

Development of Carbon-Based Materials for Improved Sodium-Ion Battery Anodes

by

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Author's declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contribution included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contribution

Section 3 is adapted from a coauthored publication (*Improved Performance of Graphene-Based Sodium-Ion Battery Anodes using Low Surface Area, Low Temperature Reduced Graphene Oxide*) that has been submitted to Carbon (submission ID: CARBON-D-25-01091). This research was done as part of a collaboration with the University of Duisburg-Essen (UDE) and includes contributions from the following researchers (co-authors on the publication): Sarah Jankhani, Lars Grebener, Doris Segets, Hartmut Wiggers, and Michael A. Pope.

I am the first author on this publication and responsible for all experiment planning, methodology, data collection and analysis, and draft writing and editing. Dr. Michael Pope assisted in supervision, experiment planning, and reviewing and editing the manuscript. Sarah Jankhani assisted in conducting the initial experiments on the spray drying of graphene oxide to determine the optimal parameters for a low surface area material. Lars Grebener assisted with reviewing and editing the manuscript. Dr. Doris Segets and Dr. Hartmur Wiggers assisted in supervision and reviewing and editing the manuscript.

Abstract

Sodium-ion batteries (SIBs) are an important future technology for large-scale grid energy storage due to the abundance and lower cost of sodium compared to lithium. However, there are many challenges that continue to hamper their commercial development, including sluggish reaction kinetics, large volume expansions during cycling, and unstable solid-electrolyte interface (SEI) formation. Additionally, more work needs to be done to understand the storage mechanisms of sodium ions in anode materials and to understand what material properties are important for high performance. This thesis focuses on two areas: the development of a new anode material made of red phosphorus nanoparticles (RPNPs) wrapped in reduced graphene oxide (rGO) sheets and an in-depth investigation into the impact of rGO material characteristics on its performance as a SIB anode.

In the first section, the synthesis of an rGO@RPNP composite through a scalable spray drying process provides increased performance when compared to the individual components or when the individual components are simply mixed together. This proof of concept is the starting point for future work on increasing red phosphorus loading within the core-shell structures, improving the reduction process to maximize the conductivity of the composite, and investigating methods to improve the initial coulombic efficiency (ICE) through optimization of material properties.

The second section attempts to decouple the effects of rGO chemistry and oxygen content from its surface area to understand the effect of the material characteristics on its electrochemical performance. It is found that a non-exfoliated sample slowly reduced to a low temperature of 400 °C provides the best performance in terms of desodiation capacity (216 mAh g⁻¹ at 100 mA g⁻¹), and stability (85% retention over 200 cycles) while reducing the irreversible capacity loss by two to threefold compared to previous literature.

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Dedication

This thesis is dedicated to Maddy, who is my guiding light through it all.

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List of Abbreviations

BET	Brunauer, Emmett, and Teller
CE	Coulombic efficiency
CNCs	Carbon nanocages
CNTs	Carbon nanotubes
CTAB	Hexadecetyltrimethylammonium bromide
DLS	Dynamic light scattering
EDX	Energy-dispersive X-ray spectroscopy
FWHM	Full-width half-max
GC	Galvanostatic cycling
GO	Graphene oxide
ICE	Initial coulombic efficiency
LIBs	Lithium-ion batteries
N/A	Not applicable
OCV	Open-circuit voltage
PDI	Polydispersity index
rGO	Reduced graphene oxide
RP	Red phosphorus
RPNPs	Red phosphorus nanoparticles
SEI	Solid-electrolyte interface
SEM	Scanning electron microscopy
SIBs	Sodium-ion batteries
SSA	Specific surface area
TEM	Transmission electron microscopy
XRD	X-ray diffraction

1 Introduction

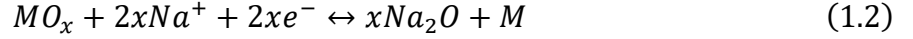
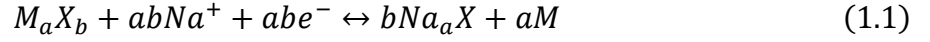
Sodium ion batteries (SIBs) are often presented as next-generation energy storage systems due to their reaction mechanisms similar to lithium-ion batteries (LIBs) and low costs.¹ Sodium is more evenly distributed in the Earth's crust compared to the highly localized lithium. It also benefits from more environmentally benign processing and is inexpensive compared to lithium, whose price will only rise along with demand.²

The cathode (positive electrode) of an SIB is commonly made of a layered sodium transition-metal oxide, Prussian blue analogues, or polyanions.³ Materials for the anode (negative electrode) can benefit from different sodium ion storage mechanisms and include intercalation into hard and soft carbons, conversion reactions with oxides and sulfides, and alloying reactions with metals or metalloids.¹ As SIB technology continues to grow, there is a need for research into new anode materials to allow it to reach its full potential. SIB anodes are generally broken up into the following categories: alloy-type, conversion-type, and intercalation-type anodes.

Alloy-based anodes use materials such as tin, antimony, germanium, silicon, and phosphorus along with their corresponding sulfides, selenides, and phosphides.⁴ These materials have high specific capacities and Earth abundance, which makes them an attractive alternative to other of anode materials, however, they suffer from large volume expansions during cycling. This leads to the pulverization of the electrode and poor cycling stability.⁴ An example of an alloy-based anode is one made of a carbon-red phosphorus (RP) composite; this system will be explored in greater detail in future sections of this thesis.

Conversion-type anodes are based on a redox reaction occurring between two materials to store the sodium ions and are not dependent on the size or lattice structure of the cation.⁵ However, as is common for many SIB anodes, conversion-type anodes still suffer from poor initial coulombic

efficiencies (ICE) and cycling stability.¹ These anodes undergo multi-step processes that deliver high capacities as the oxides or sulfides undergoing the conversion process can then undergo an alloying reaction after being released through the conversion reaction.¹ The general reaction mechanism for the conversion reaction is show below.⁵



Equation 1.1 describes the conversion reaction where M is an inactive transition metal and X is an anion. Equation 1.2 describes the subsequent alloying reaction that can occur with an oxide if M is an electrochemically active metal.⁵

Intercalation-type anodes are layered structures made of carbon or titanium-based materials.⁶ Those made of carbon materials can be further divided into two main categories: ordered carbons and disordered carbons. Ordered carbons include graphite, 2D graphene, and 1D carbon nanotubes. Disordered or amorphous carbons include hard carbon and soft carbons and are often used due to their increased lattice defects, disorder, and interlayer spacing – all of which contribute to an increased ability to store sodium ions. Hard carbon is non-graphitizable as the carbon layers are strongly bonded and are unable to be rearranged even at high temperatures. Soft carbons on the other hand, have weak crosslinking and the carbon layers are mobile through heat treatment.⁷ The major challenges with these sorts of materials include low-rate capability, slow reaction kinetics, and low ICEs.⁸

This thesis focuses on the use of disordered and amorphous carbons, and their important role in the future of SIBs. Hard carbons have been an ideal anode for SIBs and have shown promise, though they have a low average sodiation potential which can lead to the formation of sodium dendrites at higher current densities and short the batteries. They also suffer from poor electronic

and ionic conductivity.⁸ Soft carbon addresses many of these issues with a semi-graphitic structure and higher orders of crystallinity and conductivity. However, though it has been studied extensively as a material for LIBs, its narrow interlayer distances have hampered its use in SIBs.⁸ In order to improve the amount of sodium storage possible in soft carbons, many strategies have been developed, including low-temperature carbonization, heteroatom doping, and microstructure adjustments.⁹ All of these aim to control the defects present in the carbon materials and limit the degree of graphitization to preserve the large interlayer spacing needed to properly intercalate sodium ions.

The overall objective of this thesis is to develop new and improved anode materials for SIBs and to more fully understand how their material properties affect their electrochemical performance. As SIBs are a growing technology, this work will contribute to the improvement of carbon-based materials and how they can be advanced to a commercial level. This is explored in depth through (1) the development of a reduced graphene oxide (rGO) and red phosphorus nanoparticle (RPNPs) composite (rGO@RPNP) and (2) an investigation into the impact of rGO chemistry and surface area on its electrochemical performance.

1.1 Background

1.1.1 Working principles of a battery

Batteries are electrochemical energy storage devices. They are composed of two electrodes, generally made of a film coated onto a metal current collector (aluminum or copper) separated by a conductive electrolyte and a porous separator to electrically isolate the electrodes. A schematic of the operation of a SIB is shown in Figure 1. During cell charging, electrons and sodium ions are released from the cathode. The electrons travel through an external circuit while the sodium ions travel through the electrolyte and separator to be stored in the anode. During discharging, the

opposite happens – sodium ions are released from the anode and move through the electrolyte and separator to be stored in the cathode.

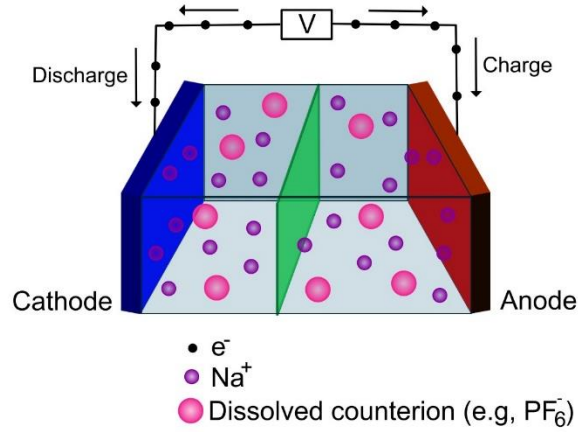


Figure 1: Schematic of SIB operation

A full cell electrochemical reaction consists of an independent half cell reaction occurring at each electrode, where these half cell reactions describe the actual chemical changes taking place at the electrode. The reactions occurring are driven by a difference in electric potential between the positive and negative electrode, where the redox reaction occurring at the negative electrode (anode during discharging) will have a more negative redox potential than the redox reaction at the positive electrode (cathode during discharging).

The cell voltage of a full cell is equal to the difference between the electrode potentials at the anode and cathode:¹⁰

$$E_{cell} = E_{cathode} - E_{anode} \quad (1.3)$$

The reduction potential at each electrode can be calculated through the Nernst equation using the standard reduction potential of the electrode and the activities of the chemical species involved:¹⁰

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{a_O^{v_O}}{a_R^{v_R}} \right) \quad (1.4)$$

where E^0 is the standard reduction potential of the electrode, R is the gas constant, T is the temperature, z is the number of electrons transferred per unit of the half cell reaction, F is Faraday's constant, a_O and a_R are the activities of the oxidizing and reducing species, and ν_O and ν_R are their stoichiometric coefficients. As the activity coefficients are often unknown, the formal potential can be substituted into Equation 1.4. The formal potential is the measured potential when the oxidizing and reducing species are present in a concentration ratio equal to 1 ($C_O^{\nu_O}/C_R^{\nu_R} = 1$) and any other cell parameters are specified (e.g., pH):¹⁰

$$E^{0'} = E^0 + \frac{RT}{nF} \ln \frac{\gamma_O}{\gamma_R} \quad (1.5)$$

Substituting Equation 1.5 into Equation 1.4 allows Equation 1.4 to be expressed in terms of the concentration of the chemical species instead of their activity coefficients, though the formal potential still depends on concentration through the activity coefficients:¹⁰

$$E = E^{0'} + \frac{RT}{nF} \ln \left(\frac{C_O}{C_R} \right) \quad (1.6)$$

These equations for cell potentials are valid when no current flows through the system. When current is flowing through the system, there are additional resistances and overpotentials to consider, such as the overpotential of ion transport across the solid electrolyte interface (SEI).

Cell potentials also play an important role in understanding the kinetics of the electrode reactions. The interfacial potential difference can be used to control the reactivity of the system, so it is important to understand how the rate constants of the anodic and cathodic reactions depend on potential. The potential dependence of the net system current can be expressed through the Butler-Volmer model:¹⁰

$$i = F A k^0 \left[C_O(0, t) e^{-\alpha f(E - E^{0'})} - C_R(0, t) e^{(1-\alpha)f(E - E^{0'})} \right] \quad (1.7)$$

where i , is the net current of the system, F is Faraday's constant, A is a pre-exponential factor, k^o is the standard rate constant, C_O and C_R are the surface concentration of the oxidizing and reducing species, α is the transfer coefficient, f is Faraday's constant divided by the gas constant multiplied by temperature, E is the cell potential, and $E^{0'}$ is the standard formal potential. The transfer coefficient is a measure of the symmetry of the energy barrier and the standard rate constant determines how quickly the system will achieve equilibrium (higher values means this will happen faster). At the equilibrium potential, the reactions rate of the anodic and cathodic reactions will be equal. Increasing the potential to more positive values will raise the barrier for reduction and increase the oxidation reaction rate, while decreasing the potential to a more negative value will do the opposite. When mass transfer effects are negligible, the surface concentrations are approximately equal to the bulk concentrations and Equation 1.7 simplifies to the Butler-Volmer equation (Equation 1.8), which relates the system overpotentials to the net current:¹⁰

$$i = F A k^o C_O^{*1-\alpha} C_R^{*\alpha} [e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}] \quad (1.8)$$

where η is the overpotential. Equation 1.8 can be used to assess how much overpotential is needed to induce current flow through the system.

When a battery is cycling, the two electrodes are connected to an external circuit through which electrons flow. The amount of charge flowing through this circuit is determined by the energy storage capacity of the active material and how much charge can be stored within. The capacity of an electrode is expressed in units of mAh (where 1 mAh = 3.6 C) and normalized by the mass of the active material. The maximum theoretical capacity of an electrode can be calculated using Faraday's Law:¹⁰

$$C_{theor.} = \frac{nF}{M} \quad (1.9)$$

where n is the number of electrons transferred per unit of the half cell reaction, F is Faraday's constant, and M is the molar mass of the active material. The theoretical capacity of a full cell can be determined from the individual capacities of the anode and cathode by modelling the electrodes as two capacitors in series with equivalent absolute capacities:¹⁰

$$C = \frac{1}{\frac{1}{C_{cathode}} + \frac{1}{C_{anode}}} \quad (1.10)$$

1.1.2 Metrics for assessing battery performance

One of the most useful metrics for assessing battery performance is the capacity, or the amount of charge stored in the electrode, especially compared to its theoretical capacity as expressed in Equation 1.9 (or Equation 1.10 for a full cell). The capacity can be normalized by the active material mass in the electrode to get the specific capacity (in units of mAh g⁻¹) and further multiplied by the areal mass loading of the active material to get the specific areal capacity (in units of mAh cm⁻²).

The electrode capacity can be broken down into reversible capacity and irreversible capacity. In a half cell, the reversible capacity is defined as the amount of charge stored during the sodiation process that is then released during the desodiation process (i.e., its storage was reversible). The difference between the sodiation and desodiation capacities is the irreversible capacity - capacity that is stored during sodiation and not released during desodiation. The capacities reported in the work are the desodiation capacities as these values represent the reversible capacity and are a better measure of the true performance of the electrode. As the counter-electrode in the half cells is sodium metal, there is an excess of sodium ions available for the sodiation process, which would not be the case in a full cell.

During the first cycle of a half cell, the capacity of the sodiation process is much larger than the capacity of the desodiation process due mainly to the formation of the SEI, though other irreversible side reactions could also play a role. The percentage of reversible capacity is the initial coulombic efficiency (ICE) and is an important metric for the translation from half cells to full cells. If the first cycle eats up 50% of the sodium ions originally available, it can be difficult to achieve high performance in later cycles.

$$ICE = \frac{C_{Desodiation, cycle\ 1}}{C_{Sodiation, cycle\ 1}} * 100\% \quad (1.11)$$

The coulombic efficiency (CE) for all the other cycles can be calculated in the same way as the ICE in Equation 1.10. It is important that the CE is as close to 100% as possible to extend the lifetime of the cell and minimize the capacity loss and sodium ion consumption throughout cycling.

In addition to tracking the CE of the cell over its lifetime, the cumulative irreversible capacity is an important metric. This metric tracks the sum of the irreversible capacity over the course of the cell lifetime. While the bulk of the cumulative irreversible capacity is seen in the first cycle, high irreversible capacities in further cycles can be an indication of continued SEI formation or SEI instability and can be used to compare different electrode materials. Once the battery stabilizes during cycling and the CE begins to approach 100%, the cumulative irreversible capacity should also stabilize, something that should happen as soon as possible for the best performance.

The capacity and CE of cells are greatly impacted by the applied current rates during the charge and discharge (or sodiation and desodiation) processes. High performance at high rates is important for commercialization and real-life applications. These rates are expressed in terms of current densities (in units of $A\ g^{-1}$) based on the electrode mass or a C rate based on the theoretical capacity of the cell. A C rate of 1C means that a current is applied such that the cell charges or discharges

in 1 hour. A C rate of 10C means that the cell will charge or discharge in one tenth of an hour, or six minutes.

1.1.3 Challenges of SIBs

Although the research into SIBs and LIBs started around the same time, the commercialization of SIBs has been much slower because of challenges including sluggish reaction kinetics and ion diffusion, the formation of sodium dendrites through uneven sodium plating, poor cycling stability, and low ICEs.^{3,11–13} The larger atomic radius of sodium ions in comparison to lithium ions also affects many aspects of battery performance including phase stability, ion transport properties, and volume swelling during cycling, and prevents the use of current commercial LIB materials, such as graphite, as an SIB anode.³ Graphitic materials generally have an interlayer spacing around 0.335 nm, while to allow for proper intercalation of sodium ions into a layered material, the interlayer spacing must be at least 0.37 nm, making graphite unsuitable for use in SIBs.¹⁴

Low ICE has been a major challenge in the development of many new anode materials. There are four main categories that limit the ICE of SIBs: irreversible decomposition of electrolyte, poor reversibility of sodiation/desodiation of the anode, ‘trap’ effects of defects and other functional groups, and other side reactions including the effect of surface area and porosity.¹¹ SEI formation is crucial to the cycling stability of a battery and has a great impact on the ICE of a cell.¹³ SEI formation consumes large amounts of sodium ions that cannot be released in the next charging cycle. If the SEI formed is not structurally sound and of even thickness, it can break apart during the cycling process and electrically isolate active material, lowering the CE and capacity in future cycles. Defects, such as heteroatoms or vacancies, can have a ‘trap’ effect, where the binding energy of these active sites with the sodium ions is too high and they are unable to be released during the next charging cycle.¹⁵

In alloy-type anodes, including those containing RP, one of the biggest challenges is the volume change brought about by the stress produced in the multi-electron transfer reaction, which can be greater than 300%.^{4,16} Undergoing this volume change over many cycles leads to the pulverization of the RP, reducing contact with the current collector and damaging the integrity of the electrode and reducing the lifetime of the cell. As the RP is being pulverized, it is also continuously exposing fresh surfaces onto which the SEI is then formed. This continuous SEI formation consumes many sodium ions, reducing the CE and cycle life of the cell. Having the thickness of the SEI layer continuously increase also increases the interface impedance and slows the transport rate of sodium ions through the SEI.¹⁶ Studies have shown that the critical fracture diameter (the diameter at which pulverization may occur) of RP particles is at least 200 nm,¹⁷ therefore the average diameter of the RPNPs is desired to be less than 200 nm, and ideally closer to 100 nm to prevent pulverization. Material designs should also incorporate void space for the volume change to minimize the stress exerted on the electrode.

1.2 Literature Review

1.2.1 Current standard of SIB anodes

The current standard for SIB anodes are those made of hard carbon due to their high surface area and potentially low cost.^{18,19} However, hard carbon suffers from low initial coulombic efficiencies (ICEs) of approximately 80% and poor rate performance.^{15,18,20} The storage mechanism of sodium ions in hard carbon is also debated, limiting its design and optimization.^{18,20} Due to the more complex structure of hard carbon compared to the layered graphite structure, many different mechanisms have been proposed: intercalation-pore filling, adsorption-intercalation-pore filling, adsorption-insertion, and multistage mechanisms.^{18,19} Hard carbon can be obtained from a number of different sources such as biomass-derived hard carbon, polymer-

based hard carbon, and soft carbon-based hard carbon, all with their own advantages and disadvantages.¹⁸

Many groups are working on the improvement of hard carbon materials, such as Liu et al., who developed a presodiation technique that increased the ICE of a full-cell with a hard carbon anode to 95% and the half cell ICE to 100%.²¹ Though this is a major improvement on current hard carbon ICEs, the sodiation and desodiation capacities exhibited in the first cycle are lower than those of a pristine hard carbon anode. The open circuit voltage (OCV) is also decreased from 2.83 V to 0.51 V. Due to the presodiation process, it is more accurate to say that this high CE is the CE of the 2nd cycle, although it shows promise for the general development of SIBs. One of the advantages of hard carbon is that it can be produced from environmentally friendly materials. This is showcased in the development of a hard carbon material made through the carbonization of natural potato starch at 1400 °C. This material was able to achieve an initial capacity of 303.5 mAh g⁻¹ and an ICE of 90.6% at a current density of 0.2 A g⁻¹.²² However, there are still many processing disadvantages when it comes to the production of hard carbon. They are often produced at high temperatures between 1000 °C and 2000 °C, which can be very energy intensive.²⁰ The structural properties of hard carbon are also difficult to control or alter after the high temperature step, presenting consistency issues with pore size and defect formation.²³

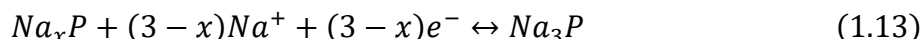
On the commercial side, Selian Energy currently has a SIB available with a hard carbon anode on an aluminum current collector and a cobalt-free layered sodium transition metal oxide cathode. Although these SIB anodes have thicker coatings than commercial LIB options, they showed a specific energy of over 120 Wh kg⁻¹ which is comparable to commercial lithium iron phosphate-type LIBs.²⁴ This is promising, however, a SIB cell with the same coating thickness as a graphite

anode in an LIB had a lower specific energy, underlining the need for further optimization of these technologies as well as the exploration of new technologies and battery chemistries.

1.2.2 Red phosphorus as an anode material

One important alloy material for use in SIB anodes is the red phosphorus allotrope. It has the highest theoretical capacities of all potential alloy materials at 2,596 mAh g⁻¹ and a low redox potential of only 0.4 V vs Na/Na⁺.²⁵ This is lower than its lithiation potential of 0.7 V vs Li/Li⁺, making it a more promising anode material for SIBs than LIBs.²⁶ It is also the most suitable of the phosphorus allotropes as white phosphorus is incredibly flammable and will self-ignite in air and black phosphorus remains an expensive material.²⁷ Unfortunately, red phosphorus (RP) has a very low electrical conductivity (~10⁻¹⁴ S cm⁻¹) and suffers from volume changes up to 300% during cycling.²⁵

The alloying reaction to store sodium ions in RP-based anodes is a two-step reaction process that proceeds through an intermediate phase before forming Na₃P as the final alloy.²⁶ The reaction proceeds as shown below in Equation 1.12 and 1.13.



Many works have combined red phosphorus with other more conductive materials such as carbon to increase the conductivity and lead to the development of fast-charging materials.²⁸ Carbon can increase the conductivity of the overall material as well as act as a buffer for the volume expansion.²⁷ It has also been shown that using nanosized RP in the range of 100-200 nm can increase its conductivity by a factor of 10¹⁰ S m⁻¹ and showed good cycling performance in LIBs.¹⁷

Currently, the most widely used methods for combining carbon and nano-sized phosphorus are through ball-milling²⁹ and vaporization-condensation conversion.³⁰ Ball-milling provides easy

control over the RP loading in the final composite. However, limited contact between the carbon and RP is an issue as the volume changes cannot be effectively buffered and the conductive pathways between the carbon and RP for fast sodium ion transport are disrupted; the composites also continue to struggle from low cycle stability.^{26,31} Vaporization-condensation techniques have been shown to improve the electrical conductivity of the composite, but the mass loading is uncontrollable and the process involves the conversion to white phosphorus before cooling the system down and initiating the conversion back to red phosphorus, which can be quite dangerous.³¹

One of the first examples of using ball-milling to produce an RP-carbon composite in SIBs is the work of Kim et al.²⁹ They synthesized an amorphous RP-carbon composite that delivered a reversible capacity of 1890 mAh g⁻¹ at a current density of 143 mA g⁻¹ as well as a specific capacity of 1540 mAh g⁻¹ at a current density of 2.86 A g⁻¹. The ICE was 85%. This work opened the door for more exploration into the use of these composites as SIB anodes.

Though RP is more suitable for SIBs, RP-carbon composites are also used as an anode material in LIBs and many of the techniques can be learned from and applied to the use of these materials in SIBs. Li et al. used a vaporization-condensation strategy to load RP into wrinkled carbon spheres.³² The loading was done at 480 °C which produces white phosphorus before the conversion to RP and requires the use of carbon disulfide to wash away any traces. They were able to achieve a specific capacity of 690.7 mAh g⁻¹ at 250 mA g⁻¹ after 200 cycles, but this highlights the need for safer processing techniques that can avoid high temperatures and the conversion to white phosphorus. A spraying method was used by Wang et al. to prepare a sandwich-like hybrid of red phosphorus nanoparticles (RPNPs) and reduced graphene oxide (rGO) nanosheets.³³ The exposed RPNPs provided storage sites for lithium ions while the rGO nanosheets acted as a conductive backbone to ensure fast electron transport and they achieved a reversible capacity of 990 mAh g⁻¹

after 50 cycles. More recently, RP was encapsulated inside the micropores of a carbon matrix up to a RP loading of 65.0 wt%.³⁴ As an anode material, this composite was able to deliver a reversible capacity of 1260 mAh g⁻¹ after 400 cycles at 0.2 A g⁻¹. The structure of the composite was optimized and carbon micropores showed a better performance than mesopores, highlighting the importance of the composite structure when designing high performance anodes.

To optimize the use of RP-carbon composites in SIBs, there needs to be high phosphorus loading, good contact between the carbon and RP, and high electrical conductivity. The structure of the electrode and active material is especially important to attempt and mitigate the large volume expansion during cycling. Liu et al. investigated the use of carbon nanocages (CNCs) as a vessel for encapsulating nanosized RP in SIB anodes.³¹ This is a convenient carbon matrix due to its large surface area, big interior cavities, and high conductivity. They were able to achieve an RP loading of 85.3 wt% and a specific capacity of 1363 mAh g⁻¹ at a current density of 100 mA g⁻¹. The carbon shells were interconnected to form a conductive network, while the interior cavities provided excellent sites for the deposition of RP during the filling process as well as space to accommodate the large volume change. Zhu et al. developed another strategy for mitigating the volume expansion of RP by encapsulating the RP within an rGO aerogel.³⁵ This anode delivered a specific capacity of 619 mAh g⁻¹ at 5.2 A g⁻¹. Both works devoted a lot of effort to the composite structure to improve the anode performance, highlighting the importance of not only the materials used, but how they are arranged. Expanded graphite was also modified with red phosphorus to increase its sodium storage and delivered a reversible specific capacity of 418 mAh g⁻¹ at 100 mA g⁻¹.³⁶ This anode was also tested at low temperatures and achieved a reversible capacity of 228 mAh g⁻¹ at -10 °C, showcasing the potential of this chemistry in cold use cases.

A selection of works using RP-carbon composites as an anode material is summarized in Table 1 (LIBs) and Table 2 (SIBs). The main challenges of volume expansion during cycling and low electrical conductivity remain to be solved through strategies such as buffer materials, carbon composites, or element doping. The ICE of these electrodes is often low due to irreversible reactions between the electrode and electrolyte and remains an active area of research.²⁶ Further improvement can be achieved by designing a stable SEI through the investigation of binders, electrolytes, and other additives. Mitigating the volume expansion of the RP during cycling will also improve the CE as the pulverization of the RP and rupturing/reforming of the SEI with each cycle is detrimental to the CE and capacity retention.

Table 1: Selected works on RP-carbon composites as an anode material in LIBs

Sample	RP loading method	RP loading	ICE	Discharge capacity
RP-wrinkled carbon spheres ³²	Vaporization-condensation	Not given	65.2%	788.2 mAh g ⁻¹ at 250 mA g ⁻¹
Sandwich-like RP-rGO composite ³³	High-pressure-assisted spraying	Not given	72.3%	1580 mAh g ⁻¹ at 50 mA g ⁻¹
RP-zeolite-templated carbon with micropores ³⁴	Vaporization-condensation	65.0 wt%	87.44%	1520 mAh g ⁻¹ at 200 mA g ⁻¹
RP on N-doped carbon bubble-carbon nanotube network ³⁷	Vaporization-condensation	53%	87.5%	1736.3 mAh g ⁻¹ at 100 mA g ⁻¹
RP in porous carbon ³⁸	Vaporization-condensation	~50 wt%	70.4%	1320.2 mAh g ⁻¹ at 260 mA g ⁻¹

Table 2: Selected works on RP-carbon composites as an anode material in SIBs

Sample	RP loading method	RP loading	ICE	Discharge capacity
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Amorphous RP-carbon composite ²⁹	Ball-milling	70 wt%	85%	1890 mAh g ⁻¹ at 143 mA g ⁻¹
RP in carbon nanocages ³¹	Evacuation-filling	85.3 wt%	67.5%	1100 mAh g ⁻¹ at 500 mA g ⁻¹
RP in rGO aerogel ³⁵	Electrostatic interaction	Not given	83.7%	1224 mAh g ⁻¹ at 260 mA g ⁻¹
RP inserted in expanded graphite ³⁶	Vapor deposition	1.89 wt%	56.1%	418 mAh g ⁻¹ at 100 mA g ⁻¹
RP in PVDF-derived carbon ³⁹	Magnetic stirring, high temperature calcination	53.3 wt%	25% *	414.2 mAh g ⁻¹ at 100 mA g ⁻¹
RP in N-doped graphene/CNT aerogel ⁴⁰	Vaporization-condensation	32 wt%	~80%	786 mAh g ⁻¹ at 200 mA g ⁻¹
RP/rGO nanocomposite ⁴¹	Ball-milling	47.6 wt%	83.05%	1495.6 mAh g ⁻¹ at 780 mA g ⁻¹
Nanoporous RP on rGO ⁴²	Redox reaction and boiling process	67.6 wt%	78.5%	2080.2 mAh g _{RP} ⁻¹ at 256 mA g _{RP} ⁻¹
RPNPs in graphene scrolls ⁴³	Quick-freezing and reduction	52.2 wt%	77% *	2355 mAh g ⁻¹ at 250 mA g ⁻¹

*ICE values are estimated from graphs given in the reference

The discharge capacities from Table 1 and Table 2 are plotted below in Figure 2a. Many works show high discharge capacities, highlighting the potential of using these composites in SIB anodes. RP-carbon composites are very effective in SIBs and can perform at similar levels to these composites in LIBs. This motivates the continued research into the use of these materials in SIBs. For the references that reported an electrode mass loading, the areal specific capacity vs areal current density is plotted in Figure 2b. RP-carbon composites in SIBs still perform well at higher areal capacities and current densities and future works should focus on pushing values farther into the top right corner of the plot.

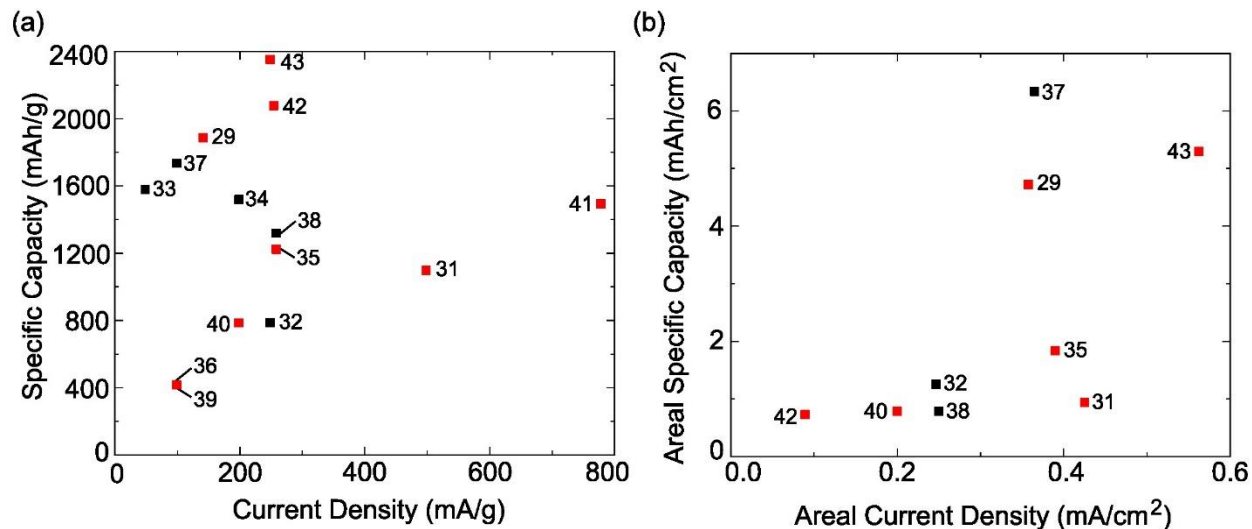


Figure 2: (a) Specific discharge capacity versus current density and (b) areal specific discharge capacity versus areal current density for selected works on RP-carbon composites in LIB (black squares) and SIB (red squares) anodes

1.2.3 Reduced graphene oxide as an anode material

Reduced graphene oxide (rGO) is an amorphous carbon material and can be produced in bulk quantities starting from graphene oxide (GO). GO can be synthesized top-down through a modified Hummer's method⁴⁴ and then reduced through a variety of methods, many of which are scalable. The GO produced through Hummer's method can consist of 30 - 50% oxygen and suffers from low conductivity, making it unsuitable as an anode material.⁴⁵ The reduction process is then needed to remove the oxygen-containing functional groups from the GO and restore the sp^2 conjugation to produce large amounts of graphene-like sheets or flakes.⁴⁶ The reduction of GO can occur through multiple different methods including chemical,⁴⁷ thermal,⁴⁸ electrochemical,^{49–51} and more recently through microwave irradiation.⁵²

Chemical reduction is considered one of the more efficient ways to reduce GO as it operates at low temperatures ($< 100\text{ }^{\circ}\text{C}$) and the final product can have an electrical conductivity approaching that of graphene. It can be done with different reducing agents; common options include hydrazine hydrate, sodium borohydride, ascorbic acid, and sodium dithionite.⁴⁶ These

reactions can either can be done in vapor or liquid phase.⁵³ Studies have shown that high electrical conductivities can be obtained by using ascorbic acid, sodium dithionite, or hydrazine hydrate, however a superior electrochemical performance is achieved by using sodium borohydride.⁴⁶ These results show that optimizing the chemical reduction of rGO is dependent on the end use of the material.

Electrochemical reduction is considered a ‘green’ synthesis as there is no special chemical agent needed. The reduction is caused by the electron exchange between the GO and electrodes. GO can be directly transferred from a suspension on to the anode through the application of an electrical field. The direction of the electrical field can then be switched, and the reduction of the GO film occurs on the cathode at room temperature.⁵⁴ This process is also unique as the type of oxygen functional groups removed can be controlled through the applied potential, however the final product is a film, which may not be suitable for all applications and limits further processing of the material.⁵⁵

Thermal reduction is the most effective at removing intercalated water molecules and oxygen-containing functional groups on the surface; achieving the highest degree of reduction.⁵⁴ Thermal reduction can be achieved in a furnace under an argon or argon/hydrogen atmosphere and the maximum temperatures used range from 700 °C to 1000 °C. In most cases, thermal reduction is accompanied by exfoliation. Rapid autoexothermic heating of the GO and the build-up of decomposition gases such as carbon monoxide, carbon dioxide, and water vapor build pressure between the GO/rGO layers which exceeds the van der Waals attraction.⁵⁶ To avoid the exfoliation, sufficient time must be given for the gas molecules to diffuse out of the interlayer space prior to significant pressure build-up. For example, reduction without exfoliation was achieved in early mechanistic studies by McAllister et al. using a slow heating rate of $< 1\text{ }^{\circ}\text{C min}^{-1}$.⁵⁷ The heating

rate can then be used to tune the surface area of the rGO and either maintain a low surface area, or produce a high surface area material approaching the theoretical surface area of graphene, $2630 \text{ m}^2 \text{ g}^{-1}$.⁵⁷

Microwave reduction has emerged as an alternative to both thermal and chemical reduction, as it eliminates the need for toxic chemical reducers as well as the need for exposing the GO to high temperatures for prolonged periods of time. While the mechanism of microwave heating may be complicated, the microwaves are essentially used to rapidly heat up the GO and remove both oxygen functional groups and defects in the graphene lattice. Currently, the physics of microwave heating are not yet well understood, and it has been difficult to design a continuous process that can produce large yields of high-quality rGO.⁵⁵

Given the wide variety of reduction methods and relative ease of scaling up this process, there are many works investigating the use of rGO as part of an anode for SIBs. Wang et al. were the first researchers to explore the use of thermally exfoliated rGO in SIB anodes.⁵⁸ They were able to show significant sodium ion insertion due to the large interlayer distances and disordered structure. The anode showed a reversible capacity of 173 mAh g^{-1} at a current density of 40 mA g^{-1} and 93.3 mAh g^{-1} at 200 mA g^{-1} after 250 cycles, though the initial coulombic efficiency (ICE) was approximately 18%. Since then, many groups have published studies showing improvements in the rate capability of an rGO-based anode. rGO nanosheets were synthesized by Ali et al. through a microwave reduction procedure and showed an initial reversible capacity of 330 mAh g^{-1} at 50 mA g^{-1} and an ICE of 26%.⁵⁹ Iodine-doped reduced graphene oxide was synthesized through a thermal reduction process and showed a capacity of 275 mAh g^{-1} at 50 mA g^{-1} , although it was still only able to achieve an ICE of approximately 31%.⁶⁰ Through a chemical reduction method, an rGO material was able to achieve a capacity of 192 mAh g^{-1} at 100 mA g^{-1} with an ICE of 17%.⁶¹

Many rGO materials presented in the current studies have a high specific surface area (between 500 and 1000 m² g⁻¹) and this is considered to be a major contributor to the capacity losses during the first cycle (and accompanying low ICEs) as there is more surface area for SEI formation and parasitic reactions with the electrolyte.⁸ Structural properties, such as the surface area, can greatly influence the electrochemical performance of rGO, and as such, it is important to be able to control the morphology and exfoliation of the rGO powder through the synthesis path.⁶²

Spray-drying is used as a technique to manufacture powders in many fields, particularly in the pharmaceutical industry.^{63,64} Many works have shown that the size and morphology of the particles produced can be controlled by adjusting the parameters of the spray-dryer, such as outlet temperature, feed flow rate, and pressure.^{63,65} Shi et al. also investigated the impact of feed concentration and how it influenced the structure and morphology of spray-dried GO and increased its dispersibility.⁶⁶ It was observed that a higher feed concentration led to a more ordered and layered structure with a larger particle size, while a lower feed concentration led to a more crumpled and ‘ball-like’ structure. However, there is no work assessing the impact of these morphological changes on the performance of the material in SIBs. While the work of Verma et al. briefly touches on the impact of thermal reduction (exfoliation versus non-exfoliation) on the storage of sodium ions, their work does not go in depth about the effect of specific surface area at different reduction temperatures or decouple the effects of rGO chemistry versus morphology.⁶²

The rGO chemistry is also important for optimizing its performance. Defects can lead to a ‘trap effect’, however, the doping of carbon materials with heteroatoms such as oxygen has been shown to improve the rate capability and ICE of SIB anodes as the redox reaction between sodium ions and carbonyl groups is rapid and reversible.⁶⁷ Chen et al. synthesized an oxygen-rich carbon anode through pyrolysis and a consecutive hydrothermal reaction achieving an ICE of 81.5% for a

carbon sample with 20.2% oxygen-doping, which is attributed to the increased oxygen functional groups on the surface.⁶⁸ A carbon material doped with 19.33% oxygen was developed by Ning et al. through a stainless-steel ball milling process and was able to achieve a reversible capacity of 353 mAh g⁻¹ at 100 mA g⁻¹ as well as an ICE up to 83.1%.⁶⁹ Both these works have greatly improved the viability of a carbon-based anode for commercial SIBs.

The table below shows a selection of the current research on rGO and related carbon materials in SIB anodes, including two entries for hard carbon works, the current standard for SIB anodes and the best performing sample from Section 3 of this thesis. Most studies looking at rGO through various reduction methods show large surface areas and corresponding low ICEs. Though the rate performance of anodes made with rGO are approaching those made of hard carbon, the ICE continues to lag behind. Further work into these carbon materials should focus on the improvement of this ICE and reduction of irreversible capacity, especially as full cells are developed.

Table 3: Physical properties and electrochemical performance of rGO and related carbon materials in SIB anodes

Sample	Reduction method	Surface area	ICE	Rate capability
rGO400 ^{This work}	Thermal reduction (400 °C)	21.3 m ² g ⁻¹	53.6%	226 mAh g ⁻¹ at 100 mA g ⁻¹
Chemically-presodiated hard carbon ²¹	Pyrolysis (1100 °C)	N/A	~95% (full cell)	301 mAh g ⁻¹ at 30 mA g ⁻¹ (full cell)
Potato-starch based hard carbon microspheres ²²	Carbonization (1400 °C)	2.1 m ² g ⁻¹	90.6%	303.5 mAh g ⁻¹ at 20 mA g ⁻¹
Reduced graphene oxide ⁵⁸	Thermal reduction (750 °C)	330.9 m ² g ⁻¹	17.7% *	174.3 mAh g ⁻¹ at 40 mA g ⁻¹
Crumpled graphene ⁷⁰	Thermal reduction (800 °C) and sintering (2800 °C)	6.4155 m ² g ⁻¹	55% *	247 mAh g ⁻¹ at 50 mA g ⁻¹
Expanded graphite ⁷¹	N/A	5.04 m ² g ⁻¹	30% *	268 mAh g ⁻¹ at 100 mA g ⁻¹

Reduced graphene oxide nanosheets ⁵⁹	Microwave irradiation reduction (1600 W)	743 m ² g ⁻¹	26%	330 mAh g ⁻¹ at 50 mA g ⁻¹
Oxygen-functionalized graphene nanosheets ⁷²	Thermal reduction (700 °C)	567.07 m ² g ⁻¹	51%	603 mAh g ⁻¹ at 50 mA g ⁻¹
Reduced graphene oxide ⁶¹	Chemical reduction (hydrazine, 100 °C)	637 m ² g ⁻¹	17%	192 mAh g ⁻¹ at 100 mA g ⁻¹
Iodine-doped reduced graphene oxide ⁶⁰	Thermal reduction (950 °C)	359.3 m ² g ⁻¹	32% *	275 mAh g ⁻¹ at 50 mA g ⁻¹
Reduced graphene oxide ⁷³	Chemical reduction (tin (II) chloride, RT)	198 m ² g ⁻¹	25%	268 mAh g ⁻¹ at 50 mA g ⁻¹
Expanded graphite ⁷⁴	Thermal reduction (600 °C)	30.22 m ² g ⁻¹	49.53%	284 mAh g ⁻¹ at 20 mA g ⁻¹
Activated crumpled graphene ⁷⁵	Thermal reduction (500 °C) and activation (350 °C)	318 m ² g ⁻¹	38%	280 mAh g ⁻¹ at 40 mA g ⁻¹
Oxygen-rich carbon ⁶⁸	Annealing of potassium citrate (750 °C) and hydrothermal reaction (90 °C)	565 m ² g ⁻¹	66.7% *	447 mAh g ⁻¹ at 200 mA g ⁻¹
Oxygen-rich carbon ⁶⁹	N/A – ball milling	72.9 m ² g ⁻¹	83.1%	353 mAh g ⁻¹ at 100 mA g ⁻¹
Reduced graphene oxide nanosheets ⁷⁶	Microwave irradiation reduction (750 W)	240 m ² g ⁻¹	46%	280 mAh g ⁻¹ at 1 A g ⁻¹

*ICE values are estimated from graphs given in the reference

The discharge capacity versus current density for the references cited in Table 3 is plotted in Figure 3a below. For those works that reported an electrode mass loading, the specific capacities and current densities have been converted to areal values in Figure 3b. The bulk of the rGO works

show capacities that are slightly under those seen in hard carbon anodes (shown with purple squares), however some works are surpassing hard carbon in rate performance, if not yet in ICE. This provides increased motivation for the continuation of works into other carbon-based materials rather than just hard carbon.

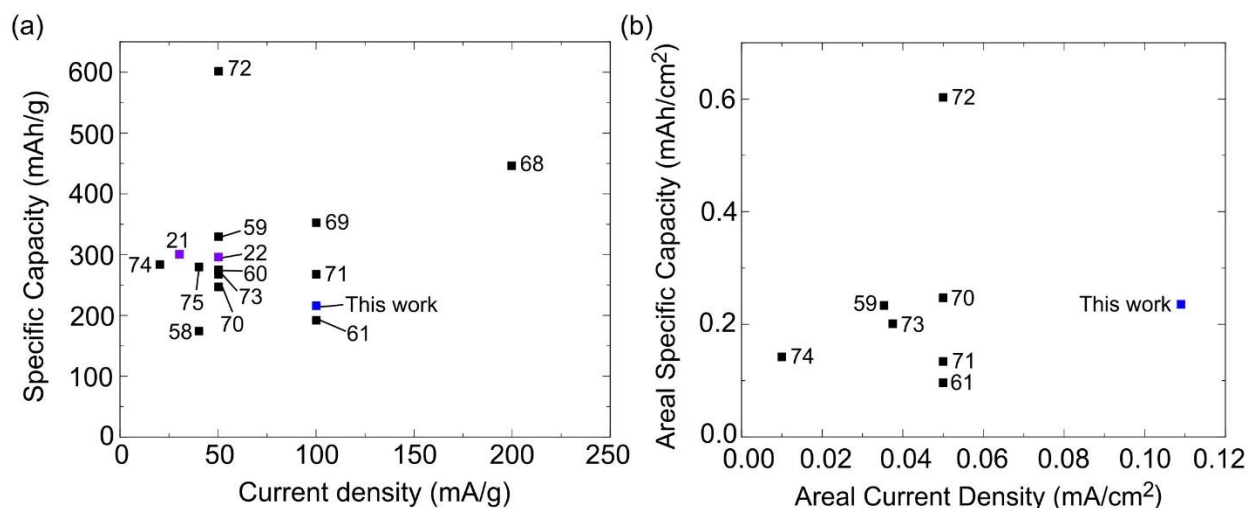


Figure 3: (a) Specific discharge capacity versus current density and (b) areal specific discharge capacity versus areal current density of selected current works on carbon-based anodes for SIBs. Hard carbon works are shown in purple, and this work (rGO400) is shown in blue.

1.3 Objectives

The overall objective of this thesis is to understand the material properties of active materials to optimize their performance in SIB anodes. This will lead to the development of next-generation anode materials and lay the foundation for future work in these areas. This work is split into two sub-objectives.

The first objective (Section 2) is to develop an rGO@RPNP composite through a scalable spray drying method. This aims to address two challenges inherent to the use of red phosphorus as an anode material: low conductivity and extreme volume changes during cycling. Red phosphorus nanoparticles and graphene oxide flakes are synthesized and then combined in a core-shell structure through a scalable spray drying process. The core-shell structures are reduced and used

as the active materials in electrodes during cycling testing. The impact of the material properties and structures is discussed with the goal of understanding how they affect the conductivity and structural integrity of the electrodes.

To expand on some of the questions from the first objective, the second objective (Section 3) is to decouple the effects of rGO chemistry and surface area to better understand their impact on performance as an anode material in SIBs. By producing a low surface area GO through spray drying, the effects of chemistry and surface area are able to be separated from each other for a more complete understanding of their impact. GO samples are thermally reduced in a tube furnace and used as is in electrode slurries during cycling testing. Different reduction temperatures are compared, as well as comparisons of exfoliated vs non-exfoliated samples at a single reduction temperature. This work also sets up future work to link back to Section 2 and use some of the findings about the rGO properties to improve the core-shell structures.

2 Development of an RP-carbon core-shell structure to improve the performance of SIB anodes

The work in the following section will discuss the development and exploration of an anode material for SIBs made of RPNPs encased in a conductive shell made of rGO. This chapter shows that the rGO@RPNP composite has better electrochemical performance than either component individually, showcasing the importance of the composite structure, and aims to address two of the main setbacks associated with an RP anode: extreme volume change while cycling that leads to the pulverization of the electrode, and low conductivity.

2.1 Methodology

2.1.1 Synthesis of RPNPs

The synthesis for the RPNPs was adapted from the procedure described in the work by Chang et al.¹⁷ First, two solutions were prepared. 58.3 mg of hexadecyltrimethylammonium bromide (CTAB; Sigma-Aldrich) was measured outside of the glovebox into a 20 mL scintillation vial. Into a second 20 mL scintillation vial, 3 mL of iodobenzene (98%, Thermo Scientific Chemicals) was measured. Both vials were transferred into an Ar-filled glovebox (Inert IL-2BG, < 1 ppm oxygen and water). 10 mL of ethylene glycol (99.8%, anhydrous, Sigma-Aldrich) is added to the vial containing the CTAB for a concentration of 0.016 M. 1.2 g of phosphorus triiodide (PI₃; 99%, Sigma-Aldrich) is added to the vial containing the iodobenzene to achieve a concentration of 1 M. Both vials are stirred to ensure the full dispersion of the solute within the solvent. The vials are then sealed within the glovebox and transferred to a glove bag (Sigma-Aldrich) filled with nitrogen to avoid exposure of PI₃ to air and to avoid hygroscopic ethylene glycol from absorbing any water. This procedure can also be done within a glovebox if the proper materials and setup are present.

The vial with CTAB/ethylene glycol is set to stir upon a stir plate at 1000 rpm. The PI_3 /iodobenzene solution is slowly added to the CTAB/ethylene glycol vial. It should be added over the course of 5 min to ensure proper dispersion and the synthesis of evenly sized RPNPs. Within approximately 10 s the color of the solution will change to a bright orange, indicating the formation of nanosized RP, though the entire reaction should be kept stirring for 5-10 min after the entirety of the PI_3 /iodobenzene solution has been added.

Once the reaction is complete, the mixture is centrifuged (accuSpin 3, Fisher Scientific) at 4000 rpm for 20 minutes. The supernatant is discarded, and the remaining particles are dispersed in toluene (Sigma-Aldrich) and ethanol in a 1:2 volume ratio. The particles are rinsed three times in the toluene/ethanol mixture before being dispersed in ethanol for storage if needed. When a powder is desired, the particles can be dried in a vacuum oven.

2.1.2 *Synthesis of graphene oxide*

The GO was synthesized through a modified Hummer's method based on the procedure described in Tour's paper.^{44,77} The reaction occurs in a round-bottom flask with a heating mantle to control the temperature and a mechanical stirring attachment. 720 mL of sulfuric acid (Sigma-Aldrich) and 80 mL of phosphoric acid (≥ 85 wt% in water, Sigma-Aldrich) are added to the reaction vessel. While the acid mixture is stirring, 36 g of potassium permanganate (ACS, LabChem) and 6 g of graphite flakes (99% metals basis, -10 mesh, Alfa Aesar) are added. The heating mantle is set to 52 °C and the reaction is left to stir for 17 h.

Once the reaction is complete, the slurry is purple with sliver sheets visible. The reaction vessel is removed from the heating mantle and the slurry is slowly added to a beaker containing 800 g of ice. Approximately 22 mL of hydrogen peroxide (H_2O_2 ; 30 wt% in water, Sigma-Aldrich) is added to the diluted slurry under stirring. The slurry undergoes a color change from purple to yellow as

the H_2O_2 is added. The slurry then undergoes two rounds of centrifugation at 4000 rpm with ethanol as a solvent and four rounds of centrifugation at 4000 rpm with 10% hydrochloric acid (Sigma-Aldrich) as a solvent. The final product is a GO paste in ethanol.

2.1.3 Preparation of electrode active material

The synthesized GO paste and batch of RPNPs are dispersed in water. 200 mg of RPNPs were dispersed along with 448.8 mg of GO in 900 mL of water. The dispersion is spray dried using a BUCHI B-290 Mini Spray Dryer with the following parameters: 180 °C inlet temperature, 30% pump power, 100% aspirator, and 600 L h⁻¹ nitrogen gas flow to achieve a powder with the RPNPs encapsulated within a shell of GO material.

The reduction is then done through a chemical reduction process with hydrazine hydrate (35 wt% in water, Sigma-Aldrich) in either a liquid phase reaction or vapor phase reaction. In a liquid phase reaction, spray-dried GO@RPNP powder is dispersed in water and hydrazine hydrate is added at a concentration of 1 µL hydrazine per 3 mg powder. Once the reaction is complete, the solution is centrifuged and filtered to end up with a dry powder. In a vapor phase reaction, a dish with GO@RPNP powder is suspended over top of a dilute hydrazine hydrate solution on a hot plate. The container is sealed allowing hydrazine vapor to fill the head space and reduce the dry powder. Thermal reduction is not an option as it runs too hot for red phosphorus; there is a high risk of a transformation to white phosphorus during this process.

2.1.4 Preparation of electrodes

The active material was combined with polyethylene glycol (average M_n 6000, Aldrich Chemistry) and Super C45 conductive carbon black (MTI Corporation) using either a mortar and pestle or homogenizer (Power Tool x120, CAT). The resulting slurry was cast on 15 µm copper foil with a doctor blade (MTI Corporations) set to a wet height of 100 µm. Electrode discs were

cut out with a diameter of 12 mm and transferred into an Ar-filled glovebox (Inert IL-2BG, < 1 ppm oxygen and water) to be assembled into coin cells. The average mass loading of the electrodes was 0.5 mg cm^{-2} . CR2032 button-type coin cells (casings from MTI Corporation) were assembled using the prepared electrodes, glass fiber membranes (Whatman glass microfiber filters, $1.6 \text{ }\mu\text{m}$ pore size), and a sodium metal (Sigma-Aldrich) or lithium metal (MTI Corporation) counter electrode. The electrolyte used is 1 M sodium hexafluorophosphate (NaPF_6 ; Sigma-Aldrich) in a binary mixture of ethylene carbonate and dimethyl carbonate in a 50:50 volume ratio.

Rate capability and lifetime testing was performed on a LANHE battery cycler.

2.1.5 Material Characterization

Size measurements were performed using a DLS instrument (VASCO III, Cordouan Technologies) on a dispersion of RPNPs in ethanol to determine the mean diameter of the particles as well as the size distribution. Transmission electron microscopy (TEM; Jeol JEM-2200FS) images were taken of a dispersion of RPNPs in ethanol. Energy dispersive X-ray spectroscopy (EDX) measurements were also taken on the same TEM. Raman measurements were done on a Renishaw InVia confocal microscope with a laser wavelength of 532 nm.

2.2 Results and Discussion

The objective of this work is to develop a procedure for the encapsulation of red phosphorus nanoparticles into crumpled rGO core-shell structures. This would address two main challenges associated with SIBs and specifically with the use of red phosphorus in SIBs: the sluggish diffusion kinetics and extreme volume change during cycling. Red phosphorus suffers from low conductivity, so the addition of conductive rGO will provide faster paths for ion transport during cycling. The void space within the core shells and between the RPNPs should provide enough void space to accommodate the volume changes during cycling, promoting the stability of the

electrodes. This work is based off of previously works from our group and other groups describing a similar system for the encapsulation of silicon within rGO for LIB anodes.⁷⁸ A schematic of the ideal spray drying and reduction process for synthesizing the composite material can be seen in Figure 4.

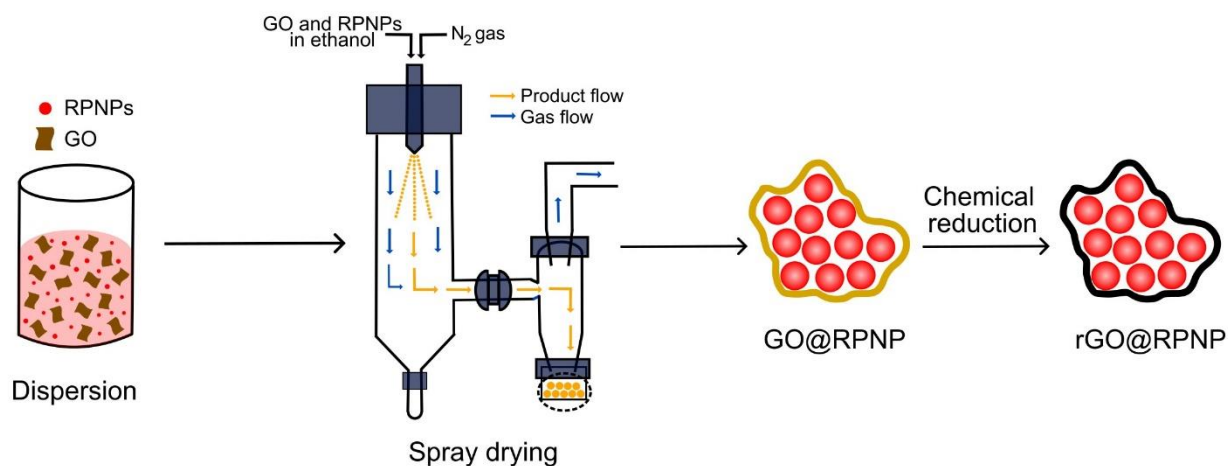


Figure 4: Schematic illustration of the composite synthesis process

2.2.1 Material development and characterization

2.2.1.1 Synthesis of RPNPs

As RPNPs are not commercially available for purchase, the synthesis procedure was adapted from Chang et al.¹⁷ using PI₃ as the precursor with ethylene glycol as a reducing agent and CTAB as a surfactant. PI₃ is a red powder in its bulk form, however the formation of nanosized RP is characterized by a color change to a bright orange (Figure 5), one indication of a successful reaction.



Figure 5: Dispersion of RPNPs synthesized using PI_3 as a precursor with the orange color characteristic of nanosized RP.

Several optimization steps were first undertaken to try and achieve the best morphology and smallest diameter possible, in order to be smaller than the critical fracture diameter (200 nm).¹⁷ Additionally, the width of the size distribution is important as it is hypothesized that more evenly sized RPNPs will be better wrapped by the GO sheets during spray drying. The width of the size distribution is quantified through the polydispersity index (PDI). Large PDI values indicate that the particles are widely distributed and polydisperse, while small PDI values (< 0.1) indicate their size is tightly clustered around an average (monodisperse, most particles have the same diameter).

To study the impact of surfactant concentration on the size and polydispersity of the RPNPs, the concentration of the surfactant (CTAB) was varied from its original concentration of 0.0163 M in ethylene glycol by either increasing or decreasing the concentration by 50%. To test the limits of increasing the surfactant concentration, the maximum concentration of CTAB that was able to be dissolved in ethylene glycol of 0.128 M was also tested (maximum concentration as determined by visual inspection). The results are summarized in Figure 6. The mean diameter of the RPNPs was slightly decreased when varying the concentration by 50% but was increased when the maximum concentration was used. Decreasing the concentration greatly increased the PDI, implying that a concentration of at least 0.0163 M CTAB in ethylene glycol is necessary to ensure

a narrow size distribution. Based on this set of testing, the original CTAB concentration of 0.0163 M is optimal as it can be fully dissolved in ethylene glycol and produces RPNPs with a small diameter and a low PDI, indicating a monodisperse sample.

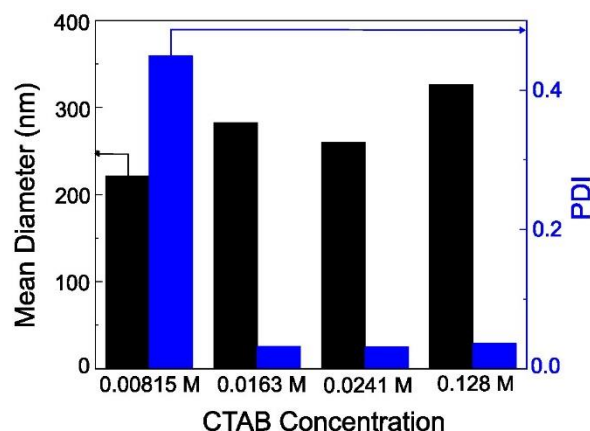


Figure 6: Impact of surfactant concentration of the mean diameter and polydispersity of RPNPs after synthesis

As CTAB is a cationic surfactant with positively charged functional groups on the surface, non-ionic surfactants were also tested to try and understand what the effect of ionic interactions were on the size of the RPNPs. Tween 20 and Span 80 were used as the surfactant in place of CTAB. However, they both resulted in much larger mean diameters of 426 nm and 359 nm. As it is clear the ionic interactions are important for the formation of small RPNPs, CTAB was used as the surfactant for the remaining syntheses.

The ratio between PI_3 and CTAB was also varied and this proved to make the biggest difference in the size of the RPNPs. When the concentration of PI_3 in iodobenzene was decreased from 1.5 M to 1 M (lowering the mass ratio between PI_3 and CTAB from 0.03 g PI_3 :1 mg CTAB to 0.02 g PI_3 :1 mg CTAB), the median diameters of the RPNPs dropped to 110 nm (as compared to a previous average size of 283 nm). It was also shown that 90% of the RPNPs had a diameter under 200 nm (Figure 7), which means the vast majority of the RPNPs were smaller than the critical

fracture diameter. The distribution of the sample is also generally monodisperse with a PDI of less than 0.1.

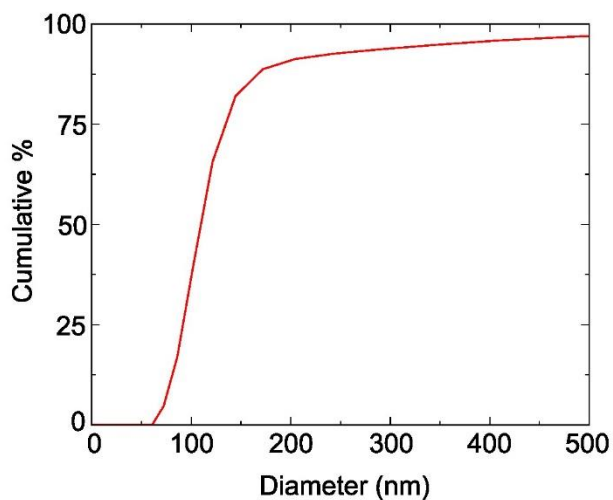


Figure 7: Diameter of RPNPs measured using the DLS showing the cumulative percentage of RPNPs, which is the percentage of particles that would pass through a pore of a certain diameter (i.e. that have a diameter smaller than that value).

TEM images (Figure 8a) of the RPNPs show a spherical morphology and even size distribution. EDX measurements taken on the samples confirm that it is phosphorus present in the particles as shown in red (Figure 8b).

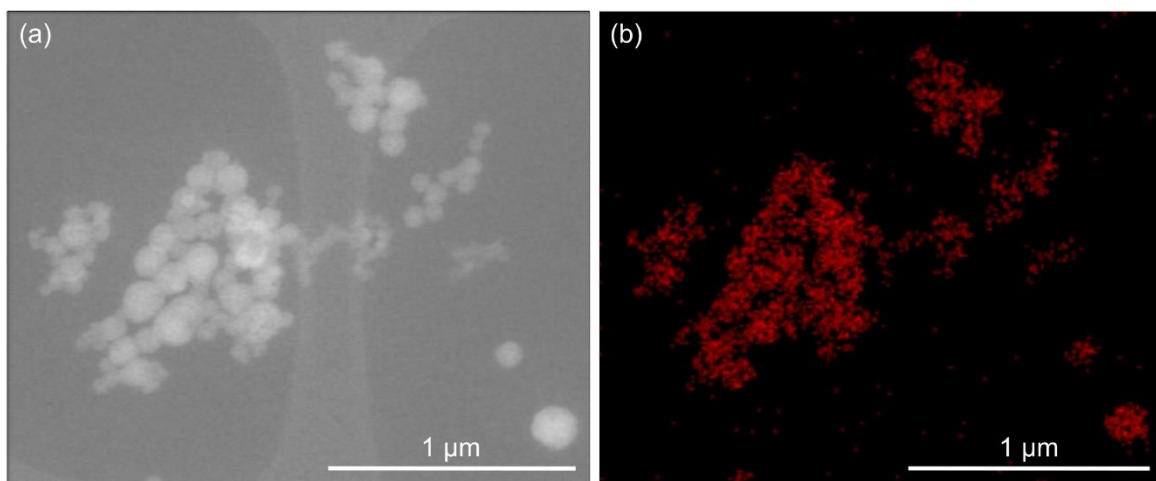


Figure 8: (a) TEM image of RPNPs and (b) EDX mapping of the phosphorus present in (a)

The RPNPs appeared to be sensitive to the moisture present in ambient conditions. The dispersions of RPNPs after synthesis were quite acidic and would become more acidic as the solution was stored in ambient conditions. It is hypothesized that the RPNPs were reacting with moisture to form phosphoric acid. The RPNPs may benefit from an additional drying process after the synthesis to remove any moisture, after which they could be stored in inert conditions.

2.2.1.2 *Synthesis and Characterization of rGO@RPNP Composites*

The RPNPs were dispersed along with GO in water to ahead of the spray drying process. As the RPNPs are smaller than the GO flakes, when the dispersion is aerosolized in the spray dryer, they migrate to the middle of the droplet, while the larger GO flakes remain on the surface of the droplet. As the droplet dries, the RPNPs end up in the center of the particle with GO flakes wrapped around them, creating the desired core-shell structures.

SEM images taken of the final spray dried powder show a significantly different morphology than GO spray dried without any RPNPs present. Both samples were spray dried with the same parameters. Figure 9a shows the GO@RPNP composite with a distinctive crumpled shape,

implying the RPNPs are enclosed inside. Figure 9b shows GO alone after spray drying; the flakes have a much flatter morphology and large flakes are still present.

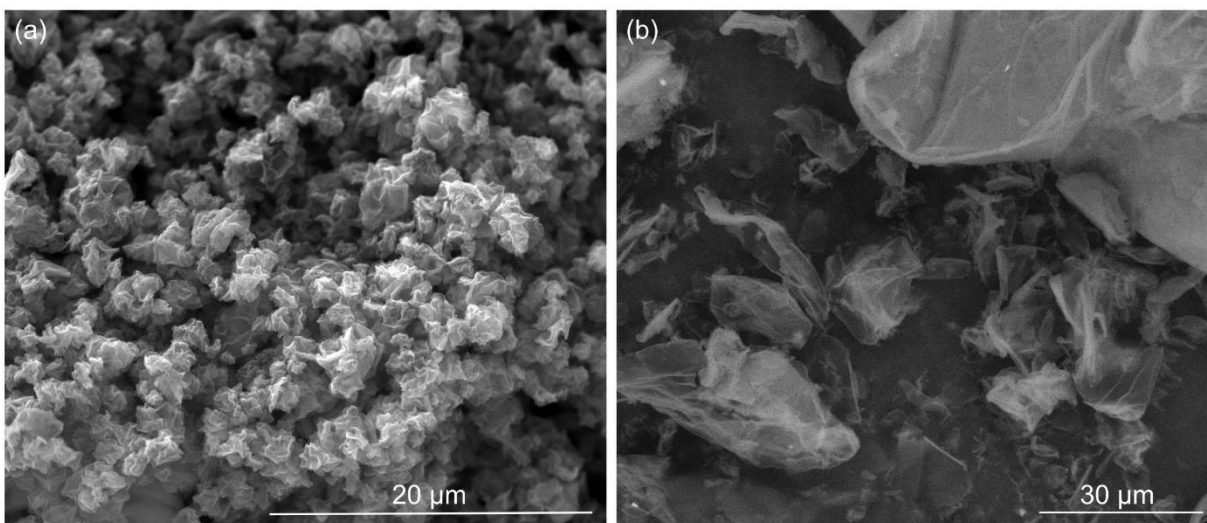


Figure 9: SEM images of (a) GO@RPNP composite and (b) GO flakes

The TEM image in Figure 10a of the GO@RPNP composite also shows dark spherical shapes within the GO core-shell (Figure 10a), which are confirmed to be RPNPs through EDX measurements (Figure 10c). The RP appears to be evenly distributed throughout the core-shell structure, through the EDX measurements only reported a weight fraction of 20% for the RP. This is the value for a single core shell structure able to be analyzed; TGA analysis on the bulk material was unable to give reliable results for any of the composite materials. The theoretical weight fraction should be upwards of 30% based on the weight ratio of the components in the spray drying dispersion.

The difference between the theoretical and experimental mass loading could be related to the hypothesis that the RPNPs are reacting with water to form phosphoric acid. This unwanted reaction could be occurring when the RPNPs were dispersed along with the GO in water. More work should be done to understand their instability and if the presence of phosphorus acid or other surface groups on the RPNPs is preventing the wrapping around of the GO sheets.

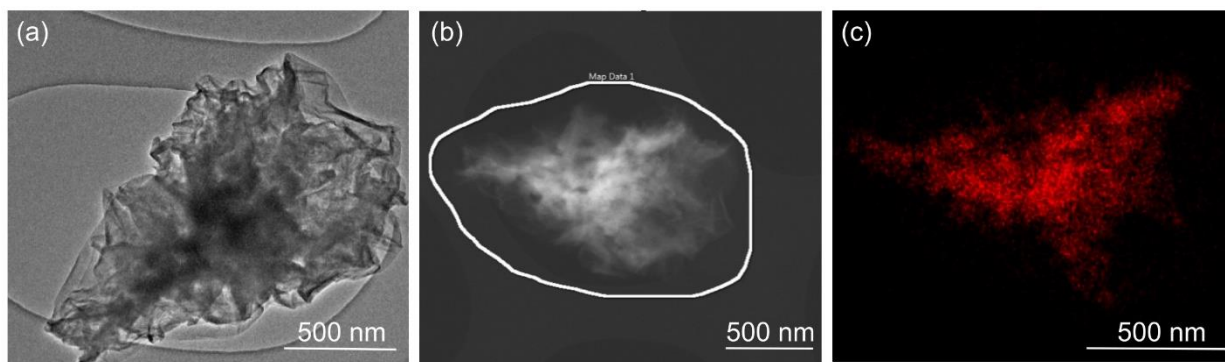


Figure 10: TEM image of (a), (b) GO@RPNP composite and (c) EDX mapping of the phosphorus present in (b)

The liquid-phase reduction is conducted by dispersing the GO@RPNP composite in water and adding hydrazine hydrate at a concentration of 1 $\mu\text{L}/\text{mg}$ of powder. Once the reaction has been completed (characterized by a dispersion color change from amber to black) and the sample has been vacuum filtered and dried, SEM images show an uncrumpling of the core-shell structures (Figure 11). While there is still phosphorus present, it is in much smaller amounts than pre-reduction and the morphology of the composite has changed compared to the pre-reduction SEM images seen in Figure 9. The crumpled structure is no longer noticeable; some flakes seem to have straightened out. The dissolution of the composite in water for the liquid-phase chemical reduction could be the reason for this uncrumpling as there is no sealing step between the spray drying and reduction steps.

To try and protect the core-shell structures, vapor phase reduction was explored to eliminate the need for dissolution of the composite in water. This was minimally successful – EDX analysis on core-shell structures reduced through a vapor-phase process showed inconsistent results of the removal of oxygen and this remains an avenue for future optimization. The reduced composites presented later in this section are reduced in the liquid-phase.

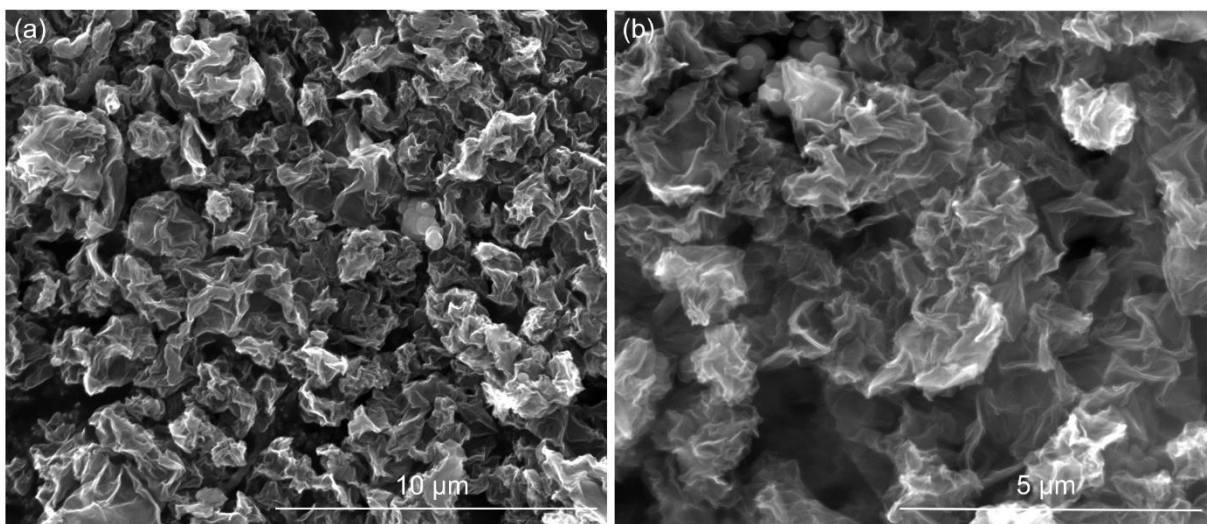


Figure 11: SEM images of (a), (b) rGO@RPNP

To assess the strength of the liquid-phase reduction process on the resulting powder, Raman spectroscopy was conducted on samples reduced for different times. The time was varied from 2 to 12 h for both spray dried GO and spray dried GO@RPNP. The Raman signal for all samples post-reduction can be seen in Figure 12a. All samples retain the G ($\sim 1580\text{ cm}^{-1}$) and D peak ($\sim 1350\text{ cm}^{-1}$) seen in the unreduced GO.⁷⁹ The G peak is present in all sp^2 carbon systems and occurs due to the in-plane C-C stretching mode.^{80,81} The intensity of the D peak is proportional to the number of aromatic domains, so long as the domain size is not large and is interrupted by defects.⁸² For pristine, or few layer graphene the 2D peak ($\sim 2700\text{ cm}^{-1}$) can be induced by an in-plane breathing-like mode of the carbon rings.⁸⁰ The ratio between the defects and graphene peaks in the Raman spectra (I_D/I_G) can be used to assess the disorder levels in the reduced materials. In all cases (2 h, 6 h, and 12 h for the reduction), an increase in the I_D/I_G (integrated peak intensity ratios after deconvolution with a Lorentzian model) was observed when compared to the unreduced sample. This indicates that the reduction process is creating more aromatic domains in the sample. A decrease in this ratio would occur with very large aromatic domains, which would be unexpected in rGO samples.

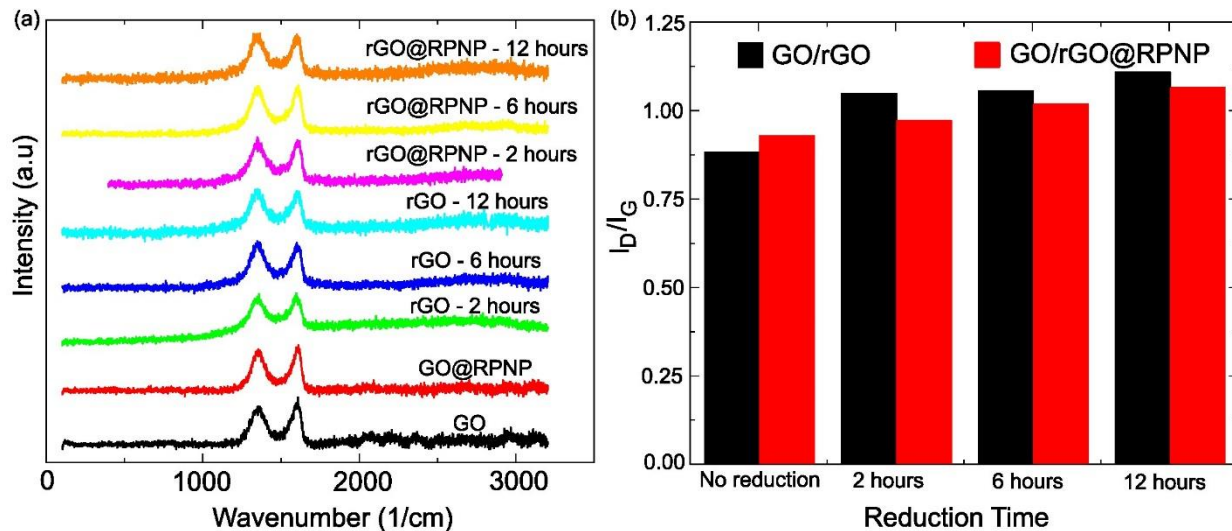


Figure 12: (a) Raman signals from rGO and rGO@RPNP at different reduction times and (b) I_D/I_G from the Raman signals in (a). The peak intensity ratios are integrated peak intensity ratios after deconvolution with a Lorentzian model.

A very wide 2D peak was observed in the longer reduction times (6 h and 12 h) for the rGO and rGO@RPNP samples, indicating that 2 h is not enough time to fully reduce the material. The chosen reduction time for the liquid-phase reduction reaction was 6 h due to minimal difference in quality when the time was increased to 12 h.

2.2.2 Investigation into the influence of composite structure on electrochemical performance

As this composite material is developed, it is important to understand how it provides a performance improvement over using only RPNPs or only GO as the active material, even before the reduction process. This can provide insights into how the spray dried core-shell structures provide a performance increase, hypothesized to be through increased electrode stability and prevention of RP pulverization. This comparison can also be used to understand how sodium ion storage and transport differs in the core-shell structures versus exposed RPNPs or GO.

When cycled in half cells, it is clear that using only RPNPs as the active material or GO only as an active material produces cells that do not reach acceptable specific capacities and show poor electrochemical stability when the current density is increased to higher rates. The combination of

these two components through the spray drying procedure greatly improves the cycling capacity and stability of the cells. This is hypothesized to be because of the structure and the core-shell structures providing void space that can accommodate large volume changes during cycling. This boost in performance occurs even when no heat treatment has been performed to increase the conductivity of the composite.

The rate capability of the individual components (RPNP and GO) as well as the spray dried GO@RPNP composite is plotted in Figure 13a. Using GO alone shows the worst performance. RPNPs show a slight improvement, especially at slower current rates, while the spray dried composite clearly outperforms both sets. It is immediately clear that the structure of the active material is important for boosting performance.

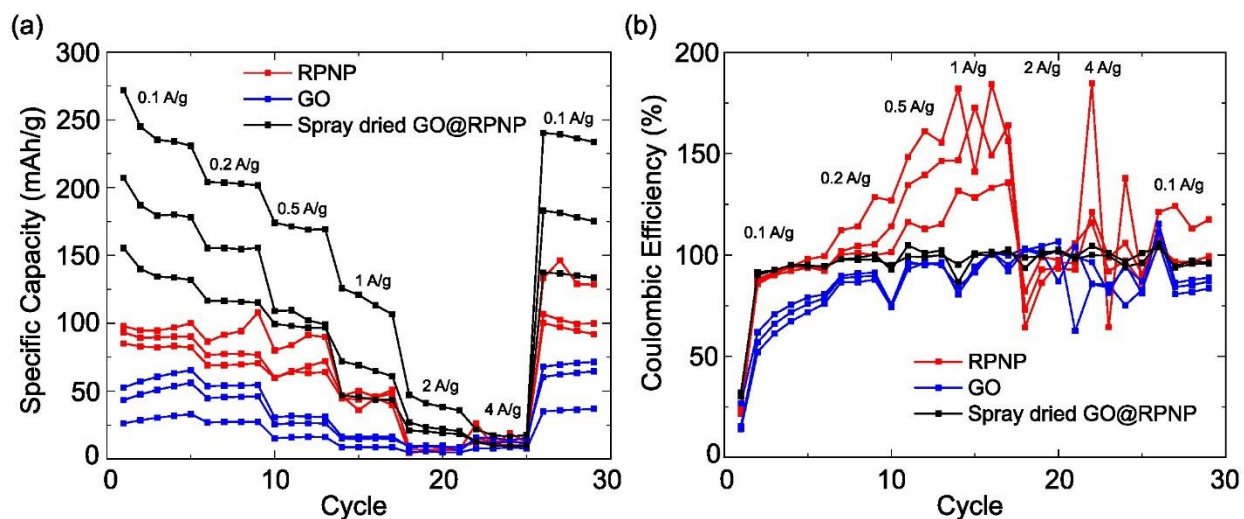


Figure 13: (a) Rate capability and (b) coulombic efficiency for RPNP, GO, and spray dried GO@RPNP against Na. The active material loading is approximately 0.5 mg cm^{-2} .

The use of the composite GO@RPNP as the active material also increases the ICE against sodium counter electrodes, as seen in Table 4 and Figure 13b. Although the ICE remains outside of acceptable commercial ranges, it is promising that a significant increase can be seen through such this process. In the first 10 cycles, the CE of the GO alone is significantly lower than the spray dried composite as sodium ions continue to be consumed through irreversible reactions past

the first cycle. Additionally, the RPNPs alone as an active material show a large amount of instability in the CE at the higher current densities. CEs higher than 100% in a half cell indicate that the desodiation capacity is higher than the sodiation capacity. This may be happening because the SEI formed in the previous cycle is dissolving and releasing sodium ions during the desodiation process. Taking one of the RPNP cells to investigate this claim, all irreversible capacity is assumed to the result of SEI formation. Summed up over all cycles, this is equal to 354 mAh g⁻¹. Assuming all desodiation capacity greater than the sodiation capacity for that cycle is the result of SEI dissolution, the capacity due to SEI dissolution summed up over all cycles is equal to 325 mAh g⁻¹, less than the amount of SEI formed. The same is true for the other two cells (362 mAh g⁻¹ SEI formed versus 155 mAh g⁻¹ SEI dissolved; 342 mAh g⁻¹ SEI formed versus 77 mAh g⁻¹ SEI dissolved), therefore, it is reasonable to assume that SEI dissolution is responsible for the CE values above 100%.

This implies that the use of RPNPs alone does not promote a stable SEI during cycling. In the spray dried GO@RPNP composite, the GO may act to protect some of the RPNPs from reacting with the electrolyte to irreversible form the SEI, leaving more sodium ions to be released in the following charging cycle. From these results, it is clear that the individual components do not provide acceptable cycling performances, and the combination of both elements through spray drying provides a significant performance boost.

Table 4: ICE and CE values for RPNP and spray dried GO@RPNP electrodes against Na

	Initial sodiation/lithiation capacity (mAh g⁻¹)	1st cycle capacity loss (mAh g⁻¹)	ICE	2nd cycle capacity loss (mAh g⁻¹)	CE 2nd cycle
RPNP	408.1	310.3	24.0%	14.3	86.9%
	391.9	306.9	21.7%	11.1	88.1%
	378.0	284.9	24.6%	15.0	85.7%

GO	169.7	143.6	15.4%	21.6	56.9%
	307.8	264.5	14.1%	43.6	52.1%
	197.3	144.7	26.7%	35.2	61.8%
Spray dried GO@RPNP	896.6	624.8	30.0%	22.6	91.6%
	646.6	439.7	32.0%	20.7	90.0%
	512.3	357.1	30.3%	12.8	91.6%

The charge/discharge curves for the first cycle of cells made with an active material of GO, RPNP, and spray dried GO@RPNP are shown in Figure 14a. There is a clear difference in the shape of the curves for electrodes made with GO, RPNP, and spray dried GO@RPNP. The RPNP seems to lead to a more sloping profile in the mid-voltage range. When the electrode is made of only GO, the curve has a much higher slope. The addition of RPNP adds additional storage sites and improves the capacity.

When comparing the charge/discharge curves for spray dried GO@RPNP over the various current densities (Figure 14b), it appears as though the impact of the RPNP disappears at the higher current densities of 2 A g^{-1} and 4 A g^{-1} . Those discharge curves have a similar shape to the GO only curve, suggesting that the RPNPs are becoming inactive at the higher current densities. However, when the current density is returned to the low rate of 0.1 A g^{-1} , the shape of the charge/discharge curve from cycle 2 is recovered. This could mean the RPNPs are not destroyed when the current is increased, they are simply inaccessible and are able to be reused as storage sites once the current density is lowered again. More work is then needed to understand why they are not being utilized at the higher current densities and how the sodium transport through the rGO shells can be improved.

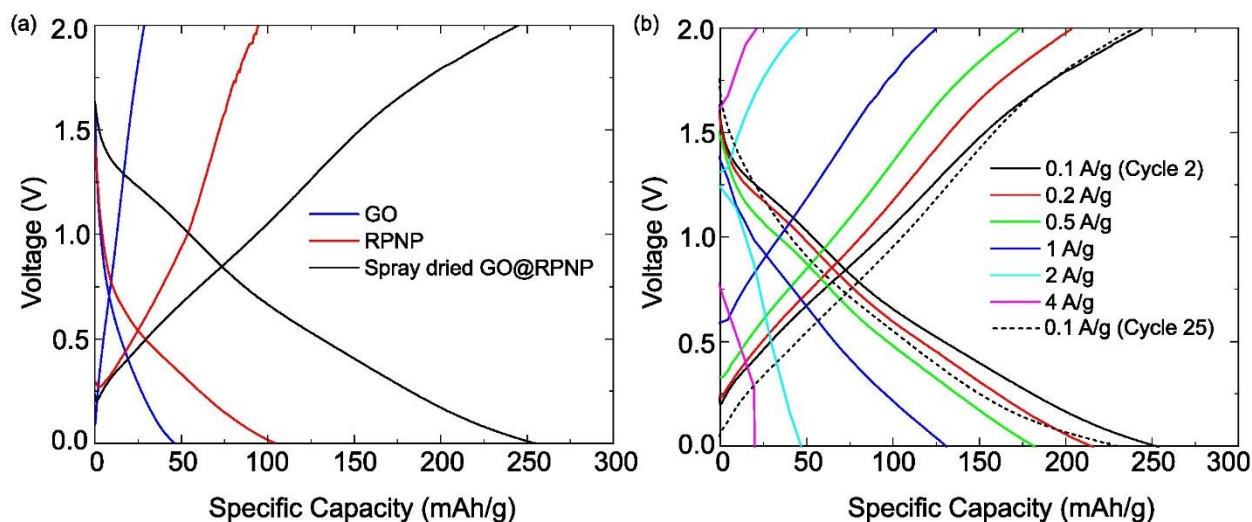


Figure 14: Charge/discharge curves (a) at 0.1 A/g and (b) for spray dried GO@RPNP at various current densities.

2.2.2.1 Comparison of methods of composite formation

While it is clear that the combination of GO and RPNPs is essential for increasing the performance, it was important to understand how the core-shell structures were able to impact performance. Spray-drying was shown to provide an increase in rate capability performance compared to the same formulations that were simply mechanically mixed with the same proportions (Figure 15a). This indicates that the spray drying is creating void space for the sodium ions to access the red phosphorus nanoparticles while eliminating the massive volume change during cycling. It is not enough to simply mix the components together and see a performance boost, it is the spray drying that really provides the benefit. In this study, it was also clear that the reduction process delivers an increase in performance compared to unreduced mixed samples. This is expected as the oxygen functional groups in GO samples promote irreversible reactions through unstable SEI formation. Though the performance difference between the reduced and unreduced samples is much smaller for the spray dried structures, this could be related to the reduction process and is an avenue for future work.

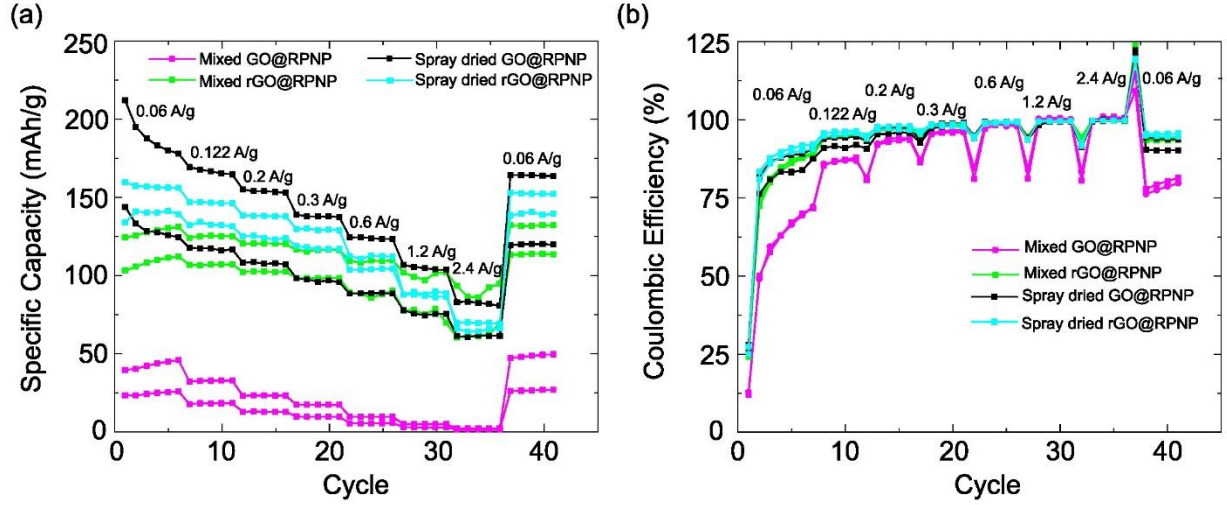


Figure 15: (a) Rate capability and (b) CE for mixed vs spray dried materials. The active material loading used is approximately 0.5 mg cm^{-2} .

As seen in Table 5, the spray drying and reduction process both increase the ICE and the CE in the second cycle compared to the mixed GO@RPNP. Though all ICE values are quite low, the improvement in the 2nd cycle CE is important as the cells need to approach 100% efficiency as fast as possible. Based on Figure 15b, the mixed GO@RPNP sample is the slowest to approach 100% efficiency. Its CE also drops when the current density is returned to 0.06 A g^{-1} , implying that irreversible reactions, such as SEI formation, are still happening.

Table 5: ICE and CE values for mixed vs spray dried materials

	Initial sodiation/lithiation capacity (mAh g^{-1})	1 st cycle capacity loss (mAh g^{-1})	ICE	2 nd cycle capacity loss (mAh g^{-1})	CE 2 nd cycle
Mixed GO@RPNP	398.5	350.5	12.1%	48.9	50.0%
	221.5	193.0	12.9%	29.4	49.1%
Mixed rGO@RPNP	592.7	442.6	25.3%	57.9	72.4%
	514.1	389.5	24.2%	44.9	74.0%
Spray dried GO@RPNP	756.2	582.4	23.0%	66.2	70.8%
	914.0	658.2	28.0%	52.8	81.7%
Spray dried rGO@RPNP	645.8	484.2	25.0%	40.0	80.9%
	703.1	510.5	27.4%	37.8	83.4%

These results are important to show that a combination of the reduction and spray drying process can create an effective anode material for SIBs. Though the mechanically mixed samples perform only slightly worse than the spray dried samples when the material has been reduced, it is still clear that the structure of the active material plays a significant role in the storage of sodium ions during cycling.

2.2.3 Comparison of cycling behaviour between LIBs and SIBs

Another important point to consider in this analysis are the differences between SIBs and LIBs during cycling. As systems for LIBs are generally more understood than those for SIBs, the differences in cycling performance and storage mechanisms can provide important insight into improving SIBs.

When the active material are RPNPs only or spray dried GO@RPNP, the lithium cells outperform the corresponding sodium cells in rate capability testing (Figure 16a and b) with higher specific capacities across all current densities. The difference is especially large when spray dried GO@RPNP is used as the active material where the LIBs show approximately double the specific capacity.

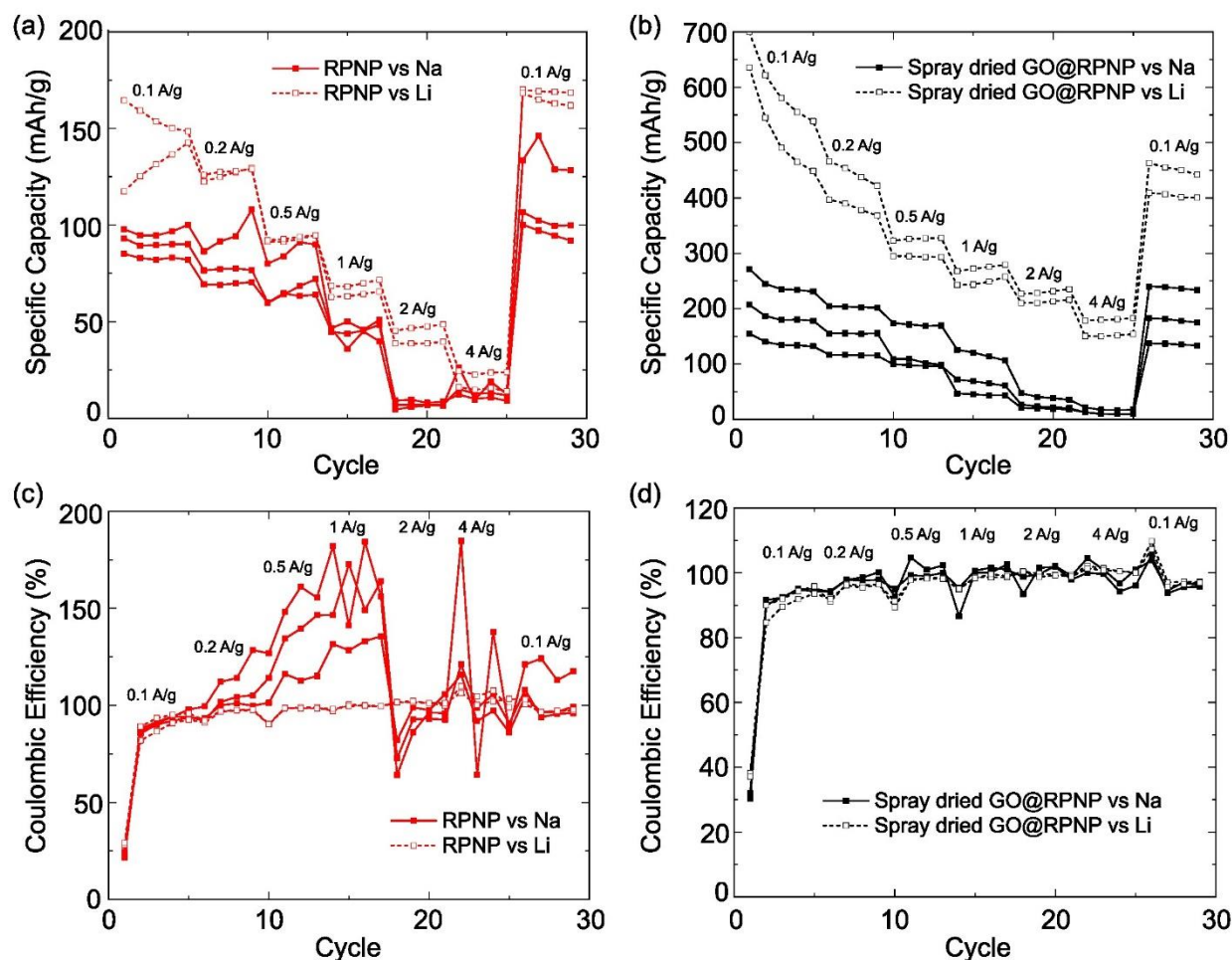


Figure 16: Rate capability of (a) RPNP versus Na and Li and (b) spray dried GO@RPNP versus Na and Li and coulombic efficiency of (c) RPNP versus Na and Li and (d) spray dried GO@RPNP versus Na and Li. The mass loading is approximately 0.5 mg cm^{-2} .

Lithium cells outperform the corresponding sodium cells in specific capacities; they also have slightly improved ICE values compared to the sodium cells (Table 6). This could be due to the formation of a more stable SEI during the first cycle. Based on the CEs during rate capability testing when using RPNPs only (Figure 16c), it seems as though the lithium cells show better stability. However, their stability is the same of slightly worse than the sodium cells when spray dried GO@RPNP is used as the active material (Figure 16d). This could indicate that the introduction of the GO and the spray drying process is providing sufficient space for the volume expansion against sodium and can stabilize the electrode/SEI to the same degree as in lithium cells.

Table 6: ICE and CE values for RPNP and spray dried GO@RPNP electrodes against Na and Li

	Initial sodiation/lithiation capacity (mAh g⁻¹)	1st cycle capacity loss (mAh g⁻¹)	ICE	2nd cycle capacity loss (mAh g⁻¹)	CE 2nd cycle
RPNP vs Na	408.1	310.3	24.0%	14.3	86.9%
	391.9	306.9	21.7%	11.1	88.1%
	378.0	284.9	24.6%	15.0	85.7%
RPNP vs Li	417.8	300.4	28.1%	27.7	81.9%
	563.1	398.6	29.2%	19.5	89.1%
Spray dried GO@RPNP vs Na	896.6	624.8	30.0%	22.6	91.6%
	646.6	439.7	32.0%	20.7	90.0%
	512.3	357.1	30.3%	12.8	91.6%
Spray dried GO@RPNP vs Li	1835.4	1135.8	38.1%	69.2	90.0%
	1713.9	1078.1	37.1%	99.0	84.6%

The stability of the spray dried GO@RPNP electrodes appear to be improved against sodium when the current density is returned to 0.1 A g⁻¹. This can be seen in both Figure 16b and d and Figure 17b and c. In Figure 16b, the specific capacities for the first 5 cycles against lithium continue to decrease, while they appear to stabilize after the second cycle against sodium. In the charge discharge curves shown in Figure 17b, the second cycle and 25th cycle against sodium have almost identical curves, while against lithium (Figure 17c), there is a gap between the two that could indicate the continued formation of SEI or slow ion transport through a thickened SEI layer.

The charge/discharge curves for spray dry GO@RPNP versus sodium and lithium, shown in Figure 17, show generally the same shape, indicating that the storage mechanisms of the ions is similar for both systems. A long plateau region is missing around 1 V, which has been attributed to the sodiation and lithiation of RPNPs,^{17,33} however, the slopes of the curves are much flatter than traditional carbon materials, indicating that additional storage sites are provided by the RPNPs within the electrode active material.

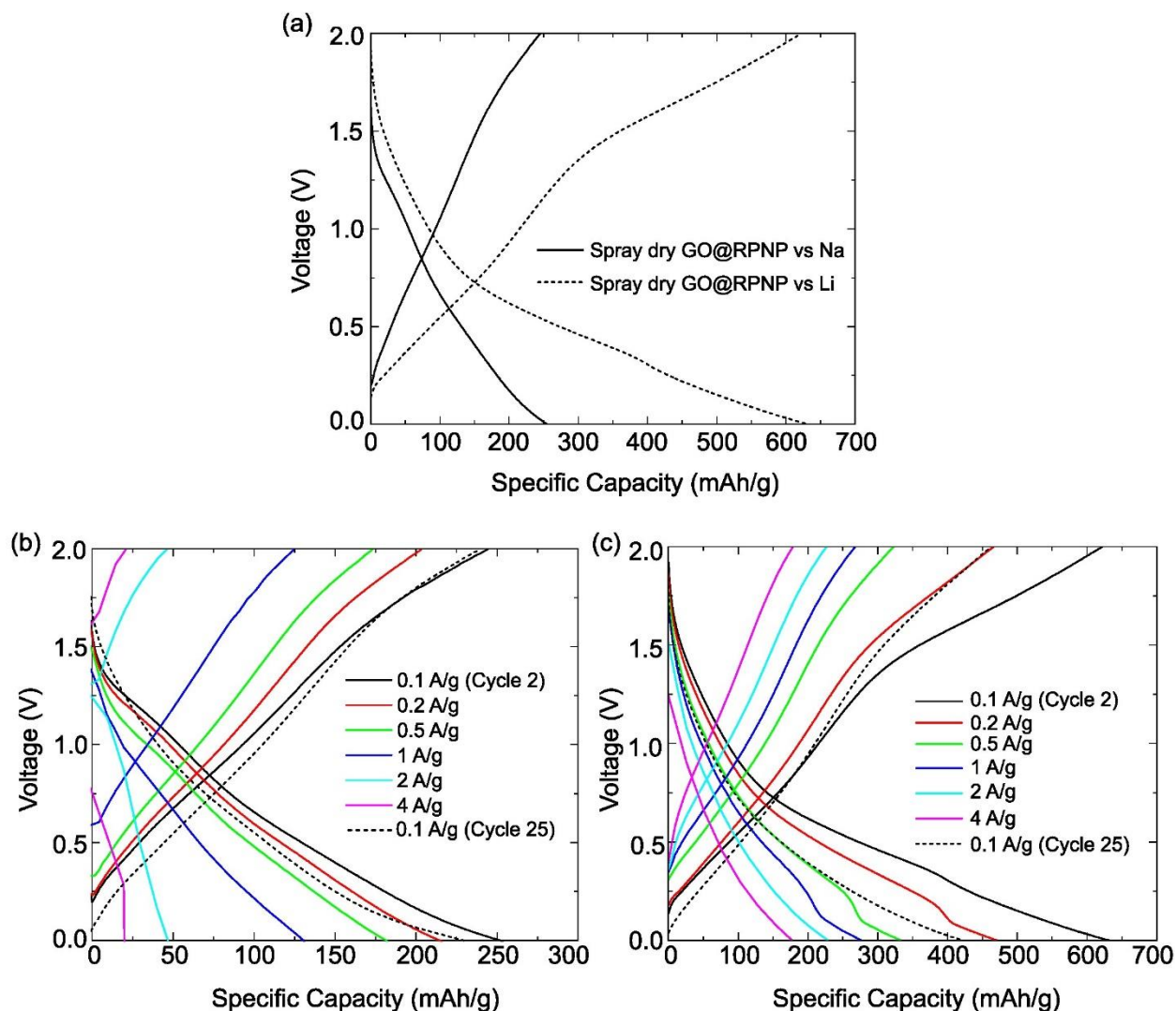


Figure 17: Charge/discharge curves (a) at 0.1 A/g, (b) for spray dried GO@RPNP versus Na at various current densities, and (c) for spray dried GO@RPNP versus Li at various current densities

2.3 Conclusion

It was shown through this work that the individual components (RPNPs and GO) performed worse on their own than when they were combined through the spray drying process. Additionally, the cycling performance was worse when the RPNPs and GO/rGO were simply mixed together instead of being spray dried together. This is a clear indicator that the structure of the composite is incredibly important to its performance. The volume changes brought about through the alloying reaction with phosphorus can be very detrimental to the cycling performance and the core-shell

structures seem effective at providing stable void space for this to occur. The reduction process also provided an increase in performance, both in mixed and spray dried samples, proving the importance of the reduction to increase the conductivity of the composite. The rGO@RPNP composite was able to achieve a reversible capacity of 192 mAh g^{-1} at 60 mA g^{-1} and an ICE of 27%.

The difference between cycling the composite against sodium and lithium counter electrodes was also studied. Though the lithium cells provided increased rate capability performance and ICE, the sodium cells seemed to show better stability at lower current densities. The charge/discharge curves for both types of cells exhibited similar shapes, indicating that the storage mechanisms for both systems are similar.

3 Improved performance of graphene-based sodium-ion battery anodes using low surface area, low reduction temperature reduced graphene oxide

While the work of the previous section mainly explored the impact of RP in spray dried core-shell structures, questions remain about how the rGO properties will affect its performance and how the reduction process can be tuned to optimize the composite. There exists no systemic work on how rGO material properties such as oxygen content and surface area affect performance in SIBs; the objective of this section is to fill this gap for a more complete understanding of carbon-based anode materials. The results from this section can then be transferred to composite materials, so that the entirety of the active material can be used as effectively as possible. Samples were reduced up to various maximum reduction temperatures to investigate the effect of oxygen content. The effects of the rGO chemistry were also decoupled from the effects of surface area by synthesizing an exfoliated and non-exfoliated sample at each reduction temperature. This allowed for the analysis of the effects of both oxygen content and exfoliation on the electrochemical performance in SIBs.

3.1 Methodology

3.1.1 Synthesis of rGO materials

The GO was synthesized in the process described in Section 2.1.2. The GO was then dispersed in a solution of ethanol at a concentration of 12 g of GO per L of ethanol. The suspension was stirred for 6 h and tip sonicated (Sonics Vibra Cell) for 10 min at 60% power. The resulting dispersion was spray-dried using a BUCHI B-290 Mini Spray Dryer with the following parameters: 12 g L⁻¹ feed concentration, 180 °C inlet temperature, 30% pump power, 100% aspirator, and 601 L h⁻¹ nitrogen gas flow. The BUCHI Inert Loop B-295 system was used to ensure

oxygen-free conditions to prevent any explosion hazard and to recapture ethanol in the condensing system.

To achieve different degrees of reduction, the spray-dried GO powder was heated in a tube furnace (Thermo Scientific, Lindberg Blue M) in a 95% argon (Ar)/5% hydrogen (H) atmosphere up to different maximum temperatures and with different ramping rates depending on whether the rGO was to be exfoliated (high surface area) or non-exfoliated (low surface area). The boat used to hold the samples in the furnace was made of aluminum oxide (MTI Corporations) and the sample mass was 200 mg of GO powder each time. The maximum reduction temperatures used were 200 °C, 300°C, 400 °C, 600 °C, 800 °C, and 1000 °C. The heating procedure for both sets of samples are shown in Table 7.

Table 7: Ramping rates for the reduction of the GO powder

Temperature range	Ramping rate non-exfoliated	Ramping rate exfoliated
RT – 150°C	1 °C min ⁻¹	5 °C min ⁻¹
150 °C hold, 2 h		
150°C - 300°C *	0.5 °C min ⁻¹	0.5 °C min ⁻¹
300 °C hold, 2 h		
300°C – max reduction temperature	1 °C min ⁻¹	5 °C min ⁻¹
Hold at max reduction temperature for 3 hours		

* For the sample with a maximum reduction temperature of 200°C, the temperature was ramped at 0.5°C min⁻¹ from 150°C up to 200°C and then held there for 5 h.

The rGO samples were removed from the furnace and used as is.

3.1.2 Preparation of electrodes

The electrodes with non-exfoliated material were prepared by making a slurry in water made up of active material, sodium alginate (Acros Organics), and Super C45 Conductive Carbon (MTI Corporation) in a 70:20:10 weight ratio. The final solid content of the slurry was approximately

8%. Unreduced GO electrodes were also prepared by making a slurry in water made up of GO, Super C45, and sodium alginate in a 50:30:20 weight ratio. The final solid content of the slurry was approximately 6%, which is less than the rGO slurries due to the higher oxygen content of the GO. Slurries were cast with a doctor blade (MTI Corporation) onto 15 μm copper foil at a wet gap of 50 μm and dried overnight at 110 $^{\circ}\text{C}$. Electrodes were then punched into discs with a diameter of 12 mm and transferred into an Ar-filled glovebox (Inert IL-2BG, < 1ppm oxygen and water) to be assembled into coin cells. Due to high surface area of the exfoliated rGO, high solids content slurries could not be formulated. Instead, electrodes were prepared by cutting out discs of copper mesh (McMaster-Carr) with a 12.7 mm diameter. They were then placed in a die press (MTI Corporation) and the exfoliated rGO material was added on top. The die was pressed at a pressure of approximately 69 MPa for 2 min, embedding the rGO into the copper mesh.

CR2032 button-type coin cells (casings from MTI Corporation) were assembled using the prepared electrodes, glass fiber membranes (Whatman glass microfiber filters, 1.6 μm pore size), and a sodium metal counter-electrode (Sigma-Aldrich). The electrolyte used is 1 M sodium hexafluorophosphate (NaPF_6 ; Sigma-Aldrich) in a binary mixture of ethylene carbonate and dimethyl carbonate in a 50:50 volume ratio.

3.1.3 *Material characterization*

Scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM and EDX; FEI Quanta Feg 250 ESEM) was performed for structural analysis and to understand the elemental composition of the samples. X-ray diffraction (XRD; Rigaku Miniflex II) was used over a range of 5° to 40° at a scan rate of $1^{\circ} \text{ min}^{-1}$ to provide an understanding of the crystal structure of the materials. The surface area of the samples was determined with nitrogen as the probing gas in a

surface area analyzer (SAA; Micromeritics Gemini 2390a) using the Brunauer-Emmett-Teller (BET) method.

3.1.4 Electrochemical measurements

Rate capability and lifetime testing were collected from the battery cells on a LAND battery testing system (LAHNE). Rate capability tests were performed based on current density. After a formation cycle at 100 mA g^{-1} , the cells underwent 4 cycles at each of the following current densities: 100 mA g^{-1} , 200 mA g^{-1} , 500 mA g^{-1} , 1000 mA g^{-1} , 2000 mA g^{-1} , 4000 mA g^{-1} , followed by a final 4 cycles at 100 mA g^{-1} once again. Lifetime testing on the cells was also performed based on current density. After an initial 15 cycles at 100 mA g^{-1} , the rate was increased to 1000 mA g^{-1} for 200 cycles. The cells were cycled between 0 and 2 V for all tests performed.

3.2 Results and Discussion

In this chapter, we attempt to decouple the effects of rGO chemistry from electrolyte-accessible surface area on sodium-ion insertion capacity, irreversible capacity loss and stability. To do so, sodium anodes fabricated from rGO powders which have been reduced and exfoliated are compared to powders that have been reduced to the same levels but have deliberately not been exfoliated (Figure 18). Low surface area GO powder precursors are prepared by spray drying in ethanol-based dispersions that facilitate restacking and granulation of the GO. Slow heating retains this low surface area, resulting in a restacked rGO powder maximizing ICE. Fast heating produces a high-surface area, exfoliated rGO powder.

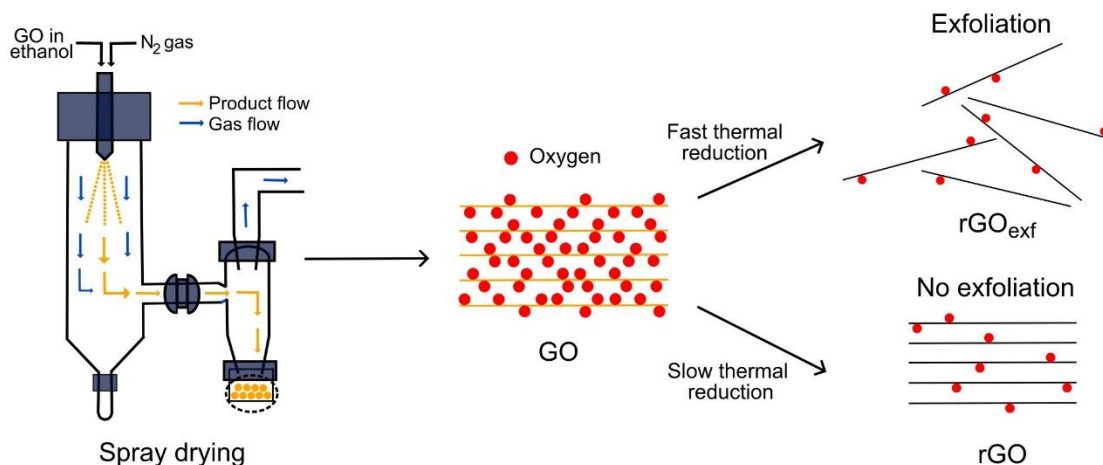


Figure 18: Process schematic of the spray drying process, and the slow and fast thermal reduction

3.2.1 Material characterization

The first aim of our study was to produce a low specific surface area (SSA) GO powder and to determine whether this low SSA can be retained during slow thermal reduction. The GO slurry obtained from the last washing step of the improved Hummer's method was spray-dried with a feed concentration of 12 g L^{-1} in ethanol. This yielded a GO powder with a SSA of $25.3 \text{ m}^2 \text{ g}^{-1}$. Spray drying from ethanol allows us to pump higher concentration dispersions into the spray dryer that we find produces a powder with lower SSA than aqueous-based dispersions. Shi et al.,⁶⁶ also showed that a higher feed concentration promotes the formation of the nematic phase during spray drying and a final product with a more layered structure and a lower surface area. A lower feed concentration promotes the formation of a more crumpled ball-like structure.⁶⁶

An SEM image of the GO flakes after spray drying are seen in Figure 19. They show a wide distribution in the size with some flakes larger than $100 \text{ }\mu\text{m}$ in lateral size. Many sheets appear to be folded, likely a result of the rapid drying process which does not allow all sheets to align and register under the action of capillary forces. Some smaller pieces of the GO also appear to be

crumpled. The GO was found to be $37.7\% \pm 0.7\%$ oxygen ($C/O = 1.57$) as estimated by EDS which is close to the ratios seen in similar methods, which are around 2.^{77,83,84}

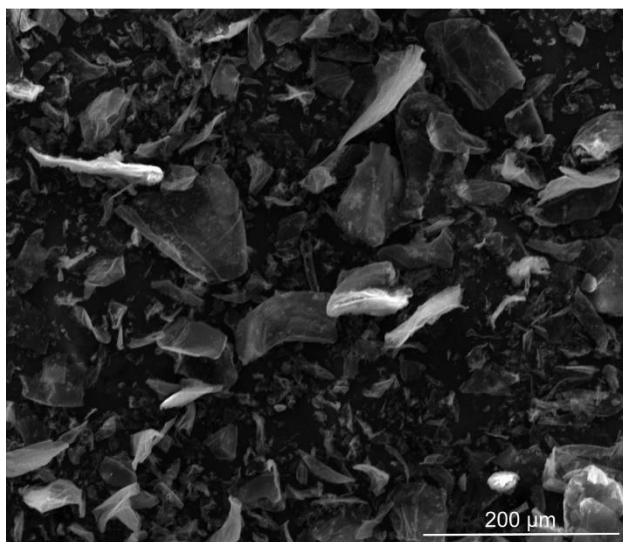


Figure 19: SEM image of GO flakes

The reduction of the GO was done in a tube furnace under an Ar/H₂ atmosphere up to a maximum reduction temperature of 200 °C, 300 °C, 400 °C, 600 °C, 800 °C, and 1000 °C following the procedures described in Table 7. The rGO samples are denoted by their reduction temperature and whether they have been exfoliated or not: rGO200, rGO200_{exf}, etc.

Figure 20 shows SEM images of the non-exfoliated samples that were slowly ramped between 150 and 300 °C at 0.5 °C/min which is where a significant amount of GO decomposition to rGO occurs. A very similar morphology to the original GO powder is observed. There is still a large variation in flake size and some sheets appear folded onto themselves. The reduction process at the lower temperature ramping rates does not significantly affect the morphology and structure of the flakes. This is also confirmed through surface area measurement by gas adsorption, showing no significant changes in the SSA for any of the reduced samples compared to the original GO powder.

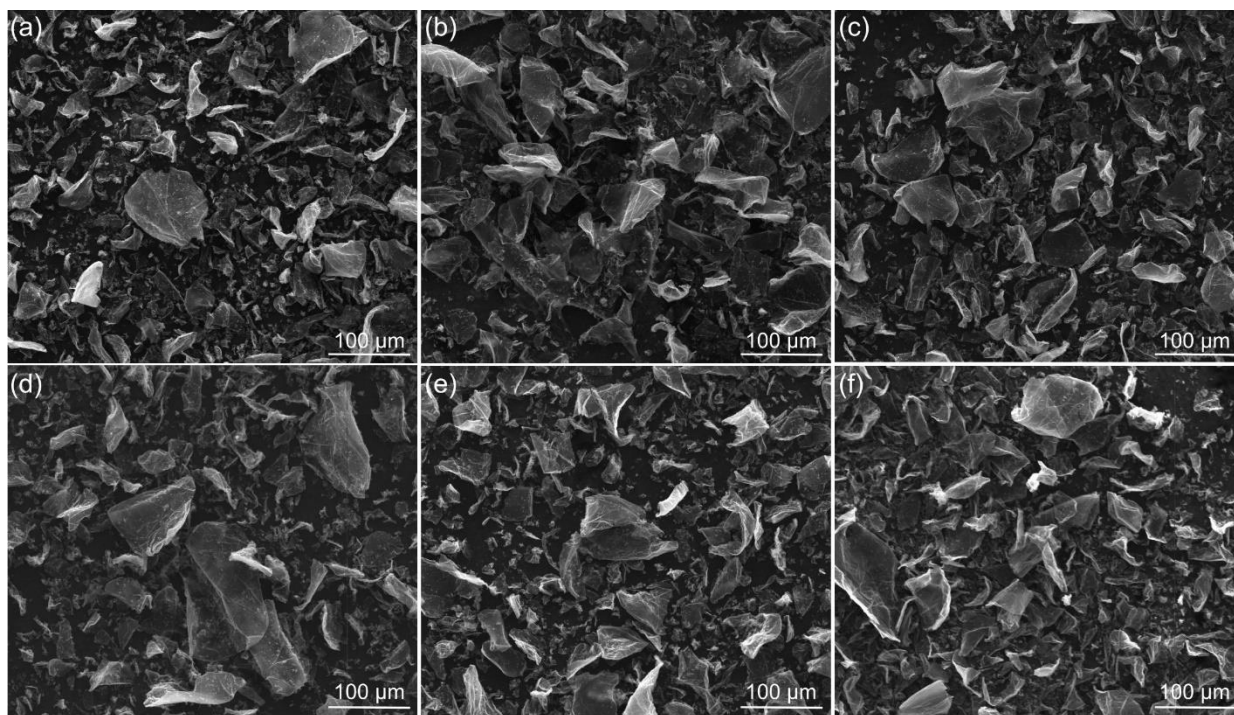


Figure 20: SEM images of (a) rGO200, (b) rGO300, (c) rGO400, (d) rGO600, (e) rGO800, (f) rGO1000

The exfoliated rGO samples synthesized with the higher heating rate show a very different morphology in SEM images. They have a more accordion-like structure caused by the rapid expansion of decomposition gases between the layers (Figure 21). In both the exfoliated and non-exfoliated samples, the reduction temperature does not appear to have an impact on the morphology of the sample.

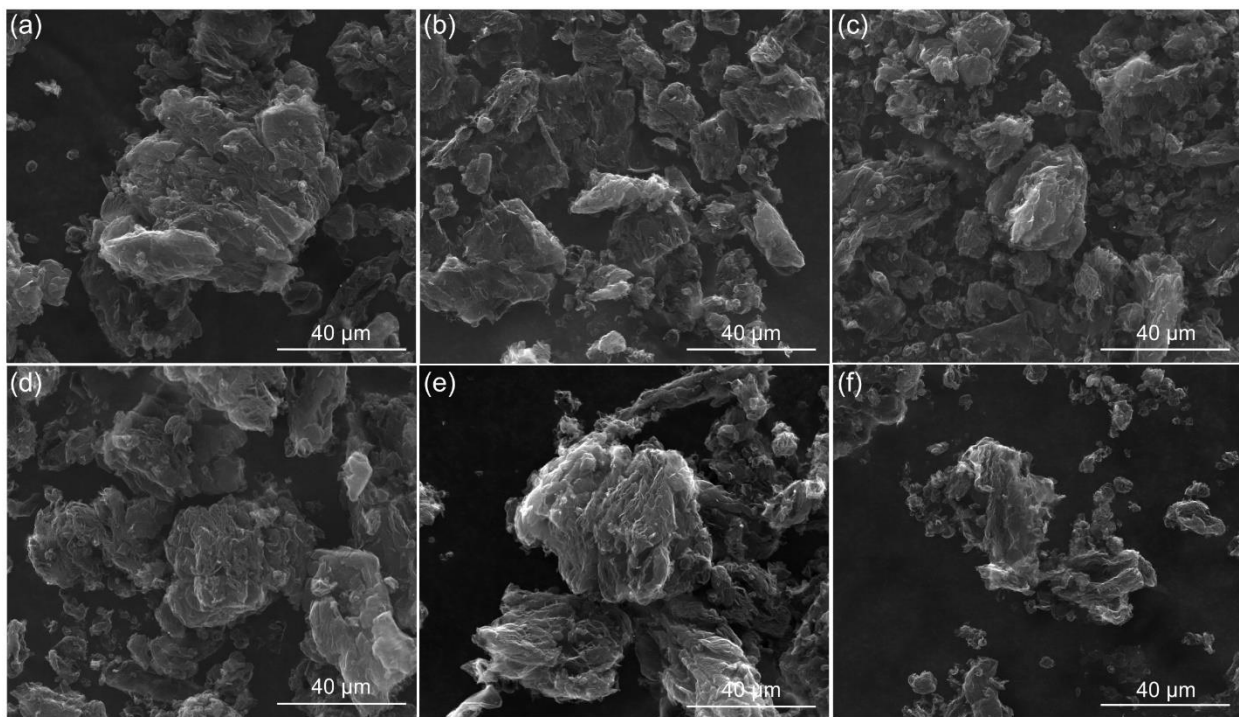


Figure 21: SEM images of (a) rGO200_{exf}, (b) rGO300_{exf}, (c) rGO400_{exf}, (d) rGO600_{exf}, (e) rGO800_{exf}, (f) rGO1000_{exf}

Following what can be observed from the SEM images, significantly increased SSAs are observed for the exfoliated samples compared to their non-exfoliated counterparts. The difference in SSA is clear (Figure 22a), where the taller cross-hatched bars belong to the exfoliated samples and are compared to the surface area of the non-exfoliated samples at the same reduction temperature. Visually, it's also easy to see that the same mass of GO, rGO400, and rGO400_{exf} occupy significantly different apparent volumes (Figure 22b). While the GO and rGO400 are more sand-like and settle at the bottom of the vial, rGO400_{exf} is very fluffy and occupies a larger portion of the vial.

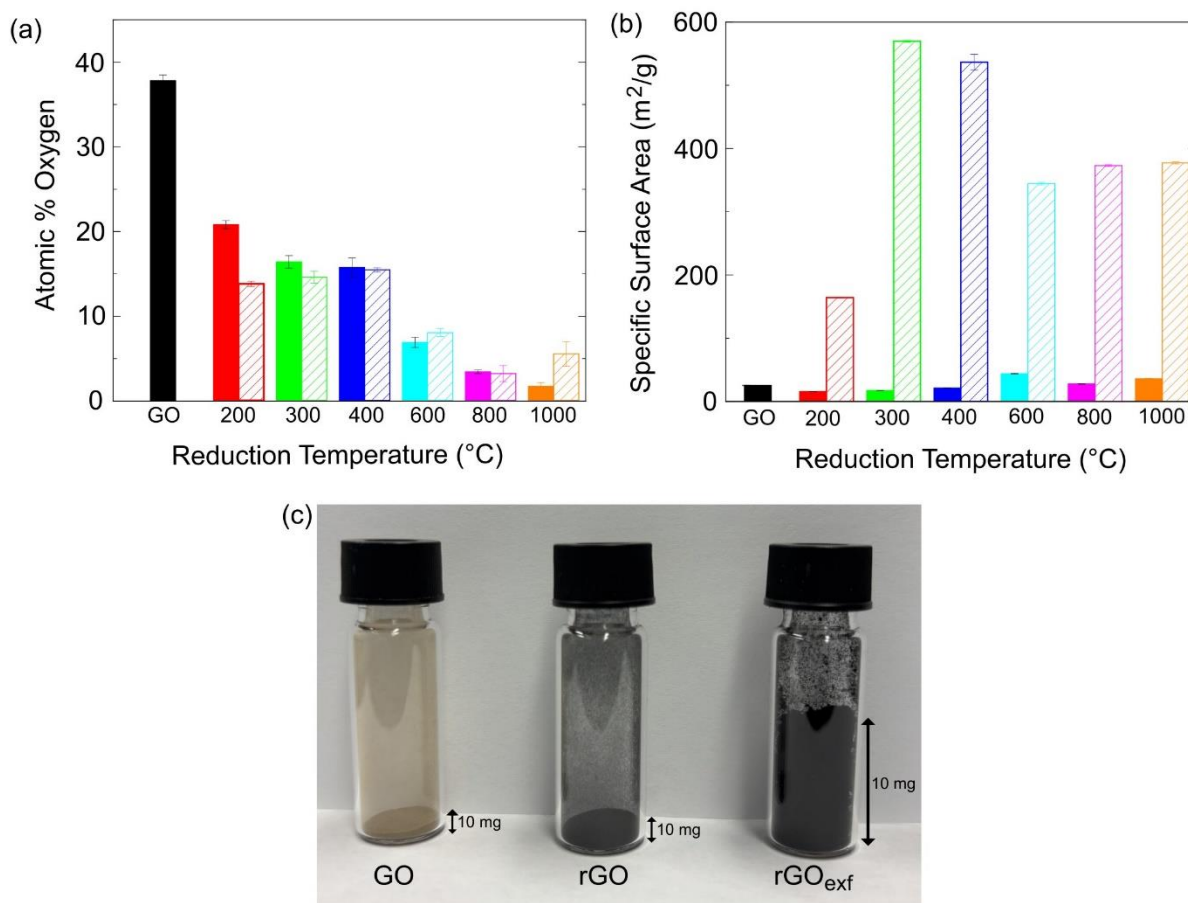


Figure 22: (a) Atomic oxygen percentage of non-exfoliated samples (solid colored bars) and exfoliated samples (cross-hatched bars), (b) BET measurements for non-exfoliated samples (solid colored bars) and exfoliated samples (cross-hatched bars), and (c) from left to right, 10 mg each of GO, rGO₄₀₀, and rGO₄₀₀_{exf}

EDX measurements taken on the non-exfoliated samples show a clear trend with a decrease in the oxygen content when the reduction temperature is increased, which is expected (Figure 22c).⁸⁵ The oxygen content values found through EDX measurements are averaged over six measurements taken at various spots on a pressed pellet of rGO material. Even with a low reduction temperature of 200 °C, the oxygen content is significantly decreased from the starting GO powder.

For the exfoliated samples, the oxygen content values are similar to their non-exfoliated counterparts at higher reduction temperatures. However, for the lower reduction temperatures of 200 °C and 300 °C, the oxygen content is lower when the sample is exfoliated. The reduction process is autoexothermic and generates heat, meaning that the exfoliated samples will likely

experience higher local temperatures due to the higher heating rate than the non-exfoliated samples which undergo a lower heating rate. The effect of the autoexothermic reaction is negligible when the reduction temperature goes to 400 °C and above as the oxygen content values start to more closely align between the exfoliated and non-exfoliated samples.

Based on XRD measurements, the crystallinity and d-spacing of the materials is heavily affected by whether exfoliation occurred or not and the remaining oxygen functional groups. The GO results exhibit a characteristic peak around $2\theta = 9^\circ$ owing to the main 001 reflection.⁸⁵ As calculated using Bragg's Law, the d-spacing of the GO material is 0.960 nm, which is larger than the interlayer spacing of graphite due to the oxygen functional groups. The non-exfoliated samples show a peak shifted to $2\theta = \sim 23\text{-}26^\circ$ as the lattice spacing is significantly reduced through the reduction process as those functional groups are removed.⁸⁵ The exfoliated samples have no XRD signal due to the complete loss of layered crystalline structure. As an example of this amorphous character, the signal for rGO400_{exf} is shown in Figure 23a. For the non-exfoliated samples, the d-spacing decreases with increasing reduction temperature as more oxygen groups are removed from the surface and the carbon layers can fit together more closely (Figure 23b). The interlayer spacing approaches that of graphite (0.335 nm).¹⁴ From the full-width-at-half-maximum (FWHM) values, the long-range crystallinity of the reduced samples decreases compared to the GO (Figure 23c). It is clear from both the calculated values and the plotted signals that higher reduction temperatures produce more amorphous samples, especially when the intensity of the rGO signals are normalized to the height of the GO peak.

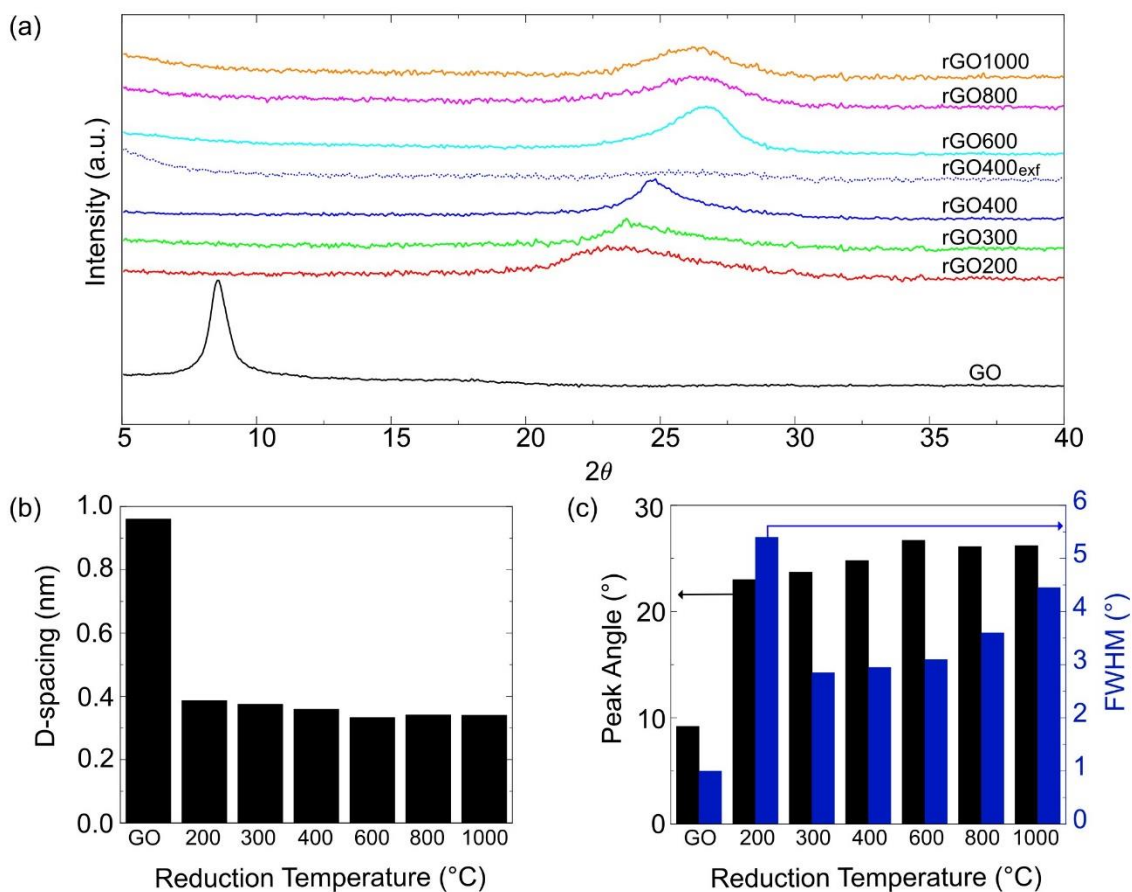


Figure 23: (a) XRD signals from GO, non-exfoliated samples, and rGO400_{exf}, (b) D-spacing of GO and non-exfoliated samples, (c) peak angle and FWHM values for GO and non-exfoliated samples

3.2.2 Differences in rate capability between exfoliated and non-exfoliated rGO

Rate capability results for all samples show that rGO400 (non-exfoliated) has the best performance, which is a surprising result. The lower reduction temperatures and slow heating rate samples (rGO400, rGO300, and rGO200) outperform the higher reduction temperatures (rGO600, rGO800, and rGO1000) by a significant margin. This is hypothesized to be because the remaining oxygen functional groups on the surface of the rGO can act as additional sodium storage sites. The larger interlayer spacing of the lower reduction temperature samples may also play a role in the increased specific capacity as the larger sodium ions are able to access more storage sites within the layered structure. For example, rGO1000 has very few oxygen groups remaining on the surface

and so the storage mechanism depends on surface adsorption. While this can be an effective storage mechanism, the low specific surface area and small interlayer spacing renders a large number of the surface storage sites inaccessible to the sodium ions and drastically lowers the specific capacity. In past works, 700 °C had been identified as the optimal reduction temperature for performance.⁷² The material was a high surface area rGO (567.07 m² g⁻¹) with an increased interlayer spacing of 0.46 nm and an oxygen content of 6.69%. Of the reduction temperatures investigated (700 °C, 800 °C, 900 °C, and 1000 °C), the reduction temperature of 700 °C produced the lowest surface area and highest interlayer spacing and oxygen content. However, they did not investigate any temperatures lower than 700 °C, prompting the question of if better performance could be achieved by lowering the reduction temperature and continuing to tune the material properties, such as lowering the SSA while maintaining an expanded interlayer spacing.

Figure 24a shows that the non-exfoliated samples reduced at higher reduction temperatures (600 °C, 800 °C, and 1000 °C) perform at a similar rate to each other and perform worse than the samples reduced at a lower temperature. rGO200 and rGO300 perform at a similar level to each other, while rGO400 shows the best performance overall. All samples regain their capacities when the cycling rate returns to 100 mA g⁻¹; this is evidence of the good reversibility of the storage mechanisms. Additionally, all samples perform better than the unreduced GO samples, confirming that the reduction process is essential for good electrochemical performance.

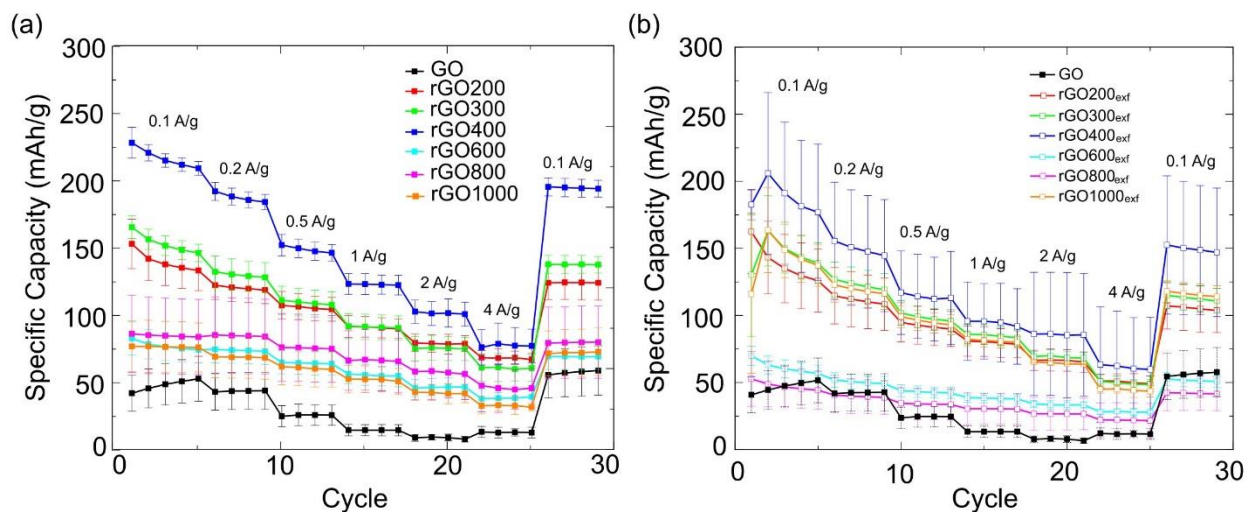


Figure 24: Rate capability performance of (a) non-exfoliated materials and (b) exfoliated materials. Errors bars indicate the corresponding standard deviation from three cells. All results are done with an active mass loading of 0.8 mg cm^{-2} .

The exfoliated samples were synthesized to be able to assess the impact of the surface area on the electrochemical performance of the cells overall, along with being able to assess the impact of the surface area at a single reduction temperature. When slurries were made using the same procedure and formulas as the non-exfoliated samples, it was immediately clear that the increased surface area of the exfoliated samples requires too much solvent to properly wet. Even a slurry with 2% solid content was unable to be properly cast onto copper foil. This would be an issue for scaling up production and commercialization, as the non-exfoliated samples could be easily integrated into a continuous, roll-to-roll process, while this is not currently possible for the exfoliated samples.

In general, the rate capability performance of the exfoliated rGO materials, seen in Figure 24b follow the same trends seen in the non-exfoliated samples, with the notable exception of rGO1000. rGO400_{exf} continues to show the highest performance, along with rGO200_{exf}, rGO300_{exf}, and rGO1000_{exf}. The cells made of rGO600_{exf} and rGO800_{exf} perform the worst. The rGO1000_{exf} cells show better performance compared to the other reduction temperatures; this is a change from the non-exfoliated sample set where rGO1000 had the worst performance. This could be because the

surface area exposed in the exfoliation process makes more of a difference in the rGO1000_{exf} sample as the interlayer spacing is among the smallest of the materials and there is the lowest number of oxygen functional groups remaining after the reduction process. This is an interesting finding as it implies that the impact of surface area depends on the reduction temperature, and by extension, the oxygen content.

The rate capability for the non-exfoliated versus exfoliated samples were compared for all reduction temperatures in Figure 25. The closed symbols are the exfoliated samples, and the open symbols indicate the non-exfoliated samples. For the lower reduction temperatures (200 °C, 300 °C, and 400 °C), the exfoliated samples seem to perform about the same as the non-exfoliated samples. This could indicate that the increased surface area does not affect or improve the performance during rate cycling at these reduction temperatures and oxygen contents. The interlayer spacing of the low surface area samples may be large enough due to the remaining oxygen groups that the sodium ions can still access the same amount of storage sites. For the samples reduced to 600 °C and 800 °C, it was observed that the non-exfoliated samples perform better than the exfoliated samples. This is an interesting result as the interlayer spacings of the non-exfoliated materials are slightly lower due to the decreased number of oxygen functional groups, which should lead to lower capacities when compared with the exfoliated samples that have a high specific surface area. While in theory the increased surface area could lead to a larger number of storage sites, it could be that the SEI formation occurs over such a large amount of material that the extra storage sites are consumed in this process and rendered inaccessible to the sodium ions. The only reduction temperature at which the exfoliated material performed better is 1000 °C. This could be attributed to the fact that rGO1000 has a smaller interlayer spacing than the lower reduction temperatures and the least amount of oxygen functional groups remaining. Thus, the

increased number of storage sites provided by the exfoliation process does play a role in increasing the capacity.

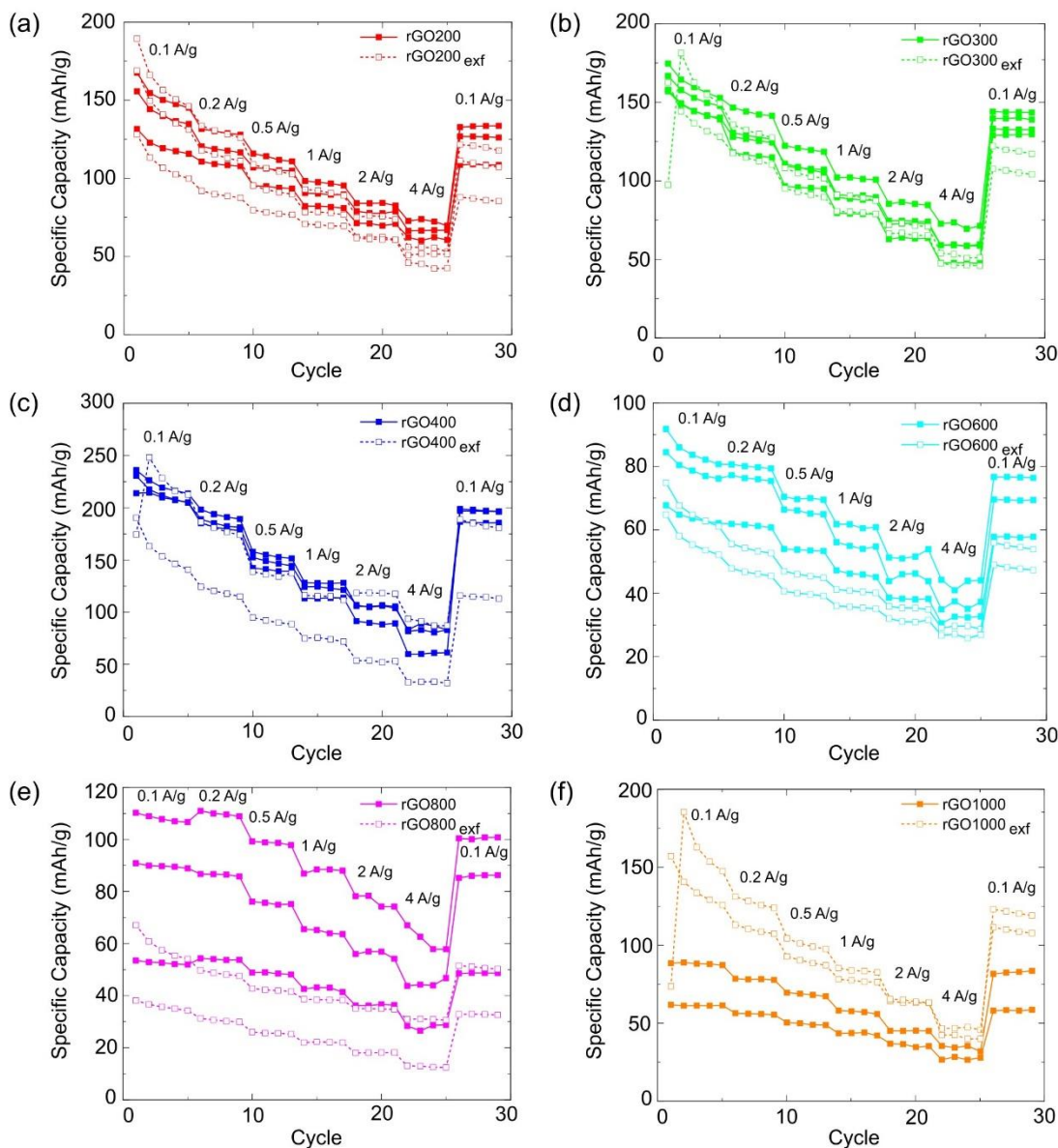


Figure 25: Rate capability comparison for (a) rGO200 versus rGO200_{exf}, (b) rGO300 versus rGO300_{exf}, (c) rGO400 versus rGO400_{exf}, (d) rGO600 versus rGO600_{exf}, (e) rGO800 versus rGO800_{exf}, and (f) rGO1000 versus rGO1000_{exf}. The active material loading used is 0.8 mg cm⁻².

Figure 26 shows the coulombic efficiency for all samples tested. The ICE for all non-exfoliated samples is within the range of 45-60% (see Table 8 for specific values), which falls in the range seen for many carbon materials,⁷⁴ but is too low for commercial applications. The CE for the

second cycle is improved over the ICE, with rGO400 having the highest second cycle CE. However, much lower ICEs are observed in the exfoliated samples, with the highest ICE being only 20%. This is due to the massive amount of SEI that needs to be formed on the surface of the electrode during the first cycles. This process consumes large amounts of sodium ions that are not released during the next charging cycle, leading to low efficiencies. This is a significant advantage of the non-exfoliated samples, as there is simply less surface area exposed for the SEI to form on, therefore reducing the number of sodium ions consumed in the first cycle.

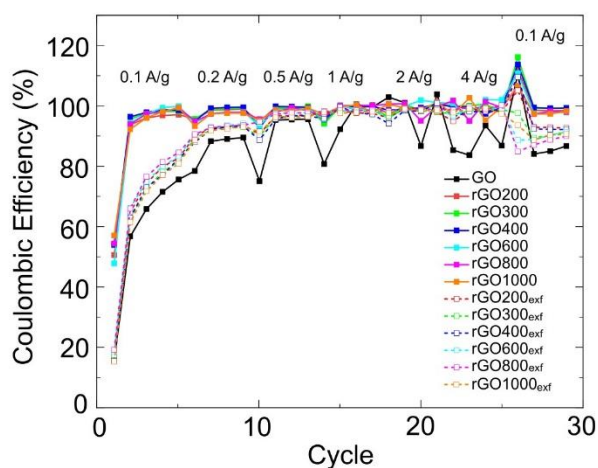


Figure 26: CE during rate capability testing for exfoliated and non-exfoliated samples. The jump at cycle 25 occurs because of the current rate switching from 4 A g^{-1} to 0.1 A g^{-1} . A representative cell for each sample is chosen with an active material loading of 0.8 mg cm^{-2} .

From Figure 26 it is clear to see that the exfoliated samples take approximately 10 cycles to reach the same CEs as the non-exfoliated samples. The non-exfoliated samples quickly stabilize, while the exfoliated samples continue to consume sodium ions in irreversible reactions, most likely SEI formation, well into cycling. Additionally, it can be noted that the CE for the last 4 cycles (when the current density is returned to the low values of 100 mA g^{-1}) drops off once again for the exfoliated samples, while it remains at or close to 100% for the non-exfoliated samples. This may be because there are still parts of the active material that are not covered in SEI in the exfoliated samples and once the current density is lowered, the slow charging rate allows sodium ions time

to reach those areas and form the missing SEI, using up sodium ions and once again reducing the CE. As the non-exfoliated samples have less exposed surface area to consume sodium ions through SEI reactions, there is no remaining surface area to be covered in those final cycles and the CE remains high.

Table 8: Electrochemical parameters from the first and second cycles of rate capability testing (at 0.1 A g^{-1}) for all samples. The active material loading used is 0.8 mg cm^{-2} .

	Initial sodiation capacity (mAh/g)	1st cycle capacity loss (mAh/g)	ICE	2nd cycle capacity loss (mAh/g)	CE 2nd cycle
GO	169.7	143.6	15.4%	21.6	56.9%
	307.8	264.5	14.1%	43.6	52.1%
	197.3	144.7	26.7%	35.2	61.8%
rGO200	307.4	151.7	50.6%	9.3	94.0%
	294.6	127.0	56.9%	9.7	94.1%
	258.5	126.9	50.9%	8.7	93.4%
rGO300	324.1	149.5	53.9%	7.1	95.9%
	313.1	146.3	53.6%	6.4	96.1%
	274.8	117.3	57.1%	6.4	95.9%
	310.4	152.5	50.9%	9.2	94.2%
rGO400	436.0	200.1	54.1%	7.9	96.6%
	415.4	184.9	55.9%	9.2	95.9%
	421.9	207.9	50.7%	9.0	96.0%
rGO600	190.4	105.9	44.4%	16.3	83.2%
	191.7	99.9	47.9%	4.9	94.6%
	137.1	69.3	49.4%	9.9	86.8%
rGO800	113.0	59.5	47.3%	11.3	82.4%
	202.3	92.1	54.5%	6.7	94.2%
	148.0	57.2	61.4%	4.2	95.5%
rGO1000	108.7	46.5	57.1%	5.0	92.5%
	137.2	48.4	64.7%	3.6	96.1%

rGO200_{exf}	1116.4	926.0	17.0%	89.7	64.9%
	1007.8	838.9	16.8%	85.1	63.7%
	683.6	555.5	18.7%	54.3	67.6%
rGO300_{exf}	932	769.4	17.4%	85.6	62.9%
	486.9	389.5	20.0%	588.5	23.5%
rGO400_{exf}	1225.4	1035.2	15.5%	95.5	63.1%
	961.0	786.6	18.2%	351.7	41.4%
rGO600_{exf}	404.5	329.6	18.5%	34.4	66.3%
	353.5	288.7	18.3%	28.1	67.3%
rGO800_{exf}	349.0	281.9	19.2%	31.1	66.1%
	225.7	187.6	16.9%	20.8	63.8%
rGO1000_{exf}	1031.1	873.6	15.3%	88.0	61.6%
	609.4	535.4	12.1%	511.8	26.7%

3.2.3 Differences in lifetime cycling between exfoliated and non-exfoliated rGO

During lifetime cycling, rGO400 electrodes still consistently perform the best when compared to the other reduction temperatures and compared to the exfoliated samples, though the difference in performance is much smaller when compared to the rate capability testing. All reduced material outperforms the unreduced samples made with GO, which have specific capacities less than 10 mAh g⁻¹ once the current density is increased to 1 A g⁻¹.

The capacity retention of the cells made with non-exfoliated material shows a clear difference based on the reduction temperature. The lower reduction temperatures (200 °C, 300 °C, 400 °C) show improved capacity retentions across all cells when compared to the higher reduction temperatures (600 °C, 800 °C, 1000 °C), as seen in Figure 27a. 100% capacity retention is defined as the capacity in the 16th cycle – the first cycle run at 1 A g⁻¹ after the 15 break-in cycles at 100 mA g⁻¹. There is little variation between the non-exfoliated cells at a certain reduction temperature.

As the capacity retention does not reach values that would be appropriate for commercial applications, it is important to understand this parameter and why there is such a clear difference between the reduction temperatures. The higher reduction temperatures see a very steep loss in capacity over the first 25 cycles before the rate of capacity loss slows, while the lower reduction temperatures see less of a drop over the initial cycles. The interlayer spacing of the samples could play a role in this phenomenon as sodium ions end up irreversibly trapped between layers that are closer together, reducing the number of accessible storage sites and capacity available for future cycles.

For the exfoliated samples, the capacity retention over the lifetime cycling of the cells is worse overall. In Figure 27b, after 200 cycles, all samples have retained less than 80% of their capacity, with rGO400_{exf} showing the worst retention and rGO1000_{exf} showing the best retention. The trend of lower reduction temperatures showing increased capacity retention over those with higher reduction temperatures is not clear to see in the exfoliated samples. The lower retention is hypothesized to be due to the instability of the SEI formed on the surface of the exfoliated material as more active material is rendered unusable through its breaking and reformation.

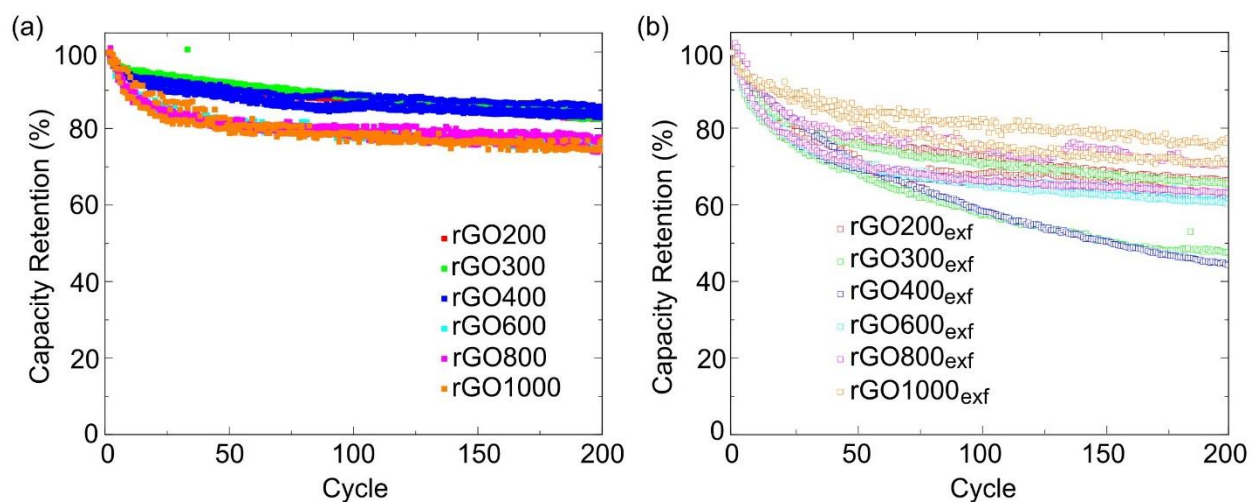


Figure 27: Capacity retention for lifetime cycling at 1 A g^{-1} of (a) non-exfoliated samples, and (b) exfoliated samples. 100% capacity is taken as the discharge capacity in the first cycle at 1 A g^{-1} . All results are from cycling at 1 A g^{-1} and an active material loading of 0.8 mg cm^{-2} .

The lifetime cycling results for the non-exfoliated versus exfoliated samples were compared for all reduction temperatures in Figure 28. In all cases, the non-exfoliated samples show higher specific capacities and better capacity retention than the exfoliated samples during lifetime testing, although the difference is less pronounced at the higher reduction temperatures. $\text{rGO1000}_{\text{exf}}$ performs at a very similar level to rGO1000 , unlike in the rate capability testing where it showed a large improvement, though there is variation within the samples.

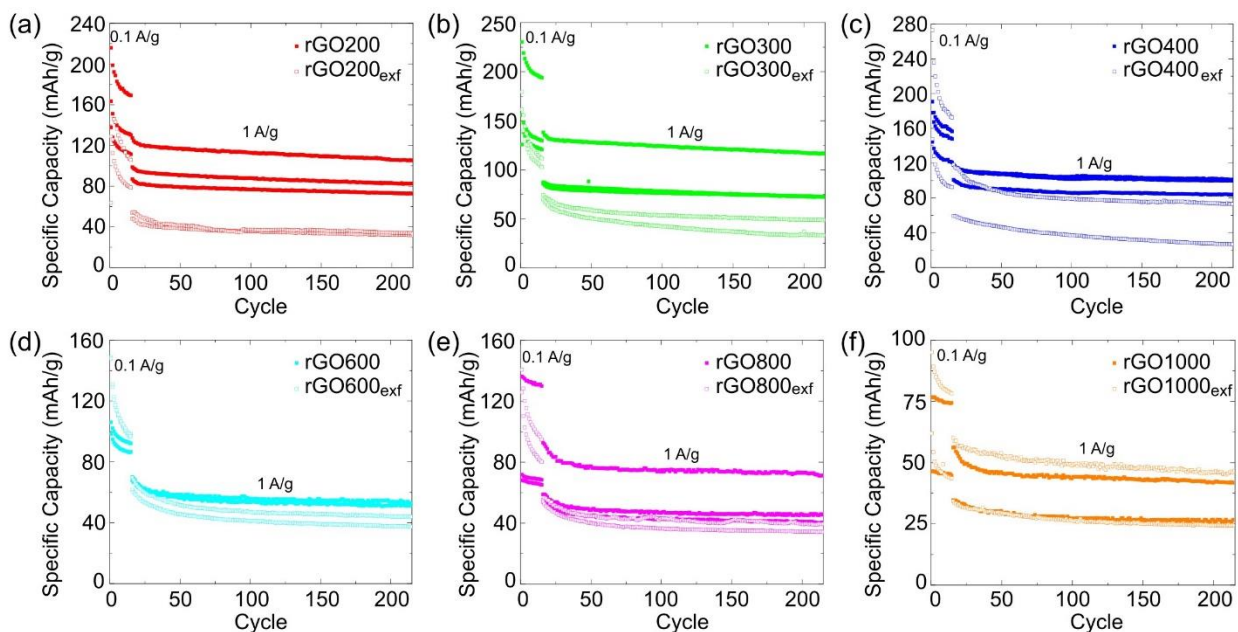


Figure 28: Lifetime cycling comparison for (a) rGO200 versus $\text{rGO200}_{\text{exf}}$, (b) rGO300 versus $\text{rGO300}_{\text{exf}}$, (c) rGO400 versus $\text{rGO400}_{\text{exf}}$, (d) rGO600 versus $\text{rGO600}_{\text{exf}}$, (e) rGO800 versus $\text{rGO800}_{\text{exf}}$, and (f) rGO1000 versus $\text{rGO1000}_{\text{exf}}$. Cells are cycled for 15 cycles at 0.1 A

The non-exfoliated samples show better stability over the first 200 cycles of their lifetime when compared to their exfoliated counterparts (Figure 29). The low surface area achieved through keeping the heating rate low during the reduction process does not promote uneven SEI formation and breaking in the same way the high surface area of the exfoliated material do. Once again, $\text{rGO1000}_{\text{exf}}$ performs at a very similar level to rGO1000 . The limited number of oxygen groups

present in these samples seems to negate the effect of surface area when it comes to capacity retention.

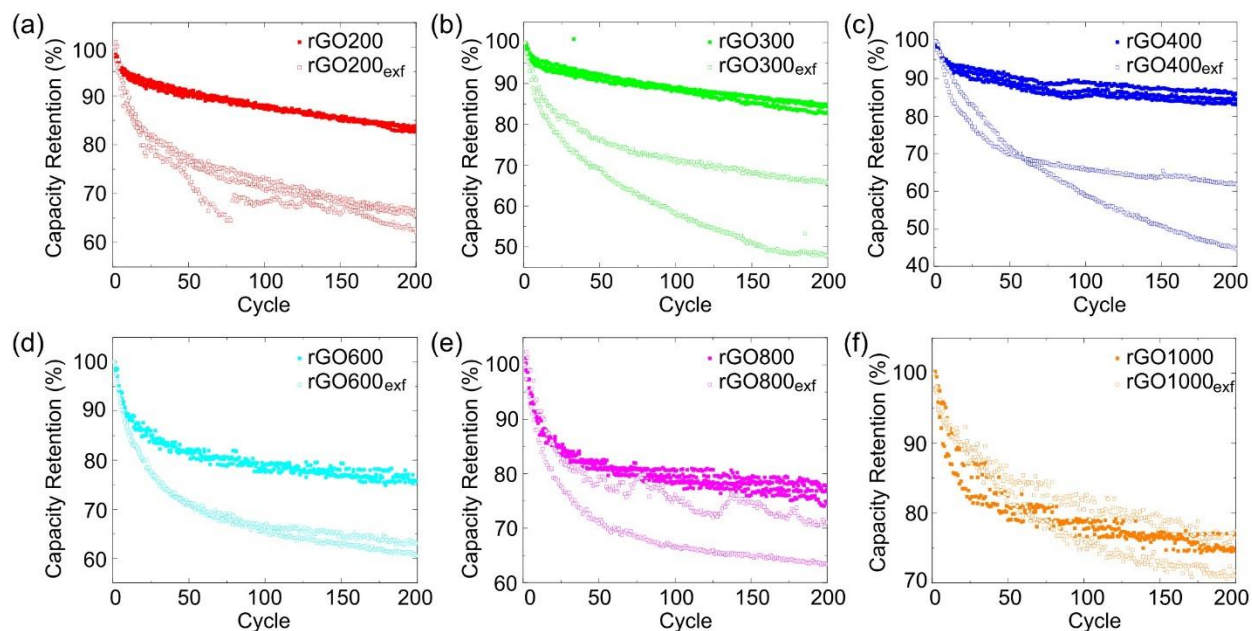


Figure 29: Capacity retention comparison for (a) rGO200 versus rGO200_{exf}, (b) rGO300 versus rGO300_{exf}, (c) rGO400 versus rGO400_{exf}, (d) rGO600 versus rGO600_{exf}, (e) rGO800 versus rGO800_{exf}, and (f) rGO1000 versus rGO1000_{exf}. 100% capacity is taken as the discharge capacity in the first cycle at 1 A g⁻¹. The active material loading used is 0.8 mg cm⁻².

3.2.4 Comparison of charge/discharge curves between exfoliated and non-exfoliated rGO

The sodiation/desodiation curves for rGO400 and rGO400_{exf} (as rGO400 is the best performing sample) were analyzed to attempt to understand the storage mechanisms of each sample and if they differ between exfoliated versus non-exfoliated samples. Based on the curves for the second cycle at 100 mA g⁻¹ (Figure 30a), the main difference is in the low voltage region. For rGO400_{exf}, a long low-voltage plateau can still be observed in the second cycle, attributed to continuing SEI formation. In rGO400, the low-voltage plateau is only seen during the first cycle, and then disappears for the second cycle, once again providing evidence that a stable SEI takes longer to form in the exfoliated samples.

The desodiation curves for rGO400 and rGO400_{exf} show similar shapes at the various current densities, indicating that the storage mechanisms are similar, though it should be noted that during both sodiation and desodiation, the exfoliated sample has a larger voltage at the same capacity. During sodiation, the shift of the rGO400_{exf} curve to the right could be a product of increased irreversible capacity loss compared to rGO400. During desodiation, the shift of the rGO400_{exf} curve to the left could be due to a larger IR drop across a thicker SEI layer. As previously commented on based on the ICE and second cycle CE values, the SEI layer is hypothesized to be thicker and less stable for the exfoliated samples, potentially slowing down ion transport. In lithium-silicon batteries, the SEI was found to be less conductive to lithium ions than the electrode material, inhibiting ion transport and slowing reaction kinetics.⁸⁶ The conductivity of the SEI layer was also suggested to be related to the type of electrolyte used. Similar studies should be undertaken with this system to understand differences in ion transport across the SEI layer in exfoliated and non-exfoliated samples and to further optimize SEI formation.

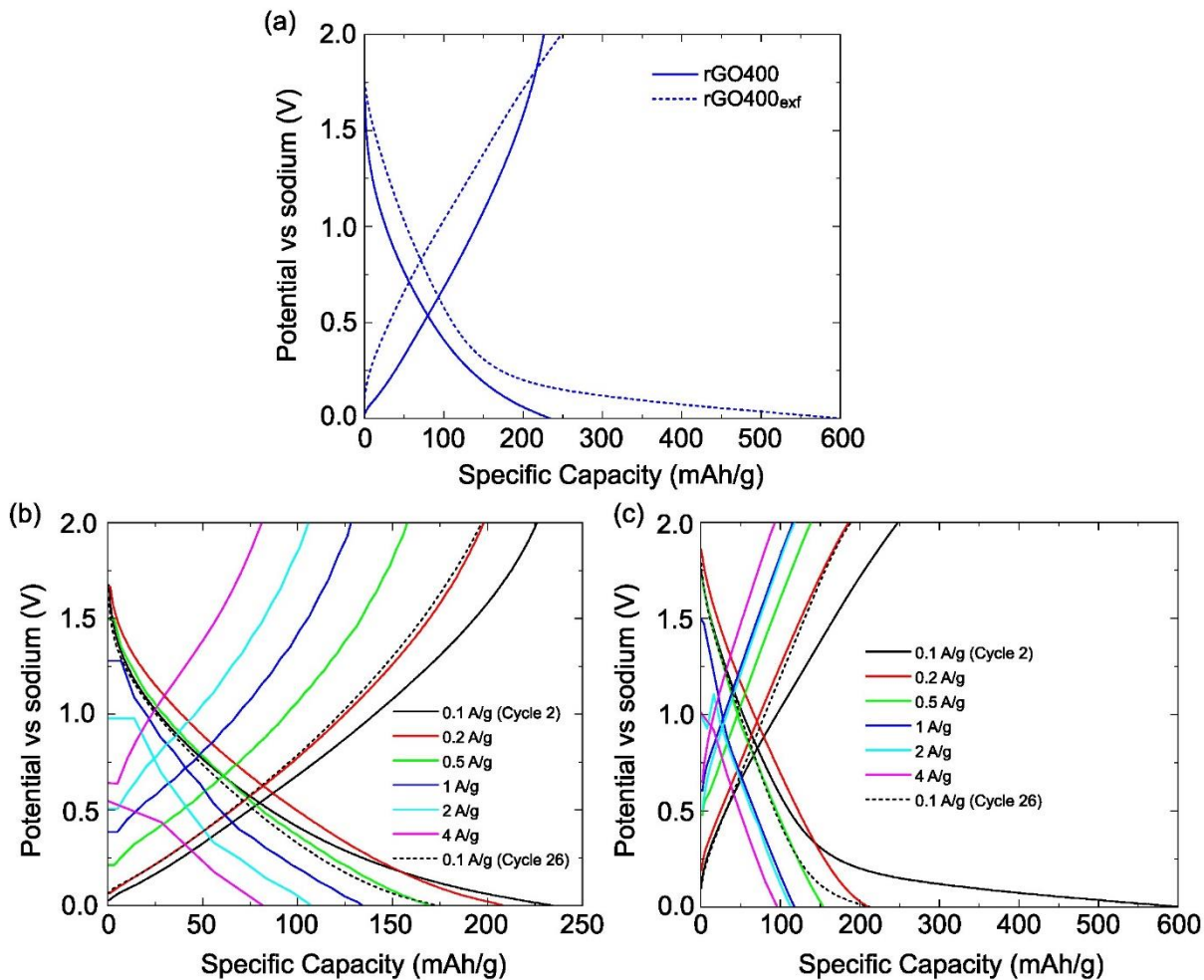


Figure 30: Sodiation/desodiation curves for (a) rGO400 and rGO400_{exf} at 0.1 A g⁻¹, (b) rGO400 at various current densities, and (c) rGO400_{exf} at various current densities. All results are taken with an active mass loading of 0.8 mg cm⁻².

3.2.5 Effects of rGO surface area and oxygen content on overall performance

Based on the totality of the electrochemical data and the comparison between non-exfoliated and exfoliated material, it was observed that the non-exfoliated material provides better performance and stability compared to the exfoliated material at the same reduction temperature. This is shown to be the case in both rate capability tests and lifetime tests. The only exception is rGO1000; rGO1000_{exf} has better rate performance due to its increased surface area and increased accessible storage sites for sodium ions. The exfoliated material does not show an increase in performance at any of the other reduction temperatures.

When considering just the non-exfoliated samples, it appears that there is a maximum oxygen content concentration that leads to peak performance and it's approximately 15%. When the oxygen content is lower (rGO600, rGO800, and rGO1000), the number of storage sites available for the sodium ions is much lower and reduces the capacity. When the oxygen content increases above 15% (rGO300, rGO200, GO), the capacity drops once again and the performance decreases. This could be due to a lower conductivity of the samples, which makes it more difficult for the sodium ions to migrate through the material and reach additional storage sites, as many studies have linked an increase in reduction temperature with an increase in conductivity.^{72,85,87} Though rGO400 is expected to have a lower conductivity than the samples with a higher reduction temperature due to the higher number of oxygen functional groups remaining, it could be that rGO400 is the balance of accessible sodium ion storage sites versus decreased conductivity to achieve peak performance.

Compared to the performance achieved in other studies, as shown in Table 9, that use thermally reduced rGO as an anode material, as well as the current standard in hard carbon anodes, the low surface area rGO400 performs well in rate capability and in ICE, showing good performance for a much lower reduction temperature and lower SSA. The highest ICE currently seen is that of a presodiated hard carbon anode, achieved by immersing the hard carbon anodes in a sodium biphenyl solution.²¹ Though they report an ICE of 100% in a half cell and 95% in a full cell, the sodiation and desodiation capacities of the first cycle are lower than those of a pristine hard carbon anode. The OCV is also decreased from 2.83 V to 0.51 V. Due to the presodiation process, it's more accurate to say that this high CE is the CE of the 2nd cycle.

Table 9 presents the SSA and cumulative irreversible capacity over the first 3 cycles for all rGO samples produced in this work, as well as other rGO samples from the literature. The cumulative irreversible capacity increases with the SSA, a trend showcased in Figure 31.

Table 9: SSA and cumulative irreversible capacity values for select rGO in SIB anode works

Sample	Reduction method	SSA	Cumulative Irreversible Capacity (3 cycles)
rGO200 ^{This work}	Slow thermal reduction (200 °C)	15.6 m ² g ⁻¹	150 mAh g ⁻¹
rGO200 _{exf} ^{This work}	Fast thermal reduction (200 °C)	164.2 m ² g ⁻¹	895.1 mAh g ⁻¹
rGO300 ^{This work}	Slow thermal reduction (300 °C)	17.3 m ² g ⁻¹	153 mAh g ⁻¹
rGO300 _{exf} ^{This work}	Fast thermal reduction (300 °C)	269.7 m ² g ⁻¹	986.6 mAh g ⁻¹
rGO400 ^{This work}	Slow thermal reduction (400 °C)	21.3 m ² g ⁻¹	210.8 mAh g ⁻¹
rGO400 _{exf} ^{This work}	Fast thermal reduction (400 °C)	536.5 m ² g ⁻¹	1225.8 mAh g ⁻¹
rGO600 ^{This work}	Slow thermal reduction (600 °C)	38.8 m ² g ⁻¹	109.5 mAh g ⁻¹
rGO600 _{exf} ^{This work}	Fast thermal reduction (600 °C)	344.4 m ² g ⁻¹	359.8 mAh g ⁻¹
rGO800 ^{This work}	Slow thermal reduction (800 °C)	27.6 m ² g ⁻¹	81.1 mAh g ⁻¹
rGO800 _{exf} ^{This work}	Fast thermal reduction (800 °C)	373 m ² g ⁻¹	275.8 mAh g ⁻¹
rGO1000 ^{This work}	Slow thermal reduction (1000 °C)	36 m ² g ⁻¹	53.7 mAh g ⁻¹
rGO1000 _{exf} ^{This work}	Fast thermal reduction (1000 °C)	377.3 m ² g ⁻¹	1083.3 mAh g ⁻¹
Reduced graphene oxide ⁵⁸	Thermal reduction (750 °C)	330.9 m ² g ⁻¹	627 mAh g ⁻¹ **
Crumpled graphene ⁷⁰	Thermal reduction (800 °C) and sintering (2800 °C)	6.4155 m ² g ⁻¹	186 mAh g ⁻¹ *
Oxygen-functionalized graphene nanosheets ⁷²	Thermal reduction (700 °C)	567.07 m ² g ⁻¹	750 mAh g ⁻¹ *
Iodine-doped reduced graphene oxide ⁶⁰	Thermal reduction (950 °C)	359.3 m ² g ⁻¹	625 mAh g ⁻¹ **
Activated crumpled graphene ⁷⁵	Thermal reduction (500 °C) and activation (350 °C)	318 m ² g ⁻¹	580 mAh g ⁻¹ *

Reduced graphene oxide nanosheets ⁵⁹	Microwave irradiation reduction (1600 W)	743 m ² g ⁻¹	923.2 mAh g ⁻¹ ***
Reduced graphene oxide ⁶¹	Chemical reduction (hydrazine, 100 °C)	637 m ² g ⁻¹	1460 mAh g ⁻¹ **
Reduced graphene oxide ⁷³	Chemical reduction (tin (II) chloride, RT)	198 m ² g ⁻¹	602 mAh g ⁻¹ **
Reduced graphene oxide nanosheets ⁷⁶	Microwave irradiation reduction (750 W)	240 m ² g ⁻¹	340 mAh g ⁻¹ ***

* Cumulative irreversible capacity is estimated from charge/discharge curves given in the reference.

** Cumulative irreversible capacity is only estimated for the first 2 cycles due to data availability. Value is estimated from charge/discharge curves given in the reference.

*** Cumulative irreversible capacity is only estimated for the first cycle due to data availability. Value is estimated from charge/discharge curves given in the reference.

Figure 31 shows an increasing trend with cumulative irreversible capacity versus SSA. All of the non-exfoliated samples produced in this work fall in the bottom left corner of the plot, while the exfoliated samples shift to up and to the right compared to their non-exfoliated counterparts. When data points from other works are added, it becomes more clear that SSA is a relatively good predictor of irreversible capacity. With increased surface area, more sodium ions are required to form the SEI over the entirety of the electrolyte-accessible surface, increasing the irreversible capacity. This once again motivates the need for the development of low-surface area materials that can limit the amount of SEI formed. Additionally, there is not a clear impact of reduction temperature on the cumulative irreversible capacity, implying that we have successfully teased out the impact of surface area on the electrochemical performance and decoupled it from the impact of the rGO chemistry.

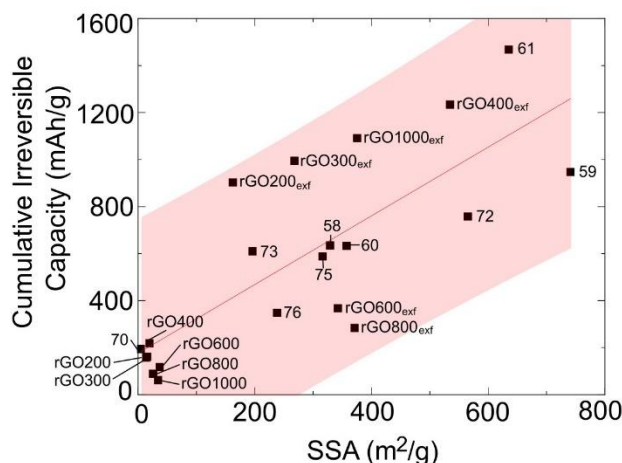


Figure 31: Cumulative irreversible capacity compared to specific surface area in other carbon material works. The red line indicates a linear trendline. The shaded red area indicates a 95% prediction interval – the interval where 95% of future values are expected to fall.

3.3 Conclusion

In conclusion, a systemic study of the impact of oxygen content and specific surface area on the performance of rGO as an anode material in SIBs was conducted. It was found that non-exfoliated material reduced to a maximum temperature of 400 °C showed the best overall performance, an interesting result that hasn't been seen before. This is hypothesized to be because rGO400 has a balance of increased storage sites due to remaining oxygen functional groups and increased interlayer spacing, while maintaining the high conductivity needed to be an effective anode material. It was also shown that increasing the specific surface area of the material by exfoliating it during the reduction process did not provide any major performance increases, except at the high reduction temperature of 1000 °C. The increased surface area only impacts the performance when there are not enough accessible storage sites in the non-exfoliated sample, such as is the case for rGO1000. The ICE of the exfoliated samples was also drastically decreased compared to the non-exfoliated samples as there is more surface to be covered by the SEI, a process that consumes sodium ions and renders them unusable for the following discharge cycle. Increased surface area makes it more difficult to make and cast slurries, as the increased folds and layers of

the material require large amounts of water or other solvents to wet it and it cannot be effectively dispersed. The non-exfoliated material was shown to be better in rate capability testing, lifetime testing, ICE metrics, and in processability as higher solid content slurries were able to be achieved. This is true for all reduction temperatures studied with the exception of the rGO1000_{exf} which showed improved rate performance over its non-exfoliated counterpart.

4 Conclusions

In this thesis, different carbon-based anode materials were investigated for sodium-ion batteries. The overall objective is to understand how the material properties and structure of the active material plays a role in optimizing electrochemical performance. As SIB technology continues to advance, being able to answer these questions will be essential for the commercialization of this technology.

In Section 2, a spray dried rGO@RPNP composite was developed. The core-shell structure produced through spray drying was made of RPNPs wrapped in GO sheets. The composite was then reduced through a liquid phase chemical reduction with hydrazine. There were many processing challenges as the RPNPs are a difficult and unstable material to work with and their interaction with the GO sheets during spray drying is not fully understood. Nonetheless, it was shown that this composite could achieve a reversible capacity of 192 mAh g^{-1} at 60 mA g^{-1} and an ICE of 27%. While this performance is not commercially viable, the performance of the composite is improved over that of only RPNPs or only GO as an active material, indicating that the core-shell structures provide increased stability and can prevent the pulverization of the RP. The difference between this active material in LIBs and SIBs was also investigated. While the composite exhibited higher specific capacities in rate capability testing with LIBs, it showed increased stability in SIBs based on the charge-discharge curves. This provides a starting point for further optimization into this system, including additional work into how the material properties beyond the composite structure can influence the performance.

In Section 3, the impact of reduction temperature and heating rate was investigated on the electrochemical performance of rGO in SIB anodes. Through the work in Section 2, questions still remaining about how the material properties and structures of the RPNPs and rGO affected the

electrochemical performance of the composite. While rGO is a popular anode material for SIBs, there is no systemic study that decouples the effects of rGO chemistry and surface area to understand their individual impact on performance. Therefore, rGO samples were synthesized through a thermal reduction process to a maximum temperature in the range between 200 °C and 1000 °C. The heating rate was also varied to produce an exfoliated (high surface area) and non-exfoliated (low surface area) sample at each reduction temperature. It was found that a maximum reduction temperature of 400 °C and a slow reduction process to maintain a low surface area provided the best performance, achieving a reversible capacity of 226 mAh g⁻¹ at 100 mA g⁻¹. The non-exfoliated samples at all reduction temperatures showed increased ICEs and reached CEs close to 100% much sooner than their exfoliated counterparts, exhibiting improved SEI stability and reduced irreversible capacities. It was shown that increased surface area leads to larger amounts of irreversible capacity, which is detrimental for using these materials in full cells where the sodium available is limited. This work sets up the motivation for using low temperature and low surface area carbon materials in SIB anodes.

4.1 Future work

4.1.1 Improvements for spray dried rGO@RPNP composites

Section 2 showed the potential of using this system as an anode material but also exposed limitations that need to be addressed. To start, the RPNP loading within the core-shell structures should be improved and optimized. Work can be undertaken at two steps in the process to increase the loading: the spray drying step and reduction process. Spray drying parameters should be systematically investigated to achieve high loadings, as well as parameters earlier in the synthesis process, such as the size of the RPNPs. The amount of RPNPs present in the core-shell structures also seems to decrease after the liquid-phase reduction. This needs to be addressed as it is clear

that the reduction is essential for increasing the conductivity of the active material and improving the ICE. There are three avenues that could be worth further investigation.

- 1) Vapor-phase reduction removes the need to dissolve the spray dried powder in water. It is hypothesized that the dissolving of the powder in water could be causing the uncrumpling of the core-shell structures.
- 2) A sealing process could be used to seal the core-shell structures before the spray dried powder is dissolved in water. This could be in the form of a thermal annealing step of a chemical sealing, such as with polydopamine.⁷⁸
- 3) Based off the work in Section 3, a low temperature thermal reduction process could be used on the core-shell structures. This would avoid the need for the high temperatures that induce the transformation to white phosphorus. As the low temperature process was also shown to provide the best performance, this could improve the overall performance of the composite compared to other reduction methods.

Next, the ICE of the spray dried material needs to be improved to be on par with both existing carbon-red phosphorus composites and commercially available materials. Strategies to increase the ICE may also improve the rate capability to meet the current benchmarks. Section 3 showed that using a low surface material improved the ICE in SIB anodes, so a low surface area GO material could be used in the spray drying step. Additional routes for improvements could include artificial SEI coatings or electrolyte additives to reduce irreversible side reactions.

Finally, more detailed studies should be undertaken in order to understand the transport of sodium through the rGO shells. Preliminary analysis of the charge/discharge curves suggest that the RPNPs are not being utilized at higher current densities but are being used at the lower rates. A better understand of the transport of sodium through the rGO shells would be able to shed some

light on why this is occurring. It would also be interesting to investigate whether the thickness of the shells surrounding the RPNPs is controllable and has an impact on the cycling performance. The SEI formation on these shells is also important to understand as thick SEI layers will impede sodium ion transport.

4.1.2 Improvements for low temperature and low surface area rGO materials

This study opens up the door for future works into the advancement of rGO as an SIB anode material. This work has shown the importance of being able to separately understand the effects of surface area and rGO chemistry on the electrochemical performance to continue improving performance and reducing irreversible capacity. The discovery that a low temperature reduction process can provide increased performance over higher reduction temperatures is important for future commercialization and has implications for the processability of these materials.

There are many future avenues for research that should be undertaken to further this work.

- 1) The ICE needs to be increased. This could be achieved through the development of an artificial SEI layer or investigation into electrolyte additives that could promote the rapid formation of a stable SEI.
- 2) More work should be done to understand the storage mechanisms of the sodium ions. This could be done through CV testing at different scan rates to see the impact of surface storage versus intercalation storage. Theoretical calculations or modelling could also be done.
- 3) Combining this work with the work in Section 2, the impact of surface area and rGO chemistry could be analyzed when the material is used as part of the rGO@RPNP composite. Low surface area and increased defects in the core-shell structures should improve the sodium ion transport through the shells and allow the RPNPs to be fully

utilized at higher current rates. A low temperature reduction could also be an important safety feature and reduce or eliminate the transformation to white phosphorus.

Investigations into rGO400 as part of composite materials would also be interesting. In addition to attempting to integrate it into the system described in Section 2 with RP, its utility should be tested as part of composites with other materials capable of alloying with sodium such as tin, antimony, or silicon.^{4,12} The increased ICE of the low surface area rGO could help improve the ICE for the entire composite.

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