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DESIGN AND OPTIMIZATION OF LITHIUM ION BATTERY FOR HIGH TEMPERATURE APPLICATIONS

by

KHALID ABABTAH

DISSERTATION

Submitted to the Graduate School

of Wayne State University,

Detroit, Michigan

in partial fulfillment of requirements

for the degree of

DOCTOR OF PHILOSOPHY

2016

MAJOR: Mechanical Engineering

Approved By:

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Advisor Date

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DEDICATION

To My Lovely Parents — Abdullatife and Nedaa, My Wife — Maha and children —

Faris and Aseel,

To my sisters and brothers — Yasser, Hind, Majed, Hajar, and Mohammed
ACKNOWLEDGEMENTS

I would like to express my deep gratitude and special appreciation to my supervisor, Dr. Leela Mohana Reddy Arava, for his great support and constant inspiration throughout this study. I always appreciate his vast knowledge in many areas (e.g., battery, and so on) and his great assistance and invaluable guidance in writing this dissertation. He has always inspired me to become an independent researcher and helped me notice the power of critical reasoning. I also would like to thank my committee members, Dr. Golam Newaz, Dr. Simon Ng, and Dr. Guru Dinda for their assistance and support in the preparation of this study. My sincere thanks are given to Dr. Babu Ganguli for his considerable support in performing experiments and analysis.

Great thanks to Dr Hesham Alsalem for his good suggestions. He is a true brother and a supporter. Also special thanks to Abdualrazzag Sawas for uncountable help and support. I would like to thank Nirul Masurkar for his great assistance in the clean room lab. He was so helpful and patient to answer all my questions. Thanks to Dr. Naresh Thangavel and Deepesh Gopalakrishnan for their great help in proofreading my papers and dissertation.
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CHAPTER 1 INTRODUCTION

Batteries for some specific applications such as downhole oil drilling, surgical tools, automotive, mining, defense, and power generation have to withstand temperatures greater than 75 °C (Figure 1.1). For example, temperature range in an oil reservoir is between 60 to 120 °C. At present, lithium thionyl chloride (Li-SOCl₂) based chemistries are heavily used in the form of primary batteries for a majority of these applications (see Table 1.1 for the state-of-the-art of high temperature batteries). Though these primary batteries can perform reasonably well at these severe conditions, changing the batteries after each discharge has practical constraints, and discarding raw materials is not economical. Moreover, Li-SOCl₂ is a hazardous material (HAZMAT) due to the toxicity of the liquid SOCl₂ when in contact with water. Hence, use of secondary batteries with a relatively limited cycle life for such applications will have a huge impact on both the environment and the economy. The celebrated and high energy density Li-ion batteries (LIBs) thus appear to be a promising alternative, but performances of these LIBs with conventional organic solvents-based electrolytes pose a safety concern to operate beyond 60 °C. The employed volatile electrolytes and unstable charged graphite anode in current LIBs lead catastrophic failure under heat. Specifically, the use of carbonate solvents such as ethylene carbonate (EC), dimethyl carbonate (DMC), or diethyl carbonate (DEC) restricts battery operation to less than 60 °C due to their volatile and highly flammable nature. Further, these solvents are highly reactive with Li salts, like lithium hexafluorophosphate (LiPF₆), which form a resistive film on the electrode surface affording poor cycle life.
Moreover, these side reactions become more vigorous at higher temperatures above 60 °C as the rate of chemical reaction between the dissolved lithium salt and electrolyte solvent increases. Thus, there is an unmet need for alternative electrolytes with superior thermal and chemical stability to expand the use of rechargeable LIBs to wider working temperatures above 75 °C without a compromise on electrochemical performance. Hence, the proposed research is based on the central objectives that use room-temperature ionic liquids-based electrolytes in conjunction with thermally stable electrodes would lead to the realization of rechargeable LIBs for high temperature applications.

Room temperature ionic liquids (RTILs), which are liquids over a wide range of temperatures, possess high thermal and chemical stability and are characterized by negligible vapor pressure, non-flammability, as well as a broad electrochemical window.
(greater than 4V). However, several RTILs suffer from low or negligible Li-ion conductivity at room temperature and electrode compatibility at high temperature (cations of RTILs get intercalated in conventional graphite anode at high temperatures). Hence, development of high temperature LIBs involves a selection of appropriate RTILs, their modification to achieve reasonable Li-ion conductivity at RT without compromising on thermal stability, and also design of alternative electrodes.

**Table 1.1** State-of-the-art of LIB for high temperature application

<table>
<thead>
<tr>
<th>Providers</th>
<th>Safety Reliability</th>
<th>Rechargeability</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochem</td>
<td>Lithium thionyl chloride (Corrosive, explosive, HAZMAT)</td>
<td>No</td>
<td>&lt; 150 °C</td>
</tr>
<tr>
<td>Saft</td>
<td>Lithium thionyl chloride (corrosive, explosive, HAZMAT)</td>
<td>No</td>
<td>&lt; 150 °C</td>
</tr>
<tr>
<td>Seeo</td>
<td>Solid polymer electrolyte (no flammable or volatile components)</td>
<td>Yes</td>
<td>&lt; 70 °C</td>
</tr>
<tr>
<td>Seiko</td>
<td>Lithium cobalt oxide cathode and Lithium titanate anode</td>
<td>Yes</td>
<td>&lt; 85 °C</td>
</tr>
<tr>
<td>Tadiran</td>
<td>Lithium thionyl chloride (Corrosive, explosive, HAZMAT)</td>
<td>No</td>
<td>&lt; 130 °C</td>
</tr>
</tbody>
</table>
CHAPTER 2 BACKGROUND AND LITERATURE REVIEW

2.1 Current battery options for high temperature applications

2.1.1 Non-rechargeable batteries

Among the currently available energy storage technologies, the Li-thionyl chloride (Li/SOCl₂) battery is one of the heavily used primary cells for high temperature applications (up to 150 °C) \(^1\). It is the most common battery used in the oil and gas industry \(^{10,11}\). In this system, Li metal is used as anode, lithium perchlorate (LiClO₄) dissolved in thionyl chloride (SOCl₂), which acts as catholyte (cathode + electrolyte), \(^{12,13}\) and polytetrafluoro ethylene (PTFE)-bonded porous carbon as counter electrode. During discharge, oxidation takes place at Li anode, electrons flow through external circuit to provide power, and at the same time Li-ions move from anode to catholyte wherein SOCl₂ is disproportionate as follows:

At anode: \( \text{Li} \rightarrow \text{Li}^+ + e^- \)

At cathode: \( 4\text{Li}^+ + 4e^- + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S} \)

Overall reaction: \( 4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S} \)

These batteries can tackle severe conditions such as drilling operation and can survive up to 150 °C. However, Li metal is used in this kind of battery, which is considered a highly reactive material that can lead to fire or explosion in case of a thermal runaway, especially under high discharge rates \(^{12-14}\). The other drawback of these batteries is non-rechargeability, which limits their use in many applications.

Lithium sulfur dioxide (Li-SO₂) primary battery is one of the commonly used types in military and aerospace technologies. In this system, SO₂ coupled with carbon as cathode and liquid SO₂ mixed with acetonitrile (ACN) as electrolyte can produce high
power and stable capacity for a temperature range of -55 to 60 °C. This system needs two atmospheres of pressure in order to maintain the electrolyte in a liquid state and should be vented to avoid pressure build-up. Moreover, the energy density is 50% less than Li/SOCl₂. Another primary battery is lithium manganese dioxide (Li/MnO₂), where lithium perchlorate (LiClO₄) is mixed with propylene carbonate (PC) and dimethoxyethane (DME) as electrolyte (temperature range -30 to 60 °C). This system suffers from poor performance above 60 °C and a high self-discharge rate.

The lithium copper oxide (Li/CuO) is a primary battery that can operate at a temperature range of -30 to 150 °C. The electrolyte consists of LiClO₄ dissolved into dioxolane (DOL) and mixed with polyethylene oxide (PEO) and dimethyl sulfone (DMSO₂). The drawback of this system is the high difference between the open circuit and the nominal voltage. Hence, the Li/CuO battery was later replaced with lithium iron sulfide (Li/FeS₂), which uses molten salts as electrolyte that can operate at a temperature range of 400 to 500 °C. A higher range of temperature (up to 600 °C) was achieved by using a new design of lithium chloride batteries (Li/Cl₂). In this system, molten lithium chloride was used as electrolyte and a carbon full of chloride gas and liquid lithium as electrodes.

2.1.2 Rechargeable batteries

Recent attempts at using rechargeable LIB concepts for these applications could only result in reaching temperatures up to 55 °C, with a combination of lithium titanate (Li₄Ti₅O₁₂) as anode, lithium manganese oxide (LiMn₂O₄) as cathode, and 1.2 M LiPF₆ in propylene carbonate - ethyl methyl carbonate (3:7 in volume) as electrolyte. Choosing Li₄Ti₅O₁₂ as an alternative to conventional graphite anode, though it addresses stability
issues of SEI, results in a relatively low cell voltage (~2.5 V) due to high lithiation potential of anode (1.55 V)\textsuperscript{2,19,20}. Further, it is found that Mn undergoes a dissolution reaction with electrolytes, resulting in poor cycle life and columbic efficiency at high temperatures\textsuperscript{19,21,9,18,22}.

Sodium sulfur (Na-S) batteries are widely used in industry for extremely high temperature application, such as grid energy storage\textsuperscript{23,24}. This system works at temperature range of 400 to 700 °C, where solid ceramic and sodium-β-alumina (NaAl\textsubscript{11}O\textsubscript{17}) are used as electrolyte, molten sodium as anode and molten sulfur as cathode\textsuperscript{25}. In spite of the high energy density (150 W h kg\textsuperscript{-1}), the dendritic sodium, which forms in Na-S battery makes it a safety issue. Hence, the zeolite Battery Africa (ZEBRA) battery was reported, which uses molten sodium tetrachloroaluminate (NaAlCl\textsubscript{4})/sodium-β-alumina and molten sodium as electrolyte, molten nickel and nickel chloride (Ni/NiCl) as anode and cathode respectively (operation temperature range of 270 to 350 °C)\textsuperscript{26}.

Liquid–metal battery is another extreme temperature battery that can work in the range of 500 to 1000 °C in order to keep the electrolyte in liquid form. Cathode and anode in this system are also in liquid form during operation\textsuperscript{27,28}. One negative point about this system is the corrosion of all the cell components and packaging materials due to the high operation temperature and high reactivity of the electrodes.

2.2 Limitations of conventional LIBs for using high-temperature application

Conventional LIBs employ non-aqueous electrolytes based on organic solvents, like ethylene carbonate (EC), dimethyl carbonate (DMC), or diethyl carbonate (DEC), pose a safety concern due to their volatile and highly flammable nature (low boiling
points or low flash points)\textsuperscript{2, 3, 12, 29-32}. In addition, the salt, such as LiPF\textsubscript{6} being a critical component of the electrolyte system, is thermally unstable due to high reactivity of its decomposed products (LiF↓ and PF\textsubscript{5}↑) with the organic solvents\textsuperscript{33, 34}. The effect of LiPF\textsubscript{6} salt on the gas generation during battery operation has been understood using accelerating rate calorimetry (ARC) technique. Actually, the gas production originates from low-boiling organic electrolyte solvent decomposition when it reacts with salt and its decomposition products, especially with highly reactive Lewis acid PF\textsubscript{5}. Further, reaction of PF\textsubscript{5} with trace amounts of water in the electrolyte produces strong acids such as HF, which triggers the solvent decomposition, electrode depletion, and gas generation\textsuperscript{35}. This phenomenon is more sensitive to temperature, which may lead to further thermal runaway. Hence, thermal stability of these organic solvent-based electrolytes mixed with LiPF\textsubscript{6} salts are unacceptable at temperatures above 60 °C\textsuperscript{29, 30, 34, 36}.

Another important factor to be considered for high temperature LIBs is stability of solid electrolyte interphase (SEI), as it is one of fundamental sources for capacity fade. SEI typically forms as a thin passivation layer results from decomposition products of electrolyte solvent and salt at the negative electrode. Such a formed SEI stability is critical for LIB performance as it further prevents the electrolyte depletion and protects the electrode against solvent decomposition. The nature of SEI is mostly dependent on the type of electrolyte solvents, salts, and the rate or mode of formation cycle. Unfortunately, the SEI tends to decompose at anode, which leads to parasitic reactions with temperatures particularly above 60 °C\textsuperscript{19}. Thus, in order to use LIBs at high
temperature applications, organic-based electrolyte solvents and LiPF₆ salt need to be replaced with thermally stable electrolyte systems capable of forming stable SEI.

### 2.3 Prior attempts at using novel electrolytes for HT batteries

In general, electrolytes for LIBs are classified into three categories viz.: organic liquids, polymer, and solid-state electrolytes. Organic electrolytes are completely ruled out for presently targeted applications due to their volatility. On the other hand, there are two other options of electrolytes rather than the liquid type for LIBs, which are polymer and ceramic electrolytes. Polymer electrolytes can be either a dry solid polymer electrolyte which serves as a solvent or gelled polymers when combined with conventional electrolytes. Poly (ethylene oxide) (PEO), which is considered a dry polymer, has poor ionic conductivity in the range of $10^{-5}$ S cm$^{-1}$ due to the sluggish conduction mechanism of the Li-ion hosted by the polymer chain. Hence, PEO’s ionic conductivity is far below the minimum conductivity ($10^{-3}$ to $10^{-2}$ S cm$^{-1}$) needed for a LIB. The other promising type is the gel polymer electrolyte (GPE), which utilizes conventional organic electrolytes to form gel and improve the ionic conductivity at ambient temperatures to display comparable conductivity as liquid electrolyte. However, presence of organic solvents in polymer electrolytes would again pose safety concerns at high temperature, thus limiting their further use in targeted applications.

On the contrary, the feasible option for high-temperature battery applications is typically the ceramic-based electrolytes as they exhibit high stability against chemical reactions with the electrodes and are generally leak-proof (i.e. safe). Moreover, they have a wide electrochemical stability window and high thermal stability (up to 200 °C) due to their high melting points and robustness. Na super conductors (NASICON) are
well-known ceramic electrolytes that showed high conductivity of \( (10^{-3} \text{ to } 10^{-2} \text{ S cm}^{-1}) \) at room temperature \(^{42,43}\). However, using ceramic electrolyte in batteries is limited to thin films (\(<1 \mu\text{m} \text{ thick})\), where the electrolyte resistance is minimized. In addition, such thin films use sputtering techniques, which are complicated to produce on a large or commercial scale \(^1\). Further, these ceramic electrolytes have SEI compatibility with electrodes, which leads to increase in the internal resistance.

During the last decade, room temperature ionic liquids (RTILs) have been studied extensively as electrolytes for Li-ion batteries due to their negligible vapor pressure and high boiling points. They are also promising for high-temperature LIBs due to their wide electrochemical potential window and structural stability across a large temperature range \(^{36,44-50}\). However, formulating desirable ionic liquid-based electrolytes is challenging because of their poor ionic conductivity, inadequacy to form stable SEI on typical Li-ion battery electrodes, stability issues toward anodic potential, etc. It is well-known that ionic liquid is a combination of large cation mostly based on organic compounds, which carry a positive charge and relatively small anions with negative charge. Towards this direction, quaternary ammonium-based cation with either heterocyclic structure or without conjugation have been considered as electrolytes for Li-ion battery applications \(^{51}\). In addition, Li-salt has to be dissolved to conduct Li-ions effectively between cathode and anode of battery \(^{51}\). Among various cations, imidazolium-based cations have gained prime importance due to their tendency to form low-viscous ionic liquids with a wide range of anions and salts \(^7\).

Initially, imidazolium-based electrolytes are considered in LIB for example, the electrolyte consists of ethylmethyl imidazolium bis (trifluoromethanesulfonylimide) with
TFSI has been successfully demonstrated for the feasibility \(^7, ^{52}\). However, these electrolytes are reported to be unstable towards anodic potential (\(<1\ \text{V vs. Li/Li}^+\)) and have limitations in forming protective SEI \(^7, ^{53}\). Recently, an introduction of new combinations based on cation structures, especially pyrrolidinum, piperidinium and its derivatives, attract greatly due to their capability to expand electrochemical stability. Pyrrolidinum-based RTILs are reported to provide comparatively high conductivity (>10\(^{-4}\) S cm\(^{-1}\)), high Li\(^+\) transference number, and low viscosity than that of its imidazolium counterpart \(^7, ^{54}\). Adversely, the lithium dendrite growth on anode, especially at high current rates and long cycling, is still a concern \(^{55, 56}\). Another major drawback of these novel electrolytes is their poor formation of SEI with respective LIB anodes. For example, Seki et al studied LiTFSI in 1-methyl-1-propyl pyrrolidinum bis (fluorosulfonyl) imide (Py13-FSI) extensively as an electrolyte for LIBs; however poor reversibility and low-coulombic efficiency (<80 \%) were reported due to its instability on graphitic anode \(^{57}\).

Similarly, heterocyclic cation, resembles pyrrolidinum, i.e., piperidinium-based ionic liquid electrolyte, was also investigated for Li-ion applications \(^{58-60}\). Electrolytes based on both 1-methyl-1-propyl piperidinium bis (fluorosulfonyl) imide and 1-ethyl-1-butyl piperidinium bis (trifluoromethanesulfonyl) imide were studied and showed relatively higher ionic conductivity than other ILs and appreciable electrochemical properties \(^{58, 59}\). In spite of several advantages, piperidinium cation was found to co-intercalate with graphite anodes at 0.5 V, which poses a safety concern when using it for conventional lithium battery configurations \(^7\).
In line with cation, anions are also an essential component, which generally determine the melting point and are equally important to regulate electrochemical stability of ionic liquids. Similar to their counterparts, several anions are reported with their possibility as stable salts in ionic liquid-based electrolytes, such as tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), bis (trifluoromethylsulfonyl) amide (NTf₂⁻), triflate (OTf⁻), and bis (trifluoromethanesulfonyl) imide (TFSI-)⁶¹,⁶². Based on the thermal stability, the [PF₆⁻] and [BF₄⁻] anions have a tendency to decompose and produce hydro-fluoric acid (HF) at a temperature above 60 °C⁶³. Such a formed HF results in an adverse effect on cycle life and capacity of the battery. On the other hand, TFSI⁻ was found to be thermally stable and also has the ability to form stable SEI on anodes⁴⁰.

Moreover, solubility of lithiated TFSI⁻ in ionic liquids is comparatively high due to large dissociation constant. For instance, the synergistic effects of piperidinium cation and imide anion-based ionic liquid electrolytes showed electrochemical stability up to 6 V⁴⁰.

On the other hand, lithium salts also play a crucial role in stabilizing the electrolytes and on overall LIB performance⁶⁴. Various salts are reported such as LiPF₆, (Lithium tetrafluoroborate) LiBF₄, (Lithium bisoxalatoborate) LiBOB, (lithium bistri fluoromethane sulfonimide) LiTFSI etc. Among them, LiPF₆, LiBF₄ and LiBOB⁶⁵ were reported to be thermally stable up to 70 °C ³⁴. However, these salts tend to decompose at a temperature above 70 °C ³⁴ when they are in contact with charged electrodes. Moreover, LiBOB was reported to exhibit very low conductivity of 4.5 mS cm⁻¹ and has limited solubility in carbonate solvents or ILs. Therefore, LiTFSI was thoroughly studied and showed a higher thermal stability (up to 250 °C) than other counterpart salts⁶⁴. In addition LiTFSI showed comparable conductivity to the
commercially used LiPF₆ salt.

2.4 Thermal stability issues of conventional anodes

Commercially used graphite anodes suffer from lithium plating at low lithiation potential. Moreover, the multilayer SEI tends to decompose at temperature above 70 °C. Furthermore, the use of RTILs-based electrolytes has found that the co-intercalation of cations from IL causes poor electrochemical performance. Such co-intercalation of cations of IL in graphite results in structural instability in electrodes and loss of charge neutrality in the electrolyte. Hence, an identification of compatible ionic liquid-based electrolytes with thermally stable electrodes gains utmost importance.

In search of an alternative anode to graphite, Li₄Ti₅O₁₂ (LTO) has been found to be attractive due to its stable capacity, high conductivity, and potential to avoid SEI formation and Li plating. Kalaga et al reported half-cell Li/LTO where PP13-TFSI mixed with dry bentonite clay as electrolyte. The cell showed stable battery performance at 120 °C with ionic conductivity of 3.0 mS cm⁻¹ (Figure 2.1). However, the high lithiation potential of LTO (1.55 V vs Li⁺/Li) anode makes it difficult to achieve high overall cell potential when combined with any current cathode materials. Additionally, LTO has a lower capacity (175 mAh/g) than graphite (372 mAh/g) and poor rate capability.
Figure 2.1 (a) Cycle stability of Li/LTO at 120 °C. (b) rate capability of Li/LTO at 120 °C with different c-rates 66.

Hence, in order to effectively use piperidinium ILs in LIBs for high temperature applications, a non-intercalating anode is required, such as one based on Si, Sn, or Ge. Among various available high capacity anodes, silicon is an attractive material as it eliminates co-intercalation issues along with other attractive features, such as high thermal stability, low lithiation potential (~0.3V vs Li/Li$^+$), and high theoretical capacity (4200 mAh/g) 67.

The main challenge of using silicon for LIBs is the huge volume expansion upon the large amount of Li insertion. During cycling, silicon undergoes around a 400 % volume expansion as a result of the full lithiation of the Si electrode (Li$_{4.4}$Si) 67-69. Large contractions of volume during the delithiation of Si result in stress within the silicon particles 67,70-74. This stress causes fractures and cracks in the electrode, which eventually lead to the pulverization of the electrode during repeated cycling 68. This will lead to the formation of unstable solid electrolyte interphase (SEI). Such a pulverization process results in huge capacity fade due to weak bonding between Si particles and carbon conducting agent 75, 76. Furthermore, the electronic conductivity of Si is relatively low
Li-ion diffusion in silicon electrode is low ($10^{-14}$ to $10^{-13}$ cm$^2$ s$^{-1}$), which limits the use of its full capacity and hampers the rate capability of the silicon electrode. To address these issues, nano Si studies have been reported on silicon to overcome the structural damage of silicon electrodes during cycling.

Nano Si has the tendency to minimize the adverse effects of huge stresses associated with bulk silicon. In general, nano Si morphologies are broadly classified as 0D (nanoparticles), 1D (nanowires and nanotubes), 2D (thin film) and 3D (porous) structures.  

2.4.1 0D (nanoparticles)

Nanoparticles of silicon have great potential to reduce Li-ion transport paths and enable far higher Li-Si alloy/de-alloying rates. Several groups demonstrated the connotation of nano-sized Si on battery performance. For example, Li et al reported that a nano-Si powder as anode with better capacity retention compared to its counterpart bulk Si powder. Nanoparticles allow quick relaxation of stress caused during insertion/extraction of lithium, and these are more resistant to electrode fracture than bulk particles. Misfit stress energy calculations of Li-Si phases reveal that fractures could be minimized by using silicon nanoparticles with diameters less than 10nm. However, in practice, silicon nanoparticles tend to disintegrate each other and peel-off from the current collector during repeated cycling (Figure 2.2). As a result, continuous breaking and formation SEI on silicon when using nanoparticles structure cannot be prevented.
Recently, several polymeric binders have been used as an alternative to conventional poly (vinylidene fluoride) (PVDF) to address the volume changes problem in silicon nanoparticles electrodes during cycling. The functionality, polarity, flexibility, and conductivity of binders are also believed to be crucial factors to stabilize the performance of silicon electrodes. In this regard, Chan et al reported that use of elastomeric polymer binder such as poly (vinylidene fluoride-tetrafluoroethylene-propylene) strongly tethered Si nanoparticles to one another, and the current collector resulted in an improved electrochemical performance. Li et al reported that using a sodium carboxymethyl cellulose (NaCMC) binder would improve the cycling performance of the Si nanoparticles due to its flexibility, elasticity, and strength. Similarly, Kovalenko et al introduced a naturally occurring polysaccharide, i.e. alginate, as a binder for silicon electrodes and demonstrated the enhanced electrochemical properties, such as capacity and rate capability. Such a significant improvement of performance was attributed to weak interactions between binders and electrolytes, which are capable of Li-ion conductivity and forming stable SEI.

**Figure 2.2** Failure mechanism of silicon nanoparticles during charge-discharge
Figure 2.3 a) Traditional nonconductive binder and failure mechanism b) conductive binder and with dual functions which can maintain both electronic and mechanical integrity of the silicon nanoparticles during charge-discharge performance c) two key function groups in poly (9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic acid) (PFFOMB), carbonyl and methylbenzoic ester have been used to modify the polymer. 

On the other hand, conductive polymer-based binders also used by altering their functional groups to improve the overall silicon electrode conductivity and mechanical strength. For instance, Liu et al evaluated the performance of silicon nanoparticles electrode as shown in Figure 2.3. The conductive binder was modified with carbonyl and methylbenzoic esters groups to enhance conductivity and mechanical strength of silicon electrodes. As a result, capacity retention upon cycling was two times higher with conducting polymer and functional groups when compared to conducting polymers without functional groups. In short, binders, which are non-reactive with electrolytes, flexible, have mechanical strength, and are capable of stabilizing SEI gain of paramount importance to improve the silicon electrode performance. Lately, porous silicon nanoparticles were reported to have enough space for silicon expansion during cycling.
Although porous structure will improve the performance, volumetric capacity of the electrode will be compromised \(^75\). Furthermore, many other techniques have been reported to fabricate silicon nanoparticles; Table 2.1 summarizes some of the key milestones \(^75\).

**Table 2.1** Key developments on using various Si nanoparticles of LIB \(^75\)

<table>
<thead>
<tr>
<th>Fabrication Method Name</th>
<th>Reported By</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow Silicon particles</td>
<td>Yao et al. and Chen et al.</td>
<td>Enhance cycling performance</td>
<td>Costly and reduced volumetric energy density</td>
</tr>
<tr>
<td>Core-shell silicon</td>
<td>Gao et al.</td>
<td>Enhance cycling performance</td>
<td>Costly and reduced volumetric energy density</td>
</tr>
<tr>
<td>Graphene Composite</td>
<td>Lee et al. and Zhu et al.</td>
<td>Large surface area, mechanical flexibility, chemical stability and excellent conductivity</td>
<td>High carbon loading</td>
</tr>
<tr>
<td>Carbon nanotubes (CNTs)</td>
<td>Wang et al. and Martin et al.</td>
<td>Large surface area, mechanical flexibility, chemical stability and excellent conductivity and good cycling performance</td>
<td>High carbon loading complicated fabrication process and the loose binder between Silicon and CNTs.</td>
</tr>
<tr>
<td>Porous Carbon</td>
<td>Guo et al.</td>
<td>Easy to scale up, good performance and low fabrication cost.</td>
<td>High carbon loading, low volumetric capacity due to the Porous structure</td>
</tr>
</tbody>
</table>

### 2.4.2 1D (nanowires and nanotubes)

1D nanostructures consisting of silicon nanowires and nanotubes can accommodate volume expansion during lithium insertion/extraction. Generally, nanotubes experience highly anisotropic expansion, exhibiting relatively small (\(-35%\)) axial direction and larger (\(-120%\)) radial growth. It has been believed that such a large radial expansion due to free surfaces of inner and outer tubes could accommodate volume expansions, which occur during lithium insertion/extraction. Sha and co-workers were the
first group to successfully fabricate silicon nanotubes and demonstrated an improved electrochemical performance\textsuperscript{75, 103}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{synthesis.png}
\caption{Synthesis of Si nanotubes coated with carbon reported by Yoo et al\textsuperscript{75}}
\end{figure}

Similarly, silicon nanotubes were reported by Yoo et al using electrospun polyacrylonitrile nanowires as the template as shown in Figure 2.4\textsuperscript{75}. Further, conductive amorphous carbon has been coated on inner and outer surfaces of the silicon tube to combat electrical conductivity and SEI stability. Such a composite silicon-carbon nanotube electrode exhibits a specific capacity of 2000 mAh/g for a number of cycles. Also, Song et al reported arrays of silicon nanotubes using ZnO nanorods as a template\textsuperscript{75}. Though, silicon nanotubes will improve cycling performance and specific capacity, the fabrication process and scalability of the production are very difficult\textsuperscript{75}. Additionally, silicon nanotube electrodes are extremely porous; hence, the mass density is much lower than silicon nanoparticles\textsuperscript{75}. As a result, volumetric capacity will be reduced dramatically.
Silicon nanowires are promising 1D nanostructures to accommodate volume expansion and to provide direct current pathway when grown directly onto the current collectors [75, 81, 104-107]. Silicon nanowires were first reported by Wagner and Ellis in the 1960’s by using vapor-liquid-solid mechanism [75, 108]. Later, there were several reports on growing Si nanowires using chemical vapor deposition (CVD), wherein diameters and lengths can be controlled precisely [75] to reduce crack initiation and propagation during lithiation/de-lithiation. For example, Figure 2.5 shows SEM of silicon nanowires produced using electroless-etching method [103, 109]. However, removing such aligned Si nanowires from the substrate without cracking them remains a complicated process [110]. The formation of a stable SEI on high surface-to-volume ratio for this morphology is very important as it consumes more electroactive species and causes irreversibility loss. Moreover, the roughness of nanowire surfaces which grow with repeated electrochemical
cycling have been reported for significant loss of active material.

2.4.3 2D (thin films)

Recently, there has been enormous progress in the application of thin film technology to develop silicon electrode with improved electrochemical performances\textsuperscript{111-113}. In general, there are four methods to coat silicon thin film, which are: physical vapor deposition (PVD)\textsuperscript{114,115}, E-beam evaporation\textsuperscript{116}, low pressure chemical vapor deposition CVD\textsuperscript{117,118} and plasma enhanced chemical vapor deposition (PECVD)\textsuperscript{75,119}. Thickness, surface morphology and crystallinity of the Si thin film can be tuned based on their application\textsuperscript{75}. There are several advantages of Si thin film compared to powder-type coated electrodes such as (i) uniform and intimate contact with current collectors (higher charge transfer per area than powder-type) (ii) short pathway for Li diffusion (higher power). However, Graetz et al reported Si thin films of 100 nm thick synthesized by thermal evaporation method, where fractures and cracks on the surface of silicon were observed due to the volume expansion of silicon\textsuperscript{75}. The cracks resulting from tension force usually lead to stress relaxation, which prevents film delamination from the current collectors\textsuperscript{120}. However, these cracks usually generate new surfaces on the silicon electrode, which lead to new SEI formation that consumes more lithium irreversibly, resulting in a huge capacity reduction\textsuperscript{120}. Moreover, in other studies amorphous silicon was deposited with 1.2 um using PECVD. Such a thin film of silicon exhibited a poor electrochemical performance in terms of capacity retention due to the cracks and fractures associated with volume expansion of rigid silicon\textsuperscript{121,122}. Furthermore, Wang et al deposited 300nm silicon on fabricated Si–Ni nanorod structures. However, low Si loading per area becomes a major concern in such current collectors.
Towards this direction, there is an increased interest to design and develop roughened, binder-free current collectors to enhance silicon loading and accommodate the silicon expansion issues.

Hence, based on the central objectives of this proposal, we will synthesize different pore size current collectors to deposit Si thin films and, as a result, 3D silicon electrodes. Plasma-enhanced chemical vapor deposition (PECVD) process will be used for silicon deposition due to its unique ability to control the size and morphology of Si nanostructures as well as its feasibility to deposit Si on a variety of substrates. In a typical PECVD process, a silane precursor will be used to deposit Si thin films on the substrate. To achieve uniform, crack-free Si coatings and to vary Si loading, several experimental parameters will be varied, such as carrier/reacting gas mixture flow, substrate temperature, chamber pressure, and deposition time.

2.5 Thermal stability issues with conventional cathodes

Apart from electrolyte and anode materials, cathodes (positive electrodes) are other key components for successful deployment of lithium-ion batteries for high temperature applications. Similar to anode materials, identification and preparation of thermally stable cathode materials is a challenge; however, these electrodes have some drawbacks, such as lower deliverable capacity, inferior C-rate performance and lesser energy density. Hence, looking for cathode materials with thermally stable, high voltage, compatible capacity, long cycle performance, inherent safety and economic viability has become one of the research focus topics in recent years.

Generally, cathode materials for LIB applications have been classified into three categories based on their crystal structures, namely layered LiMO$_2$ (M=Co, Ni and Mn),
Spinel LiM₂O₄ and Olivine LiFePO₄ (Figure 2.6)¹²³,¹²⁴,¹²⁵. Among them, LiCoO₂ is the most commonly used cathode in commercial Li-ion batteries due to its high voltage (3.7 V) and reasonably specific capacity (150 mAh/g)¹²⁶. However, LiCoO₂ suffer from lack of stability at high temperature or even upon overcharge. At 200 °C and above, LiCoO₂ will release oxygen, which is hazardous in presence of flammable electrolyte solvents¹²⁷⁻¹³⁰. In addition, other drawbacks are low deliverable capacity (theoretical capacity ~274 mAh/g), expensive coat, and toxicity (due to presence of cobalt).

<table>
<thead>
<tr>
<th>Framework</th>
<th>Compound</th>
<th>Specific capacity (mAh/g)</th>
<th>Average potential (V vs Li⁰/Li⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered</td>
<td>LiCoO₂</td>
<td>272 (140)</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>LiNi₁/₃Mn₁/₃Co₁/₃O₂</td>
<td>272 (200)</td>
<td>4.0</td>
</tr>
<tr>
<td>Spinel</td>
<td>LiMn₂O₄</td>
<td>148 (120)</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>LiMn₃/₂Ni₁/₂O₄</td>
<td>148 (120)</td>
<td>4.7</td>
</tr>
<tr>
<td>Olivine</td>
<td>LiFePO₄</td>
<td>170 (160)</td>
<td>3.45</td>
</tr>
<tr>
<td></td>
<td>LiFe₁/₂Mn₁/₂PO₄</td>
<td>170 (160)</td>
<td>3.4/4.1</td>
</tr>
</tbody>
</table>

**Figure 2.6** (a) Electrochemical properties of three structures of cathode material; (b) three crystal structures used in lithium ion battery¹²⁵

LiMn₂O₄, another popular spinel cathode, exhibits an operating voltage of 4.2 V vs. Li/Li⁺. This electrode has been studied extensively for its structural stabilization with variant doping in Mn sites. Though spinel LiMn₂O₄ cathodes are successful at moderate
temperatures, they are plagued by capacity fade at elevated temperatures (>60 °C). LiMn$_2$O$_4$ showed no oxygen release at temperature below 400 °C; however, poor Li-ion intercalant will happen above 190 °C $^{131, 132}$. Hence, based on its structural feasibility, LiMn$_2$O$_4$ will be considered as one of the cathode candidates to fabricate Li-ion batteries for high temperature applications below 190 °C $^{133, 134-136, 123, 134, 137-139}$.

Recently, an exciting cathode material based on tetrahedral polyanion (PO$_4$)$_3^-$ and the use of M$^{3+}$/M$^{2+}$ red-ox couple was reported, and it is distinctive in nature of olivine class cathodes from the ordered rock-salt system. Herein, the oxygen atoms are strongly bonded by both iron and phosphorous atoms, which resulted in an increase in structure stability at high temperatures than in the layered oxides such as LiCoO$_2$. Thermal stability of LiFePO$_4$ as a material is up to 300 °C $^{140}$ while LiCoO$_2$ starts to decompose at 250 °C. Such a high structural stability at their lattice points leads to excellent cyclic performance and safety. On the other hand, the strong covalent oxygen bonds between Fe and P atoms also lead to low ionic diffusivity ($10^{-13}$ to $10^{-16}$ cm$^2$ s$^{-1}$) and poor electronic conductivity ($10^{-9}$ S cm$^{-1}$) $^{141}$. In recent years, researchers were able to prepare successfully electrochemically highly active LiFePO$_4$ using carbon coating and preparation at nano scale dimensions. Figure 2.7 shows thermal ramp results reported by E. P. Roth $^{142}$ of some cathode materials for LIBs $^{134}$. LiFePO$_4$ showed the lowest self-heating rate and the most resistant to thermal abuse $^{134}$. 
Several possible cathode materials were studied for their thermal stability by fabricating the respective LIB\textsuperscript{143}. The studied cathode materials are: LiCoO\textsubscript{2}, LiNiO\textsubscript{2}, LiNi\textsubscript{0.8}Co\textsubscript{0.2}, Li\textsubscript{x}Ni\textsubscript{0.8}Co\textsubscript{0.15}Al\textsubscript{0.05}O\textsubscript{2}, LiNi\textsubscript{0.7}Co\textsubscript{0.2}Ti\textsubscript{0.05}Mg\textsubscript{0.05}O\textsubscript{2}, Li[Ni\textsubscript{3/8}Co\textsubscript{1/4}Mn\textsubscript{3/8}]O\textsubscript{2}, and LiFePO\textsubscript{4}, etc.\textsuperscript{143-148} LiFePO\textsubscript{4} as cathode was the safest material among all studied materials\textsuperscript{143}. Based on these electrifying results, nano-carbon coated LiFePO\textsubscript{4} is also considered for high temperature LIB investigations.

2.6 Physicochemical measurements

2.6.1 Linear sweep voltammetry (LSV)

LSV experiment is a method to understand electrochemical stability using a three-electrode cell consisting of a stainless steel working electrode and lithium as a counter and a reference electrode over the temperature range. The cell is fabricated in an argon-filled glove box with oxygen and water contents lower than 0.1 ppm. LSV is carried out at different scan rates using a Bio-logic (VM3) electrochemical workstation in the voltage range from 0 to 5V. The same procedure is repeated for all the electrolyte mixtures under investigation.
2.6.2 Cyclic voltammetry (CV)

CV is an electrochemical method used to measure the resulting current from the applied voltage. In the CV test, voltage is applied to the working electrode, where it is ramped linearly vs. time and then will reverse the ramp to the initial voltage. The measured current is plotted vs. the applied potential to get the CV graph. CV plot is an important technique to understand: oxidation and reduction peaks, reversibility of the reaction, number of the transferred electrons, formal potential of the material and stability of the reaction, etc.

2.6.3 Ionic conductivity and viscosity

Ionic conductivity of the electrolyte is measured using a calibrated digital conductivity meter (K912 Consort). This conductivity meter has a 4-electrode cell to prevent the polarization error and fouling of the electrode. In order to remove any trace amount of moisture before testing, the pip electrolytes are dried at 100 °C under high-vacuum overnight. A heating block is used to control the temperature and stirring is maintained during the measurement to maintain homogeneity. A 30-minute equilibration time is used at each temperature. Viscosity was obtained for all electrolytes using AR1000 (TA Instruments) rheometer equipped with temperature control.

2.6.4 Thermal stability

Thermalgravimetric analysis (TGA) measurements are performed on these electrolytes using TGA Q50. TGA is usually used to determine the material mass loss due to decomposition or oxidation of the tested material. Therefore, Pip electrolyte with different PC addition is studied in the temperature range from 20 to 500 °C. The
decomposition point is marked as the weight loss of the original sample weight. In addition, long-term thermal stability is determined.

2.6.5 X-ray photoelectron spectroscopy (XPS)

XPS is a technique to measure the surface elemental composition of the material. The number of electrons from the top 0 to 10 nm of the material can be measured using the XPS method. Measurements were carried out with a Thermo Scientific K-Alpha XPS (ESCA) using focused mono-chromatized Al Ka radiation (hn 1/4 1486.6 eV).

2.6.6 X-ray diffraction (XRD)

XRD is a method to understand and study the crystallinity of a compound. XRD can be used to distinguish between amorphous and crystalline material. Moreover, it can quantify the percentage crystallinity of the sample. XRD was obtained using a Rigaku Miniflex-600 diffractometer with Cu K-α (λ = 1.54 Å).

2.7 Summary

Based on state-of-art and scientific knowledge, there is an unmet need for alternative electrolyte and electrode materials with superior thermal and chemical stability to expand the use of rechargeable LIBs to wider working temperatures (above 75 °C) without compromising electrochemical performance. Hence, to fill the gap in advancement requires serious consideration of room temperature ionic liquids-based electrolytes (RTILs) in conjunction with high-capacity electrodes that should solve the problem and would lead to the realization of rechargeable LIB for high temperature applications. Piperidinium cation and imide anion-based ionic liquid electrolytes offer a potential solution to this challenge due to their negligible vapor pressure, thermal stability up to 385 °C which makes it a feasible approach to address the safety of the LIB at high
temperatures. However, based on the literature of anode material and due to the fact that graphite will intercalate with Piperidinium cation-based ionic liquid electrolytes and in order to increase the capacity, an alternative anode material is needed to support the goal of this approach. Hence, Silicon was selected for investigation due to its attractive features, such as high thermal stability, low lithiation potential (≈0.3V vs Li/Li$^+$), and high theoretical capacity (4200 mAh/g). On the other hand, introducing a new cathode to replace LiCoO$_2$ is crucial to support the goal of this thesis, which develops a LIB that can work safely with desired energy density at high temperature.

2.8 Dissertation objectives

Batteries for high temperature applications such as needed for avionics, defense, space, surgical tools, downhole drilling etc., are required to withstand temperatures over 75 °C. However, state-of-the-art military grade rechargeable batteries have an operational temperature limit of 60 °C. Higher temperature tolerance is still a high-sought requirement, most expedient to oil drilling, defense and space industries. Hence, there is a critical need for developing rechargeable batteries that can operate beyond 75 °C. Though conventional rechargeable LIBs used in consumer electronics and electric vehicles (EV) have exceptional performance at ambient temperatures, they undergo catastrophic failure under heat due to presence of volatile electrolytes. Thus, the central objectives of this thesis are that use of room temperature ionic liquids-based (RTILs) electrolytes in combination with high capacity electrodes would result in thermally stable and rechargeable high-energy density LIBs. The main research objectives of this research are:

(1) To understand the effect of additives on thermal, chemical and electrochemical stabilities of RTILs based electrolytes
(2) To design and develop high capacity Si anodes and study its electrochemical performance at various temperatures ranging from RT to 150 °C

(3) To understand electrochemical performance of RTIL electrolyte against LiFePO$_4$ cathodes and evaluate its performance in a full-cell Li-ion battery at various temperature ranging from RT to 120 °C

At the completion of this research, it is expected to understand the fundamental electrode-electrolyte interactions as a function of temperature in rechargeable LIBs.
3.1 Introduction

With continued success in the portable electronic device market, LIBs are of increasing interest for applications in electric and hybrid vehicles, surgical tools, oil and gas drilling etc., due to their superior energy density and long cycle life. However, current LIBs employ conventional liquid electrolytes based on organic solvents, which poses a safety concern, especially at elevated temperatures. Specifically, the use of carbonate solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC) or diethyl carbonate (DEC), restricts battery operation to less than 60 °C due to their volatile and highly flammable nature. Moreover, when these solvents are used with Li salts, such as lithium hexafluorophosphate (LiPF₆), a resistive film forms on the electrode surface affording poor cycle life. These side reactions become more dominant at higher temperatures as the rate of chemical reaction between the dissolved lithium salt and electrolyte solvent increases. Thus, there is an unmet need for alternative electrolytes with superior thermal and chemical stability to expand the use of LIBs to a wider working temperature range without compromising the electrochemical performance.

Room temperature ionic liquids (ILs) offer a potential solution to this challenge due to their negligible vapor pressure, wide electrochemical potential window and structural stability across a large temperature range. However, many ILs exhibit high viscosity and poor Li-ion conductivity at room temperature, along with reduced cathodic stability. Among the studied ILs, piperidinium-based ionic liquids are...
promising for LIB due to their wide electrochemical potential stability up to 5.0 V, high thermal stability up to 385 °C, and moderate Li-ion conductivity at room temperature (RT) (1.4 mS cm$^{-1}$). However, co-intercalation of the piperidinium cation, at lower potentials, along with the Li-ion during charge-discharge process significantly limits its use with intercalation graphite-based electrodes. Hence, in order to effectively use piperidinium ILs in Li-ion batteries, a non-intercalating anode is required, such as one based on Si, Sn, or Ge.

Silicon is an attractive material for the anode because it has high thermal stability, low lithiation potential ($\sim$0.3V vs Li/Li$^+$), and its theoretical capacity is 10 times that of carbon anodes (4200 mAh g$^{-1}$). Owing to their brittleness, they undergo large volume expansion during lithiation, wherein the electrodes need to be designed in a way to preserve the mechanical integrity of the silicon structures, extending the cycle life of the cell. Nanostructured silicon has attracted attention in the past few years as a solution for this problem, as these structures can allow better accommodation of the strains generated by cycling and offer the space necessary to allow volumetric expansion of the silicon structures without physical deterioration. Various engineered structures have reported this purpose, ranging from nanoparticles, 2D nanorods and 3D architectures. We recently reported porous three-dimensional (3D) nano Si electrodes, which exhibit minimal volume expansion, and studied their electrochemical performance in the presence of conventional organic electrolytes at room temperature. Yet, their performance in the presence of ionic liquids at elevated temperatures is unknown. Herein, we combine a piperidinium IL/ propylene carbonate electrolyte with a 3D nano Si anode and construct a cell that operates between 25 and 100 °C. In this
chapter, we show the: 1) ionic conductivity, viscosity and Li-ion transference number of 1-methyl-1-propyl piperidinium bis (trifluoromethanesulfonyl) imide mixed with propylene carbonate; 2) thermal and electrochemical stability of the electrolyte; 3) battery operation over a wide temperature range from room temperature up to 100 °C; 4) rate capability as a function of temperature; and 5) morphological investigation and compositional study of the SEI on the Si anode.

3.2 Experimental details

3.2.1 Preparation of electrolyte mixtures

Thermally stable room temperature ionic liquid electrolyte is prepared using 0.8 M of lithium bis (trifluoromethanesulfonyl) imide (99.8%, Sigma Aldrich) salt dissolved in 1-methyl-1-propylpiperidinum bis (trifluoromethylsulfonyl) imide (99%, io-li-tec) solvent. The electrolyte mixtures are prepared by mixing propylene carbonate (99.7%, Sigma Aldrich) and RTIL (v/v) with constant lithium salt concentration (0.8M). All electrolytes used in the study were prepared in an argon-filled glove box with oxygen and water contents lower than 0.1 ppm.

3.2.2 Preparation and evaluation of 3D Si electrode

Firstly, 3D porous Ni current collectors were prepared by the galvanostatic electrodeposition method as reported previously. Then, the Si deposition process was carried out on the 3D porous Ni current collectors (deposited at pH-1.5 and current-10 mA cm⁻²) using plasma enhanced chemical vapor deposition (PECVD) process, which has a capability of remotely cracking Si precursor (Figure 3.11). The silane precursor was used to deposit Si thin films. To achieve conformal Si coating on 3D porous Ni, experimental parameters such as carrier/reacting gas mixture flow, substrate temperature,
chamber pressure and deposition time were tuned. Prior to testing ionic liquid-based electrolytes, electrochemical performance of 3D Si had been verified by fabricating cells with 1 M of LiPF₆ in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as an electrolyte with celgard separator; the results are displayed in Figures 3.14 & 3.15. The electrochemical measurements of the ionic liquid-based electrolytes with 3D Si were performed on CR2032 coin cells in the potential range between 1.5 and 0.05 V vs Li/Li⁺ at different current rates from room temperature (RT) to 100 °C.

3.2.3 Cell fabrication and characterizations

Coin cells of standard 2032 were fabricated using prepared pure RTIL and RTIL-based electrolyte mixtures with 3D porous silicon as working electrode, metallic lithium as counter/reference electrode and quartz membrane separator. Cyclic voltammograms (CV) were recorded in the potential range from 1.5 to 0.05 V with different electrolytes using Bio-logic (VM3) electrochemical work station. Charge-discharge studies at different current rates (from C/10 to 1 C rate) were carried out in the potential range of 1.5 - 0.05 V using ARBIN charge-discharge cycle life tester. The morphology of the samples was characterized by a JSM 401F (JEOL Ltd., Tokyo, Japan) SEM operated at 3.0 kV and a JEM 2010 (JEOL Ltd., Tokyo, Japan). Crystallinity of 3D Si was identified using XRD.

3.3 Results and discussion

1-methyl, 1-propylpiperidinum bis (trifluoromethanesulfonyl) imide (Pip) was chosen as the base solvent for the electrolyte formulation due to its wide electrochemical potential window and thermal stability. Propylene carbonate (PC) was chosen as an additive to enhance room-temperature ionic conductivity of highly viscous ILs¹⁶⁷,¹⁶⁸ and
also to contribute to the formation a stable solid-electrolyte interphase (SEI) film during the electrochemical process. Lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) salt was added (0.8 M) to the above mixture to afford the final electrolyte.

3.3.1 Physicochemical characterizations

3.3.1.1 Thermal gravimetric analysis (TGA) and flammability tests

The Pip electrolyte exhibited thermal stability up to 385 °C as evidenced from negligible weight loss during the TGA experiment (Figure 3.1). However, with the addition of PC, these electrolytes (PC/Pip mixtures) were thermally stable up to 120 °C, and the stability decreased with increasing PC concentration from 10 to 30% v/v to Pip electrolyte, due to solvent vaporization. The PC/Pip mixtures were not flammable when exposed to an open flame, demonstrating the safety of the electrolytes even with doping of PC as high as 30% (Figure 3.2).
Figure 3.1 Thermal behavior of Pip electrolyte and propylene carbonate (PC) added Pip electrolytes

Figure 3.2 Flammability test to demonstrate the safety of Pip and Pip-PC electrolyte mixtures
3.3.1.2 Viscosity measurements

Viscosity was subsequently measured as a function of PC addition (10, 20 and 30% v/v) to the Pip/LiTFSI electrolyte. Viscosity of the three electrolyte formulations as a function of PC content and temperature was determined. The viscosity decreased with increasing PC addition from 0.50 to 0.13 Pa·s with the addition of 30% PC at 25 °C (Figure 3.3). The most significant temperature dependence was observed for the neat Pip ionic liquid, decreasing from 0.50 (25 °C) to 0.11 Pa·s (95 °C). As a comparison, the viscosity of 20PC-Pip decreased from 0.14 Pa·s at 25 °C to 0.084 Pa·s at 95 °C. The values for the viscosity of 20PC-Pip and 30PC-Pip converged at about 0.084 Pa·s at 95 °C.

![Figure 3.3](image)

**Figure 3.3** Viscosity of the Pip electrolytes and its variation upon addition of PC at different temperatures
3.3.1.3 Electrochemical stability and corrosion measurements

The electrochemical stability of the Pip, 10PC-Pip, 20PC-Pip and 30PC-Pip electrolytes was determined. A linear sweep voltammetry (LSV) experiment was performed using a three-electrode system consisting of a stainless steel working electrode, and lithium as a counter and reference electrode over the temperature range of 25 to 100 °C. At 25 °C, comparable results were observed for all of the electrolytes with anodic stability up to 4.35 V vs. Li/Li⁺ (Figure 3.4). The observed increase in the current for the 30PC-Pip electrolyte, at relatively low voltage, may be due to carbonate solvent decomposition on the stainless steel working electrode. Upon increasing the electrolyte temperature to 100 °C, the overall electrochemical stability remained with a slight decrease in anodic stability at about 0.2V (Figure 3.5). Similarly, LSV test had been conducted to understand the effect of TFSI⁻ anion on Al current collector corrosion at 100 °C (Figure 3.6). The system was stable up to 4.2 V, indicating the feasibility of currently investigated electrolyte (20PC-Pip) for silicon-based full cell applications.

![Figure 3.4](image)

**Figure 3.4** Electrochemical stability of Pip and Pip-PC electrolyte mixtures at room temperature from -0.1 to 5.0V
Figure 3.5 linear sweep voltammetry traces for pure Pip and PC-Pip electrolytes at 100 °C from -0.1 to 5.0V

Figure 3.6 Al current collector corrosion test using three-electrode system with 20PC-Pip electrolyte

3.3.1.4 Ionic conductivity measurements

The ionic conductivity of the electrolytes depended heavily on temperature. As shown in Figure 3.7, the Arrhenius plots for the ionic conductivities of Pip, 10PC-Pip,
20PC-Pip and 30PC-Pip revealed increased conductivity at higher temperatures. The ionic conductivity of the Pip electrolyte was 0.23 mS cm\(^{-1}\) at 25 °C and increased by one order of magnitude with the addition of PC. Although the slopes were slightly different between the electrolyte PC/Pip compositions, the ionic conductivities converged at about 10 mS cm\(^{-1}\) at 100 °C (373 K).

**Figure 3.7** Ionic conductivity of the Pip and PC added Pip electrolytes

### 3.3.1.5 Vogel-Tammann-Fulcher (VTF)

The measured ionic conductivities were found to present a Vogel-Tammann-Fulcher (VTF) behavior with temperature and were fitted using the Equation (eq 1),

\[
\sigma = \frac{A}{\sqrt{T}} e^{-\frac{E_a}{R(T-T_o)}}
\]

(eq 1),

where \(\sigma\) is the ionic conductivity, \(A\) is a pre-exponential factor, \(E_a\) is the pseudo activation energy, \(T_o\) is the ideal glass transition temperature, \(R\) is the gas constant and \(T\) is the absolute temperature \(^{169-171}\). The fitted parameters are presented in Table 3.1 and the VTF plot for all of the PC/Pip compositions are presented in Figure 3.8. The pseudo
activation energy \((E_a)\) value initially dropped with addition of PC, later increasing at larger volume fraction of PC (Table 3.1). Although a preferential solvation of \(\text{Li}^+\) by PC explained the initial behavior, the interplay between free volume and increased PC content is still under investigation.

For RTIL-organic solvent mixtures, a decrease in \(T_o\) with solvent addition is a commonly reported result. However, the pseudo activation energy follows a trend that seems to be strongly dependent on the nature of the RTIL and the solvents being mixed, rendering its behavior rather unpredictable. Since the VTF model assumes a free volume-mediated ionic motion,\(^{169}\) the pseudo activation energies reflect the actual solvation state of the charge carriers in solution, which can be expected to change with salt concentration, RTIL structure, mutual solubility of the two liquids and content of organic solvent. Nevertheless, stoichiometry for the RTIL-organic solvent mixtures have been reported in \(\text{wt}\%\),\(^{170, 171}\) \(\text{vol}\%\) and \(\text{mol}\%\),\(^{169}\) extending the system to a broad range of composition and making comparisons difficult.

At higher temperatures, the viscosity of the PC/Pip electrolyte decreased with all of the electrolytes and exhibit similar values of ionic conductivities due to the contribution from ionic liquid. Addition of PC to the Pip enhanced the ionic mobility at lower temperatures without critically compromising the overall thermal stability up to 100 °C.\(^{31, 167}\).
Figure 3.8 Vogel-Tammann-Fulcher ionic conductivity plot for the LiTFSI solutions in RTIL and solvent mixtures

Table 3.1 Parameters obtained by fitting the ionic conductivity data with the VTF equation

<table>
<thead>
<tr>
<th>PC content / vol%</th>
<th>A / S K^{0.5} cm^{-1}</th>
<th>Ea / kJ mol^{-1}</th>
<th>T_0 / K</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.4</td>
<td>7.4</td>
<td>185.9</td>
<td>0.99993</td>
</tr>
<tr>
<td>10</td>
<td>3.2</td>
<td>4.0</td>
<td>205.1</td>
<td>0.99996</td>
</tr>
<tr>
<td>20</td>
<td>3.3</td>
<td>4.6</td>
<td>185.0</td>
<td>0.99818</td>
</tr>
<tr>
<td>30</td>
<td>5.2</td>
<td>6.2</td>
<td>142.2</td>
<td>0.99501</td>
</tr>
</tbody>
</table>

*Correlation coefficient for the fitting.

3.3.1.6 Lithium ion transference number

The Li-ion transference number (T_{Li^+}) was measured, using the polarization technique described by Evans et al.\textsuperscript{172} and the values were determined to be 0.05, 0.20 and 0.33 for Pip, 10PC-Pip, and 20PC-Pip, respectively. An increase in the T_{Li^+} was found with addition of PC to the electrolyte consistent with the reduction in viscosity and solvation of the Li-ions resulting in an increase in the relative diffusion coefficient of Li^+. 
The observed increase in Li-ion transport with addition of organic solvents to IL-based electrolytes agrees with previous reports in the literature \(^{173}\).

### 3.3.2 Fabrication of 3D silicon electrodes

#### 3.3.2.1 Preparation of 3D nickel current collectors

As discussed earlier, our motivation is to evaluate the feasibility of using Si as an anode for an IL-electrolyte based high temperature LIB. Following our previously reported method \(^{165}\), 3D Ni current collectors were prepared by optimizing bath solution pH and deposited currents. Figure 3.9 shows the electrodeposition setup to prepare Ni-Cu alloy on the stainless steel substrate galvanostatically at \(-10\) mA/cm\(^2\) for 2h. The selective etching of Cu component from Ni-Cu alloy film resulted in 3D porous Ni current collector. Herein, pH and deposition current play vital roles in controlling pore size as rate copper and nickel components are sensitive to these parameters (Figure 3.10).

**Figure 3.9** Schematic representation of 3D Ni current collector fabrication
Figure 3.10 Electrodeposited Ni-Cu films at different pH dipped in copper etchant 49-1(Transcene) for 6h and corresponding porous 3D Ni current collectors (inset)

3.3.2.2 Silicon coating optimization and morphology studies

Conformal coating of silicon on the 3D Ni current collector is done using plasma-enhanced chemical vapor deposition (PECVD) technique. The process was tailored by optimizing deposition time, flow rate, power, etc., so that deposition of 500 nm of silicon is equivalent to planar thicknesses on 3D Ni under vacuum. The surface morphology of the electrodeposited 3D porous Ni before and after the Si deposition is shown in Figure 3.11 along with the schematic representation of PECVD technique used for Si deposition. Microscopy studies revealed that 3D Ni current collector which is electrodeposited at pH-1.5 and current -10 mA cm\(^{-2}\) exhibited the desired porosity of 1~2 µm, and the same could be tuned by changing deposition parameters. During optimization of electrodeposition method, it is observed that pH and deposition current play key role to determine the pore size from few µm to nm (Figure 3.12). For instance,
we observed the pore size of 100 nm with the conditions of pH-4.5 and deposition current of -4mA/cm$^2$ since rate of copper/nickel deposition is highly sensitive to these experimental parameters. Herein, at high pH and low current, copper deposition is slow compared to that with more acidic solution and high deposition current. Therefore, copper concentration in deposition of Cu/Ni film is much less at these conditions, which is directly proportional to pore size after etching the copper component. The thickness of deposited silicon (>400 nm) on 3D Ni structure has been understood from the difference in 3D Ni wall thickness before and after coating (Figure 3.11). XRD was used to identify the crystallinity of 3D silicon electrodes. Amorphous silicon was obtained from the PECVD process as shown in Figure 3.13.

**Figure 3.11** FE-SEM images of a) bare porous 3D Ni current collector and b) the same deposited with 500 nm of silicon to form 3D Si electrode
Figure 3.12 FE-SEM images of porous 3D Ni current collectors at different pH of electrochemical deposition bath solution

Figure 3.13 XRD of 3D Silicon electrodes
3.3.2.3 Verification of silicon electrode performance

Prior to testing ionic liquid based electrolytes, electrochemical performance of 3D Si was verified by fabricating CR2032 coin cells with 1 M of LiPF₆ in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as an electrolyte with celgard separator. The electrochemical performance of 3D Si anode at 25 °C was verified, and the results agreed with literature values (Figures 3.14 and 3.15). It was seen from the study that the 3D silicon anode delivered a capacity as high as 2400 mAh/g (0.45 mAh/cm²) with an appreciable capacity retention and a negligible capacity fade of 7% corresponding to 50 cycles. Also, rate capability test was performed to understand the feasibility of 3D Si for high rate applications; it was observed that stable reversible discharge capacities of 2400, 2000, 1450 and 970 mAh/g were observed at C/10, C/5, C/2 and C-rates, respectively. Based on these intriguing results, extended rate capability behaviour of silicon anode was studied and an appreciable capacity of > 1000 mAh g⁻¹ was observed with 500 nm of Si on 3D Ni for 50 cycles with ~99% capacity retention. Also, it was confirmed that unsuitability of organic electrolyte for high temperature applications as cell failed after few cycles at 100 °C (Figure 3.16). Having confirmed structural and electrochemical properties of the 3D nano Si electrodes with conventional organic electrolytes, the best-identified electrodes were subsequently studied with the novel PC/Pip electrolytes.
Figure 3.14 Typical charge-discharge profiles of 3D Si electrode with organic electrolyte

Figure 3.15 Electrochemical properties of 3D Si electrode with organic electrolyte a) specific capacity vs. cycle number, b) rate capability and c) cycling behavior at 1C
Figure 3.16 Electrochemical performance of silicon electrode with organic electrolyte at 100 °C

3.3.3 High temperature electrochemical studies

For the high temperature studies, the separator was replaced by a quartz membrane, and coin cells were fabricated with PC/Pip electrolyte following the similar procedure outlined in the previous section.

3.3.3.1 Cyclic voltammetry (CV)

CV experiments were performed on the PC/Pip electrolytes at room temperature with a scan rate of 0.2 mV s\(^{-1}\), as shown in Figure 3.17. The absence of prominent reduction and oxidation peaks in the Pip electrolyte was a consequence of its poor ionic conductivity at room temperature. Upon the addition of PC to Pip (e.g., 10PC-Pip electrolyte), a broad cathodic peak was observed around 0.4 V, likely due to the formation of a solid electrolyte interphase (SEI), as commonly seen in organic electrolyte-based systems \(^{160, 174-176}\). However, the broad reduction and oxidation peaks
attributed to the lithiation/de-lithiation of silicon suggested that the electrolyte kinetics were still slow. Upon increasing the concentration of PC to 20%, a significant enhancement in redox peaks current was observed, indicating improved electrochemical properties. Further increases in PC concentration to 30% afforded only a marginal enhancement in electrochemical performances over the 20PC-Pip electrolyte. Hence, in order to retain the best performance of the electrolyte while minimizing the PC content, the 20PC-Pip electrolyte was selected for subsequent experiments.

![Cyclic voltammograms comparison](image)

**Figure 3.17** Comparison of cyclic voltammograms (all four electrolytes) at room temperature

### 3.3.3.2 Rate capability, charge-discharge profiles and cycle life

To understand the rate capability and cycle life of the 3D Si anode, galvanostatic charge/discharge measurements were conducted by operating cells between C-rates of C/40 and C/5 at 25 °C (Figures 3.18 and 3.19). The Pip electrolyte in concert with the Si anode exhibited excellent charge-discharge properties with capacity of 0.3 mAh cm\(^{-2}\) and
voltage plateaus around 0.4 V/0.2 V when the cell operated at C/40 (Figure 3.18). The trend in voltage plateaus continued with slightly higher C-rates up to C/10 with a gradual decrease in specific capacity values. However, at higher C-rates, such as C/5, a significant drop in the specific capacity was observed (95%) and attributed to the poor ionic conductivity of the Pip electrolyte at 25 °C. On the other hand, the 20PC-Pip electrolyte exhibited excellent characteristic features of lithiation and de-lithiation of silicon at 25 °C with desired potentials of 0.2 and 0.45 V vs Li/Li⁺, respectively (Figure 3.20). Furthermore, comparative cycle life tests at a C/5 rate for the Pip, 10PC-Pip, and 20PC-Pip highlight this point (Figure 3.21). At the end of the 100th cycle, the specific capacities of 3D Si electrode are 0.01, 0.04 and 0.21 mAh cm⁻² for Pip, 10PC-Pip and 20PC-Pip electrolytes, respectively. Addition of 20% PC to Pip resulted in improved electrochemical performance of the Si anode at a C/5 rate with a drastic enhancement in capacity and stability over 100 cycles.

![Figure 3.18](image-url) Charge-discharge profiles at different C-rates for Pip electrolyte
Figure 3.19 Cycle life of different C-rate at RT for Pip electrolyte

Figure 3.20 Comparative charge-discharge profiles with different PC concentration in RTIL electrolyte at RT
Based on the encouraging results above, the performance of the 3D Si / 20PC-Pip LiTFSI / Li coin cell configuration was evaluated at higher temperatures, as the compatibility of Si anodes with ILs in general and Pip IL in particular are unknown at higher temperatures. First, we performed CV studies with the Pip and 20PC-Pip electrolytes at 25, 60, 80 and 100 °C. The electrochemical activity of the 3D Si anode in the presence of both electrolytes improved at higher temperatures, due to the increased ionic conductivity and reaction kinetics (Figure 3.22a and b). The enhanced reduction and oxidation peak currents observed in the case of 20PC-Pip, without changing peak position at 100 °C, confirmed not only the improved electrochemical properties but also the unaltered thermal stability upon PC addition to the Pip electrolyte (Figure 3.22b). The lithiation/de-lithiation of silicon at elevated temperatures occurred in two stages. Interestingly, these two-stage lithiation/de-lithiation peaks overlapped with each other in
the CV cycles without altering their position, which further confirmed the thermal stability of the system.

![Figure 3.22](image)

**Figure 3.22** Temperature-dependent performance of 3D Si electrodes: cyclic voltammograms (a) with Pip electrolyte and (b) 20PC-Pip electrolyte

The charge-discharge profiles of Si electrodes with Pip and 20PC-Pip electrolytes at different temperatures are shown in Figure 3.23a and b. During the first discharge, there was a small plateau region around the potential of 0.6 V, and then a stable large plateau occurred below 0.4 V corresponding to SEI formation and lithium-silicon alloy formation, respectively \(^{177, 178}\). In view of volume expansion-driven electrode destabilization, the discharge cut-off voltage was restricted to 50 mV at the expense of deep discharge capacity. Upon cycling at different temperatures, the charge-discharge plateau, corresponding to alloy/de-alloy of Li-Si, remained unaltered due to the improved ion transport properties of the PC-Pip electrolyte. In comparison, the large polarization observed at 25 °C, as a consequence of the high viscosity impeding Li-ion conductivity, afforded a lower specific capacity of 0.18 mAh/cm\(^2\).
Figure 3.23 Temperature-dependent performance of 3D Si electrodes: capacity vs. voltage profiles at different temperatures (a) with Pip and (b) with 20PC-Pip electrolytes

The capacity versus cycle number as a function of temperature from 100 °C to 25 °C was investigated at a constant current rate of C/5 (Figure 3.24a and b). As the ionic conductivities of both electrolytes were comparable at higher temperatures, their capacities were also expected to be of similar magnitudes. Figure 3.24 c and d shows a plot that compares the ionic conductivity, viscosity and capacity of Pip and 20PC-Pip, respectively. At 100 °C, silicon exhibited high specific capacity of 0.41 (1912 mAh g⁻¹) and 0.52 mAh cm⁻² (2230 mAh g⁻¹) when using the Pip and 20PC-Pip electrolytes, respectively (Figure 3.25 a and b shows consequent capacities of Pip and 20PC-Pip electrolytes in gravimetric capacity correspondingly). A similar result was observed at 80 °C, with the cell containing the 20PC-Pip electrolyte showing slightly higher capacities. At high temperatures, the ionic conductivity did not limit the cell operation (Table 3.2). The higher $T_{Li^+}$ values measured in the presence of PC-Pip were in agreement with the improved performance of the mixed electrolytes. Differences in the specific capacity values were more apparent at working temperatures below 60 °C. For
instance, at 25 °C, the Pip electrolyte-containing cell afforded a capacity of 0.01 mAh cm\(^{-2}\), whereas the 20PC-Pip electrolyte cell presented a capacity of 0.19 mAh cm\(^{-2}\).

**Figure 3.24** High-temperature electrochemical properties: capacity vs. cycle number studies of (a) Pip and (b) 20PC-Pip electrolyte at different temperatures (c) temperature dependent parameters of Pip electrolyte (d) temperature-dependent parameters of 20PC-Pip electrolyte
Table 3.2. Comparison of ionic conductivity vs. viscosity vs. capacity with respect to temperature variation for Pip and 20PC-Pip

<table>
<thead>
<tr>
<th></th>
<th>Pip Electrolyte</th>
<th>20PC-Pip Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (C)</td>
<td>RT 60 80 100</td>
<td>RT 60 80 100</td>
</tr>
<tr>
<td>Ionic Conductivity mS/cm</td>
<td>0.23 0.86 2.28 4.37</td>
<td>1.31 2.6 4.45 6.98</td>
</tr>
<tr>
<td>Viscosity Pa.s</td>
<td>0.5 0.26 0.16 0.11</td>
<td>0.14 0.12 0.09 0.08</td>
</tr>
<tr>
<td>Capacity mAh/cm2</td>
<td>0.025 0.24 0.37 0.42</td>
<td>0.17 0.41 0.48 0.52</td>
</tr>
</tbody>
</table>

Figure 3.25 Capacity vs. cycle number studies of (a) Pip and (b) 20PC-Pip electrolytes at different temperatures represented in gravimetric unit (mAh/g)

The poor electrochemical performance of the Pip at 25 °C was consistent with its low conductivity and transference number. Importantly, both cells regained their high
electrochemical performance and high energy density when returned to operation at 100 °C. In order to evaluate the long-term performance of the electrolytes at high temperature, cycling stability tests were conducted at 100 °C (Figure 3.26). Excellent capacity retention over 30 cycles at 0.2 C rate with specific capacity values of 0.42 and 0.46 mAh cm\(^{-2}\) were observed for the Pip and 20PC-Pip electrolytes, respectively as, shown in Figure 3.26a. Further, at 2C, specific capacity around 0.21 mAh cm\(^{-2}\) was obtained for 60 charge-discharge cycles with coulombic efficiency of 96%, as shown in Figure 3.26b. Additional rate capability tests were performed to understand the suitability of the PC containing cell for high power applications at 100 °C (Figure 3.27).

![Figure 3.26](image)

**Figure 3.26** (a) Comparative cycling behavior of Pip and 20PC-Pip electrolytes, (b) high rate (2C) cycling performance of silicon electrode at 100 °C with 20PC-Pip electrolyte
3.3.3.3 Electrochemical Impedance Spectroscopy (EIS)

EIS studies were performed at RT and at 100 °C to probe the charge transfer resistance for cells using the investigated electrolytes (Figure 3.28). The drastic difference on the diameter of the semicircles (charge transfer resistance) after addition of 20% of PC (195 Ω) compared to that with pure Pip electrolyte (2750 Ω) highlight the improved reaction kinetics in the presence of organic solvents as shown in Figure 3.28a. Interestingly, the impedance spectra for both systems presented a perfect overlap at 100 °C (Figure 3.28b), showing that the role of propylene carbonate is to improve the cell performance at low temperatures without affecting it to a large extent once the temperature goes up. The suitability of 20PC-Pip electrolyte for silicon-based full cell configurations was also verified by fabricating half-cells with conventional cathode material (LiCoO₂), and the obtained results have been displayed in Figure 3.29.
Figure 3.28 Electrochemical impedance spectroscopy studies of silicon electrodes with Pip and 20PC-Pip electrolytes at (a) RT and (b) 100 °C

Figure 3.29 Feasibility tests of 20PC- Pip electrolyte mixture for LiCoO₂ cathodes
3.3.3.4 X-ray photoelectron spectroscopy (XPS)

XPS experiments were performed on the silicon anodes used with the Li metal cells containing the Pip, 20PC-Pip, or organic (1M LiPF$_6$ in EC: DEC=1: 1 v/v) electrolytes to probe the chemical nature of solid-electrolyte interphase (SEI) (Figures 3.30-3.33). The disassembled silicon electrodes (on lithiated state) were carefully transferred from the glove box to XPS fast entry lock using transferable vacuum chamber without exposing them to atmospheric air. The chemical composition of the SEI formed was strongly dependent on the type of electrolyte employed for cell preparation $^{179}$, as listed in Table 3.3. The C1s spectra data collected for both the electrolytes indicated that the C-C and C-F were mostly from the reduction of the alkyl carbonates and LiTFSI salt (Figure 3.30a). The oxygen content, determined from the O 1s, was found to be higher when the carbonate-based organic electrolyte was used, resulting in formation of Li$_2$CO$_3$ and oxygenated organic compounds (Figure 3.30b). Surprisingly, the intensity of the S 2p and F 1s peaks was only appreciable for the 20PC-Pip electrolyte, but still with a very reduced atomic fraction, possibly in the form of LiF and other products from the decomposition of TFSI$^{-}$$^{180}$ (Figure 3.32). One of the most interesting features in the spectrum is that the Si 2p peak was nearly invisible for the electrode cycled with the Pip, indicating the formation of a thicker SEI (Figure 3.33). Although contributing for cyclic stability, the growth of a thick surface layer further increased cell resistance in support of the observed lower capacities obtained for cells using a low conductive electrolyte. The absence of detectable amounts of S and F may suggest that the SEI surface was formed primarily by decomposition products of the cation or carbonate solvents. Addition of 20% PC, however, led to an increased contribution of TFSI$^{-}$ decomposition products to
the SEI and formation of a thinner passivation layer. Such changes are likely a consequence of changes in the molecular environment of Li⁺ after addition of PC. The structure, porosity, and morphology of the 3D silicon anode were maintained even upon lithiation, confirming the robustness of structure (Figure 3.34 a, b and c for Pip, 20PC-Pip and Organic electrolytes respectively).

Table 3.3 Atomic composition of the SEI formed on silicon electrodes using different electrolytes

<table>
<thead>
<tr>
<th>Element</th>
<th>1:1 EC/DEC + 1M LiPF₆</th>
<th>RTIL + 0.8M LiTFSI</th>
<th>RTIL + 20 vol% PC + 0.8M LiTFSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>44.29</td>
<td>37.06</td>
<td>26.08</td>
</tr>
<tr>
<td>C</td>
<td>31.51</td>
<td>40.23</td>
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<tr>
<td>Si</td>
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<td>1.05</td>
</tr>
<tr>
<td>Li</td>
<td>22.96</td>
<td>21.79</td>
<td>15.54</td>
</tr>
<tr>
<td>F</td>
<td>0.13</td>
<td>0.26</td>
<td>0.59</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
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<td>0.07</td>
</tr>
<tr>
<td>N</td>
<td>0.18</td>
<td>0.38</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Figure 3.30 XPS spectra of 3D silicon electrode with Pip and 20PC-Pip electrolytes interface: (a) deconvoluted high resolution C1s spectra, (b) O1s spectra
Figure 3.31 Survey and high resolution X-ray photoelectron spectra of silicon electrode with organic electrolyte (discharged state)
Figure 3.32 Survey and high-resolution X-ray photoelectron spectra of silicon electrode with Pip 20PC-Pip electrolyte mixture (discharged state)
Figure 3.33 Survey and high-resolution X-ray photoelectron spectra of silicon electrode with Pip electrolyte (discharged state)
Figure 3.34 Morphology of 3DSi electrode: (a) with pip, (b) 20PC-Pip, and (c) organic electrolytes respectively on discharged state

3.4 Conclusion

Enhancing room temperature Li-ion transport properties of IL-based electrolytes and maintaining high energy density, without compromising thermal stability, is key for developing safe LIBSs and extending their use to additional applications that require operation at >60 °C. To address these challenges, we evaluated novel high energy density 3D nano Si electrodes paired with 1-methyl-1-propyl piperidinium bis (trifluoromethanesulfonyl) imide (Pip) ionic liquid / propylene carbonate (PC) / LiTFSI electrolytes. A systematic study of the physical and electrochemical properties of PC-containing Pip electrolytes shows that the 20%PC formulation provides LIB operation from 25 to 100 °C. Measurement of transference numbers and ionic conductivity reveals that the addition of PC overcomes the slow kinetics of Pip electrolyte, due to its positive contribution in reducing the viscosity of the electrolyte. For the 20PC-Pip electrolyte, a drastic improvement in capacity is observed for the Si electrodes at 25 °C with stability over a 100 charge/discharge cycles. At 100 °C, the capacity further increases by 3-4 times to 0.52 mAh cm\(^{-2}\) (2230 mAh g\(^{-1}\)) with minimal loss during cycling. The use of high
capacity Si anodes in combination with IL-based electrolytes demonstrates a validated approach to address both the safety and energy density limitations of current Li-ion batteries. Continued research on thermally stable and high energy density energy storage devices, especially those operating over a wide temperature range, will provide advances in basic science and novel devices for use in routine day-to-day operation as well as those for broader industrial applications.
CHAPTER 4 BINDER-FREE SILICON ELECTRODES FOR LI-ION BATTERY OPERABILITY UP TO 150 °C

4.1 Introduction

Enhancing thermal stability of LIBs is one of today’s crucial needs in order to cater safety issues and expand their applications beyond portable electronics, such as hybrid electric vehicles, oil drilling tools, medical appliances, oil and gas field sensors, etc. \(^\text{181,182}\). Batteries for high temperature applications with capability of operability over 60 °C are still dominated by primary batteries relying on toxic chemistries like metallic lithium vs. thionyl chloride \(^\text{12}\). Though conventional rechargeable energy storage technologies including high energy density LIBs have exceptional performance at ambient temperatures, these often experience catastrophic failure under heat due to thermally unstable electrodes, electrolytes and their interface namely solid-electrolyte interface (SEI) \(^\text{183,184}\).

Towards an extendable temperature operability of LIBs, room temperature ionic liquids (RTILs) have recently evolved as potential alternatives to flammable organic solvent electrolytes due to negligible vapor pressure and chemical stability at high temperature segment \(^\text{182,185}\). However, RTILs suffer from poor anodic compatibility at high temperature; for example, cations of RTILs get intercalated in conventional graphite anode and results in poor electrochemical performance \(^\text{186}\). Hence, development of thermally stable anodes with stable SEI is key to progress in LIBs for extendable temperature applications. In this context, \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) (LTO) as anode was studied extensively to replace carbon materials owing to its zero-strain structure and high lithium insertion potential (1.55 V vs. \(\text{Li}/\text{Li}^+\)); this results in thermal stability and stubbornness against electrolyte decomposition \(^\text{40,114}\). Despite the safety advantageous of LTO, low
lithium storage capability (160mAh/g) and prosaic operational cell potential (∼1.85 V vs. LiFePO₄) pull back from wide-spread of commercial applications. For example, Manev’s Knowledge Foundation reported that LiFePO₄/ Li₄Ti₅O₁₂ full cell showed only 50-60 Wh/kg which is slightly more than Ni/MH battery. As a result, the commercial impact of Li₄Ti₅O₁₂ as anode in the market is limited and search for an alternative anode continues for high temperature LIB applications.

Recently, the possibility of using next-generation silicon anode by morphing three-dimensional porous structure for high temperature applications with propylene carbonate (PC)-RTIL based electrolyte was examined. Though such an ever-first attempt was successful up to 100 °C vs. Li/Li+ (infinite Li-ions), structural integrity of silicon electrodes and its dependable solid electrolyte interface (SEI) in-conjunction with practically viable cathode (limited Li-ions) is unknown. It is well reported that stabilizing the silicon electrode interface is key to obtaining reliable electrochemical performance, as electrolyte tends to decompose continuously. On the other hand, LiFePO₄ cathode gains paramount importance owing to structural stability originating from stronger bonds between metal to oxygen through phosphorus compared to that in LiCoO₂ wherein oxygen is directly bonded to metal and readily released at higher temperature. The use of LiFePO₄ not only provides thermal stability but also reduces cost and environmental concerns significantly compared to cobalt-based cathodes. However, poor ionic and electronic conductivity and thermodynamically feasible impure phosphate phases necessitate carbon coating and optimization during synthesis of LiFePO₄.
Towards this direction, studies attempted so far to stabilize SEI on silicon electrodes are in half-cell configuration wherein silicon is cycled against unlimited Li-ion source (metallic lithium) 179, 189, 194, 195. To the best of our knowledge, very few studies reported the performance of silicon electrode and its associated formation cycle in full-cell configurations; however, it was at room temperature 196-200. On the other hand, the formation of SEI on silicon electrode and its stability at higher temperatures with combination of thermally stable battery components such as electrolyte and cathode has never been reported. It is intriguing to develop LIBs operable at higher temperatures to combat an ever-warming world and amplify their applications beyond portable electronics and electric vehicles.

4.2 Experimental details

4.2.1 Preparation of 3D Si electrodes

3D porous Ni current collectors were prepared by galvanostatic electrodeposition method as reported previously 123, 201. Si was deposited on the 3D porous Ni current collectors (deposited at pH-1.5 and current -10mA cm\(^{-2}\)) using plasma-enhanced chemical vapor deposition (PECVD) process 201.

4.2.2 Synthesis of lithium iron phosphate (LiFePO\(_4\)/C)

Firstly, Lithium acetate (CH\(_3\)COOLi), Iron (II) Oxalate Dihydrate (FeC2O4.2H\(_2\)O) and Ammonium dihydrogen phosphate (NH\(_4\)H\(_2\)PO\(_4\)) were mixed together and treated with water at 80 °C for 12 hours. Diluted HNO3 was used to dissolve the solution completely to obtain a clear solution. Then, the solution was mixed with 3 wt % tartaric acid to precursors and simultaneously was heated and stirred until thick
gel was produced. The resulting gel was heated to 300 °C (Ar:H₂=90:10) and followed by product at 700 °C for 8 hours to obtain LiFePO₄/C powder.

4.2.3 Electrolyte, electrode and cell fabrication and characterizations

Room temperature ionic liquid electrolyte was prepared using 0.8 M of lithium bis (trifluoromethanesulfonyl) imide (99.8%, Sigma Aldrich) salt dissolved in 1-methyl-l-propylpiperidinium bis (trifluoromethylsulfonyl) imide (99%, io-li-tec) solvent. An argon-filled glove box with oxygen and water contents lower than 0.1 ppm was used to prepare the electrolyte and coin cell fabrication. LFP electrodes were prepared using a mixture of LFP powder, poly (vinylidene fluoride) (PVDF) binder and super P carbon in a ratio of 80:10:10 wt/wt% and N-Methyl-2-pyrrolidone (NMP) as solvent. Coin cells of standard 2032 were fabricated using prepared RTIL (Pip) with 3D porous silicon or LFP as working electrodes, metallic lithium as counter/reference electrode and quartz membrane separator. The full cell was balanced in specific capacity wise per unit weight, wherein LFP was 3% more in capacity than the capacity of 3D Si in respective half-cell configurations. Cyclic voltammograms (CV) were recorded in the potential range from 1.5 to 0.05 V and 4.5 to 3 V for 3D silicon and LFP, respectively, using Bio-logic (VM3) electrochemical workstation. The CVs for full cells were conducted in the potential range of 2.4 -3.6 V at a scan rate of 0.1 mV/s. Charge-discharge studies at different current rates (from C/5 to C/2 rate) were carried out in the potential range of 1.5 - 0.05 V and 4.5 to 3 V for 3D silicon and LFP correspondingly, using ARBIN charge-discharge cycle life tester. The morphology of the samples was characterized by a JSM 401F (JEOL Ltd., Tokyo, Japan) SEM operated at 3.0 kV and a JEM 2010 (JEOL Ltd, Tokyo, Japan).
4.3 Results and discussion

4.3.1 Morphological studies of LiFePO$_4$/C composite

In order to understand the feasibility of silicon electrode and the formed SEI on its surface in full-cell configuration at high temperature, olivine structured LiFePO$_4$/C composite cathode (LFP) was chosen due to its known PO$_4^{3-}$ polyanion driven structural stability. Citric acid assisted sol-gel chemistry route was used to prepare desirable conductive carbon-coated nano-sized LFP composite to overcome its inherent conductivity issues. Prior to constructing a full-cell LIB, prepared olivine structured LFP composite cathode has been tested thoroughly against Li/Li$^+$ for its stability at high temperature. The recorded X-ray diffraction pattern indicates that the crystal structure was matched to the orthorhombic phase of LFP (JCPDS File No.: 81-1173) (Figure 4.1) without any impure phases. From transmission microscopy images (Figure 4.2), the clusters of nanoparticles with spherical shape were observed for LFP synthesized at 700 °C. Hence, the formation of narrowly distributed nanoparticles (<100 nm) with uniform size was attributed to the chelating agent (citric acid) assisted sol-gel process, controlling the growth and wider distribution of particles via slow-rate of heating (2 °C/min.) along with the process of intermittent grinding. Similarly, high-resolution transmission microscopy (HRTEM) images of the LFP composite are furnished in Figure 4.2 (bottom row). The study authenticate the fact that the residual carbon derived from starting precursors as well as from gelling agent (citric acid) are uniformly covered LFP particles as a thin layer. Thus, the uniform coating of the carbon layer on nanoparticles with thickness less than ~8 nm advances the conductivity and electrolyte percolation by means of interconnecting the LFP particles.
4.3.2 Electrochemical studies of LFP

The electrochemical properties of LFP composite cathode were studied in half-cell configuration with RTIL electrolyte at various temperatures from 60 to 120 °C. From
Figure 4.3, it is understood that electrochemical activity (currents in CV) of LFP electrodes in Pip electrolyte increases with the increase of temperature due to change in ionic conductivity. The observed red-ox peaks for LFP cathode at 3.25, and 3.65 V correspond to one-step reversible de-intercalation and intercalation of Li-ions into FePO₄ phase (LiFePO₄/FePO₄) at all the studied temperatures indicate thermal stability. Similarly, the temperature effect on solution resistance and electrode-electrolyte interface resistance with temperature was revealed using electrochemical impedance spectroscopy (EIS) studies (Figure 4.4). To understand the influence of the temperature on the specific capacity and cycle life, galvanostatic charge-discharge experiments were conducted. Figure 4.5 depicts the typical voltage vs. capacity plots of LFP cathode, wherein well-defined charge and discharge plateaus were observed around 3.5/3.4 V and insignificant changes with rise in temperature confirm the thermal stability of cathode due to polyanion structure. Further, the cycling behavior of currently prepared LFP cathode at 0.2C rate is illustrated in Figure 4.6. The excellent specific capacity of 140 mAh g⁻¹ (0.8 mAh cm⁻²) was exhibited at 120 °C with consistent performance over 100 charge-discharge cycles. More notably, superior capacity retention (80%) and coulombic efficiency (99%) signify the potentiality of LFP cathode for high temperature applications.
Figure 4.3 Cyclic voltammograms of LFP electrodes at different temperatures

Figure 4.4 Recorded EIS of LFP electrodes at different temperatures
Figure 4.5 Charge-discharge profiles of LFP electrodes at various temperatures

Figure 4.6 Cycling performance of prepared LFP cathode at 0.2C rate for various temperatures
4.3.3 Electrochemical studies of 3D silicon electrodes

On the other hand, electrochemical studies of 3D silicon electrodes were conducted using Pip electrolyte in half-cell configurations vs. Li/Li+. Fabrication procedures of 3D Ni current collectors and 3D silicon electrodes with desired porosity and thickness were reported previously. In spite of the excellent electrochemical properties of 3D silicon electrodes at ambient temperature, performance and stability for extreme conditions were not explored. Hence, in order to understand the thermal and electrochemical properties of 3D Silicon electrodes, CV studies were conducted on (3D Si vs. Li) using Pip electrolyte at various temperatures ranging from 60 to 150 °C at a scan rate of 0.05 mV s⁻¹. From Figure 4.7, it is understood that electrochemical activity of 3D Si electrodes in Pip electrolyte increases with the increase of temperature due to decrease in viscosity of electrolyte. Further, it is observed that lithiation of silicon at elevated temperatures occurs in two stages at about 0.1 and 0.25V associated with formation of LiₓSi alloy phases. Similarly, anodic peaks around 0.3 and 0.49 V correspond to de-lithiation of silicon which signifies the reversible nature of system. At 60 °C, the slight shifts in the peaks corresponded to the low ionic conductivity of the Pip electrolyte, which will improve with increase in temperature. Remarkably, these two-stage lithiation/de-lithiation peaks overlap with the number of CV cycles at high temperature without altering their position, which confirms the stability of the silicon electrodes. The peaks at 0.5, 0.55 and 0.48 V at 60, 120 and 150 °C, respectively, in the cathodic region (lithiation) attributed to the formation of the solid electrolyte interface (SEI) layer. Such results reveal that the decomposition of electrolyte to form SEI is
temperature-sensitive, and it is important to understand the effect of SEI on electrochemical stability.

**Figure 4.7** Cyclic voltammograms of 3D silicon electrodes at different temperatures

Typical charge-discharge profiles of silicon at different temperatures are illustrated in Figure 4.8. During the first discharge, there was a small plateau region around the potential of 0.6 V, and then a stable large plateau occurs well below 0.4 V conforming SEI formation and lithium-silicon alloy formation, respectively. In order to minimize the volume expansion, which will affect the electrode stabilization, discharge cut-off voltage was constrained to 50 mV at the expense of deep discharge capacity. To understand the cycle life of 3D Si electrodes at high temperature up to 150 °C, capacity vs. cycle number studies were conducted by operating cells at C/5-rate from 60 °C to 150 °C for 100 cycles. As shown in Figure 4.9, 3D Si/Pip electrolyte/Li system exhibited excellent charge-discharge properties when operated at high temperature above 60 °C. For instance, the specific capacity values for 3D silicon vs.
Li/Li+ at 60, 120 and 150 °C were 0.32, 0.49 and 0.44 mA h cm\(^{-2}\), correspondingly. The discharge (Li dealloying) capacities at these temperatures (60, 120 and 150 °C) after 100 cycles were 0.26, 0.4, 0.31 mA h cm\(^{-2}\), respectively, resulting in about 81% of capacity retention. Further, the rate capabilities of 3D Si anode (Figure 4.10) were understood by conducting tests from C/10 to C rates at 150 °C. The silicon anode in concert with the Pip electrolyte exhibited excellent high-rate properties with capacity of 0.43, 0.41, 0.4 and 0.35 mA h cm\(^{-2}\) when the cell operated at C/10, C/5, C/2 and 1C, respectively. Such stability in the capacity values at high-rates (1C) and high-temperature (150 °C) are an indication of suitability of the silicon electrode for extreme conditions.

**Figure 4.8** Typical charge-discharge profiles of silicon at different temperatures
Figure 4.9 Cycle life of 3D Si electrodes at high temperatures up to 150 °C

Figure 4.10 Rate capability of 3D Silicon electrodes at 150 °C
4.3.4 LIB full-cell electrochemical studies at high temperatures

4.3.4.1 Full cell formation cycle optimization

Though the electrochemical performance of 3D Si as anode and LFP as cathode using the Pip electrolyte in half-cell configurations vs. Li/Li+ were excellent, the feasibility and operability of full-cell (3D Si/Pip electrolyte/LFP) at various temperatures, which depend on the stability of SEI on silicon is unexplored. Towards this direction, forming SEI at different conditions namely galvanostatic mode, CC-CV mode (constant current and constant voltage) and potentiostatic mode (CV) at room temperature was considered. By monitoring charge-transfer resistance across such formed SEI, the fabricated full-cells were subjected to electrochemical performance from room temperature to higher temperatures to reveal the practicability of the system.

During galvanostatic charge at low C-rate (C/20), the electrolyte solvent including salt decompose effectively at the negative electrode to form the thin passivation layer on anode. This process occurs usually at lower potential in commercial LIB, which is comprised of organic electrolyte and graphite anode. Surprisingly, electrolyte reduction process (SEI formation) occurred slightly at higher potential (1.75 V vs. LFP) in present study, wherein RTIL-based electrolyte and silicon electrode were used. Such unusual behavior may be due to the chemical nature of RTIL electrolyte at room temperature with respect to comparatively less oxidative surface of the silicon electrode. Though electrolyte reduction (SEI formation) occurred in all three cases, their potential was highly sensitive to current rate and mode of formation cycle. For instance, formation cycle formed via potentiostatically exhibited electrolyte reduction at comparatively higher potential (2.0 V) compared to that of galvanostatic mode (1.6 V). Figure 4.11
sketches the charge-discharge behavior of the full-cell at C/20 wherein poor reversibility and large charge transfer resistance (Figure 4.12) was witnessed possibly due to undesirable formation SEI. On the other hand, excellent reversibility with charge-discharge plateaus and CV peaks at appropriate potential (3.2/3.0 V) were observed when the full-cell was subjected to CC-CV mode (C/100) and potentiostatic mode (0.01mV/s) (Figure 4.13 and 4.14). The reduced charge-transfer resistance values for later studies compared to that of galvanostatic mode are direct evidence that the nature of the passivation layer is vital for reversibility in full-cell configuration (Figure 4.15 and 4.16). Specifically, the SEI formed from CV results in much lesser resistance value of 170 Ω considering RTIL electrolyte and silicon electrode (Figure 4.16).

Figure 4.11 Charge-discharge behavior of full cell at C/20 (room temperature)
Figure 4.12 Charge transfer resistance of full-cell after SEI formation cycled at C/20

Figure 4.13 Formation cycle using CC-CV mode of full-cell
**Figure 4.14** Formation cycle of full-cell using potentiostatic mode (CV)

**Figure 4.15** Charge transfer resistance of full-cell after SEI formation using CC-CV mode
4.3.4.2 Cyclic voltammograms of LIB full-cell

Based on reduced charge-transfer resistance at electrode-electrolyte interface and excellent reversibility, further studies are performed on full-cells with potentiostatically formed SEI at various temperatures. Upon increasing the temperature, red-ox peaks of full cell at 2.92/3.18 V evolved in terms of peak current and sharpening of red-ox peaks due to drastic change in ionic conductivity of electrolyte (Figure 4.17). Moreover, the appearance of second red-ox peak at 2.6/2.8 V from 60 °C indicate that the lithiation/delithiation of full cell resemble silicon half-cell electrode (Si vs. Li/Li+), wherein the Li-Si alloy/dealloy formation occurred at distinguished potentials with increase in temperature. Though intercalation potential for LFP electrode was similar at all the studied temperatures, full-cell based on the same LFP electrode exhibits multiple red-ox peaks at higher temperatures. Positively, such formed secondary red-ox peaks of full-cell along with primary red-ox peaks were perfectly reversible in nature even upon
repeated CV sweeps. To understand the electrochemical cycling behavior of the presently configured full-cell, CR2032 coin cells were fabricated using pre-studied electrodes such as 3D silicon and LFP vs. Li/Li\(^+\) and tested after forming SEI potentiostatically at different temperatures viz., from RT to 120 °C.

![Figure 4.17 Cyclic voltammograms of full-cell at different temperatures](image)

**4.3.4.3 Charge-discharge profiles and cycle life of full-cell at high temperatures**

Typical charge-discharge profiles of full-cell (3D silicon Vs LFP) with Pip electrolyte at different temperatures are illustrated in Figure 4.18. Perfectly aligned charge-discharge plateau at around 3 V for full-cell at all the temperatures evidence the potentiality of the system. A reversible discharge capacity of 0.18, 0.32 and 0.25 mAh cm\(^{-2}\) for RT, 60 and 120 °C, respectively, was observed. To understand the electrochemical cycling stability, capacity vs. cycle number studies were conducted at a constant current rate of C/5 and at different temperatures from RT to 120 °C as shown in Figure 4.19. Exceptionally, silicon-based full-cell delivered excellent reversible specific capacity of 0.16 mAh cm\(^{-2}\) for over 50 charge-discharge cycles with appreciable capacity retention of 98%. Coulombic efficiency of the present system at RT is 99.2% indicates
compatibility of electrode-electrolyte and their interfaces. With the rise in temperatures, the full-cell exhibits remarkably enhanced specific capacity values of 0.33 and 0.27 at the initial cycle for 60 and 120 °C, correspondingly, as shown in Figure 4.19. At 60 °C, the capacity retention for a full-cell over 50 charge-discharge cycles was around 70%. Further, the stability of specific capacity over a repeated cycling at even high temperature (120 °C) was comparatively poor due to parasitic reactions at electrode-electrolyte interface and may due to continuous formation of SEI on the newly exposed silicon electrode surface. As a note, coulombic efficiency above 99% as an indicator of full cell feasibility was substantial at all the studied temperatures, which is noteworthy.

**Figure 4.18** Typical charge-discharge profiles of full cell at different temperatures
4.3.4.4 EIS studies of full cell at high temperatures

At room temperature, Nyquist plots recorded after initial charge-discharge cycle showed high electrolyte resistance (100 Ω) and charge transfer resistance (290 Ω) attributed to the poor Li-ionic conductivity of Pip electrolyte (Figure 4.20). As expected, significantly reduced resistances (120 Ω) were observed at higher temperatures owing to enhanced ionic conductivity in electrolyte and temperature driven electrolyte decomposition during passivation layer formation on silicon electrode.
4.3.5 Post-mortem SEM of 3D Si electrodes at high temperatures

In order to understand the silicon structural stability at higher temperatures, scanning electron images were recorded on silicon electrodes after electrochemical cycling at different temperatures. Figure 4.21 shows typical SEM images of 3D silicon, wherein the morphology of the electrode was stable even after 20 cycles at 60 °C. Similarly, 3D tubular morphology was invariable when temperature increased to 120 and 150 °C as shown in Figures 4.22 and 4.23, respectively. Hence, structural integrity and robustness of binder-free 3D silicon electrodes developed in this study were potential electrodes for full-cell configurations with combination of thermally stable cathodes, especially for high temperature applications.
Figure 4.21 SEM of 3D silicon at 60 °C after 20 cycles

Figure 4.22 SEM of 3D silicon at 120 °C after 20 cycles
4.4 Conclusion

Developing a thermally stable anode that can work safely with compatible cathode and electrolyte holds the key for developing LIBs with extendable temperature applications. Herein, we have demonstrated successfully that 3D silicon electrode exhibits not only high capacity in conventional manner but also extreme stability up to 150 °C in combination with RTIL electrolyte. The silicon electrode displayed high capacity of 0.4 mAh cm$^{-2}$ (2000 mAh/g) at 150 °C with excellent capacity retention (~70%) and near perfect coulombic efficiency (>99%) for 200 charge-discharge cycles. Among various modes of formation cycle to form passivation layer on silicon electrode, the potentiostatic method reveals the preferential reversibility due to reduced charge transfer resistance. Further, electrochemical properties of silicon electrode in full-cell configuration have been inferred using thermally stable LFP electrodes as cathode. Such a system revealed exceptional stability at RT over 50 cycles with the capacity of 0.16 mAh cm$^{-2}$. The feasibility of currently studied full-cell for high temperature
applications was explored by forming a passivation layer at RT, and the results are encouraging with high initial capacity of 0.27 mAh cm$^{-2}$ at 120 °C. This study opens the new avenue of developing silicon-based electrodes in conjunction with thermally stable electrolytes to extend operable temperature range of LIBs for next generation applications.
CHAPTER 5 POROUS GRAPHENE CURRENT COLLECTORS FILLED WITH SILICON AS ANODE FOR HIGH PERFORMANCE LITHIUM ION BATTERY APPLICATIONS

5.1 Introduction

Nowadays, LIB is the leading source of power option in consumer electronics due to its high specific energy, light weight, minimal self-discharge and durability. In addition, LIBs are forecasting as potential candidates to utilize renewable energy to replace the current sources of power, such as hydro-thermal energy, burning of coal, gasoline and diesel, etc. However, the energy and power density attained from commercially available battery is far below the optimum needs for electric vehicles (EVs) and advanced electronics. These shortcomings mainly originate from low specific capacity and poor power capability electrode materials in currently used commercialized LIBs. For example, graphite is used as an anode material with one lithium storage per six carbon atoms which accounts for specific capacity of 370 mAh/g. Hence, rechargeable batteries with high energy density and ultrafast charge/discharge capability inspire the scientist toward exploring alternative electrode materials that can exhibit such performance.

On the other hand, silicon nanostructures have attracted extensive interest as a next generation anode due to its high chemical stability, low lithiation potential (~0.3V vs. Li/Li$^+$), and high theoretical capacity (4200 mAh/g) which is 10 times higher than existing carbon anode. Nevertheless, earlier studies on Si anode suffer from enormous capacity fade resulted from electrode pulverization and loss of contact between electrode/current collectors due to silicon’s large volume expansion during the lithiation/delithiation process. Recent importance has been given to binder/carbon-based nanocomposites, as these structures have the potential for enhancing
strain/stress accommodation compared to its bulk forms \(^{152-158, \ 216}\). But, such binder/carbon-based nanocomposites can increase electrode volume due to low binder/carbon density, and will eventually will lead to high electrode thickness and result in low silicon loading per unit footprint area (reduced volumetric and gravimetric energy density).

Therefore, binder-free silicon electrodes have been used as an alternative to increase silicon loading; however, such direction showed poor cycle life due to delamination of silicon from the current collector during cycling. Thus, the number of approaches has been reported to overcome the huge capacity degradation of binder-free silicon electrodes, by (i) silicon in nanowire format, (ii) three-dimensional porous silicon structures and (iii) design current collectors to deposit silicon conformally by deposition methods. In all these methods key to obtaining stable performance is adhesion between silicon anode/current collectors \(^{201, \ 217, \ 218}\). Another important parameter to be considered to construct robust silicon electrodes is the deposition method.

Silicon was deposited using different methods such as chemical vapor deposition (CVD) or physical vapor deposition (PVD) with standard thickness \(\leq 500\) nm on different morphologies of current collectors \(^{114, \ 117}\). In the same line, it was recently reported that the plasma-enhanced chemical vapor deposition (PECVD) method was used deposit silicon on 3D porous nickel current collectors with enhanced electrochemical performance. However, passivation issues of Ni current collectors with electrolytes especially at lower potential always remained a concern. Herein, there is an essential need to develop a binder-free silicon electrode coupled with porous current collector that can (i) reduce the interface resistance between silicon and current collectors (improve
charge/discharge rates), (ii) accommodate the silicon volume expansion (longer cycle life and less capacity fade), and (iii) adopt more silicon per unit area (higher capacity). Hence, in this study, 3D porous graphene (3D G) current collectors were synthesized using chemical vapor deposition process (CVD). Further, conformal deposition of Si on 3D G current collectors was achieved using optimum PECVD process prior to using them as lithium storage capability.

5.2 Experimental details

5.2.1 Synthesis of 3D graphene structures

Commercial stainless steel foils (Type 304) (0.1 mm) were brought from Sigma Aldrich. Foils were punched into 9.5 mm diameter circles using electrode punch. The punched stainless steel foils were then loaded into a quartz tube kept in a single zone furnace. Vacuum was created in the tube; reaching the pressure of 2 x 10^{-2} mTorr. Perfluorohexane (99.99% pure) (PFH) brought from Sigma Aldrich was used as precursor for growth of graphene. The furnace was heated to 950 °C at ramp rate of 25 °C/min in a reducing atmosphere of Ar/H₂. Once the temperature was reached, gas flow was stopped. PFH was passed into the tube at the rate of 500 mTorr for 12 min. After this, the tube temperature was quenched to 850 °C by opening the furnace mouth. At this moment, PFH flow was stopped and Ar was flown instead. The furnace was then allowed to cool down in air. Samples were taken out of the tube by releasing the vacuum inside the tube. Scanning Electron Microscopy (SEM) (FEI, Quanta 400 ESEM FEG), Raman spectroscopy (Renishaw inVia) was done on the samples for preliminary characterization.
5.2.2 Preparation of 3D Si/G electrode as anode

Optimized Si coating was deposited on the 3D porous G current collectors using plasma-enhanced chemical vapor deposition (PECVD) process. The 100% silane gas was used to deposit Si thin films. In order to attain conformal coating of Si on the 3D G current collectors with desired adhesion and electronic conductivity, deposition parameters such as flow rate (5 sccm), substrate temperature (150 °C), deposition pressure (450 mTorr) and time (100 min) were tuned.

5.2.3 Cell fabrication and characterizations of 3D Si/G Vs. Li

Coin cells of standard 2032 were fabricated using 1 M of LiPF₆ in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as an electrolyte with celgard separator. 3D porous Si/G was used as working electrodes, and metallic lithium as counter/reference electrode. All cells were fabricated inside an argon-filled glove box with oxygen and water contents lower than 0.1 ppm.

5.2.4 Battery performance evaluation

Charge-discharge studies at different current rates (from C/5 to 5C rate) were carried out in the potential range of 1.5 - 0.05 V, using ARBIN charge-discharge cycle life tester. The morphology of the samples was characterized by a JSM 401F (JEOL Ltd., Tokyo, Japan) SEM operated at 3.0 kV and a JEM 2010 (JEOL Ltd, Tokyo, Japan). The interface resistance was measured by EIS technique using Bio-logic (VM3) electrochemical work station.

5.3 Results and discussion

Three-dimensional porous current collector has advantages over planar current collectors for a number of reasons. Firstly, it can accommodate volume expansion and
weak adhesion of binder-free silicon electrode. Secondly, loading per unit area of anode material can be increased compared to the planar current collectors used in conventional thin film battery. These current collectors are expected to adopt more Si material than conventional current collectors due to the extra space between the inner walls. As a result, the thickness of the coated film on G current collectors will be less than the thickness of the same film coated on other conventional collectors. By increasing the surface area of the current collector, the rate capability of the electrode is expected to enhance.

The synthesis process of 3D G current collectors using chemical vapor deposition technique (CVD) is illustrated in Figure 5.1. Currently synthesized 3D porous graphene current collectors were characterized systematically prior to use for silicon electrode fabrication by PECVD. Raman spectroscopy and scanning electron microscopy (SEM) were used to characterize the 3D G current collector. Typical Raman spectra were recorded, and the results indicated two sharp G and 2D peaks at 1580 and 2690 cm\(^{-1}\), respectively (Figure 5.2). It can be seen from Figure 5.3a and b that 3D G current collectors display highly porous and continuous in nature with a pore distribution of \(~ 0.8\) um. These porous structures are expected to improve (i) adhesion between 3D G and Si that leads to better electronic conductivity, and (ii) Si dissemination due to the high surface area that will improve the Li diffusion (high rate performance). Notably, porous structure was uniformly distributed throughout the surface with a large amount of void space. Such homogenous porous structure leads to excellent cycle performance when coated with Si as anode for LIBs as it can accommodate volume expansion/contraction of Si during cycling.
Figure 5.1 CVD parameters used to synthesize graphene current collectors

Figure 5.2 Typical Raman spectra for graphene current collectors
In order to understand the Si loading capacity of 3D G current collectors, PECVD process was optimized to coat various Si thickness viz., 100, 200, 500, 1000 nm (equivalent to planar thickness), respectively. These 3D porous current collectors are expected to adopt more Si material than conventional 2D planar current collectors due to the extra space between the inner walls. As a result, the thickness of the coated film on G current collectors will be less than the thickness of the same film coated on conventional planar current collectors. From Figure 5.4, the conformal coating of silicon on 3D graphene current collectors, especially with the thickness from 100 to 500 nm (Figure 5.4a, b and c) with porous structure to percolate ionic conductivity through electrolyte, clearly seen. On the other hand, 3D G current collators can accommodate more Si loading up to 1000 nm (figure 5.4d) leaving nanopores in structure without compromising on the robust integration of Si. Further, well-textured Si coating on G current collectors is demonstrated in the cross-section SEM image (inset of Figure 5.4b). Interestingly, a large amount of void spaces were formed and rooted underneath Si, which works as electrolyte percolation channels to enhance Li-ion conductivity and as well as a hotel to accommodate the volume expansion of Si during lithiation/dellithiation.
Figure 5.4 SEM images of 3D graphene current collectors (a) 100 nm thickness of Si (b) 200 nm thickness of Si (c) 500 nm thickness of Si (d) 1000 nm thickness of Si

However, inspecting the cross section area shows that Si was not coated all the way to the inner wall, and as a result, some of the current collector was not utilized to load silicon. Therefore, an optimization of the Si coating process was needed to (i) utilize the inner pore surface area (improving the aerial capacity) and (ii) better Si mass distribution (reduced thickness and as a result higher rate capability). Hence, optimization experiments were executed by varying some of the PECVD process parameters such as flow rate, power, time, silane gas concentration (SiH₄) and temperature. It was found that using 100 % SiH₄ and low power of 25 W minimized the defect density (residual stress) of the deposition. Additionally, high temperature (150 °C) would produce better
adhesion of the Silicon to the graphene current collectors than low temperature (90 °C) (Silicon films will peel off when low temperature is used). Flow rate and time were varied while film thickness was monitored and measured after each experiment. Results indicated that when flow rate of 25 sccm and 15 minutes time (fast deposition) were used to coat 500nm, surface area of the current collector was not completely utilized as shown in the inset of Figure 5.4b. On the contrary, conformal Si inside the inner wall of the graphene pores was achieved when the flow rate was reduced to 5 sccm and the time increased to 100 min to coat 500 nm.

To illustrate the influence of graphene current collectors for silicon electrodes on power capability, the interface resistance between the electrode and the current collectors was measured using electrochemical impedance spectroscopy (EIS) technique as shown in Figure 5.5a. Typical Nyquist plots were drawn to understand the charge transfer resistance of 3D Si/G electrode toward Li-ion diffusion compared with other reported current collectors, such as 3DNi and stainless steel (SS). The charge transfer resistance drastically increased toward Li-ion diffusion using current collectors such as 3DNi and SS due to the poor adhesion and increase of interface resistance between silicon and current collector. Notably, Nyquist plots showed that silicon electrode coating on graphene current collector with reduced flow rate exhibited low charge transfer resistance indicating fast charge transfer due to the excellent conductivity of the 3D G current collectors and its adhesion to silicon (Table 5.1). Raman spectroscopy revealed the graphene surface coverage from coated silicon with various thicknesses by appearing silicon related peaks at 300, 500 and 900 cm$^{-1}$ (Figure 5.5b). In addition, Raman spectra show that graphene-related peaks co-exist with silicon peaks for 100 and 200 nm infer the
possibility to increase thickness further. Accordingly, Raman peaks of 2G and D bonds corresponding to graphene disappeared for thicker silicon coating of 500 and 1000 nm indicating complete utilization of current collector.

![Figure 5.5](image)

**Figure 5.5** (a) Interface resistance comparison of different current collectors (b) Raman spectroscopy of the 3D Si/G electrodes

**Table 5.1** Interface resistance comparison

<table>
<thead>
<tr>
<th>Silicon Coating</th>
<th>3D Ni Fast</th>
<th>3D G Fast</th>
<th>3D G Slow</th>
<th>SS fast</th>
<th>SS slow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs=4.5 ohm</td>
<td>8</td>
<td>17</td>
<td>3</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Rct</td>
<td>460</td>
<td>237</td>
<td>720</td>
<td>2200</td>
<td></td>
</tr>
</tbody>
</table>

Electrochemical performance of 3D Si/G electrodes was evaluated using standard 2032 coin cell configuration against metallic lithium as reference/counter electrodes. All fabricated cells were cycled initially at a low rate of C/20 for two cycles to stabilize solid electrolyte interface (SEI). Typical charge-discharge profiles of various Si electrode thicknesses with organic electrolyte are illustrated in Figure 5.6. All samples showed
typical lithiation/delithiation plateaus at around (0.21/0.4) V, (0.25/0.41) V, (0.3/0.44) V, and (0.28/0.42) V for 100, 200, 500nm, slow 500nm, respectively. The increase in the lithiation/delithiation plateaus voltage was due to the increase of resistance associated with increasing film thickness. Notably, the optimized Si coating showed comparatively lower lithiation/delithiation plateau voltage than regular fast coating due to the decrease of the resistance resulting from the improved adhesion of Si to the current collectors. During the first discharge of the 100nm thickness of Si, there was small plateau region around the potential of 0.6 V, and then a stable large plateau occurred well below 0.4 V corresponding to SEI formation and lithium-silicon alloy formation, respectively (Figure 5.7) 177, 178. A reversible capacity of 0.17 mAh/cm² was obtained in the consequent cycles (10th and 20th cycles). This reversible capacity was enhanced by increasing the Si loading to 200, 500 nm as shown in Figures 5.8 and 5.9, respectively. In order to minimize the volume expansion issues, discharge cut-off voltage was restricted to 50 mV at the expense of deep discharge capacity.

Figure 5.6 Typical charge-discharge profiles of various Si thicknesses with organic electrolyte
Figure 5.7 Typical charge-discharge profiles of 100 nm thickness of Si

Figure 5.8 Typical charge-discharge profiles of 200 nm thickness of Si
Figure 5.10 shows the cycling performance of electrodes at room temperature at C/5-rate between 0.05 and 1.5 V for various Si thicknesses. Apparently, the 3D Si/G electrodes exhibit excellent stable capacity of 0.14, 0.21, 0.33, 0.58, 1.23 mAh/cm$^2$ after 50 cycles for 100, 200, 500 nm, slow 500nm, slow 1000nm of Si, respectively. Interestingly, 3D G current collectors were able to adopt up to 1000nm thickness of Si; however, the capacity retention after 50 cycles was not satisfactory like (slow 500nm), and therefore further studies were restricted to 500nm thickness. To understand the rate capabilities of the 3D Si/G anode, galvanostatic charge/discharge measurements were conducted by operating cells between rates of C/5 and 5C (Figure 5.11). Interestingly, 200nm Si coating in concert with the graphene current collectors exhibited excellent charge-discharge properties with capacity of 0.38, 0.3, 0.2, 0.14 mAh/cm$^2$ for the rate of C/5, C/2, C, 5C, respectively.
Figure 5.10 Cycling performance of electrodes at room temperature with different thickness

Addition of slow Si loading (500nm) to G current collectors resulted in improved reversible capacity of up to 0.37 mAh/cm² at the high rate of 5C with a loss of less than 3% compared to C rate capacity as shown in Figure 5.11. Furthermore, to understand the effect of high rate currents on the reversible capacity for high Si loading (slow 500nm), charge-discharge profiles were plotted as shown in Figure 5.12. Amazingly, at high rates such as 1c and 5c, electrodes maintained high capacity retention with around 99% coulombic efficiency.
Figure 5.11 Rate capability of the 3D Si/G electrodes (500 nm) at RT

Figure 5.12 Typical charge-discharge profiles of 500 nm thickness of Si with different rates

5.4 Conclusion

Developing a Li-ion battery that can operate safely with high charge/discharge rates and high energy density holds the key for developing practical Li-ion batteries to meet today’s emerging technology. In this work, we have reported highly conductive 3D
porous graphene current collectors filled with Si as anode for the LIB. The optimized Si coating using PECVD process can effectively improve the adhesion between the electrode and current collector as well as increase the Si loading. Such optimized configuration of silicon electrodes exhibits excellent current rates up to 5C with reversible capacity of 0.72 mAh/cm$^2$ (500 nm Si thickness). Moreover, graphene current collectors in conjunction with a porous network enable maximization of the silicon loading results in high energy density of 1.8 mAh/cm$^2$ with respect to 1000 nm planar equivalent thickness. Thus, constructing highly conductive and porous electrodes results in enhancing electronic and ionic conductivities and as a result improved electrochemical performance.
CHAPTER 6 CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

Developing thermally stable electrolyte that can work safely with compatible cathode and anode holds the key for developing LIBs for high temperature applications. In this work, we have demonstrated successfully that (i) new electrolytes materials chemistry (RTILs and PC), and (ii) new engineering design and optimization (3D silicon electrodes) implemented to address LIB high temperatures issues. This dissertation focuses on designing electrolyte mixture using propylene carbonate (PC) as an additive to enhance the room temperature (RT) ionic conductivity of RTILs to suit the industrial demands for a safe practical LIB that serves the high temperature applications. A systematic study on the physical and electrochemical properties of PC-containing Pip electrolytes shows that the 20%PC formulation provides LIB operation from RT to 100 °C. PC as an additive plays a main key in stabilizing the SEI formation by reducing the electrode/electrolyte interactions. Furthermore, ionic conductivity of the Pip electrolyte at RT was enhanced using 20%PC from 0.29 to 1.31 mS/cm attributed to the reduction of the viscosity of the electrolyte from 0.5 to 0.14 Pa.s. As a result, the overall capacity of the cell was improved from 0.025 to 0.17 mAh/cm² at RT using 3D silicon electrodes.

This dissertation also focuses on the development of three-dimensional (3D) current collectors and electrodes that exhibit high capacity up to 0.5 mAh/cm² at 120 °C in conjunction with RTIL-based electrolyte which resulted in thermally stable and rechargeable high-energy density LIBs.

3D current collectors such as Nickel and Graphene showed the ability to accommodate more electrode active materials and improve adhesion between the
electrode and current collectors (improved conductivity and as a result more power). Energy per footprint area was significantly improved when 3D current collectors were adapted. By using 3D Ni current collectors, we have created porous electrodes with the ability to engineer pore dimensions. This has assisted to mitigate the volume expansion issues associated with some of the materials such as silicon and hence enhancing the battery performance. Compatibility of the engineered 3D Si/Ni electrodes with RTILs were successfully proven to offer a thermally stable LIB that can work up to 150 °C (0.4 mAh/cm²) due to the non-intercalating, binder-free Silicon electrode and also attributed to the non flammable and low vapor pressure electrolyte.

LFP as a cathode material was synthesized and tested with RTILs at high temperatures up to 120 °C. Here, we used carbon as a conducting source to effectively enhance the LFP conductivity. Stable cyclic performance of more than 100 cycles at 120 °C with a capacity of 0.85 mAh/cm² was achieved using modified LiFePO₄/C electrodes. Finally, a first of its kind full-cell LIB was fabricated using the engineered 3D Si/Ni vs. LiFePO₄/C electrodes and RTILs electrolyte. Here, we have observed an important phenomenon for future high temperature LIB using CV mode to form a stable SEI. This approach is a key to having a workable full cell LIB with a reversible capacity of 0.27 mAh/cm² at high temperatures up to 120 °C.
6.2 Future work

Future work could focus on developing lithium ion battery operable above 120 °C. Toward this direction, we recommend the following materials and strategies for future high temperature LIB:

- Identification of a new thermally stable binder that can enhance cathode (LFP) performance above 120°C
- Identification of new additives to the RTILs electrolyte to mitigate the capacity fade of the full cell LIB at high temperature
- 3D engineering current collectors could be used in other battery systems such as lithium sulfur to enhance the energy density of the battery.
REFERENCES


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ABSTRACT

DESIGN AND OPTIMIZATION OF LITHIUM ION BATTERY FOR HIGH TEMPERATURE APPLICATIONS

by

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December 2016

Advisor: Dr. Leela Mohana Reddy Arava

Major: Mechanical Engineering

Degree: Doctor of Philosophy

With massive commercial success of lithium ion battery (LIB), the ability to operate at and above 70 °C is still a crucial issue and a safety concern to combat ever-increasing global warming and to extend applications beyond portable electronics. Among various components of battery, anode and electrolyte and the passivation layer formed between them are crucial towards the development of LIBs for extendable temperature ranges. In this regard, room temperature ionic liquids (RTILs) have the capability to tackle thermal stability issues of LIBs, but their poor compatibility with traditional graphite anodes limits their practical application. Towards addressing this issue, we explore the feasibility of engineered three-dimensional Si (3D Si) anodes in conjunction with modified RTIL as an electrolyte and their electrochemical performance up to 150 °C. Detailed electrochemical studies such as electrochemical stability, ionic conductivity, specific capacity, rate capability, and coulombic efficiency reveal that 3D Si anode and RTIL combinations are thermally stable for high temperature rechargeable battery applications. Further, silicon electrode in full cell configuration has been demonstrated in association with LiFePO₄/C cathode to develop next generation LIBs
with enhanced safety and thermal stability. Interaction between electrode and electrolyte has been evaluated by conducting X-ray photoelectron spectroscopy and electron microscopy studies at various electrochemical conditions.
AUTOBIOGRAPHICAL STATEMENT

EDUCATION

M.S, Mechanical Engineering, Wayne State University, 2012.


PUBLICATIONS AND PATENTS

1. Ababtain, Khalid, Ganguli Babu, and Leela Mohana Reddy Arava. "High Porous Graphene Current Collectors for High Capacity Lithium ion Battery " Manuscript is under communication

2. Ababtain, Khalid, Ganguli Babu, and Leela Mohana Reddy Arava. "Binder Free-Silicon Electrodes for Li-Ion battery operability up to 150°C" Manuscript is under communication

