

Tin Anode for Sodium-Ion Batteries Using Natural Wood Fiber as a Mechanical Buffer and Electrolyte Reservoir

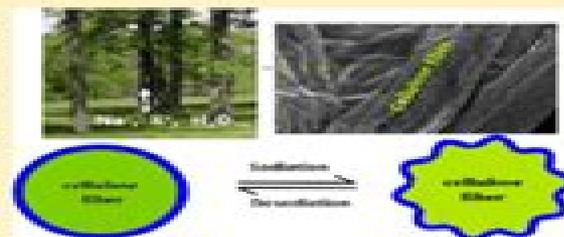
Hongli Zhu,^{1,8} Zheng Jia,^{2,8} Yuchen Chen,[†] Nicholas Weadock,[†] Jiayu Wan,[†] Oeyvind Vaaland,[‡] Xiaogang Han,[†] Teng Li,^{*,‡} and Liangbing Hu^{*,†}

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 Supporting Information

ABSTRACT: Sodium (Na)-ion batteries offer an attractive option for low cost grid scale storage due to the abundance of Na. Tin (Sn) is touted as a high capacity anode for Na-ion batteries with a high theoretical capacity of 847 mAh/g, but it has several limitations such as large volume expansion with cycling, slow kinetics, and unstable solid electrolyte interphase (SEI) formation. In this article, we demonstrate that an anode consisting of a Sn thin film deposited on a hierarchical wood fiber substrate simultaneously addresses all the challenges associated with Sn anodes. The soft nature of wood fibers effectively releases the mechanical stresses associated with the sodiation process, and the mesoporous structure functions as an electrolyte reservoir that allows for ion transport through the outer and inner surface of the fiber. These properties are confirmed experimentally and computationally. A stable cycling performance of 400 cycles with an initial capacity of 339 mAh/g is demonstrated, a significant improvement over other reported Sn nanostructures. The soft and mesoporous wood fiber substrate can be utilized as a new platform for low cost Na-ion batteries.

KEYWORDS: Na-ion battery anode, Sn nanostructures, wood fibers, mechanical buffer, ion diffusion



Grid scale storage is a crucial component of an energy landscape that incorporates a wide variety of renewable energy sources. Li-ion batteries and other electrochemical storage methods are considered among the most promising technologies for energy storage due to their high energy density and cyclability.^{1–3} Grid scale storage requires a low cost, safe, and environmentally benign battery system. Na is an earth abundant material and Na-ion batteries fulfill these requirements better than Li-ion batteries. Widespread implementation of Na-ion batteries is limited by several factors: (1) slow Na ion diffusion kinetics, (2) large volume changes and structural pulverization during charging/discharging, and (3) difficulty in maintaining a stable solid electrolyte interphase (SEI).⁴ These challenges are related to the large size of the Na ion (372% larger in volume than Li ion for a coordination number of four; $R_{Li} = 59$ pm, $R_{Na} = 99$ pm),⁵ which makes it impossible to simply adopt the recent knowledge and strategies developed for high-performance Li-ion batteries. Several cathode materials and electrolyte systems have been studied for Na-ion batteries, including bilayered $Na_2V_2O_7$, P2 $Na_{0.44}Fe_{0.33}Mn_{0.23}O_2$, and fluorinated ethylene carbonate (FEC) as an electrolyte additive.^{6–14} Anode materials that have been investigated include metal oxides and alloys, hard carbon, and nano-composites.^{15–20} Sn is a promising anode material because it alloys with Na at a high specific capacity of 847 mAh/g when $Na_{1-x}Sn_x$ is formed. Studies of Sn film and nanostructured anodes were reported; the cycle life, however, is limited to 20

cycles due to pulverization.^{17–19} The pulverization is primarily due to a 420% volume expansion associated with the formation of $Na_{0.1}Sn_x$.²⁰ Recently developed Sn nanostructures and SnO_2 @graphene nano-composites improve cycling performance but lack the processability and cycling performance required for low cost grid scale storage.^{21,22}

Wood naturally absorbs ions and water as part of the metabolism process. Specifically, this function is performed by wood fibers, or tracheids. The wood fibers are intrinsically soft, porous, and form into a multichannel structure.²³ In this study, we develop a nature inspired low cost electrode consisting of an electrodeposited Sn film on conductive wood fiber. Conductivity is achieved by a solution-based coating of carbon nanotubes (CNT) on the fiber surface. We find that the wood fiber increases the cyclability of Sn for Na-ion batteries by alleviating: 1) the capacity loss due to electrode pulverization, and 2) the poor rate performance as a result of slow ion diffusion kinetics. The stress reduction mechanism predicted by modeling the sodiation stresses throughout the Sn film on wood fiber agrees well with the experimental results. Control experiments with atomic layer deposition (ALD) confirm the role of the wood fiber as a mechanical buffer and electrolyte reservoir for ion diffusion. The Sn anode described is ideal for

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Nanomaterials for Electrochemical Energy Storage Devices Poulomi Roy, S. K. Srivastava, 2019-10-14 Energy storage devices are considered to be an important field of interest for researchers worldwide. Batteries and supercapacitors are therefore extensively studied and progressively evolving. The book not only emphasizes the fundamental theories, electrochemical mechanism and its computational view point but also discusses recent developments in electrode designing based on nanomaterials, separator fabrication of advanced devices and their performances. [Advanced Battery Materials](#)

Chunwen Sun, 2019-03-26 This book details the latest R D in electrochemical energy storage technologies for portable electronics and electric vehicle applications. During the past three decades, great progress has been made in R D of various batteries in terms of energy density increase and cost reduction. One of the biggest challenges is increasing the energy density to achieve longer endurance time. In this book, recent research and development in advanced electrode materials for electrochemical energy storage devices is covered. Topics covered in this important book include: Carbon anode materials for sodium ion batteries; Lithium titanate based lithium ion batteries; Rational material design and performance optimization of transition metal oxide based lithium ion battery anodes; Effects of graphene on the electrochemical properties of the electrode of lithium ion batteries; Silicon based lithium ion battery anodes; Mo based anode materials for alkali metal ion batteries; Lithium sulfur batteries; Graphene in Lithium Ion Lithium Sulfur Batteries; Graphene ionic liquid supercapacitors; Battery electrodes based on carbon species and conducting polymers; Doped graphene for electrochemical energy storage systems; Processing of graphene oxide for enhanced electrical properties. [Cellulose Nanocrystal/Nanoparticles Hybrid Nanocomposites](#)

Denis Rodrigue, Abou el Kacem Qaiss, Rachid Bouhfid, 2021-08-26 Cellulose Nanocrystal Nanoparticles Hybrid Nanocomposites: From Preparation to Applications presents a broad survey of the main innovations in the field of functionalized cellulose at the nanoscale and for hybrid nanoparticles based nanocomposites for industrial application. The book covers the properties and applications of cellulose including particle extraction, synthesis, functionalization of cellulose at the nanoscale and hybrid nanoparticles and their processing and characterizations. Readers will find this to be a single and comprehensive reference for future research on polymer based nanocomposites. Hybrid nanocomposites based on cellulose at the nanoscale and hybridized with other reinforcement agents represent a key advance in polymer based materials. Cellulose is considered the most abundant polymer on the planet and an essential renewable resource. There is considerable research interest in the simple extraction and synthesis of nanoscale dimensions, high aspect ratio, mechanical, electrical and thermal properties of cellulose at the nanoscale and its hybridized materials. Nanocomposites and bio nanocomposites with hybrid reinforcements, for example, are novel materials with enhanced properties due to the integration of cellulose with other nanoparticles and new methods have been developed to extract cellulose at the nanoscale. The extracted cellulose shows potential applications in nanocomposites and functionalization techniques are essential to create enhanced nanocomposites.

particularly for hybrid nanoparticles Presents the state of the art in functionalized cellulose at the nanoscale along with industrial applications of hybrid nanoparticles based nanocomposites Details the properties and applications of cellulose at the nanoscale and for hybrid nanocomposites Gives updates on hybrid nanoparticles including the processing and characterization of nanocomposites Brings together expertise from chemistry polymer science engineering and manufacturing

Sustainable Nanomaterials for Biosystems Engineering Junaid Ahmad Malik, Megh R.

Goyal, Mohamed Jaffer M. Sadiq, 2023-05-04 This new volume explores the integration of bionanomaterials and sustainable resources for the development of new and emerging sustainable processes It highlights the concept of essential bionanomaterials derived from sustainable resources with examples of interdisciplinary methodologies and research that highlight the reuse of biomass waste as well as the proper usage of green technologies The volume considers the most recent trends challenges and applications in bionanomaterials derived from sustainable sources in energy production and environmental mitigation The book looks at state of the art trends in the use of bionanomaterials for renewable energy such as in production of solar energy for energy harvesting and for energy conversion and storage Chapters consider the application of bionanomaterials for the development of improved optical and electrical biosensors The volume goes on to address the promising use of bionanomaterials for environmental remediation such as for recovering heavy metals radioactive metals and other pollutants from wastewater from river water from soils etc Other topics include the use of sustainable nanomaterials in the food industry in the biomedical field in ecological research and more

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Nanostructured Anode Materials for Li-ion and Na-ion Batteries Yong-Mao Lin,2013 The demand for electrical energy storage has increased tremendously in recent years especially in the applications of portable electronic devices transportation and renewable energy The performances of lithium ion and sodium ion batteries depend on their electrode materials In commercial Li ion batteries with graphite anodes the intercalation potential of lithium in graphite is close to the reversible Li Li half cell potential The proximity of the potentials can result in unintended electroplating of metallic instead of intercalation of lithium in the graphite anode and frequently leads to internal shorting and overheating which constitute unacceptable hazards especially when the batteries are large as they are in cars and airplanes Moreover graphite cannot be readily used as the anode material of Na ion batteries because electroplating of metallic sodium on graphite is kinetically favored over sodium intercalation in graphite This dissertation examines safer Li ion and Na ion battery anode materials

Tin Oxide Based Anode Materials for Rechargeable Li-ion Batteries Ruifen Zhang,2001 **Titanate Anodes for Sodium Ion Batteries** ,2013 *Nanostructured Tin-Based Anodes for Lithium Ion Batteries with X-Ray Absorption Fine Structure Studies* Dongniu Wang,2013 The practical applications of lithium ion batteries are highly dependent on the choice of electrodes where boosting the materials innovations to design and achieve high capacity excellent cycling performance rate capability low cost and safe electrode materials provide the best solution Based on this tin based anodes have gained great attention due to its high theoretical capacity low cost and nontoxic nature to environment Nevertheless it undergoes significant volume variation 259% during the operation of the battery leading to pulverization and significant capacity fade Thus the practical application of tin based anodes is still quite challenging This thesis tackles issues related to tin based

anodes It is demonstrated that designing hierarchical nanostructured tin and tin based carbon composites particular tin based graphene composites are the most effective routes to achieve excellent electrochemical properties In this thesis we reported the rational design and fabrication of nanostructured tin based anodes which began with the synthesis of relevant electrode materials as well as evaluation of their electrochemical performance Further synchrotron based X ray absorption spectroscopy was conducted to unveil the electronic structure of these composites for better understanding of the mechanism behind the performance Various strategies of material design have been used These include i SnO₂ nanowires on conducting substrates are successfully obtained using hydrothermal process The electronic structure and the optical properties study revealed the different crystallinity and surface defect states related luminescence ii Further we extend the research to fabricate the hierarchical tin based graphene composites such as graphene SnO₂ nanoparticles and SnO₂ nanowire graphene carbon composites using hydrothermal method The hierarchical nanocomposites exhibit better performance in both high and stable capacity benefitting from the buffering effect of carbonaceous materials as well as high capacity of tin dioxide iii In addition Sn C graphene was obtained using chemical vapor deposition method The core shelled Sn C nanoparticles are well embedded in graphene matrix with superior electrochemical performances iv Refer to Sn C nanowires on metallic substrates obtained by the same route the high cyclic capability is achieved benefitting from the one dimensional core shell structure v Most interestingly through surface coating of Al₂O₃ on SnO₂ electrodes via atomic layer deposition we found that the well defined and optimized Al₂O₃ layer could relieve mechanical degradation and form an artificial SEI layer leading to improved electrochemical performances compared with bare SnO₂ electrodes The element specific X ray absorption spectra uniquely characterize the Sn C and O specified edge of target samples providing the information of the crystallinity and surface defect states revealing the strong chemical bonding and interactions between Sn or SnO₂ with graphene or carbon layer allowing for better understanding of the performance The study in this thesis demonstrates nanostructured tin based anodes can be alternative high performance anodes in the next generation lithium ion batteries

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