SOCIETY OF PHYSICS STUDENTS
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SPS Chapter Research Award Proposal

Project Proposal Title	Partially Lithiophilic Non-Conductive Matrix as Lithium Host for Lithium Metal Battery
Team Leader	Abdullah Al Maruf
Name of School	South Dakota State University
SPS Chapter Number	6514
Total Amount Requested	$2,000.00

Abstract

The Lithium (Li) metal has attracted considerable attention in the scientific community due to its application in lithium ion (Li-ion) batteries with high theoretical specific capacity and low reduction potential. This project is devoted to developing a high energy density and safe lithium metal battery, and tackle one of its crucial performance limitation – to solve the dendrite formation problem of lithium metal anode. We proposed a novel lithium host (partially lithiophilic non-conductive matrix (PLNM)) to guide the lithium deposition behavior. South Dakota State University's (SDSU) SPS chapter will lead this research project, which will potentially help to solve the current limitation of Li-ion batteries, as well as help undergraduate students prepare for graduate studies.

Proposal Statement

Overview of Proposed Project

In this project, we are trying to achieve a long cycling life and safe lithium (Li) metal battery by guiding the Li deposition behavior. The current Li ion battery technology uses graphite as anode material, which has the capacity of only 372 mAh/g. Because Li metal has a high specific capacity of 3860 mAh g^{-1}, storing Li in its metallic form instead of storing Li atoms into graphite host leads to much higher energy density. However, there are several issues while using Li metal as electrode such as the dendrites growth, uncontrolled interfacial reaction and degradation, and large volume changes during the Li plating and stripping. As shown in the Figure 1a, dendrites form after plating on the planar Cu surface due to the uneven Li flux. On one hand, the dendrite may short the battery if it penetrates the separator and cause serious safety issue. On the other hand, the dendrites may break down during the following stripping step and become isolated as inactive Li ("dead Li"). Therefore, to avoid dendrite growth and obtain a smooth and dense Li is critical for commercializing Li metal anode in the next-generation batteries.

This project proposed a ***partially lithiophilic non-conductive matrix (PLNM)*** as the lithium host, which constructed based on a glass fiber matrix with only one side lithiophilic coating. As shown in Figure 1b, Li was able to nucleate on bottom of the glass fiber matrix due to its lithiophilic property. With the increase amount of the Li deposition, Li is forced to grow into the non-conductive matrix because Li can only epitaxially grow from former Li layer. The non-conductive matrix itself acts as an ion distributer, reducing the ion gradients, which helps Li get a smoother Li deposition. [1]

The objectives of this project are:

(1) Prepare PLNM with optimized lithiophilic coating:

Many materials have been demonstrated to be lithiophilic such as gold (Au)[2], silver (Ag)[3], and silicon (Si)[4]. These materials either react with or form alloy with Li. All these materials will be used in PLNM as lithiophilic decoration by using the methods of sputtering or thermal evaporation on one side of GF matrix.

(2) Demonstrate that PLNC has better electrochemistry performance in Li metal battery:

Li plating/stripping cycling test will be used to determine the cycling stability of the Li metal anode. A high coulombic efficiency with long cycling stability of more than 500 cycles can be expected.

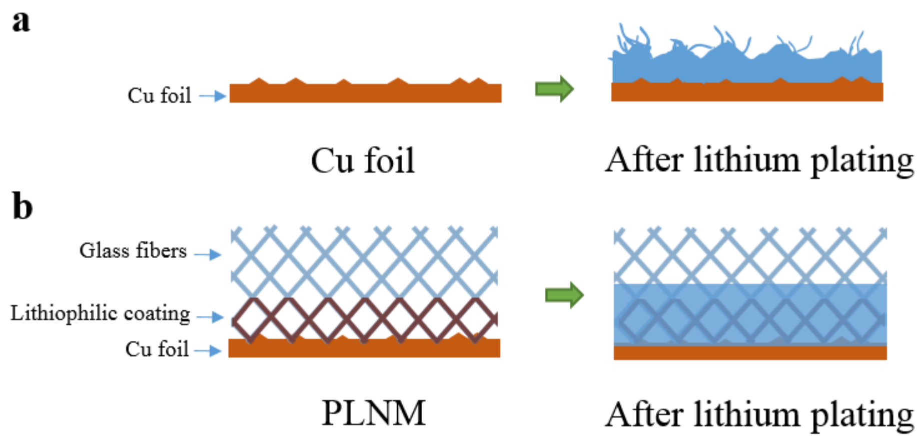

Figure 1. Lithium plating behavior on Cu foil (a) and PLNM (b)

(3) Benefit of the proposed study and the SPS involvement:

Our project will help the local SPS chapter by creating undergraduate research opportunities for SPS students at SDSU and prepare them for graduate school. This will also help our chapter to grow as we do more interdepartmental outreach through Physics colloquiums, besides SPS programs/activities, and get more students excited about the research, potentially recruiting more members for our local and national SPS. Additionally, the SPS research will help facilitating our chapter's public relationship with companies like Dactronics, Raven Industries, 3M, etc. in South Dakota, since our proposed project has direct applications in industries with an interest in highly efficient Li ion batteries. The industry relationship can be also useful in terms of fundraising for our local SPS chapter to organize large meetings in the future, boosting the overall image of our local SPS community in the university and nationally. Our project is also helpful in green energy technology revolution, since high density energy storage capacity is much needed to store energy as we are building highly efficient perovskite solar cells at SDSU research labs. Moreover, in continuation of previous years, we will present our work in the annual SPS regional/national meetings. This year, an officer of SDSU SPS chapter, Abdullah Al Maruf, won the best (research) poster award in the SPS Zone-11 Meeting-2019 at the University of South Dakota. The national SPS will be acknowledged in the final manuscript as we're aiming to publish our work in a reputed scientific journal by the end of the project.

Background for Proposed Project

Lithium ion batteries have completely changed modern life by revolutionized the way of people's communications and transportations.[7] The 2019 Nobel Prize in Chemistry was awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino "for the development of lithium ion batteries". The concept proposed by these scientists was to use carbon-based anode (e.g. graphite) and metal oxide base cathode (e.g. lithium cobalt oxide). During charging, Li travels through the electrolyte and inserted into the layered graphite drove by the external power force. During discharge, the Li ions go back to $LiCoO_2$ and the electrons travels through external circuit, powering electronic devices. Since Li ion battery with graphite anode and $LiCoO_2$ was commercialized at 1990s, the specific energy have been increased to 250 Wh·Kg^{-1}, nearly approaching the theoretical value of cathode/anode materials.[8] However to meet the fast-growing energy demands and develop high-energy batteries for electric vehicles and grid storage applications, researchers have explored extensive studies on batteries beyond LIB nowadays. With the high specific capacity (3860 mAh g^{-1}) and low reduction potential (-3.04 V vs standard hydrogen electrode), lithium metal battery (LMB) have the potential to achieve a much higher specific density (> 500 Wh Kg^{-1}).[9] Moreover, the high capacity of Li metal anode opens up great opportunity for the application in the next generation energy storage cells including Li sulfur (Li-S) and Li air batteries. They hold the potential to deliver theoretical energy densities of 2567 Wh kg^{-1} and 3505 Wh kg^{-1} respectively, which are much higher than the performance in the present commercial battery technology.[10 11]

However, there are several issues while using Li metal as electrode such as the dendrites growth, uncontrolled interfacial reaction and degradation, and large volume changes during the Li plating and stripping. When Li is plated/stripped, the huge volume fluctuation breaks the fragile SEI layer and the fresh Li is exposed to the electrolyte, leading to continuous formation of new SEI. In the same time, the Li dendrites form uncontrollably due to the uneven Li-ion flux and SEI cracks.[12] Li dendrites can be broken during stripping and produce "dead" Li.[13] Consequently, LMB faces the problems of low coulombic efficiency (CE) and fast battery failure.[14] Therefore, to efficiently accommodate volume changes and avoid dendrite growth need to be addressed for a working LMB. Considerable efforts have been devoted to stabilizing Li metal anode such as introducing electrolyte additives,[15-17] and developing protective layer on Li.[18-21] However, these methods failed to reduce the large volume changes during the Li plating/stripping process.

To avoid volume changes, use of a porous current collector as the host for Li metal has been demonstrated as a promising approach. The porous Li host can be mainly divided into two categories: conductive and non-conductive host. The conductive Li host are usually made of Cu, Ni, or carbon. Because of their high conductivity, Li nucleates on the top surface, leading to volume change and dendrites shooting out of the matrix.[24] Some non-conductive matrix have been proposed such as glass fiber cloth and polyimide nanofibers.[1, 22] Li nucleation does not happen on this matrix itself. Li tends to grow under it on the current collector. Li is not deposited inside the matrix but pushes up the matrix. The matrix itself only acts as an ion distributer, reducing the ion gradients, which helps Li get a smoother Li deposition.[1] However, dendrites still form after extensive cycling because the non-conductive host did not solve the volume change issues. With this idea, this project proposed a partially lithiophilic non-conductive matrix as the Li host, which constructed based on a glass fiber matrix with only one side lithiophilic coating. In this design, Li preferentially nucleated on the lithiophilic side and Li is forced to grow into the non-conductive matrix because Li can only epitaxially grow from former Li layer. Further, the not coated part of this matrix will help to smooth the Li surface.

Expected Results

By conducting this project, we will able to develop a suitable Li host which could both acomendate the volume fluctuation and supress the dendrites growth. Li/PLNM cells will be assembled to test the Li plating/stripping behaviors. The battery with the proposed Li host is expected to have higher columbic efficiency and longer cycling life than other kind of Li host.

Scaning electron microscope (SEM) will be used to exam the Li anode morpology after Li plating. The surface morphology of Li inside PLNM will be compared with normal Li surface in after plating, with a hope to gain overall higher effeciency and sotarage capacity in the Li ion battery.

Description of Proposed Research - Methods, Design, and Procedures

Objective 1. Prepare PLNM with optimized lithiophilic coating.

- Step 1. Au, Ag and Si will be deposited on one side of the glass fiber using sputtering system to get PLNM. The coating time will be controlled to get different thickness of coating layer.
- Step 2. The surface morpholgy after lithiophilic coating will be examined by Scanning Electron Microscpe (SEM).

Objective 2. Demonstrate that PLNC has better electrochemistry performance in Li metal battery.

- Step 1. Coin cell batteries with metal Li as anode and PLNM as cathode will be assambled in an Ar filled glovebox. The control cells with planer Cu as cathode will also be assembled
- Step 2. The coin cells will be test on a battery analyzer. Li will be first plated on to PLNM by dischaging to the capacity of 1 mAh/cm^2 , then Li will be removed from PLNM by charging to the cutoff voltage of 0.5V. The coulumbic efficenecy will be calculted to estimate the Li lost at each plating/striping cycles.
- Step 3. Different current density will be used for the coulumbic efficiency test, such as 1mA/cm^2, 2mA/cm^2, 3mA/cm^2.
- Step 4. The Li metal full cell with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$(NMC811) as cathode, the pre-deposited Li@PLNM as anode will be assembled. The batteried will be kept charging and discharging between voltage rage of 2.5V-4.2V for 500 cycles to test the battery stablity.

Plan for Carrying Out Proposed Project

This research will be performed with a collaboration between South Dakota State University's (SDSU) SPS Chapter in the Physics Department and the Electrical Engineering Department. SDSU's University Center for Commercialization of Sustainable Energies and Precision Agriculture Sensors Technologies has clean room facilities where all the necessary equipment are stationed, and the Physics Department is also located in the same building.

Only local and national SPS student members in the university will be directly involved in the research, which will also count as their Undergraduate Research Experience during the academic year. Majority of the SPS members have previous experience in Physics research during summer, and have sufficient knowledge on designing, fabrication, characterization, and analysis to perform the project successfully. Dr. Qiquan Qiao at the EE department will be our research advisor for the project. The SPS team members, Abdullah Al Maruf, Ke Chen, Rajesh Pathak, and Nick Carlson will conduct research. The SDSU SPS advisor and Zone-11 councilor, Dr. Robert McTaggart, will oversee the project, and help the SPS research team with guidance during the project.

Project Timeline

1. Assemble all previous work on this project including, but not limited to, previous research reports, ideas, prototypes, and compile useful materials and begin research on instruments. – **Finish by end Jan 2020**
2. Prepare PLNM with Au, Ag and Si coating using sputtering system to get PLNM. **– Finish by mid-March 2020**.
3. Characterize PLNM using Scanning Electron Microscope (SEM), X-ray Photoelectron Spectroscope (XPS), and Transmission Electron Microscope (TEM) and– **Finish by end April 2020**.
4. Collect all the analyzed data of materials' characterization and testing, and prepare a report – **Finish by mid-May 2020.**
5. Complete assembling and testing coulombic efficiency of Li/PLNM cells using Argon glovebox and LAND (CT2001A) battery analyzer **– Finish by end June 2020**.
6. Test Li/PLNM at different current LAND (CT2001A) battery analyzer **– Finish by mid-Aug 2020**.
7. Test the full cell performance LAND (CT2001A) battery analyzer and Electrochemical Station – **Finish by end Sep 2020**.
8. Complete the analysis of all the obtained data on Origin Software **– Finish by end Oct 2020**.
9. Summarize all the data and complete writing a manuscript to publish in a scientific journal – **Finish by mid-Dec 2020**.

Budget Justification

To conduct the SPS research project, we request $2000 to cover the software subscription, materials, and supplies required for the experiments. The cost associated with this project comes largely from CR2032 coin cell case, LiNiCoMnO2 (Ni:Co:Mn=8:1:1) powder, lithium chips, battery electrolyte, cutter and OriginPro software to execute the project. The lab equipment (i.e. SEM, glovebox, glassware and tubes, etc.) will be provided by the university. Another cost that contributes to the budget is paying for the TEM and XPS facilities (two hours each) in Dactronics. We have also requested SDSU Physics Department for additional budget to pay for undergraduate students' salaries and they agreed to support the participating students if we secure $2000 SPS Chapter Research Award.

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Facilities

Some of the SDSU research facilities are shown in the following: