Thin film solid electrolytes and electrodes for rechargeable lithium-ion batteries

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Abstract

Various modifications of chemical vapour deposition (CVD), and electrostatic spray deposition (ESD) have been developed recently for the production of solid-state battery components. In addition, the DSM–Solufill™ process will be explored for the production of thin films of these battery components. The principles of these techniques will be discussed, with examples of materials used for these thin film Li-ion batteries. © 1977 Elsevier Science S.A.

Keywords: Chemical vapour deposition; Electrostatic spray deposition; Thin film deposition; Lithium-ion batteries

1. Introduction

The enormous demand for portable electronic equipment requires the introduction of new rechargeable batteries with higher energy densities than the existing ones. Among these, lithium-ion batteries are very promising. Moreover, not only the consumer electronics industry, using high capacity batteries, is interested in this new generation of rechargeable batteries, also the chip industry, credit card factories, and even the feedstock industry. Chips can be made smart, credit cards can be used as bank account, and cattle can wear small implants for data storage of their daily behaviour, etc. However, it should be clear that these latter industries are merely interested in microbatteries in a kind of thin film construction. Reported thin film Li-ion batteries often use lithium metal oxides ($LiMn_2O_4$, $LiCoO_2$, $LiNiO_2$, $Li_xV_yO_z$) as the cathode, and, for instance, carbon, TiS_2, or other lithium metal oxides as the anode. Most thin film rechargeable lithium-ion batteries operate with certain solid electrolytes that are either polymer or ceramic. Chemical vapour deposition (CVD) has been recognized as an important production method for thin films and powders of structural and functional ceramics. It is of particular interest for the formation of non-oxidic layers. Electrostatic spray deposition (ESD), recently developed for the formation of inorganic thin films, is a simple method to form oxidic layers. Both deposition techniques have been applied for the production of thin films of components for

solid-state lithium batteries. Furthermore, the DSM–Solufill™ process has been explored for the production of thin films of electrodes and electrolytes. The powders needed for the Solufill™ process are prepared by concentrated sol–gel methods. The principles of these advanced thin-film techniques will be reviewed with emphasis on the lithium battery components TiS_2, $LiMn_2O_4$, $LiCoO_2$, and $BPO_4 \cdot yLi_2O$ ($0 < y < 0.15$). In addition, unique morphologies of ESD-grown films of electrodes will be presented.

2. Thin film technologies for Li-ion batteries

In the following sections various thin film technologies will be discussed together with examples of production of characteristic battery components. These technologies reviewed are CVD, ESD, and the DSM–Solufill™ process.

2.1. Chemical vapour deposition

In CVD processes gases or vapours are used to form solid compounds. The reaction takes place on the surface (film deposition) or in the gas phase (powder formation). In order to activate the reaction, various techniques exist. Among them thermal activation in either a hot-wall or a cold-wall reactor is the simplest. In addition, laser activation, plasma activation, and microwave activation were also applied (see Fig. 1). Furthermore, particle precipitation aided CVD (PP–CVD) and electrochemical vapour deposition (EVD) are
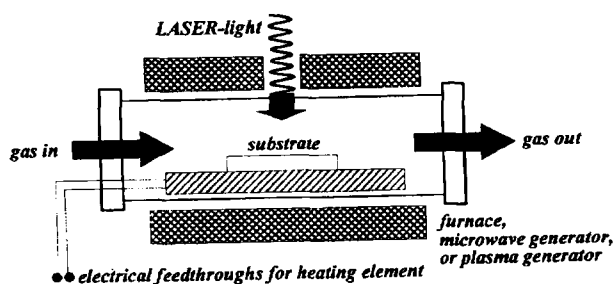
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Fig. 1. Schematic outline of the set-up used for various CVD techniques. Combinations of different energy sources are possible, often useful, and sometimes indispensible.
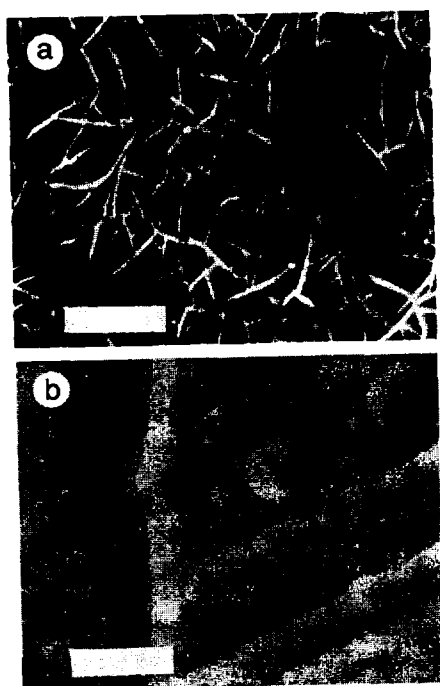

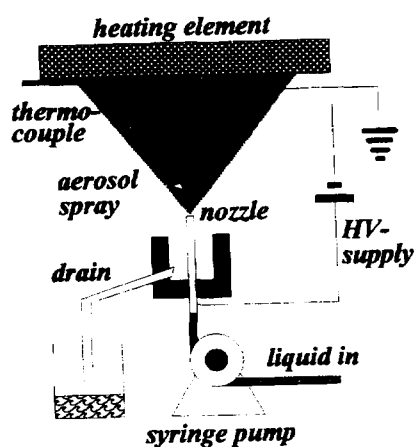Fig. 2. CVD-grown layer of TiS_2 (a) (bar = 4 μm), and MEEP (b) (bar = 20 μm).

Fig. 3. ESD set-up. The set-up can be also used in the horizontal configuration.

options for the production of components for solid-state lithium batteries.

CVD of TiS_2 is relatively well studied, probably due to the ready availability of a volatile, reactive, and cheap precursor of titanium, i.e. $TiCl_4$. For the alternatives, i.e. manganese, cobalt, nickel, and vanadium, the precursors are very expensive, non volatile, and extremely toxic. CVD of TiS_2 is studied with $TiCl_4$ and various sulfur-containing precursors, such as H_2S, t-butylthiol, and hexametyldisilathiane (HMDST) at several temperatures, pressures, and reactant concentrations. In addition, a variety of CVD set-ups were applied in order to find the best reactor geometry [1]. Surprisingly, most of the deposits wherever made, whatever precursor used, revealed the same typical star-like structure as shown in Fig. 2(a). Even vacuum techniques yield this morphology.

CVD is also applied to deposit polymer electrolytes, such as poly-(methoxy(ethoxyethoxy))phosphazene (MEEP). Deposition is carried out with phosphonitrilic chloride trimer and 2-(2-methoxyethoxy)ethanol as the precursors at low pressure (10 mbar). Fig. 2(b) shows an as-deposited layer that need to be annealed afterwards in order to form the proper electrolyte component.

2.2. Electrostatic spray deposition

ESD or electrospraying (see Fig. 3) comprises the generation of an aerosol by applying a high voltage to the surface of a liquid, which contains certain precursor materials [2]. The method was used commonly to form nanocrystalline oxidic ceramic powders [3]. However, the method adapted here is modified in order to deposit thin films, using the aerosols as the adsorbing species [4,5]. The micron-sized aerosol particles are charged, thus preventing agglomeration in the gas phase. ESD opens the opportunity to control the morphology of a layer [6]. This morphology is determined by the droplet size of the spray of the incoming droplet at the substrate surface, but also by the deposition temperature, and the spreading rate of the droplets on this surface. In addition, at low deposition temperatures and/or using a high boiling point solvent, the solution chemistry including the precipitation process and the pyrolysis or reaction of the solutes are also important parameters. However, the main factor determining the morphology of the layer is the substrate temperature, since the temperature influences all the parameters mentioned above. The higher is the substrate temperature, the more porous is the layer. The layer formed at relatively high temperatures using ethanol as solvent is very porous and reveal a fractal-like appearance (Fig. 4(a)). At moderate temperature and at an early stage the deposited layer on a metal substrate is relatively dense (Fig. 4(b)), but it becomes porous with increasing thickness. The concentration of the precursor solution has a minor effect on the morphology of the layer. Actually, it seems easier to obtain a denser layer using a higher concentration compared to using a lower concentration. The electric field strength can influence the flying time of the charged particles. Above the onset voltage, the

Fig. 4. ESD-grown layers of LiCoO₂: (a) fractal-like layer; (b) dense layer, and (c) layer with a unique structure. All bars agree with 20 μm.

Fig. 5. Powders of LiMn₂O₄: (a) (bar = 2 μm), and (b) BPO₄:Li (bar = 4 μm) synthesized by the sol–gel method.

higher the applied voltage, the denser the layer. For a ceramic substrate, its surface roughness (or smoothness) can affect the morphology of a deposited layer. Cracks or cavities present in the substrate will lead to the formation of more agglomerates. At the same deposition temperature, a layer formed using a precursor solution with a high boiling point solvent is generally denser than one obtained using a low boiling point solvent. In addition, however, a unique porous structure can be obtained with a high boiling point solvent at deposition temperatures below 230 °C [7] (see Fig. 4(c)).

2.3. DSM–Solufill™ process

The principle of the process is the incorporation of a ceramic powder in an ultra high molecular weight polyethylene (UHMwPE) matrix. This matrix can incorporate up to 60 mass% ceramic powder. The ceramic powder, UHMwPE, and additives form a suspension that can be extruded into a
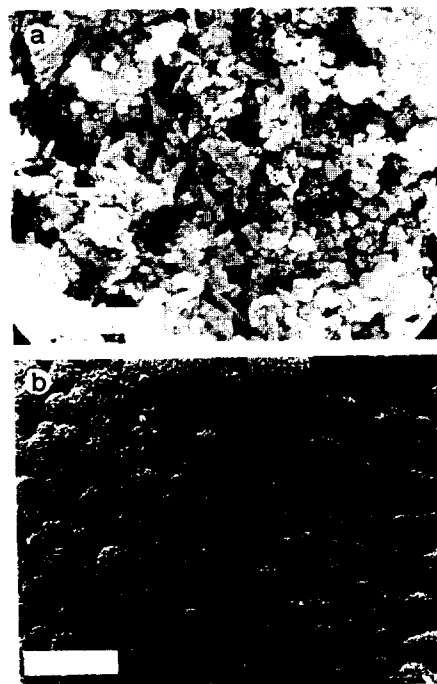
tape. This tape can be enlarged in two dimensions, leading to a final green tape with a typical density of 60–80%.

The DSM–Solufill™ process will be employed for the production of films of the cathode material LiMn₂O₄ and the elctrolyte material BPO₄·yLi₂O $(0 < y < 0.15)$. Submicron powders of LiMn₂O₄ were synthesized by the sol–gel technique using a concentrated manganese acetate tetrahydrate $(Mn(CH_3COO)_2 \cdot 4H_2O)$ solution to which a proper amount of lithium hydroxide monohydrate $(LiOH \cdot H_2O)$ is added [8]. The homogeneous paste formed is calcined in a programmable furnace using an optimized temperature programme. BPO₄·yLi₂O is produced by calcining stoichiometric mixtures of either boric acid and phosphoric acid, or boric acid and dihydrogen ammonium phosphate, both with a proper amount of lithium hydroxide [9]. The calcination step took place in a programmable furnace using an optimized temperature programme. The obtained powders (see Fig. 5) are dried, ground in a ball mill, and dried again prior to the DSM–Solufill™ processing. Subsequently, layers of foils of the current collector, anode, electrolyte, cathode, and current collector are composed in order to form a complete battery.

Acknowledgements

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