

The invention relates to a galvanic cell having: a nickel-plated steel cup serving as a current collector; pressed into this steel cup a cathode substantially comprising manganese dioxide and a conductor means; a zinc anode; a separator; and an aqueous alkaline electrolyte.

It is in accordance with general experience that alkaline manganese dioxide/zinc cells of the genus described above have substantially worse discharge data after storage at temperatures going well beyond room temperature than they do in the freshly manufactured state. In particular, losses in capacitance occur.

The cause of this phenomenon has proved to be the construction of a transition resistance or phase boundary resistance between the MnO_2 electrode pressed into an annular shape and the nickel coating of the steel cup. As has emerged from appropriately designed tests, a plurality of influences of differing importance may contribute to the occurrence of this phase boundary layer. Excluded from this is clearly the choice of electrolyte used, since between cells having pure KOH, NaOH or LiOH electrolyte no specific differences in their electrical behaviour are manifested.

In contrast, manganese has a decidedly negative effect as regards the phase boundary resistance. This can be concluded from the increase in the resistance of nickel plates when the latter are dipped in an alkaline MnSO_4 solution and briefly polarized therein to be positive. Here, thin layers of what is assumed to be the composition $\text{Mn}(\text{OH})_x$, where $x > 2$, are formed on the nickel surface. These are also produced in pure MnSO_4 solutions reacting weakly acidically as a result of hydrolysis, and in this case they result in an even greater rise in the resistance.

With respect to the capacity for storage at high temperatures of the manganese dioxide, it was found that polarization in the direction of charge at a current quantity amounting to approximately 2% of the total manganese dioxide capacitance does not additionally impair the capacitance loss in accordance with experience, but a corresponding polarization in the direction of discharge (pre-discharge), in which the phase

boundary resistance is significantly increased, probably does have this effect.

Further factors influencing the phase boundary resistance were recognized to be, inter alia, the dissolving out of metal impurities from the manganese dioxide, resulting in an increase in resistance, or the compression pressure during fabrication of the electrode. High compression pressures are clearly unfavourable, since the electrode bodies thus produced are relatively brittle and then become mechanically soft all the faster during the inevitable swelling.

A known measure which is intended to serve to reduce the phase boundary resistance is applied not to the electrode material but to the collector, and provides for the latter to be above all chemically inert. Thus, DE-PS 1 421 582 proposes that the positively polarized steel cup of galvanic primary cells be provided on the inside with a plating which is preferably of gold. The disadvantages of this measure are the high price of gold and the working steps and costs associated with its galvanic application.

The object of the invention is to specify an alkali manganese cell which has a housing cup of steel conventionally nickel-plated and which has a substantially improved capacity for storage at high temperature by comparison with empirical values.

In accordance with the invention, the object is achieved by the means specified in the characterizing part of Claim 1.

In accordance with this, it was not only possible to confirm that an undesirable transition resistance between cathode and cup is fundamentally responsible for capacitance losses which are perceptible in a particularly damaging way after storage of the cells at high temperature, but it could also be confirmed that this transition resistance is connected in particular to the formation of a high-resistance nickel oxide layer on the nickel coating of the cup collector. In particular, it was found that certain additives to the manganese dioxide electrode or to the electrolyte, these being compounds which form strong complex salts with nickel in a strongly alkaline medium, clearly prevent the formation of the oxidic cover layer, since the phase boundary

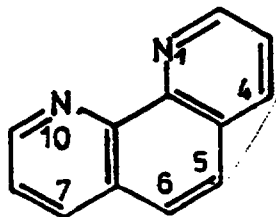
resistance is reduced in their presence. Here, those complex formers have been found to be particularly effective which were selected from the group comprising mono- or multi-nuclear N-heterocycles having either a 1,3-diazole structure, an o-phenanthroline structure or a structure having at least one carboxyl group in the ortho position with respect to an N-atom, or from the group comprising 1,2-dioximes, or from the group comprising o-dihydroxybenzene-sulphonic acids and the salts thereof.

Additives according to the invention with an Ni-complexing effect are from the N-heterocyclic compounds first mentioned:

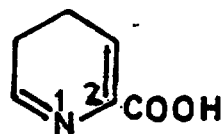
Imidazole



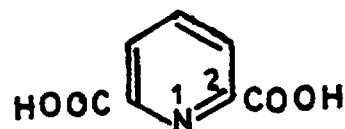
1,10 phenanthroline



2-picolinic acid
(pyridine-carboxylic acid-(2))

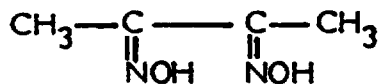


Pyridine-2,6-dicarboxylic acid



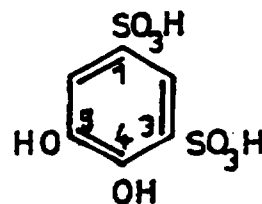
An additive according to the invention from the group comprising 1,2-dioximes is:

Dimethyl glyoxime



and from the last-mentioned group is:

o-dihydroxybenzene-1,3-disulphonic acid
(Tiron)



The surprising action of the additives according to the invention were tested by experiment in a special resistance-measuring apparatus. To this end, manganese dioxide electrode tablets having a content of 0.2% by weight in each case of one of the said complex formers were pressed onto nickel plates at a pressure of 75 kp/cm², impregnated with 40% strength KOH and stored at 90°C. The measurement apparatus was encapsulated such that drying out or a reaction of CO₂ with the air was prevented. For the measurement, a current was applied across the contact surface of the manganese dioxide tablet towards the nickel plate and the voltage drop at the contact surface was recorded. The dimensions of the manganese dioxide tablets were 10 mm x 5 mm (diameter x height) and their basic composition was 88% by weight of MnO₂, 10% by weight of graphite to improve the electrical conductivity and 2% by weight of polyethylene as a binder.

Under the conditions of a measurement current of 500 mA, the test electrodes were in each case measured in three different states:

- a) directly after assembly of the measurement arrangement
- b) after 24 h storage time at 90°C
- c) after 96 h storage time at 90°C.

The relatively short storage time in combination with the relatively high storage temperature is sufficient to recognize the positive action of an additive and to compare it with another additive. The result of a 90°C storage for a month corresponds approximately to a storage time of 1 to 1.5 years at room temperature.

The figure shows by means of bar charts how the voltage drop at the transition from manganese dioxide tablet to nickel plate as a measure of the phase boundary resistance between cathode and cup owing to the various additives is reduced by comparison with

an additive-free manganese dioxide tablet. Here, the bars of each triplet correspond, in sequence, to the states a), b) and c) defined above. The additives to the tablet are designated as follows:

- 1 = standard (without additive)
- 2 = imidazole
- 3 = 2-picolinic acid
- 4 = dimethyl glyoxime
- 4 = 4,5-dihydroxybenzene-1,3-disulphonic acid
- 6 = 1,10 phenanthroline

As can easily be seen, the phase boundary resistance can be reduced by means of 2-picolinic acid by a factor of almost 3 by comparison with the standard sample.

It is assumed that the action of the additives consists in the fact that they release the poorly conductive nickel oxides at the surface of the cathode collector and thus allow good electronic contact with the nickel substrate.

In the manufacture of galvanic cells according to the invention, the addition of complex formers can be added to the conventional manufacturing process without problems. It is simplest for the active substances to be admixed in the dry form with the positive electrode active mass, which in addition to the active constituent MnO_2 also contains a conductor means (graphite, carbon black) and a binder, before the pressing. However, it is also possible to dissolve the substances, unless they are themselves liquid, in a little electrolyte and to impregnate the electrode with them.

The quantity of additive should, in accordance with the invention, be between 0.001 and 1% by weight with respect to the cathode active mass. An increase in the quantity of additive exceeding 1% by weight does not promote the favourable action of the substances.

Claims

1. Galvanic cell having: a nickel-plated steel cup serving as a current collector; pressed into this steel cup a cathode substantially comprising manganese dioxide and a conductor means; a zinc anode; a separator; and an aqueous alkaline electrolyte, characterized in that for lowering the transition resistance between the cathode and the cup there is added to the electrolyte or the cathode active mass a complex former which in a strongly alkaline medium reacts with nickel oxide coatings to form a strong complex salt.
2. Galvanic cell according to Claim 1, characterized in that the complex former is selected from the group comprising mono- or multi-nuclear aromatic N-heterocycles having either a 1,3-diazole structure, an o-phenanthroline structure or a structure having at least one carboxyl group in the ortho position with respect to an N-atom, or from the group comprising 1,2-dioximes, or from the group comprising o-dihydroxybenzene-sulphonic acids and the salts thereof.
3. Galvanic cell according to Claim 1, characterized in that the complex former is one of the N-heterocyclic compounds comprising imidazole, 1,10 phenanthroline, 2-picolinic acid (pyridine-carboxylic acid-(2)) and pyridine-2,6-dicarboxylic acid.
4. Galvanic cell according to Claim 2, characterized in that the complex former is dimethyl glyoxime.
5. Galvanic cell according to Claim 2, characterized in that the complex former is 4,5-dihydroxybenzene-1,3-disulphonic acid.
6. Galvanic cell according to Claims 1 to 5, characterized in that it contains the complex former in each case in a quantity of 0.001 to 1% by weight with respect to the cathode active mass.



7. Process for manufacturing a galvanic cell according to one of Claims 1 to 6, characterized in that the nickel-complexing compound of the cathode active mass is admixed in the dry state before it is pressed.

8. Process for manufacturing a galvanic cell according to one of Claims 1 to 6, characterized in that the cathode is impregnated with nickel-complexing compound in liquid form or dissolved in the cell electrolyte.



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