

Solid State Thin Film Lithium Microbatteries

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Abstract—Solid state thin film lithium microbatteries fabricated by pulsed-laser deposition (PLD) are suggested. During deposition the following process parameters must be considered, which are laser energy and fluence, laser pulse duration, laser pulse frequency, target composition, background gasses, substrate temperature, target-substrate distance and orientation. The effects of the variations of the process parameters can be obtained by measuring stoichiometry, thickness, phases and structure (grain size and texture), and stress of the deposited films. Electrochemical measurements will be conducted to test the microbattery properties through open-circuit voltage, charge-discharge cycling, cyclic voltammetry, and impedance analysis.

Index Terms—Lithium microbatteries, Pulsed-laser deposition, Solid state thin films.

I. INTRODUCTION

A battery is an electrochemical power source that is capable to convert chemical energy into electrical energy. It consists of negative and positive electrodes, electrolyte, battery housing, as shown in Fig. 1. Chemical reactions take place at the two spatially separated electrodes and electrical power can be generated in an external conducting circuit connecting the two electrodes. Electrolytes conduct electricity by the motion of ions and exhibit negligible electronic transport. Electrodes conduct both ions and electrons. To reach a higher voltage the batteries can be connected in series with others, and for a higher capacity it is necessary to link them parallel. There are three broad categories of batteries: primary batteries, rechargeable batteries, and fuel cells. In a primary battery one or both of the electrode reactions is irreversible and the battery can not be recharged. In a secondary battery the electrochemical reactions can be reversed and the battery thereby recharged hundreds or even thousands of times. In a fuel cell the reactants are continuously fed into the cell from outside.

The various existing types of electrochemical storage systems differ in the nature of chemical reaction, structural features and form, reflecting the large number of possible applications. Typical fields of applications for electrochemical systems are batteries and electric devices for providing

emergency powering for mobile systems such as cars and airplanes, power supplies to stationary appliances beyond the reach of the electricity grid such as remote transmitters and automatic weather stations, backup power sources to equipment that must be kept operational even in the event of a failure of the grid such as lighting and equipment in hospital operating theatres and flight control equipment. A growing number of new areas of applications are also accessible such as current sources for portable devices such as notebooks and cellular phones. These new applications are often related to the necessity for low weight. They also should have a large storage capacity and high specific energy densities.

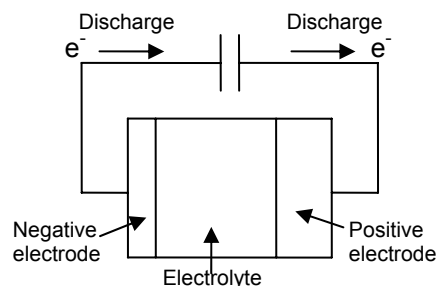


Fig. 1. Schematic picture of an electrochemical battery.

II. SOLID STATE THIN FILM LITHIUM BATTERIES

Most of the applications mentioned above could be covered by primary batteries, but economic and ecological reasons lead to the use of secondary batteries. The desire to obtain high performance secondary batteries has spurred the development of a variety of materials for electrodes and electrolytes. These materials include metals, metal hydrides, carbon and graphite, and metal oxides for electrodes, liquids, polymers, and solids for electrolytes. The assessment criteria of batteries should be based on their most important features: open-circuit voltage, specific capacity, energy density, power density, charge and discharge characteristics, current-voltage diagram, energy efficiency, cycle life, and overcharge reactions.

Solid state batteries using solid-electrolyte have attractive advantages compared to conventional liquid-electrolyte batteries such as lead-acid batteries or nickel-cadmium cells. These advantages include ease of utilization, high reliability, thermal stability, resistance to shocks and vibrations, absence

of self-discharge, extremely long active life, absence of possible pollution due to liquid electrolyte, possible miniaturization, and possible integration with microcircuits.

Thin-film techniques are used in battery technology mainly for the purpose of reducing the internal resistance due to geometrical reasons. In addition it offers various advantages:

(i) Thin-film technology has been widely used in advanced microelectronics.

(ii) Thinning of layers gives a lower electrical resistance in the transverse direction.

(iii) Thin-film technology provides clean surface of the compound and may improve the electrode-electrolyte interface contact reducing the interface resistance and permitting a high degree of reversibility.

(iv) Film deposition of alkali metals such as lithium is easy.

(v) Film deposition of lamellar compound allows the orientation of the layers with the van der Waals planes perpendicular to the separator surface.

(vi) Deposition of the fast ionic conductor in vacuum chamber avoids possible moisture problems.

(vii) Thin film technologies generally give very good adhesion between layers and large areas can also be obtained with these techniques.

(viii) Convenient substrate materials such as silicon wafers can be used.

(ix) Encapsulation of the battery can be achieved by the deposition of an insulating layer on the top of the device.

Another advantage is that it can allow the exploration for preparation of new materials with different chemical stoichiometries, perhaps providing better performances. However, thin film batteries have low capacities. Therefore rechargeability is an essential condition for technical feasibility of thin film technologies.

Rechargeable lithium batteries have received much attention in recent years. There is great interest in the application of solid electrolytes for high performance secondary lithium batteries because of high electrical, chemical, and mechanical stability of many lithium compounds. These lithium batteries can be fabricated by successive deposition of contacts, electrodes and an oxide electrolyte. This makes them ideal for integration with microelectronics.

A. Negative Electrodes

A number of materials have been used as the negative electrode in lithium batteries, such as lithium, carbon and graphite, lithium-aluminum, lithium-silicon, lithium-tin, and intercalation compounds, such as Li_xWO_2 , Li_xMoO_2 , and Li_xTiS_2 .

1) *Lithium*: Lithium has two unique properties which make it highly suitable as a negative electrode for batteries. Firstly, it is the lightest metal in the periodic table. This is a most attractive property for a lightweight battery. The specific capacity of lithium metal is 3.86 Ah/g. Secondly, lithium has a high electrochemical potential of -3.045 V vs NHE, which holds out the promise of a 3 V battery when combined with a suitable positive electrode. In order to obtain a reasonable cycle life, a three- to fivefold excess of lithium is required. The difficulties associated with the use of metallic lithium

stem from its reactivity with the electrolyte and the changes and dendrite formation that occur after repetitive charge-discharge cycling. After cycling the surface area of lithium increases with a corresponding increase in the reactivity. This lowers the thermal stability of the system.

2) *Carbon Materials*: The major problem with lithium is the battery safety because of the high reactivity of lithium. Carbon materials can reversibly accept and donate significant amounts of lithium without significant swelling on prolonged cycling. There is no dendrite formation. The usage of carbon and graphite for the negative electrode does not affect the mechanical and electrical properties. The battery becomes safer and is used more efficiently. The chemical potential of a lithiated carbon material is close to that of metallic lithium, thus an electrochemical battery made with a lithiated carbon material will have almost the same open-circuit voltage as one made with metallic lithium. The specific capacity or energy of the lithium ion battery depends largely on the type of carbon materials used, the lithium intercalation efficiency, and the irreversible capacity loss associated with the first charge process.

B. Positive Electrodes

A variety of materials have been investigated for the positive electrode of lithium batteries, such as intercalation solid compounds, soluble inorganic cathodes, and polymeric materials. The best positive electrodes for rechargeable batteries are those where there is little bonding and structural modification of the active materials during the charge and discharge reaction. The intercalation compounds, such as MnO_2 , V_2O_5 , LiMnO_2 , LiVO_2 , LiCoO_2 , LiMn_2O_4 , and LiNiO_2 , are among the most useful positive electrode materials. In these compounds, a guest species such as lithium can be inserted interstitially into the host lattice during discharge and subsequently extracted during recharge. Key requirements for these compounds for the positive-electrode are: high free energy of reaction with lithium, wide range of the amount of intercalation, little or no structural change on reaction, highly reversible reaction, rapid diffusion of lithium ions in solid, good electronic conductivity, no solubility in electrolyte, readily available or easily synthesized from low cost reactants.

1) *LiCoO₂*: LiCoO_2 gives a high capacity (155 mAh/g) and cycle numbers. It has a voltage of 4.1 V vs. lithium. It is used in most of the lithium batteries in production in spite of its limited availability and cost. LiCoO_2 has a layer structure, where lithium and transition metal cations occupy alternate layers of octahedral sites in a distorted cubic close-packed oxygen-ion lattice. The layered metal oxide framework provides a two dimensional interstitial space, which allows for easy removal of the lithium ions. The dimensional changes on charge-discharge cycling are small.

2) *LiMn₂O₄*: LiMn_2O_4 has a lower capacity (120 mAh/g) but a higher voltage (4.2 V) than LiCoO_2 . It offers an advantage in terms of the availability of natural resources and cost. LiMn_2O_4 has a spinel or tunnel structure which possesses

a three-dimensional space via face sharing octahedral and tetrahedral structures. This provides conducting pathways for the insertion and extraction of lithium ions.

3) LiNiO_2 : LiNiO_2 has a higher capacity (200 mAh/g) but a lower voltage (4.0 V) than LiCoO_2 . It has a layer structure. The dimensional changes are small. Despite its high capacity and low cost, LiNiO_2 is not widely used commercially because of the energy involved upon decomposition, the relatively low temperature at which self heating ensues, and the difficulty of preparing the material consistently in quantity.

C. Solid Electrolytes

Ionic transport in solids is related to the atomic disorder in real crystals. The most important defects are vacancies and interstitials. Charged defects have an effect on electronic concentration and accordingly on electronic leakage current. An ionically conducting material may readily turn into an electronic conductor. The most important driving forces for the motion of ionic defects and electrons in solids are the migration in an electric field and the diffusion under the influence of a chemical potential gradient. Depending on the majority charge carriers, quite different driving forces and fluxes apply for the ions and electrons in solid electrolytes and electrodes. The majority carriers are transferred in an electric field whereas the minority charge carriers are moved by diffusion. The solid electrolyte therefore carries the mobile ions according to Ohm's law and the electronic carriers according to Fick's law. The electrodes carry the ions towards the interfaces with the electrolyte by diffusion. The mobility rather than concentration of electrons and holes has to be small in electrolytes.

Solid electrolytes for battery applications require high ionic conductivities and wide range of appropriate thermodynamic stability. Four major aspects should be taken into consideration for the design of suitable solid electrolytes: (i) optimizing the lattice structure spatially and energetically to improve the number and mobility of ionic defects, (ii) developing synthesis routes which lead to materials of amorphous or polycrystalline structure with high overall conductivity, (iii) optimizing the stability range to prevent chemical reactions with the electrodes, (iv) optimizing the electrolytic domain with negligible electronic conduction over the activity range employed. It is difficult to prepare all-solid-state batteries — except possibly thin film batteries — with good contacts between the electrolyte and electrodes because of differences in the thermal expansion coefficients of different materials and because of undesirable side reactions at high temperatures.

The electrolyte generally used in solid state thin film lithium batteries is lithium phosphorus oxynitride (LiPON). LiPON has a good lithium ion conductivity and excellent stability in contact with metallic lithium.

III. PLD-GROWN LITHIUM MICROBATTERY

A. Pulsed-Laser Deposition (PLD)

Several methods have been used in preparing solid state thin film batteries. These methods include RF sputtering deposition, evaporative deposition, chemical vapor deposition (CVD), pulsed-laser deposition (PLD), and spin-on coating.

Our project is to use PLD to grow materials that can lead to lithium microbatteries with high power and energy density. PLD is a successful evaporative deposition technique in the growth of materials containing volatile components with complex stoichiometry. For this reason, it is well suited to films of lithiated transitional metal oxides, where lithium loss due to volatilizations could occur in conventional evaporation technologies. PLD can preserve the stoichiometries of the target sources, therefore can grow films of constant stoichiometries. In this project, KrF excimer laser (wavelength 248 nm) will be used. During deposition the following process parameters will be investigated: laser energy/fluence, laser pulse duration, laser pulse frequency, target composition, background gasses, substrate temperature, target-substrate distance and orientation. The effects of the variations of the process parameters on film stoichiometry, film thickness, film phases and structure (grain sizes and film texture), and film stress will be studied.

B. Lithium Microbatteries

In our project the lithium microbattery will consist of the following main components: platinum current collector on the substrate, LiCoO_2 positive electrode, LiPON electrolyte, lithium foil negative electrode, and protective coating. The thickness of the lithium foil was determined by its availability and was generally present in excess.

C. Testing and Characterization Techniques

The properties and performance of the solid state thin film lithium microbatteries will be tested and characterized through the following measurements: open-circuit voltage, specific capacity, energy density, power density, energy efficiency, cyclic voltammetry, charge and discharge characteristics, cycle life, overcharge reactions, complex impedance plot, x-ray diffraction (XRD), Raman scattering spectra, scanning electron microscopy (SEM).

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