

**Description:**

The invention relates to alkaline primary cells comprising a zinc gel as the anode material, an aqueous alkaline electrolyte, a separator and a cathode material containing manganese dioxide.

The cathodes used in alkaline primary cells customarily comprise manganese dioxide, graphite and a binder.

Additionally, electrolyte, surfactants and further additives may be present.

The manganese dioxide is used, particularly in the form deposited electrochemically (EMD), as the active cathode material.

Synthetic graphite of high purity or alternatively expanded graphite, prepared from natural graphites, in the form of a powder having a typical particle size of, e.g. 10-50 μm in the case of synthetic graphites and particle size of 1-20 μm in the case of expanded graphites, are added to the cathode material as electroconductive material. Graphite has the function, when uniformly dispersed within the cathode compression-molded electrode as a conductive skeletal first-order matrix, of ensuring the electric charge transfer within the cathode. Customarily, the graphite content is from 7 to 10% by weight when synthetic graphites are used. If expanded graphites are used, it is possible, employing special blending techniques, to reduce the graphite content to about 5% by weight, an improvement in the discharge characteristics of the cathode being achieved at the same time.

In many cases, the cathode is composed of cathode rings inserted into the cell jar. The mechanical strength required of these cathode compacts is brought about by a binder. Modern fabrication plants for alkaline primary cells run at very high speed. Thus it is possible, for example, to achieve a production rate of 1000 cells of size LR6 per minute. These so-called "high-speed lines" pose certain minimum requirements with respect to the mechanical strength of the cathode rings which are



conveyed in feeder sections and holding plates.

A drawback of most binders is that they require a volume which is not available for active material. Furthermore, many binders are hydrophobic and impede electrolyte uptake of the cathode during the cell fabrication process. This has adverse effects on cell performance.

Typical binders are powdered plastics from the group of the polyethylenes (PE), polypropylenes (PP), polyethylene terephthalates (PET), polytetrafluoroethylene (PTFE), polyacrylates (PA), polybutadienes (PB) and block polymers or copolymers of the abovementioned compounds. The introduction of binders in the form of aqueous dispersions is also known (e.g. PTFE or PE dispersions), the added water likewise having some of the characteristics of a binder with respect to the cathode compact.

The cathode material further contains additions of alkaline electrolytes, preferably aqueous potassium hydroxide in concentrations of from 10 to 55%. Binary electrolytes such as KOH/NaOH or KOH/LiOH and ternary electrolytes such as KOH/NaOH/LiOH can be used.

Electrolyte is meant to fill the pores of the cathode to achieve ion conductivity in the cathode. A number of positive characteristics are thus achieved. Thus the use of binders can be entirely or partially dispensed with, since alkalis likewise have some of the characteristics of a binder with respect to the cathode compact. A suitable choice of the amount of electrolyte allows an optimum porosity of the cathode to be set, with the result that the diaphragm resistance of the cathode compact is minimized. A reduced diaphragm resistance in turn distinctly improves the performance of the complete cells. A cathode comprising, e.g., 6% by weight of a 50% strength KOH electrolyte improves the discharge characteristics of the cells fabricated therewith, compared with a cathode containing much less or no electrolyte. Moreover it is possible, by means of a high concentration of the electrolyte, to distinctly reduce post-storage



contact resistance from the cell jar to the cathode ring.

The fabrication of a cathode with a high electrolyte content in the cathode material does, however, have drawbacks with respect to the process, compared with a dry cathode mix. The fabrication of the cathode compact customarily makes use of so-called carousel-type compression mould. These carousel-type compression mould as a rule are made of special steel alloys which are subject to significantly increased wear as the electrolyte content in the cathode formulation increases.

The addition of surfactants to the cathode materials improves electrolyte uptake of the cathode. The surfactant is customarily added in very low concentrations of, for example, 1-100 ppm, based on the cathode weight, and can be added to the cathode mix both homogeneously and applied to the graphite component in a preliminary step, to reduce the hydrophobic properties of the graphite.

Customary surface-active substances can be liquid or solid and may be of the nonionic, anionic or cationic type. Thus, for example, aliphatic fluorine compounds, aromatic and aliphatic phosphonic acids or polyethylene glycols are suitable.

A drawback of such surfactants is occasionally observed, however, in that these, owing to their high molecular mobility, reach the zinc electrode as the counter electrode and there, with certain discharge modes (e.g. pulsed discharge), cause the voltage level to be lowered.

Further additives used include, inter alia, titanium compounds.

US Patent No. 5,342,712 proposes anatase TiO_2 as an additive to the cathode. The addition of from 0.1 to 2% by weight of the titanium dioxide modification anatase to the cathode material of alkali primary cells is claimed to enable an increase in the period of use by 15% with higher currents (3.9 ohm discharge).

What still remains desirable, however, is a dry-component cathode, i.e. without added electrolyte or with

less added electrolyte, which cathode nevertheless in the assembled cell has the advantages of a pasted cathode. Another objective is to extend the service life of carousel-type compression moulds for cathode fabrication, which results in cost savings in the production process.

It is an object of the present invention to provide a solution for the abovementioned problems.

The object is achieved according to the invention, in that the cathode material of alkaline primary cells contains 0.1-5% by weight of alkali metal titanates and/or alkaline earth metal titanates.

Preferably, the cathode material of the alkaline primary cells contains magnesium titanate (MgTiO_3) and/or calcium titanate (CaTiO_3) and/or lithium titanate (Li_2TiO_3).

The addition of magnesium titanate (MgTiO_3) and/or calcium titanate (CaTiO_3) and/or lithium titanate (Li_2TiO_3) to the cathode material improves the discharge behavior of the battery and reduces gassing in the cell.

The process according to the invention for fabricating alkaline primary cells comprises the addition of the alkali metal titanates and/or alkaline earth metal titanates in the form of a powder to the cathode material having an electrolyte content of from 4 to 5% by weight.

Preferably, the alkali metal titanates and/or alkaline earth metal titanates added to the cathode material have a particle size of from 0.1 μm to 200 μm and a BET surface area of 0.5-500 m^2/g .

The alkali metal titanates and/or alkaline earth metal titanates are preferably added to the cathode material in a purity of more than 95%.

The present invention is described with reference to the following examples.

Example

Cathode mixes comprising the components:

86.0% of EMD

9.0% of graphite

4.5% of electrolyte (50% strength KOH)

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are admixed with 0.2% by weight, 0.5% by weight or 2% by weight, respectively, of the following titanium compounds:

	MgTiO ₃	Magnesium titanate,
5	CaTiO ₃	Calcium titanate or
	Li ₂ TiO ₃	Lithium titanate.

For comparative purposes, a cell (reference cell) without added titanate and a cell containing 0.5% by weight of anatase TiO₂ in the cathode material are fabricated.

The mixes are granulated and then densified to produce annular compacts. These are pushed into the cell jar, after which the separator is inserted, either in the form of a honeycomb or in the form of a convolute separator. Then the gel-type zinc electrodes are metered in. The zinc anode comprises 68% by weight of a zinc powder having a particle size distribution of, typically, 50-500 μ m particle size and about 32% by weight of an alkaline electrolyte (e.g. a 40% strength KOH). This anode is additionally admixed with small amounts of a gassing inhibitor (e.g. In₂O₃ or In(OH)₃), a gelling agent (e.g. Carbopol 940), a surface-active substance (e.g. glycol, polyethylene glycol or a fluoro surfactant).

Table 1 shows the results of the experiments with various titanium compounds in terms of performance and gassing. This demonstrates that MgTiO₃, CaTiO₃ or Li₂TiO₃, as well as improving the continuous and intermittent discharge characteristics, also reduce gassing of the cell.

Figure 1 shows the comparison of an LR20 containing CaTiO₃ (1) with a reference cell (2) with continuous discharge across a 2 ohm resistor. At switch off voltages below 0.95 V significant run time advantages can be observed.

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Table 1

Type LR 6	Titanium compound	3.9 ohms cont. Ah → 0.75 V	Pulse cycles → 0.9 V 15 s/m, 7 d/w - 1.8 ohms	Flash cycles → 1 V 15 s/m, 1 h/d, 7 d/w - 2 ohms	Gassing without initial discharge (ml) 7d at 70°C	Gassing with initial discharge (ml) 7d at 70°C
Mignon	0.5% MgTiO ₃	1.81	604	505	0.3	0.3
	0.5% Li ₂ TiO ₃	1.80	555	495	0.3	0.3
	0.5% TiO ₂ anatase	1.78	519	393	0.4	0.4
	0.2% MgTiO ₃	1.84	578	485	0.3	0.3
	Reference	1.731	525	471	0.4	0.4

Type LR 20	Titanium compound	2 ohms cont. Ah → 0.9 V	Gassing without initial discharge (ml) 7d at 70°C	Gassing with initial discharge (ml) 7d at 70°C
Mono	0.5% CaTiO ₃	9.2	3.3	5.5
	0.5% Li ₂ TiO ₃	9.4	3.7	6.3
	0.5% TiO ₂ anatase	8.8	3.8	6.3
	2% MgTiO ₃	9.1	3.9	5.8
	2% CaTiO ₃	9.1	2.9	6
	Reference	8.6	3.9	7.7

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Claims

1. Alkaline primary cell comprising a zinc gel as the anode material, an aqueous alkaline electrolyte, a separator and a cathode material containing manganese dioxide, wherein the cathode material contains 0.1-5% by weight of alkali metal titanates and/or alkaline earth metal titanates.
2. The alkaline primary cell as claimed in claim 1, wherein the cathode material contains magnesium titanate (MgTiO_3) and/or calcium titanate (CaTiO_3) and/or lithium titanate (Li_2TiO_3).
3. A process for fabricating an alkaline primary cell as claimed in either claim 1 or 2, wherein the alkali metal titanates and/or alkaline earth metal titanates are added in the form of a powder to the cathode material having an electrolyte content of from 4 to 5% by weight.
4. The process as claimed in claim 3, wherein the alkali metal titanates and/or alkaline earth metal titanates added to the cathode material have a particle size of from $0.1 \mu\text{m}$ to $200 \mu\text{m}$ and a BET surface area of $0.5\text{-}500 \text{ m}^2/\text{g}$.
5. The process as claimed in claim 3 or 4, wherein the alkali metal titanates and/or alkaline earth metal titanates are added in a purity of more than 95%.



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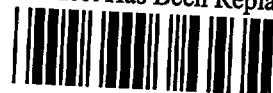


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Abstract

The invention relates to alkaline primary cells comprising a zinc gel as the anode material, an aqueous alkaline electrolyte, a separator and a cathode material containing manganese dioxide, wherein the cathode material contains 0.1-5% by weight of alkali metal titanates and/or alkaline earth metal titanates.

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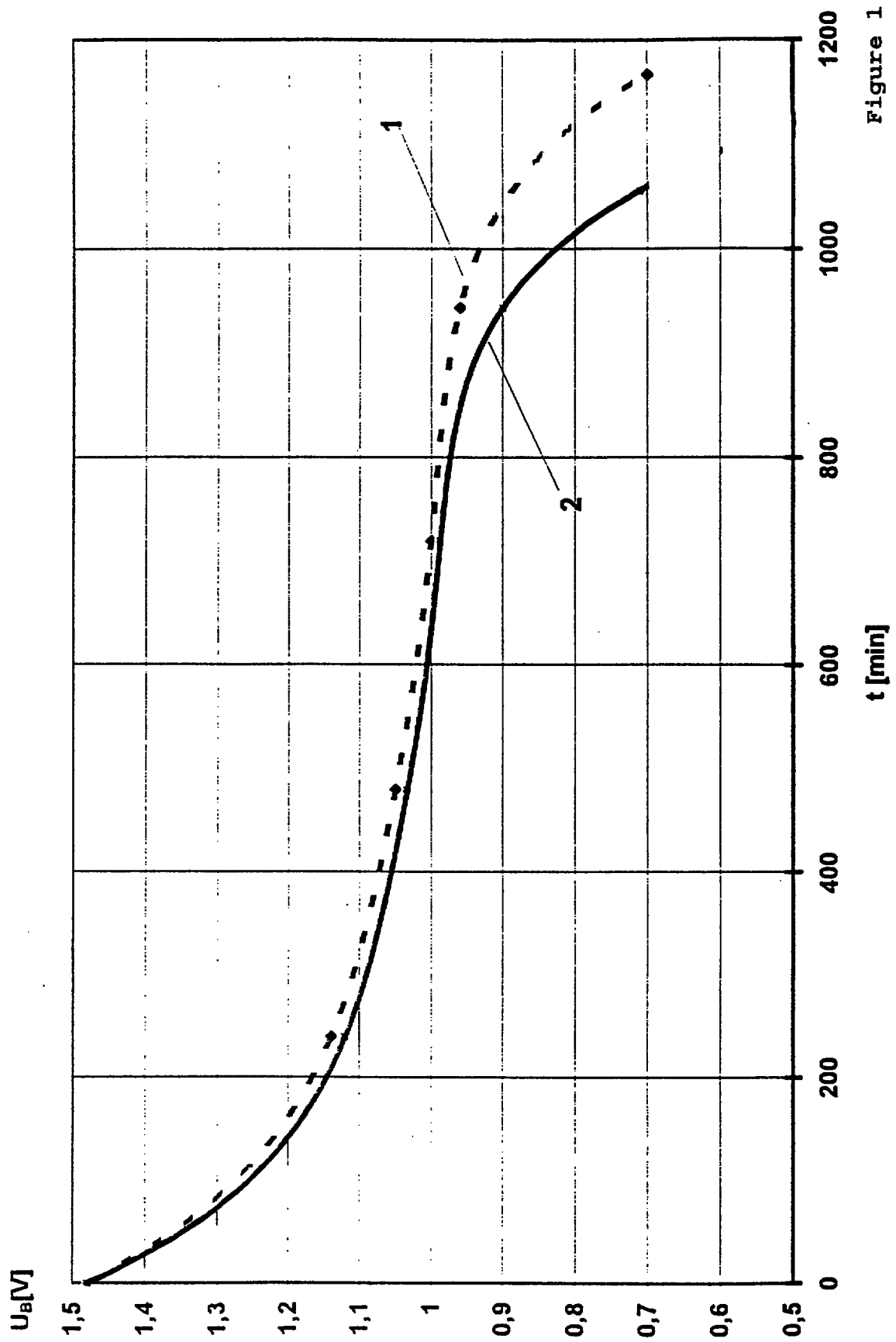


Figure 1

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CATHODE ADDITIVE FOR ALKALINE PRIMARY CELLS

Description:

The invention relates to alkaline primary cells comprising a zinc gel as the anode material, an aqueous alkaline electrolyte, a separator and a cathode material containing manganese dioxide.

The cathodes used in alkaline primary cells customarily comprise manganese dioxide, graphite and a binder.

Additionally, electrolyte, surfactants and further additives may be present.

The manganese dioxide is used, particularly in the form deposited electrochemically (EMD), as the active cathode material.

Synthetic graphite of high purity or alternatively expanded graphite, prepared from natural graphites, in the form of a powder having a typical particle size of, e.g. 10-50 μm in the case of synthetic graphites and particle size of 1-20 μm in the case of expanded graphites, are added to the cathode material as electroconductive material. Graphite has the function, when uniformly dispersed within the cathode compression-molded electrode as a conductive skeletal first-order matrix, of ensuring the electric charge transfer within the cathode. Customarily, the graphite content is from 7 to 10% by weight when synthetic graphites are used. If expanded graphites are used, it is possible, employing special blending techniques, to reduce the graphite content to about 5% by weight, an improvement in the discharge characteristics of the cathode being achieved at the same time.

In many cases, the cathode is composed of cathode rings inserted into the cell jar. The mechanical strength required of these cathode compacts is brought about by a binder. Modern fabrication plants for alkaline primary cells run at very high speed. Thus it is possible, for example, to achieve a production rate of 1000 cells of size LR6 per minute. These so-called "high-speed lines" pose certain minimum requirements with respect to the mechanical strength of the cathode rings which are

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conveyed in feeder sections and holding plates.

A drawback of most binders is that they require a volume which is not available for active material. Furthermore, many binders are hydrophobic and impede electrolyte uptake of the cathode during the cell fabrication process. This has adverse effects on cell performance.

Typical binders are powdered plastics from the group of the polyethylenes (PE), polypropylenes (PP), polyethylene terephthalates (PET), polytetrafluoroethylene (PTFE), polyacrylates (PA), polybutadienes (PB) and block polymers or copolymers of the abovementioned compounds. The introduction of binders in the form of aqueous dispersions is also known (e.g. PTFE or PE dispersions), the added water likewise having some of the characteristics of a binder with respect to the cathode compact.

The cathode material further contains additions of alkaline electrolytes, preferably aqueous potassium hydroxide in concentrations of from 10 to 55%. Binary electrolytes such as KOH/NaOH or KOH/LiOH and ternary electrolytes such as KOH/NaOH/LiOH can be used.

Electrolyte is meant to fill the pores of the cathode to achieve ion conductivity in the cathode. A number of positive characteristics are thus achieved. Thus the use of binders can be entirely or partially dispensed with, since alkalis likewise have some of the characteristics of a binder with respect to the cathode compact. A suitable choice of the amount of electrolyte allows an optimum porosity of the cathode to be set, with the result that the diaphragm resistance of the cathode compact is minimized. A reduced diaphragm resistance in turn distinctly improves the performance of the complete cells. A cathode comprising, e.g., 6% by weight of a 50% strength KOH electrolyte improves the discharge characteristics of the cells fabricated therewith, compared with a cathode containing much less or no electrolyte. Moreover it is possible, by means of a high concentration of the electrolyte, to distinctly reduce post-storage

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contact resistance from the cell jar to the cathode ring.

The fabrication of a cathode with a high electrolyte content in the cathode material does, however, have drawbacks with respect to the process, compared with a dry cathode mix. The fabrication of the cathode compact customarily makes use of so-called carousel-type compression mould. These carousel-type compression mould as a rule are made of special steel alloys which are subject to significantly increased wear as the electrolyte content in the cathode formulation increases.

The addition of surfactants to the cathode materials improves electrolyte uptake of the cathode. The surfactant is customarily added in very low concentrations of, for example, 1-100 ppm, based on the cathode weight, and can be added to the cathode mix both homogeneously and applied to the graphite component in a preliminary step, to reduce the hydrophobic properties of the graphite.

Customary surface-active substances can be liquid or solid and may be of the nonionic, anionic or cationic type. Thus, for example, aliphatic fluorine compounds, aromatic and aliphatic phosphonic acids or polyethylene glycols are suitable.

A drawback of such surfactants is occasionally observed, however, in that these, owing to their high molecular mobility, reach the zinc electrode as the counter electrode and there, with certain discharge modes (e.g. pulsed discharge), cause the voltage level to be lowered.

Further additives used include, inter alia, titanium compounds.

US Patent No. 5,342,712 proposes anatase TiO_2 as an additive to the cathode. The addition of from 0.1 to 2% by weight of the titanium dioxide modification anatase to the cathode material of alkali primary cells is claimed to enable an increase in the period of use by 15% with higher currents (3.9 ohm discharge).

What still remains desirable, however, is a dry-component cathode, i.e. without added electrolyte or with

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less added electrolyte, which cathode nevertheless in the assembled cell has the advantages of a pasted cathode. Another objective is to extend the service life of carousel-type compression moulds for cathode fabrication, which results in cost savings in the production process.

It is an object of the present invention to provide a solution for the abovementioned problems.

The object is achieved according to the invention, in that the cathode material of alkaline primary cells contains 0.1-5% by weight of alkali metal titanates and/or alkaline earth metal titanates.

Preferably, the cathode material of the alkaline primary cells contains magnesium titanate (MgTiO_3) and/or calcium titanate (CaTiO_3) and/or lithium titanate (Li_2TiO_3).

The addition of magnesium titanate (MgTiO_3) and/or calcium titanate (CaTiO_3) and/or lithium titanate (Li_2TiO_3) to the cathode material improves the discharge behavior of the battery and reduces gassing in the cell.

The process according to the invention for fabricating alkaline primary cells comprises the addition of the alkali metal titanates and/or alkaline earth metal titanates in the form of a powder to the cathode material having an electrolyte content of from 4 to 5% by weight.

Preferably, the alkali metal titanates and/or alkaline earth metal titanates added to the cathode material have a particle size of from 0.1 μm to 200 μm and a BET surface area of 0.5-500 m^2/g .

The alkali metal titanates and/or alkaline earth metal titanates are preferably added to the cathode material in a purity of more than 95%.

The present invention is described with reference to the following examples.

Example

Cathode mixes comprising the components:

86.0% of EMD

9.0% of graphite

4.5% of electrolyte (50% strength KOH) _

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are admixed with 0.2% by weight, 0.5% by weight or 2% by weight, respectively, of the following titanium compounds:

	MgTiO_3	Magnesium titanate,
5	CaTiO_3	Calcium titanate or
	Li_2TiO_3	Lithium titanate.

For comparative purposes, a cell (reference cell) without added titanate and a cell containing 0.5% by weight of anatase TiO_2 in the cathode material are fabricated.

The mixes are granulated and then densified to produce annular compacts. These are pushed into the cell jar, after which the separator is inserted, either in the form of a honeycomb or in the form of a convolute separator. Then the gel-type zinc electrodes are metered in. The zinc anode comprises 68% by weight of a zinc powder having a particle size distribution of, typically, 50-500 μm particle size and about 32% by weight of an alkaline electrolyte (e.g. a 40% strength KOH). This anode is additionally admixed with small amounts of a gassing inhibitor (e.g. In_2O_3 or $\text{In}(\text{OH})_3$), a gelling agent (e.g. Carbopol 940), a surface-active substance (e.g. glycol, polyethylene glycol or a fluoro surfactant).

Table 1 shows the results of the experiments with various titanium compounds in terms of performance and gassing. This demonstrates that MgTiO_3 , CaTiO_3 or Li_2TiO_3 , as well as improving the continuous and intermittent discharge characteristics, also reduce gassing of the cell.

Figure 1 shows the comparison of an LR20 containing CaTiO_3 (1) with a reference cell (2) with continuous discharge across a 2 ohm resistor. At switch off voltages below 0.95 V significant run time advantages can be observed.

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Table 1

Type LR 6	Titanium compound	3.9 ohms cont. Ah → 0.75 V	Pulse cycles → 0.9 V 15 s/m, 7 d/w - 1.8 ohms	Flash cycles → 1 V 15 s/m, 1 h/d, 7 d/w - 2 ohms	Gassing without initial discharge (ml) 7d at 70°C	Gassing with initial discharge (ml) 7d at 70°C
Mignon	0.5% MgTiO ₃	1.81	604	505	0.3	0.3
	0.5% Li ₂ TiO ₃	1.80	555	495	0.3	0.3
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	0.2% MgTiO ₃	1.84	578	485	0.3	0.3
	Reference	1.731	525	471	0.4	0.4

Type LR 20	Titanium compound	2 ohms cont. Ah → 0.9 V	Gassing without initial discharge (ml) 7d at 70°C	Gassing with initial discharge (ml) 7d at 70°C
Mono	0.5% CaTiO ₃	9.2	3.3	5.5
	0.5% Li ₂ TiO ₃	9.4	3.7	6.3
	0.5% TiO ₂ anatase	8.8	3.8	6.3
	2% MgTiO ₃	9.1	3.9	5.8
	2% CaTiO ₃	9.1	2.9	6
	Reference	8.6	3.9	7.7

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Claims

1. Alkaline primary cell comprising a zinc gel as the anode material, an aqueous alkaline electrolyte, a separator and a cathode material containing manganese dioxide, wherein the cathode material contains 0.1-5% by weight of alkali metal titanates and/or alkaline earth metal titanates.
2. The alkaline primary cell as claimed in claim 1, wherein the cathode material contains magnesium titanate (MgTiO_3) and/or calcium titanate (CaTiO_3) and/or lithium titanate (Li_2TiO_3).
3. A process for fabricating an alkaline primary cell as claimed in either claim 1 or 2, wherein the alkali metal titanates and/or alkaline earth metal titanates are added in the form of a powder to the cathode material having an electrolyte content of from 4 to 5% by weight.
4. The process as claimed in claim 3, wherein the alkali metal titanates and/or alkaline earth metal titanates added to the cathode material have a particle size of from $0.1 \mu\text{m}$ to $200 \mu\text{m}$ and a BET surface area of $0.5\text{-}500 \text{ m}^2/\text{g}$.
5. The process as claimed in claim 3 or 4, wherein the alkali metal titanates and/or alkaline earth metal titanates are added in a purity of more than 95%.



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-8-CATHODE ADDITIVE FOR ALKALINE PRIMARY CELLS**Abstract**

The invention relates to alkaline primary cells comprising a zinc gel as the anode material, an aqueous alkaline electrolyte, a separator and a cathode material containing manganese dioxide, wherein the cathode material contains 0.1-5% by weight of alkali metal titanates and/or alkaline earth metal titanates.

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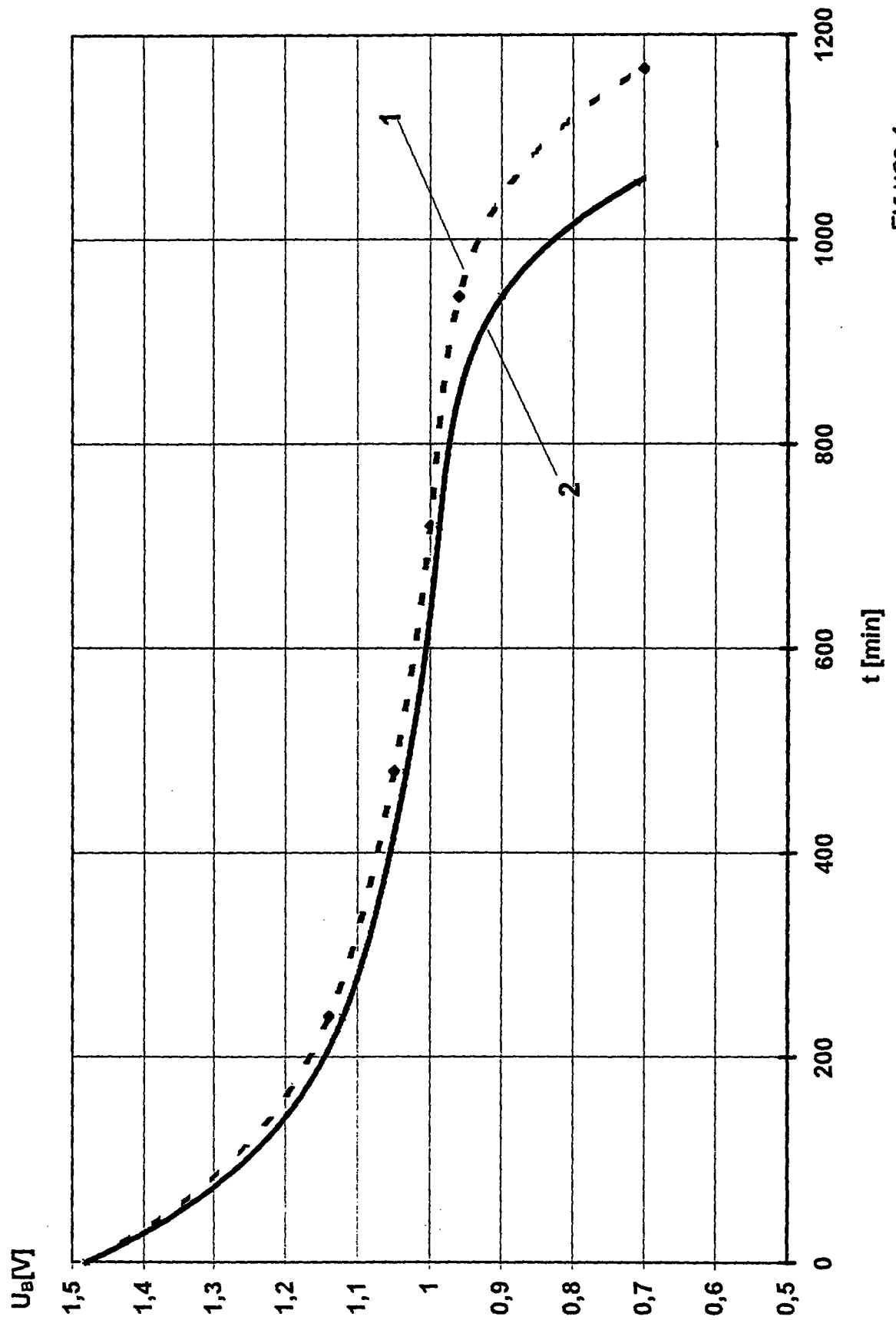
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FIGURE 1