

The present invention relates to a gas-tight sealed alkaline secondary cell with at least one positive electrode, a negative electrode, an intermediate separator and a lamellar auxiliary electrode connected in an electron-conducting manner with the negative electrode to reduce oxygen pressure.

The scope of the invention extends to cover all types of gas-tight alkaline cells operating in the oxygen consumption cycle, in particular Ni/Cd, Ni/Zn and Ni/hydride storage cells.

As is known, the accumulation of oxygen arising when these cells are overcharged may effectively be prevented if the area of the negative electrode is virtually enlarged by short-circuiting it with an auxiliary electrode on which the oxygen consumption reaction below



is kinetically less inhibited than on the main negative electrode. The auxiliary negative electrode thus contains at least catalysts such as metallic platinum, silver, copper or also carbon and additionally preferably has a large internal surface area due to high porosity.

The quantity of electrolyte also has a critical influence upon oxygen consumption since, on the one hand, an electrolyte deficit should be used for reasons of overcharging safety, while, on the other hand, high current loads on the cell demand large quantities of electrolyte. In any case, the quantity of electrolyte should be such that the triphase equilibrium absolutely necessary for oxygen conversion can be established on the active electrode surface.

Unlike in gas-tight Ni/Cd cells, complete sequestration of gaseous oxygen is important in Ni/hydride cells not least because the storage alloy corrodes in its presence.

Due to the customarily confined electrode accommodation in storage cells with high energy and power density, the auxiliary

electrodes in these cells are, like the electrode plates, thin lamellar structures and often lie closely adjacent to the negative plates in the plate stack.

DE-AS 15 96 223 even describes a Ni/Cd storage cell in the form of a wound cell with an auxiliary electrode, in which cell the auxiliary electrode covers the final spiral of the negative electrode and is simultaneously in close contact with the internal wall of the case, which constitutes the negative pole of the cell. This outer layer on the negative contains finely divided silver or another metal of a highly electropositive nature such as cadmium on a porous, hydrophobic support, so that when in contact with the negative it forms a negative mixed electrode on which the rate of oxygen reduction is increased.

In a metal oxide/lanthanum nickel hydride storage cell known from German patent DE 28 38 857, the oxygen reduction electrode consists of a nickel mesh coated with carbon black, which mesh is short-circuited with the negative electrode via a wire and is shielded from the positive electrode by a separator, which has lower electrolyte affinity than the two main electrodes, so that it only slightly inhibits the flow of oxygen. The hydride electrodes, on the other hand, are as far as possible protected from oxygen diffusing towards them by being isolated with a second separator material which is only slightly gas permeable when moist.

The object of the invention is more effectively and long-lastingly to promote oxygen conversion in a gas-tight alkaline secondary cell operating with an auxiliary electrode than previously, while simultaneously as far as possible suppressing the NO_2/NH_3 self-discharge shuttle which is also catalysed by the auxiliary electrode.

The object is achieved according to the invention with a secondary cell as described in patent claim 1.

According to the invention, it has proved very favourable to provide such a cell with an auxiliary electrode having a three-layer structure in which, thanks to special properties, each layer in its own way plays a part in fulfilling the requirements for rapid oxygen consumption.

Thus, thanks to high porosity and hydrophobic behaviour, the electrically non-conductive first layer, forms a gas transmission layer through which oxygen gains ready access to the reaction zone, while electrolyte liquid is prevented from penetrating.

The presence of water which is, however, necessary for oxygen reduction, is ensured by a second layer being hydrophilic and, with the assistance of a moisture reservoir, constantly wetting the catalyst layer, the actual consumption layer, which is the adjoining third layer.

Since the catalyst layer is on the other hand rendered hydrophobic by the addition of a plastic binder to the catalyst, there is a zone between the second and third layers of the auxiliary electrode according to the invention which is simultaneously hydrophobic and hydrophilic, so creating ideal conditions for a triphase equilibrium.

The third layer is at least in electronic contact, moreover as a rule in close physical contact, with the main negative electrode of the cell.

The material on which the first two layers of the novel auxiliary electrode are based is a single-layer, highly porous synthetic fibre non-woven fabric with a pore volume of 90 to 99%. Its hydrophobic properties ensure the passage of the oxygen flowing from the gas space, even over long-term operation.

By coating one side of the non-woven fabric with a Tylose mixture containing water (Tylose = collective term for a large range of water-soluble cellulose ethers, in particular methyl cellulose

and carboxymethyl cellulose), a hydrophilic layer (second layer) is produced in the non-woven fabric, which retains its original hydrophobicity on the other side (first layer), by the Tylose penetrating the non-woven fabric to a certain depth and, due to its hydrophilic nature, always binding to itself a quantity of electrolyte which is sufficient permanently to wet the adjoining catalyst or consumption layer. In this manner, desiccation and thus a reduction in the effectiveness of the auxiliary electrode is avoided.

The material of the catalytically active third layer is composed on 50 to 80 wt.% activated carbon, 3 to 20 wt.% carbon black, optionally graphite, as the conductive substance, and 10 to 30 wt.% PTFE. This material is present in the form of a rolled mixture of the stated components. A particularly favourable mixture is composed of approximately 75 wt.% activated carbon, approximately 7.5 wt.% conductive carbon black and approximately 17.5 wt.% PTFE.

The combination of activated carbon and water-repellent PTFE ensures that there are present in the transitional zone with the hydrophilic second layer containing Tylose many triphase interfaces with large internal surface areas, which are important for O_2 conversion. The added conductive carbon black ensures the ready transfer of electrons to the consumption domains contained in this zone. The electrons originate here from the negative electrode of the gas-tight storage cell, to which the consumption layer is directly, preferably areally, connected.

The subject matter of the invention is clarified by means of several figures.

Figure 1 is a schematic diagram of the layer structure of the novel auxiliary electrode.

Figure 2 shows the manner of production of the auxiliary electrode according to the invention.

Figures 3 and 4 show possible arrangements of the novel auxiliary electrode in wound cells.

Figures 5 to 7 show possible arrangements of the novel auxiliary electrodes in prismatic cells.

According to figure 1, the first layer 1a of the three-layer electrode 1 comprises the side of the synthetic fibre non-woven fabric 2 left in its original state, while the second layer 1b is the result of impregnating the other side of the non-woven fabric with an aqueous Tylose mixture 3. Layer 1b of the non-woven fabric is consequently hydrophilic. The third layer 1c is a rolled sheet 4 made from the activated carbon mixture stated above. This layer may additionally contain a metallic mesh insert, for example made of nickel, and make electrical contact with the main negative electrode via this reinforcement.

The mechanism of oxygen degradation on the auxiliary electrode is also indicated: O_2 from the gas or electrolyte space readily penetrates the highly porous layer 1a which is largely free of electrolyte and reacts with H_2O in the hydrophobic layer 1c in accordance with the above-stated reaction equation, which water is kept permanently available in the immediate vicinity by layer 1b which is hydrophilic or has an affinity for the electrolyte. Hydroxyl ions are produced as the reaction product by acquisition of electrons from the negative electrode.

In accordance with figure 2, production of an auxiliary electrode according to the invention is very simple: in separate operations, a powder mixture of the above-stated components of the catalyst layer is rolled into a sheet 4 and a 1 to 2% aqueous Tylose mixture 3 is applied to a synthetic non-woven fabric 2. The non-woven fabric and the sheet are thereupon introduced into a calender 5, preferably as a continuous ribbon, and are gently compressed and bonded together by the still moist Tylose coating, which acts as a welcome adhesive. The joined laminated material then passes through a drying section 6.

Figures 3 to 7 illustrate several possibilities for the positioning of auxiliary electrodes 1 according to the invention, both in gas-tight round cells and in prismatic cells.

Thus, in a round cell with wound electrodes, the auxiliary electrode may either according to figure 3 lie against the outer end of the spiral winding formed by the negative, or according to figure 4 it may be arranged in the form of a disk, optionally as a stack of two or more disks opposite one end face of the winding, for example close the base of the cell. The auxiliary electrode may particularly advantageously be combined there with a multi-contact plate which has proved effective as a current collector for the negative in wound cells with sintered sheet electrodes.

In detail, the figures show in each case the auxiliary electrode 1, the negative electrode 7, the positive electrode 8, the separator 9, the electrical contact 10 of the negative electrode (multi-contact plate) and the cell can 11. The O_2 arrows indicate the preferred orientation of the auxiliary electrode, namely with the first layer 1a which is exposed to gaseous oxygen outwards.

A particularly advantageous arrangement of the auxiliary electrode according to the invention (not shown) may be achieved in wound cells by providing a separator between the positive electrode and the negative electrode, the latter being the outer spiral of the winding, which separator is extended beyond the end of the negative electrode as a continuation of the winding such that it encircles the electrode winding once more, and applying an aqueous Tylose paste to one side of this extended end of the separator and pressing a pre-rolled catalyst mixture onto the side moistened with Tylose.

The side of the separator extension to be treated with Tylose is preferably the side facing away from the can wall such that, in the completely assembled roll inserted in the can, the free end of the separator lies with its dry side against the can wall and

with its catalyst side against the negative electrode. This also corresponds to the section according to figure 3.

By means of this measure according to the invention, the non-woven fabric separator is additionally used as a base material for the auxiliary electrode, namely as a former for the hydrophobic layer 1a and for the hydrophilic layer 1b (c.f. figure 1), to which only the catalyst layer 1c is then to be added. It is here immaterial for the functioning of the auxiliary electrode whether it is the consumption layer 1c or the gas transmission layer 1a which is adjacent to the negative electrode. What is, however, important is that the auxiliary electrode is arranged outside the area of influence of the self discharge shuttle. Since the shuttle proceeds between a positive and a negative electrode, it is absolutely essential that the auxiliary electrode, if it is not to promote this phenomenon, is arranged outside the ion path between counterpolar electrodes. This condition may at least be fulfilled, as is shown by most of the examples listed here (figures 3 and 5 to 7), by the auxiliary electrode being positioned between two negative electrodes or by the auxiliary electrode being at least screened from a positive electrode by a negative electrode.

Laminated auxiliary electrodes may also be arranged in many different ways in gas-tight prismatic cells. Thus, in figure 5, the auxiliary electrode 1 is applied to the end negative plate of the plate block consisting of negative electrodes 7, positive electrodes 8 and separators 9, a large area of the auxiliary electrode lying with its consumption layer 1c or catalyst sheet 4 against the negative.

In figure 6, a sandwich structure of the auxiliary electrode according to the invention is provided such that the synthetic fibre non-woven fabric 2 is impregnated with Tylose on both sides, a central zone remaining unchanged and acting as a hydrophobic gas transmission layer, and that the consumption layers 1c are adjacent to the impregnated layers 1b on both

sides. The electrode stack is arranged in this case such that there is always a sandwich-type auxiliary electrode located between two negative electrodes.

Figure 7 is an enlargement of the circled section of figure 6.

Claims

1. Gas-tight sealed alkaline secondary cell with at least one positive electrode, a negative electrode, an intermediate separator and a lamellar auxiliary electrode connected in an electron-conducting manner with the negative electrode to reduce oxygen pressure, characterised in that the auxiliary electrode (1) is a three-layer electrode made from a hydrophobic and electrically non-conductive first layer (1a) which promotes oxygen access, a hydrophilic second layer (1b) and a hydrophobic third layer (1c) which is in electronic contact with the main negative electrode and which maintains catalytic oxygen reduction.
2. Secondary cell according to claim 1, characterised in that the first and the second layer are based on a single-layer synthetic fibre non-woven fabric (2), onto one side of which is applied a cellulose ether mixture (3) containing water, and that the third layer consists of an activated carbon mixture (4) rolled into a sheet, which is laminated to the side of the synthetic fibre non-woven fabric treated with the cellulose ether.
3. Secondary cell according to claim 2, characterised in that the rolling mixture containing activated carbon is composed of 50 wt.% to 80 wt.% activated carbon, 3 wt.% to 20 wt.% conductive carbon black and 10 wt.% to 30 wt.% PTFE.
4. Secondary cell according to claim 3, characterised in that the rolling mixture containing activated carbon is composed of approximately 75 wt.% activated carbon, approximately 7.5 wt.% conductive carbon black and approximately 17.5 wt.% PTFE.
5. Secondary cell according to one of claims 1 to 4, characterised in that the auxiliary electrode is arranged outside the ion path between counterpolar electrodes.



6. Secondary cell according to claim 5, characterised in that the auxiliary electrode is at least screened from a positive electrode by negative electrodes.
7. Secondary cell according to claim 5, characterised in that in an electrode winding the auxiliary electrode is formed by an elongation of the separator extending beyond the end of the negative electrode as a continuation of the winding, one side of which separator is coated with cellulose ether and is provided with a catalytically active layer, and that the separator elongation which encloses the electrode winding having the negative electrode in the form of the outer spiral lies against the inner wall of the cell can.
8. Secondary cell according to claim 7, characterised in that the side of the separator elongation coated with cellulose ether and provided with a catalyst layer is the side facing away from the can wall.
9. Secondary cell according to claim 5, characterised in that in an electrode winding the auxiliary electrode is arranged in the form of one or more disks opposite one end face of the winding.
10. Secondary cell according to claim 9, characterised in that the auxiliary electrode is incorporated in an multi-contact plate (10) as a current collector for the negative electrode.

