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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

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## 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落, 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  $370.7\mu Ah/cm^2 \cdot \mu m$ , 100 次循环后还保留  $83.4\mu Ah/cm^2 \cdot \mu m$ , 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  $\text{Li}^+$  intercalation and improves the capacity and cycle performance of  $\text{V}_2\text{O}_5$  thin film electrode. However, copper doping increase the first irreversible capacity loss of  $\text{V}_2\text{O}_5$  thin film. The doping content of copper has a significant influence on the electrochemical performance of  $\text{V}_2\text{O}_5$ .  $\text{Cu}_{2.1}\text{VO}_{4.4}$  thin film displays the highest discharge capacity of  $370.7 \mu\text{Ah}/\text{cm}^2 \cdot \mu\text{m}$  at the first cycle and the best cycle performance with a capacity of  $83.4 \mu\text{Ah}/\text{cm}^2 \cdot \mu\text{m}$  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.  $\text{V}_2\text{O}_5/\text{LiPON}/\text{LiCoO}_2$  and  $\text{Cu}_{2.1}\text{VO}_{4.4}/\text{LiPON}/\text{LiCoO}_2$  all solid state thin film Li-ion batteries were fabricated with  $\text{V}_2\text{O}_5$  or copper doped  $\text{V}_2\text{O}_5$  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  $\text{Cu}_{2.1}\text{VO}_{4.4}$  is significantly improved than undoped  $\text{V}_2\text{O}_5$  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  $\text{V}_2\text{O}_5$  and  $\text{Cu}_{2.1}\text{VO}_{4.4}$  respectively. At a discharge current of 50nA, the first cycle capacity was 3.71nAh and 10.3nAh for the thin film batteries with undoped  $\text{V}_2\text{O}_5$  and  $\text{Cu}_{2.1}\text{VO}_{4.4}$  respectively.

The main innovations in this thesis are: studied the optimal doping ratio of copper to improve the electrochemical performance of  $\text{V}_2\text{O}_5$  thin film electrode; prepared  $\text{V}_2\text{O}_5$  and copper doped  $\text{V}_2\text{O}_5$  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

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