学校编码：10384　　　　分类号_______密级 ______

学号：19920060153195　　　　UDC ______

厦门大学

博 士 学 位 论 文

铜掺杂五氧化二钒薄膜电极的制备及其在微型全固态锂离子电池中的应用

Preparation of Copper doped Vanadium Pentoxide Thin Films Electrodes and Its Application in Micro-scale All Solid State Li-ion Batteries

张 梁 堂

指导教师姓名： 吴 孙 桃 教 授

专 业 名 称： 测试计量技术及仪器

论文提交日期： 2015 年 7 月

论文答辩时间： 2015 年 9 月

学位授予日期： 2015 年 月

答辩委员会主席：____________

评 阅 人：____________

2015 年 7 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为(　　　　　　　　　　　　　　)课题(组)的研究成果，获得（　　　　　　　　　）课题（组）经费或实验室的资助，在（　　　　　　　　　）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

年　　月　　日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1.经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

（　　）2.不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年　　月　　日

中文摘要

随着微机电系统（MEMS）的发展，微型设备已经进入人们的生活。大体积的外接电源限制了微设备的推广应用，同时电源也逐渐向微小型化方向发展，进一步研究将微电源跟微设备集成在同一芯片上成为了新的发展趋势。全固态薄膜锂离子电池具有能量密度高、电压高、循环性能好和安全稳定等优点，并且制备工艺与 MEMS 的集成相兼容，是最适合应用于 MEMS 器件上的集成微能源。本论文目的是研究铜掺杂对 V_2O_5 薄膜的电化学性能的影响，并以 V_2O_5 及其掺杂铜的 $Cu_{2.1}VO_{4.4}$ 薄膜做为负极薄膜，研制了微型全固态薄膜锂离子电池。研究成果对今后的微型薄膜锂离子电池的研究和应用都具有重要的借鉴参考意义。

在本论文中，首先对全固态薄膜锂离子电池中的负极材料 V_2O_5 及其掺杂铜薄膜进行研究。研究中采用钒和铜靶材，利用磁控共溅射制备 V_2O_5 及其掺杂不同比例的铜的薄膜，并对所制备后的薄膜进行表征和分析，研究铜的掺杂比例对 V_2O_5 薄膜的结构、表面形貌和化学成分的影响。再将制备后的薄膜组装成纽扣电池，测试薄膜的电化学性能。主要结论如下：

利用射频磁控溅射钒靶材，可获得晶态 V_2O_5，而掺杂铜后，可获得无定形态的铜钒氧化物。晶态的 V_2O_5 薄膜表面粗糙，颗粒成片状结构。铜的掺杂不仅增加了薄膜生长速率，还提高了 V_2O_5 薄膜表面的平整度，使薄膜表面更加平整光滑，同时降低了表面的颗粒尺寸，提高了薄膜的致密性。掺杂铜后的铜钒氧化物，XPS 结果表明铜离子以二价铜形式存在于化合物中，随着铜的掺杂增多，V2p 电子结合能会随之下降，并导致低价态钒原子的增多。

对所组装的薄膜电极进行循环伏安法和恒电流充放电测试表明，V_2O_5 掺杂铜后有利于更多的 Li^+ 的嵌入，提高了 V_2O_5 薄膜电极的容量和循环性能，但铜的掺杂也增加了 V_2O_5 首次不可逆容量损失。铜的不同掺杂比例对 V_2O_5 电化学性能影响很大，其中 $Cu_{2.1}VO_{4.4}$ 薄膜电极首次放电容量达到 370.7μAh/ cm^2·μm，100 次循环后还保留 83.4μAh/ cm^2·μm，在整体上体现了较高的放电容量和较好的循环性能。

结合厦门大学萨本栋微机电中心的实验条件，本论文设计了一种可制备全固态薄膜锂离子电池的微加工工艺。以 V_2O_5 及其掺杂铜的 $Cu_{2.1}VO_{4.4}$ 薄膜作为负极，制备了 V_2O_5/LiPON/$LiCoO_2$ 和 $Cu_{2.1}VO_{4.4}$/LiPON/$LiCoO_2$ 全固态薄膜锂离子电池，并对所制备的微电池进行形貌和电化学分析。所制备的微电池的活性材料层与层之间界面光滑平整，未见裂缝、微孔等缺陷。掺杂铜的 $Cu_{2.1}VO_{4.4}$ 微电池比未掺杂的 V_2O_5 微电池在放电容量和循环性能都有明显提高。V_2O_5 微电池和 $Cu_{2.1}VO_{4.4}$ 微电池，在 10nA 的放电电流下，首次容量分别为 4.1nAh 和 12.1nAh，在 50nA 放电电流下，首次容量分别为 3.71nAh 和 10.3nAh。

本论文的主要创新性工作有：研究优化铜的掺杂比例对提高 V_2O_5 薄膜电极的电化学性能，利用磁控溅射技术制备了 V_2O_5 及其掺杂铜的薄膜，并系统研究了铜的掺杂对 V_2O_5 薄膜的晶体结构、表面形貌、化学成分以及电化学性能的影响；以 V_2O_5 及其掺杂铜的 $Cu_{2.1}VO_{4.4}$ 薄膜作为负极，研制了 V_2O_5/LiPON/$LiCoO_2$ 和 $Cu_{2.1}VO_{4.4}$/LiPON/$LiCoO_2$ 微型全固态薄膜锂离子电池；采用光刻工艺、溅射工艺、剥离工艺、腐蚀工艺等 MEMS 微加工工艺，制备出微型全固态薄膜锂离子电池，开发出一整套工艺流程。

关键词：全固态薄膜锂离子电池；微加工；V_2O_5 及其掺杂铜薄膜

Abstract

With the development of micro electro mechanical systems (MEMS), the micro devices have entered people's life. However large volume of external power sources limits the popularization and application of micro devices. Microminiaturization of power sources and integration of micro power sources into the same chip with micro devices have gradually become the development focus for further research. All solid state thin film Li-ion battery has the advantages of high energy density, high voltage, good cycle performance and safety and stability. Besides, its fabrication process is compatible with the techniques of MEMS industry, which makes it the most suitable power source for MEMS devices. The purpose of this thesis is to study the electrochemical properties of copper doped V_2O_5 thin films, and to develop a micro all solid state thin film Li-ion battery by using V_2O_5 and copper doped V_2O_5 films as the anode. The research in this thesis will have an important impact on the future research and application of micro thin film Li-ion battery.

In this thesis, at first the preparation and characterization of V_2O_5 thin film and Cu-doped V_2O_5 thin films as the anode material in Li-ion battery were carried out. The V_2O_5 thin film and Cu-doped V_2O_5 thin films with different doped concentrations were deposited by magnetron sputtering. The influence of degrees of Cu doping in V_2O_5 thin films on their structures, surface morphologies and chemical compositions were investigated. Subsequently, the prepared films were assembled into coin cells and the electrochemical properties of the films were tested. The main conclusions are as follows:

V_2O_5 thin film prepared by radio frequency magnetron sputtering from vanadium target shows crystalline structure, while copper doped vanadium oxide thin films is amorphous. The crystalline V_2O_5 thin film has rough surface with granular structure. The copper doping not only increases the growth rate but also improves its flatness at the surface. It also decreases the particle size and results in more dense V_2O_5 thin film.

The XPS results indicate the Cu in the copper-doped vanadium oxide is divalent. With the increase of the Cu doping, V2p binding energy shifts to lower energy, showing an increase of vanadium with low valance state.

Cyclic voltammetry and constant current charge/discharge tests show that the copper doping is beneficial to Li^+ intercalation and improves the capacity and cycle performance of V_2O_5 thin film electrode. However, copper doping increase the first irreversible capacity loss of V_2O_5 thin film. The doping content of copper has a significant influence on the electrochemical performance of V_2O_5. $Cu_{2.1}VO_{4.4}$ thin film displays the highest discharge capacity of 370.7 μAh/ cm^2·μm at the first cycle and the best cycle performance with a capacity of 83.4 μAh/ cm^2·μm after 100 cycles.

Based on the experimental conditions of the Sa Bendong micro computer center of Xiamen University, a fabrication process for the preparation of all solid state thin film Li-ion battery has been designed. V_2O_5/LiPON/$LiCoO_2$ and $Cu_{2.1}VO_{4.4}$/LiPON/$LiCoO_2$ all solid state thin film Li-ion batteries were fabricated with V_2O_5 or copper doped V_2O_5 thin films as the anode. The surface and cross-section morphologies and electrochemical properties of thin film Li-ion batteries were characterized. The interfaces between the active material layers of the prepared thin film batteries were smooth and flat, and no cracks, pores and other defects were found. The performance of the thin film batteries with $Cu_{2.1}VO_{4.4}$ is significantly improved than undoped V_2O_5 in terms of discharge capacity and cycling performance. At a discharge current of 10nA, the first cycle capacity was 4.1nAh and 12.1nAh for the thin film batteries with undoped V_2O_5 and $Cu_{2.1}VO_{4.4}$ respectively. At a discharge current of 50nA, the first cycle capacity was 3.71nAh and 10.3nAh for the thin film batteries with undoped V_2O_5 and $Cu_{2.1}VO_{4.4}$ respectively.

The main innovations in this thesis are: studied the optimal doping ratio of copper to improve the electrochemical performance of V_2O_5 thin film electrode; prepared V_2O_5 and copper doped V_2O_5 film by magnetron sputtering technology, and systematic studied the influence of doping on the crystal structure, surface

morphology, chemical composition and electrochemical performance of V_2O_5 thin film;, developed V_2O_5/LiPON/$LiCoO_2$ and $Cu_{2.1}VO_{4.4}$/LiPON/$LiCoO_2$ miniature solid state thin film Li-ion batteries with V_2O_5 and copper doped V_2O_5 as anode; developed a whole set of process flow with MEMS micro processing technology to prepare miniature solid state thin film Li-ion battery, including a photolithography, sputtering, stripping, corrosion.

Key words: All Solid State Thin Film Li-ion Battery; Micro Machining; V_2O_5 and Copper doped V_2O_5 Thin Film

目　录

Table of Contents