

The invention relates to a process for the production of a positive electrode in strip form for primary and secondary cells, in which a dry powder mixture comprising the electrochemically active material and a binder is applied by means of rollers to a metal netting or an expanded metal as the current collector.

The preferred field of application of the positive electrodes produced in accordance with the novel process is that of winding cells having liquid electrolyte, based on systems containing Li electrodes or H_2 electrodes as negative counter-electrodes, that is to say both aqueous and non-aqueous systems. In this case, as a rule the counter-electrodes are also, together with the positive electrode and with the interposition of a separator, rolled up in a spiral.

Winding technology primarily requires of the strip-shaped or film-shaped electrodes a high degree of flexibility. In accordance with practice which has been conventional hitherto, winding electrodes are produced in a wet process, for example by brushing a metal oxide paste onto both sides of a perforated metal strip in accordance with DE-OS 2 903 074. The individual production steps, beginning with making up the paste and maintaining a suitable viscosity and ending with a careful drying process, in which the formation of cracks in the adhering mass layers have to be avoided, require considerable technical expenditure.

However, there is furthermore known from DE-PS 1 496 289 a dry process in which the pulverulent active material is pressed continuously between rollers into the openings of an expanded metal as the support net. Here, filling of the openings takes place in the compression region of the rollers, from one side.

The publication gives only an imprecise hint of the final thickness of the resulting electrode strip, stating that the support net has an initial thickness of 0.5 to 2.5 mm and is compressed by rolling to preferably 25% of the original

thickness.

The object of the invention is to specify a process for the production of positive strip electrodes for winding cells, which are distinguished by improved use of the mass and in particular are suitable for lithium systems.

In accordance with the invention, the object is achieved by a process as specified in Claim 1.

In accordance with this, a grid-shaped current collector, which can be a metal netting or expanded metal, is acted upon on both sides with the active material in a dry rolling process. Taking as a starting point a dry powder mixture which is composed of the actual electrochemically active material and a smaller proportion of binder, application to the support in the desired way is, however, not achieved directly but in accordance with the invention by way of a preliminary processing of the dry powder to give strips of mass which are then used to coat a current collector strip on both sides in a rolling-on process.

For the sake of better understanding, the process sequence according to the invention will be described with reference to a figure illustration which shows the structure of the rolling apparatus to be used.

This rolling system includes two powder supplies 1 for the simultaneous production of two films of the mass. The powder supplies comprise a charging funnel through which the mass is first supplied, in dependence on consumption, to a beater mill 2. As a measurement of and a regulating variable for consumption there serves the level of filling of the powder in the supply channel 3, which is measured by means of a light barrier 4 which is for its part coupled back to a metering apparatus (stirrer in the charging funnel, not illustrated).

The beater mill comminutes any lumps which may have arisen during

production of the mass and supplies the powder to the rolling head 5 by way of the supply channel. In the rolling head 5, the powder is compressed and rolled to give a solid strip of mass or a film. By exchanging rollers having different diameters, strips or films of different thicknesses can be produced. A precise adjustment on the rolling heads serves to correct the thickness within the relatively small range. The rolled strip of mass 6 is supplied from two sides by way of a sliderail with edge control 9, 10 to the rolling-on mill 14.

Since the strip of mass does not always have to be supplied synchronously, the drives are controlled individually by means of light barriers 8 in dependence on the length of a strip compensation 7.

The current collector in the form of a netlike support strip and/or expanded metal sheet is drawn from a reel 12 located above the rolling-on mill by way of braking, deflecting and guide rollers 13 into the rollers, is coated on both sides with the strips or films of mass, and after excess material has been stripped off (stripper 15) is wound onto a driven reel 16. The tensile force of the reel is matched by a slip clutch to the electrode material in order to prevent damage. Collection plates and a suction means above the reel prevent the electrodes from being damaged by mass particles falling down. The electrode strip wound onto the reel can be removed as a coil after rolling. The shape of the cathode is punched out of the electrode strip, the cathode may be subjected to a heat treatment and is prepared for winding.

Electrodes produced in accordance with the novel rolling process give cells into which they are incorporated a comparatively high energy content relative to their weight and a high energy density per unit volume. Moreover, such cells (size AA) can be used for various discharge current densities. If, with a pulsed discharge operation, a ratio of discharge time:interpulse time of 1:2 is chosen, then the cells can be loaded at 1.5 A during the

discharge times. Even with a long-term load of 100 mA, the energy density predetermined for these cells only falls by 20%.

The electrode strips produced in accordance with the invention, having a thickness which is at most 2.00 mm, but preferably only 0.40 to 0.20 mm, have a larger active surface than strips coated on one side. At the same time, porosity values which are at least 24% but preferably 28% to 30% are achieved. These rolled electrodes can particularly advantageously be combined with negative counter-electrodes such as Li and H₂ and used in primary and secondary systems.

A preferred active material for the electrode production in accordance with the invention comprises MnO₂, FeS₂, CuO, α -Cu₂V₂O₇, or Li_xMnO_y, where $1.5 < x < 2$ and $2.5 < y < 3$. However, oxides of manganese, iron, copper and vanadium, as well as sulphites of molybdenum, titanium and vanadium, are generally possible.

Moreover, all the positive active materials which are used in conventional alkaline accumulators, namely Ni(OH)₂, Fe(OH)₂, Co(OH)₂ or Zn(OH)₂, can be processed in accordance with the novel rolling process to give electrodes. The nickel/hydrogen storage cell also provides an advantageous possibility of applying this technique.

In addition to the active material, the dry powder mixture also contains conventional small quantities of PTFE as a binder and, in some cases, a small amount of carbon black.

Some examples are given below for lithium winding cells (size AA) which were equipped with positive rolled electrodes according to the invention and then subjected to a discharge test. In all cases, a solution of LiClO₄ in a propylene carbonate/dimethoxyethane mixture served as the electrolyte.

Example 1:

The cathode strip was produced by rolling a dry powder mixture comprising MnO_2 and 10% PTFE and carbon black onto a netlike current collector on both sides.

It had a strip thickness of 0.40 mm. Its porosity was 33% and its BET surface $20 \text{ m}^2/\text{g}$. With a pulsed discharge, with a 3-second discharge time at 1.3 A and a 7-second interpulse time, the lithium cell produced therewith reached a specific capacity of 197 mAh/g of cathode mass. With a lithium cell whereof the cathode was produced by coating its collector strip on one side (conventional rolling technique!) and which, at 0.45mm, had a similar thickness, a specific capacity of only 180 mAh/g of cathode mass was determined.

Example 2:

A similar cathode strip to that of Example 1 was rolled down to a thickness of 0.30 mm, using rollers of smaller diameter and a narrower nip. The expansion which is associated with this means that the geometric electrode surface is enlarged by 20%.

A lithium winding cell built using this cathode could still be discharged without problems at 1.5 A in pulsed operation, the specific capacity being 5% higher than with the electrode which was 0.40 mm thick.

This finding shows that as a consequence of reducing the thickness of rolled electrodes coated on both sides in accordance with the invention, the loading capacity of the cell grows, in particular because of the relatively large cathode surface with the same amount of active mass. The porosity and the BET surface - measured at 31% and $19 \text{ m}^2/\text{g}$ respectively: compare the numerical values in Example 1 with these - are on the other hand barely altered by the reduction in thickness.

Example 3:

As further tests showed, the novel rolling process can be advantageously transferred not only to the production of cathodes in winding cells of the Li/MnO₂ primary system but equally to the cathodes of the primary systems LiFeS₂ or Li/CuO, and furthermore those of the secondary systems Li/Cu₂V₂O₇ or Li/Li_xMnO_y. In these cases, winding cells having corresponding cathode strips rolled in accordance with the invention were only tested with a continuous discharge current of 1.3 A/cell (current density = 1 mA/cm²).

Purely for clarity, the specific current yields achieved, as in Example 1 expressed by the capacity values per 1 g of cathode mass, and the thicknesses d of the electrodes are given below.

FeS₂: 295 mAh/g; d = 0.30 mm

CuO: 278 mAh/g; d = 0.37 mm

The BET surface of the FeS₂ electrode corresponded, at 20 m²/g, to that of the MnO₂ electrode of Example 1 which was 0.40 mm thick, and the porosity was 24.2%.

A reduction in thickness ($d < 0.30$ mm) is necessary in producing cathode strips of α - Cu₂V₂O₇ or Li_xMnO_y for secondary systems. Only thus is it possible to obtain a higher specific capacity value of between 230 and 200 mAh/g of active mass and a higher loading capacity of the cell. Using the Li/Li_xMnO_y secondary cell, approximately 100 cycles were achieved, although the life expectancy of the cycles of such a cell is not exhausted by this, since in this test it was the lithium electrode which provided a limit to the capacity in the subsequent cycles.



Claims

1. Process for the production of a positive electrode in strip form for primary and secondary cells, in which a dry powder mixture comprising the electrochemically active material and a binder is applied by means of rollers to a metal netting or an expanded metal as the current collector, characterized in that two strips of mass are rolled out of the dry powder mixture at the same time, in that these strips of mass are supplied to the nip of a rolling mill from two sides, while a grid-shaped or net-shaped current collector passes into the rolling mill between them and is coated on both sides with the material of the strips of mass, filling the grid openings, and in that after excess material has been stripped off the finished electrode strip is rolled up for storage.
2. Process according to Claim 1, characterized in that the electrode strip is rolled to a final thickness of at most 2.0 mm, preferably 0.2 to 0.4 mm.
3. Process according to Claim 2, characterized in that the porosity of the electrode strip is at least 24%, preferably 28 - 30%.
4. Process according to one of Claims 1 to 3, characterized in that MnO_2 , FeS_2 or CuO are used as the electrochemically active material of the electrode.
5. Process according to one of Claims 1 to 3, characterized in that $\alpha - \text{Cu}_2\text{V}_2\text{O}_7$, or Li_xMnO_y having the parameters $1.5 < x < 2$ and $2.5 < y < 3$ is used for secondary systems as the electrochemically active material.
6. Process according to one of Claims 1 to 5, characterized in



that the final thickness of the electrode is controlled using measuring and metering devices which, before the strips of mass are rolled out, determine and regulate the requirement thereof for dry powder mixture.

7. Apparatus for carrying out the process for producing an electrode according to Claims 1 to 6, characterized in that it has two powder supplies comprising mass charging funnels and stirrers, having downstream rolling heads for simultaneously producing two strips of mass from a dry powder mixture, and devices for metering the dry powder, and in that it includes a rolling-on mill, into the roll nip whereof a grid-shaped current collector strip can be drawn in with the rolled strips of mass, one on each side, to form an electrode strip coated on either side, and in that devices for stripping off the collector net adhering excess mass are arranged downstream of the rolling-on mill.