University of Rhode Island

DigitalCommons@URI

Open Access Dissertations

2019

THE EFFECT OF ADDITIVES AND SURFACE MODIFYING AGENTS ON THE SOLID ELECTROLYTE INTERFACE IN LITHIUM ION BATTERIES

Dilni Kaveendi Chandrasiri Koggala Wellalage
University of Rhode Island, dilnikaveech@gmail.com

Follow this and additional works at: https://digitalcommons.uri.edu/oa_diss

Recommended Citation

Koggala Wellalage, Dilni Kaveendi Chandrasiri, "THE EFFECT OF ADDITIVES AND SURFACE MODIFYING AGENTS ON THE SOLID ELECTROLYTE INTERFACE IN LITHIUM ION BATTERIES" (2019). *Open Access Dissertations*. Paper 863.
https://digitalcommons.uri.edu/oa_diss/863

This Dissertation is brought to you for free and open access by DigitalCommons@URI. It has been accepted for inclusion in Open Access Dissertations by an authorized administrator of DigitalCommons@URI. For more information, please contact digitalcommons-group@uri.edu.

THE EFFECT OF ADDITIVES AND SURFACE MODIFYING AGENTS ON THE
SOLID ELECTROLYTE INTERFACE IN LITHIUM ION BATTERIES

BY

DILNI KAVEENDI CHANDRASIRI KOGGALA WELLALAGE

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

ANALYTICAL CHEMISTRY

UNIVERSITY OF RHODE ISLAND

2019

DOCTOR OF PHILOSOPHY DISSERTATION
OF
DILNI KAVEENDI CHANDRASIRI KOGGALA WELLALAGE

APPROVED:

Dissertation Committee:

Major Professor	Brett L. Lucht
	David R. Heskett
	Matthew Kiesewetter
	Arijit Bose
	Nasser H. Zawia

DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
2019

ABSTRACT

Lithium ion batteries have become the most widely used and state of the art energy storage device in the current century, due to its high volumetric and gravimetric capacity, which makes portable electronic devices a possibility. The new and improved battery material have further increased the energy density of lithium ion batteries which made it possible to be used in high power applications such as electric and hybrid electric vehicles, aerospace applications as well as grid energy storage.

Many problems still exist with the use of Li-ion batteries, such as safety, cost, material availability, environmental impact of used material, and etc. With the gain of the popularity of these devices, the need for even higher energy density keep on arising. Researchers have constantly been working on understanding the reactions taking place in the batteries as well as developing materials to improve the inherent problems of these systems.

One major concern is the inability of li-ion batteries to work in a wide temperature window. Batteries tend to freeze at low temperatures during winter. Although this does not destroy the battery, it makes it harder for use and reduces the reliability. Also, at higher temperatures, due to the use of organic solvents, batteries have the tendency to catch fire. One approach to overcome this problem is to use a solvent like propylene carbonate, which has a working temperature range from -42 to 240 °C. But propylene carbonate tends to co-intercalate into graphite anode and reduce in-between the graphite layers leading it to exfoliate and destroy the cell. In this study alkali metal ions were used as additives to understand the effect of them on the solid

electrolyte interphase, that can improve the overall cell performance and use of propylene carbonate as a co-solvent.

Another major problem is the low gravimetric capacity of the commercially used graphite anode. Many scientists have been working on using high energy density material such as silicon, which has ten times the capacity of graphite, as an anode material. But silicon has a propensity to change its volume up to ~300% in the charge discharge cycle which leads to cracking of the silicon particles and continuous consumption of the electrolyte.

Binders play a large role in the performance of silicon-based electrodes. The binder not only helps in the direct mechanical properties of the electrode, but also participate in the solid electrolyte interphase (SEI) formation. Most studies conducted by the research community show the use of polymers as binders. This study shows that the use of single molecules with similar functional groups, can still act as good binders as they react on the surface of silicon to form a better SEI.

One study shows that citric acid, which is a tri carboxylic acid, when used as a binder gives similar performance to polyacrylic acid, which is a polycarboxylic acid binder. When looking at the surface, lithium citrate was observed on the SEI. This gave an insight to functionalize the surface of silicon nanoparticles with citric acid, in order to form an artificial SEI containing lithium citrate. These surface modified nanoparticles have shown better performance with the conventional binders compared to unmodified particles consistent with the findings in the previous study.

Many natural polymeric gums such as chitosan, guar gum, xanthan gum, pine resins etc, have been studied as binders. This led us into using a single molecular

natural glue, casein, a cheap, alternative binder material for silicon based electrodes.

This has shown better performance compared to the conventional PVDF binder.

ACKNOWLEDGMENTS

“It always seems impossible until it’s done”

Nelson Mandela

The path towards the success of this dissertation has been arduous. I would extend my deepest appreciation to all those who supported me and stuck with me throughout this journey.

Foremost, I consider myself most fortunate to have Prof. Brett Lucht as my major professor, and I greatly appreciate the support and guidance he has have given me with my projects, making tough decisions and believing that I could do more in lab than I thought I had the ability to. This gave me the chance to learn so many different areas of li-ion batteries and work with many different collaborators that motivated me to become a better scientist every day.

Next, I want to thank my family, my mother, father, brother, sister in law and her parents and my friends Maheeka, Kaveesha, Shalini and Danuka, who stood by me as a rock, supporting me and picking me up every time I fell.

I would also like to thank my wonderful PhD committee members Prof. Bose, Prof. Heskett and Prof. Kieseewetter. All of whom I have worked with to different levels and it had always been a pleasant experience. I would also thank all the department chairs and all the professors who have helped me in numerous ways.

In addition, I would like to thank my colleagues, who taught, helped and challenged me, without which I wouldn’t have seen my true potential. I am utterly grateful to my second family in Lucht’s Lab Maheeka, Mickdy, Bharathy, Cao, Julien, Teaho, Sunhyung, Nina, Navid, Satu, Zach, Usha, Nuwanthi, Chamithri and many others for making these five years pleasant and unforgettable.

Lastly, I would like to thank the numerous collaborators, and everyone outside my lab who have helped me with instrumentation.

Thank you!

PREFACE

This dissertation is following the manuscript format. Chapters 1-3 are published material and chapter 4 is in preparation. The first chapter addresses a common problem which arises with graphite-based electrodes. The study reveals an additive that can be utilized to use a wide temperature range solvent. Surface characterization studies have shown the impact of this additive on the solid electrolyte interphase.

Chapters 2-4 focus on silicon as an anode material and the investigation of novel binders and a study that focuses on how they alter the SEI formation. Understanding the SEI have inspired the formation of an ex situ artificial SEI that can improve the performance of silicon-based anodes.

The appendix includes the background to li-ion batteries, a brief review of the problem, the experimental methods used as well as a summary of all the instrumentation techniques utilized in preparation of this dissertation.

TABLE OF CONTENTS

ABSTRACT	ii
ACKNOWLEDGMENTS	v
PREFACE.....	vii
TABLE OF CONTENTS.....	viii
CHAPTER 1 - INTRODUCTION.....	1
1.1. Background	1
1.2. How a Li ion battery works.....	2
1.3. Review of the problem.....	3
1.4. References.....	3
 CHAPTER 2 – SYSTEMATIC INVESTIGATION OF ALKALI METAL IONS AS ADDITIVES FOR GRAPHITE ANODE ON PROPYLENE CARBONATE BASED ELECTROLYTE	 5
2.1. Abstract	6
2.2. Introduction.....	7
2.3. Experimental.....	10
2.3.1. Material.....	10
2.3.2. Electrochemical Characterization.....	10
2.3.3. Surface Characterization.....	11
2.4. Results and Discussion.....	12
2.4.1. Electrochemical Properties.....	12
2.4.2. FTIR-ATR.....	14

2.4.3. XPS.....	15
2.4.4. TEM.....	17
2.4.5. ICP-MS.....	17
2.4.6. Electrochemical cycling of harvested electrodes.....	18
2.5. Conclusion.....	18
2.6. References.....	20
2.7. List of Figures.....	27
2.8. List of Tables.....	28
2.9. Figures.....	29
2.10. Tables.....	36
 CHAPTER 3- HIGH CYCLING PERFORMANCE OF SI	
NANOPARTICLE ANODE UTILIZING CITRIC ACID AS AN	
EFFICIENT BINDER	38
3.1. Abstract	39
3.2. Introduction.....	40
3.3. Experimental.....	44
3.4. Results and Discussion.....	45
3.4.1. Electrochemical cycling behaviour.....	45
3.4.2. Ex-Situ characterization of the SEI.....	47
3.5. Conclusion.....	52
3.6. References.....	54
3.7. List of Figures.....	61
3.8. Figures.....	62

CHAPTER 4- USE OF CITRIC ACID TO FORM AN ARTIFICIAL SEI ON SILICON NANOPARTICLES TO ENHANCE THE PERFORMANCE IN LI-ION BATTERY ANODES.....	69
4.1. Abstract	70
4.2. Introduction.....	71
4.3. Experimental.....	72
4.3.1. Surface modification of silicon nanoparticles.....	73
4.3.2. Preparation of Electrodes.....	73
4.3.3. Cell Construction.....	74
4.4. Results and Discussion.....	75
4.4.1. Electrochemical Performances.....	76
4.4.2. Surface Analysis of the electrodes.....	78
4.4.3. Electrochemical Cycling of full cells.....	80
4.5. Conclusion.....	80
4.6. References.....	82
4.7. List of Figures.....	86
4.8. List of Tables.....	87
4.9. Figures.....	88
4.10. Tables.....	96
 CHAPTER 5- CASEIN FROM BOVINE MILK AS A BINDER FOR SILICON BASED ANODES.....	 97
5.1. Abstract	98
5.2. Introduction.....	100

5.3. Experimental.....	102
5.3.1. Preparation of Electrode laminates.....	102
5.3.2. Cell construction and cycling procedure.....	104
5.4. Results and Discussion.....	105
5.4.1. Electrochemical performance.....	105
5.4.2. Surface Analysis.....	107
5.4.3. Understanding Surface Morphology.....	109
5.5. Conclusion.....	110
5.6. References.....	112
5.7. List of Figures.....	118
5.8. Figures.....	119
APPENDICES	129

CHAPTER 1

INTRODUCTION

1.1. Background

With the increase of greenhouse gas emission from industry and motorized vehicles, governments around the world took the initiative to fuel greener energy research¹. Preceded by numerous inventions carried out by researchers such as Goodenough³, and Yazami⁴, the first Li ion battery was commercialized by Sony Co. in 1990s. Although battery research at the beginning was very slow, technological advancement in the field of electronics led to a boom in popularity². Soon the Li ion batteries became the power source of all mobile consumer electronic devices, such as laptops, cell phones, cameras etc. Battery manufactures have invented new ways to increase the energy density of materials and develop better cell architecture as well as improve safety aspects of lithium ion batteries to be used in consumer electronics. Continuous research and development are still required with the rise of battery usage in electric vehicles, use in medical implants, grid storage etc⁵.

1.2. How a Li ion Battery works

A li-ion battery, like most other batteries, consists of two electrodes, a positive electrode (Cathode) and a negative electrode (Anode). The two electrodes are separated by a porous membrane called the separator, which is either made out of glass fiber or polyolefin. There is an electrolyte solution which is the ion carrier in the cell. The anode usually consists of a host material such as graphite, silicon, tin etc. And the cathode consists of a lithium transition metal oxide electrode, such as LiCoO_2 , LiMnO_2 , LiNiCoMnO_2 and etc. This acts as the supplier of Li^+ ions. The electrolyte solution consists of a lithium salt such as LiPF_6 , LiTFSI , LiClO_4 etc. and a carbonated based electrolyte mixture. When a battery is charged, the Li^+ ion in the cathode solvates with the electrolyte and moves to the anode and intercalates or alloys. When the cell is connected to an external circuit, these ions deintercalate from the anode and

intercalate back in the cathode, while electrons are passed through the external circuit giving current.

In the first few charging cycles, as the solvated Li ions approach the anode, they reduce on the surface due to the working potential forming a passivation layer called the solid electrolyte interphase (SEI). The SEI is a Li ion conducting but electron insulating layer. This acts as a protective layer on the electrode to minimize the electrolyte from further decomposing on the surface⁶.

Optimization of the SEI formation is important because the consumption of the electrolyte will lead to faster capacity fade.

1.3. Review of the problem

Continuous improvement of Li ion batteries is required due to cost of material, need for higher energy density, improved working voltage range, temperature range, lifetime and safety. Both anode and cathode material development is needed for use in high power applications. Electrolyte and additive development is required to address the other challenges. This work confronts these challenges by

1. Investigating additives to work on a wider temperature range
2. Investigating binders and surface functionalization to improve the performance of high energy density material, Silicon

1.4. References

1. M. Li, J. Lu, Z. Chen, K. Amine, *J. Advanced Mat.*, 1800561, 1-24, 2018
2. T. Nagaura and K. Tozawa, *Progress in Batteries and Solar Cells*, 9, 20(1990)
3. J. Goodenough and K. Mizushima, *US Patent 4302518*, Nov. 24, 1981

4. R. Yazami and P. Touzain, *J. Power Sources*, 9, 365(1983)
5. F. Schipper, E. M. Erickson, C. Erk, Ji-Y. Shin, F. F. Chesneau, D. Aurbach, *J. Electrochem. Society*, 164 (1) A6220-A6228 (2017)
6. K.Xu, *Chem Reviews*, 104(10), pp 4303-4418, 2004

CHAPTER 2

Systematic Investigation of Alkali Metal Ions as Additives for Graphite Anode in Propylene Carbonate Based Electrolytes

K.W.D. Kaveendi Chandrasiri, Cao Cuong Nguyen, Yuzi Zhang,

Bharathy S.Parimalam, Brett L. Lucht*

Electrochimica Acta, Volume 250, 1 October 2017, Pages 285-291

2.1. Abstract

Propylene carbonate (PC) is an electrolyte co-solvent with a wide working temperature range, which can improve the performance of lithium ion batteries (LIBs). Unfortunately, PC co-intercalates into graphite with lithium ions leading to exfoliation and rapid capacity decay. Incorporation of low concentrations of Cs⁺ or K⁺ ions as additives improves the performance by inhibiting graphite exfoliation and leading to better first cycle efficiency. The electrochemical behavior of graphite anodes with a series of electrolytes containing added alkaline metal acetate salts, Li, Na, K, and Cs, has been investigated. Cells containing K and Cs acetate have the highest first cycle efficiency and reversible cycling capacity. In an effort to better understand the role of the cation on performance, the solid electrolyte interphase (SEI) on the graphitic anodes cycled with the different electrolytes has been investigated via a combination of X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Infrared Spectroscopy (ATR-IR), Transmission electron microscopy (TEM) and Inductive coupled plasma mass spectrometry (ICP-MS). The presence of the heavier cations (K and Cs) leads to a thinner SEI with higher LiF content which is likely responsible for the performance enhancement.

Keywords

Lithium ion batteries, electrolyte additives, Solid electrolyte interphase, anode

2.2. Introduction

Interest in Li ion batteries (LIB) has significantly increased over the last two decades due to the widespread use of consumer electronics such as cellular phones, laptops, and cameras. There is also interest in the use of LIB for high power and wide temperature range applications such as electric vehicles[1], electric torpedoes[2], as well as military and aerospace applications[3]. While many materials such as lithium (Li), graphite, silicon (Si) and tin (Sn) have been recently investigated as anodes for LIB, graphite is the most widely used anode material in commercial LIB[4]. This is due to a low flat working potential vs. Li, and good cycling stability which provides long operational lifetimes[5][6]. Graphite also offers good electronic conductivity, stable capacity, and low cost[7][8]. Lithium is intercalated into the graphite structure as LiC_6 with a specific capacity of 372 mAh/g. LIB electrolytes consist of a highly dissociating salt dissolved in a mixture of linear and cyclic carbonate solvents. The most frequently used cyclic carbonates are ethylene carbonate (EC) and propylene carbonate (PC). EC is considered an essential component in the electrolyte due to the importance of EC in formation of a stable solid electrolyte interphase (SEI), allowing reversible lithium intercalation/deintercalation for graphite electrodes[9–11]. However, EC has a relatively high melting point (36.4°C) limiting low temperature performance. In order to enable LIB operation at low temperature, EC is blended with linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC)[12,13]. Another approach is to replace EC with PC which has a broader operating temperature window of -48.8°C to 242.0 °C[14][15].

Unfortunately, PC co-intercalates into graphite during cycling resulting in graphite exfoliation and destruction of the anode[16].

One effective method to prevent graphite exfoliation with PC electrolytes is to generate a stable SEI during the first cycle. A more stable SEI can be generated via incorporation of electrolyte additives or electrolytes with high salt concentrations[17]. While electrolytes containing high salt concentrations have received significant recent interest, high concentrations of lithium salts typically reduce the conductivity of the electrolyte. Thus, most commercial LIB electrolytes have salt concentrations between 1.0 and 1.2 M[18–20]. The SEI formed on the graphite anode consumes lithium irreversibly from the electrolyte resulting in a decrease in the first cycle coulombic efficiency. Therefore, formation of a stable and uniform surface film with minimum electrolyte reduction is critical for LIB[21][22]. Low concentrations of SEI forming electrolyte additives have been investigated to generate a stable SEI[23]. The additives are typically preferentially reduced before the carbonate solvents and lead to improved cycle life[24]. Recent reports have described the use of many different additives including sulfur containing species, unsaturated compounds, and other alkali metal cations[16][25][23][26]. Investigations of electrolytes containing both sodium and lithium salts, show that lithium intercalates into graphite in the presence of sodium without sodium intercalation or deposition[27]. A recent study has revealed that cesium cations can enhance the performance of lithium ion batteries containing PC based electrolytes [28–30]

The role of different alkali metal ions as additives for graphite electrodes in PC based electrolytes has been systematically investigated via electrochemical and ex-situ

surface analytical methods. The electrochemical performance of Li||graphite cells has been investigated with 1M LiPF₆ in EC: PC: EMC (5:2:3) with and without added lithium, sodium, potassium and cesium acetates. The coulombic efficiency improves with an increase in cation radius of the acetate salt. Ex situ surface analysis was conducted via a combination of TEM, IR-ATR, XPS and ICP-MS to develop a better understanding of SEI formation, structure, and function for the SEI generated in the presence of different alkali metal ions.

2.3. Experimental

2.3.1. Material

Battery grade lithium hexafluorophosphate (LiPF_6), ethylene carbonate (EC), propylene carbonate (PC), and ethyl methyl carbonate (EMC) were obtained from BASF. Trace metal grade 70% nitric acid ($>99.9\%$), dimethyl carbonate (DMC), cesium and potassium standards, anhydrous cesium, potassium, sodium and lithium acetates ($\geq 99.9\%$), were purchased from Fisher Scientific. The acetate salts were used since high purity acetate salts of all of the different cations are commercially available. Graphite electrode laminates ($55\text{ }\mu\text{m}$ thickness and a loading of 6 mg/cm^2) and high purity Li chips (15.5 mm diameter and 0.25 mm thickness) were purchased from MTI. Graphite anodes were punched at 15 mm diameter and dried in a vacuum oven for 24 hours at $110\text{ }^\circ\text{C}$. Preparation of electrolyte solutions, cell assembling and disassembling was done in an argon glove box (M-Braun) with water and oxygen contents $< 1\text{ ppm}$.

2.3.2. Electrochemical Measurements

All electrochemical measurements were performed in triplicate ($< 1\%$ variation) on 2032 coin cells using an Arbin BT2000 battery cycler. The cells consist of a graphite working electrode, lithium foil counter electrode, one 19 mm and one 15 mm separator (Celgard 2325) sandwiched with a 16 mm Whatmann glass microfiber separator, and electrolyte ($100\text{ }\mu\text{L}$). The formation cycles for $\text{Li}||\text{graphite}$ cells were carried out with one cycle at $\text{C}/20$, two cycles at $\text{C}/10$ at a voltage range of $0.005\text{--}1.2\text{ V}$. The subsequent cycling was conducted at a rate of $\text{C}/5$. All cycles included a taper charge at $1/10^{\text{th}}$ the respective rate. The rate was calculated based on the nominal capacity of

the graphite electrode, 350 mAh/g. All cells were cycled at 25°C. Electrolyte solutions were prepared inside an Argon filled glove box. The STD electrolyte is 1M LiPF₆ + EC: PC: EMC (5:2:3). Li-Ac, Na-Ac, K-Ac and Cs-Ac electrolytes consists of the STD electrolyte with 0.02M of added acetate.

2.3.3. Surface Characterization

Graphite electrodes were removed from cycled Li||graphite cells in an Ar filled glovebox. All electrodes were washed 4 times with 500 μ L aliquots of DMC unless otherwise specified. The electrodes were dried under vacuum overnight. The infrared spectra with attenuated total reflectance (IR-ATR) were conducted inside a N₂-filled glovebox with a Bruker Tensor 27 IR spectrometer equipped with an LaDTG detector. All spectra were collected with 512 scans and with a spectral resolution of 4 cm⁻¹. All samples were transferred into the N₂ glovebox without exposure to air. Ex-situ XPS was conducted using a K α spectrometer (Thermo scientific) with a spot size of 400 μ m, an energy step size of 0.05 eV, and a pass energy of 50 eV without charge compensation for cycled electrodes. XPS of alkali metal acetate powders was collected for reference. The flood gun was used for charge compensation. XPS samples were transferred via a vacuum sealed transfer vessel without exposure to air. The binding energy was corrected based on C 1s of hydrocarbon at 285 eV. TEM imaging was conducted using a JEOL JEM-2100F TEM (Perbody, MA) at 160 eV. TEM samples were prepared as follows: the cycled electrodes were treated with ultrasonication in DMC for 15 mins to allow homogenous dispersion of the active materials in solution, and then copper TEM grids (500 mesh) were dipped into the dispersed solution and dried overnight in a vacuum oven. The TEM grids were

transferred into the TEM chamber using tightly-closed vials. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of the digested cycled electrodes was conducted using iCAP Q ICP-MS with He KED interference reduction. Disassembled electrodes were rinsed 4 times with aliquots of 500 μ L of DMC and then separated from the copper foil into an HDPE vial. Samples were sonicated for 15 mins and digested in 2% HNO_3 for 72 hours. The solution was filtered multiple times using 0.45 μ m wattman syringe filter before measurement. All samples were measured in triplicate.

To investigate the role of cesium and potassium ions in the anode SEI, cells containing Cs-Ac and K-Ac as additives were cycled at C/20 for a single cycle and carefully disassembled. The electrode was carefully rinsed twice using 500 μ L portions of the carbonate solvent mixture (EC: PC: EMC 5:2:3) to remove residual electrolyte. The electrode was further rinsed with three 500 μ L portions of DMC to remove residual EC. These electrodes were dried for 10 minutes under vacuum in the antechamber of an argon filled glovebox and then used as an electrode for a new cell with the STD electrolyte formulation without added Cs-Ac or K-Ac. The cell was cycled at C/20 for one cycle and the voltage profiles were compared.

2.4. Results and Discussion:

2.4.1. Electrochemical Properties

The voltage profiles for the first cycle for each cell are provided in Figure 1. A plateau at ~0.7 V is observed for cells cycled with standard, Li-Ac and Na-Ac electrolytes. This can be attributed to the reduction of PC and EC. The plateau ends and the

voltage decreases below 0.25 V characteristic of lithiation of the graphite electrode. In contrast, cells containing the K-Ac electrolyte have a much smaller plateau, which starts at a slightly lower voltage, ~0.6 V[31]·[32]. Interestingly, cells containing the Cs-Ac electrolyte have a very small shoulder in the 0.4-1.0 V range suggesting little PC reduction and have excellent reversible capacity. All of the cells have similar voltage plateaus below 0.25 V which results from the lithium intercalation into graphite to form Li_xC_6 ($0 \leq x \leq 1$)[9].

The voltage profiles after 10 cycles are provided in figure 1(b) and contain no high potential (> 0.4 V) shoulders consistent with no further PC reduction, and the reversible capacity and efficiency are good for all cells. The discharge capacity and coulombic efficiency are provided in Figure 1c and d, respectively. As the ionic radius of the alkali metal increases, the first cycle efficiency increases as depicted in Figure 1. The first cycle efficiency for cells containing the STD, Li-Ac and Na-Ac electrolytes is around 25%. The first cycle efficiency is increased to 40-50% for K-Ac and is further increased above 80% for Cs-Ac. The first cycle discharge capacity is similar for all electrolytes, suggesting that while there are significant differences in the quantity of electrolyte reduced, graphite damage and exfoliation is minimal during the first cycle. Cells cycled with the Cs-Ac and K-Ac electrolytes have higher specific capacity after 10 cycles than cells cycled with Na-Ac, Li-Ac, or STD electrolytes. Cells containing Na-Ac, Li-Ac and STD electrolytes have relatively similar efficiency and capacity retention and more capacity fade over the first 10 cycles (~20 %). While all the cells have reasonable efficiency after 6 cycles, the electrodes extracted from cells cycled with the STD, Li-Ac or Na-Ac electrolytes have signs of considerable

damage as evidenced by very poor contact with the current collector. Alternatively, the electrodes extracted from cells cycled with the Cs-Ac or K-Ac electrolytes adhere well to the current collector after 10 cycles. Oddly, these results differ from previous investigations where Na was beneficial while K had a negative impact on the graphite anodes [33].

2.4.2. *Fourier Transformation Infrared Spectroscopy - ATR*

Ex-situ surface analysis has been conducted on electrodes cycled with the different electrolytes to develop a better understanding of the difference in the performance of the cells containing the standard electrolyte and the cells containing electrolytes with added alkali metal acetates. The IR-ATR spectra for fresh and cycled (1 cycle and 10 cycles) graphite electrodes extracted from Li/graphite cells are provided in figure 2.

The fresh electrode has absorptions at 1579, 1425, and 1230 cm^{-1} consistent with the presence of the SBR-CMC binder[34]. After the first cycle, the IR spectra of the electrodes are changed for all electrolytes. Interestingly, the IR spectra are very similar for all electrolytes investigated. Strong new absorptions are observed at 1492 and 868 cm^{-1} consistent with the presence of Li_2CO_3 [35][36]. Weaker new absorptions are observed at 1662 and 1778 cm^{-1} characteristic of lithium alkyl carbonates and poly(carbonate)s, respectively[37][36]. In addition, all the electrodes investigated contain medium absorptions at 1579 and 1184 cm^{-1} which is likely a combination of lithium carboxylates such as lithium acetate and the SBR-CMC binder[38]. Lithium alkyl carbonates, Li_2CO_3 , poly(carbonate)s, and lithium carboxylates are commonly observed components of the anode SEI. However, the similarity of the IR spectra for the different electrodes is surprising considering the significant difference in first cycle

efficiency for the different electrolytes. The IR spectra of electrodes after 10 cycles with the different electrolytes are also provided in Figure 2. The spectra are similar for all electrolytes investigated, suggesting that the organic components of the SEI are similar for all electrolytes investigated.

2.4.3. X-ray photoelectron spectroscopy

The C 1s, F 1s, and O1s XPS spectra of graphite electrodes extracted from cells after 1 and 10 cycles with different electrolytes are provided in Figure 3. The XPS spectra of electrodes cycled with all of the different electrolytes are similar. The C 1s spectra contain a peak at 290 eV characteristic of the CO₃ present in Li₂CO₃ and lithium alkyl carbonates[39]. In addition, the C1s spectra contain peaks characteristic of C-O (286.5 eV), C-H (285 eV), and graphite (284 eV). The primary difference in the C 1s XPS spectra for the different electrolytes is the intensity of the graphite peak at 284 eV. The relative intensity of the graphite peak is greatest for the Cs-Ac and K-Ac electrolytes, suggesting that the SEI is thinner for these electrolytes since the SEI is thinner than the depth of penetration of XPS, ~ 5 nm[40]. The O 1s spectra of electrodes cycled with all of the electrolytes are dominated by a broad peak centered at ~533 eV consistent with the presence of a mixture of C-O and C=O containing species characteristic of lithium acetate, lithium alkyl carbonates and Li₂CO₃[41]. The F1s spectra of electrodes cycled with the different electrolytes contain two peaks characteristic of LiF at 685 eV and Li_xPF_yO_z at 687 eV. After the first cycle, the electrodes cycled with most of the electrolytes have similar intensity for the LiF and Li_xPF_yO_z peaks. However, the F 1s peak for LiF has much greater intensity for the electrode cycled with the Cs-Ac electrolyte. The F 1s spectra of the electrodes after

10 cycles also contain the same two peaks, but the LiF peak intensity is greater for the electrodes cycled with the STD and Li-Ac electrolytes. The P2p spectra of the cycled electrodes contain weak peaks between 134 and 137 eV (not shown) characteristic of $\text{Li}_x\text{PF}_y\text{O}_z$ and residual LiPF_6 [42]. The electrode cycled with the Cs-Ac electrolyte also contains very weak Cs 3d peaks (Figure 4) consistent with the presence of a low concentration Cs in the SEI.

The elemental atomic concentrations of the electrode surfaces after 1 and 10 cycles as determined by XPS are provided in table 1. After one cycle, the concentration of F is higher for the cells cycled with the Cs-Ac and K-Ac electrolytes. In addition, the element concentrations have only small changes for the Cs-Ac and K-Ac electrolytes when comparing electrodes after 1 and 10 cycles suggesting that the SEI is stable and does not evolve with additional cycling. Alternatively, the elemental concentrations of the electrodes cycled with the STD and Li-Ac electrolytes have significant changes in the elemental concentrations after 10 cycles suggesting a significant evolution of the SEI with additional cycling.

The atomic concentrations of electrodes cycled with the STD and the Cs-Ac electrolytes as a function of sputtering time are provided in Figure 5. Initially the concentration of C is ~ 50 % for both electrodes. Upon sputtering the concentration of C increases for both the electrodes, although the increase is much faster for the electrode cycled with the Cs-Ac electrolyte. The increase in C concentration is consistent with removal of the SEI components via sputtering to reveal the underlying graphite anode. Thus, the faster removal of the SEI components is consistent with a thinner SEI for the Cs-Ac electrolyte. Similar trends are observed for the decreasing

concentrations of O and F providing additional support for a thinner SEI on the electrode cycled with the Cs-Ac electrolyte.

2.4.4. Transmission Electron Microscopy (TEM)

TEM images (figure 6) of the electrodes cycled with different electrolytes reveal significant differences in the thickness of the anode SEI and are in agreement with the XPS sputtering data. Electrodes cycled with the STD, Li-Ac and Na-Ac electrolytes have a very thick film on the electrode. The SEI is amorphous and discontinuous consistent with significant deposits of electrolyte reduction products. The cells cycled with electrolyte containing added K-Ac and Cs-Ac have a thin grainy SEI which has a similar morphology to the LiF rich SEI generated on graphite electrodes with concentrated electrolytes[42]. The grains are ~10 nm diameter and densely packed on the graphite surface. The TEM and XPS data suggest the presence of a LiF rich SEI composed of LiF nano-particles. The presence of Cs^+ or K^+ appears to initiate the formation of a thin LiF nano-particle passivation layer. The larger cations may initiate LiF nanoparticle aggregation by impeding the kinetics of Li ion intercalation into the graphite or providing a site for initial CsF generation acting a seed for LiF aggregation.

2.4.5. Inductive couple plasma – Mass Spectrometry (ICP-MS)

To further investigate the presence of cesium or potassium in the SEI, elemental analysis of the extracted electrodes was conducted by ICP-MS. The concentrations of Cs and K for the cycled electrodes are provided in Table 2. The concentrations of Cs and K are 100 times greater when cells are cycled with Cs-Ac or K-Ac, respectively,

consistent with incorporation of the Cs or K into the SEI during formation cycling, as previously observed by XPS data (Figure 4).

2.4.6. Electrochemical Cycling of Harvested Electrodes

In an effort to confirm the generation of a stable SEI for cells cycled with Cs-Ac or K-Ac electrolytes, cells were prepared with the STD, K-Ac, and Cs-Ac electrolytes. Electrodes were extracted from cells after one cycle and the pre-cycled electrodes were used to prepare new cells containing STD electrolyte (no added Cs-Ac or K-Ac). The 1st cycle (C/20) voltage profiles of the cells prepared with the pre-cycled electrodes are provided in Figure 7. The cells constructed with the electrodes pre-cycled with the STD electrolyte have very low first cycle efficiency, < 30%. However, the cells constructed with the pre-cycled electrodes with either the Cs-Ac or K-Ac electrolytes have a high first cycle efficiency, > 75 %. This demonstrates the presence of a stable SEI on the electrodes cycled with the Cs⁺ and K⁺ ions.

2.5. Conclusion

A systematic investigation was carried out on the incorporation of alkali metal acetates as additives for PC based electrolytes for graphite anodes in lithium-ion batteries. The electrochemical performance and ex-situ surface analysis of cells containing the STD electrolyte and the Li-Ac electrolyte are nearly identical suggesting that the effect of the acetate anion on the electrochemical performance and SEI structure is small. Upon increasing the ionic radius of the alkali metal ions, a significant improvement in the performance was observed along with significant decrease in PC reduction. A combination of ex-situ surface analysis via XPS, IR-ATR, and TEM suggests that the organic SEI components are similar for all electrolytes, but higher concentrations of

LiF are observed after the first cycle for electrodes cycled with the Cs-Ac and K-Ac electrolytes. A morphological difference of the surface films was observed for the different electrolytes. Electrodes cycled with the STD, Li-Ac, and Na-Ac electrolytes are thick and inhomogeneous while electrodes cycled with the K-Ac and Cs-Ac electrolytes are thin and grainy. The larger cations may initiate LiF nano-particle aggregation and facilitate the generation of a thin, homogeneous, and robust LiF rich SEI.

2.6. Acknowledgement

The authors gratefully acknowledge funding from Department of Energy Office of Basic Energy Sciences EPSCoR Implementation award (DE-SC0007074).

2.7. References

- [1] K. Zaghib, A. Mauger, H. Groult, J.B. Goodenough, C.M. Julien, Advanced electrodes for high power Li-ion batteries, *Materials (Basel)*. 6 (2013) 1028–1049. doi:10.3390/ma6031028.
- [2] R. Gitzendanner, F. Puglia, C. Martin, D. Carmen, E. Jones, S. Eaves, High power and high energy lithium-ion batteries for under-water applications, *J. Power Sources*. 136 (2004) 416–418. doi:10.1016/j.jpowsour.2004.03.032.
- [3] A. Ritchie, W. Howard, Recent developments and likely advances in lithium-ion batteries, *J. Power Sources*. 162 (2006) 809–812. doi:10.1016/j.jpowsour.2005.07.014.
- [4] B. Wang, B. Luo, X. Li, L. Zhi, The dimensionality of Sn anodes in Li-ion batteries, *Mater. Today*. 15 (2012) 544–552. doi:10.1016/S1369-7021(13)70012-9.
- [5] C. Wang, A.J. Appleby, F.E. Little, Charge-discharge stability of graphite anodes for lithium-ion batteries, *J. Electroanal. Chem.* 497 (2001) 33–46. doi:10.1016/S0022-0728(00)00447-2.
- [6] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. Proietti Zaccaria, C. Capiglia, Review on recent progress of nanostructured anode materials for Li-ion batteries, *J. Power Sources*. 257 (2014) 421–443. doi:10.1016/j.jpowsour.2013.11.103.
- [7] A. Patil, V. Patil, D. Wook Shin, J.W. Choi, D.S. Paik, S.J. Yoon, Issue and challenges facing rechargeable thin film lithium batteries, *Mater. Res. Bull.* 43 (2008) 1913–1942. doi:10.1016/j.materresbull.2007.08.031.
- [8] B. Scrosati, J. Garche, Lithium batteries: Status, prospects and future, *J. Power Sources*. 195 (2010) 2419–2430. doi:10.1016/j.jpowsour.2009.11.048.

- [9] K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, *Chem. Rev.* 104 (2004) 4303–4417. doi:10.1021/cr030203g.
- [10] K. Xu, Electrolytes and interphases in Li-ion batteries and beyond, *Chem. Rev.* 114 (2014) 11503–11618. doi:10.1021/cr500003w.
- [11] S.S. Zhang, A review on electrolyte additives for lithium-ion batteries, *J. Power Sources.* 162 (2006) 1379–1394. doi:10.1016/j.jpowsour.2006.07.074.
- [12] D. Aurbach, Y. Talyosef, B. Markovsky, E. Markevich, E. Zinigrad, L. Asraf, J.S. Gnanaraj, H.J. Kim, Design of electrolyte solutions for Li and Li-ion batteries: A review, *Electrochim. Acta.* 50 (2004) 247–254. doi:10.1016/j.electacta.2004.01.090.
- [13] S.S. Zhang, T.R. Jow, K. Amine, G.L. Henriksen, LiPF₆ ± EC ± EMC electrolyte for Li-ion battery, *J. Power Sources.* 107 (2002) 18–23. doi:10.1016/S0378-7753(01)00968-5.
- [14] H. Zhao, S.J. Park, F.F. Shi, Y.B. Fu, V. Battaglia, P.N. Ross, G. Liu, Propylene Carbonate (PC)-Based Electrolytes with High Coulombic Efficiency for Lithium-Ion Batteries, *J. Electrochem. Soc.* 161 (2014) A194–A200. doi:10.1149/2.095401jes.
- [15] D.M. Seo, S. Reininger, M. Kutcher, K. Redmond, W.B. Euler, B.L. Lucht, Role of mixed solvation and ion pairing in the solution structure of lithium ion battery electrolytes, *J. Phys. Chem. C.* 119 (2015) 14038–14046. doi:10.1021/acs.jpcc.5b03694.
- [16] M.D. Bhatt, C. O'Dwyer, The Role of Carbonate and Sulfite Additives in Propylene Carbonate-Based Electrolytes on the Formation of SEI Layers at Graphitic

- Li-Ion Battery Anodes, *J. Electrochem. Soc.* 161 (2014) A1415–A1421. doi:10.1149/2.0931409jes.
- [17] S. Dalavi, P. Guduru, B.L. Lucht, Performance Enhancing Electrolyte Additives for Lithium Ion Batteries with Silicon Anodes, *J. Electrochem. Soc.* 159 (2012) A642-A646. doi:10.1149/2.076205jes.
- [18] R. Younesi, G.M. Veith, P. Johansson, K. Edstrom, T. Vegge, Lithium salts for advanced lithium batteries: Li-metal, Li-O₂, and Li-S, *Energy Environ. Sci.* 8 (2015) 1905–1922. doi:10.1039/C5EE01215E.
- [19] H.P. Chen, J.W. Fergus, B.Z. Jang, The Effect of Ethylene Carbonate and Salt Concentration on the Conductivity of Propylene Carbonate|Lithium Perchlorate Electrolytes, *J. Electrochem. Soc.* 147 (2000) 399-406. doi:10.1149/1.1393209.
- [20] S.K. Jeong, H.Y. Seo, D.H. Kim, H.K. Han, J.G. Kim, Y.B. Lee, Y. Iriyama, T. Abe, Z. Ogumi, Suppression of dendritic lithium formation by using concentrated electrolyte solutions, *Electrochem. Commun.* 10 (2008) 635–638. doi:10.1016/j.elecom.2008.02.006.
- [21] Y.Y. Zhang, Y.Y. Zhang, S. Xia, P. Dong, L. Jin, J. Song, Challenges in the Development of Film-Forming Additives for Lithium Ion Battery: A Review, *Am. J. Anal. Chem.* 4 (2013) 7–12. doi:10.4236/ajac.2013.46A002.
- [22] S. Uchida, M. Yamagata, M. Ishikawa, Effect of Electrolyte Additives on Non-Nano-Si Negative Electrodes Prepared with Polyimide Binder, *J. Electrochem. Soc.* 162 (2014) A406–A412. doi:10.1149/2.0581503jes.

- [23] A.M. Haregewoin, A.S. Wotango, B.-J. Hwang, Electrolyte additives for lithium ion battery electrodes: progress and perspectives, *Energy Environ. Sci. Energy Environ. Sci.* 9 (2016) 1955–1988. doi:10.1039/c6ee00123h.
- [24] L.E. Downie, K.J. Nelson, R. Petibon, V.L. Chevrier, J.R. Dahn, The Impact of Electrolyte Additives Determined Using Isothermal Microcalorimetry, *ECS Electrochem. Lett.* 2 (2013) A106–A109. doi:10.1149/2.010310eel.
- [25] C. Korepp, H.J. Santner, T. Fujii, M. Ue, J.O. Besenhard, K.C. Möller, M. Winter, 2-Cyanofuran-A novel vinylene electrolyte additive for PC-based electrolytes in lithium-ion batteries, *J. Power Sources.* 158 (2006) 578–582. doi:10.1016/j.jpowsour.2005.09.021.
- [26] J. Zheng, P. Yan, R. Cao, H. Xiang, M.H. Engelhard, B.J. Polzin, C. Wang, J.G. Zhang, W. Xu, Effects of Propylene Carbonate Content in CsPF₆-Containing Electrolytes on the Enhanced Performances of Graphite Electrode for Lithium-Ion Batteries, *ACS Appl. Mater. Interfaces.* 8 (2016) 5715–5722. doi:10.1021/acsami.5b12517.
- [27] K. Matsuki, K. Ozawa, Lithium Ion Rechargeable Batteries: Materials, Technology, and New Applications, *Lithium Ion Recharg. Batter. Mater. Technol. New Appl.* (2009) 1–9.
- [28] H. Xiang, D. Mei, P. Yan, P. Bhattacharya, S.D. Burton, A. Von Wald Cresce, R. Cao, M.H. Engelhard, M.E. Bowden, Z. Zhu, B.J. Polzin, C.M. Wang, K. Xu, J.G. Zhang, W. Xu, The Role of Cesium Cation in Controlling Interphasial Chemistry on Graphite Anode in Propylene Carbonate-Rich Electrolytes, *ACS Appl. Mater. Interfaces.* 7 (2015) 20687–20695. doi:10.1021/acsami.5b05552.

- [29] C. Wang, K. Xu, J. Zhang, W. Xu, Wide-Temperature Electrolytes for Lithium-Ion Batteries, *ACS Appl. Mater. Interfaces*, (2017) 11826-11835, doi:10.1021/acsami.7b04099.
- [30] M.S. Ding, Q. Li, X. Li, W. Xu, K. Xu, Effects of Solvent Composition on Liquid Range, Glass Transition, and Conductivity of Electrolytes of a (Li, Cs)PF₆ Salt in EC-PC-EMC Solvents, *J. Phys. Chem. C*. (2017) 11178-11183, doi:10.1021/acs.jpcc.7b03306.
- [31] W. Luo, J. Wan, B. Ozdemir, W. Bao, Y. Chen, J. Dai, H. Lin, Y. Xu, F. Gu, V. Barone, L. Hu, Potassium Ion Batteries with Graphitic Materials, *Nano Lett.* 15 (2015) 7671–7677. doi:10.1021/acs.nanolett.5b03667.
- [32] M. Arakawa, J. Yamaki, Anodic-Oxidation of Propylene Carbonate and Ethylene Carbonate on Graphite-Electrodes, *J. Power Sources*. 54 (1995) 250–254. doi:10.1016/0378-7753(94)02078-H.
- [33] S. Komaba, T. Itabashi, T. Kimura, H. Groult, N. Kumagai, Opposite influences of K⁺ versus Na⁺ ions as electrolyte additives on graphite electrode performance, *J. Power Sources*, 146 (2005) 166–170. doi:10.1016/j.jpowsour.2005.03.121.
- [34] C.C. Nguyen, T. Yoon, D.M. Seo, P. Guduru, B.L. Lucht, Systematic Investigation of Binders for Silicon Anodes: Interactions of Binder with Silicon Particles and Electrolytes and Effects of Binders on Solid Electrolyte Interphase Formation, *ACS Appl. Mater. Interfaces*. 8 (2016) 12211–12220. doi:10.1021/acsami.6b03357.

- [35] G. V Zhuang, H. Yang, P.N. Ross, K.Xu, R. Jow, Lithium Methyl Carbonate as a Reaction Product of Metallic Lithium and Dimethyl Carbonate, *Electrochemical and Solid-State Letters* 9(2) (2006) A64-A68, doi: 10.1149/1.2142157
- [36] F.A. Miller, C.H. Wilkins, Infrared Spectra and Characteristic Frequencies of Inorganic Ions, *Anal. Chem.*, 1952, 24 (8), pp 1253–1294, doi: 10.1021/ac60068a007
- [37] D.M. Seo, D. Chalasani, B.S. Parimalam, R. Kadam, M. Nie, B.L. Lucht, Reduction Reactions of Carbonate Solvents for Lithium Ion Batteries, *ECS Electrochem. Lett.* 3 (2014) A91–A93. doi:10.1149/2.0021409eel.
- [38] M. Nie, B.L. Lucht, Role of Lithium Salt on Solid Electrolyte Interface (SEI) Formation and Structure in Lithium Ion Batteries, *J. Electrochem. Soc.* 161 (2014) A1001–A1006. doi:10.1149/2.054406jes.
- [39] D. Aurbach, I. Weissman, A. Schechter, H. Cohen, X-ray Photoelectron Spectroscopy Studies of Lithium Surfaces Prepared in Several Important Electrolyte Solutions. A Comparison with Previous Studies by Fourier Transform Infrared Spectroscopy, *Langmuir*. 12 (1996) 3991–4007. doi:10.1021/la9600762.
- [40] J. Sun, I.G. Hill, Understanding the Role of Prop-1-ene-1, 3- Sultone and Vinylene Carbonate in $\text{LiNi}_{1/3}\text{Mn}$, *J. Electrochem. Soc.* 2015 volume 162, issue 14, A2635-A2645. doi:10.1149/2.0741512jes.
- [41] S. Leroy, F. Blanchard, R. Dedryvère, H. Martinez, B. Carré, D. Lemordant, D. Gonbeau, Surface film formation on a graphite electrode in Li-ion batteries: AFM and XPS study, *Surf. Interface Anal.* 37 (2005) 773–781. doi:10.1002/sia.2072.

[42] M. Nie, D. Chalasani, D.P. Abraham, Y. Chen, A. Bose, B.L. Lucht, Lithium ion battery graphite solid electrolyte interphase revealed by microscopy and spectroscopy, *J. Phys. Chem. C* 117 (2013) 1257–1267. doi:10.1021/jp3118055.

2.8. List of Figures

Figure 1. Cycling data, a) Voltage profiles for the 1st cycle b) Voltage profile for 10th cycle c) Specific capacity vs cycle number d) Coulombic efficiency vs cycle number

Figure 2. IR-ATR spectra for graphite electrodes after one cycle and after 10 cycles.

Figure 3. XPS spectra of graphite electrodes cycled and rinsed after 1 cycle and 10 cycles

Figure 4. Cs3d XPS Spectra for cycled electrodes (1 cycle)

Figure 5. Relative Atomic Concentration for a) Standard electrolyte (1M LiPF₆ EC: PC: EMC 5:2:3) and b) Standard electrolyte + 0.02M Cs-Ac electrodes after rinsing and sputtering for 0, 60, 180, 420, 900 s

Figure 6. Transmission Electron microscopy data for electrodes harvested after one cycle

Figure 7. First cycle voltage profiles of electrodes (harvested post one formation cycle with 0.02M Cs-Ac and K-Ac) cycled with 1M LiPF₆ + EC: PC: EMC 5:2:3 (STD)

2.9. **List of Tables**

Table 1. Elemental composition of cells cycled a) first cycle and b) 10 cycles

Table 2. ICP-MS data for digested graphite electrodes. Data given in milligrams of metal in an electrode.

2.10. Figures

Figure 1. Cycling data, a) Voltage profiles for the 1st cycle b) Voltage profile for 10th cycle c) Specific capacity vs cycle number d) Coulombic efficiency vs cycle number

Figure 2. IR-ATR spectra for graphite electrodes after one cycle and after 10 cycles.

Figure 3. XPS spectra of graphite electrodes cycled and rinsed after 1 cycle and 10 cycles

Figure 4. Cs3d XPS Spectra for cycled electrodes (1 cycle)

Figure 5. Relative Atomic Concentration for a) Standard electrolyte (1M LiPF₆ EC: PC: EMC 5:2:3) and b) Standard electrolyte + 0.02M Cs-Ac electrodes after rinsing and sputtering for 0, 60, 180, 420, 900 s.

Figure 6. Transmission Electron microscopy data for electrodes harvested after one cycle

Figure 7. First cycle voltage profiles of electrodes (harvested post one formation cycle with 0.02M Cs-Ac and K-Ac) cycled with 1M LiPF₆ + EC: PC: EMC 5:2:3 (STD)

2.11. Tables

a)

Element	STD	Li-Ac	Na-Ac	K-Ac	Cs-Ac
O1s %	44.3	40.5	39.9	34.7	28.5
F1s %	6.8	13.4	17.2	17.6	21.4
C1s %	48.2	44.4	41.3	46.7	49.8
P2p %	0.7	1.7	1.6	1	0.3

b)

Element	STD	Li-Ac	Na-Ac	K-Ac	Cs-Ac
O1s %	29.3	33.2	41.9	36.8	32.9
F1s %	32.7	25.5	11.4	19.9	18.9
C1s %	36.3	39.9	45.6	41.7	47.3
P2p %	1.7	1.4	1.1	1.6	0.9

Table 1. Elemental composition of cells cycled a) first cycle and b) 10 cycles

Sample	Average Cs ⁺ Content /mg	Average K ⁺ Content /mg
Cs-Ac	0.018 ±0.002	<10 ⁻⁵
K-Ac	<10 ⁻⁵	0.008 ±0.002
STD	<10 ⁻⁵	<10 ⁻⁵

Table 2. ICP-MS data for digested graphite electrodes. Data given in milligrams of metal in an electrode.

CHAPTER 3

High Cycling Performance of Si Nanoparticle Anode utilizing Citric Acid as Efficient Binder

Cao Cuong Nguyen, K.W.D.K. Chandrasiri, Daniel M. Seo and Brett L. Lucht*

Langmuir 2017, Volume 33, 37, 9254-9261

3.1. Abstract

Citric acid and its analogues have been investigated as surface-modifying agents for Si nanoparticle anodes using electrochemical cycling, attenuated total reflectance infrared (ATR IR), and X-ray photoelectron spectroscopy (XPS). A Si nanoparticle anode prepared with citric acid (CA) has better capacity retention than one containing 1,2,3,4-butanetetracarboxylic acid (BA), but both electrodes outperform Si-PVDF. The Si-CA anode has an initial specific capacity of 3530 mA h/g and a first cycle efficiency of 82%. Surprisingly, the Si-CA electrode maintains a high specific capacity of ~2200 mA h/g after 250 cycles, corresponding to 64% capacity retention, which is similar to the Si prepared with long-chain poly(acrylic acid) (PAA). On the contrary, the silicon electrode prepared with PVDF has a fast capacity fade and retains only 980 mA h/g after 50 cycles. The IR and XPS data show that the Si-CA electrode has an SEI composed primarily of lithium citrate during the first 50 cycles, resulting from the electrochemical reduction of citric acid. Only low concentrations of electrolyte reduction products are observed. The lithium citrate layer derived from CA stabilizes the silicon surface and suppresses electrolyte reduction, which likely contributes to the enhanced cycling performance of the Si nanoparticle anode.

3.2. Introduction

The rapid development of portable electronic devices such as smartphones, tablets, and laptops requires a new generation of lithium ion batteries (LiB's) with higher energy density. High-energy LiB's are also urgently needed to increase the driving range of electric vehicles. Graphite is the most common anode used in commercial LiB's, but graphite has a moderate theoretical capacity of 372 mA h/g.(1) Much attention has been devoted to the development of silicon anodes for lithium ion batteries because of the high theoretical capacity, 3579 mA h/g.(2) However, the large volume change of Si during cycling (up to 280%) leads to the pulverization of active particles and the loss of electrical contact between electrode components.(3, 4) Furthermore, this enormous morphology change causes the continuous breakdown of the solid electrolyte interphase (SEI) on the Si surface. The reformation of the SEI consumes electrolyte and active lithium, which can result in complete electrolyte consumption and cells drying out. The combination of these detrimental reactions leads to a rapid capacity loss for silicon electrodes.

Modification of the SEI using sacrificial additives such as fluoroethylene carbonate (FEC), vinylene carbonate (VC), or methylene ethylene carbonate (MEC) is one of the effective methods of improving the cycling performance of Si nanoparticle electrodes. (5-8) These additives are reduced on the surface of silicon to form a more robust SEI mainly consisting of poly(carbonate) and inorganic salts such as lithium carbonate and lithium fluoride. This SEI was found to be effective at passivating the surface of silicon electrodes and suppressed the reduction of solvents such as EC, resulting in less lithium alkyl carbonate.(6-8)

Polymer binders are an important component to maintaining the integrity of the electrode structure. The choice of binder has a large effect on the cycling performance of Si electrodes. For example, silicon has poor cycling performance with poly(vinylidene difluoride) (PVDF), the most widely used binder in LiB's.(9, 10) Heat treatment of Si-PVDF electrodes at high temperature improves the cycling performance due to PVDF melting and homogeneous coverage of the silicon surface, leading to a significant enhancement in the adhesion strength of the electrode laminate.(11) Chen et al. improved the cycling performance of amorphous SiSn composite by using a cross-linked elastomeric polymer, poly(vinylidene fluoride-tetrafluoroethylene-propylene), together with an adhesion promoter to tolerate the large volume change of silicon and to increase the adhesion strength.(12) On the contrary, Li et al. found that Si with sodium carboxymethoxy cellulose (CMC), a very stiff binder, performed better than the more elastic PVDF and CMC/SBR mixture.(10) The formation of covalent bonds and/or strong hydrogen bonding between silicon particles and CMC is believed to be the reason for preserving electrode structure and the improved performance.(13-17) In addition, the cycling performance of Si is enhanced as the number of carboxylic groups per monomer(16) or the length of the polymer chain are increased.(17) The cycle life of Si was also greatly improved with other functional binders such as poly(acrylic acid) (PAA),(18) alginate extracted from brown algae,(19) and cross-linked PAA with CMC.(20) Jeong et al. showed that Si electrodes prepared with hyperbranched polysaccharides have excellent adhesion because of the strong ion-dipole interactions between the binders and silicon nanoparticles as well as the binders and copper current collectors. As a result, the

electrodes show a significant improvement in capacity retention compared to CMC and alginate.(21) In summary, the development of a binder for the silicon nanoparticle anode lies primarily in enhancing the mechanical strength and adhesion ability of the binder.

It has been previously reported that the binder structure can play an important role in the modification of SEI.(22, 23) For silicon electrodes, binders are not inactive components that simply adhere the laminate to the current collector but also incorporate into the SEI on silicon nanoparticle electrodes. Binders such as PAA and CMC can uniformly coat the surface of silicon nanoparticles during electrode preparation because of their strong interactions with the native surface oxide on silicon nanoparticles via carboxylic and hydroxyl groups. The binders are then electrochemically reduced during formation cycling, converting the carboxylic acids to lithium carboxylates.(23) The lithium carboxylate layer functions as a protective SEI and suppresses the decomposition of electrolyte, producing a thinner, more stable SEI than observed with the PVDF binder, which is likely related to the enhanced cycling performance. However, some electrolyte decomposition products are observed on Si-PAA and Si-CMC electrodes after the first cycle, and the concentration of electrolyte decomposition products becomes significant after five cycles.(23) Better surface coverage of the Si particles might be obtained with small-molecule surface modifiers as a result of the superior orientational flexibility. This should increase the protection of silicon from exposure to the electrolyte and improve the cycling performance of the Si anode. Citric acid was chosen because it is a small molecule and contains multiple functional groups, i.e, carboxylic acids and alcohol, to ensure a

strong interaction with silicon nanoparticles during electrode preparation. Thus, a more uniform layer of citric acid is expected to cover surface silicon nanoparticles. This layer is also expected to undergo an electrochemical reduction process, resulting in a citric acid-derived SEI that protects the electrode from the electrolyte reduction in a manner similar to that observed for PAA.⁽²³⁾ In addition, citric acid is inexpensive, which is important for practical use.

We have investigated the electrochemical cycling performance of Si nanoparticles utilizing citric acid as a surface-modifying agent and binder. Several other carboxylic acids have been investigated along with the effect of PVDF and PAA binders on SEI formation on silicon nanoparticle anodes. The changes to the surface of the Si nanoparticles has been investigated via infrared spectroscopy with attenuated total reflection (IR-ATR) and X-ray photoelectron spectroscopy (XPS). The use of citric acid as a SEI modifier and binder provides improved capacity retention and a more stable SEI.

3.3. Experimental Section

Silicon nanoparticles (Alfa Aesar), super C (Timcal), and carboxylic acids (Acros) with a weight ratio of 50:25:25(23) were thoroughly mixed with a mortar and pestle for 1 h using N-methyl-2-pyrrolidone (NMP) as a solvent. The slurry was then transferred to a vial containing a magnetic stirring bar and stirred for 3 h. The well-mixed slurry was spread on a copper foil and dried in a convection oven at 60 °C. Si electrodes with a PVDF ($M_w = 600\,000$, MTI) and PAA ($M_w = 450\,000$, Sigma-Aldrich) binder were also prepared in the same way for reference. The electrodes were punched into 14-mm-diameter disks and dried in a vacuum oven at 110 °C overnight. The dry electrodes were not calendared. The thickness of the electrode laminates was $\sim 15\,\mu\text{m}$ (excluding copper foil), and the total material loading was $\sim 1.2\,\text{mg}/\text{cm}^2$ ($0.6\,\text{mg}/\text{cm}^2$ for Si).

Battery-grade solvents, salts, and additives were received from BASF. Coin cells (2032) were assembled in an Ar-filled glovebox and used for the evaluation of the electrochemical cycling performance. The cells consist of a Si working electrode, a lithium foil counter electrode, an electrolyte (100 μL), and separators (one Celgard 2325 and one glass fiber (GF/D, Whatman)). The electrolyte was 1.2 M LiPF_6 in ethylene carbonate (EC)/diethylene carbonate (DEC) (1:1 w/w) with 10 wt % fluoroethylene carbonate (FEC). The cells were cycled between 0.005 and 1.5 V at a rate of C/20 (0.179 A/g) for the first cycle (formation cycle) and then at C/7 (0.511 A/g) for additional cycles using an Arbin BT2000 battery cycler at 25 °C. The rate was calculated on the basis of the theoretical capacity of Si at 3579 mA h/g. Multiple samples for each electrode formulation were tested to confirm the reproducibility.

The delithiated electrodes were extracted from cycled cells and carefully rinsed with DMC four times (1 mL in total) to remove residual electrolyte and then dried in a glovebox for ex situ analysis. ATR IR (with the instrument equipped with a Bruker Tensor 27 LaDTG detector) was conducted inside a N₂-filled glovebox to prevent the reactions of samples with O₂ and moisture. All spectra were collected from 512 scans at a spectral resolution of 4 cm⁻¹. Ex situ XPS was conducted using a K-Alpha spectrometer (Thermo Scientific) with a spot size of 400 μm, an energy step size of 0.05 eV, and a pass energy of 50 eV. The electrodes were transferred from the glovebox to the XPS chamber using a vacuum-sealed transfer module (thermo) without exposure to air at any time. The binding energy was corrected on the basis of C 1s of the hydrocarbon at 285 eV.

3.4. Results and Discussion

3.4.1. Electrochemical Cycling Behavior

The structures of some examples of carboxylic acids that have been investigated are depicted in Figure 1. Slurries prepared with carboxylic acids with two or fewer –COOH groups such as oxalic and maleic acid result in poor mixing of the materials, which results in an inhomogeneous laminate. The mixing of NMP slurries with carboxylic acids having a greater number of –COOHs such as BA and CA allows good homogeneous electrode laminates to be prepared as depicted in Figure 2.

Plots of voltage profiles, capacity, and efficiency vs cycle number of Si-BA and Si-CA at different cycle numbers are presented in Figure 3. Cycling data of Si-PVDF and Si-PAA are also added for reference. Note that all electrodes contain 25 wt % super C as conductive carbon to ensure good electrochemical cycling performance as previously

reported in the literature.(17, 20, 21, 23, 24) It has been reported that conductive carbon, i.e., super C, has a reversible capacity of about 180 mA h/g,(25) which is very low when compared to 3579 mA h/g for silicon. Thus, the specific capacity of silicon electrodes is primarily from silicon. Si-PVDF shows lithiation and delithiation capacities of 3750 and 2680 mA h/g (based on the weight of silicon), respectively, corresponding to a first cycle efficiency of 71.4% (Figure 3a,c). The voltage profile for the first cycle of Si-PVDF (Figure 3a) shows several small plateaus from 1.4 to 0.8 V that are due to the reduction of electrolytes.(26, 27) In addition, there is a large polarization in the voltage profiles as the cycle number increases, indicating a significant increase in cell impedance. After 50 cycles, Si-PVDF retains only ~980 mA h/g (Figure 3a,b), corresponding to a very poor capacity retention of 36.5%. On the contrary, the Si-CA has higher first cycle lithiation and delithiation capacity of 4300 and 3530 mA h/g, respectively, and a first cycle efficiency of 82% (Figure 3b–d). In the first voltage profile curve of Si-CA (Figure 3b), plateaus at ~2 and 0.8 V could be due to the reduction of carboxylic/hydroxyl groups of CA and electrolyte reduction, respectively.(23, 26, 27) Surprisingly, the Si-CA electrode maintains a capacity of ~2200 mA h/g and a capacity retention of ~64% after 250 cycles, similar to the Si electrode prepared with long-chain binder PAA (Figure 3c). The electrode prepared with BA delivers an initial delithiation capacity of 3650 mA h/g and a first cycle efficiency of 75% (Figure 3c,d). After 50 cycles, the Si-BA cell retains a capacity of 2200 mA h/g and a capacity retention of 60%. Although the rate of the capacity fade for the Si-BA cells is faster than for the Si-CA cells, the Si-BA cells are much better than Si-PVDF.

The superior performance of Si-CA compared to that of Si-PVDF suggests that CA plays an important role in enhancing the cycling performance of the Si electrode. Because CA is small molecule, the mechanical and adhesion strength, which are considered to be critical properties for binders, are poor compared to those of the long-chain PAA binder. However, the comparable cycling performance of Si-CA and Si-PAA suggests that the primary factor contributing to the performance enhancement is the reactivity of the CA, which modifies the surface of the silicon similarly to that reported previously for PAA and CMC.(23) The small molecular size of CA allows better uniform coverage of the surface of Si via the strong interactions of a large number of carboxylic and hydroxyl groups. Therefore, ex situ surface analysis has been conducted via a combination of ATR IR and XPS to investigate the SEI on fresh and cycled Si-CA anodes.

3.4.2. *Ex Situ Characterization of the SEI Formed on Si-CA Electrodes*

The IR spectra for fresh and cycled Si electrodes with PVDF and citric acid are provided in Figure 4. The Si electrodes prepared with PVDF are dominated by signals originating from PVDF at 1402, 1175, 878, and 840 cm^{-1} .(28) After the first cycle, the Si-PVDF electrode shows new peaks at 1806 cm^{-1} characteristic of poly(FEC),(6, 7) at 1653 cm^{-1} characteristic of lithium alkyl carbonate ROCOOLi, and at 1493 cm^{-1} characteristic of Li_2CO_3 .(6, 7, 29-31) Another new peak at 1605 cm^{-1} is from a lithium carboxylate.(32, 33) The peak intensity of the electrolyte decomposition products is much stronger than the intensity of the absorption associated with the PVDF binder at 1178 cm^{-1} , consistent with the formation of a thick SEI. The signal of PVDF completely disappears after 10 cycles, suggesting SEI thickening due to the

severe electrolyte reduction. The intensity of the peak at 1493 cm^{-1} for lithium carbonate slightly increases at the expense of the lithium alkyl carbonate at 1653 cm^{-1} . The change in the ratio of Li_2CO_3 to lithium alkyl carbonate is consistent with the decomposition of lithium alkyl carbonates to Li_2CO_3 upon prolonged cycling, as previously reported.(34)

The IR spectrum of the fresh Si-PAA electrodes contains a strong peak at 1708 cm^{-1} , characteristic of the $-\text{COOH}$ group in PAA. Small peaks at 1610 and 1803 cm^{-1} are attributed to hydrogen bonding carboxylic dimers and an anhydride, $-\text{OCOOC}-$.(1, 23) After the first cycle, the peak at 1708 cm^{-1} disappears and a new peak is observed at 1574 cm^{-1} , consistent with the conversion of PAA to PAALi by electrochemical reduction.(23) Small new peaks at 1806 , 1653 , and 1493 cm^{-1} are observed and are characteristic of poly(FEC), lithium alkyl carbonate, and lithium carbonate, respectively, as seen in the Si-PVDF electrodes. The intensity of those peaks is much weaker than the signal of PAALi, indicating that the reduction of solvent is less than on Si-PVDF. As the cycle number increases, the peaks for poly(FEC), lithium alkyl carbonate, and lithium carbonate increase and become stronger than for PAALi, consistent with a thickening of the SEI.

The fresh Si-CA electrode contains peaks at 1745 and 1700 cm^{-1} resulting from the presence of carboxylic acid groups of citric acid. After the first cycle, these peaks are replaced by new peaks observed at 1583 and 1414 cm^{-1} , characteristic of $-\text{COOLi}$ from lithium citrate.(35-37) Lithium citrate is generated via the electrochemical reduction of citric acid during cycling in a similar manner to the reduction of poly(acrylic acid) as previously reported.(23) Interestingly, lithium alkyl carbonates at

1653 cm^{-1} and lithium carbonate at 1493 cm^{-1} are not observed. The peak characteristic of poly(FEC) at 1806 cm^{-1} is present but very weak compared to those of the Si-PVDF and Si-PAA electrodes after one cycle. The spectrum of the Si-CA electrode after 10 cycles is almost identical to that of the electrode after the first cycle with lithium citrate as the main component of the SEI. As the number of cycles increases to 30 and 50 cycles, the intensity of the peaks characteristic of poly(FEC) and lithium carbonate is slightly enhanced but remains relatively small compared to peaks for lithium citrate. The lithium citrate derived from citric acid likely forms a uniform surface film on the Si nanoparticles, which inhibits electrolyte decomposition. The C 1s, F 1s, and O 1s XPS spectra of the Si-PVDF, Si-PAA, and Si-CA electrodes are provided in Figure 5. The elemental atomic concentrations are provided in Figure 6. XPS provides information on the top layer of the SEI, ~ 10 nm depth, whereas ATR IR provides information to a greater depth of ~ 600 nm. The fresh Si-PVDF electrode contains peaks at 291 and 688 eV in the C 1s and F 1s spectra, respectively, characteristic of the CF_2 group of the PVDF binder. The peak at 286.5 eV in the C 1s spectrum is from the CH_2 of PVDF, and the peak at 284 eV corresponds to super C. The broad peak at 532.5 eV in the O 1s spectrum is from surface SiO_x . After the first cycle, new peaks characteristic of electrolyte decomposition are observed at 290 and 286.5 eV in the C 1s spectrum due to the presence of ROCOOLi and Li_2CO_3 .^(6, 31, 38) In addition, a small peak at 288.7 eV is assigned to lithium carboxylate.^(33, 38, 39) The presence of poly(FEC) is supported by the peak at 291 eV in the C 1s spectrum and the peak at 534 eV in the O 1s spectrum.⁽⁶⁾ The signal of PVDF at 688 eV in the F 1s spectrum disappears and is replaced by a new peak at 685 eV,

characteristic of LiF, and a weak shoulder at 687 eV from $\text{Li}_x\text{PO}_y\text{F}_z$. The presence of LiF results from a combination of the reduction of FEC and the decomposition of LiPF_6 .(40-42) The atomic concentration of F is increased from 13 to 19% after the first cycle (Figure 6), suggesting a high concentration of LiF in the SEI. With increased cycling of the Si-PVDF electrodes, the concentrations of carbon and oxygen increase while the concentration of F decreases, consistent with the increased concentration of poly(FEC), lithium carbonate, and lithium alkyl carbonates on top of the SEI.

The fresh Si-PAA contains peaks at 284, 286.5, and 289.5 eV in the C 1s spectrum, characteristic of super C and the $-\text{C}-\text{O}$ and $-\text{COOH}$ groups of PAA, respectively.(23) The peak in the O 1s spectrum centered at 532.7 eV results from a combination of SiO_x , $\text{C}-\text{O}$, and $\text{C}=\text{O}$ from the silicon surface oxide and PAA binder. The changes in the spectra after the first cycle are similar to Si-PVDF: new peaks are observed in the C 1s spectrum at 291 eV from poly(carbonate), 290 eV from lithium alkyl carbonate and lithium carbonate, 288.5 eV from lithium carboxylate, and 286.5 eV from the $-\text{C}-\text{O}$ groups.(33, 39) Related changes are observed in the O 1s spectrum, the peaks at 531.8 and 534 eV in O 1s are characteristic of $-\text{CO}_3$, $-\text{CO}_2$, and $\text{C}-\text{O}$, supporting the presence of poly(carbonate), lithium alkyl carbonate, and lithium carbonate. A strong peak at 685 eV is observed in the F 1s characteristic of LiF formed by the reduction of FEC and LiPF_6 . The high concentration of fluoride, $\sim 25\%$ (Figure 6), indicates a significant decomposition of electrolyte. With increased cycling, the composition of the outer SEI is similar to that observed for the Si-PVDF electrode.

The C 1s spectrum of the fresh Si-CA electrodes contains a peak at 284 eV characteristic of super C and peaks at 286.5 and 289.5 eV from the -C-O and -COOH groups of citric acid. The O 1s spectrum shows a peak at 532.5 eV and a shoulder at 533.5 eV from surface SiO_x , Si-O-C , and C-O . After the first cycle, the peak of -COOH disappears and the spectrum is dominated by a new strong peak at 288.8 eV, characteristic of lithium carboxylate groups (-COOLi)(33, 39) of lithium citrate. The presence of -COOLi is also supported by the sharp peak at 531.5 eV in the O 1s spectrum. A peak is also observed at 286.7 eV in the C 1s spectrum from the C-O in lithium citrate. Interestingly, the peaks for poly(FEC) at 291 eV (C 1s) and 534 eV (O 1s) and lithium alkyl carbonate/lithium carbonate at 290 eV (C 1s) are very small. The XPS results are consistent with the IR-ATR results discussed above. In addition, the results suggest that the initial lithium citrate layer on Si-CA suppresses electrolyte reduction. The F 1s spectrum contains weak peaks at 685 eV from LiF and at 686.8 eV from Li_xPOyFz . The atomic concentration of F, from both LiF and Li_xPOyFz , is $\sim 4\%$, which is much lower than the 19 and 25% F observed on the Si-PVDF and Si-PAA electrodes (Figure 6). This again supports a decrease in electrolyte reduction on Si-CA electrodes after the first cycle, compared to that for Si-PVDF electrodes. The C 1s, F 1s, and O 1s spectra do not change significantly after 10 cycles. When the cycle number exceeds 10, peaks characteristic of poly(FEC) at 291 eV and lithium alkyl carbonates/lithium carbonate at 290 eV increase in intensity, but the peak at 288.7 eV for lithium citrate remains dominant. The SEI on Si-CA is primarily composed of lithium citrate during the first 50 cycles. Overall, XPS and IR data reveal that the electrolyte reduction, including the reduction of the FEC additive, is decreased for Si-

CA electrodes compared to that for Si-PVDF and Si-PAA electrodes, which is likely responsible for the enhanced cycling performance of Si-CA electrodes. Unlike graphite electrodes, which require a small amount of additive to form a stable SEI during the first few formation cycles, Si electrodes continuously consume sacrificial additives, such as FEC, during cycling to repair the SEI. Complete consumption of the FEC leads to cell failure.^(43, 44) The modification and stabilization of the SEI upon incorporations of citric acid as a surface-modifying agent and binder is a promising method of inhibiting electrolyte reduction and prolonging the cycle life of silicon electrodes.

3.5. Conclusions

Several carboxylic acids were investigated as surface-modifying agents and binders for Si nanoparticle anodes. Si-CA electrodes have better capacity retention than Si-BA electrodes, but both electrodes outperform Si-PVDF. The Si-CA anodes have a first cycle specific capacity and Coulombic efficiency of ~ 3530 mA h/g and 82%, respectively. After 250 cycles, Si-CA retains a high capacity of ~ 2200 mA h/g, corresponding to 64% capacity retention, which is comparable to that of Si-PAA. The CA binder uniformly covers the surface of Si because of the strong interactions between the carboxylic acids and hydroxyl groups and the surface oxide, SiO_x, along with the orientational flexibility of the small molecule. Surface analysis via IR and XPS reveals that the surface layer of CA is reduced to lithium citrate during the first cycle, which provides a protective layer on the Si nanoparticles dramatically suppressing electrolyte reduction. The reduction products of the electrolyte, poly(FEC), lithium alkyl carbonate, lithium carboxylate, lithium carbonate, and

lithium fluoride are minor during the first 10 cycles. The concentration of the electrolyte reduction products slowly increases with increased cycling but remains low compared to that of lithium citrate. The layer of lithium citrate derived from citric acid effectively stabilizes the surface of silicon. The modification and stabilization of the SEI with citric acid appear to be the primary contributors to the enhancement of the cycling performance of Si electrodes. The results suggest a new approach to designing functional binders for enhancing the performance of silicon anodes.

The authors declare no competing financial interest.

Acknowledgment

The authors gratefully acknowledge funding from a Department of Energy, Office of Basic Energy Sciences EPSCoR Implementation award (DE-SC0007074)

3.6. References

1. Komaba, S.; Shimomura, K.; Yabuuchi, N.; Ozeki, T.; Yui, H.; Konno, K. Study on Polymer Binders for High-Capacity SiO Negative Electrode of Li-Ion Batteries J. Phys. Chem. C 2011, 115, 13487– 13495 DOI: 10.1021/jp201691
2. Obrovac, M. N.; Chevrier, V. L. Alloy Negative Electrodes for Li-Ion Batteries Chem. Rev. 2014, 114, 11444– 11502 DOI: 10.1021/cr500207
3. Obrovac, M. N.; Christensen, L. Structural Changes in Silicon Anodes during Lithium Insertion/Extraction Electrochem. Solid-State Lett. 2004, 7, A93– A96 DOI: 10.1149/1.1652421
4. Ryu, J. H.; Kim, J. W.; Sung, Y.-E.; Oh, S. M. Failure Modes of Silicon Powder Negative Electrode in Lithium Secondary Batteries Electrochem. Solid-State Lett. 2004, 7, A306– A309 DOI: 10.1149/1.1792242
5. Choi, N.-S.; Yew, K. H.; Lee, K. Y.; Sung, M.; Kim, H.; Kim, S.-S. Effect of Fluoroethylene Carbonate Additive on Interfacial Properties of Silicon Thin-Film Electrode J. Power Sources 2006, 161, 1254– 1259 DOI: 10.1016/j.jpowsour.2006.05.049
6. Etacheri, V.; Haik, O.; Goffer, Y.; Roberts, G. a; Stefan, I. C.; Fasching, R.; Aurbach, D. Effect of Fluoroethylene Carbonate (FEC) on the Performance and Surface Chemistry of Si-Nanowire Li-Ion Battery Anodes Langmuir 2012, 28, 965– 976 DOI: 10.1021/la203712s
7. Nguyen, C. C.; Lucht, B. L. Comparative Study of Fluoroethylene Carbonate and Vinylene Carbonate for Silicon Anodes in Lithium Ion Batteries J. Electrochem. Soc. 2014, 161, A1933– A1938 DOI: 10.1149/2.0731412jes

8. Nguyen, C. C.; Lucht, B. L. Improved Cycling Performance of Si Nanoparticle Anodes via Incorporation of Methylene Ethylene Carbonate Electrochem. Commun. 2016, 66, 71– 74 DOI: 10.1016/j.elecom.2016.03.005
9. Buqa, H.; Holzapfel, M.; Krumeich, F.; Veit, C.; Novák, P. Study of Styrene Butadiene Rubber and Sodium Methyl Cellulose as Binder for Negative Electrodes in Lithium-Ion Batteries J. Power Sources 2006, 161, 617– 622 DOI: 10.1016/j.jpowsour.2006.03.073
10. Li, J.; Lewis, R. B.; Dahn, J. R. Sodium Carboxymethyl Cellulose: A Potential Binder for Si Negative Electrodes for Li-Ion Batteries Electrochem. Solid-State Lett. 2007, 10, A17– A20 DOI: 10.1149/1.2398725
11. Li, J.; Christensen, L.; Obrovac, M. N.; Hewitt, K. C.; Dahn, J. R. Effect of Heat Treatment on Si Electrodes Using Polyvinylidene Fluoride Binder J. Electrochem. Soc. 2008, 155, A234– A234 DOI: 10.1149/1.2830545
12. Chen, Z.; Christensen, L.; Dahn, J. R. Large-Volume-Change Electrodes for Li-Ion Batteries of Amorphous Alloy Particles Held by Elastomeric Tethers Electrochem. Commun. 2003, 5, 919– 923 DOI: 10.1016/j.elecom.2003.08.017
13. Munao, D.; van Erven, J. W. M.; Valvo, M.; Garcia-Tamayo, E.; Kelder, E. M. Role of the Binder on the Failure Mechanism of Si Nano-Composite Electrodes for Li-Ion Batteries J. Power Sources 2011, 196, 6695– 6702 DOI: 10.1016/j.jpowsour.2010.11.072
14. Vogl, U. S.; Das, P. K.; Weber, A. Z.; Winter, M.; Kostecki, R.; Lux, S. F. Mechanism of Interactions between CMC Binder and Si Single Crystal Facets Langmuir 2014, 30, 10299– 10307 DOI: 10.1021/la501791q

15. Lestriez, B.; Bahri, S.; Sandu, I.; Roué, L.; Guyomard, D. On the Binding Mechanism of CMC in Si Negative Electrodes for Li-Ion Batteries *Electrochem. Commun.* 2007, 9, 2801– 2806 DOI: 10.1016/j.elecom.2007.10.001
16. Hochgatterer, N. S.; Schweiger, M. R.; Koller, S.; Raimann, P. R.; Wöhrle, T.; Wurm, C.; Winter, M. Silicon/Graphite Composite Electrodes for High-Capacity Anodes: Influence of Binder Chemistry on Cycling Stability *Electrochem. Solid-State Lett.* 2008, 11, A76– A76 DOI: 10.1149/1.2888173
17. Bridel, J.-S. S.; Azai, T.; Morcrette, M.; Tarascon, J.-M. M.; Larcher, D.; Azais, T. Key Parameters Governing the Reversibility of Si/Carbon/CMC Electrodes for Li-Ion Batteries † *Chem. Mater.* 2010, 22, 1229– 1241 DOI: 10.1021/cm902688w
18. Magasinski, A.; Zdyrko, B.; Kovalenko, I.; Hertzberg, B.; Burtovyy, R.; Huebner, C. F.; Fuller, T. F.; Luzinov, I.; Yushin, G. Toward Efficient Binders for Li-Ion Battery Si-Based Anodes: Polyacrylic Acid *ACS Appl. Mater. Interfaces* 2010, 2, 3004– 3010 DOI: 10.1021/am100871y
19. Kovalenko, I.; Zdyrko, B.; Magasinski, A.; Hertzberg, B.; Milicev, Z.; Burtovyy, R.; Luzinov, I.; Yushin, G. A Major Constituent of Brown Algae for Use in High-Capacity Li-Ion Batteries *Science* 2011, 334, 75– 79 DOI: 10.1126/science.1209150
20. Koo, B.; Kim, H.; Cho, Y.; Lee, K. T.; Choi, N.-S.; Cho, J. A Highly Cross-Linked Polymeric Binder for High-Performance Silicon Negative Electrodes in Lithium Ion Batteries *Angew. Chem., Int. Ed.* 2012, 51, 8762– 8767 DOI: 10.1002/anie.201201568
21. Jeong, Y. K.; Kwon, T.; Lee, I.; Kim, T.-S.; Coskun, A.; Choi, J. W. Millipede-Inspired Structural Design Principle for High Performance Polysaccharide Binders in

- Silicon Anodes Energy Environ. Sci. 2015, 8, 1224– 1230 DOI: 10.1039/C5EE00239G
22. Komaba, S.; Yabuuchi, N.; Ozeki, T.; Okushi, K.; Yui, H.; Konno, K.; Katayama, Y.; Miura, T. Functional Binders for Reversible Lithium Intercalation into Graphite in Propylene Carbonate and Ionic Liquid Media J. Power Sources 2010, 195, 6069– 6074 DOI: 10.1016/j.jpowsour.2009.12.058
23. Nguyen, C. C.; Yoon, T.; Seo, D. M.; Guduru, P.; Lucht, B. L. Systematic Investigation of Binders for Silicon Anodes: Interactions of Binder with Silicon Particles and Electrolytes and Effects of Binders on Solid Electrolyte Interphase Formation ACS Appl. Mater. Interfaces 2016, 8, 12211– 12220 DOI: 10.1021/acsami.6b03357
24. Liu, W.-R.; Yang, M.; Wu, H.-C.; Chiao, S. M.; Wu, N.-L. Enhanced Cycle Life of Si Anode for Li-Ion Batteries by Using Modified Elastomeric Binder Electrochem. Solid-State Lett. 2005, 8, A100– A100 DOI: 10.1149/1.1847685
25. Fransson, L.; Eriksson, T.; Edström, K.; Gustafsson, T.; Thomas, J. Influence of Carbon Black and Binder on Li-Ion Batteries J. Power Sources 2001, 101, 1– 9 DOI: 10.1016/S0378-7753(01)00481-5
26. Zhang, X.; Kostecki, R.; Richardson, T. J.; Pugh, J. K.; Ross, P. N. Electrochemical and Infrared Studies of the Reduction of Organic Carbonates J. Electrochem. Soc. 2001, 148, A1341– A1345 DOI: 10.1149/1.1415547
27. Zhuang, G. V.; Yang, H.; Blizanac, B.; Ross, P. N. A Study of Electrochemical Reduction of Ethylene and Propylene Carbonate Electrolytes on Graphite Using ATR-

- FTIR Spectroscopy *Electrochem. Solid-State Lett.* 2005, 8, A441– A445 DOI: 10.1149/1.1979327
28. Bormashenko, Y.; Pogreb, R.; Stanevsky, O.; Bormashenko, E. Vibrational Spectrum of PVDF and Its Interpretation *Polym. Test.* 2004, 23, 791– 796 DOI: 10.1016/j.polymertesting.2004.04.001
29. Xu, K.; Zhuang, G. V.; Allen, J. L.; Lee, U.; Zhang, S. S.; Ross, P. N.; Jow, T. R. Syntheses and Characterization of Lithium Alkyl Mono- and Dicarbonates as Components of Surface Films in Li-Ion Batteries *J. Phys. Chem. B* 2006, 110, 7708– 7719 DOI: 10.1021/jp0601522
30. Aurbach, D.; Markovsky, B. A Comparative Study of Synthetic Graphite and Li Electrodes in Electrolyte Solutions Based on Ethylene Carbonate-Dimethyl Carbonate Mixtures *J. Electrochem. Soc.* 1996, 143, 3809– 3820 DOI: 10.1149/1.1837300
31. Nie, M.; Abraham, D. P.; Seo, D. M.; Chen, Y.; Bose, A.; Lucht, B. L.; Chalasani, D. Silicon Solid Electrolyte Interphase (SEI) of Lithium Ion Battery Characterized by Microscopy and Spectroscopy *J. Phys. Chem. C* 2013, 117, 13403– 13412 DOI: 10.1021/jp404155y
32. Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd ed.; Wiley: Chichester, 2001.
33. Ota, H.; Sakata, Y.; Inoue, A.; Yamaguchi, S. Analysis of Vinylene Carbonate Derived SEI Layers on Graphite Anode *J. Electrochem. Soc.* 2004, 151, A1659– A1659 DOI: 10.1149/1.1785795
34. Young, B. T.; Heskett, D. R.; Nguyen, C. C.; Nie, M.; Woicik, J. C.; Lucht, B. L. Hard X-Ray Photoelectron Spectroscopy (HAXPES) Investigation of the Silicon Solid

- Electrolyte Interphase (SEI) in Lithium-Ion Batteries ACS Appl. Mater. Interfaces 2015, 7, 20004– 20011 DOI: 10.1021/acsami.5b04845
35. Tobón-Zapata, G. E.; Piro, O. E.; Etcheverry, S. B.; Baran, E. J. Crystal Structure and IR-Spectrum of Lithium Citrate Monohydrate, $\text{Li}(\text{C}_6\text{H}_7\text{O}_7) \cdot \text{H}_2\text{O}$ Z. Anorg. Allg. Chem. 1998, 624, 721– 724 DOI: 10.1002/(SICI)1521-3749
36. Guo, Y.; Wang, Z.; Shao, H.; Jiang, X. Hydrothermal Synthesis of Highly Fluorescent Carbon Nanoparticles from Sodium Citrate and Their Use for the Detection of Mercury Ions Carbon 2013, 52, 583– 589 DOI: 10.1016/j.carbon.2012.10.028
37. Spectral Database for Organic Compounds, SDBS http://sdb.db.aist.go.jp/sdb/cgi-bin/cre_frame_disp.cgi?spectrum_type=ir&sdbno=12695, accessed Aug 30, 2016.
38. Schroder, K. W.; Celio, H.; Webb, L. J.; Stevenson, K. J. Examining Solid Electrolyte Interphase Formation on Crystalline Silicon Electrodes: Influence of Electrochemical Preparation and Ambient Exposure Conditions J. Phys. Chem. C 2012, 116, 19737– 19747 DOI: 10.1021/jp307372m
39. Moulder, J. F.; Chastain, J. Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data; Physical Electronics Division, Perkin-Elmer Corp.: Eden Prairie, MN, 1992.
40. Campion, C. L.; Li, W.; Lucht, B. L. Thermal Decomposition of LiPF_6 -Based Electrolytes for Lithium-Ion Batteries J. Electrochem. Soc. 2005, 152, A2327– A2334 DOI: 10.1149/1.2083267

41. Aurbach, D.; Weissman, I.; Schechter, A.; Cohen, H. X-Ray Photoelectron Spectroscopy Studies of Lithium Surfaces Prepared in Several Important Electrolyte Solutions. A Comparison with Previous Studies by Fourier Transform Infrared Spectroscopy *Langmuir* 1996, 12, 3991– 4007 DOI: 10.1021/la9600762
42. Nadimpalli, S. P. V.; Sethuraman, V. a.; Dalavi, S.; Lucht, B.; Chon, M. J.; Shenoy, V. B.; Guduru, P. R. Quantifying Capacity Loss due to Solid-Electrolyte-Interphase Layer Formation on Silicon Negative Electrodes in Lithium-Ion Batteries *J. Power Sources* 2012, 215, 145– 151 DOI: 10.1016/j.jpowsour.2012.05.004
43. Petibon, R.; Chevrier, V. L.; Aiken, C. P.; Hall, D. S.; Hyatt, S. R.; Shunmugasundaram, R.; Dahn, J. R. Studies of the Capacity Fade Mechanisms of LiCoO₂/Si-Alloy: Graphite Cells *J. Electrochem. Soc.* 2016, 163, A1146– A1156 DOI: 10.1149/2.0191607jes
44. Jung, R.; Metzger, M.; Haering, D.; Solchenbach, S.; Marino, C.; Tsiouvaras, N.; Stinner, C.; Gasteiger, H. A. Consumption of Fluoroethylene Carbonate (FEC) on Si-C Composite Electrodes for Li-Ion Batteries *J. Electrochem. Soc.* 2016, 163, A1705– A1716 DOI: 10.1149/2.0951608jes

3.7. List of Figures

Figure 1. Structure of some carboxylic acids.

Figure 2. Digital photographs of Si electrode prepared with citric acid (Si-CA) and 1,2,3,4-butanetetracarboxylic acid (Si-BTCA)

Figure 3. Voltage profile plots of Si-PVdF and Si-CA at different cycle number. Capacity and efficiency vs. cycle number of Si-PVdF and Si-CA in 1.2 M LiPF₆/ EC : DEC +10 wt.% FEC.

Figure 4. Specific capacity and efficiency of Si-graphite composite electrode using citric acid as binder in 1.2 M LiPF₆/ EC : DEC +10 wt.% FEC.

Figure 5. IR spectra of Si-CA and Si-PVdF before and after cycling.

Figure 6. High resolution C 1s, F 1s and O 1s XPS spectra of the Si-CA and Si-PVdF at different cycle number.

Figure 7. Elemental atomic concentration of fresh and cycled Si-PVdF and Si-CA.

3.8. Figures

Figure 1. Structure of some carboxylic acids.

Figure 2. Digital photographs of Si electrode prepared with citric acid (Si-CA) and 1,2,3,4-butanetetracarboxylic acid (Si-BTCA)

Figure 3. Voltage profile plots of Si-PVdF and Si-CA at different cycle number. Capacity and efficiency vs. cycle number of Si-PVdF and Si-CA in 1.2 M LiPF_6 / EC : DEC +10 wt.% FEC.

Figure 4. Specific capacity and efficiency of Si-graphite composite electrode using citric acid as binder in 1.2 M LiPF₆/ EC : DEC +10 wt.% FEC.

Figure 5. IR spectra of Si-CA and Si-PVdF before and after cycling.

Figure 6. High resolution C 1s, F 1s and O 1s XPS spectra of the Si-CA and Si-PVdF at different cycle number.

Figure 7. Elemental atomic concentration of fresh and cycled Si-PVdF and Si-CA.

CHAPTER 4

Citric Acid based pre-SEI for Improvement of Silicon Electrodes in Lithium Ion Batteries

K. W. D. Kaveendi Chandrasiri, Cao Cuong Nguyen, Bharathy S. Parimalam,
Sunhyung Jurng, Brett L. Lucht^{*}

Journal of The Electrochemical Society, 165 (10) A1991-A1996 (2018)

4.1. Abstract

Silicon electrodes are of interest to the lithium ion battery industry due to high gravimetric capacity (~3580 mAh/g), natural abundance, and low toxicity. However, the process of alloying and dealloying during cell cycling, causes the silicon particles to undergo a dramatic volume change of approximately 280% which leads to electrolyte consumption, pulverization of the electrode, and poor cycling. In this study, the formation of an ex-situ artificial SEI on the silicon nanoparticles with citric acid has been investigated. Citric acid (CA) which was previously used as a binder for silicon electrodes was used to modify the surface of the nanoparticles to generate an artificial SEI, which could inhibit electrolyte decomposition on the surface of the silicon nanoparticles. The results suggest improved capacity retention of ~60% after 50 cycles for the surface modified silicon electrodes compared to 45% with the surface unmodified electrode. Similar improvements in capacity retention are observed upon citric acid surface modification for silicon graphite composite/ LiCoO₂ cells.

4.2. Introduction

Lithium ion batteries have been widely used in the portable electronic device market for over two decades due to high energy density, good rate capability, and long cycle life¹⁻³. Graphite is the most frequently used commercial anode material. Although graphite has good performance, low cost and high capacity retention, the relatively modest storage capacity (~370 mAh/g) has driven investigations of alternative anode materials⁴. Different anode materials with greater storage capacity have been investigated including lithium metal, tin, silicon and other metal alloys. While lithium metal anodes are very appealing, dendrite formation after long term cycling results in significant safety concerns⁵⁻⁷. Therefore, the use of lithium alloying compounds has been intensively investigated over the last decade. Silicon is the most attractive alloying anode material due to its high theoretical capacity. Lithiation of silicon results in the formation of alloys such as $\text{Li}_{15}\text{Si}_4$ with a theoretical capacity of 3580 mAh/g^{8,9}. In addition, silicon has a high volumetric capacity of 9786 mAh/cm³.¹⁰

Silicon is abundant and has low toxicity which makes it a good candidate for an anode material for commercial batteries. Silicon also exhibits a discharge voltage of ~0.4 V vs Li/Li^+ which allows it to maintain an open circuit potential which avoids lithium plating^{9,11-13}. While theoretically interesting, there are numerous factors that make silicon electrode use difficult. Some of the important factors include the volume variation during the lithiation and delithiation process of 280% which leads to pulverization of the electrode, instability of the SEI due to the volume variation, and damage to the electrode laminate^{14,15}. Numerous strategies have been undertaken to solve these stress induced problems that affect the electrochemical properties of the

electrode including the use of nanoparticles, which limit the stress induced damage of from large volume changes^{16,17}, containing the capacity of silicon to 1200 mAh/g¹⁸, the use of electrolyte additives for better SEI formation¹⁹, novel binders that can accommodate the stress or modify the surface of the silicon particles^{20,21} and structure modification of the electrode materials²².

This investigation is focused on improving the interfacial properties of the silicon electrode by using surface modification. Citric acid (CA) has been previously reported as a binder for silicon-based anodes²³. The use of citric acid binder provided comparable electrochemical performance to silicon anodes prepared with poly(acrylic acid) (PAA), one of the better binders reported for silicon anodes^{24,25}. Ex-situ surface analysis of the citric acid based anodes indicates that the citric acid decomposes on the surface of the electrode to form lithium citrate which functions as a pre-formed SEI. Our previous manuscript investigated the use of citric acid and a binder for silicon anodes.²⁵ In this manuscript, we investigate citric acid as a pre-treating agent to modify the surface of the silicon particles, which therein could generate an artificial SEI on the silicon particles. The use of citric acid as a surface modifying agent also allows the use of citric acid modified silicon in silicon/graphite composite electrodes.

4.3. Experimental

Silicon nanoparticles (< 50nm, Alfa Aesar), Super C (Timcal), Graphite G8 (C-preme), SFG6 (Timcal), Anhydrous NMP (sigma Aldrich), PVDF binder ($M_w = 600\,000$, MTI), and Citric Acid (CA) (99.5%, Acros organics) were purchased. Battery grade Lithium hexafluorophosphate (LiPF_6), Ethylene Carbonate (EC), Dimethyl Carbonate (DMC) and Fluoroethylene Carbonate (FEC) were obtained from a commercial supplier with water content < 50 ppm and stored in an Ar glovebox. High purity lithium chips (15.6 mm diameter) were purchased from MTI corporation.

4.3.1. Surface modification of Silicon nanoparticles with citric acid

Surface modification was carried out through sonication and subsequent stirring of silicon nanoparticles (Si-np) and citric acid in NMP. 10% citric acid solution was prepared via sonication of citric acid with NMP for 30 minutes. 0.2 g of silicon nanoparticles were sonicated for three hours in 20 mL of 10% citric acid-NMP solution. The mixture was stirred for 12 hours with 10 minutes of sonication every 3 hours to prevent aggregation of the nanoparticles. The particles were collected with centrifugal separation, washed twice with NMP to remove the unreacted citric acid, and washed 3 times with acetone to remove the residual NMP. The samples were dried under air at 40 °C in a convection oven for 2 hours and transferred to a vacuum oven at 35 °C and dried for 24 hours. The same procedure was repeated two more times to complete the surface modification. The samples were analyzed using infrared spectroscopy with attenuated total reflectance (IR-ATR) to confirm the formation of the silyl ester bonds.

4.3.2. Preparation of silicon and silicon graphite composite electrode laminates

Laminates were prepared with both fresh silicon nanoparticles (Si-np) and modified silicon nanoparticles (M-Si-np). Citric acid, PVDF, graphite and carbon black powders, were dried in a vacuum oven overnight at 110 °C, and Si-np powder was dried for 48 hours in a vacuum oven at 35 °C before slurry preparation. The electrode slurry was prepared in a nitrogen filled glovebox, to minimize agglomeration of the nanoparticles, oxidization in air, and reaction with moisture²⁶. The fresh Si-np or M-Si-np, super C65 conductive carbon, and PVDF binder were mixed thoroughly in 2:1:1 ratio using a mortar and pestle with extra dry NMP as a solvent for one hour. Subsequently the mixture was stirred for 3 hours using a magnetic stirrer and then coated on copper foil using a doctor blade. The laminates were dried in a convection oven under air flow for one hour and dried overnight under vacuum at room temperature. Electrodes were punched with 14 mm diameter and dried under vacuum at 110 °C for another 24 hours and transferred into an argon filled glovebox for coin cell preparation.

Similarly, silicon nanoparticle graphite composite electrodes were prepared with Si-np or M-Si-np, Super C -65, Graphite SFG6, Graphite G8, and PVDF binder at a ratio of 15:5:30:40:10 using mortar and pestle and NMP as a solvent in a N₂ filled glovebox.

4.3.3. Cell construction

Coin cells (2032 type) were constructed in an argon filled glovebox. Cells were assembled using a 14 mm Si-np anode, one 19 mm Celgard 2325 separator, one 15.6 mm Whatman GF/D glass microfiber separator, and a 15.6 mm lithium chip with 100

μL of electrolyte containing 1.2 M LiPF_6 in EC: DEC: FEC 40: 40: 10 (by mass). All Si-np||Li cells were cycled between 0.005 and 1.50 V at a rate of C/20 for 1 formation cycle, with a C/40 taper charge followed by cycles at C/3 with a C/20 taper charge. Cell cycling was carried out with an Arbin BT 2000 battery cycler at 25 °C. All cells were tested in triplicate. After the 1st lithiation and 2nd and 20th delithiations, cells were rested for 12 hours followed by electrochemical impedance spectroscopy using a potentiostat with an amplitude of 10 mV and frequency range of 300 kHz–20 mHz. Representative data is presented.

Delithiated electrodes were extracted from the cycled cells, carefully rinsed with DMC three times (1.5 mL in total) to remove residual electrolyte and then dried in a glovebox for ex-situ surface analysis. Ex-situ X-ray photoelectron spectroscopy (XPS) was conducted using a K-Alpha spectrometer (Thermo Scientific) with a spot size of 400 μm , an energy step size of 0.05 eV, and a pass energy of 50 eV. The electrodes were transferred from the glovebox to the XPS chamber using a vacuum-sealed transfer module (Thermo Scientific) without exposure to air. The binding energy was corrected based on the C 1s peak of hydrocarbons at 285 eV. Infrared spectroscopy with attenuated total reflectance (IR-ATR) (Bruker Tensor 27 with LaDTG detector) was conducted inside a N_2 -filled glovebox to prevent the reactions of samples with O_2 and moisture. All spectra were collected with 512 scans at a spectral resolution of 4 cm^{-1} .

4.4. Results and discussion

The surface modification was carried out as described in the experimental section and the nanoparticle powders were analyzed by IR-ATR. The spectra of the Si-np and M-

Si-np along with pure citric acid powder are provided in Figure 1. Pure citric acid has two characteristic absorptions at 1748 and 1702 cm^{-1} corresponding to the C=O stretch of the carbonyl groups. The carbonyl peaks of the citric acid are shifted upon reaction with the surface of the silicon nanoparticles to 1725 and 1630 cm^{-1} characteristic of the conversion to silyl esters (-Si-O- C(O)-C-) as previously reported^{23,27,28}.

Prior to conducting electrochemical studies, thermogravimetric analysis (TGA) was conducted on the fresh and CA surface modified silicon nanoparticles to determine the quantity of citric acid on the surface of the active material. The results are displayed in Figure 2. Both samples were dried under vacuum and analyzed under nitrogen. The Si-np undergoes no weight loss up to 350° C, while the M-Si-np has a small weight loss of ~0.7%. Since both samples were processed under similar conditions, the weight loss observed for the M-Si-np can be assigned to the removal of citric acid. The mass loss of citric acid corresponds to approximately one monolayer resulting from the generation of silyl esters (Figure 3).

4.4.1. Electrochemical Performance

Silicon nanoparticle (with 50% Si) and silicon nanoparticle graphite (Si-np/Gr) composite electrodes (with 15% silicon) were prepared with PVDF binder. While PAA binders have been typically reported to improve the performance of silicon anodes, PVDF was selected since the focus of the investigation is on the effect of citric acid modification of the surface of the silicon nanoparticles and the carboxylic acid functional groups of the PAA have similar reactions with the silicon surface as observed for citric acid.²³ Si-np||lithium cells were constructed and analyzed. Better performance was observed in cells with M-Si-np than the Si-np. The cycling

performance data is provided in Figure 4. The first cycle delithiation capacity for M-Si-np is 3550 mAh/g while the Si-np has a first cycle delithiation capacity of 2650 mAh/g. While we do not have a strong understanding of this large increase in capacity, it may be due to the etching of surface SiO₂ from the silicon nanoparticles during the citric acid pre-treatment. In addition, after the first lithiation, the cells containing Si-np have greater impedance than cells containing M-Si-np. This is consistent with either a more conductive SEI or less damage to the electrode laminate for the M-Si-np electrodes. While the first cycle efficiencies are similar for the M-Si-np and Si-np, the second cycle efficiency is much higher for M-Si-np (90%), than Si-np (77%), suggesting that the M-Si-np generates an SEI after fewer cycles and thus the surface modification results in the generation of a pre-SEI. The change in the first two cycles results in a large improvement in the capacity of the electrode. However, after the first two cycles the capacity loss is similar for the two electrodes suggesting that capacity fade from electrode damage during the large volumetric changes upon cycling becomes dominant. However, the overall capacity retention is significantly better for the M-Si-np electrode.

Silicon graphite composite electrodes which contain 15% silicon have also been prepared and investigated in Si-np/Gr||lithium cells as depicted in Figure 5. The first cycle discharge capacity and efficiency are similar for cells with M-Si-np/Gr and Si-np/Gr. The similarity of first cycle discharge capacity is surprising when compared to the large increase in capacity for the M-Si-np electrodes compared to the Si-np electrodes as described above. While we do not have a strong understanding of why citric acid modification significantly improves the second cycle efficiency for the Si-

np electrodes and does not change the second cycle efficiency for Si-np/Gr composite electrodes, silicon nanoparticle electrodes have been previously reported to have low efficiency (< 80 %) with PVDF binders,²³ while silicon/graphite composite electrodes have been reported to have high second cycle efficiencies²⁹. However, the cells containing M-Si-np/Gr have lower impedance after the first cycle, similar to that observed for the EIS for the Si-np electrodes. Upon continued cycling, the cells with Si-np/Gr composite electrodes have more capacity fade than the cells containing M-Si-np/Gr composite electrodes. The cells containing M-Si-np/Gr have ~70 % capacity retention after 50 cycles while the cells containing Si-np/Gr have only ~50% capacity retention after 50 cycles. The improved capacity retention of the M-Si-np/Gr composite electrodes is consistent with the reduced impedance after the first cycle and the improved capacity retention of the silicon electrodes.

4.4.2. Surface analysis of the electrodes

In an effort to develop a better understanding of the source of performance improvement of the citric acid modified silicon particles, ex-situ surface analysis of the electrodes before and after cycling has been conducted. XPS and IR-ATR spectra of the fresh and cycled electrodes were obtained without exposure to air.

The IR-ATR spectra of the Si-np/Gr composite electrodes and the M-Si-np/Gr composite electrodes before and after cycling are depicted in Figure 6. The fresh electrodes have peaks at 1416, 1177, 975, 880 and 828 cm^{-1} characteristic of the PVdF binder^{24,30}. Since the surface modification is only a mono-layer on the silicon particle and there is only 15 % silicon in the composite electrode, the spectra of the fresh electrodes are very similar. The cycled electrodes are all dominated by peaks

characteristic of Li_2CO_3 at 1420 and 1490 cm^{-1} . In addition, weak absorptions are observed at 1790 cm^{-1} characteristic of poly(FEC) for all cycled electrodes^{24,31}. After two cycles, the composite electrodes containing M-Si-np have new absorptions at 1590 cm^{-1} characteristic of $-\text{CO}_2\text{Li}$ from lithium citrate as previously reported,^{24,23} consistent with citric acid modification of the SEI.

The XPS spectra of the Si-np/Gr composite electrodes and the M-Si-np/Gr composite electrodes before and after cycling are depicted in Figure 7 and the elemental concentrations are provided in Table 1. The fresh electrodes are dominated by C and Si from the active materials along with high concentrations of O and F from the surface coating of SiO_2 on the silicon nanoparticles and the PVDF binder, respectively. After cycling, the concentrations of C and Si are decreased while the concentrations of Li, F, and O are increased characteristic of the generation of an SEI on the surface of the anode. The XPS spectra of the fresh electrodes are very similar and are dominated by PVDF binder (C1s, 284.3, 286.5 and 291 eV; F1s, 687.5 eV), graphite (C1s, 284.3 eV), and silicon (99.4 eV), as expected since the M-Si-np/Gr electrode contains only a very thin layer of citric acid. The XPS spectra of the electrodes after cycling are very similar. The C 1s spectrum contains broad C1s peak between 287 and 291 eV characteristic of a combination of C-O, C=O, and CO_3 . After cycling, both electrodes contain a strong peak at 685 eV and a weak peak at 687 eV in the F 1s spectrum characteristic of LiF and $\text{Li}_x\text{PF}_y\text{O}_z$, respectively, from the reduction of FEC and LiPF_6 ^{19,32}. After cycling, the silicon 2p spectra contains only weak peaks consistent with the generation of an SEI which is thicker than the depth of penetration of XPS. The O1s spectra contain a broad peak between 531 and 534 eV

characteristic of a combination of $-\text{CO}_3$, $-\text{CO}_2$, and $\text{C}-\text{O}$, supporting the presence of poly(carbonate), lithium alkyl carbonate, lithium carboxylate, and lithium carbonate. Overall the XPS spectra are similar for both the Si-np/Gr and M-Si-np/Gr electrodes suggesting that the composition of the SEI is similar for both electrodes after 20 cycles.^{4,33}

4.4.3. Electrochemical cycling of silicon graphite composite electrodes with LiCoO_2 electrodes

The silicon graphite composite electrodes were further investigated in full cells with a LiCoO_2 cathode to examine the effect of the surface modification in cells with a limited supply of lithium for cycling. LiCoO_2 electrodes are commonly used in many commercial lithium ion batteries due to excellent capacity retention^{34,35}. Electrochemical cycling of silicon graphite composite|| LiCoO_2 cells have been conducted with the same electrolyte and similar cycling protocol to the silicon graphite composite/lithium cells discussed above. The cycling performance of the graphite silicon composite/ LiCoO_2 cells containing M-Si-np or Si-np is depicted in Figure 8. The cycling performance is similar to that observed for the Si-np/Gr composite||lithium cells. The cells containing M-Si-np have significantly better capacity retention (78 %) than the cells containing Si-np (60%). The results suggest that surface modification of silicon nanoparticles may improve the performance of silicon graphite composite electrodes in commercial cells.

4.5. Conclusion

Surface modification of silicon nanoparticles with citric acid, a small molecule tricarboxylic acid, has been investigated to generate a more stable SEI and reduce

electrolyte consumption during the lithiation and delithiation of silicon electrodes. The study has shown improved performance for the surface modified silicon-based electrodes due to the formation of the pre-SEI. The surface modified Si-np/Gr composite/lithium cells have much better capacity retention, 60%, than the unmodified Si-np/Gr composite||lithium cells, 45%, after 50 cycles. The surface modified Si-np/Gr composite||LiCoO₂ cells also have much better capacity retention, 78%, compared to the unmodified Si-np/Gr composite||LiCoO₂ cells. The results suggest that surface modification of the silicon nano-particles with citric acid can significantly improve the performance of silicon/graphite composite electrodes.

Acknowledgements

The authors gratefully acknowledge funding from Department of Energy Office of Basic Energy Sciences EPSCoR Implementation award (DE-SC0007074)

4.6. References

1. M. Armand and J. M. Tarascon, *Nature*, **451**, 652–657 (2008).
2. K. Xu, *Chem. Rev.*, **114**, 11503–11618 (2014).
3. Aurbach, D.; Talyosef, Y.; Markovsky, B.; Markevich, E.; Zinigrad, E.; Asraf, L.; Gnanaraj, J. S.; Kim, H. J. *Electrochim. Acta*, **50**, 247–254, (2004)
4. Chandrasiri, K. W. D. K.; Nguyen, C. C.; Zang, Y.; Parimalam, B. S.; Lucht, B. L., *Electrochimica acta*, **250**, 285--291, (2017)
5. Shen, X.; Tian, Z.; Fan, R.; Shao, L.; Zhang, D.; Cao, G.; Kou, L.; Bai, Y. *J. Energy Chem.*, **0**, 1–24, (2018)
6. Goriparti, S.; Miele, E.; De Angelis, F.; Di Fabrizio, E.; Proietti Zaccaria, R.; Capiglia, C. *J. Power Sources*, **257**, 421–443, (2014)
7. Cheng, X. B.; Zhang, R.; Zhao, C. Z.; Wei, F.; Zhang, J. G.; Zhang, Q. *Adv. Sci.*, **3**, 1500213, (2016)
8. Luo, F.; Liu, B.; Zheng, J.; Chu, G.; Zhong, K.; Li, H.; Huang, X.; Chen, L. *J. Electrochem. Soc.*, **162** (14), A2509–A2528, (2015)
9. Zuo, X.; Zhu, J.; Müller-Buschbaum, P.; Cheng, Y. *J. Nano Energy*, **31**, 113–143, (2017)
10. K. Xu, *Chem. Rev.*, **104**, 4303–4417 (2004).
11. B. Scrosati and J. Garche, *J. Power Sources*, **195**, 2419–2430 (2010).
12. K. M. Abraham, *J. Phys. Chem. Lett.*, **6**, 830–844 (2015).

13. W. J. Zhang, *J. Power Sources*, **196**, 13–24 (2011)
14. Beattie, S. D.; Loveridge, M. J.; Lain, M. J.; Ferrari, S.; Polzin, B. J.; Bhagat, R.; Dashwood, R. *J. Power Sources*, **302**, 426–430, (2016)
15. M. N. Obrovac and L. J. Krause, *J. Electrochem. Soc.*, **154**, A103 (2007)
16. Mazouzi, D.; Karkar, Z.; Hernandez, C. R.; Manero, P. J.; Guyomard, D.; Roué, L.; Lestriez, B. *J. Power Sources*, **280**, 533–549, (2015)
17. Kim, N.; Oh, C.; Kim, J.; Kim, J.; Jeong, D.; Bae, J.; Hong, E.; Kyoo, J., *J. Electrochem. Soc.*, **164** (1), 6075–6083, (2017)
18. T. Yoon, C. C. Nguyen, D. M. Seo, and B. L. Lucht, *J. Electrochem. Soc.*, **162**, A2325-A2330, (2015)
19. C. C. Nguyen and B. L. Lucht, *J. Electrochem. Soc.*, **161**, A1933–A1938 (2014)
20. Magasinski, A.; Zdyrko, B.; Kovalenko, I.; Hertzberg, B.; Burtovyy, R.; Huebner, C. F.; Fuller, T. F.; Luzinov, I.; Yushin, G., *ACS Appl. Mater. Interfaces*, **2**(11), 3004–10, (2010)
21. Lacey, M. J, Jeschull, F., Edstrom, K., Brandell, D., *J. Power Sources*, **264**, 8–14, (2014)
22. Chevrier, V. L.; Liu, L.; Le, D. B.; Lund, J.; Molla, B.; Reimer, K.; Krause, L. J.; Jensen, L. D.; Figgemeier, E.; Eberman, K. W. *J. Electrochem. Soc.*, **161** (5), A783–A791, (2014)
23. Nguyen, C. C.; Yoon, T.; Seo, D. M.; Guduru, P.; Lucht, B. L. *ACS Appl. Mater. Interfaces*, **8** (19), 12211–12220, (2016)

24. Porcher, W.; Chazelle, S.; Boulineau, A.; Mariage, N.; Alper, J. P.; Rompaey, T. Van; Bridel, J.; Haon, C. *J. Electrochem. Soc.*, **164** (14), 3633–3640, (2017)
25. Nguyen, C. C.; Seo, D. M.; Chandrasiri, K. W. D. K.; Lucht, B. L. *Langmuir*, **33**(37), 9254-9261, (2017)
26. Aslanov, L. a.; Zakharov, V. N.; Zakharov, M. a.; Kamyshny, a. L.; Magdassi, S.; Yatsenko, a. V. *Russ. J. Coord. Chem.*, **36** (5), 330–332, (2010)
27. S. C. Feifel and F. Lisdat, *J. Nanobiotechnology*, **9**, 59 (2011)
28. García, S. J.; Fischer, H. R.; White, P. A.; Mardel, J.; González-García, Y.; Mol, J. M. C.; Hughes, A. E. *Prog. Org. Coatings*, **70** (2–3), 142–149, (2011)
29. T. Schott, J. L. G, P. Nov, and S. Trabesinger, *J. Electrochem. Soc.*, **164**, 190–203 (2017).
29. T. Schott, J. L. G, P. Nov, and S. Trabesinger, *J. Electrochem. Soc.*, **164** (2) A190-A203 (2017)
30. Papp, J. K.; Forster, J. D.; Burke, C. M.; Kim, H. W.; Luntz, A. C.; Shelby, R. M.; Urban, J. J.; McCloskey, B. D. *J. Phys. Chem. Lett.*, **8** (6), 1169–1174, (2017)
31. Jung, R.; Metzger, M.; Haering, D.; Solchenbach, S.; Marino, C.; Tsiouvaras, N.; Stinner, C.; Gasteiger, H. A. *J. Electrochem. Soc.*, **163** (8), A1705-A1716 (2016)
32. Brown, L. A.; Rhinehart, J. L.; Long, B. K. *ACS Catal.*, **5** (10), 6057–6060, (2015)
33. Leroy, S.; Blanchard, F.; Dedryvère, R.; Martinez, H.; Carré, B.; Lemordant, D.; Gonbeau, D. *Surf. Interface Anal.*, **37** (10), 773–781, (2005)
34. Huang, B.; Jang, Y.; Chiang, Y.; Sadoway, D. R. *J. Appl. Electrochem.*, **28** (3), 1365–1369, (1998)

35. Julien, C. M.; Mauger, A.; Zaghib, K.; Groult, H. *Inorganics*, **2**, 132–154, (2014)

4.7. List of Figures

Figure 1 – FTIR – ATR spectra of silicon nanoparticles(black), citric acid powder(red) and CA modified silicon nanoparticles(Blue).

Figure 2 – TGA of the fresh silicon nanoparticles (black) and CA surface modified silicon nanoparticles (red).

Figure 3 – Schematic representation of the surface modification of silicon nanoparticles.

Figure 4 – Cycling performance of silicon electrodes a) specific capacity and b) coulombic efficiency vs cycle number plots, c) first cycle voltage profile and d) 1st lithiation impedance spectra.

Figure 5 – Cycling performance of silicon graphite composite electrodes a) specific capacity and b) coulombic efficiency vs cycle number plots, c) first cycle voltage profile and d) 1st lithiation impedance spectra.

Figure 6 – FTIR- ATR data for a) Si-np/Gr and b) M-Si-np/Gr electrodes. (black) fresh electrode, (red) electrode extracted after 2 cycles, (red) electrode extracted after 20 cycles.

Figure 7 – XPS data for silicon nanoparticle and modified silicon nanoparticle electrodes a) C1s, b) F1s, c) Si2p, and d) O1s. Fresh electrode(black), electrodes extracted after cycling, (red) after 20 cycles.

Figure 8 – Cycling performance data for Silicon graphite composite electrode/ LCO full cells, a) specific capacity and b) coulombic efficiency vs cycle number.

4.8. List of Tables

Table 1 - Elemental concentrations obtained by XPS for fresh and cycled (20 cycles)

Si-np/GR and M-Si-np/Gr electrodes.

4.9. Figures

Figure 1: FTIR – ATR spectra of silicon nanoparticles(black), citric acid powder(red) and CA modified silicon nanoparticles(Blue).

Figure 2: TGA of the fresh silicon nanoparticles (black) and CA surface modified silicon nanoparticles (red)

Figure 3. Schematic representation of the surface modification of silicon nanoparticles

Figure 4: Cycling performance of silicon electrodes a) specific capacity and b) coulombic efficiency vs cycle number plots, c) first cycle voltage profile and d) 1st lithiation impedance spectra.

Figure 5: Cycling performance of silicon graphite composite electrodes a) specific capacity and b) coulombic efficiency vs cycle number plots, c) first cycle voltage profile and d) 1st lithiation impedance spectra.

Figure 6: FTIR- ATR data for a) Si-np/Gr and b) M-Si-np/Gr electrodes. (black)fresh electrode, (red) electrode extracted after 2 cycles, (blue) electrode extracted after 20 cycles

Figure 7: XPS data for silicon nanoparticle and modified silicon nanoparticle electrodes a) C1s, b) F1s, c) Si2p, and d) O1s. Fresh electrode(black), electrodes extracted after cycling, (red) after 20 cycles

Figure 8: Cycling performance data for Silicon graphite composite electrode/ LCO full cells, a) specific capacity and b) coulombic efficiency vs cycle number

4.10. Tables

Element	Atomic %			
	Fresh		20 cycles	
	M-Si-np/Gr	Si-np/Gr	M-Si-np/Gr	Si-np/Gr
C1s	54.8	67.6	24.6	24.3
F1s	12.6	8.6	24.8	25.5
Li1s	N/A	N/A	31.1	31.4
O1s	11.2	8.9	18.9	17.9
P2p	N/A	N/A	0.4	0.5
Si2p	21.4	14.9	0.2	0.4

Table 1: Elemental concentrations obtained by XPS for fresh and cycled (20 cycles) Si-np/GR and M-Si-np/Gr electrodes

CHAPTER 5

Casein from Bovine Milk as a Binder for Silicon based Electrodes

K. W. D. Kaveendi Chandrasiri, Maheeka Yapa Abeywardana, Brett L. Lucht*

Manuscript in Progress for *Journal of Power Sources*

5.1. Abstract

High capacity electrode material has been studied over the years due to the constant demand for high energy density applications in li ion batteries. Among others, silicon has been considered a more promising candidate for its high theoretical capacity of ~ 3600mAh/g, abundant resources, low cost and low toxicity. However, silicon-based electrodes face rapid degradation due to the extensive volume variation (~300%) in the charge discharge process. Binders used in the electrode fabrication plays a crucial role in these high-performance electrodes since it can reduce the mechanical fracture in the cycling process.

Utilization of polymeric material as binders to hold the active material has been the most common approach used in the li ion battery electrode preparation. Recent studies carried out by Nguyen et. al have shown the use of small molecular carboxylic acids as binders which showed an improvement in the cell performance for silicon electrodes. In this study we introduce a cheap and environmentally friendly alternative that could be used as a non-polymeric binder for silicon electrodes. Further, the electrode preparation can be done in water medium which reduces the introduction of toxic organic solvents such as NMP to the environment. Casein is a milk protein found in bovine milk rich in amine groups and carboxylic acid groups which can form bonds with the silanol groups in silicon. A comparative study conducted between PVDF and Casein as binders have shown that when casein was used as binder, it shows better performance compared to PVDF. It has 30% higher capacity retention compared to PVDF with a 1300 mAh/g capacity after 200 cycles. Surface morphology and Solid

electrolyte interface was analyzed using electron microscopy techniques and spectroscopic methods and the results will be discussed.

5.2. Introduction

The demand for high energy density material for lithium ion battery electrodes increase by the day due to the boom in the electric and hybrid electric vehicle market. The current electric vehicle battery has a rather low driving range per single charge and has a high price tag associated with the production making it unaffordable to the wide population. Utilization of a high volumetric energy density electrode can give a high driving range with a similar sized unit cell which could drop the cost and make it affordable¹. Currently, most commercial batteries use graphite as the anode material which was introduced in 1991. Graphite has good cycle life, low cost, low flat working potential vs Li, good electronic conductivity and good overall performance^{2,3}. Advancement in technology have made it possible to almost reach the theoretical capacity of graphite (~372 mAh/g), which is a specific energy of ~150 Wh/kg. This is still far too less for the energy demand of the electric vehicles and power grid energy storage applications⁴. Many alternative anode materials have been studied over the years and silicon has been the most promising candidate with a theoretical capacity of ~3600 mAh/g in its alloyed form (Li₁₅ Si₄)^{4,5} which is almost 10 times higher than graphite. At higher temperatures the Li₂₂Si₄ alloying state can be reached which can give up to ~4200 mAh/g capacity⁶⁻⁸, making it the best of all other known anode material. This is due to silicon being able to alloy with about four lithium atoms whereas, six carbon atoms are needed to bond with one lithium atom. The half reactions for silicon and graphite are as follows⁹.

Silicon has many other advantages apart from the higher volumetric and gravimetric energy density. The working potential (0.5 V vs Li/Li⁺) reduces the safety concerns of lithium deposition and dendrite formations. It is the second most abundant element on earth crust making it a cheap alternative and it is environmentally friendly¹⁰

However, the practical implementation of silicon as an anode material has been challenging. The alloying/ dealloying of silicon with lithium experiences a volume variation of ~300%. This expansion induces stress on the particles which leads to instability, loss of contact between active material and the current collector which leads to pulverization of the electrode. This in turn leads to low capacity stability. Secondly, the continuous formation of the SEI contributes to the fast capacity fade. In a conventional cell, the first cycle produces an SEI which acts as a barrier to stop the electrolyte from being further consumed. But due to the effects of pulverization, silicon exposes fresh surfaces throughout the cycling process which leads to consumption of lithium leading to capacity fade^{6,11,12}.

Investigating binders is one of the various methods used to improve cycling stability of silicon-based electrodes. A common approach used by many researchers is to work with polymeric binders because of the polymeric structures ability to hold the silicon particles with each other as well as the current collector more stably. But in the case of silicon as well as most other high capacity material, the structure of the binder also play a significant role in the SEI formation in the charge and discharge process. In a study by Nguyen et. al. it was shown that small molecules, that has the ability of forming a functionally and morphologically more stable SEI can act as a good binder. In the study a small molecular tricarboxylic acid, citric acid when used as a binder has

outperformed the properties of PVDF and showed comparable performance to polyacrylic acid binder^{13,14}.

Many naturally occurring adhesives such as xanthan gum¹⁵, guar gum¹⁶, chitosan¹⁷, cellulose, gelatin etc. has been studied in lithium ion batteries as binders. All these structures are known biopolymers. In this study another alternative single molecular structure, casein was used as a binder. Casein is a naturally occurring milk protein, which can easily be extracted from bovine milk in a very cost-effective method and can be used as a natural adhesive. Instead of harmful chemicals, water can be used for processing casein as a binder. Electrochemical studies were conducted to compare the performance of electrodes made with casein in multiple methods vs the common PVDF binder and the SEI was characterized using XPS, IR and SEM.

5.3. Experimental

Silicon nanoparticles (< 50nm, Alfa Aesar), Super C (Timcal), Graphite G8 (C-preme), SFG6 (Timcal), Anhydrous NMP (sigma Aldrich), PVDF binder ($M_w = 600$ 000, MTI) and Casein Sodium salt from bovine milk (Sigma) were purchased. Battery grade Lithium hexafluorophosphate ($LiPF_6$), Ethylene Carbonate (EC), Dimethyl Carbonate (DMC) and Fluoroethylene Carbonate (FEC) were obtained from a commercial supplier with water content < 50 ppm and stored in an Ar glovebox. High purity lithium chips (15.6 mm diameter), and Lithium Cobalt Oxide Cathode were purchased from MTI corporation.

5.3.1. Preparation of Electrode Laminates

Si-Casein: Material ratio, Si: Casein: C-65, 50: 25: 25. Laminates were prepared by mixing Casein with water (2.5ml) in a mortar and pestle. This starts creating a sticky foamy mixture. C-65 and silicon nanoparticles were then mixed until a homogenous slurry is formed. This mixture is then stirred for 3 hours using a magnetic stirrer. The resulting mix is then coated on a copper foil using a Doctor blade. The punched electrodes are shown in figure 2(a).

The silicon PVDF: Material ratio, Si: PVDF: C-65, 50: 25: 25. Laminates were prepared in a nitrogen filled glovebox using NMP as a solvent (1.9 ml). A mix of silicon nanoparticles, C-65 and PVDF was ground until a homogenous slurry is formed. Mix is then stirred using a magnetic stirrer for 3 hours and coated on a copper foil using a Doctor blade.

Si-Casein excess water: Material ratio, Si: Casein: C-65, 50: 25: 25. Similar to the other two electrodes, silicon nanoparticles, C-65 and casein was mixed thoroughly in a mortar and pestle with water. In this procedure double the amount of water was used as the solvent (5 ml). Excess was to make the mixture less viscous and reduce bubble formation. The mixture was stirred using a magnetic stirrer for 3 hours followed by sonication for 10 minutes under vacuum to remove any bubbles. The electrode was then coated using a doctor blade shown in figure 2(b).

Si-Casein-PVDF: Material ratio, Si: PVDF: Casein: C-65, 50: 20: 5: 25. Silicon nanoparticles were mixed with 5% casein in water and let the water evaporate completely. The powder was crushed and mixed with PVDF, C-65 and NMP to form a slurry and coated using a doctor blade. 20% PVDF was used in the mixture. No foaming was observed, and the electrode is shown in figure 2(c).

5.3.2. *Cell construction and Cycling Procedure*

All electrodes were punched to 14 mm diameter electrodes and dried overnight under vacuum at 110 °C before cell preparation. Coin cells (2032 type) were constructed in an argon filled glovebox. Cells were assembled using a 14mm Si-np anode, one 19mm Celgard 2325 separator, one 15.6mm Whatman GF/D glass microfiber separator, and a 15.6 mm lithium chip with 100 μ L of electrolyte containing 1.2 M LiPF₆ in EC: DEC: FEC 40: 40: 10 (by mass). All Si-np||Li cells were cycled between 0.005 and 1.50 V at a rate of C/20 for 1 formation cycle, with a C/40 taper charge followed by cycles at C/3 with a C/20 taper charge. Cell cycling was carried out with an Arbin BT 2000 battery cycler at 25 °C. All cells were tested in duplicate. After the 1st and 50th delithiations, cells were rested for 12 hours followed by electrochemical impedance spectroscopy using a potentiostat with an amplitude of 10 mV and frequency range of 300 kHz–20 mHz. Representative data is presented.

Delithiated electrodes were extracted from the cycled cells, carefully rinsed with DMC three times (1.5 mL in total) to remove residual electrolyte and then dried in a glovebox for ex-situ surface analysis. Ex-situ X-ray photoelectron spectroscopy (XPS) was conducted using a K-Alpha spectrometer (Thermo Scientific) with a spot size of 200 μ m, an energy step size of 0.05 eV, and a pass energy of 50 eV. The electrodes were transferred from the glovebox to the XPS chamber using a vacuum-sealed transfer module (Thermo Scientific) without exposure to air. The binding energy was corrected based on of C 1s peak of hydrocarbons at 285 eV, F1s peak of LiF at 685 eV, and PVDF at 688 eV.

Infrared spectroscopy with attenuated total reflectance (IR-ATR) (Bruker Tensor 27 with LaDTG detector) was conducted inside a high purity N₂-filled glovebox to prevent the reactions of samples with O₂ and moisture. All spectra were collected with 512 scans at a spectral resolution of 4 cm⁻¹.

The surface morphology and elemental distribution of fresh and cycled electrodes was examined by scanning electron microscopy, coupled with EDS (JEOL 5900).

5.4. Results and Discussion

Four types of electrodes have been prepared and compared in this study. In each case 25% binder was used. First one is a conventional silicon electrode prepared with the most commonly used polymeric binder PVDF, shown in figure 2(d). In the same way a casein-based electrode was prepared with a similar slurry consistency. However, it was observed that when using a small amount of solvent, (solvent : solid = ~1 v/v) casein tend to foam producing air bubbles which cannot be removed using conventional methods such as vacuum suction or sonication. Electrodes were coated with the air bubbles with a higher thickness using a doctor blade. The punched electrode is shown in figure 2(a). A second method was then utilized to reduce the foamy nature of the electrode slurry. With the addition of more solvent (2.5 ml was further increased to 5 ml), the foaming could be reduced. Also, sonication with vacuum suction further reduced the formation of these large bubbles giving a smoother electrode as shown in figure 2(b). Furthermore, an electrode was prepared with a combination of casein and PVDF as the binders where no foaming was observed.

5.4.1. Electrochemical performance

Cell cycling was carried out in 2032 type cells according to the procedure described in the experimental section. The specific capacity of half cells is depicted in figure 3(a). A rapid capacity fade is observed in both the electrodes containing PVDF. After 50 cycles cells the PVDF electrode retains a capacity of ~1000 mAh/g. The electrode with a mixture of PVDF and casein has a much lower first cycle capacity, but the capacity retention is slightly better than the PVDF electrodes after the first 80 cycles. The casein electrode with the textured surface retains a capacity of ~1550 mAh/g after 50 cycles, which is significantly better than PVDF electrodes. The casein electrodes with excess water retains more than 1200 mAh/g capacity after 200 cycles, which is a significant improvement compared to all other electrodes. The first cycle efficiency is lowest for the electrode containing casein + PVDF consistent with the low first cycle capacity, while the casein electrode prepared with excess water had the highest first cycle efficiency.

An equivalent circuit diagram for a typical Nyquist plot for Li/electrode/Si electrode is shown in figure 3(e). The semicircle, which is in the high to moderate frequency range is usually attributed to the impedance caused due to the SEI and charge transfer. The semicircle in the low frequency range is attributed to Li-ion diffusion¹⁸.

Surprisingly the electrochemical impedance spectra (EIS) for the first cycle have a significantly different trend. Both electrodes containing PVDF have much lower impedance than the electrodes containing only casein. However, after 50 cycles, the electrodes with only casein maintained comparable impedance while the PVDF electrodes have a large increase in impedance. The large difference in morphology may be the source of the trends in impedance spectra. While quantitative analysis of

the EIS data for composite electrodes is difficult, the first semicircle is typically assigned to the formation of the anode SEI^{19–21}. The surface roughness resulting from foaming likely leads to the higher initial impedance. After 50 cycles the large increase in impedance for electrodes containing PVDF is due to the formation of a thicker SEI and loss of contact between the particles. This could be due to the morphological change to the electrode laminate.

There is a 20% increase in the first cycle efficiency in the full cell data with LiCoO₂ electrode when casein was compared to PVDF, which resulted in the initial drop in the capacity. There was no difference in the cycling performance of textured vs, excess water-based casein electrode in full cells. After ~50 cycles the casein-based electrodes have shown significantly higher performance compared to the PVDF based electrodes.

5.4.2. Surface Analysis

Ex-situ surface characterization was performed on fresh and cycled electrodes to understand the varying difference in the cycling performance. X-ray photoelectron spectroscopy reveal a few noteworthy differences in the fresh electrodes as shown in figure 5(a). The Si2p is dominated by 2 main peaks in all four electrodes corresponding to Si-Si at ~99.5 eV and Si-O at 104 eV. The electrodes that contain casein contain an extra peak at ~102 eV, which is characteristic of Si-N^{22–24}. Since casein contains amino groups, this suggests that casein reacts on the surface of the silicon to generate Si-N bonds. There is also an increase in the Si-O peak in both the Si2p spectrum and the O1s spectrum for the electrode processed with excess water. Previous studies have shown that the oxide layer on silicon increases with increased exposure to air and moisture²⁵. Therefore, this could be attributed to the thickening of

the oxide layer. The carbon spectrum of the fresh electrodes containing PVDF have peaks corresponding to conductive carbon at 285 eV and PVDF at 286.6 and 290 eV^{26,27}. While the cells with Casein have peaks corresponding the conductive carbon at 285 eV and casein at 285.5 eV (C-N), 286 eV (C-O), and 288-289 eV (C=O)^{28,29}. An interesting observation is the absence of the nitrogen peak in casein containing sample with excess water. Although after 1 cycle, this electrode shows a nitrogen peak which corresponds to the amides in casein in the N1s spectrum. A depth profile on the fresh electrode is shown in figure 6. It shows a nitrogen peak appearing after a short period of etching. This could mean that the slight change in morphology is changing the binder presence on the surface of the electrode. The XPS spectra of the cycled electrodes all have very similar carbon spectra consisting of Li_2CO_3 and Li-alkyl carbonate from electrolyte reduction products around 290.8 eV, and 287.5 eV respectively.

The FTIR-ATR spectra of the fresh and cycled electrodes are provided in Figure 7. Surprisingly, while the electrodes prepared with casein and casein with excess water, both consists of the same components, the two electrodes have a slightly different chemical functionalization. The peaks 1650, 1514 and 1441 and cluster of peaks around 3200 cm^{-1} are peaks corresponding to casein. The amide group stretching of casein shows another peak at 1585 cm^{-1} ³⁰. This peak is well observed in the fresh electrodes with excess water and the ones with the combination binder system. But, this peak was not observed in casein electrode with the textured surface. Some researchers have found that foaming of the particles are mainly due to the micelle formation³¹⁻³³. This could be a potential reason to the change in the functionalization on casein-textured

electrodes that are seen on the FTIR spectra. PVDF peaks are observed at 1416, 1177, 975, 880 and 828 cm^{-1} ¹²⁷. After cycling all electrodes contain new IR absorptions characteristic of electrolyte reduction products. The new absorptions include peaks at 1490 and 1450 cm^{-1} characteristic of Li_2CO_3 , peaks around 1620 cm^{-1} characteristic of lithium alkyl carbonates, and peaks around ~ 1750 and ~ 1800 cm^{-1} characteristic to polycarbonate. These compounds are commonly observed SEI components resulting from the reduction of EC and FEC. Both casein containing electrodes show similar SEI immediately after one cycle. Although a significant difference on the fresh electrode surface is observed, as it cycles, reduction products of casein, and the electrolyte covers the surface. This could also be the reason why not much of a difference in cycling performance is observed in the first few cycles.

5.4.3. *Understanding surface morphology*

Surface analysis has shown that the change in the processing method used when utilizing casein as a binder not only improves the overall performance of the electrode but also alters the surface species and the distribution of the binder. Therefore scanning electron microscopy studies were conducted. As shown on figure 8(a) the casein electrode clearly shows large holes or deformities formed on the surface due to popping of the foam bubbles as they dry. Comparatively the casein with excess water electrode show much smoother surface. Yet it also shows some deformity and random pore structure. The pores in this electrode are 20 times smaller. The PVDF, Casein mixture gave a coarser electrode that look grainy in the material distribution. PVDF electrode is a smoother surfaces electrode compared to the others. After cycling the zoomed in images are shown in figure 9. The large popped bubble surface is

significantly covered by the SEI formation in the casein electrode, although some pores are still observed. Comparatively the electrode prepared with excess water still shows a much less damaged surface with some porosity left on the electrode similar to the original electrode. The casein PVDF combination electrode shows a much thicker SEI producing a thick mossy surface on the electrode. PVDF only electrode shows a thick SEI formed on the electrode and cracks are observed on the surface.

5.5. Conclusion

Casein was investigated as potential binder for silicon-based electrodes. The usual processing method tend to foam casein giving a large pore containing structure. An alternate processing method was used with casein and double the amount of solvent, which got rid of the formation of larger air bubbles. SEM images have shown the casein electrode with excess water still consists of pores 20 times smaller than the ones with casein only electrodes. This change in the surface morphology has changed the cycling performance giving the best performance with casein with excess water, showing the viability of using casein as a binder for silicon-based anodes. Further studies need to be conducted to improve the processing method to further smoothen the surface that could show even better performance.

Acknowledgements

The authors would like to Acknowledge the funding from the Department of Energy Office of Basic Energy Sciences EPSCoR implementation award (DE-SC 0007074), And Dr.Irene Andreu from the center for nanotechnology in the University of Rhode Island Department of Engineering for assisting in obtaining SEM data.

5.6. References

- (1) Bordes, A.; Eom, K.; Fuller, T. F. The Effect of Fluoroethylene Carbonate Additive Content on the Formation of the Solid-Electrolyte Interphase and Capacity Fade of Li-Ion Full-Cell Employing Nano Si-Graphene Composite Anodes. *J. Power Sources* **2014**, *257*, 163–169.
<https://doi.org/10.1016/j.jpowsour.2013.12.144>.
- (2) Chandrasiri, K. W. D. K.; Nguyen, C. C.; Zhang, Y.; Parimalam, B. S.; Lucht, B. L. Systematic Investigation of Alkali Metal Ions as Additives for Graphite Anode in Propylene Carbonate Based Electrolytes. *Electrochim. Acta* **2017**, *250*, 285–291. <https://doi.org/10.1016/j.electacta.2017.08.065>.
- (3) Yim, C.; Niketic, S.; Salem, N.; Naboka, O.; Abu-lebdeh, Y. Towards Improving the Practical Energy Density of Li-Ion Batteries : Optimization and Evaluation of Silicon : Graphite Composites in Full Cells. **2017**, *164* (1), 6294–6302. <https://doi.org/10.1149/2.0481701jes>.
- (4) Shen, X.; Tian, Z.; Fan, R.; Shao, L.; Zhang, D.; Cao, G.; Kou, L.; Bai, Y. Research Progress on Silicon/Carbon Composite Anode Materials for Lithium-Ion Battery. *J. Energy Chem.* **2018**, *0*, 1–24.
<https://doi.org/10.1016/j.jechem.2017.12.012>.
- (5) Ashuri, M.; He, Q.; Shaw, L. L. Silicon as a Potential Anode Material for Li-Ion Batteries: Where Size, Geometry and Structure Matter. *Nanoscale* **2016**, *8* (1), 74–103. <https://doi.org/10.1039/C5NR05116A>.
- (6) Zuo, X.; Zhu, J.; Müller-Buschbaum, P.; Cheng, Y. J. Silicon Based Lithium-Ion Battery Anodes: A Chronicle Perspective Review. *Nano Energy* **2017**, *31*

- (October 2016), 113–143. <https://doi.org/10.1016/j.nanoen.2016.11.013>.
- (7) Dalavi, S.; Guduru, P.; Lucht, B. L. Performance Enhancing Electrolyte Additives for Lithium Ion Batteries with Silicon Anodes. *J. Electrochem. Soc.* **2012**, *159* (5), A642. <https://doi.org/10.1149/2.076205jes>.
 - (8) Liang, B.; Liu, Y.; Xu, Y. Silicon-Based Materials as High Capacity Anodes for next Generation Lithium Ion Batteries. **2014**, 267.
 - (9) Casimir, A.; Zhang, H.; Ogoke, O.; Amine, J. C.; Lu, J.; Wu, G. Nano Energy Silicon-Based Anodes for Lithium-Ion Batteries : Effectiveness of Materials Synthesis and Electrode Preparation. *Nano Energy* **2016**, *27*, 359–376. <https://doi.org/10.1016/j.nanoen.2016.07.023>.
 - (10) Yin, Y. X.; Wan, L. J.; Guo, Y. G. Silicon-Based Nanomaterials for Lithium-Ion Batteries. *Chinese Sci. Bull.* **2012**, *57* (32), 4104–4110. <https://doi.org/10.1007/s11434-012-5017-2>.
 - (11) Goriparti, S.; Miele, E.; De Angelis, F.; Di Fabrizio, E.; Proietti Zaccaria, R.; Capiglia, C. Review on Recent Progress of Nanostructured Anode Materials for Li-Ion Batteries. *J. Power Sources* **2014**, *257*, 421–443. <https://doi.org/10.1016/j.jpowsour.2013.11.103>.
 - (12) Erk, C.; Brezesinski, T.; Sommer, H.; Schneider, R. Toward Silicon Anodes for Next-Generation Lithium Ion Batteries: A Comparative Performance Study of Various Polymer Binders and Silicon Nanopowders. **2013**. <https://doi.org/10.1021/am401642c>.
 - (13) Nguyen, C. C.; Seo, D. M.; Chandrasiri, K. W. D. K.; Lucht, B. L. Improved Cycling Performance of a Si Nanoparticle Anode Utilizing Citric Acid as a

Surface-Modifying Agent. *Langmuir* **2016**, acs.langmuir.6b04310.

<https://doi.org/10.1021/acs.langmuir.6b04310>.

- (14) Chandrasiri, K. W. D. K.; Nguyen, C. C.; Parimalam, B. S.; Jurng, S.; Lucht, B. L. Citric Acid Based Pre-SEI for Improvement of Silicon Electrodes in Lithium Ion Batteries. **2018**, *165* (10), 1991–1996. <https://doi.org/10.1149/2.0161810jes>.
- (15) He, J.; Zhong, H.; Wang, J.; Zhang, L. Investigation on Xanthan Gum as Novel Water Soluble Binder for LiFePO₄ Cathode in Lithium-Ion Batteries. *J. Alloys Compd.* **2017**, *714*, 409–418. <https://doi.org/10.1016/j.jallcom.2017.04.238>.
- (16) Vieira, D.; Loef, N.; Hekmatfar, M.; Moretti, A.; Kim, G.; Passerini, S. Electrochimica Acta Evaluation of Guar Gum-Based Biopolymers as Binders for Lithium-Ion Batteries Electrodes. **2018**, *265*.
<https://doi.org/10.1016/j.electacta.2018.01.083>.
- (17) Chai, L.; Qu, Q.; Zhang, L.; Shen, M.; Zhang, L.; Zheng, H. Electrochimica Acta Chitosan , a New and Environmental Benign Electrode Binder for Use with Graphite Anode in Lithium-Ion Batteries. *Electrochim. Acta* **2013**, *105*, 378–383. <https://doi.org/10.1016/j.electacta.2013.05.009>.
- (18) Yang, L.; Smith, C.; Patrissi, C.; Schumacher, C. R.; Lucht, B. L. Surface Reactions and Performance of Non-Aqueous Electrolytes with Lithium Metal Anodes. *J. Power Sources* **2008**, *185* (2), 1359–1366.
<https://doi.org/10.1016/j.jpowsour.2008.09.037>.
- (19) Aurbach, D.; Levi, M. D.; Levi, E.; Schechter, A. Failure and Stabilization Mechanisms of Graphite Electrodes. *J. Phys. Chem. B* **2002**, *101* (12), 2195–2206. <https://doi.org/10.1021/jp962815t>.

- (20) Levi, M. D.; Aurbach, D. Simultaneous Measurements and Modeling of the Electrochemical Impedance and the Cyclic Voltammetric Characteristics of Graphite Electrodes Doped with Lithium. *J. Phys. Chem. B* **2002**, *101* (23), 4630–4640. <https://doi.org/10.1021/jp9701909>.
- (21) Yu, Y.; Zhang, Y.; Maglia, F.; Karayaylali, P.; Giordano, L.; Lund, I.; Tatara, R.; Jung, R.; Shao-Horn, Y.; Schmidt, J. P. The Effect of Electrode-Electrolyte Interface on the Electrochemical Impedance Spectra for Positive Electrode in Li-Ion Battery. *J. Electrochem. Soc.* **2018**, *166* (3), A5090–A5098. <https://doi.org/10.1149/2.0121903jes>.
- (22) Ravizza, E.; Spadoni, S.; Piagge, R.; Comite, P.; Wiemer, C. XPS Composition Study of Stacked Si Oxide / Si Nitride / Si Oxide Nano-Layers †. **2012**, No. February, 1209–1213. <https://doi.org/10.1002/sia.4943>.
- (23) Akazawa, M.; Hasegawa, H. Instructions for Use Formation of Ultrathin SiN_x / Si Interface Control Double Layer on „ 001 ... and „ 111 ... GaAs Surfaces for Ex Situ Deposition of High- k Dielectrics. <https://doi.org/10.1116/1.2750344>.
- (24) Zhang, P.; Tan, D.; Zhang, X.; Xu, J.; Li, W.; Zhang, P. Observation of “ Fast ” and “ Slow ” Decay Processes in Oxygen-Doped Hydrogenated Amorphous Silicon Nitride Thin Films. **2015**, *5* (1), 22–28. <https://doi.org/10.1364/OME.5.000022>.
- (25) Zhang, L.; Liu, Y.; Key, B.; Trask, S. E.; Yang, Z.; Lu, W. Silicon Nanoparticles : Stability in Aqueous Slurries and the Optimization of the Oxide Layer Thickness for Optimal Electrochemical Performance. **2017**. <https://doi.org/10.1021/acsami.7b09149>.

- (26) Papp, J. K.; Forster, J. D.; Burke, C. M.; Kim, H. W.; Luntz, A. C.; Shelby, R. M.; Urban, J. J.; McCloskey, B. D. Poly(Vinylidene Fluoride) (PVDF) Binder Degradation in Li–O₂ Batteries: A Consideration for the Characterization of Lithium Superoxide. *J. Phys. Chem. Lett.* **2017**, 8 (6), 1169–1174.
<https://doi.org/10.1021/acs.jpcllett.7b00040>.
- (27) Nguyen, C. C.; Yoon, T.; Seo, D. M.; Guduru, P.; Lucht, B. L. Systematic Investigation of Binders for Silicon Anodes: Interactions of Binder with Silicon Particles and Electrolytes and Effects of Binders on Solid Electrolyte Interphase Formation. *ACS Appl. Mater. Interfaces* **2016**, 8 (19), 12211–12220.
<https://doi.org/10.1021/acsami.6b03357>.
- (28) Veith, G. M.; Adamczyk, L. A.; Guo, B.; Brown, S. S.; Dai, S.; Dudney, N. J. Electrochemical and Solid-State Lithiation of Graphitic C₃N₄. **2013**, No. February.
- (29) Burgain, J.; Petit, J.; Burgain, J.; Petit, J.; Scher, J.; Rasch, R.; Bhandari, B.; Gaiani, C. Surface Chemistry and Microscopy of Food Powders Progress in Surface Science Review Article Surface Chemistry and Microscopy of Food Powders. *Prog. Surf. Sci.* **2017**, No. August.
<https://doi.org/10.1016/j.progsurf.2017.07.002>.
- (30) Sun, N.; Liang, Y.; Yu, B.; Tan, C.; Cui, B. Food Hydrocolloids Interaction of Starch and Casein. *Food Hydrocoll.* **2016**, 60, 572–579.
<https://doi.org/10.1016/j.foodhyd.2016.04.029>.
- (31) Horne, D. S. *Casein Micelle Structure and Stability*, Second Edi.; Elsevier Inc., 2014. <https://doi.org/10.1016/B978-0-12-405171-3/00006-4>.

- (32) Horne, D. S. Casein Structure , Self-Assembly and Gelation. **2002**, 7, 456–461.
- (33) Holt, C.; Carver, J.; C, D. Invited Review : Caseins and the Casein Micelle :
Their Biological Functions , Structures , and Behavior in Foods 1. *J. Dairy Sci.*
2013, 96 (10), 6127–6146. <https://doi.org/10.3168/jds.2013-6831>.

5.7. List of Figures

Figure 1. Structure of Casein

Figure 2. Images of the different electrodes used. a) Si-Casein excess water, b) Si-Casein, c) Si-Casein-PVDF, d) Si-PVDF

Figure 3. Cycling Performance of Half Cells a) Specific Capacity, b) Coulombic Efficiency, and Electrochemical Impedance of the c) 1st cycle, d) 50th cycle

Figure 4. Cycling performance of Si/ LCO full cells

Figure 5. X-ray photoelectron Spectroscopy data for the a) Fresh electrodes, b) After 1st Cycle

Figure 6. X-ray photoelectron Spectroscopy N1s depth profile data for Si-Casein excess water fresh electrode

Figure 7. FTIR- ATR spectra of a) Fresh, b) After 1 cycle, electrodes

Figure 8. SEM images of fresh electrodes a) Si- Casein, b) Si- Casein excess water, c) Si-Casein PVDF and d) Si-PVDF

Figure 9. SEM images of electrodes after 1 cycle a) Si- Casein, b) Si- Casein excess water, c) Si-Casein PVDF and d) Si-PVDF

Figure 10. SEM -EDS elemental concentration of Si-Casein excess water electrodes a) fresh, and b) after 1cycle

5.8. Figures

Figure 1. Structure of Casein

Figure 2. Images of the different electrodes used. a) Si-Casein excess water, b) Si-Casein, c) Si-Casein-PVDF, d) Si-PVDF

Figure 3. Cycling Performance of Half Cells a) Specific Capacity, b) Coulombic Efficiency, and Electrochemical Impedance of the c) 1st cycle, d) 50th cycle e) An equivalent circuit diagram for a typical Nyquist plot for Lithium /Silicon half cells.

Figure 4. Cycling performance of Si/ LCO full cells

Figure 5. X-ray photoelectron Spectroscopy data for the a) Fresh electrodes, b) After 1st Cycle

Figure 6. X-ray photoelectron Spectroscopy N1s depth profile data for Si-Casein excess water fresh electrode

Fresh Electrodes

1st Cycle

Figure 7. FTIR- ATR spectra of a) Fresh, b) After 1 cycle, electrodes

Figure 8. SEM images of fresh electrodes a) Si- Casein, b) Si- Casein excess water, c) Si-Casein PVDF and d) Si-PVDF

Figure 9. SEM images of electrodes after 1 cycle a) Si- Casein, b) Si- Casein excess water, c) Si-Casein PVDF and d) Si-PVDF

Figure 10. SEM -EDS elemental concentration of Si-Casein excess water electrodes a) fresh, and b) after 1cycle

APPENDICES

Methods and Procedures

Research Materials

Electrodes and separators required for the study which includes graphite, lithium chips, $\text{Li}(\text{NiCoMn})\text{O}_2$ (Ni: Co: Mn = 1:1:1 and 5:2:3), LiFePO_4 , LiCoO_2 , celgard-polyolefin and glass fiber separators were purchased from MTI corp. or BASF. The powders required for slurry coating were purchased from Sigma, Fischer Scientific, Timcal. All electrodes and separators were dried in a vacuum oven for moisture control. Battery grade electrolyte solutions were used as provided from BASF. High purity metal acetate additives, ICP-MS standards and solvents were purchased from Sigma. Cell parts required for 2032 type cell construction were purchased from MTI Corp. Solvents that do not meet moisture requirements as received were dried in schlenk lines or vacuum ovens before use.

Metal cell parts, glassware and plastic vials, plastic spatulas and pipette were washed with DI water and acetone and dried overnight in a vacuum oven before being introduced into the argon or nitrogen filled glove boxes. All the work required for the projects were carried out in a nitrogen or argon filled glovebox due to air and moisture sensitivity of the materials used in cell preparation.

Electrode Coating Procedures and Equipment

Mortar and pestle as well as an Ultra turax tube dispenser were used for electrode slurry preparation. A doctor blade coupled with an MSK-AFA-iii Automatic thin film coater from MTI corp. was used for electrode laminate preparation. Depending on the

type of material used, and the particle size the methods used in slurry preparation differ. Calendaring of electrodes were carried out using MSK-HRP MR100DC high precision rolling press from MTI.

Cell Construction, Cycling, and Deconstruction

Coin cells type 2032 were constructed in an argon glove box to avoid exposure to air and moisture. Cells contain an exoskeleton of a can and a cap with a gasket to help create an air tight seal. Half cells consist of an electrode that needs to be analyzed with a lithium counter electrode and full cells will consist of graphite or silicon electrode as the negative electrode and lithium metal oxide electrode as the positive electrode. Two polyolefin discs each 15mm and 19mm, or two 19mm with a 16mm or 17mm glass fiber disc sandwiched between them were used as the separator. Each cell consists of exactly 100 μL of the electrolyte solution. The separators were sandwiched between the electrodes and the cell are sealed using an MTI crimper. Cell construction is subject to change based on the needs of the experiment but doesn't change drastically.

All cells were cycled on a battery cycler, at a given current rate based on the study conducted, and will undergo a charge, taper, a rest, a discharge, a rest, and will repeat as many times as necessary. The current rates are calculated in accordance with the theoretical capacity of the limiting electrode. If the capacity of the limiting electrode is X mAh, 1 C will represent X mA. Cells are cycled at different rates, and at different voltage ranges depending on what is needed for the experiment.

Cells were deconstructed in an argon filled glove box to isolate the anode and cathode for surface analysis as needed.

Electrode Preparation for Surface Analysis

All electrodes that will be used in surface analysis will be washed three times with dimethyl carbonate (DMC) or the electrolyte solvent mix without the salts and additives and dried overnight in an argon filled glove box antechamber. These samples are extremely air sensitive and thereby will be transferred to instrument used for analysis using Argon filled vials or vacuum sealed holders.

Instrumentation and Equipment

Battery Cyclers

Cell cycling is carried out in Arbin BT2000 battery cyclers coupled with temperature-controlled ovens.

Electrochemical Impedance Spectroscopy (EIS)

Princeton and Biologic VSP instruments were used for electrochemical impedance spectroscopic studies. This information will provide details about the cell impedance at various stages of the SEI formation and cell cycling. This instrument have also been used for cyclic voltammetry measurements which can be used to understand voltage ranges and reduction potentials.

Argon and Nitrogen Glove Boxes

Since LIB are sensitive to moisture, and oxygen even at very low levels, and argon glove box is needed to build and disassemble cells. The moisture content of the glove

box should be kept below 0.1 ppm. In addition to cell building, the glove boxes are used for other moisture and air sensitive experiments such as electrolyte additive synthesis, electrolyte degradation studies and electrode slurry preparation.

Inductive Coupled Plasma Mass Spectrometry (ICP-MS)

ICP- MS analysis of the digested cycled electrodes was conducted using iCAP Q ICP- MS in Inbre Laboratory, Department of Pharmacy. ICP-MS is a very sensitive technique that can be used to quantify trace amounts of metals on the SEI. When metal containing additives are used, it is important to analyze the SEI to verify the presence of the added metal.

Scanning Electron Microscope (SEM)

SEM Joel 5900, was used to characterize the surface morphology, of the electrode and the solid electrolyte interphase at different stat of charge and cycling conditions. EDX is used to understand the elemental distribution on the SEI.

Transmission Electron Microscopy (TEM)

TEM imaging was conducted using a JEOL JEM-2100F TEM (Perbody, MA). Is used to characterize the solid electrolyte interphase thickness.

X-ray Photoelectron Spectroscopy (XPS)

XPS, Fisher Thermo Scientific K-Alpha using Al-K α radiation source ($h\nu = 1486$ eV), was used. XPS help reveal bonding information on the surface of the electrodes, giving insight on the functional groups and oxidation states of the SEI components. It

can also be used for depth profiling of the electrode where the surface is etched with argon to analyze the chemical composition and oxidation states at deeper levels. It can also be used for area mapping of elements on the electrode surface.

Fourier Transform Infrared Spectroscopy (FTIR)

Brüker Tensor 27 FTIR with Attenuated Total Reflectance (ATR), and Diffuse reflectance accessories are used for surface analysis. The ATR accessory is equipped with germanium and diamond crystals. The instrument is stored in a nitrogen filled glove box to avoid any contamination to the electrodes during the analysis. FTIR can give information about the functional groups on the surface of the electrodes to help analyze the SEI

Thermo Gravimetric Analysis (TGA)

The TGA (TA Instruments Q5000) was used with nitrogen purge gas to quantify the extent of surface modification. Platinum pans were used for the analysis

Vacuum and Convection ovens

Fisher Scientific Isotemp vacuum oven-282A was used for drying cell parts, vials and powders. Jeio Tech TC-ME wide temperature chamber was used to carry out analysis at negative temperatures and higher temperatures. Fisher Scientific Isotemp incubators were used to maintain temperatures for cell cycling from 10 to 60°C. Thermo Scientific Precision convection ovens are used for all other drying purposes.

Data Analysis Software

Cycling, electrochemical impedance and cyclic voltammetry data were analyzed using MS Office Excel, EC lab and Origin lab. FTIR and XPS data were characterized using OPUS, Thermo Advantage and XPS Peak Fit software respectively. NMR data were processed using Mestre Nova. Chem Draw were used for drawing chemical structures.