Short communication

Separators for nickel metal hydride and nickel cadmium batteries designed to reduce self-discharge rates

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Abstract

This study gives a short overview for current nonwoven separator materials used in nickel–metal-hydride (NiMH) and nickel–cadmium (NiCd) cells.

In this context, a new material is presented, which combines the characteristics of ammonia trapping (which is synonymous to a reduced self-discharge of NiMH batteries) together with a neither environmentally nor toxicologically questionable production method, in which either free acrylic acid or fuming sulfuric acid is used.
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1. Introduction

Nonwoven separators used in rechargeable alkaline batteries commonly consist of either polyamide, polyolefine, or a mixture of both. Since a permanently hydrophilic surface is a key item for separator materials (the separator must not "dry out" during cycling), from this point of view, polyamide with its polar groups should be the favoured material choice. Consequently, polyamide separators are mostly used in nickel–cadmium (NiCd) cells. Polyolefine-based materials have to be post-treated to obtain a hydrophilic surface. Additionally, homogeneity of the material has to be as good as possible to avoid electrical shorts inside the battery, especially after high numbers of storage/discharge cycles.

For nickel–metal-hydride (NiMH) cells, another item has become of major importance: A common problem of these cells is their high rate of self-discharge, meaning that a completely charged battery continuously loses its charge during storage. As described later, this disadvantageous behaviour can be largely influenced by the separator [1–8].

Following Senyarich and co-workers, three general reasons are seem to be responsible for this behaviour [4]:

- Self-decomposition of the nickel hydroxide electrode.
- Release of hydrogen gas from the hydride electrode, leading to a reduction of the Ni(III)oxyhydroxide NiOOH in the nickel electrode.
- Redox shuttles.

The redox shuttles include (a) metal ions present in different oxidation states like cobalt, or manganese, respectively, which are released from the electrode materials [3–5] and (b) the so-called "nitrite/nitrate–ammonia-shuttle" [4]. In the latter case, which has major influence on self-discharge, nitrogen-containing impurities are oxidized at the charged nickel electrode and form nitrite, or nitrate, respectively, which migrate through the separator to the cathode. Due to the high activity of the hydrogen atoms in the hydrogen storage electrode, the anions are rapidly reduced to N(−III). Due to the strongly alkaline environment (containing > approx. 5 mol/kg hydroxide compared with 10^{-4} mol/kg N(−III) species, and the fact that hydroxide is a much stronger base than ammonia), the balance of the acid–base equilibrium reaction

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$
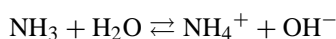
is nearly completely on the left side, and thus, ammonia is the predominant N(−III) species. This ammonia again passes through the separator and reaches the nickel electrode; the shuttle is complete. The mechanism is schematically illustrated in Fig. 1.

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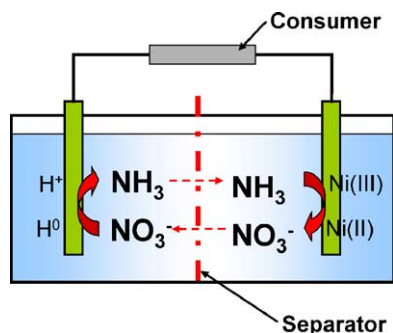*E-mail address:* peter.kritzer@freudenberg-nw.com (P. Kritzer).

Fig. 1. Schematic mechanism for the chemical self-discharge of a charged NiMH battery. Note that instead of nitrate, also nitrite is seen as the oxidized form. Note also that the self-discharge reaction does not cause electrical currents through the consumer.

Elevated temperatures increase the self-discharge of NiMH cells due to the fact that both diffusion process and chemical reaction rates increase with temperature.

In principle, this mechanism is similar in NiCd cells, where a nitrate/nitrite shuttle seems to occur [4]. Due to the lower reactivity of the Cd electrode compared to that of a metal hydride electrode, the reduction rate of the oxidised species is much lower resulting in a lower self-discharge rate for NiCd cells [4].

Origin of the nitrogen impurities are/might be [4]:

- The nickel hydroxide active materials, which are prepared (precipitated) from a nitrate-containing solution. Elimination of the nitrate cannot be avoided, since this would lead to a lower performance of the cell. Additionally, nickel hydroxides with very low levels of nitrogen compounds are extremely expensive, and thus, currently not interesting for an economic industrial use.
- Coating layer on negative electrode.
- The AB_5 alloy.
- The separator. It was found in earlier studies that polyamide separators decompose in a remarkable extent [6,9] and thereby release nitrogen compounds. Thus, if polyamide separators are used, their contribution to the total amount of nitrogen impurities is dominant. When polyolefine-based separators are used, their contribution to the amount of total nitrogen becomes negligibly low.

Senyarich and co-workers quantified the contribution ratios as follows [4]:

- Nitrogen released from the nickel hydroxide: 73%.
- Nitrogen released from the coating layer: 10%.
- Nitrogen released from the AB_5 alloy: 9%.
- Nitrogen released as trace impurities from a polyolefine separator: 7%.

It was found in the past that ammonia absorbing separators successfully depress the nitrogen-induced self-discharge [4,7,8]. In this case the separator is not only no nitrogen source, but it is even a nitrogen "sink". The nitrogen in form of ammonia is trapped at the separator surface, and the

shuttle is blocked or (at least) slowed down. Therefore, the "ammonia-trapping capacity" has become a synonym for a "high-performance" NiMH separator. It was shown in different studies that without an ammonia-trapping separator, the self-discharge ratio of a NiMH cell stored for 30 days at room temperature is in the range of 30%, whereas the same cell equipped with an ammonia-trapping separator shows self-discharge values of approximately 20% under the same conditions [3,8].

Current production-scaled methods to obtain an ammonia-trapping separator include the following post-treatments:

- Sulfonation process, in which a polyolefine material is treated in fuming sulfuric acid, followed by a multi-step washing in less and less concentrated acid and water [10]. Besides the separator as product, a sulfuric acid waste stream results from this process.
- UV light induced grafting of acrylic acid (AA). The grafting is induced by initiating the polymer chain to generate radical sites on the polymer chains, and afterwards an application of an organic solution containing AA monomers [11]. To suppress the possible side reaction of AA polymerisation, certain stabilizers have to be present in the solution. The waste stream resulting from this process is contaminated with organic compounds, and in order to dispose of this waste, a thermal or biological post-treatment is necessary. The new technology of supercritical water oxidation could be an interesting alternative for the treatment of this waste stream [12].

2. Experimental and discussion

2.1. Preparation and analysis of the new separator material

In the present study, a new separator is presented, which contains a functional polymer with ammonia-trapping properties. The polymer powder used is Style T316237 from Freudenberg KG, Germany, a high-density polyethylene-based material, which is grafted with AA within the polymer melt and then milled. No undesired by-products are formed by this treatment. The AA content is about 6%. The AA thereby is homogeneously distributed through the polymer. From this polymer, a powder was milled to particle sizes below 250 μm. Milling was performed by a ball mill cooled with liquid nitrogen. This powder is applied together with polyolefine fibres (Type NBF; Daiwabo Co., Japan) to form a wet-laid nonwoven material. Thermo-bonding of the web, necessary to obtain a sufficient strength, is obtained by using bi-component polyolefine fibres, which possess a core of polypropylene (PP) and a shell of polyethylene (PE). Applying heat at temperatures above the melting temperature of PE, but below that of PP, and a simultaneous application of pressure leads to bonding points at the crossings of the single fibres. The functional polymer is distributed in form
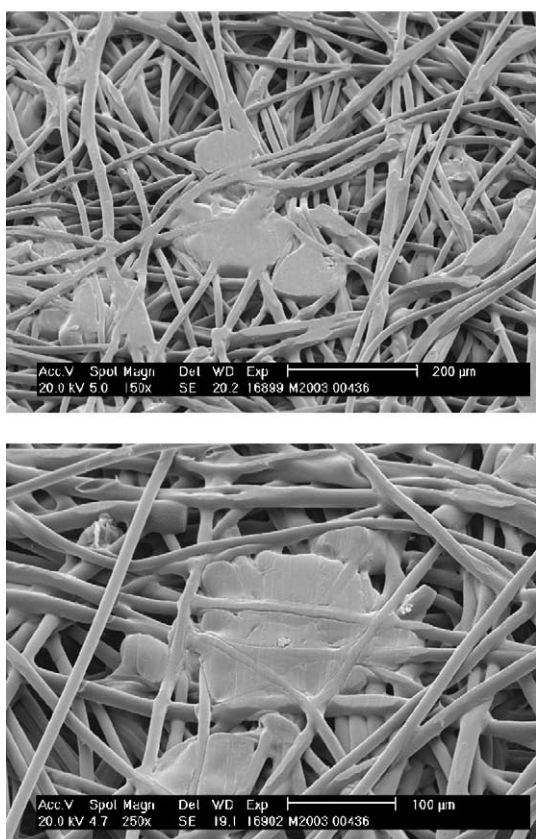
Fig. 2. Scanning electron microscope pictures of separator material FS 23955-12 containing functional polymers. Particle sizes are around 100–200 μm.

of maximum 200 μm large "islands" within the web (see Fig. 2). The particles do not penetrate through the whole thickness of the material, so that the important electrolyte storage capability is not decreased significantly.

The following materials have been produced in an industrial scaled process; the materials are now commercially available (see Table 1).

The ammonia trapping was measured after [4] using a Kjeldahl device.

To prove if a thermal or a thermo-mechanical post-treatment causes a loss in functionality, three derivatives of FS 23967-21 have been produced:

- Derivative A was calendered with two steel rolls at $T = 110\,°C$ and a line pressure of 20 N/mm to a thickness of 140 μm.
- Derivative B was calendered at $50\,°C$ and a line pressure of 80 N/mm to a thickness of also 140 μm.
- Derivative C is stored for 24 h at $100\,°C$ in an air atmosphere, without applying any mechanical pressure.

Ammonia trapping is measured as described above. The values determined for all three derivatives were the same as the value of the base material FS 23967-21. Therefore, it is concluded that a thermal or a thermo-mechanical post-treatment does not negatively influence the functionality of the separator.

Functionality is also neither lost after storage in hot electrolyte nor in strongly oxidizing solution (see Table 1).

3. Battery results

To prove the performance of the new separator, self-discharge tests have been performed with NiMH batteries containing different separator materials (see Fig. 3). Therefore, AA NiMH type cells were charged to 110% and stored under different conditions. After this storage, the remaining charge is determined.

As shown in Fig. 3, the separators can be classified into three classes. Polyamide separators show an extremely high self-discharge of NiMH cells leading to a complete discharge after short times [3,6]. Separators consisting of chemically stable and nitrogen-free polymers like polyoxy alkylene or polyolefines, respectively, which are post-treated by either fluorination or plasma treatment, show values of self-discharge at 28 days at room temperature of 30%, which is an acceptable value for most applications. However, towards higher temperatures, the self-discharge of cells equipped with these separators increases significantly.

Table 1
Technical data of separator material equipped with a functional polymer

	Product name[a]				
	FS 23955-12	FS 23967-21	FS 23967-18	FS 23967-14	FS 23980-21
Area weight (g/m^2)	55	67	67	67	80
Thickness (μm)	120	210	180	140	210
Average pore size (μm)	22	27	21	16	23
Mass loss in KOH storage[b] (%)	<0.5	<0.5	<0.5	<0.5	<0.5
Ammonia-trapping value ($\times10^{-4}$ mol/g)	2	2	2	2	2
Ammonia-trapping value after KOH storage[b] ($\times10^{-4}$ mol/g)	2	2	2	2	2
Ammonia trapping after KMnO$_4$ storage[c] ($\times10^{-4}$ mol/g)	2	2	2	2	2

[a] Nomenclature for the product name: FS, Freudenberg separator; "230", product class; 4th and 5th digit represent the area weight; digits after hyphen represent thickness.

[b] Twenty-eight days in 30% KOH at $70\,°C$.

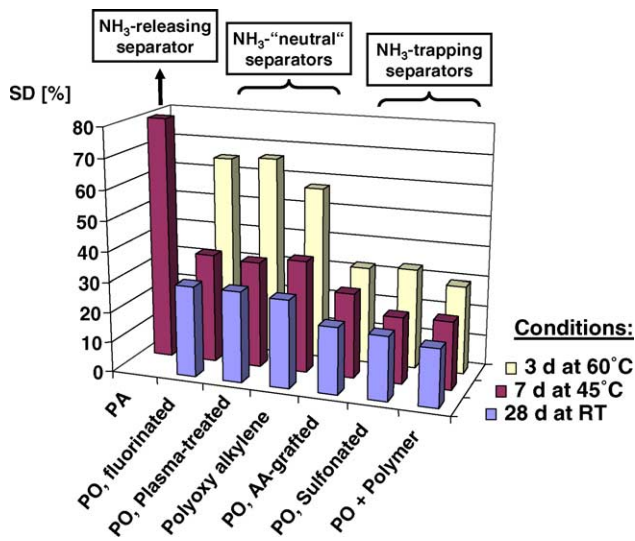[c] Seven days in 2 mol/kg KMnO$_4$ at $70\,°C$.

Fig. 3. Self-discharge (SD) results of NiMH AA cells equipped with different nonwoven separators consisting of polyamide (PA) or post-treated polyolefine (PO), respectively. The polyoxy alkylene material is produced after Ref. [13]. SD data are measured by Varta NBT, Germany. Data for polyamide after Ikoma et al. [3]. The PO + polymer material is FS 23955-12 mentioned in Table 1.

PO separators, which are post-treated either by acrylic acid grafting, by sulfonation, or by introduction of a functional polymer as described in the present paper, show a significant improvement already at room temperature. Typical self-discharge values are 20%, compared with 30% for separators from the second class. These results are in coincidence with the values obtained in earlier studies [1,3]. At higher temperatures, the difference between class two and class three separators is even more pronounced. A storage for 3 days at 60 °C leads to self-discharge values of 30%, compared with 60% for separators from the second class.

The different behaviour of the three classes can be explained as follows:

- *Ammonia-releasing separators.* Such materials consist of nitrogen-containing fibres like polyamide, which are slowly decomposed during cell life. This decomposition is very slow and does not lead to a failure of the separator, but the released nitrogen compounds additionally contribute to the existing level of nitrogen impurities, and thus, lead to an accelerated shuttle and an increased self-discharge. It must be mentioned that because of the much lower susceptibility of NiCd cells regarding self-discharge, polyamide is still the standard separator material.
- *Ammonia-neutral separators.* These separators do not release additional nitrogen compounds into the electrolyte and thus do not worsen the nitrogen shuttle reaction. On the other hand, they do not absorb the existing impurities and consequently, they also do not suppress the existing shuttle.

- *Ammonia-trapping separators* absorb more nitrogen compounds than they release ("ammonia sink separators"). Consequently, such materials block or slow down the nitrate/ammonia shuttle and thus, reduce self-discharge. This behaviour is more pronounced at higher temperatures, due to the thermally accelerated chemical reactions and diffusion/migration processes of the shuttle shown in Fig. 1. As mentioned above, this shuttle is not the only reason for self-discharge in NiMH cells. This means that if a separator completely blocked the nitrate/ammonia shuttle, there would still be a significant self-discharge, especially caused by the decomposition of the electrode materials.

All these results can be more or less transferred to NiCd cells. However, for these cells, the difference of self-discharge obtained from batteries with class one, two, and three separators is less distinct. Therefore, the substitution of the standard polyamide separators by, e.g. class three separators should only be interesting for cells, which are stored in a charged state at higher temperatures and for long times.

4. Conclusion

In this study, the influence of different types of separator materials on the self-discharge of NiMH cells is investigated. Separator materials can be classified into three classes. Such materials, which release nitrogen impurities, such materials which neither release nor absorb such impurities and such materials, which absorb nitrogen impurities.

Ammonia-trapping separators show the best performance regarding self-discharge. Such materials can fix the nitrogen impurities in their reduced speciation, and thus, can suppress the detrimental shuttle reactions, and reduce the value of self-discharge.

In this study, a new ammonia-trapping separator material is presented. It is shown that this material is not inferior to the existing "high-performance" materials, and thus, is a promising alternative as separator material for NiMH and high-performance NiCd cells.

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