁₃ TFSI	1650	69			0.1-1.5		⁵³
(LaSi ₂ /Si) Li	Gas deposition	Thin film, 2 - 4μm		1 M LiTFSI in PP ₁₃ FSl	3200			2900 (250)	0.005-2.0	0.25	²¹
(LaSi ₂ /Si) Li	Gas deposition	Thin film, 2 - 4μm		1 M LiTFSI in PP ₁₃ TFSI	1500			1500 (250)	0.005-2.0	0.25	²¹
Si Li	Gas deposition	Thin film, 2μm		1 M LiTFSI in PP _{1MEM} TFSI	2670	85	100 (100)	1000 (100)	0.005-2.0	0.12	²²
Si Li	Gas deposition	Thin film, 2μm		1 M LiTFSI in PP ₁₆ TFSI	1770	70	99 (100)	1000 (100)	0.005-2.0	0.12	²²

cSi Li ^a	Mechanical milling	Particles, 50 nm	cPAN ^b	1.2 M LiFSI in PYR ₁₃ FSI	>2000		100 (200)	76.7 % (100)	0.05-1.0	0.1	¹⁹
cSi Li	Mechanical milling	Particles, 50 nm	cPAN	0.6 M LiTFSI in PYR ₁₃ TFSI	1000	80	75 (100)		0.05-1.0	0.1	¹⁹
cSi Li	Mechanical milling	Particles, 50 nm	cPAN	1.2 M LiFSI in EMIFSI	2500	94	100 (100)	2000 (100)	0.05-1.0	0.1	¹⁹
cSi NMC111	Mechanical milling	Particles, 50 nm	cPAN	1.2 M LiFSI in PYR ₁₃ FSI	2000	100	100 (1000)	50% (1000)	2-4.15	0.5	¹⁹

a. cSi, crystalline silicon.

b. cPAN, cyclized polyacrylonitrile.

Acknowledgements

This research is supported by the U.S. Department of Energy, Vehicle Technologies Office. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC, under contract DE-AC02-06CH11357.

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