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Novel Sustainable Anode Materials and Interfacial Chemistry for Improved Rechargeable Batteries

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I am submitting herewith a dissertation written by Yunchao Li entitled "Novel Sustainable Anode Materials and Interfacial Chemistry for Improved Rechargeable Batteries." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Energy Science and Engineering.

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ABSTRACT

The fast growth of the renewable energy market leads to a rapidly increased demand for high-performance energy storage. Despite the great success of the current lithium-ion batteries (LiBs) in portable electronics, the findings of new applications such as in electric vehicles and in large-scale energy storage revealed the limitations of current LiBs in terms of performance, cost, life time and safety. To meet the future application requirements, this dissertation is focused on the innovation and improvement of anode materials, characterization and understanding of material surface properties and modification of the anode materials.

A new carbon material recovered from waste tire with higher capacity and lower cost is discovered. In the meantime, there are also some issues for the application of such material. Various characterization techniques, such as neutron vibrational spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy were utilized to better understand the carbon surface properties. Several methods were applied for surface modification to future improve the interface between electrode and electrolyte, resulted in better performance of tire-derive carbon in LiBs.

Another way for alleviating interfacial problem on the anode side is through the use of high voltage anode materials such as lithium titanates. Mono-dispersed nanosized lithium titanates was synthesized with shape controlled method, which
showed high rate capability and long cycle life. Moreover, a sustainable lithium source is tested for application as battery material precursor.

By integration of materials modification, interfacial engineering, and the advanced characterization techniques, we could potentially build a low-cost, safe and long cycling advanced rechargeable batteries.
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CHAPTER 1
INTRODUCTION
1.1 Research Background

With the fast development of portable electronics, electric vehicles and renewable energy generation, the demand for high-performance energy storage system increases rapidly. Moore’s Law in semiconductor industry predicts that there is a doubling of memory capacity in every two years. However, when compared, the energy storage capacity increasing rate is much slower than this trend. The lag in the energy storage development results in the delay of many great technologies applications. The renewable energy sources, such as wind and solar could reduce the dependence on fossil fuels and greenhouse gas emissions. However, due to the variability of these sources, large-scale energy storage is required to secure the reliability of the electric grid. Thus, it is very urgent for us to develop a safe, cost efficient, and reliable large energy storage device.

Since its first introduction by the SONY Corp. in 1991 of a wireless cell phone powered by a rechargeable lithium-ion battery (LIB), the LIB has been used extensively in our daily life in many areas such as portable computers, cells phones, digital cameras and hand-held tools. Currently, LIBs have been considered as the best candidates for electric vehicles (EVs) and harvesting energy from renewable sources due to their relative high energy density, low self-discharge and long-term cyclability. Lithium is the lightest metal (density $\rho=0.53$ g cm$^{-3}$) and it is the most electropositive metal (-3.04 V versus standard hydrogen electrode) [1]. Hence, lithium ion batteries can offer more energy per unit weight and volume than the typical nickel metal hydride (NiMH) batteries. Nonetheless, today’s battery technologies are lagging behind the needs for EVs and grid storage. A significant improvement in energy density, rate capability and lifetime is
required for LIBs to meet the current society needs. Such improvements should arise from changes in battery chemistry and cell architecture engineering.

The electrode materials play the biggest role in the battery chemistry since they host the lithium ions and determine the cell operational voltage and cycling properties. In a battery, Li ions migrate across the ionic conducting electrolyte solution located between the two host structures, which serve as the positive and negative electrodes. The interaction between Li ion and the electrode materials influence the power output and cycle life of the battery. The advances in designing and discovering of new electrode materials are crucial to improve the battery chemistry.

At the same time, the battery properties such as, cycle life, safety, energy and power density, are not only relying on the materials used and their morphologies, but also on their compatibility with one another and the chemistries at the interfaces. Finding the best combination of the electrode-electrolyte system could minimize the decomposition of the electrolyte and reduce the formation of the solid-electrolyte interfaces (SEI), which promotes lithium transportation and enhance the battery safety.

1.2 Objective

As discussed above, the electrochemical performance of lithium-ion batteries is determined by multiple factors in a battery system, such as the properties of the cathode materials, anode materials, electrolytes and the electrode-electrolyte interfaces formed during battery cycling. Hence, it requires a system engineering to build a better battery.
In this dissertation, we focus on the improvements of the energy storage by synthesis of novel anode materials to improve the capacity and lower the cost. In the meantime, we also conduct the study of materials surface properties to better understand its relationship with the performance and provide guidance for further modification.

Chapter 1 gives an introduction on the research motivation and objectives. In Chapter 2, a brief overview of energy storage devices is discussed, which includes the development of cathodes, anodes and the electrode-electrolyte interface of Li-ion batteries. In the meantime, beyond lithium battery systems such as sodium-ion batteries and potassium-ion batteries are also included since they are regarded as the potential low-cost alternative solutions for large scale stationary energy storage. Chapter 3 describes the background and mechanism for the characterization techniques used in this dissertation to better understand the data achieved. By synthesizing a new tire-derived carbon as potential anode material for electrochemical energy storage systems, in Chapter 4, we identified that it would be possible to realize next-generation electrical energy storage systems with long life at an affordable cost. However, there are several obstacles need to be overcame for tire-derived carbon towards applications. Three methods were proposed and studied to solve the issues we identified and to further improve the anode performance as a battery electrode material. Surface carbon coating using Toluene and pre-lithiation were utilized to significantly improved the first cycle efficiency of tire-derived carbon during cycling. Tin (II) oxides were ball milled and formed a composite with tire-derived carbon which has transition metal oxides reinforced by carbon matrix. The obtained composite material presented a capacity of 690 mAh g⁻¹ after
300 cycles, which is over 85% capacity increase when comparing with commercial graphite that has a capacity of 372 mAh g\textsuperscript{-1}. This composite avoids the fast capacity fade associated with tin based alloying materials with the help of the ideal pore size of tire-derived carbon matrix to adsorb volume expansion. In Chapter 5, combining with the advanced characterization techniques, we revealed the surface functional groups and understood the surface chemistries of the tire-derived carbon. The information acquired from vibrational neutron spectroscopy together with many other surface analysis techniques such as XPS and Raman provided the solution to further improve the performance of the material. To further reduce the cost of rechargeable battery systems for large scale stationary energy storage, the application of tire-derived carbon as anode materials in beyond lithium system is given in Chapter 6. In addition to their great abundance and availability, since sodium and potassium will not have alloying reaction with aluminum, both sodium ion batteries (SIBs) and potassium ion batteries (KIBs) could use Al current collector on both cathode and anode side. In order to minimize the influence of solid-electrolyte interface (SEI), a mono-dispersed Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} (LTO) is synthesized to serve as a high-power anode material as shown in Chapter 7. The LTO anode with controlled morphology maintained 92% of its initial capacity after 2000 cycles at 1C rate when paring with LiFePO\textsubscript{4} cathode. The last chapter concludes the dissertation and proposes the new tire-derived carbon research direction and possible future improvement forwards.
CHAPTER 2
OVERVIEW OF BATTERIES AS ENERGY STORAGE DEVICES
2.1 Lithium-ion Batteries

The first practical battery was invented over two centuries ago, which is known as Volta cell. Ever since several types of batteries based on different chemistries were invented. In general, a battery provides two main functions: the ability to store energy and supply of power over a duration of time.

A primary battery is one that cannot be easily recharged and the chemistry reaction within the cell is non-reversible. Most primary cells utilize electrolytes that are contained within absorbent material or a separator (i.e. no free or liquid electrolyte), and are thus termed dry cells. Alkaline, Silver-oxides and Zinc carbon batteries are examples of primary batteries. In contrast, in a secondary or rechargeable battery, the reverse reaction will occur due to the reverse chemical difference during charging. Among them, lead-acid and lithium-ion battery are the most commonly used secondary batteries.

A conventional lithium-ion battery (LIB) typically consists of two different lithium insertion compounds as electrodes and these electrode materials are separated by a porous polymer film, namely a separator. The electrodes and separator are immersed in an ionically conducting organic solution namely electrolyte. Generally, the commercial Li-ion cells use graphite as an anode material and lithium metal oxides, such as LiCoO₂, serve as the cathode. The schematic of a LiCoO₂/graphite cell is shown in Figure 2.1. Both electrodes can reversibly insert and remove Li ions from their respective structures. Because of the differences in chemical potential of the two electrodes, when they are connected to an external circuit, the electrons will spontaneously travel from the negative
Figure 2.1. Schematics of a LiCoO$_2$/Graphite cell.
part (anode) to the positive part (cathode). Meanwhile, in order to keep the charge balance, the ions move through the electrolyte and separator from anode to cathode. Specifically, during discharging, Li-ions are removed from the lithiated graphite side (Li\textsubscript{x}C\textsubscript{6}) and intercalated into the layered Li\textsubscript{1-x}CoO\textsubscript{2} part. The detailed chemical reactions are listed below in equation 2.1.

\[
\begin{align*}
\text{Cathode: } & \text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \\
\text{Anode: } & C_6 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_xC_6 \\
\text{Overall: } & \text{LiCO}_2 + C_6 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_xC_6
\end{align*}
\]  

(2.1)

2.1.1 The History and Development of Lithium-ion Batteries

TiS\textsubscript{2} was first used as a positive electrode with Li metal as the negative electrode and lithium perchlorate in dioxolane as electrolyte by Exxon in 1972 [2]. In the following decade, significant number of other compounds was studied as the potential electrode materials, which includes, TiO\textsubscript{2}, MnO\textsubscript{2}, V\textsubscript{2}O\textsubscript{5}, and V\textsubscript{6}O\textsubscript{13} [1]. The success of intercalation electrodes stimulated large number of discoveries from academic and industrial researchers. In 1985, Moli Energy Ltd. first developed and introduced a Li-MoS\textsubscript{2} battery system into the market. However, it soon encountered the lithium metal dendritic growth issues and led to catch fire or explosion of the cell. This battery system was soon abandoned. To circumvent the safety issues associated with the use of highly reactive lithium metal, a second insertion material, graphite was found to meet the safety requirements and was used as the anode. A rechargeable Li-ion battery consisted of a LiCoO\textsubscript{2} cathode and a graphite anode was developed and commercialized by Sony Corp. in 1991. This so-called Li-ion battery thus consists of two intercalation electrodes that can
host lithium ions during cycling and also known as a “rocking chair” battery. This battery sets the foundation of the materials and chemistry for the conventional Li-ion battery industry.

2.1.2 Cathode Materials

To compensate for the increase in potential and loss of lithium source by replacing lithium metal, high-potential lithium insertion compounds were discovered and utilized. LiCoO₂ introduced by Professor Goodenough is the first and the most commonly used cathode material in commercial Li-ion batteries today due to its high working potential, low self-discharge, good structure stability and long cyclability. The theoretical specific capacity of LiCoO₂ is 274 mAh g⁻¹, while only half of the lithium could be removed to avoid the collapse of the structure. The major limitation of LiCoO₂ is the high-cost, low thermal stability, and fast capacity fade at high current density. Because Co is an expensive and toxic element and much effort has been made to find a cheaper alternative. Other commercial cathode materials include LiMn₂O₄ (spinel), LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ (layered), LiFePO₄ (olivine) and LiNi₁/₃Mn₁/₃Co₁/₃O₂ (layered). Continuous research efforts on developing cathode materials have been made to develop new cathode with higher work potential (e.g. LiNi₀.₅Mn₁.₅O₄ with 4.7 V vs. Li⁺/Li) and larger capacities (e.g. Li₁+xM₁-xO₂, lithium rich layered oxides, capacity ~270 mAh g⁻¹). However, all of these advanced cathode materials suffers from fast capacity fade and structure degradation. Recently, sulfur attracts a lot of attention as a potential cathode material, which provides a theoretical capacity of 1675 mAh g⁻¹, almost one order of magnitude higher than that of
conventional compound. However, sulfur will form soluble polysulphides and cause severe capacity fade.

2.1.3 Anode Materials

As mentioned before, anode materials are necessary in the batteries, as they would greatly avoid lithium dendrite formation which enhances the cell safety. In this work, the main emphasis of the materials innovation is on the anode side.

Currently, the most commonly used anode material in commercial batteries is still graphite, as same as the first Li-ion battery that was introduced 25 years ago. However, several advances have been made on the anode side and some of them are in transition to be commercialized. Extensive research has been conducted to evaluate the new mechanism and materials. Novel synthesis techniques and strategies have also been adopted to enhance the electrode performance including: controlling the particle size and morphology [3], coating [4] and encapsulation of the active material [5], and composite formation [6]. There are generally four groups of the materials which attract most attentions as anode materials, namely, carbonaceous materials, alloying anode materials, conversion materials, and lithium titanates and titanium oxides.

2.1.3.1 Carbon-based Anode Materials

Carbon is one of the most abundant element on earth and shows an almost infinitely large amount of structural variations, ranging from highly ordered graphite to randomly oriented amorphous carbon. The structure, morphology, grain size, crystallinity and carbonization temperature all influence the capacity and cyclability of the
carbonaceous host material. Carbon anodes can be divided into two types, graphitic carbon and hard carbons.

Graphite is an intercalation material that has the combined properties of low cost, low delithiation potential (~0.1V vs. Li⁺/Li), high lithium diffusivity and good electronic conductivity. The crystal structure of graphite is shown in Figure 2.2a. It consists of parallel graphene sheets, stacked with alternate layers on top of each other (A-B-A-B-A stacking). It can intercalate up to one Li atom per six C atoms under ambient conditions, which results in a theoretical capacity of 372 mAh g⁻¹ [7]. In LiC₆, the Li atoms occupy next nearest-neighbor sites, separated by 3.75 Å, within the van der Waals space between the energy pairs of carbon sheets. One of the major influence of the presence of lithium in the graphite structure is the adjacent parallel graphene sheets rotate from A-B-A-B-A stacking into A-A-A-A-A stacking, as illustrated in Figure 2.2b. At this stage, the honeycombs are directly above and below one another. Li atoms are located at the center of the honeycombs between above and below [8]. However, graphitic carbons do not work well with propylene carbonate (PC) based electrolyte, which has lower melting point and fast lithium transport.

Hard carbons are mostly disordered and can contain significant amount of nanoscale porosity, which can be modeled by a series of graphene sheets arranged much like a house of cards (as shown in Figure 2.3) [9]. Dahn et al. revealed that Lithium will insert between the parallel graphene layers, resulting a distribution of chemical environments and this leads to a sloping voltage profile during the discharge and charge process [10]. The nanovoids and defects also provide excess capacity, where can allow
Figure 2.2. (a) Schematics of graphite structure, (b) different atoms arrangement of graphene layers.

Figure 2.3. A schematic of a “House of card” model for hard carbon materials.
lithium to fill the pores in the structure in a process analogous to adsorption. The low voltage plateau during the discharge is associated with such process. In the meantime, the nanopores and defects inside the hard carbons could also reduce the isotropic volume expansion. Currently, many studies were conducted to discover the lithium storage performance of hard carbons from different precursors, such as, sucrose, banana peels, and dopamine etc. Most of the precursors are relatively high cost or require complex treatments, which prevent the application in many cost sensitive fields.

### 2.1.3.2 Alloying materials

Alloying materials are typically elements those can electrochemically alloy and form compounds with Li at a lower potential. These elements include Al, Sn, Sb, and Si, etc. [11]. Among them, silicon has attracted greatest attention since it has a theoretical capacity of 4200 mAh g⁻¹, which is more than 11 times higher than that of graphite. However, the alloying materials are notorious for their colossal volume expansion during lithiation process (e.g. 270% for Silicon, 250% for Tin). Such large volume expansion will cause material fracture and loss of contact, which results in fast capacity decrease and poor cycling life. To alleviate such issues, different synthesis techniques were applied. In general, the most successful strategy is developing carbon composites which could absorb the expansion and increase the electronic and ionic conductivities. Additionally, hollow structures encapsulation of active silicon materials or silicon nanowires were investigated and used to intentionally reserve the space for volume expansion. However, the great cost associated with achieving advanced structure for this type of material will hinder its application.


2.1.3.3 Conversion materials

In 2000, Poizot et al. reported that nano-sized transition-metal oxides (MO) (M=Co, Fe, Ni, Cu, etc.) could be utilized to store lithium through a reversible heterogeneous conversion reaction [12].

\[
\text{MO}_x + 2x\text{Li} \rightarrow \text{M}_0 + x\text{Li}_2\text{O}
\]  

This type of transition-metal oxides provides electrochemical capacities ranging from 400-1100 mAh g\(^{-1}\), with 100% capacity retention for up to 100 cycles and high charging rates. The reason for reversible Li\(_2\)O formation in such a reaction at room temperature is believed to be related to the presence of extremely small separation between Li\(_2\)O and metal nanograins. Since then, reversible lithium storage was also observed in transition metal fluorides, sulfides, nitrides and phosphides [11].

For anode materials based on the conversion reaction, there are three main disadvantages, which are low columbic efficiency, high average charging voltage and large polarization. These drawbacks will significantly decrease the materials cyclability, energy density and the efficiency of the charge storage. Hence, a lot of improvements such as material morphology and conductivity are still needed for this type of materials before commercialization.

2.1.3.4 Lithium titanates and titanium oxides

Spinel Li\(_4\)Ti\(_5\)O\(_12\) (LTO) with a structure of \(Fd\bar{3}m\) space group has attracted significant attention as a safe and high-power anode owing to its unique electrochemical
properties. Unlike the commonly used graphite, LTO is a zero-strain insertion material. Each LTO structure unit can intercalate up to three lithium ions without any volume changes, converting Li$_4$Ti$_5$O$_{12}$ to rock salt Li$_7$Ti$_5$O$_{12}$ [13]. Such unique structure packing features of LTO leads to excellent reversibility and cyclic stability for fast lithium ion intercalation-deintercalation. In addition, LTO has a stable and relatively high lithiation potential of 1.55V vs. Li$^+$/Li to suppress the formation of SEI and consequently avoid the deposition of lithium dendrites, making the LIBs safe. Unfortunately, some kinetic problems of low intrinsic electrical conductivity (ca. $10^{-13}$ S·cm$^{-1}$) and poor lithium-ion diffusivity (ca. $10^{-9}$–$10^{-13}$ cm$^2$·s$^{-1}$) limit such material to realize its full capacity at high rates. Hence, various methods were developed to improve the performance of the material. By doping to reduce partial Ti$^{4+}$ into Ti$^{3+}$, a mixture of Ti$^{3+}$/Ti$^{4+}$will be generated and hence its electronic conductivity will be increased. Nanostructure engineering is also used to form unique nanostructure-dependent functions. Small particle size increases the contact areas of electrode/electrolyte interface and shortens the Li$^+$ transport distance, and hence enhances the battery power outputs.

In addition to Li$_4$Ti$_5$O$_{12}$, titanium oxide (TiO$_2$) has also been extensively studied. Rutile is the most thermodynamically stable polymorphs of TiO$_2$. Its bulk crystalline form can only insert negligible Li at room temperature [14]. However, nanostructured morphology could greatly improve its properties and Liu et al. reported that mesoporous rutile could accommodate more than 0.7 Li$^+$ (235 mAh g$^{-1}$) during the first cycle and maintain a reversible capacity of 0.55 Li$^+$ (185 mAh g$^{-1}$) between 1.0 and 3.0 V vs. lithium [15]. Anatase has a reversible capacity of 0.5 Li$^+$ in bulk material and the operation voltage
is 1.7 V vs. Li/Li⁺ [16]. TiO₂-B has the largest capacity compared with other compounds in the Li-Ti-O system. TiO₂-B is the least dense polymorphs and its theoretical capacity is 335 mAh g⁻¹. Its high rate capability and no SEI formation properties attract several research interests. Liu et al. reported mesoporous TiO₂-B microspheres with superior rate performance while discharging at 1.75 V. It was shown that the microspheres of TiO₂-B had a capacity of 311 mAh g⁻¹ at C/10, 165 mAh g⁻¹ at 10 C, and only 10% of the capacity loss after 5000 cycles [17].

2.1.4 Interfacial Phenomena

Interfaces play an important role towards chemical energy storage cells since they are always the determinant factors on the performance of LIBs. Among them, the electrolyte-electrode interface is partially crucial. It is well known that lithium is thermodynamically unstable in contact with both liquid and polymer electrolytes. If an anode has a potential $\mu_A$ above the lowest unoccupied molecular orbital (LUMO) of the electrolyte, a small amount of organic electrolytes will spontaneously react with the anode during the first several cycles and eventually stabilized by forming a solid electrolyte interface (SEI) passivation layer. Several research efforts have been conducted on studying the properties and influence of such an SEI layer. It is proven that the SEI composition and behavior can significantly affect the battery's cycle life, power capability and even the safety.

As shown in Figure 2.4, the operating voltage of the graphite is close to that of lithium potential and it can also maximize the cell voltage. However, by using the anode material that has a potential above the LUMO of the electrolyte, such as the LiPF₆ in 1:1
Figure 2.4. Schematic energy diagram of a Li-ion battery.
ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte, results in a reduction of the electrolyte on the graphite surface due to the transfer of electrons from the graphite anode to the LUMO of the organic solvent (EC and DEC) in the electrolyte. Hence, an anode with a potential above LUMO of electrolyte will irreversibly consume both the charge carriers and the electrolyte, which finally cause the irreversible capacity loss of the cell. However, the formation of a thin but stable film is necessary to maintain passivation of the negative electrode and thus prevent further electrolyte reduction. There also exists some high voltage anode materials such as TiO2 and Li4Ti5O12 mentioned before, which operate at potentials above the electrolyte reduction voltage to avoid SEI formation. These types of materials are known for fast-charging, long cyclability and safety. However, due to the high anode working potential, the full cell voltage will be reduced which sacrifices the cell overall energy density.

2.2 Beyond lithium-ion batteries

With the concerns of the limited global availability of lithium resources and relatively high cost of lithium, new alkali-ion based batteries were proposed and developed to find an alternative for the conventional Li-ion batteries. Among the potential candidates, sodium-ion and potassium-ion batteries are the most studied systems.

2.2.1 Sodium-ion Batteries

The concept of high energy density rechargeable batteries with sodium as negative electrodes started earlier than the development of Li-ion batteries. A sodium-sulfur (Na-S) battery has been utilized since 1960s with a molten sulfur cathode and a Na metal
anode, which separated by a sodium ion conducting solid electrolyte ceramic tube. However, this type of battery requires operation at relatively high temperature (300°C) and the materials suffer from corrosion problems.

The rechargeable sodium ion batteries based on intercalation materials that employ non-aqueous electrolytes was first explored in the mid-1980s. Due to its low cost, high abundance, and suitable working chemical potential (-2.7 V versus Standard Hydrogen Electrode), rechargeable Na-ion batteries are considered as one of the potential alternative energy storage solutions for stationary grid energy storage of electricity produced from renewable sources.

The chemical properties of sodium share many similar chemical properties with lithium because of its location in the periodic table and the similarities of fundamental principles of sodium-ion batteries (SIBs) and lithium-ion batteries (LIBs). During cycling, sodium ions are shuttled between the cathode and anode electrodes in an organic based electrolyte system. A remarkable number of new materials and approaches have been studied to serve as the electrode materials in the last few years. Thus far, several suitable cathode materials, such as NaNiO₂ [18], NaMnO₂ [19], NaFePO₄ [20] and Na₃V₂(PO₄)₃ [3], etc., are discovered by researchers by following the principles of cathodes for LIBs. However, good anode materials for SIBs are still under development, in particular robust anodes for sodium storage is of great importance and becomes more urgent. The most commonly used anode material in Li-ion batteries, graphitic carbons will not be able to allow Na⁺ ion to intercalate by itself due to the large ionic size of sodium. Similar as LIBs electrodes, extensive research has been conducted to develop several types of potential
materials based on different chemistry mechanisms, such as alloy, conversion, insertion reactions. Among all of the potential anode materials, hard carbons are regarded as the most promising electrodes due to their larger interlayer spacing, high capacity, low cost and the structure variety.

2.2.2 Potassium-ion Batteries

A potassium ion battery is another analogue to lithium ion battery, where a potassium ion containing cathode is used. The high abundance and lower cost of potassium raw materials (1000 USD t$^{-1}$ for K$_2$CO$_3$ vs. 6500 USD t$^{-1}$ for Li$_2$CO$_3$), mean that K-ion based electrochemical energy storage technologies can exhibit their potentials in many applications [21]. Also, like sodium, potassium does not alloy with aluminum at lower potentials, enabling the use of aluminum as the anode current collector instead of high cost copper current collectors that are used in LIBs. Moreover, the negative potential of the K$^+$/K redox couple is -2.936 V vs. standard hydrogen electrode, which is only 0.1 V higher than that of Li$^+$/Li. In addition, K$^+$ ions show higher transport numbers and mobility in non-aqueous electrolytes due to weaker Lewis acidity and smaller Stoke’s radius of solvated ions. Among alkali metal elements, potassium salts are commonly used as both electrolytes and electroactive species because of their abundance, high conductivity and low cost. Currently, metal hexacyanoferrates is still one of the best cathode candidate for potassium ion batteries, as it was used in the first prototype of a K-ion battery in 2004. Other transition metal based cathodes are also developed recently, such as FeSO$_4$F [22], amorphous FePO$_4$ [23] and layered K$_{0.3}$MnO$_2$ [21]. As for the anode, the use of K metal is not applicable due to its severe safety concerns. Hence, identifying the potential anode
materials for KIBs is of great importance. Recently, carbon based materials (graphite, graphene and hard carbons) and tin-based composites have been studied as anodes for KIBs. Among these materials, hard carbons showed the most promise because graphite and tin-based composites suffered pronounced capacity fade and lower rate capability while the high cost of graphene prevents its application in the price sensitive large-energy storage field.
CHAPTER 3
EXPERIMENTAL CHARACTERIZATION TECHNIQUES
3.1 Materials Physical Properties Characterization

The research in the fields of chemistry and materials depends on a variety of physical characterization techniques and instruments to illustrate the properties and reactions. The interpretation of a complex system like a battery usually requires application of a combination of several tools. Therefore, a good understanding of the mechanism behind each characterization techniques is important and crucial to the research.

3.1.1 X-ray Diffraction

X-ray Diffraction (XRD) is a rapid analytical technique that was first observed by Max von Laue in 1912. It utilizes the interaction of X-rays from a collection of crystallites to obtain a diffraction pattern, which could be used to reveal the information about crystal structure, chemical composition and physical properties of materials and thin films. In 1914, the father and son, William Henry Bragg and William Laurence Bragg simplified the Laue diffraction conditions and developed the angles for coherent and incoherent scattering from a crystal lattice. X-rays are often generated by means of cathode ray tubes, which consists of a tungsten filament and a current is passed through the filament to excite electrons. A high potential is applied between the tungsten filament (cathode) and a metal anode to accelerate electrons. When the electrons strike the target, and have sufficient energy to dislodge inner shell electrons of the target material, the rapid deceleration will generate characteristic X-ray spectra. These spectra are characteristic of the target materials (Cu, Fe, Mo, Cr, etc.) and consist of several different components, such as, $K_\alpha$ (include $K_{\alpha 1}$ and $K_{\alpha 2}$) and $K_\beta$. A monochromatic crystal is used as a filter and
produce monochromatic X-rays for diffraction. When radiation with wavelength comparable to the crystal atomic spacing, the diffraction of radiation by a set of parallel planes of atoms will occur and undergoes constructive interference. The Bragg’s equation (3.1) describes the condition on diffraction angle when the constructive interference to be at its strongest, as shown in Figure 3.1.

\[ 2d \sin \theta = n\lambda \]  

(3.1)

Where \( d \) is the interplanar distance, \( n \) is a positive integer and \( \lambda \) is the wavelength of incident wave, which is related to the target material.

### 3.1.2 Particle Porosity Analysis

Particle surface area and pore size are important properties for powder materials, since they influence many aspects of the material and is a valuable indicator of quality and performance. The detailed information such as surface area and pore size are critical for the industrial process and chemical reaction. The specific surface area is increased as the particle size becomes smaller. In the meantime, the specific surface area is also increased if there are pores present in the particles. In a battery, the surface area of the electrode materials will determine the contact area between the electrode materials and the electrolyte, which will be one of the key factors to determine the solid electrolyte interface (SEI) and cell impedance. Therefore, it is important to measure and modify the specific surface area preferably down to single digits and pore size of electrode materials to optimize its performance for improved battery systems.
Figure 3.1. The illustration of Bragg diffraction happens when two beams of X-ray approach a crystalline solid and the extra $2d\sin\theta$ that lower beam traveled is an integer of the wavelength.
The surface properties of battery electrode materials, such as surface area and pore size distribution are commonly analyzed by gas adsorption method from nitrogen, argon or krypton adsorption isotherm at their boiling temperatures. This method is possible to evaluate the pore size distribution from molecular size to a few hundred nanometers. Inside each pore, the condensation occurs below the saturation pressure and the adsorbed gas molecules interact with the wall of surrounding pore. The pore size is directly related to the condensation pressure.

There are five major isotherm types as shown in Figure 3.2. These are generally considered depending on the degree of adsorption, the mechanism of adsorption, the nature of the adsorbent surface and the relative strengths of the adsorbate-adsorbent interactions. Type I (Langmuir) isotherm presents as the gas adsorption rises rapidly in the initial adsorption stage with increasing gas pressure, and attains a complete monolayer coverage afterwards. Such phenomenon occurs in chemisorption for system with strong attractive interaction between adsorbate and adsorbent and weak interaction between the adsorbate themselves, such as solids with fine microporous structure. Type II isotherm is a typical physical adsorption on non-porous materials, where the adsorbate molecules have strong mutual interactions leading to multi-layer adsorption. Type III and V are in the systems where interaction between adsorbate molecules is stronger than that between the adsorbate and adsorbent. The uptake of gas molecules is initially slow until the surface coverage is sufficient so that the interactions between adsorbed and free molecules begins to dominate the process. There is no flattish portion in the curve in Type III, which indicates that monolayer formation is missing. Type IV isotherm is similar to type
Figure 3.2. Five different types of adsorption isotherms.
Il that involves formation of monolayer followed by multi-layer. It shows the phenomenon of capillary condensation of gas.

The Brunauer-Emmett-Teller (BET) technique is the most common method for determine the surface area of powders and porous materials. It was developed primarily to describe the type II isotherm. Nitrogen gas is generally employed as the probe molecule for anode materials and is exposed to a solid sample at liquid nitrogen conditions (77K). However, as for the cathode, Krypton is used for lower surface area measurement. The measured monolayer capacity and knowledge of the cross-sectional area of the molecule being used as a probe are used to evaluate the surface area.

The method of Barrett-Joyner-Halenda (BJH) is a procedure for calculating pore size distributions from experimental isotherms using the Kelvin model of pore filling. The model is based on the assumption that pores have a cylindrical shape and that the pore radius is equal to the sum of the Kelvin radius and the thickness of the film adsorbed on the pore wall.

3.1.3 Raman Spectroscopy

The Raman effect was first observed in 1928 and was named after the famous Indian Scientist C. V. Raman, who earned the Nobel Prize for Physics in 1930 with his discovery. The Raman effect is the result from the interaction between the scattering material and the light. Most of the scattered photons have exactly the same energy and wavelength as the incident photons, which is commonly referred as Rayleigh scattering as shown in Figure 3.3. In a scattering process, the incident photon excites an electron
into a higher virtual state and then the electron decays back to a lower level, emitting a scattered photon. Since the electron decays back to the same level in Rayleigh scattering, it is also referred as elastic scatter.

However, in every $10^6$ $–$ $10^8$ photons scatters, vibrational motion will cause inelastic scattering which constitute Raman effect. In this case, the Raman scattering can be classified as two types, Stokes Raman scattering and Anti-Stokes Raman scattering (Figure 3.3) depending on the molecule gains energy from or lose energy to the photon. Stoke Raman scattered light has less energy (longer wavelength) due to the energy absorption by the molecule. Conversely, if the molecule transfers energy to the scattered photon, then the photon has more energy (shorter wavelength) than the incident light and this phenomenon is referred as anti-Stokes Raman scattering.

When a laser light interacts with molecular vibrations, phonons or other excitations, it will lead to the energy of the laser photons being shifted up and down. The information about the vibrational modes in the system could be extracted from such an energy shift. In a typical Raman spectroscopy, the sample is illuminated with a laser beam and the electromagnetic radiation was collected and sent through a monochromator to filter out the elastic scattered radiation. The rest of the collected light is dispersed onto a detector to obtain a Raman spectrum. This spectrum presents the intensity of the Raman-scattered radiation as a function of its frequency difference from the incident radiation (also known as Raman shift). Since Raman scattering arises from molecular vibration causing a change in polarizability, the intense Raman scattering will occur from symmetric vibrations that induce large distortion of electron cloud. Each peak corresponds to a
Figure 3.3. Energy level diagram showing the states involved in Rayleigh scattering, Stokes and Anti-Stokes Raman scattering.
molecular bond vibration, including individual bonds such as C-C, C=C, N-O, C-H etc., and groups of bonds such as benzene ring breathing mode, polymer chain vibrations, lattice modes.

### 3.1.4 X-ray Photoelectron Spectroscopy

The surface of a material is the origin of interaction with the external environment and other materials. It is regarded as one of the most important part for materials performance. Hence, to solve the problems associated with modern materials, the understanding of the physical and chemical interactions occurs at the surface or at the interface layers is necessary.

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA) is a quantitative spectroscopic technique that measures elemental composition, chemical state and electronic state of the elements existing on the surface. It can be utilized to acquire the very top surface chemistry (1-12 nm) of a material in its “as received” state or after treatment.

XPS is typically accomplished by exciting a sample surface with mono-energetic Al Kα X-rays causing photoelectrons to be emitted from the sample surface. Then the energy of the emitted photoelectrons is measured with an electron energy analyzer. The elemental identity, chemical state and quantity of a detected element will be determined from the obtained binding energy and the intensity of a photoelectron peak.
3.1.5 Neutron Diffraction and Inelastic Neutron Scattering

The neutron is a subatomic particle with no net electric charge and its mass is slightly larger than that of a proton. Neutron has several advantages that are critical for its application: its comparable wavelength with interatomic spacings, the comparable kinetic energy with that of atoms in a solid, better bulk material penetration ability, week interaction with matter, and isotopic sensitivity.

In a powder diffractometer at a neutron source, a beam of neutrons is first directed through a monochromator to obtain a single wavelength followed by diverting to a sample. The neutrons scattered from a powder are counted by a detector and recorded as a function of the angles. Each Bragg peak in a typical diffraction pattern corresponds a diffraction from atomic planes with different interplanar spacing, d.

Inelastic neutron scattering resolves the change in kinetic energy occurs between the neutrons and the scattering system. Inelastic scattering of neutrons creates an excitation inside the sample and both the energy of the neutron and the internal state of the sample are changed, which could be detected in wavelength change.

3.2 Electrochemical Characterization

Electrochemistry is the study of the chemical response of a system to an electrical stimulation. In a battery, the energy is stored chemically which involves oxidation and reduction of both electrode materials. Electrochemical characterization techniques are the most important method to determine the performance of a battery material.
3.2.1 Coin Cell Assembly

Coin cells are the most commonly used configuration for battery materials. It provides good reproducibility and consistency for each cell made. It can be used to produce both half-cell or full-cell configurations for different test purposes. Figure 3.4 presents a schematic of a coin cell used for electrochemical studies.

3.2.2 Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the most widely used electroanalytical techniques to determine the reversible and non-reversible behavior of a system in an electrochemical reaction. CV is performed by cycling the potential of a working electrode and measuring the corresponding current. In the experiment, the working potential is ramped linearly versus time and after the pre-set potential value is reached, the working potential is ramped in the opposite direction and return to the initial potential. Such cycles of potential increase and decrease can be repeated as many times as needed. The rate of potential change is known as scan rate and the potential between the working electrode and reference/counter electrode is referred as working potential. From a CV graph, information about redox potentials and electrochemical reaction rates could be determined.
Figure 3.4. Schematic of a coin cell used for electrochemical studies.
CHAPTER 4
NOVEL WASTE TIRE-DERIVED CARBON AS ANODE FOR IMPROVED LITHIUM-ION BATTERIES
Abstract

In this chapter, morphologically tailored tire-derived carbon is utilized in lithium-ion battery anode with improved capacity as a potential solution for adding high value to waste tire-rubber-derived materials. However, this material also faces some obstacles to replace the currently widely used commercial graphite. We identify the major issues for this material and provide solutions and results to further improve the performance of this tire-derived carbon.

The first half part of this chapter that demonstrates the potential of tire-derived carbon as an anode is revised based on the following paper published in RSC Advances where I am listed as a co-author:

Amit K. Naskar, Zhonghe Bi, Yunchao Li, Sam K. Akato, Dipendu Saha, Miaofang, Chi, Craig A. Bridges, M. Parans Paranthaman, Tailored Recovery of Carbons from Waste Tires for Enhanced Performance as Anodes in Lithium-Ion Batteries, RSC Advances, 2014, 4, 38213

My primary contributions to this paper include (i) evaluate the electrochemical performance of tire-derived carbon as anode materials in lithium ion batteries, (ii) compare the performance of tire-derived carbon with the commercial graphite (iii) gathering and reviewing literature to help with paper writing.

The second part of this chapter to improve the performance of tire-derived carbon as anode is revised based on the following paper recently submitted.

4.1 Introduction

Proper disposal and recycling of worn-out rubber tires prevent the threats large piles of them pose to the environment and to public health and safety. In the past such tires were mostly placed in landfills, but in the past few decades, uses for ground rubber tires have been found. By 2009, of the nearly 290 million scrap tires generated in the United States that year, almost 90% of them were consumed either as fuel; as additives in civil engineering applications; as additives to plastics, rubbers, and asphalt; or in agriculture through various usages. Tires contain significant quantities of organic materials and have a significantly higher heat value than coal [24]. Shredded tires can be incinerated, but the typically incomplete combustion discharges smoke, toxic chemicals, and obnoxious odours. Therefore, reclamation of the materials for other value-added uses is desired.

Reclaiming the rubbery materials from waste tires requires separating the steel and textile reinforcing carcass, shredding the rubber chunks, and chemically or mechanically breaking down the cross-linked networks in the vulcanized rubber chunks, often termed devulcanization [25]. Although use of reclaimed rubber offers processing advantages, loading a significant quantity of reclaimed rubber in a new rubber formulation is impossible without a deleterious effect on product quality [26]. Despite the fact that devulcanization produces the highest-quality reclaimed rubber, it has other drawbacks,
including reduced process safety and the foul smell of the disulfide-type chemicals required in the process [27]. As an alternative, waste tire rubbers are usually cryogenically pulverized into small micron-sized rubber particles. Shredded rubber pieces are also ground in ambient conditions to produce powder buffings. Powdered tire rubbers are useful as filler in various low-cost rubber or plastic products [28, 29]. Use as low-cost additives often requires chemical modification and surface compatibilization of the tire rubber particles with the matrix, which is not always a cost-effective solution [30]. Some effective recommendations include bitumen modification and production of activated carbon [31, 32]. Tire-derived hydrocarbon fuel is another use of waste tires.

With the current demand to restart dry shale gas production in the United States, although sometimes controversial, the future market potential for tire-derived fuel needs additional support. For example, utilizing the pyrolyzed residue from waste tires after fuel extraction would boost the economics of the recycling process. In fact, the pyrolytically recovered carbon black from waste tires is one of the major products obtained from tire recycling. However, isolated carbon black from waste tires does not necessarily produce a good reinforcing filler for tire or other polymeric products [33]. Usually high-structure carbon black made from clusters of ~10–100 nm spherical particles is used in tire rubber formulations to enhance the mechanical properties of the product. Carbonaceous deposits on black particles during tire pyrolysis cause a lowering of the surface activity that can be avoided if pyrolysis is conducted at reduced pressures.\textsuperscript{20} Therefore, in general, pyrolytically recovered black from waste tires does not retain the structural characteristics necessary for the reinforcing effect. Although carbon residues, as by-
products of tire-derived-fuel manufacturing, do not normally find efficient use, it is important to mention here that tire-derived fuel is one of the solutions for tire recycling recommended by the US Environmental Protection Agency. Manufacturing value-added carbon residue from a portion of the recycled tire rubber could be beneficial. Use of tire rubber materials for significantly value-added applications would be very attractive not only from the materials recovery standpoint but also from the perspective of controlling environmental hazards caused by waste tire stockpiles. Scrap tire piles are flammable, and such fires are difficult to extinguish. They also provide breeding ground for mosquitoes and other insects, and rats. Therefore, the search for alternative uses of waste-tire-derived materials continues, and a method that significantly enhances the performance of products containing waste-derived material would be commercially attractive.

In this chapter, tire-derived carbon for its value-added use as an active material in Li-ion batteries was investigated. A detailed study of the structure of sulfonated tire-derived, its surface chemistry, the electrochemical performance with lithium metal, and the further improvement are discussed. The properties of different types of tire-derived carbons and commercial graphite were used for comparison.

4.2 Sample Preparation and Test Conditions

Pulverized tire rubber powder in the size range of 80–120 μm was obtained from Lehigh Technologies, Inc., Georgia. The powder recycled rubber contains a cross-linked rubber mix (45%), carbon black (33%), inorganic filler and vulcanization activator (10%),
and residual extractable and volatile materials. Typically, 50g of tire rubber powders were soaked in a 100 mL concentrated sulfuric acid bath (20% SO₃, kept at 70 °C for 12 hours) to yield the sulfonated tire rubber that was then washed and filtered off. The non-silica inorganic residues, such as ZnO or steel belt residues, are usually removed during oleum treatment and subsequent washing. The washed sulfonated tire rubber cake was then pressed between Teflon sheets under a hot plate inside a compression mold at 110 °C to remove moisture and to obtain a thick (2 mm) molded sheet, followed by pyrolysis in a tubular furnace under a flowing nitrogen gas atmosphere at 1000 °C. The temperature of the furnace was ramped up from room temperature to 1000 °C at 10 °C/min; upon reaching 1000 °C, the temperature was maintained for 15 min with the sample soaking inside. The furnace was allowed to cool down to room temperature and the environment was maintained under a flowing nitrogen gas before the monolithic carbon sample was removed. The sample is termed as the sulfonated tire-rubber-derived carbon or the tailored carbon. The yield of carbon based on the as-received material (non-sulfonated rubber) was 40%. A control group of tire-derived carbon that simple pyrolysis of powdered rubber at 1000 °C was also obtained as a comparison. It is well worth to note that the carbon yield of the control tire-derived carbon is only about 33%, which is about 7% lower than that of the sulfonated tire-derived carbon. A schematic of the process of tire-derived carbon and its use as a low-cost anode material in Li-ion batteries is shown in Figure 4.1. The commercial graphite with the mass-median-diameter of 20 μm was obtained from MTI Corp., Richmond, CA, USA.
**Figure 4.1.** Schematic of the recovery of carbon black from recycled tire rubber.
Thermogravimetric analysis (TGA) of the control and tailored tire rubber samples was performed in a TGA Q500 (TA Instruments) at a 10 °C/min heating rate up to 1000 °C under nitrogen. The porosity characteristics of the recovered carbons were investigated by nitrogen adsorption–desorption at –196 °C (77 K) and pressure up to an ambient condition in a Qunatachrome Nova 2000 analyzer. The pore size distributions in the carbon samples were obtained by employing non-local density functional theory (NLDFT) using the data reduction software of the instrument. Transmission electron micrographs of carbon materials were obtained with an FEI Titan 60/300S S/TEM at 60 kV. The TEM specimens were prepared by directly dispersing the carbon sample to lacey carbon TEM grids.

Electrochemical studies were performed by first preparing CR2032 coin cells. The coin half-cells were assembled in an argon-filled glove box, using recycled carbon as the working electrode and metallic lithium foil as the counter electrode. The anode was prepared by casting a slurry containing 80 wt.% ground recycled carbon material, 5 wt.% conducting commercial carbon (super C45) obtained from TIMCAL, and 15 wt.% polyvinylidene difluoride (PVDF) binder in n-methyl-2-pyrrolidone (NMP) solvent onto a copper foil. The standard electrolyte for Li-ion batteries consisted of a solution of 1.0 M LiPF6 in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by volume). Galvanostatic charge/discharge cycling between 0 and 3.0 V was performed at room temperature under different rates using an Arbin potentiostat/galvanostat multichannel system.
4.3 Characterization of Tire-derived Carbon

Thermogravimetric analysis (TGA) of the rubber powder samples was conducted to determine their compositional characteristics. Figure 4.2 (a) compares the TGA data of the control and sulfonated tire-derived carbon. The sulfonated tire-derived carbon shows a weight loss at around 150 °C, which corresponds to the desulfonation step that causes the elimination of H₂SO₃. It shifts the subsequent pyrolysis temperature of rubber to a slightly higher one. Desulfonation of rubbers or aliphatic hydrocarbons is known to form unsaturated moieties that are relatively better char-forming materials. Usually, desulfonation or elimination of sulfonic acid group (from rubber polymers) occurs with the formation of unsaturated groups in the hydrocarbon chain that undergo high temperature pyrolysis with a minimal loss of mass to yield carbon along with recovery of carbon black in the rubber matrix.

The derivative of TGA data shown in Figure 4.2 (b) indicate that after the desulfonation, the rubber pyrolysis becomes a single-step weight loss that is responsible for the creation of char from the matrix material. Thus, the tailored carbon contains carbon black particles physically bound in a synthesized carbon matrix produced from sulfonated rubber. By comparison, the control carbon does not have such process. It yields low carbon amount after pyrolysis and the isolated carbon black attains very low bulk density.

Nitrogen adsorption-desorption at liquid N₂ temperature (77 K) was used to illustrate the pore textural characteristics of the carbon samples. The surface areas were calculated using BET method form the N₂ adsorption isotherm in Figure 4.3 (Top) and the pore size distribution (Figure 4.3 bottom) was obtained by applying no-local density
Figure 4.2. (a) TGA thermograms, (b) derivative TGA thermograms of control and sulfonated tire-derived carbon.
Figure 4.3. (Top) Nitrogen adsorption-desorption plots for sulfonated and control tire-derived carbons, (bottom) pore size distribution plots (inset: magnified view of the plot in lower pore width region).
functional theory (NLDF) method. Comparing the pore size distribution between the control carbon and the sulfonated tire-derived carbon, the sulfuric acid treatment prior to pyrolysis allows formation of a very small volume fraction of pores of width 3-5 nm and prominent microporosity with pore width less than 2 nm. These micro pores are due to the gaps between the thin carbon matrix on the carbon particles produced by the pyrolysis of a char-forming sulfonated rubber matrix. In addition, during the pyrolysis process, sulfonated tire-derived carbon produce SO₂ and steam which activate the material and yield dominant microporosity. When the rubber is not sulfonated, it (matrix) does not yield any detectable char; thus, leaves highly porous carbon black lump. Further, we noticed that sulfonation creates a relatively hard carbon monolith with a less pore volume. The surface area and comparative porosity data are shown in Table 4.1.

Transmission electron microscopy (TEM) images of the control recovered carbon and the tailored counterparts are reported in Figures 4.4 and 4.5, respectively. Control carbon (Figure 4.4) has the morphology of fused particles with irregular shapes; the selected area electron diffraction (SAED) pattern indicates that the amorphous phase dominates. Originally, sulfonated tire rubber produced a carbon monolith. Hydrogen bonding in sulfonated powder rubber allowed inter-particle fusion and compaction during compression molding. The resilient control rubber powder could not be molded into a uniform sheet by compression molding; it might require two-roll milling and/or a binder.

Ground carbon produced from the sulfonated tire-rubber-derived monolith has the morphology of a uniaxial nanostructure (Figures 4.5a–b). The electron diffraction pattern in the selected area indicates the presence of both crystalline and amorphous carbon.
Table 4.1. BET surface area and porosity data of different carbon materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>BET Surface Area (m²/g)</th>
<th>Total Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite Powder</td>
<td>2</td>
<td>0.006</td>
</tr>
<tr>
<td>Controlled Tire-derived Carbon</td>
<td>95</td>
<td>0.55</td>
</tr>
<tr>
<td>Sulfonated Tire-derived Carbon</td>
<td>72</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Figure 4.4. (a–c) TEM images of control tire-rubber-derived carbon, and (d) the corresponding Selected Area Electron Diffraction pattern.
materials (inset of Figure 4.5 (b)). It is apparent that sulfonation, subsequent processing, and pyrolysis influence the alteration of the local meso-scale structure in some fraction of the recovered tire-derived carbon.

4.4 Electrochemical Performance of Waste Tire-derived Carbon as Anode and Issues

Graphite has been used widely as an anode in commercial Li-ion batteries, as it can intercalate/deintercalate Li up to a composition of LiC₆ (at which a Li atom is present between every layer of the host graphite lattice) and benefits from low cost and ready availability [34, 35]. Graphite offers a theoretical capacity of 372 mAh g⁻¹. Thus, even though carbon, in the form of high-quality graphite, has low atomic weight and low density (~2.2 g cc⁻¹), its reversible capacity is limited. Hence, low-cost materials with robust carbon architectures that can undergo unfatigued, reversible intercalation by Li ions and offer high capacity are the ones desired for electrode applications. The objective here is to compare the performances of three different anode materials: carbons derived from unmodified tire rubbers, sulfonated tire rubbers, and commercial graphite.

The first and second discharge/charge cycles of a Li/carbon cell and cycled at a rate of 0.1 C (1C = fully charge or discharge of the cell in one hour) between 3.0 and 0.005 V are shown in Figure 4.6(a)–(c). The initial reaction of the control carbon with lithium, which occurred predominantly below 1 V, generated a discharge capacity of 890 mAhg⁻¹, whereas the subsequent first charge and second discharge yielded 400 and 510 mAhg⁻¹, respectively (Figure 4.6(a)). The large irreversible capacity loss between the first and second discharge reactions could be associated with the reduction of carbon surface
Figure 4.5. (a–b) TEM images of sulfonated tire-rubber-derived carbon, and the corresponding Selected Area Electron Diffraction pattern (inset).

Figure 4.6. 1st and 2nd voltage profiles of the carbon anodes at a rate of 0.1C; (a) control carbon, (b) sulfonated tire-derived carbon, and (c) standard graphite.
groups followed by electrolyte reduction and formation of solid electrolyte interphase (SEI), if any [36]. The anodic performance of carbon recovered from sulfonated tire rubber shows the first discharge capacity around 545 mAh\(^{-1}\), and the reversible charge capacity is around 387 mAh\(^{-1}\), leading to an irreversible capacity of 158 mAh\(^{-1}\) (Figure 4.6(b)). However, both second discharge capacity and reversible charge capacity are around 390 mAh\(^{-1}\). Standard graphite based anode exhibits the first discharge capacity around 399 mAh\(^{-1}\), whereas the subsequent first charge and second discharge yielded 357 and 363 mAh\(^{-1}\), respectively (Figure 4.6(c)). In addition, Figure 4.6 shows that the voltage profiles are different for sulfonated tire-derived carbon with a sloping region between 1.5 to 0.01 V than that of graphite, which has a much sharper charge/discharge potential.

The cycling performance of the half-cell at a rate of 0.1 charge/discharge cycles per hour with anode containing the control carbon, sulfonated tire-derived tailored carbon, and standard graphite are displayed in Figures 4.7(a), (b) and (c), respectively. The control carbon exhibited an initial coulombic efficiency of 45\%, much lower than that of the tailored carbon (71\%) and graphite (~90\%). This initial coulombic efficiency data can be linked to the surface area data of the carbon (Surface area: control carbon > tailored carbon > graphite) and it can also be caused by either the presence of surface functional group or absorbed species [36].

The lowest efficiency of the control carbon is likely due to its fluffy nature and the higher surface area. Its charge and discharge capacity decreased to ~200 mAh g\(^{-1}\), and the coulombic efficiency increased slowly to 99\% after 45 cycles. The cycling performance of the half-cell with anode composed of tailored carbon exhibited excellent
Figure 4.7. Cycling performance of the carbon anode at a rate of 0.1C: (a) control carbon, (b) sulfonated tire-derived carbon, and (c) standard graphite.
cycling performance with reversible capacity of ~390 mAh g\(^{-1}\) and 100% coulombic efficiency that was maintained to 100 cycles minimally. This result is better than the experimental data with graphite (357 mAh g\(^{-1}\)) and theoretical capacity of 372 mAh g\(^{-1}\) for commercial graphite anodes.

In the case of tailored carbon derived from sulfonated tire-rubber the carbon exhibits significant nanoporosity. Also, the material has some ordered structure due to the formation of sulfonation and desulfonation induced unsaturated hydrocarbon structure. Nanoporous layers of ordered carbons can accommodate lithium ions not only on intercalated layers but also at the pores that may come from folded single layer of graphite sheet like structure. Single layer carbon that creates nanoporosity can accommodate more lithium atom in the form of \(\text{Li}_x\text{C}_6\) where \(x>1\). Further, our tailored carbon is synthesized from diene-rubber matrix containing embedded carbon black through sulfonation, a mechanism which yields crosslinked networked structure of polymer during thermal desulfonation. In such crosslinked carbon matrix lithium will very likely have more insertion position in the structure. Hence, it is normal that hard carbons will have larger capacity than graphite as anode materials [8]. The charge/discharge curves of three samples in Figures 4.6(a)-(c) clearly show the capacity differences between first cycle and second cycles which is mainly caused by SEI formation. The discharge curve indicates the SEI formation starts from about 0.8 V for graphite. Both control and tailored carbon derived from tire rubber exhibit a slightly different discharge profile likely due to its significantly higher porosity than that of the graphite powder. It is well known that the porous carbons have a different release rate of lithium from anode
during charging. Macroporous carbon-based anode has less capacity than that involving microporous carbon.

The rate performance of the control carbon anode (Figure 4.8(a)) clearly shows a capacity of $\sim 100$ mAh g$^{-1}$ at 1C and only $\sim 40$ mAh g$^{-1}$ at 5C, which is significantly less than the widely used commercial carbon anodes. A typical anode composed of active graphite materials exhibits a reversible capacity of 357 mAh g$^{-1}$. Under identical conditions, the relative drop in capacity of anode materials after too many charge/discharge cycles are likely due to the changes in carbon morphology, the formation of interphase layers, and the resulting reduced conductivity. Based on results obtained on anodes composed of the control carbon, the half-cell anode performance appears to be poor.

The rate performance of the sulfonated tire-derived carbon anodes in Figure 4.8(b) was clearly excellent, with $\sim 270$ mAh g$^{-1}$ at 1C, 160 mAh g$^{-1}$ at 5C, and over 50 mAh g$^{-1}$ at 10C, which are much higher than that obtained from the control tire-rubber-derived carbon. This result probably occurred because (1) the tailored carbon displayed both crystalline and amorphous carbon characteristics with distinct nanoporosity, but the control carbon displayed predominantly amorphous characteristics; and (2) the conductivity of the control carbon is lower, owing to the contrasting morphologies discussed earlier. The superior electrochemical performance obtained from the tailored carbon indicates that this material, originating from waste tires, has potential for use as an anode material in practical Li-ion battery applications.
Figure 4.8. (a) Rate performance of the control carbon anode, and (b) tailored carbon from sulfonated tire-rubber.
However, there are three major problems that would hinder the application of such tire-derived carbon in the commercial lithium-ion batteries. First and for most, as we can see from the comparison of Figure 4.6, there is very large discharge capacity different for tire-derived carbon, which is called the irreversible capacity. This irreversible capacity will lead to much lower first cycle efficiency and it is caused by surface functional group reaction with lithium as well as the solid-state interfaces formation. Hence, in a full cell configuration, a lot of limited lithium ions supplied by cathode material will be restricted as “dead” lithium. More cathode materials will be needed to compensate for this lithium ion loss. Second, the capacity of such carbon is only slightly larger than that of commercial graphite. Last, the average working voltage profile is higher than graphite. Graphite has a low voltage working plateau associated with Li intercalation at below 0.2V, however, for tire-derived carbon, a sloping discharge curve starting from 1.2V is observed in Figure 4.6 (b). Higher anode voltage will result in lower working potential for full cell, which will lead to lower energy density it can provide.

4.5 Solution to Improve the Performance of Tire-derived Carbon

The following two solutions are proposed and studied to improve the performance of tire-derived carbon. The first approach could improve the first efficiency of the anode material, while the second approach increase the capacity of the materials which also compensates the energy density loss from tire-derived carbon with relatively high voltage profile. It is also well-worth to note that such slightly higher lithiation voltage could also be beneficial to prevent lithium dendrite formation since it is much higher than the lithium deposition voltage.
1. Pre-lithiation and surface coating of the tire-derived carbon electrode

2. Development of tire-derived carbon and metal oxide composite to increase the capacity.

4.5.1 Pre-lithiation and Surface Coating

Pre-lithiation

Experimentally, it is difficult to pre-lithiate anode materials than cathode materials since it requires more reactive lithium source and the process is hard to control. There are some reports using stabilized lithium metal power (SLMP), however, this type of material is expensive and hard to disperse in NMP solution during the slurry preparation. It will require special complex procedure to apply the lithium.

Here, the pre-lithiation is conducted by direct contacting of lithium metal with electrolyte wetted with casted electrode, as shown in Figure 4.9 (a). Different contact periods were studied to optimize the process conditions. Since the electrode was shorted after contacting with Li, the assembled cell has almost 0V OCV and at this time, first cycle efficiency would be that of the real second cycle since the first discharge is skipped. It is noticeable that all of the pre-lithiated cells have very high efficiency (over 94%) from the beginning, compared to 71% efficiency of the cell without pre-lithiation. There are no major differences in electrochemical performances during the first 10 cycles for different electrodes shown in Figure 4.9. However, the long-term cycling test is needed to fully evaluate the influence of electrode properties.

In the meantime, new methods could be developed to pre-lithiate electrode materials and might be conducted in the future. Half cells with electrodes could be
Figure 4.9. (a) Schematic of direct contact pre-lithiation process, electrochemical test data with (b) 20 min, (c) 19 h, (d) 23 h contact.
assembled and discharged to certain voltage, followed by disassembling of the cell and washing of the electrodes, then full cells can be made with pre-lithiated electrodes. This method can precisely control the amount of lithium pre-intercalated into the electrodes. Another approach is to use Li₃N as a lithium source additive when preparing the slurry and make a pouch cell. Li₃N will decompose at 0.44V during the formation cycle and the N₂ gas generated could be released before the final sealing of the pouch cell.

The goal of using pre-lithiation treatment is to achieve first cycle efficiency of over 90% for the electrode materials.

**Surface Coating**

Pyrolytic carbon-coated graphite has been studied as potential anode materials by many researchers. The carbon surface coating could effectively eliminate the active sites and pores on the surface of hard carbon which reduce the material exposure to electrolyte and to avoid heavy SEI layer formation.

Chemical Vaper Deposition (CVD) based coating method was utilized for the tire-derived carbon to improve its performance. The coating was prepared by placing carbon powder in an alumina boat in a tube furnace with flowing N₂ atmosphere at 700 °C for 30 min with N₂ gas bubbling through toluene kept at 60°C.

As shown in Figure 4.10, the reversible capacity of tire-derived carbon increased from around 365 mAh g⁻¹ to ~ 440 mAh g⁻¹, which could be due to better lithium transport kinetics and less SEI formation on the electrode surface. In the meantime, the first cycle efficiency for tire-derived carbon increases from 59% to 66% after the carbon coating process. Figure 4.11 presents the charge-discharge voltage profiles comparison for the
Figure 4.10. Cycling performance comparison of (a) tire-derived carbon, (b) carbon coated tire-derived carbon.

Figure 4.11. Charge-discharge voltage profiles of tire-derived carbon and carbon coated tire-derived carbon.
pristine and coated carbons. As it can be seen, coated carbon presents a much larger charge capacity than the pristine sample, which means more lithium can be transported back to the lithium metal side during cycling. In contrast, without surface modification, the pristine carbon has more SEI causing higher charging potential.

### 4.5.2 Tire-derived Carbon/SnO Composite

To further improve the capacity, metal oxides are introduced to form a composite with tire-derived carbon. Tin (Sn) and its oxides forms (SnO, SnO2) are widely studied as a family of potential high capacity anodes materials [37-40]. If all the oxygen turns into Li2O, the theoretical capacities of Sn, SnO and SnO2 are 993, 1273, and 1494 mAh g⁻¹, respectively. Lithium can be accommodated into each Sn atom with a capacity of 991 mAh g⁻¹. Although Sn has a lower gravimetric capacity than that of Si, Sn is still attractive due to its comparable volumetric capacity of 2020 mAh cm⁻³ vs. Si (2400 mAh cm⁻³) [41]. Unfortunately, the huge volume change occurring during the charge and discharge process poses serious problems. The large volume change leads to pulverization and loss of electrical contact for electrons conduction between particles, resulting in fast capacity fade. Tremendous efforts have been paid to alleviate such issue, such as hollow structure to encapsulate the materials, inactive supporting material matrix and carbon nanotubes (CNTs) surface coating [41-44]. Recently, more and more studies of tin oxides have been conducted due to the variety of synthesis methods to modify their morphology and structure [45]. However, the capacity retention is still one of the biggest obstacle that hinders Sn-based materials to be commercialized. A few reports presented good stability
when integrated with graphene or CNTs, but the materials cost is way beyond for industrial application [46-48].

Here, we report a low-cost, high capacity lithium ion batteries anode by using tire-derived carbon and Tin Oxide (SnO) composite. After a simple ball milling with 25 wt. % of tin (II) oxide, two components were uniformly mixed. The tire-derived carbon served as an absorbing matrix, which effectively minimized the volume change and the degradation of the electrode. This composite anode showed a very stable electrochemical performance with a capacity of 690 mAh g⁻¹ after 300 cycles at a current density of 40 mA g⁻¹.

The morphology of tire-derived carbon (TC) was elucidated by scanning electron microscopy (SEM). As it is shown in Figure 4.12 (a), the tire-derived carbon presents a porous surface. These pores could be good confining places for SnO and bond with carbon matrix. Nitrogen adsorption–desorption plot for TC and the pore volume distribution are plotted in Figure 4.12(b). The Brunauer-Emmett-Teller (BET) specific surface area of TC is determined to be 227.1 m² g⁻¹. The pore size shows a relatively distribution with a unique mesopore widths in the range of 5 - 10 nm and a noticeable volume fraction of microporosity that than 2 nm. The microporosity could be attributed to the fact that the sulfuric acid pretreated tire powder produces SO₂ and steam which yields activated tire-derived carbon.

After ball milled with SnO for 12 hours, XRD collected the tire-derived carbon/SnO composite as shown in Figure 4.13(a). The diffraction pattern consists of both crystalline SnO peaks and the amorphous TC broad peak near ~ 26.6° which is related to its (002)
Figure 4.12. (a) SEM image of the surface of tire-derived carbon (TC), (b) nitrogen adsorption–desorption plot and the pore size distribution of TC.
Figure 4.13. (a) X-ray Diffraction (XRD) pattern, (b) nitrogen adsorption–desorption plot and the pore size distribution, (c) scanning transmission electron microscopy (STEM) dark field image, (d) STEM bright field image of the ball milled TC/SnO composite.
plane. One other noticeable point from the XRD pattern is that the SnO peaks are broadened comparing with the SnO powder data, which suggests a reduction in particle size for SnO powders. The XRD data indicates both TC and SnO kept their integrity even after 12 hours intensive ball mill and no significant chemical reaction happened to change the physical presence of TC and SnO. In Figure 4.13 (b), Nitrogen adsorption–desorption plot shows a reduced BET surface area of the ball milled TC/SnO composite to 100.8 m² g⁻¹. Such reduction in the surface area could due to the pore filling of SnO particles into the tire-derived carbon matrix. In the meanwhile, the pore size distribution for the composite still maintained the unique 5-10 nm mesoporosity and great amount of micropores from the TC. High resolution scanning transmission electron microscopy (STEM) dark field and bright field images of tire-derived carbon and SnO composite were presented in Figure 4.13(c) and (d). The arrows in the images show some tin rich particles. It can be clearly observed from the STEM images that the presence of uniformly and well bonded carbon and tin oxide composites, which is believed to be the key to tackle the volume expanse problem for tin based materials.

Typical cyclic voltammetry (CV) curves of TC and TC/SnO composition at a scanning rate of 0.1 mVs⁻¹ between 0.005 V and 2 V were compared in Figure 4.14 (a) and (b). The CV of TC shows a gradually lithium intercalation and de-intercalation process without large peak observed. The first cycle reveals large difference in discharge curve comparing with 2nd and 3rd cycle, which could be related to the solid electrolyte interfaces (SEI) and the reaction with surface functional group of the carbon materials. The small discharge peak at 0.8V may be attributed to the reduction of the solvents (mainly EC) and
co-intercalation into graphene layers [49, 50]. As for TC/SnO composite, besides the possible causes mentioned above, the strong cathodic peak observed at 0.8 V is also associated with the formation of Sn metal and Li₂O from the conversion reaction. The anodic peaks at ~0.7 V and 0.48 V are due to Li dealloying from LiₓSn. The reaction of lithium inside the TC/SnO composite is shown in equation below.

\[
\text{SnO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{O} + \text{Sn} \quad (4.1)
\]
\[
\text{Sn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn} \quad (0 \leq x \leq 4.4) \quad (4.2)
\]
\[
x\text{Li} + y\text{C} \leftrightarrow \text{Li}_x\text{C}_y \quad (4.3)
\]

The representative charge/discharge profiles of the TC/SnO composite at a current density of 40 mA g⁻¹ are shown in Figure 4.14 (c). Both TC and TC/SnO composite have gradually changing discharge voltage profiles. However, TC/SnO composite shows much larger area below 0.5 V, which is due to lithium alloying with Sn as it is shown in Equation (2). The cycling performances comparison of TC and TC/SnO composite is plotted in Figure 4.14(d). The initial capacities of discharge and charge for tire-derived carbon is 1032.8 and 645.3 mAh g⁻¹, which corresponds to a first cycle efficiency of 62.5%. After the first cycle, the TC cell efficiency went up to 93.2% for the second cycle and maintained above 98% after 15 cycles. The discharge and charge capacities after 100 cycles for TC is 463.1 and 459.8 mAh g⁻¹. Comparing with pure tire-derived carbon, the composite with SnO added shows lower first cycle efficiency of 56.3%, which is due to the irreversible reduction reaction of SnO to Sn in equation (4.1). It is well documented that Li₂O phase is electrochemically inactive and non-conductive. However, it is reported that the
Figure 4.14. (a) Cyclic voltammetry (CV) curve of TC, (b) CV curve of TC/SnO composite, (c) charge-discharge voltage profiles of TC and TC/SnO composite, (d) Cycling performance comparison of TC and TC/SnO composite.
presence of Sn as finely divided particles in a network of Li$_2$O could hinder the aggregation of Sn particles and lead to the good cyclability, which also observed in this TC/SnO composite and will be shown later [51]. The efficiency of the TC/SnO Composite cell increased to over 98% after 8 cycles. The capacity of the composite slightly decreased then gradually stabilized after 10 cycles and the discharge capacity of TC/SnO composite after 100 cycles is 632 mAh g$^{-1}$. This value is 36.5% larger than that of TC alone, which indicates the 75% of carbon matrix in the composite works well with 25% SnO. In fact, this value is also larger than the simple add up of TC and theoretical SnO capacities. There may be two reasons for such phenomenon. First of all, ball milling of TC breaks down the particle size and will allow more carbon direct to react with lithium which yields higher capacity on the carbon matrix part. Moreover, it may also attribute to the synergic effect between the carbon and tin oxides, which shows enhancement of the composite than the sum of individual performance and this effect has been reported by other studies [51, 52].

The rate capability of TC/SnO composite has also been tested and the results are shown in Figure 4.15(a). The discharge capacities of the composite are 727, 595, 483, 288 and 50 mA g$^{-1}$ with a current density of 40 mA g$^{-1}$, 100 mA g$^{-1}$, 200 mA g$^{-1}$, 500 mA g$^{-1}$, and 1 A g$^{-1}$, respectively. Undoubtedly, the composite has low performance under high current densities, which may cause by relatively low conductivity of the tire-derived carbon. However, it is noticeable that after the large current density of 1 A g$^{-1}$, the capacity of TC/SnO recovers back to its original capacity without losing much lithium storage capability at lower current density. This proves the strong carbon matrix support that
Figure 4.15. (a) Rate test of TC/SnO composite electrode, (b) long-term stability test of TC/SnO Composite at a rate of 40 mA g⁻¹.
provided by TC and cycling under large current density did not destroy the bonding and connection between the carbon matrix and SnO particles. The TC/SnO was also cycled at a current density of 40 mA g\(^{-1}\) for 300 cycles to evaluate its long-term stability since that is the biggest issue for most of the alloying anode materials. Interestingly, the TC/SnO composite shows very capacity retention and it shows a discharge capacity of 690 mA g\(^{-1}\) after 300 cycles. During the cycling, there is a capacity decrease followed by an increase at about 125 cycles, which could be associated to the expansion by Sn particles that opened more accessible locations to Li ions for storage. It is noteworthy that this composite electrode was achieved by simply ball milled of waste tire derived product and SnO without complicated synthesis process and the capacity retention performance is among many of the best Sn based materials mixed with expensive carbon nanotubes or graphene.

4.6 Summary

In this chapter, a novel sustainable anode material derived from waste tires were utilized in lithium ion batteries. This low-cost tire-derived carbon shows a good capacity and stability. The issues for such anode material to be used in real world are also identified. Through pre-lithiation and surface coating, the material will achieve a first cycle efficiency over 90%. In the meanwhile, the tire-derived carbon and SnO composite also shows over a discharge capacity of 690 mA g\(^{-1}\) after 300 cycles. This tire-derived carbon a pathway for inexpensive, environmentally benign and value-added waste tire-derived products for energy storage applications.
CHAPTER 5
NEUTRON VIBRATIONAL SPECTROSCOPY AND OTHER SURFACE PROPERTIES CHARACTERIZATION OF NOVEL WASTE TIRE-DERIVED CARBON
Abstract

To better understand the properties and further improve the performance of the tire-derived carbon for energy storage applications, it is crucial to study the fundamental surface properties of a material. In this chapter, detailed investigation and characterization including neutron vibrational spectroscopy, x-ray photoelectron spectroscopy, Raman spectroscopy were used to obtain more information about the surface properties of tire-derived carbons. This chapter is revised based on the following paper published in Physical Chemistry Chemical Physics:


5.1 Introduction

With the rapid growth of the automobile market, the disposal and recycling of end-of-life tires is becoming a serious problem for the society. It is estimated that over 231 million scrap tires were generated in the United States in 2011[53]. Large piles of old tires are threats to the environment and to public health. Uncontrolled tire fires are notoriously difficult to extinguish, which will generate hazardous smokes and pollute soil, and surface and ground water [54, 55]. In the past used tires were mostly discarded in landfills. Only in the last few decades, scrap tires have been recycled through pyrolysis to recover fuel, solvents, and carbon black for use in civil engineering applications.
A typical tire consists mainly of carbon black, natural rubber (NR), synthetic polyisoprene (PI), butadiene rubber (BR), styrene-butadiene rubber (SBR), and other fillers and additives[56]. Pyrolysis is a thermal degradation process in an oxygen-free atmosphere which results in gas, liquid and solid products. Most of the NR, PI, BR, and SBR will turn into C1-C4 hydrocarbons and higher hydrocarbons/hydrogen gases during pyrolysis. The gas and liquid products are recovered and used as fuels and the solid products containing carbon black are used as additives for civil engineering applications.

Electrical energy storage has attracted increased attention because of the rapid growth of renewable energy generation and increased demand for replacing gasoline-based vehicles with electric vehicles [57-59]. Carbon is one of the most important materials that are widely used in energy storage applications [60-62]. Graphite and amorphous hard carbon are used as anodes in rechargeable batteries and activated carbon provides good charge storage in supercapacitors [63]. Sulfonated tire-derived carbon was recently developed at ORNL, and provides another potential solution for producing high value-added products from recycled tires [64]. Tire-derived carbon was prepared by first treating tire rubber with sulfuric acid followed by a simple pyrolysis process. The unique sulfuric acid treatment functionalizes the rubber and forms sulfonated group on the rubber macromolecule matrix. During the pyrolysis step, the sulfonated rubber generates carbon matrix through desulfonation followed by char-formation and gradually forms a carbon-matrix carbon black composite. The solid carbon yield increases after the sulfonation followed by the pyrolysis process since less rubber will be lost as gas and solvents during carbonization. Electrochemical testing vs lithium
shows that a waste tire-derived carbon anode has a capacity of 390 mAh g\(^{-1}\) after 100 cycles, which is about 10% higher than the commercial lithium-ion battery (LIB) anode material of choice, namely, graphite. As for the sodium-ion batteries (SIB), tire-derived carbon shows excellent cyclability and a discharge capacity of 203 mAh g\(^{-1}\) after 100 cycles with a very large portion of the low-voltage plateau. This will be beneficial to increase the energy density of the full cells[65]. Pseudocapacitor testing also revealed that the activated sulfonated tire-derived carbon and polyaniline (PANI) composite exhibited a capacitance of 480 F g\(^{-1}\) at 1 mV s\(^{-1}\) and excellent capacitance retention of 98% after 10,000 charge/discharge cycles. This outperformed other PANI activated carbon composites [66].

To better understand the properties and further improve the performance of the tire-derived carbon for energy storage applications, it is crucial to study the fundamental microscopic physics and chemistry of the material. Dahn et al. proposed a “house of cards” model to explain the Li storage in hard carbon, in which the graphene layers are randomly stacked and both sides of the graphene are accessible to Li insertion, resulting in much larger capacity with hard carbon than with graphite[67, 68]. The surface functional groups of the pyrolyzed hard carbon play an important role towards its electrochemical performance. The reaction of lithium with surface functional groups will increase the irreversible capacity. Meanwhile the large amounts of oxygen and hydrogen present in carbon will cause a hysteresis between charge and discharge curves because a higher voltage is required for the removal of lithium from the carbon. This correlates with reduced cell potential and lower power density [69]. The edge effect on the high capacity of
carbonaceous materials heat-treated below 1000 °C could result from the presence of hydrogen atoms bonded at the periphery of the aromatic molecules which constitute the basic structural unit. Many studies have shown that the capacities of various polymers pyrolyzed below 1000 °C were correlated to the C/H atomic ratio [68-72]. Microporous layers of ordered carbon can accommodate lithium ions not only on the intercalated layers, but also at the pores that may come from folded single layer of graphite sheet-like structure. In addition, the tailored carbon synthesized from diene-rubber matrix containing embedded carbon powders through sulfonation can lead to cross-linked carbon generation that would more likely enable more lithium insertion into the anode matrix. Hence, it is important to know the surface properties of the tire-derived carbon and investigate changes during pyrolysis, and also determine the differences with commercial graphite to understand and improve the material’s electrochemical performances.

Inelastic neutron scattering (INS) reveals unique properties and important details of the micromorphology that are not accessible by other techniques. Since the neutron scattering cross-section of hydrogen (82.02 barn) is more than one order of magnitude higher than the other elements present in the samples, such as carbon (5.55 barn), oxygen (4.23 barn), and sulfur (1.03 barn), INS is particularly sensitive to the vibrational modes involving hydrogen, even if the latter is only a minor fraction of the material. At equal sample mass, the integrated intensity of the INS spectra reflects the total amount/fraction of hydrogen. Peak positions and their relative intensity are telltale indicators of the type of functional groups containing hydrogen (e.g., C-H, C-H2, C-H3, sp2 or sp3). It is anticipated that most of the hydrogen atoms present in the carbon matrix are
terminal hydrogens on the carbon ring systems. The information acquired from this study will be useful in the future to the fundamental understanding of the pyrolysis of sulfonated tire rubber and to further develop and improve advanced electrochemical storage materials.

5.2 Experimental

A. Materials

The details of the sulfonation process of the tire powders were published previously. Typically, the tire rubber powders were soaked in a hot oleum bath (20% SO3 at 70 ºC for 12 h) to yield sulfonated tire rubber followed by washing and filtering. The dried sulfonated tire rubber was then pyrolyzed in a tube furnace under nitrogen gas. The products at various stages of heat-treatment conditions, a controlled sample of pyrolysis of tire rubber without sulfonation, and commercial graphite (Source: MTI) were studied and are labeled in Figure 5.1.

B. Characterization Methods

Nitrogen adsorption-desorption isotherms were obtained using a TriStar surface area & porosity analyzer at 77 K. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained by the Barret-Joyner-Halenda (BJH) method. XPS data were collected with a Thermo Fisher K-alpha XPS with a monochromatic Al-Kalpha, a 1486.6 eV source, 400 μm spot, and an argon ion flood gun. Raman spectra were recorded with a Renishaw system 1000 Raman spectrometer equipped with an integral microscope (Leica DMLMS/N). The laser line of
Figure 5.1. Flow chart comparison of different carbon samples.
632.8 nm from a 25-mW air-cooled He–Ne laser (Renishaw) was used as an excitation source.

The INS spectra were measured at the VISION beamline of the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). About 8 g of each sample was loaded in an aluminum sample holder, and measured at 5 K for about 8 h. A spectrum was collected for the empty sample holder and subtracted from the spectra. VISION is a neutron vibrational spectrometer with a dynamic range of 0-500 meV and an energy resolution of 1 to 1.5% over the dynamics range. It determines the energy of a neutron incident on the sample by time-of-flight and sets the final neutron energy with a series of focusing graphite single crystal analyzers.

5.3 Results and Discussion

Nitrogen adsorption–desorption plots of different carbon products obtained from pyrolysis of sulfonated tire rubber and commercial graphite are compared in Figure 5.2(a), and the pore volume distribution for the samples are shown in Figure 5.2(b). The BET surface areas of CC1000, TC1100, TC1600 and graphite are 108, 189, 148, and 0.3 m$^2$ g$^{-1}$, respectively. TC1100 and TC1600 have relatively larger surface areas while CC1000 shows a slightly smaller value because that CC1000 will not go through the SO$_2$ activation process during pyrolysis. In the meanwhile, higher temperature treatment will introduce more disorder to order transformation and results in less surface area for TC1600 when comparing that with TC1100. As for pore size distribution, CC1000 shows the pore sizes range from 1 to 30 nm with dominant width larger than 5 nm [7]. However, both sulfonated TC1100 and TC1600 carbon show a wide pore size distribution with a prominent
Figure 5.2. (a) N2 adsorption-desorption plots of TC1100, TC1600, CC1000 and graphite, (b) pore size distribution comparison of TC1100, TC1600 and CC1000.
microporosity and a noticeable volume fraction of pore widths in the range of 6-8 nm. These unique pore features of the pyrolyzed sulfonated tire-derived carbon are possibly due to the production of SO₂ and steam during pyrolysis which activates the carbon surfaces [73].

Raman spectroscopy is a standard nondestructive tool for the characterization of crystalline, nanocrystalline, and amorphous carbon. Figure 5.3 shows Raman spectra comparison for commercial graphite, CC1000, TC1100, and TC1600. The graphite presents predominately G band (order) at 1590 cm⁻¹ due to its well-ordered crystalline structure. A perfect crystalline sp² carbon is characterized by a single sharp G band in the first-order Raman spectrum. CC1000, TC1100 and TC1600 show both D band at ~1360 cm⁻¹ and G band. The introduction of a disordered carbon structure breaks the crystal symmetry and thus more vibrational modes appear. In the spectra, CC1000 has the largest D band and G band peak widths among all the samples, which indicates large amounts of the functional groups on the surface of this sample. Sulfonated samples TC1100 and TC1600 have narrower peak widths and TC1600 shows less surface functional groups as the pyrolysis temperature increases. The presence of undesirable amounts of surface functional groups will greatly influence the material's electrochemical performances and often cause irreversible capacity during the first cycle, which leads to reduced first cycle efficiency [74]. It is interesting to note that the ratio of I_D/I_G for TC1600 is higher than that of TC1100. This phenomenon is more or less counterintuitive. As it has been revealed by Ferrari et al. that the value of I_D/I_G changes differently in a three-stage model [75, 76]. As the ordering increases, the carbon structure moves from sp³ bonded
Figure 5.3. Raman spectra comparison of commercial graphite, CC1000, TC1100 and TC1600.
tetrahedral amorphous carbon to amorphous carbon, then to nanocrystalline graphite and finally to ordered graphite. When sample treated at 1000 °C to 1600 °C, the carbon changes mostly from amorphous carbon to nanocrystalline graphite stage, where G peak will change from lower than 1520 cm$^{-1}$ to 1600 cm$^{-1}$ [76]. During pyrolysis process, there is a trend of decreasing in defects and increasing of cluster diameter L\textsubscript{a}. Within the nanocrystalline graphite transforms to microcrystalline graphite stage, I\textsubscript{D}/I\textsubscript{G} will decrease with decreasing disorder following the Tuinstra & Koenig relation, I\textsubscript{D}/I\textsubscript{G} $\propto$ 1/L\textsubscript{a} [77]. However, when amorphous carbon is heat-treated to nanocrystalline graphite, the Tuinstra & Koenig relation is no longer valid, but I\textsubscript{D}/I\textsubscript{G} $\propto$ L\textsubscript{a}\textsuperscript{2} [75]. Therefore, the I\textsubscript{D}/I\textsubscript{G} will decrease during this stage of graphitization. In fact, the G peak full width at half maximum (FWHM) is a measure of disorder, which confirms the disorder increase from TC1600 to TC1100 and then to CC1000.

To elucidate further the properties of pyrolyzed sulfonated tire-derived carbon, the surface chemistry of carbon was studied by X-ray photoemission spectroscopy (XPS). The atomic concentrations of C, O, and S on the carbon surfaces are listed in Table 1. The starting tire rubber (TR) shows the lowest amount of carbon atoms and the highest levels of heteroatoms. After sulfuric acid treatment, many of the surface functional groups were removed and the fraction of C was greatly improved. Comparing all the carbon products, CC1000 contains the highest oxygen and sulfur concentrations and the corresponding values are much higher than those of the acid-treated tire rubber (ATR). This result could be attributed to the acid treatment process which greatly dissolved most of the organic and inorganic components present in the tire rubber. The sulfur is added
to the tires to form cross-links between individual polymer chains and increase its durability. Typically, direct pyrolysis of tire rubber will retain approximately 78% (by weight) of the original sulfur in the pyrolyzed char, while 13% will be emitted in the gas and 9% in the liquid phase products.[78] The main difference in O and S contents of TC1100 and TC1600 carbon is due to the elimination of functional groups during heat-treatment.

The high temperature pyrolyzed carbon XPS spectra comparison is shown in Figure 5.4. The C1s data is dominated by the presence C-C and C-H bonds and lower concentrations of C-O, C=O and O-C=O bonds. Comparing all the C1s scans, the width of the C-C peak (284.8 eV) can be arranged in the following order: TR>ATR>CC1000>TC1100>TC1600>graphite. Such a trend indicates the presence of relative amounts of carbon-based functional groups on the surface. With respect to the final products, CC1000 has the highest number of heteroatoms connected with carbon atoms and TC1600 has the lowest level. As seen in the deconvolutions of the C1s scans, sulfonated tire-derived carbons TC1100 and TC1600 show significantly reduced amounts of C-O and C=O bonds. The sulfonation process removed many of the heteroatoms on the carbon and this will help to reduce the irreversible capacity of the LIBs/NIBs. The O1s data shows both CC1000 and TC1100 present relatively large amounts of C=O species on the surface. As the pyrolysis temperature was increased to 1600 ºC, the data shows a clear decrease in the C=O signal. Electrochemical testing of the carbon materials with a large portion of surface oxygen functional groups exhibited increased irreversible capacity by forming \(-\text{COOLi}\) from \(-\text{COOH}\) and \(-\text{OLi}\) from \(-\text{OH}\) [74]. The S2p data shows
Table 5.1. (a) XPS surface concentrations (in atomic percentages) of tire rubber, acid-treated tire rubber, CC1000, TC1100, TC1600, and graphite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR</td>
<td>68.3 at%</td>
<td>25.1 at%</td>
<td>6.6 at%</td>
</tr>
<tr>
<td>ATR</td>
<td>88.7 at%</td>
<td>9.8 at%</td>
<td>1.4 at%</td>
</tr>
<tr>
<td>CC1000</td>
<td>77.2 at%</td>
<td>21.1 at%</td>
<td>1.7 at%</td>
</tr>
<tr>
<td>TC1100</td>
<td>84.6 at%</td>
<td>15.1 at%</td>
<td>0.3 at%</td>
</tr>
<tr>
<td>TC1600</td>
<td>94.4 at%</td>
<td>5.3 at%</td>
<td>0.3 at%</td>
</tr>
<tr>
<td>Graphite</td>
<td>98.7 at%</td>
<td>1.3 at%</td>
<td>0 at%</td>
</tr>
</tbody>
</table>

Figure 5.4. X-ray photoemission spectroscopy (XPS) comparisons of graphite, CC1000, TC1100 and TC1600: column (a) C1s scans, (b) O1s scans, and (c) S2p scans.
that all of the pyrolyzed carbons made from tire contain the -SO\textsubscript{3}H group. Meanwhile, TC1100 also presents some thiol groups after acid treatment and this group was eliminated under 1600 °C heat-treatment conditions.

The INS spectra for all the carbon materials in the energy range of 15 meV to 450 meV are plotted in Figure 5.5. The INS spectrum for the starting raw tire powders has the highest integrated intensity due to the presence of large amounts of hydrogen in the rubber. In the raw tire powders, hydrogen exists in various forms, e.g., C-H in aromatic rings (sp\textsuperscript{2} carbon) and -CH\textsubscript{2}- and -CH\textsubscript{3} groups in the polymers (sp\textsuperscript{3} carbon). In the INS spectrum, the multiple peaks in the energy range of 20 meV to 80 meV are mainly due to ring deformation modes, whereas the peaks in the energy range of 80 meV to 200 meV can be assigned to the vibrational (wagging, rocking, twisting, bending) modes of the bonds in -CH\textsubscript{2}- and -CH\textsubscript{3} bonds, as well as the bending mode of C-H in the aromatic rings. The C-H stretching modes can be found at around 380 meV, and as a result of the various C-H bonding scenarios (aromatic C-H, >CH\textsubscript{2}, -CH\textsubscript{3}), the peak is relatively broad (see Supporting Information for illustrations of these modes obtained from ab initio calculations on related model molecules).

Upon sulfonation, a large fraction of hydrogen is removed, as indicated by the much-reduced integrated intensity, as well as the disappearance of a number of peaks in the energy range of up to 200 meV. For example, most of the ring deformation modes (20 meV to 80 meV due to aromatic ring deformation) are gone, and many of the modes believed to be due to aliphatic -CH\textsubscript{2}- and -CH\textsubscript{3} (80 meV to 200 meV) are also suppressed.
Figure 5.5. INS spectra of tire-derived samples processed under various conditions. Note: y-axis is in logarithmic scale, and the relative intensity of the spectra reflects the relative scattering power of the samples (except for the one for graphite, which was scaled by a factor of 0.2 for clarity).
The presence of a new peak at around 110 meV is consistent with some vibrational modes associated with -SO\(_3\)H (e.g., the OH bending mode and the S-O stretching mode with H riding on the O, see Supporting Information). Also, the shape of the peak at 380 meV is changed, which can be explained by the new contribution of the O-H stretching mode at a slightly different energy compared to the C-H stretching mode.

The sulfonated samples can be heat-treated at various temperatures. After 1100 °C heat-treatment one can see that the integrated intensity further decreases and the peaks corresponding to the C-H/O-H bending modes now merge into two broad peaks centered at 110 meV and 150 meV respectively, separated by a dip at 130 meV. Such a peak profile can be attributed to the out-of-plane and in-plane bending modes of the terminating hydrogen at the edges of the graphite layers, as suggested by previous INS experiments and simulations [79]. Note that this is the material that has been shown to exhibit superior performance when used in batteries and capacitors, and an explanation for the enhanced performance requires further investigation.

If the sulfonated sample is heat-treated at a higher temperature (1600 °C), almost all hydrogen will be removed, and the sample becomes very much like graphite. This is indicated by the absence of the C-H stretching peak at 380 meV, as well as the similarity of the INS spectrum to the one measured on the commercial graphite. On the other hand, the INS spectrum from the TC1600 sample shows smeared edges and broader peaks compared to the commercial graphite, meaning that the structure is probably less ordered. To better understand the role of sulfonation, the tire powder was also heat-treated directly without sulfonation. After heat treatment at only 1000 °C, almost all
hydrogen was removed. This is in stark contrast to the sulfonated sample for which some terminating hydrogen formed and survived even after 1100 °C heat treatment. Another interesting observation is that, compared to the TC1600 sulfonated sample, the structure of the CC1000 sample is even more disordered. In fact, the latter is more like the carbon black, which will not graphitize easily.

To summarize, what can we learn from the above observations? First, the sulfonation removed some >CH₂ and -CH₃ in the raw tire powders, and created -SO₃-H (and possibly SO₂-H). Second, by heat-treating the sulfonated sample at 1100 °C, almost all >CH₂ and -CH₃ were removed. The -SO₃H functional group helped to produce terminating H at the edge of the sp² bonded graphite-like layers. Previous studies also proved that the introduction of molecular hydrogen to passivate the active surface area left behind by desorbed surface oxygen groups can control the irreversible capacity to improve efficiency, increase cyclability, and enhance electro-conductive/adsorption properties.[70, 80] In contrast, heat-treating the samples without sulfonation, even at a lower temperature 1000 °C, will remove essentially all hydrogen, and the sample becomes sp² carbon with a high degree of disorder. Third, if the sulfonated sample is further treated at 1600 °C, it turns into a graphite-like structure. The INS experiment allows us to estimate the relative amounts of hydrogen content, as well as the bonding environment of hydrogen. It also reveals the different degree of order in samples heat treated at various temperatures, with and without sulfonation.
5.4. Summary

In summary, combining all the test results conducted, sulfuric acid treatment plays an important role in removing impurities in the tire rubber, producing unique pore size distribution, and modifying the surface functional groups. It is shown that CC1000 has more oxygen content and less terminating hydrogen atoms, while the sulfonation process produces more terminating H and also controls the O atom in a relatively low level. Such properties, in turn, influence the C/H ratio and the electrochemical performance of the material. The unnecessary surface oxygen groups could react with the Li ions in an irreversible manner in producing SEI layer and contributing to the lithium loss in the full cells. Hence, the sulfonation pretreatment of the tire-derived carbon improves the electrochemical performance of the material and provides a pathway to develop and further improve advanced energy storage materials.
CHAPTER 6
NOVEL WASTE TIRE-DERIVED CARBON AS ANODE FOR BEYOND LITHIUM-ION BATTERIES
Abstract

The application of low-cost tire-derived carbon as lithium ion battery anodes provides a good value-added recycling option. In this chapter, applications in beyond lithium systems for tire-derived carbon will be investigated to further reduce the cost of the energy storage systems for large scale stationary energy storage applications. This chapter consists two major parts of the applications (Sodium-ion batteries and Potassium-ion batteries).

The content of sodium-ion batteries part is revised based on the following paper published on Journal of Power Sources:


The content of potassium part is revised from the following paper published on Journal of The Electrochemical Society:

6.1 Tire-derived Carbon as Anode for Sodium ion batteries

6.1.1 Introduction

With the concerns of the limited global availability of lithium resources and high cost, sodium-ion batteries (SIBs) are considered to be an alternative to lithium-ion batteries (LIBs), especially for applications where energy density is of minor importance, such as stationary grid energy storage of electricity produced from renewable sources [81, 82]. Due to its high abundance, low cost, and suitable working chemical potential (-2.7 V vs. Standard Hydrogen Electrode), rechargeable sodium-ion batteries are gradually attracting a lot of attention [83]. Sodium shares many similar chemical properties with lithium because of its location in the periodic table and the similarities of fundamental principles of SIBs and LIBs. Thus far, several suitable cathode materials have been developed for SIBs [84-87]. However, the absence of good anode material hinders the application of SIBs. The search for suitable electrode materials for sodium-ion batteries, in particular robust anodes for Na⁺ storage therefore is of great important and becomes more urgent. Extensive research has been conducted to develop potential materials, such as alloying anodes [88], conversion anodes [89, 90], insertion anodes [91] and carbon anodes. But on the way to commercialize SIBs, carbon based materials have attracted the most attention, respecting to their unique electrochemistry functions and low cost for large-scale application [92]. Compared to carbon anodes, the disadvantages of alloying anodes and conversion anodes for SIBs should be attributed to the large volume changes during sodiation and desodiation, which causes fast capacity fade. In addition, conversion anodes also encounter relative high working potential and the large hysteresis between
discharge and charge problems. For intercalation anodes, the low capacity limits their application.

Unlike the successful application of graphite as anodes in LIBs, the electrochemical sodium insertion into graphite to form binary intercalation compound is proven to be not favorable [10, 93]. Theoretical calculations suggest that the interlayer distance of graphite is too small to accommodate the large Na⁺ ion, and a minimum interlayer distance of 0.37 nm is believed to be good for Na⁺ insertion [94]. Very recently, progress has been made by Adelhelm et al. through the use of solvent co-intercalation to address the unfavorable graphene layer intercalation [95]. A variety of carbon materials have been investigated as anodes for SIBs, such as hard carbons [96], carbon nanotubes [94], reduced graphene oxides [97], and expanded graphite [98]. Hard carbon is likely to be the most promising anode for commercialization because of its stability, relatively high capacity and easy to scale-up. However, great amounts of the currently studied hard carbon are produced from sucrose [99], banana peels [100] and dopamine [101] etc. Most of the precursors are relatively high cost or require complex treatments, which prevent the application in many cost sensitive fields [102]. A low-cost hard carbon anode material is desired for promoting the development of SIBs for large-scale energy storage market.

The widespread use of motor vehicles unavoidably results in large quantities of used tires. Globally, it is estimated that about 1.5 billion waste tires are produced every year [103]. In the past, used tires are mostly disposed in landfills, which is not a sustainable solution. As more and more discoveries find that discarded tires pose serious environmental and health threats to our society, proper recycling of worn-out tires has
become a critical issue. By now, the recycling of tires was mainly consumed as fuel, additives to plastics, rubbers, or civil engineering applications. Typically, a tire consists of natural rubber, synthetic polyisoprene, butadiene rubber, styrene-butadiene rubber, carbon black and a fractional amount of additives [56]. The regular direct pyrolysis process results in the production of about 30-40% carbon black, depending on the pyrolysis conditions [103]. A high value-added product produced from used tires will lead more opportunities for the recycling industry and generate more environmental and economic benefits.

Tires are designed to be stable in physical and chemical harsh conditions owing to their cross-linked structure and various additives, which make them hard for recycling. However, such disadvantages are also the desired properties for electrochemical energy storage applications. A method for producing sulfonated and pyrolyzed carbon composite from recycled micronized tire rubber has been reported [104, 105]. The sulfonated tire-derived carbon has ~10% higher yield than the controlled carbon that was produced from the direct pyrolysis of powder rubber. Since the vulcanized tire formulation consists of a mixture of diene-rubbers such as polybutadiene, polyisoprene, or styrene-butadiene copolymer, desulfonation of rubbers or aliphatic hydrocarbon during the pyrolysis step will form unsaturated moieties that are relatively better char-forming materials [104]. This process also improves the carbon yields. Relatively low packing density and higher operating voltage are among the main obstacles for hard carbons to be used as an anode in LiBs. However, such problem will not be a big issue for SIB application since sodium-ion batteries are mostly targeted for stationary energy storage and also the Na/Na⁺ couple
operates 0.34 V higher than Li/Li⁺ couple. To validate our hypothesis on potential use of tire-derived carbons in SIB anodes we present here the performance of these carbons, synthesized at different temperatures. Interestingly, a higher temperature of pyrolysis leads to a larger sodium storage capacity, which behaves opposite to that of some hard carbons produced in the same temperature range and used against lithium. In the meanwhile, unlike most hard carbon voltage profile in LIBs, the plateau capacity at low-potential region increases significantly as the pyrolysis temperature increases, which is beneficial to increase the cell voltage and energy density.

6.1.2 Experimental Details

**Tire-derived Carbon Synthesis**

Pulverized tire rubber powder in the size range of 80–120 μm was obtained from Lehigh Technologies, Inc., Georgia. Typically, 50g of tire rubber powders were soaked in a 100 mL concentrated sulfuric acid bath (kept at 110 ºC for overnight) to yield the sulfonated tire rubber that was then washed and filtered off. The washed sulfonated tire rubber was then pyrolyzed from room temperature to 400 ºC at 1 ºC /min then at 2 ºC /min to 1100 ºC, 1400 ºC, and 1600 ºC, respectively, in a tube furnace under flowing nitrogen gas, and they are hereafter designated as TC1100, TC1400, and TC1600. This described synthesis method can produce up to 500g materials per batch in current stage and will be scale-up to 10kg in the next few months.

**Material Characterization**

The X-ray diffraction (XRD) data were collected with a PANalytical Empyrean diffractometer equipped with Cu Kα radiation (λ=1.5406Å). Nitrogen adsorption
desorption isotherms were obtained with a Quantachrome NovaWin1000 surface area & porosity analyzer at 77.4° K. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained by the Barret-Joyner-Halenda (BJH) method. Raman spectra were collected with a Horiba LabRam HR using an excitation wavelength of 473nm, a 600 gr/mm grating and an 800 mm monochromator. A Zeiss Merlin VP scanning electron microscope (SEM) operated at 3kV was used to characterize the surface morphologies of the samples. Interlayer distances of the carbons were determined by a Hitachi HD-2300A scanning transmission electron microscope (STEM) with a field emission source operated at 200 kV in bright-field imaging mode at a 2.1Å resolution. XPS data were collected with a Thermo-Fisher K-alpha XPS with a monochromatic Al-Kα source, a 1486.6 eV source, 400 μm spot, and an argon ion flood gun.

**Electrochemical Measurements**

Electrochemical properties were characterized with half cells against a sodium-metal electrode. The working electrode was prepared by spreading the mixed slurry consisting of the active material, conductive carbon C45 and PVDF binder in N-methyl-2-pyrrolidone (NMP) solvent at a weight ratio of 80:10:10. The resulting slurry was then casted onto a copper foil current collector and transferred to a vacuum oven for drying at 120 °C overnight. The typical loading amount of active material was 2 to 2.5 mg cm⁻². The electrolyte was a solution of 1 M NaClO₄ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in vol). Coin cells (CR2032) consisting of the tire-derived carbon electrode, glass fiber, a sodium metal counter electrode and electrolyte were assembled in an Ar-
filled glove box. Galvanostatic charge/discharge was carried out on a Land CT2001 battery test system (Wuhan, China) over a voltage range of 0 – 3 V at current density of 20 mA g⁻¹ at room temperature. The sodiated electrodes were disassembled in an Ar-filled glovebox and placed in an air-sensitive sample holder for further characterizations. The ex situ XRD analysis was performed on a Rigaku Miniflex600 diffractometer with Cu Kα radiation.

6.1.3 Results and Discussion

As shown in Figure 6.1(a), XRD collected on bulk materials indicate that the tire-derived carbons pyrolyzed at different temperatures are mainly composed of poorly crystalline carbonaceous material. The broad peak near 2θ ~ 26.6° suggests lack of significant order in the bulk of the carbon materials and this peak is related to the (002) plane. The R value for TC1100, TC1400, and TC1600 are 1.58, 2.27 and 2.67, respectively. Here, R is defined as the peak height divided by the background height at the position of the peak. The value of R can be used to estimate the fraction of graphene sheets, which increases as the proportion of the graphene layers with parallel neighbors increases [106]. TC1600 shows the largest graphene fraction by the comparing three R values. Raman spectra obtained on tailored carbons are shown in Figure 6.1(b). The \text{I}D/\text{I}G ratio for TC1100, TC1400, and TC16000 increases from 0.85 to 0.96 to 0.99. Such a trend has also been reported for hard carbon material obtained from other precursors [107]. The \text{I}D/\text{I}G ratio changes differently in a three-stage model of increasing disorder as illustrated by Ferrari et al [75]. The G peak is due to the bond stretching of all pairs of sp² atoms in both rings and chains. The D peak is due to the breathing modes of sp² atoms.
in the rings [108]. The ratio of $I_D/I_G$ is proportional to the number of aromatic rings. The increased relationship in the $I_D/I_G$ ratio and G band position for the tire-derived carbons shows that more sp² amorphous carbon turns into nanocrystalline graphite at higher temperatures. This tendency can also be concluded and confirmed by the R values.

The BET surface areas of TC1100, TC1400, and TC1600 are 189, 210 and 148 m² g⁻¹, respectively. The pore volume distribution shows a relatively wide pore size distribution with prominent microporosity with a pore width of less than 2 nm and a noticeable volume fraction of pore widths in the range of 6 - 8 nm. The dominant microporosity could be attributed to the fact that the sulfuric acid pretreated tire powder produces SO₂ and steam which yields activated tire-derived carbon [104]. The interlayer distances for crystalline areas were determined high resolution scanning transmission electron microscopy (STEM) to be 4.7 Å, 4.5 Å, and 4.0 Å for TC1100, TC1400 and TC1600, respectively. These values are larger than the required distance (0.37 nm) [94] for sodium intercalation and follow the general trend that the carbon interlayer distance decreases with increasing pyrolysis temperatures. The selected area electron diffraction (SAED) patterns of three different temperature treated carbon indicate that the amorphous phase dominates. It is also clear that the TC1600 carbon has more crystalline phases compared to the lower temperature pyrolyzed carbon.

X-ray photoemission spectroscopy (XPS) of the tire-derived carbons are shown in Figure 6.2. The C1s spectrum in Figure 6.2(a) for the samples shows a sharp peak at 284.8 eV, which is due to the sp² configuration. The fitting results for C1s spectrum also
Figure 6.1. (a) X-ray diffraction patterns and (b) Raman spectra of tire-derived carbons obtained by pyrolyzing at different temperature.

Figure 6.2. X-ray photoemission spectroscopy (XPS) of sulfonated tire rubber-derived carbons (a) C1s scans (b) S2p scans. The insert in (a) shows the expanded binding energy plots.
show small amounts of C-O, C=O, and aromatic C functional groups on the surface. The small peak at around 291 eV could be related to the presence of aromatic rings in the materials and as shown in the inset that its relative intensity increases with the pyrolysis temperatures. This result also confirms the conclusion by Raman spectra that more aromatic rings are present in the higher temperature samples. Figure 6.2(b) shows the S2p scans of the samples. The doublets at about 164 eV are related to the thiol group and the peak at 169 eV is due to the sulfate group. It is shown that as the temperature increases, sulfate groups are removed from the samples. The XPS elemental analysis for the samples is shown in Table 1. The impurities of Si and Fe could be due to the additives or impurities present in the tire powders. It is clear that the purity improves as the pyrolysis temperature increases since more functional groups are eliminated at higher temperatures.

The electrochemical performances of tire-derived carbons were evaluated in sodium half cells. Figure 6.3 (a)-(c) show the cycling stability of the three samples tested under a current density of 20 mA g⁻¹. TC1100 provides an initial capacity of 520 mAh g⁻¹ for discharge and 250 mAh g⁻¹ during charge, which corresponds to only 48% coulombic efficiency for the first cycle in Figure 6.3 (a). The large irreversible capacity loss could be associated with the high surface area of the carbon material and the reduction of carbon surface functional groups followed by electrolyte decomposition and formation of solid electrolyte interphase (SEI) [36, 109]. Surface coating techniques could be used in the future to reduce the surface area and to improve the efficiency. After the 10th cycle, the coulombic efficiency increases to above 99% and the capacity becomes stabilized. The
Table 6.1. XPS surface concentration (in atomic percentages) of TC1100, 1400 and TC1600

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>S</th>
<th>C</th>
<th>O</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC1100</td>
<td>1.5</td>
<td>1.1</td>
<td>82.1</td>
<td>14.8</td>
<td>1.52</td>
</tr>
<tr>
<td>TC1400</td>
<td>0.9</td>
<td>0.6</td>
<td>92.6</td>
<td>4.4</td>
<td>-</td>
</tr>
<tr>
<td>TC1600</td>
<td>0.5</td>
<td>0.5</td>
<td>95.5</td>
<td>3.6</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6.3. Cycling performances of (a) TC1100, (b) TC1400, and (c) TC1600, and (d) a comparison of discharge and charge curves of all the carbons.
capacity at the 100\textsuperscript{th} cycle was 179.4. Compared to TC1100, the cycling results for TC1400 and TC1600 in Figure 6.3 (b) and (c) show improvements in first cycle efficiency and capacity. TC1400 exhibits 57\% first cycle efficiency and a capacity of 185 mAh g\textsuperscript{-1} after 100 cycles whereas TC1600 shows further enhancement of the first cycle efficiency to 66\% and a capacity of 203 mAh g\textsuperscript{-1} at 100\textsuperscript{th} cycle. The improved cycling performance may be related to the reduced number of surface functional groups and also reduced amount of defects in the carbon after the higher temperature treatment. Figure 6.3 (d) presents the electrochemical voltage profiles when sodium is intercalated and deintercalated from the various tire-derived carbons. It can be seen that the TC1100 voltage profile mostly consists of the sloping region during cycling. However, both the TC1400 and TC1600 charge and discharge curves can be divided into two regions, a sloping voltage region extending down to 0.2 V and a large portion of the plateau region. Similar voltage profiles of other high temperature treated carbon materials for sodium-ion batteries have also been reported previously \cite{67, 107, 110}. The observed charge capacity of the plateau region for TC1400 is 165 mAh g\textsuperscript{-1}, which is approximately 65\% of the whole capacity. For TC1600, the plateau capacity increases to 197 mAh g\textsuperscript{-1}, accounting for 71\% of the total capacity. In carbon materials, the disordered graphene layers are randomly distributed and can be modeled like a “house of cards” \cite{106}. Steve et al. revealed that the sloping region of the potential profile corresponds to the insertion of sodium between the turbostratically disordered graphene layers and the low-potential plateau region can be attributed to the insertion of the metal into the nanopores between randomly stacked layers through a process analogous to adsorption \cite{10}. When sodium
is intercalating into graphene inter-layers continuously, the overall potential decreases as the insertion of metal ions between layers changes the potential for further insertion and turbostratic stacking between the parallel sheets gives rise to a distribution of insertion-site potentials [96]. The Na chemical potential of the following step in the pore filling is close to that of the elemental sodium metal, which shows a voltage plateau close to 0 V. The improved performance of tire-derived carbon at higher firing temperature suggests that more nano-crystalline graphene layers are created and these randomly stacked layers generate more voids for sodium storage at an elevated temperature. The increased capacities below 0.2 V for tire-derived tires could also be attributed to the increment of nanopores to provide more sites for sodium plating in the low potential region. Predominant amount of micropores below 2 nm rise as the treating temperature increase for the samples which suggests more SO$_2$ related activation occurred at higher temperature.

A comparison of the discharge and charge curves of TC1600 at different cycles is shown in Figure 6.4. The plot shows that the capacity decreases with cycling. However, by comparing the discharge capacity profile, it is interesting to reveal that the sloping region is almost constant while the plateau region is reduced dramatically. This rapid plateau region decay indicates the sodium adsorption-desorption in the nanopores at the low-potential region and hence capacity fades and the Na plating into nanopores is not fully reversible or has poor kinetic properties.

Ex-situ XRD measurements (in Figure 6.5) were carried out to analyze the structural changes during sodium insertion into TC1600 carbon. For the pristine electrode,
**Figure 6.4.** Comparison of the discharge and charge curves of TC1600 at 25th, 50th, 75th, and 100th cycles.

**Figure 6.5.** Ex-situ XRD patterns of the TC1600 electrodes at different voltages.
the (002) peak centered at 25.3° and the two strong peaks located between 40° and 55° are due to the copper foil substrate. All the patterns were adjusted based on the standard 2θ position of Cu as internal standard. The coin cells were discharged from OCV to 0.8V, 0.3V, 0.2V, 0.1V, 0.05V and charged back to 0.1V and 0.3V, respectively. As sodium intercalates into the carbon electrode, the (002) peak shifts slightly to lower angle for electrodes discharged to lower voltage. Such peak shifts to lower angle indicates an increase in d-values due to sodium insertion between the parallel graphene layers and an expansion of the interlayer spacing. It is noticeable that the peaks keep the same positions once discharged below 0.3V and stay unchanged even charged back to 0.3V. This confirms the sodiation mechanism at low voltage changes from insertion between the parallel graphene layers to the filling of sodium into nanopores in the materials. It is also interesting to mention that Tarascon et al. recently reported in-situ XRD results for sodiation process for carbon nanofibers heat treated at 2200 °C [111]. No (002) peaks shift observed during the sodiation and desodiation process and this is an opposite trend for our result and some previously reported results [10, 110]. Such a difference could be possibly attributed by much higher treatment temperature for their sample, which would greatly reduce the interlayer distance between parallel graphene layers and makes it impossible for Na⁺ to intercalate between the layers.

Figure 6.6 shows the charge and discharge capacities of TC1100, TC1400 and TC1600 at different current densities. As shown in Figure 6.6 (a), TC1600 has the highest capacity at a small current density (20 mA g⁻¹). However, as the current density increases, both TC1600 and TC1400 suffer from dramatic capacity fade, dropping from 256 mAhg⁻¹
Figure 6.6. (a) Cycling capacities of TC1100, TC1400, and TC1600 at different current densities, and discharge profiles of (b) TC1100, (c) TC1400, and (d) TC1600 at different current densities.
at 20 mA g\(^{-1}\) to 72 mAh g\(^{-1}\) at 200 mA g\(^{-1}\) for TC1600 and from 204 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) to 55 mAh g\(^{-1}\) at 200 mAh g\(^{-1}\) for TC1400. Meanwhile, TC1100 exhibits much better large-current-density tolerance which has a capacity of 225 mAh g\(^{-1}\) at 20 mA g\(^{-1}\) and maintains 120 mAh g\(^{-1}\) at 200 mAh g\(^{-1}\). Figure 6.6 (b), (c) and (d) are plotted for comparing the discharge voltage profiles for all carbon samples at different current densities and they reveal the possible reasons. As discussed before, both TC1400 and TC1600 have a larger portion of the low-voltage plateau, which is caused by pore plating of sodium metal. This plateau rapidly disappears as the current density increases. TC1100 does not have a plateau and delivers a larger capacity at higher current density. These results indicate that the pore plating process will be slower and needs more time to reach equilibrium than the sodium insertion into disordered graphene layers. To further improve the high rate capability, electrode materials conductivity could be improved with a surface coating process [107].

The long-term stability test was conducted for TC1100 in 1M NaClO\(_4\) in propylene carbonate (PC) as the electrolyte, as shown in Figure 6.7. Good cyclability performance proves that the materials could also work in other electrolytes, such as PC based systems, which can be operated at lower temperature than ethylene carbonate (EC) based electrolytes. TC1100 shows a capacity of 154 mAh g\(^{-1}\) after 600 cycles at a current density of 20 mA g\(^{-1}\).

A comparison table of recently reported carbon materials for sodium ion batteries with this work is shown below in Table 6.2. As it can be seen, tire-derived carbons have comparable performance with most of the state-of-art sodium ion batteries carbons.
Figure 6.7. Long-cycle stability test of TC1100 at a current density of 20 mA g⁻¹.

Table 6.2. Comparison of the sodium storage performance for state-of-art NIB carbons.

<table>
<thead>
<tr>
<th>Performance</th>
<th>1st cycle efficiency</th>
<th>Capacity below 0.2V vs Na/Na⁺</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-doped carbon sheets[101]</td>
<td>165 mAhg⁻¹ after 600 cycles (200 mAg⁻¹)</td>
<td>26.4%</td>
<td>not reported</td>
</tr>
<tr>
<td>Porous N-doped carbon sphere[112]</td>
<td>206 mAhg⁻¹ after 600 cycles (200 mAg⁻¹)</td>
<td>39.9%</td>
<td>ca. 70 mAhg⁻¹ at 200 mAg⁻¹ (3rd cycle)</td>
</tr>
<tr>
<td>Banana peel pseudographite[100]</td>
<td>210 mAhg⁻¹ after 600 cycles (500 mAg⁻¹)</td>
<td>67.8%</td>
<td>200 mAhg⁻¹ at 50 mAg⁻¹ (10th cycle)</td>
</tr>
<tr>
<td>Hollow carbon spheres[113]</td>
<td>160 mAhg⁻¹ after 100 cycles (100 mAg⁻¹)</td>
<td>41.5%</td>
<td>ca. 100 mAhg⁻¹ at 50 mAg⁻¹ (10th cycle)</td>
</tr>
<tr>
<td>Hard carbon spherules[99]</td>
<td>290 mAhg⁻¹ after 100 cycles (30 mAg⁻¹)</td>
<td>83.0%</td>
<td>220 mAhg⁻¹ at 30 mAg⁻¹ (2nd cycle)</td>
</tr>
<tr>
<td>Carbon microspheres[114]</td>
<td>183 mAhg⁻¹ after 50 cycles (30 mAg⁻¹)</td>
<td>ca. 40%</td>
<td>ca. 120 mAhg⁻¹ at 30 mAg⁻¹ (2nd cycle)</td>
</tr>
<tr>
<td>N-doped porous carbon sheets[115]</td>
<td>155.2 mAhg⁻¹ after 260 cycles (50 mAg⁻¹)</td>
<td>34.9%</td>
<td>ca. 150 mAhg⁻¹ at 50 mAg⁻¹ (5th cycle)</td>
</tr>
<tr>
<td>Hollow carbon nanowires[116]</td>
<td>206.3 mAhg⁻¹ after 400 cycles (50 mAg⁻¹)</td>
<td>50.5%</td>
<td>ca. 150 mAhg⁻¹ at 50 mAg⁻¹ (2nd cycle)</td>
</tr>
<tr>
<td>Hierarchical porous carbons[117]</td>
<td>160 mAhg⁻¹ after 200 cycles (500 mAg⁻¹)</td>
<td>34.0%</td>
<td>ca. 100 mAhg⁻¹ at 100 mAg⁻¹ (10th cycle)</td>
</tr>
<tr>
<td>Present work</td>
<td>203 mAhg⁻¹ after 100 cycles (20 mAg⁻¹)</td>
<td>66.0%</td>
<td>197 mAhg⁻¹ at 20 mAg⁻¹ (3rd cycle)</td>
</tr>
</tbody>
</table>
Considering of the main advantage for SIBs is their low cost, especially for large-scale energy storage, price is always the most important aspect. Many of the current well-performing materials use high value precursors such as dopamine, polyaniline nanowires and graphene oxides, which could hinder their potential for application. However, the cost for waste tires is even much lower than the most common used sucrose, which costs ~$0.06 per kilogram with more than 70% yields for waste tire and $0.25 per kg with about 45% yields for sucrose [102]. In the meanwhile, the waste tire recycling is a well-developed industry and the sources are readily available in large amount when comparing with materials made with banana peels and peanut skin.

6.1.4 Summary

In summary, we have demonstrated the use of solid-waste-tire-derived carbons as anodes for sodium-ion batteries. When the pyrolysis temperature is increased from 1100 to 1600°C, the capacity of the plateau below 0.2 V increases dramatically and this could help increase the full cell energy density. The 1600°C treated carbon shows a capacity of 203 mAh g⁻¹ after 100 cycles. These tire-derived carbons demonstrate a low-cost, easily scalable option with good electrochemical capacity and stability for sodium-ion battery anodes.

6.2 Tire-derived Carbon as Anode for Potassium ion batteries

During the past two and half decades, great efforts have been devoted to Lithium-ion batteries (LiBs) [59, 118-123]. However, the limited global availability of lithium resources, safety and high cost of extraction hinder the application of LiBs in several energy storage systems. This demands alternative energy storage devices that are based
on earth-abundant elements. Recently, sodium-ion batteries (NIBs) and potassium-ion batteries (KIBs) have gradually received more attention to realize affordable rechargeable batteries for large scale systems [83, 124, 125]. Rapid progress has been made to advance NIB technologies. Many of the layered metal oxides and polyanionic compounds exhibited good capacity and cyclability as cathode materials in NIBs [83]. On one side, developing anodes for NIBs is still a great challenge as only very limited amounts of Na can be intercalated into graphite due to the larger ionic radius of sodium (1.0 Å for Na$^+$ vs. 0.76 Å for Li$^+$) [98]. On the other hand, despite its even larger ionic size (1.40 Å), potassium ion based graphite intercalation compounds (GICs) have been reported [126]. The high abundance and lower cost of potassium raw materials (1000 USD t$^{-1}$ for K$_2$CO$_3$ vs. 6500 USD t$^{-1}$ for Li$_2$CO$_3$), mean that K-ion based electrochemical energy storage technologies can exhibit their potentials in many applications [21]. Also, similar to sodium, potassium does not alloy with aluminum at lower potentials, enabling the use of aluminum as the anode current collector instead of high cost copper. Moreover, the redox potential of K/K$^+$ (-2.94 V vs. standard hydrogen electrode, SHE) is lower than that of Na/Na$^+$ (-2.71 V vs. SHE), indicating a higher working potential for K-ion batteries. In addition, K$^+$ ions show higher transport numbers and mobility in non-aqueous electrolytes due to weaker Lewis acidity and smaller Stoke’s radius of solvated ions [127]. A few potassium intercalation cathode materials such as Prussian blue and its analogues [124, 128, 129], FeSO$_4$F [22], amorphous FePO$_4$ [23] and layered K$_{0.3}$MnO$_2$ [21] have been reported. As for the anode, the use of K metal is not applicable due to its severe safety concerns. Hence, identifying the potential anode materials for KIBs is of great importance. Recently,
carbon based materials (graphite, graphene and hard carbons) and tin-based composites have been studied as anodes for KIBs [126, 130-134]. Among these materials, hard carbons showed the most promise because graphite and tin-based composites suffered pronounced capacity fade and lower rate capability while the high cost of graphene prevents its application in the price sensitive large-energy storage field [130, 133].

Here, we investigated the low-cost, tire-derived carbon as a potential anode material for potassium-ion batteries, presenting another important application for the waste-tire recycling products.

Electrochemical properties were characterized with half cells against a potassium-metal electrode. The working electrode was prepared by spreading the slurry consisting of 80% active TC1100 material, 10% conducting carbon (Timcal Super C65) and 10% PVDF binder in N-methyl-2-pyrrolidone (NMP) solvent. The resulting slurry was mixed for 20 min using a Thinky mixer and subsequently coated onto a copper foil. After drying for 12 h in a vacuum oven at 80°C, 12 mm diameter electrodes were punched out with an active material density of ~ 2 mg cm⁻². Coin cells (CR2032 type) were assembled in a high purity Argon glovebox. The electrolyte utilized consisted of 0.8 M KPF₆ dissolved in a 1:1 volume mixture of ethylene carbonate (EC)/diethyl carbonate (DEC). Whatman glass fiber was utilized as the separator. Cyclic voltammetry was performed utilizing a Gamry Reference 600+ instrument, at a scanning rate of 0.2 mV s⁻¹. Galvanostatic cycling was performed using an Arbin cycler, with 1C = 279 mA g⁻¹ utilized to calculate current densities for all C-rates described in this manuscript. The voltage range of 0.005 to 3.0 V was used for all cycling tests. Since the material will only work as anodes in K-ion
batteries, only the capacities below 1.8 V will count as effective capacity. All the discharge capacities discussed below are calculated based on the potassium storage capability between 0 to 1.8 V. All potentials listed in this manuscript are versus K/K⁺ unless otherwise stated.

The electrochemical test data of TC1100 vs. potassium metal in a half cell configuration is shown in Figure 6.8. The cyclic voltammetry (CV) plot obtained at a scan rate of 0.2 mV s⁻¹ is shown in Figure 6.8(a). The reduction process (potassiation) at the first cycle results in a small peak at about 0.91 V and a larger reduction current, which is normally attributed to the electrolyte decomposition and SEI formation. In the depotassiation process, an oxidation peak is observed at around 0.54 V. Galvanostatic discharge-charge experiments were carried out to evaluate the potassium storage performance of the samples. As shown in Figure 6.8(b), the voltage profiles of charge-discharge at C/10 (27.9 mA g⁻¹) show a very large irreversible capacity at first cycle, which results in only 37.1% efficiency. This value is quickly improved to 76.4% at the following charge-discharge cycles. Further cycling test at C/2 is shown in Figure 6.8(c) and it reveals a good cyclability of TC1100 carbon. The initial discharge capacity below 1.8V is 192 mAh g⁻¹ and it remains at a capacity of 155 mAh g⁻¹ after 200 cycles, which corresponds to 80.7% capacity retention. The rate study of TC1100 at current densities of C/10, C/5, C/2, 1C and 2C was conducted and shows a discharge capacity of 220, 173, 139, 110, and 60 mAh g⁻¹, respectively in Figure 6.8(d). As shown in Figure 6.8(d), the discharge capacity was almost recovered once the current was changed from 2C to C/10, which suggests that the structure of the material can sustain high current densities.
Figure 6.8. Electrochemical performance of TC1100 as K-ion anode. (a) Cyclic voltammetry plots at 0.2 mV s\(^{-1}\) rate, (b) First two charge-discharge cycles at a current density of C/10 (27.9 mA g\(^{-1}\)), (c) Rate capability test, and (d) Discharge capacity retention at long-cycle stability test.
6.3 Comparison Between Sodium and Potassium Performance

It is very interesting to mention that although K⁺-ion has a 40% larger ionic radius compared to Na-ion, TC1100 shows better electrochemical cycling performances at higher rates in potassium-ion batteries than those in sodium-ion batteries. Such phenomenon has also been reported in the literature for other types of hard carbons [130, 131]. For example, Ji et al. shows higher diffusion coefficients of K⁺ in hard carbons than that of Na⁺ in hard carbons and such observation was attributed to lower K-ion activation energy caused by different binding energies between K/C and Na/C as well as a lower charge density of larger K-ions. The detailed mechanism of tire-derived carbon electrochemical performance in these two systems could be focused in the future studies [131].

6.4 Summary

Waste tire-derived carbon for beyond lithium systems application were demonstrated in this chapter. The abundance of sodium and potassium make these electrochemical energy storage systems become more attractive to large scale stationary electricity storage. With the proved low-cost and good cycling performance, tire-derived carbon is one of the most promising anode candidate for application.
CHAPTER 7
ALTERNATE ANODE MATERIALS: MONO-DISPERSED LITHIUM TITANTATE AND ITS PERFORMANCE
Abstract

The rapidly growth of electric car market boosts the great need for high-power, long-life and safe lithium-ion batteries. The alternative anode material, Li$_4$Ti$_5$O$_{12}$, operating at 1.55 V could meet most of the requirements for hybrid electric vehicles (HEVs) or plug-in hybrid electric vehicles (PHEVs). In this chapter, a shape controlled synthesis was utilized to obtain a mono-dispersed lithium titanate and the great performance of the electrode material presented a promising alternative anode material for electric car battery applications. The sustainable production is extremely important to our society and the earth. Other than the use of recycled tires as starting material for electrode synthesis, we also proved the lithium salts obtained from geothermal plants as side product could also be used as lithium source in battery materials.

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7.1 Introduction

As one of the most important energy storage devices in the past decades, lithium-ion batteries (LIBs) have been widely applied in our daily life from powering cell phones, laptops and other portable electronic devices due to their relative high energy density and long cycling life [1]. However, as limited by the material functions of carbon-based anodes (mostly graphite) for fast lithium ion intercalation and deintercalation, the current commercial LIBs suffer from significant capacity degradation when working under larger-current conditions for their potential application in electric vehicles and hybrid electronic
vehicles [104, 135]. In the meantime, lithium is thermodynamically unstable in contact with the conventional organic electrolytes under $\sim 1.0$ V. This electrochemical behavior always causes the formation of an insoluble Li-ion salts passivating layer on the surface of anode materials, referred to as the solid electrolyte interphase (SEI) [136]. This SEI film not only limits the capacity and dynamic response of the batteries by consuming lithium and lowering the lithium ion conduction, but also facilitates the formation of lithium dendrite that could create internal short circuits in the cells [137]. Therefore, the development of low-cost anode materials with robust recycling stability to sustain fast lithium ions insertion and extraction, as well as with reduced or eliminated SEI formation is crucial for the high-power application of LIBs.

To avoid the formation of SEI, extensive studies were focused on titanium-based anodes including various polymorphs of TiO$_2$ [17, 138-141] and lithium titanate [142]. Among these possible alternate anode materials for high-power LIBs, spinel Li$_4$Ti$_5$O$_{12}$ (LTO) with a structure of $Fd\bar{3}m$ space group has attracted significant attention owing to its unique electrochemical properties [143]. Unlike the commonly used graphite, LTO is a zero-strain insertion material. Each LTO structure unit is able to intercalate up to three lithium ions without any volume changes, converting Li$_4$Ti$_5$O$_{12}$ to rock salt Li$_7$Ti$_5$O$_{12}$ [13]. Such unique structure packing features of LTO leads to excellent reversibility and cyclic stability for fast lithium ion intercalation-deintercalation [144]. In addition, LTO has a stable and relatively high lithiation potential of 1.55V vs. Li$^+/Li$ to suppress the formation of SEI and consequently avoid the deposition of lithium dendrites, making the LIBs safe. Unfortunately, some kinetic problems of low intrinsic electrical conductivity (ca. $10^{-13}$
S·cm\(^{-1}\)) and poor lithium-ion diffusivity (ca. \(10^{-9}–10^{-13}\) cm\(^2\)·s\(^{-1}\)) limit such material to realize its full capacity at high rates[145].

Nanostructure engineering is a commonly used strategy in the development of high-performance electrochemical materials for Li\(_\text{IBs}\), because of the unique nanostructure-dependent functions [146, 147]. For example, the reduction of particle size will change the Li-ion solubility in various phases and in turn it alters the shape of the voltage profiles [148]. Furthermore, the smaller particle size also increases the contact areas of electrode/electrolyte interface and shortens the Li\(^+\) transport distance, which thus enhances the battery power outputs. In this regard, nanostructuring LTO as monodisperse nanoparticles (30-50 nm) have been carried out to advance LTO as high-power anode in this communication. Also, as technologies become more dependent on lithium, identifying new lithium sources and supply chains are needed. Recently, Simbol materials have developed a method to extract lithium chloride from geothermal brine solutions and converted them to lithium carbonate and lithium hydroxide products. Demonstration of Li\(_\text{IBs}\) made from Simbol’s lithium salts compared with commercially available lithium salts is essential.

LTO powders are normally prepared by a solid-state reaction of lithium salts with titania in small quantities [149-151]. However, materials made by this method in large quantities also come with inhomogeneity and larger particle size issues. In order to obtain excellent electrochemical performance, solution-based method is more desired to control the stoichiometry and the particle size of the LTO. Here, we report a simple, large scale synthesis of LTO nanoparticle method with controlled size, shape, composition and
extraordinary lithium-ion batteries performance [152]. The half-cell showed a capacity of 154.8 mAh g⁻¹ at 1C after 400 cycles and it could maintain a capacity of 147 mAh g⁻¹ at 10C. Full cells with LiFePO₄ cathodes have also been assembled, in which LTO demonstrated 92.6% capacity retention under 1C after 2000 cycles. We also report our evaluation of the LTO electrode materials made with lithium salts extracted from the geothermal sources for LIBs.

7.2 Experimental Detail

Synthesis of Li₄Ti₅O₁₂

Li₄Ti₅O₁₂ powders are synthesized in three stages. In stage I, TiO₂ nanospheres are prepared; and in stage II lithium is inserted in TiO₂ nanospheres and finally in stage III it is converted to LTO nanoparticles. The reported method has been scaled up to kg batches. The details of the synthesis stages are as follows.

Stage I (Preparation of TiO₂ nanospheres): 79g hydrochloric acid solution (37%, Fisher Scientific), 7.9g citric acid monohydrate (Alfa Aesar) and 398g titanium oxychloride solution (25.1% in TiO₂, Cristal) were mixed together with deionized water in a heated reactor equipped with a glass condenser and an overhead stirrer. While being constantly stirred, the mixture was heated to 75°C and a small amount of anatase TiO₂ seeds (0.1% vs. TiO₂; Cristal) was quickly introduced. The reaction was maintained at 75°C for 2 hours and then increased to 85°C and maintained for 3 hours. The reaction mixture was cooled to room temperature and stirring was stopped. The TiO₂ slurry formed was settled for
about 3 hours and the mother liquor was removed and about the same amount of deionized water was added.

**Stage II** (Li inserted TiO$_2$ nanospheres): The stirring was restarted and 78.8g lithium hydroxide monohydrate (Alfa Aesar) was added in small portions. After stirring for about 15 minutes, the mixture was transferred in to a 2-liter hydrothermal reactor (Parr Instruments) and was treated at 120°C under autogenous pressure for 24 hours. The reaction was then cooled to room temperature, and the product was separated by filtration and washed by deionized water several times until the filtrate conductivity was lower than 500 μS cm$^{-1}$.

**Stage III** (Converted LTO nanoparticles): The washed sample was dried in an oven at 90°C. The lithium inserted TiO$_2$ nanospheres were heat-treated in a furnace at 600°C for 6 hours in air.

**Materials Characterization**

The X-ray diffraction (XRD) data were collected using X'Pert Pro MPD system equipped with Cu Kα radiation (λ=1.5406Å). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained by the Barret-Joyner-Halenda (BJH) method. A JEOL 7401F scanning electron microscope (SEM) operated at 2kV was used to characterize the surface morphologies of the samples. Transmission electron microscopy (TEM) imaging was conducted using a JEOL 2000FXII TEM operated at 200kV.
Electrochemical Measurements

Electrochemical properties of LTO were characterized in a half cell configuration against a lithium-metal electrode and a full cell configuration coupled with LiFePO$_4$ cathodes (MTI Corp.). The working electrode was prepared by spreading the mixed slurry containing active material, conductive carbon C45 and PVDF binder in N-methyl-2-pyrrolidone (NMP) solvent in a weight ratio of 80:10:10. The resulting slurry was then casted onto a copper foil current collector and transferred to a vacuum oven for drying at 110 °C overnight. The typical loading amount of active material was 2 to 2.5 mg cm$^{-2}$. The electrolyte was a solution of 1 M LiPF$_6$ in ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1 in vol). Coin cells (CR2032) consisting of the LTO electrode, Celgard separator, a lithium metal counter electrode/LiFePO$_4$ electrode and electrolyte were assembled in an Ar-filled glove box. For the LTO-Li$_4$Ti$_5$O$_{12}$ full-cell, the anode is limited and the weight ratio of the cathode and the anode is 2.7:1. Galvanostatic charge/discharge was carried out on a Land CT2001 battery test system (Wuhan, China) over a voltage range of 1 – 3 V in room temperature. The rate performance was evaluated on an Arbin BT2000 under different current densities.

7.3 Results and Discussions

Figure 7.1(a) shows the X-ray Diffraction (XRD) patterns of the TiO$_2$ nanospheres precursors, lithium inserted nanospheres and the fully converted LTO nanoparticles. The XRD collected on TiO$_2$ precursors indicates the presence of anatase phase was obtained after the hydrolysis in stage I. After the lithium insertion into TiO$_2$ nanospheres by hydrolysis, the XRD peaks shifted. The converted LTO nanoparticles have a pure spinel...
Figure 7.1. (a) XRD patterns of the TiO2 precursor, Li inserted TiO2 nanospheres, and converted LTO nanoparticles, (b) SEM images of the precursor and Li inserted TiO2 nanospheres, and converted LTO nanoparticles.
LTO pattern with much higher peak intensities, which indicates good crystallinity of this material. The average nanoparticle crystallite size was calculated to be 31.4 nm from the peak broadening. The porosity was analyzed in more detail via N$_2$ physisorption at 77 K. The BET surface area is determined to be 45 m$^2$ g$^{-1}$.

The morphology and microstructure of the materials were analyzed by electron microscopy characterization techniques. The scanning electron microscopy (SEM) images of the TiO$_2$ precursors, Li inserted TiO$_2$ and the converted LTO nanoparticles are presented in Figure 7.1(b). The particle size was well controlled and kept the same throughout the synthesis process. Almost spherical shape particles with uniform size of around 30-50 nm can be observed in all of the images. This size is also in good agreement with the determined BET surface area of 45 m$^2$ g$^{-1}$ by a rough calculation assuming perfectly spherical particles: diameter equals to 6000*BET surface area/density, where density of LTO is 3.5 g cm$^{-3}$[153].

Transmission electron microscopy (TEM) images of different magnifications of the LTO nanoparticles are shown in Figure 7.2 (a) & (b). The monodispersed size of the nanoparticles is clearly observed and the particle size distribution measured from the TEM image confirmed an average particle size of 42.7 nm. The high resolution TEM image was taken in the boxed area in Figure 7.2(b) showing the lattice fringes of the as-synthesized LTO which indicates the presence of good crystalline material. A lattice spacing of 0.48 nm was observed, which is in good agreement with the d-spacing of 0.484 nm associated with the (111) direction of spinel structure (ICDD 00-049-0207). The Fast Fourier Transform (FFT) pattern taken along the (111) zone axis in the boxed area in
Figure 7.2. (a) TEM image of the LTO nanoparticles. (b) & (c) high resolution TEM image of the LTO nanoparticles. (d) Fast Fourier transform (FFT) pattern along (111) zone axis.
Figure 7.2(b) is presented in Figure 7.2(d) confirming the formation of a highly crystalline spinel phase. TEM analyses show that \{111\} facets are present predominately while lesser amounts of \{001\} and \{110\} facets are present as edge truncations.

Coin cells with Li discs as counter electrode were used to evaluate the electrochemical performance of the as-made LTO materials cycling between 1.0V to 3.0V as shown in Figure 7.3 (a) & (b). The first 10 cycles were performed under a current density of C/10 (1C=175 mA g\(^{-1}\)) and the capacity gradually drops from 180.1 mAh g\(^{-1}\) to 174.2 mAh g\(^{-1}\). It is noticeable that the first cycle efficiency is slightly higher than 100% which could due to the oxidation of the impurities on the surface of lithium metal and the initial OCV is less than 3 V after cell assembly. With no SEI formation, the LTO electrodes show very high efficiency throughout the cycling process, which not only greatly preserve the limited lithium ion in the cell but also prolong the cell cycling life. The current was then increased to 1C and the capacity changes from 165.7 mAh g\(^{-1}\) at the beginning of such rate to 154.8 mAh g\(^{-1}\) after 400 cycles with only 6.6% capacity loss. The typical galvanostatic discharge/charge profiles of pure LTO can be observed in the inset of Figure 7.3 (a). The flat plateau corresponds to the reversible phase transition from \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) to \(\text{Li}_7\text{Ti}_5\text{O}_{12}\). As can be seen, the capacities under different current densities decrease slightly as the current rate increases in Figure 7.3 (b). The LTO electrode shows outstanding capacities of 155, 152, 147, 134 and 127 mAh g\(^{-1}\) at 2C, 5C, 10C, 20C and 30C rate, respectively. Such great power output capabilities should attribute to the nano-sized particles for facilitating more lithium ions and electrons movement at a same time. The controlled particle shape also improves the packing density of the material and
Figure 7.3. (a) Half-cell performance of LTO electrode at 1C (inset: half-cell voltage profile), (b) Half-cell performance of LTO electrode cell at different rates, (c) full-cell performance of LTO vs. LiFePO4 at 1C, (d) voltage profile of the LTO-LiFePO4 full-cell.
provides better contact between particles. As mentioned before, the BET surface area is only 45 m² g⁻¹ and such small value could suggest that the uniformly dispersed nanoparticles with controlled shapes are present rather than the porosity which is the main reason for the good electrochemical performance of this material. After 10 cycles at 30C, the current resumed to the initial C/5 and capacity recovered from 127 mAh g⁻¹ to 165 mAh g⁻¹ immediately and maintained thereafter. This effect suggests negligible damage of the lithium intercalation/deintercalation process to the material crystal lattice at large current rate and full recoverability of this material. A cyclability test of LTO electrode under high current density of 10C is plotted in Figure 7.4. The cell was charge/discharge at 1C for the first 5 cycles followed by 10C cycling. The initial capacity of the 10C cycling starts at 149 mAh g⁻¹ and has less than 6% capacity loss after more than 200 cycles high rate charge and discharge. This performance also indicates the good durability under extreme cycling conditions for the size controlled LTO nanoparticles. A rate capability comparison for state-of-art LTO anode materials and this work is presented in Table 7.1, which shows such monodispersed nano-size LTO is among the best performance materials with very good capacity retention under large current densities. It is also well-worth to mention that the synthesis method used in this work is in relatively large scale and can be easily scale-up. It can produce very uniform and excellent performance materials without complicated synthesis method.

Lithium iron phosphate is regarded as one of the safest cathode material with stable, reliable and high-rate capable properties. In order to test the potential for LTO as a safe battery anode, coin cells with LiFePO₄ as cathode electrodes were assembled and...
Figure 7.4. Charge-discharge performance of LTO under current density of 10C.

Table 7.1. Comparison of the rate capability for state-of-art LTO anodes.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Rate Capability (mAh g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2C</td>
</tr>
<tr>
<td>LTO/carbon core-shell [154]</td>
<td>161</td>
</tr>
<tr>
<td>Mesoporous LTO [142]</td>
<td>-</td>
</tr>
<tr>
<td>Sm-doped LTO [155]</td>
<td>170</td>
</tr>
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tested under C/5 for 50 cycles and followed by 1C rate charge and discharge cycling. The first cycle efficiency for the full cell is 85% and this value went up quickly to 97% for the 2nd cycle. The good cycle efficiency should be attributed to the voltage window of both LTO anodes and LFO cathodes, which will not cause any electrolyte decomposition. Extraordinary LTO capacity retention is shown in Figure 7.3 (c), where the LTO electrode has a capacity of 167 mAh g⁻¹ in the first cycle and 165 mAh g⁻¹ in 50th cycle. At the beginning of the following cycling at 1C, the initial capacity is 159 mAh g⁻¹ and it still maintains a capacity of 147.3 mAh g⁻¹ after 2000 cycles, which is only 7.36% capacity loss at this current density after about 2000 cycles. Such superior capacity retention proves the great potential of this lithium inserted TiO₂ converted LTO as anode electrodes for energy storage applications where requires long service life and high-power output, such as engine start-stop systems. The voltage profile shown in Figure 7.3 (d) reveals the working potential of the full cell is about 1.8 V with a long plateau at this voltage. This property will benefit the battery for more stable output power.

From a typical 50 MW geothermal plant in the Salton Sea, 15,000 tons of lithium carbonate or hydroxide can be produced by extracting and converting of lithium chloride. Also, there are about 390 MW of power currently produced in the Salton Sea Known Geothermal Region (SSKGR) from the deep geothermal resource. This will be equivalent to 117,000 tons of lithium salts production. Hence, the lithium salts separated from geothermal brine solutions will be low-cost and further unlimited supply of lithium source will be available. Lithium titanate (LTO) electrode materials made with Simbol Material’s lithium salts extracted from geothermal brine solutions had also been evaluated in a half-
cell configuration. Figure 7.5 shows the reversible capacity slightly over 150 mAh g\textsuperscript{-1} with a stable performance for up to 300 cycles at 1C. This result suggests that the lithium salts extracted from geothermal brine solutions could be an alternative source of lithium supply chain.

### 7.4 Summary

In summary, a novel LTO synthesis method with well-controlled nanoparticle size has been demonstrated. Its electrochemical performance test shows outstanding fast charge-discharge capability and great cyclability with more than 92.4% capacity retention in a full cell at a current rate of 1C. Such a method provides a potential way for large-scale production of LTO for energy storage applications.
Figure 7.5. Electrochemical performance of LTO made from geothermal source.
CHAPTER 8
CONCLUDING REMARKS
The method for recycling waste tire and synthesis of low-cost novel sustainable carbon anode materials were demonstrated in this dissertation. The tire-derived carbon shows larger capacity than the commercial graphite and yields very stable electrochemical cyclability.

The surface properties are the key facts to the battery material’s performance since they will greatly influence the formation of SEI. Hence, different techniques, including vibrational inelastic neutron spectroscopy, Raman spectroscopy, and X-ray spectroscopy were used to characterize the tire-derived carbon in order to provide better understanding of its surface properties and its relationship with its performance.

CVD Carbon coating was utilized to modify the surface of tire-derived carbon. The results show an improvement of capacity as well as an increase in conductivity. Pre-lithiation was also performed to reduce the first cycle efficiency loss. To further improve the capacity of tire-derived carbon, a composite was obtained by ball milling of tire-derived carbon with SnO, which yielded a capacity of 690 mAh g\(^{-1}\) after 300 cycles.

The knowledge and experiences acquired from lithium-ion application are important since they could also be applied to beyond lithium systems, such as Na-ion batteries and K-ion batteries. The electrochemical testing results in Chapter 6 reveal the potential for tire-derived carbon to be used in large-scale, low-cost stationary energy storage markets.

The SEI free anode materials, Li\(_{4}\)Ti\(_{5}\)O\(_{12}\), was synthesized with a shape control method to obtain a mono-dispersed nano-size material, which presented high rate
capability and long cycle life. The sustainable application of waste tire derivatives is extremely importance to our society and the earth. Other than tires, we also proved that the lithium salts extracted from the geothermal plant wastes could be used as precursor to make good performance LTO.

To achieve the best performance of tire-derived carbon as an anode material for rechargeable batteries, there are several areas of studies need to be carried out. On one side, the waste tires include many different types such as passenger car tires, truck tires, minivan tires, etc. These tires are manufactured with different compositions for various applications. For example, from a detailed tire composition comparison, the biggest difference between a typical passenger tire and truck tire is the amount of metal in the tire where passenger tire has 16.5% metal comparing with truck tire’s 25%. However, in terms of all the carbon-based materials, a passenger tire has a value of 74% whereas 67% of the truck tire is carbon material. Thus, a detailed comparison of the recovered tire-derived carbon per tire type is needed to better understand the carbon yields and its electrochemical performance. Once the difference is identified, a recovery plan will be developed. The sulfonation process removed most of the metal based impurities and the main difference should be on the structure of the carbon products and carbon yield. On the other side, the future direction for this research should also emphasize on the surface modification of tire-derived carbon to optimize the treating time and temperature, as well as the carbon precursors. The impurities in tire-derived carbon removal is also needed to further improve its performance. A detailed comparison study of tire-derived carbon in
Li/Na/K ion systems is also an interesting topic, since the rate performance indicated lower sodium diffusivity in the carbon than Li and K systems.


APPENDIX
Publication List


7. **Y. Li**, G. Fu, M. Watson, S. Harrison, MP Paranthaman, “Monodispersed Li$_4$Ti$_5$O$_{12}$ with Controlled Morphology as High Power Lithium Ion Battery Anodes”, *ChemNanoMat*, 2016, 2, 642-646.


Patent Applications


VITA

Yunchao Li was born in 1989 in Xuzhou, Jiangsu Province, P. R. China. He attended China University of Mining and Technology in 2007. In 2009, he transferred to University of Kentucky (UK), where he earned his Bachelor’s degree in Materials Engineering. After graduate from UK in 2012, he joined the Bredesen Center at University of Tennessee, Knoxville (UTK) to pursue his PhD degree working with Dr. M. Parans Paranthaman at Oak Ridge National Laboratory. His research interests focus on synthesis and characterization of electrode materials for various electrochemical energy storage devices, including Li-ion batteries, Na-ion batteries, K-ion batteries, and supercapacitors. He received R&D 100 award for the contribution to the invention of tire-derived carbon as a low-cost lithium-ion battery anode. He worked as a summer Intern student at Apple Inc., Cupertino, CA in 2017, where he learned a lot about industrial research and development requirements.