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硕 士 学 位 论 文

掺铜 SnO_x 为负极的全固态微型薄膜锂离子电
池的研究和制备

Investigation and Fabrication for All-Solid Thin Film
Lithium-Ion Micro-Batteries Using SnO_x Doped with Copper

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中文摘要

随着 MEMS 技术的应用发展,微能源技术越来越受到人们的关注。全固态微型薄膜锂离子电池,有着体积小,安全性高,能量密度高,开路电压高,循环性能好,制备兼容性高等优势,成为目前微电源中的最佳选择。

正负电极和电解质都大大影响了整个电池的性能。本论文系统地探讨了全固态微型锂离子电池的活性材料薄膜的制备,并将实验结果集成到全固态微型锂离子电池的微加工技术中。

首先探讨了磁控溅射方法制备 SnO_x 薄膜时金属铜的掺杂。随着铜掺杂量的增加, SnO_x 薄膜的充放电容量和循环性能有了很大的改善,但是由于铜的参与导致首圈不可逆损失增大,保证适当的铜掺杂量可以得到性能良好的负极 SnO_x 薄膜。通过 XRD 和 SEM 发现,铜的掺杂使得 SnO_x 趋于非晶态,有利于减缓 SnO_x 薄膜嵌锂时的体积膨胀。另外铜离子参与氧化还原反应也增加了负极材料 SnO_x 的嵌锂容量。

然后研究了退火温度对 LiCoO_2 薄膜的影响。从 400°C 到 600°C ,发现退火温度越高, LiCoO_2 的(003)方向的结晶度就越强,这说明形成了脱嵌锂性能最好的 HT- LiCoO_2 。经过电化学测试和参照组比较,发现在 300°C 下溅射,之后在 600°C 中退火的 LiCoO_2 薄膜具有理想的容量和稳定的循环性能。

接下来对固体电解质 LiPON 的物相和性质进行了研究。由 XRD 分析得知 LiPON 呈非晶结构,离子电导率较高。LiPON 在潮湿的空气中会发生反应,改变其性质。对所制备的 LiPON 进行交流阻抗测试,算得到其离子电导率为 $8 \times 10^{-7} \text{S/cm}$,可以满足全固态微型薄膜锂离子电池对电解质的要求。

最后结合萨本栋微纳米中心的条件,设计了制备微型薄膜锂离子电池 $\text{LiCoO}_2/\text{LiPON}/\text{SnO}_{1.48}$ 和 $\text{LiCoO}_2/\text{LiPON}/\text{Cu}_{0.18}\text{SnO}_{1.55}$ 的工艺流程。之后将制备的电池进行恒电流充放电循环测试 100 圈,发现从 40 圈之后, $\text{LiCoO}_2/\text{LiPON}/\text{Cu}_{0.18}\text{SnO}_{1.55}$ 的放电容量稳定在 10-12nAh,大大超过了 $\text{LiCoO}_2/\text{LiPON}/\text{SnO}_{1.48}$ 的容量,且循环性能良好。

关键词: 锂离子电池; 薄膜材料; 微加工

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Abstract

With the development of MEMS technology, micro energy technology attracts more and more attention. Because micro-scaled all-solid-state thin-film lithium-ion batteries have a small volume, high security, high energy density, high open circuit voltage, good cycle performance, high preparation compatibility, they have become the best choice for micro power sources.

Positive and negative electrodes and electrolyte conditions greatly affect the performance of the entire micro-scaled all-solid-state thin-film lithium-ion batteries. This paper systematically discusses the preparation of active material thin films in lithium batteries, and the results are used in the micro-fabrication techniques of all-solid-state thin-film lithium-ion batteries.

First, we discuss the metal copper doping while preparing SnO_x films by magnetron sputtering. With the increasing amount of copper doping, the charge-discharge capacity and cyclic performance of SnO_x film is greatly improved, but the first loop irreversible loss increases due to the copper doping. Ensuring the appropriate amount of copper doping can obtain cathode SnO_x film with good performance. XRD and SEM results show that copper-doping make SnO_x film tends to amorphous, this helps mitigating the volume expansion of SnO_x film while intercalating lithium. More over, the involvement of copper ions in the redox reaction also increases the lithium insertion capacity of anode material SnO_x .

Then the annealing temperature on LiCoO_2 thin films is studied. From 400°C to 600°C , the higher the annealing temperature is, the stronger the degree of crystallinity of LiCoO_2 at (003) direction is, this indicates the formation of HT- LiCoO_2 which has a best performance of lithium-ion intercalation and deintercalation. After the electrochemical measurements and comparison of the reference group, it is found that the sample which is sputtered at 300°C and annealed at 600°C has the desired capacity and stable cycling performance.

Then the phase composition and properties of solid electrolyte LiPON is studied. The

XRD analysis shows that LiPON presents amorphous structure, and the ionic conductivity is higher. LiPON in the humid air will react and change its properties. LiPON prepared is tested with AC impedance test, the ionic conductivity is calculated to be $8 \times 10^{-7} \text{S/cm}$, and it meets the requirement of micro-scaled all-solid-state thin-film lithium-ion batteries.

Finally based on the MEMS techniques in Pen-Tung Sah Micro-Nano Technology Research Center of Xiamen University, a dexterous micro-fabrication process was developed for preparing solid-state microscale lithium-ion batteries $\text{LiCoO}_2/\text{LiPON}/\text{SnO}_{1.48}$ and $\text{LiCoO}_2/\text{LiPON}/\text{Cu}_{0.18}\text{SnO}_{1.55}$. Afterwards the prepared batteries are tested with constant current charge and discharge cycle test for 100 laps, and it is found that the capacity of $\text{LiCoO}_2/\text{LiPON}/\text{Cu}_{0.18}\text{SnO}_{1.55}$ batteries after 40 laps stabilizes at 10-12nAh, which is much higher than the capacity of $\text{LiCoO}_2/\text{LiPON}/\text{SnO}_{1.48}$, and it shows excellent cycle performance.

Key words: Lithium-ion batteries; Thin film materials; Micro-fabrication

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