Title: METHOD FOR THE MANUFACTURE OF A THIN FILM BATTERY AND DEVICE COMPRISING SUCH A BATTERY

Abstract: The invention relates to a method for the manufacture of a thin film battery, comprising the steps of: depositing a first electrode layer on a substrate, depositing an electrolyte layer on the first electrode, and depositing a second electrode layer on the electrolyte layer, wherein one of the first electrode layer and the second electrode layer is an anode material and the other electrode is a cathode material. The method further relates to a thin battery obtainable by such method, and a device comprising such a battery.
Method for the manufacture of a thin film battery and device comprising such a battery

The invention relates to a method for the manufacture of a thin film battery, comprising the steps of: depositing a first electrode layer on a substrate, depositing an electrolyte layer on the first electrode, and depositing a second electrode layer on the electrolyte layer, wherein one of the first electrode layer and the second electrode layer is an anode material and the other electrode is a cathode material. The method further relates to a thin battery obtainable by such method, and a device comprising such a battery.

According to the state of the art, the manufacture of thin film batteries commonly comprises the steps of depositing a first electrode layer on a substrate (which is usually not conductive), depositing an electrolyte layer on the first electrode, and depositing a second electrode layer on the electrolyte layer, wherein one of the first electrode layer and the second electrode layer is an anode material and the other electrode is a cathode material. This layer stacking (substrate-anode-electrolyte-cathode or substrate-cathode-electrolyte-anode) can be repeated, in order to yield a serial stack of batteries. Typical depositing methods include chemical and physical vapour deposition techniques.

However, chemical and physical vapour deposition techniques are relatively expensive and time-consuming. When relatively large substrate areas need to be covered, the above-mentioned conventional deposition techniques are usually unsuitable. Also, chemical and physical vapour deposition techniques require advanced devices.

It is the object of the invention to provide a relatively simple method to prepare thin film batteries relatively fast and efficiently, in particular on larger substrates.

To achieve this object the invention provides a method according to the preamble, characterized in that at least one layer selected from the first electrode layer, the electrolyte layer and the second electrode layer is deposited using a sol-gel method. Such a sol-gel method requires relatively simple equipment compared to chemical and physical vapour deposition methods; it is relatively cheap and enables relatively rapid depositions of thin films. The method according to the invention is in particular suitable to rapidly deposit thin films on large surfaces, and offers and excellent thickness control and stoichiometry control of layer components. The sol-gel method preferably comprises the steps of: a) application of a fluid comprising at least one precursor onto a supporting surface, b) allowing
the precursor, to condense to yield a gel layer, and c) drying of the gel layer. The fluid is
commonly formed by a solution of one ore multiple precursors in a solvent, wherein the
solution is named a ‘sol’. The fluid or sol may also be a colloidal suspension. In a typical sol-
gel process, one or more precursors are subjected to a series of hydrolysis and polymerization
reactions to form the sol. Allowing the precursors to condense to yield a gel layer during step
b) is commonly performed by evaporating a solvent comprised by the sol. This evaporation
may be a natural evaporation (at room temperature) or may be a forced evaporation by
heating the sol. However, also other evaporation techniques and/or conditions, such as
reduced pressure (vacuum), a drying gas stream, heating up to the boiling point of the
solvent, or combinations of such techniques, may be applied. The technique or techniques of
choice for evaporation usually depend on the solvent that is to be removed. The final step c)
of drying of the gel layer is preferably realized by annealing the gel layer by heating.
Annealing of the gel layer by heating removes organic compounds and leads to the formation
of the desired layer from the precursors. The temperature used for annealing depends on the
nature of the precursors and solvent, as well as the desired layer. The temperature for
annealing is typically higher than 180 °C. The precursors are typically metal-organic
compounds, metal salts and/or metallic coordination complexes of the desired elements. The
precursors may be in solution or mixed with the solvent as a preferably homogeneous
dispersion or suspension. The substrate may be a two-dimensional (essentially flat) or three-
dimensional structure. The supporting surface onto which the sol is applied during step a)
may be formed by another layer, such as an electrode layer, being part of a thin film battery
to be prepared. However, it is also conceivable that the supporting surface is formed by a
substrate that is not actually part of the thin film battery to be prepared. The application of the
fluid, in particular the sol, onto the supporting surface according step a) may be performed by
using several application techniques, as will be explained further below.

In a preferred embodiment, during step a) the application of the fluid, in
particular the sol, onto the supporting surface is performed by means of spin-coating. Spin-
coating is a method to apply the sol relatively rapidly in an evenly divided, homogeneous
way to the substrate, which may lead to a relatively high production rate. Relatively large
surfaces can be treated, and by varying the speed of rotation the thickness of the formed layer
can be tuned. Spin-coating is in particular suitable for IC technology, and allows for easy
process optimization as spin-coating mainly relies on spin speed and solution viscosity.

In yet another preferred embodiment, during step a) the application of the
fluid, in particular the sol, onto the supporting surface is performed by means of dip-coating.
Dip-coating is another very rapid and convenient way to apply fluid to a relatively large area. Dip-coating is commonly well suitable for high production coating of relatively simple shapes. During dip-coating, the transfer efficiency is commonly relatively high as all contact areas of the supporting surface will be covered by the sol. Moreover, the equipment requirements are relatively low, and a further advantage of dip-coating is that the process can be applied in conveyor paths and can be automated relatively easily.

In another preferred embodiment, during step a) the application of the fluid, in particular the sol, onto the supporting surface is performed by means of spray-coating. Spray-coating is a very convenient way to apply the sol to a relatively large area. The fluid is applied in small droplets that adhere to the surface that is to be treated. The size of the droplets applied by spray coating depends on the sol and the nozzle used, which may be varied to obtain optimum results. Spray-coating is particularly suitable for continuous processes. Spray-coating is easily adaptable to different surfaces, in particular non-planar substrates. The thickness of the layer produced by spray-coating is highly reproducible.

In a particular preferred embodiment, during step a) the application of the fluid, in particular the sol, onto the supporting surface is performed by means of printing. Printing provides a very controlled way to deposit the fluid to the substrate. As a result printing is very material-efficient. A particular useful printing technique is ink-jet printing. Preferably, the fluids used in printing have a viscosity that does not exceed 30 cP. The printing equipment is easily adaptable to produce layers in specific shapes, making printing a highly versatile technique.

It is preferred if at least one of the layers deposited using a sol-gel method is deposited as a pattern. Patterns may be used to improve mechanical and electrical properties of the obtained thin film battery. Also, multiple battery units may be applied to a single substrate as a pattern.

In a preferred embodiment, the pattern is obtained by applying a mask of a predetermined pattern followed by deposition of a layer using at least one of the methods selected from the group consisting of: spin-coating, dip-coating, and spray-coating, in particularly printing. Thus, a precisely defined pattern is obtained in a rapid way. The same mask may be used multiple times on different substrates, or a separate mask may be applied to each substrate prior to application of the fluid.

Printing allows a very flexible and precise way of applying a pattern. The pattern may be easily changed, and very fine pattern structures are possible by printing techniques.
Preferably both electrode layers are deposited using a sol-gel method to enable further optimization of the manufacture of the thin film battery. More preferably, both electrode layers and the electrolyte layer are deposited by using a sol-gel method. Thus, similar manufacture steps are repeated, making the consistent use of relatively simple equipment possible. Parameters for each layer may vary; in particular the temperature used in the heating step depends on the precursor that is used for a particular layer.

It is advantageous if at least two adjacent layers are formed by oxide materials. It was discovered that oxide material layers are readily obtained by sol-gel methods, and the mutual adhesion between oxide material layers is excellent.

In a preferred embodiment, the substrate is a rigid substrate. Rigid substrates are very convenient to handle. Useful substrates are indium-tin oxide-coated glass, silicon, metals and rigid polymer materials. The rigid substrates may have a planar geometry. It is, however, also conceivable to apply a pre-shaped (three-dimensional), e.g. curved, substrate. As mentioned afore, the substrate itself may form one of the electrode layers.

In another preferred embodiment, the substrate is a flexible substrate. Flexible substrates are particularly useful in certain applications. Typical flexible substrates are PEEK (polyetheretherketone) and polyimide-polymers such as Kapton.

The invention also relates to a thin film battery obtainable by the method according to the invention. Such a thin film battery is relatively cheap to produce, and shows excellent electrical properties. The batteries obtained by the method according to the invention may be advantageously applied in electrical devices, such as displays, cell phones, sensors, energy and light applications.

The invention further relates to an electrical device comprising a thin film battery according to the invention.

The invention will now be elucidated by means of the following non-limitative example.

The following battery stacks listed in table I were prepared using the method according to the invention:
Table I: battery stacks prepared by sol-gel methods.

<table>
<thead>
<tr>
<th></th>
<th>anode</th>
<th>cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li_{4-x}Ti_{5}O_{12}</td>
<td>LiCoO₂</td>
</tr>
<tr>
<td>2</td>
<td>Li_{x}V₂O₅</td>
<td>LiCoO₂</td>
</tr>
<tr>
<td>3</td>
<td>SnO₂</td>
<td>LiCoO₂</td>
</tr>
<tr>
<td>4</td>
<td>NiVO₄</td>
<td>LiCoO₂</td>
</tr>
</tbody>
</table>

Li_{4-x}Ti_{5}O_{12}, Li_{x}V₂O₅, SnO₂ and NiVO₄ are readily obtainable as layers through sol-gel methods, although other materials are also suitable. X in Li_{4-x}Ti_{5}O_{12} may be varied from 5-7. The lithium concentration x in Li_{x}V₂O₅ may vary from 0-0.8. Between the anode and cathode, a suitable solid electrolyte was deposited. Examples of solid electrolyte materials readily obtainable by sol-gel methods are Li_{5}La_{3}Ta₂O_{12}, Li_{0.5}La_{0.5}TiO₃, LiTaO₃ and LiNbO₃. LiCoO₂ is a cathode material that is particularly convenient to obtain by sol-gel methods.

However, other cathode materials like LiNiO₂ and LiMn₂O₄ are also readily obtainable by sol-gel methods. Combined with a suitable solid electrolyte between the anode and the cathode material, well packed, stable layer stacks are obtained, in particular if an oxide material is used as the electrolyte layer.

The following steps were performed to obtain the battery stacks:

a) application of a fluid containing the precursor for the layer on a substrate,
b) evaporation of solvent to yield a gel layer, and

c) annealing of the gel layer with the substrate by heating.

All layers were stacked on top of platinum-coated silicon wafers, but this substrate could be substituted by other rigid or flexible substrates. The steps a)-c) were repeated for each subsequent layer, wherein the already deposited layers on top of the substrate material act as a new substrate.

Table II shows an example of different precursors that may be employed in order to obtain a complete battery stack by means of by sol-gel methods. The annealing temperatures for these materials vary from 200 °C to 750 °C, depending on the components.

Alcohols are particularly useful as solvents in the applied fluid, as they form soluble complexes that act as precursors, in particular for oxide materials. In particular, alcohols with relatively low boiling points such as methanol, ethanol, n-propanol and isopropanol are useful. Also, low boiling organic acids such as acetic acid are useful. For metal oxide layers,
sol-gel methods were preferred, but for some metal layers or oxide layers physical deposition techniques may also be applied.

Table II

<table>
<thead>
<tr>
<th>Layer Material</th>
<th>Precursor(s)</th>
<th>solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>Sn(OEt)₂ or SnCl₂</td>
<td>ethanol</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>Nb(OEt)₃ and Li or Li(OEt)</td>
<td>2-methoxyethanol or ethanol or propanol</td>
</tr>
<tr>
<td>LiCoO₂</td>
<td>Co(CH₃CO₂)₂ or Li(OC₃H₂)</td>
<td>isopropanol or acetic acid</td>
</tr>
</tbody>
</table>

For printing purposes, the viscosity of the applied solutions did not exceed 30 cP.

The invention is further elucidated by means of the following non-limitative figures, wherein:

Fig. 1 shows a general design of a battery stack is shown in figure 1, and Figs. 2a-d show different types of batteries.

A general design of a battery stack 10 is shown in figure 1. The stack 10 consists of a substrate 11, on top of which a barrier layer 12 is deposited, which acts as a substrate for a SnO₂ anode material layer 13. A solid electrolyte LiNbO₃ layer 14 separates the anode 13 from the LiCoO₂ cathode material layer 15. In a final step, the complete battery stack 10 was sealed by a sealing polymer 16, which is made out of a non-conductive polymer material. It is noted that the obtained stack 10 may have different forms.

Figures 2a-d show different types of batteries obtained by the method according to the invention. Figure 2a shows a rigid substrate 20 fully covered with a battery stack 21 comparable to figure 1.

Figure 2b shows a rigid substrate 30 with a pattern of battery stacks 31 deposited as separate blocks on the surface of the substrate.
Figure 2c shows a flexible substrate 40 fully covered with a battery stack 41. The battery stack is sufficiently thin and of sufficiently flexible material layers to enable the complete battery to be flexible.

Figure 2d shows a pattern of battery stacks 51 deposited as separate blocks on top of the flexible substrate 50. Such a pattern allows for a greater flexibility of material, lowering the risk of damage to the battery stack.
CLAIMS:

1. Method for the manufacture of a thin film battery, comprising the steps of:
   - depositing a first electrode layer,
   - depositing an electrolyte layer onto the first electrode, and
   - depositing a second electrode layer onto the electrolyte layer,
   wherein one of the first electrode layer and the second electrode layer is an anode and the other electrode layer is a cathode, characterized in that at least one layer selected from the first electrode layer, the electrolyte layer and the second electrode layer is deposited using a sol-gel method.

2. Method according to claim 1, characterized in that the sol-gel method comprises the steps of:
   a) application of a fluid comprising at least one precursor onto a supporting surface,
   b) allowing the precursor to condense to yield a gel layer, and
   c) drying of the gel layer.

3. Method according to claim 2, characterized in that during step a) the application of the fluid onto the supporting surface is performed by means of spin-coating.

4. Method according to claim 2 or 3, characterized in that during step A) the application of the fluid onto the supporting surface is performed by means of dip-coating.

5. Method according to any of claims 2-4, characterized in that during step a) the application of the fluid onto the supporting surface is performed by means of spray-coating.

6. Method according to claim 5, characterized in that during step a) the application of the fluid onto the supporting surface is performed by means of printing.
7. Method according to any of the preceding claims, characterized in that at least one of the layers deposited using a sol-gel method is deposited as a pattern.

8. Method according to claim 7, characterized in that the pattern is obtained by applying a mask of a predetermined pattern followed by deposition of a layer using at least one of the methods selected from the group consisting of: spin-coating, dip-coating, and spray-coating, in particularly printing.

9. Method according to any of the preceding claims, characterized in that both electrode layers are deposited using a sol-gel method.

10. Method according to claim 11, characterized in that both electrode layers and the electrolyte layer are deposited using a sol-gel method.

11. Method according to any of the preceding claims, characterized in that at least two adjacent layers are formed by oxide materials.

12. Method according to any of the preceding claims, characterized in that the substrate is a rigid substrate.

13. Method according to any of the preceding claims 1-11, characterized in that the substrate is a flexible substrate.

14. Thin film battery obtainable by the method according to any of the preceding claims.

15. Electrical device comprising a thin film battery according to claim 14.