

Polypropylene fibre material as a carrier for nickel electrodes

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Abstract

Nickel metallized polypropylene fibre material has been used as a carrier for nickel electrodes in alkaline solution. The metallization process of polypropylene has been performed chemically and electrochemically after a special fabric pretreatment. Application of this carrier allows the manufacturing of a low-cost, active nickel electrode due to elimination of an expensive nickel sinter.

Introduction

Sintered nickel is frequently used as a carrier for nickel electrodes. However, its high price and unprofitable weight ratio of carrier to active mass (NiOOH) cause the development of some different support materials. Super fine nickel fibres in the form of felts or foams are a very promising carrier for nickel electrodes [1–6]. Such support is now available in the commercial batteries developed by Sorapac, Hoppecke and some other companies. The next possibility is the use of nickel-plated fibres, e.g., carbon fabric [7]. Some artificial fibres can also be applied for supporting the active mass. Polypropylene fabric was first used for the preparation of an auxiliary electrode in our laboratory [8]. The subject of the present investigation is the replacement of sintered nickel with a nickel-plated polypropylene carrier for nickel electrodes. Polypropylene as fibre material is chemically resistant and permits the formation of a suitable fabric structure, fibre thickness and package. Such a carrier allows manufacture of a nickel electrode of high energy density for moderate rates. An increase in specific energy can be achieved due to the significant reduction of the weight of the electrode support.

Experimental

Two types of polypropylene fibre material PP(I, II), made from the same elementary fibres but differing in the packing, were used for these investigations.

These fabrics were produced in the Fibre Institute in Łódź (Poland) from elementary fibre of length 38 mm and 1.5×10^{-3} g/m linear weight. The fibre materials PP(I, II) are characterized in terms of: a real density (0.207 g/cm³(I) and 0.095 g/cm³(II)), a thickness (0.82 mm (I) and 1.9 mm (II)), a quantity of needle transitions (200 per cm² (I, II)) and a packing (22.75% (I) and 10.4% (II)).

After the initial pretreatment (degreasing, etching, sensitization, activation) the polypropylene fabrics were chemically and electrochemically nickel plated. The active material was inserted into this carrier by Kandler's method [9].

For scanning electron microscopy (SEM) examination of the metallized fabrics and nickel electrodes a JSM 35 JEOL stereoscan microscope was used.

Electrical investigations were based on galvanostatic charging and discharging of nickel electrodes (40 mm × 60 mm) in 30% KOH solution. A nickel/cadmium system was applied and a zinc sheet was the reference electrode. Discharge rates were C/2.5, C/5 and C/10.

The chemicals were of A.R. grade.

Results and discussion

Metallization of polypropylene

The metallization of polypropylene fibre material consists of two steps: (i) chemical (electroless) plating, and (ii) electrodeposition. The first step creates an initial electrically conductive nickel layer. Electrodeposition is needed because the chemical nickel layer is not sufficiently conductive for battery applications. Adequate electrical conductivity cannot be achieved through increased metallization time because thick electroless nickel layers undergo peeling. Good electrical properties of the carrier can be obtained when the nickel layer is grown electrochemically.

A very important requirement is good adhesion of the first nickel layer to the polymer, obtained by suitable preparation of the fibre material. Such preparation is based on: degreasing, etching, sensitization and activation. Surface degreasing was carried out to remove the contaminants left over from formation of the plastic or as a result of atmospheric contamination (dust, dirt). Degreasing together with etching of polypropylene fabric was achieved in an alkaline solution of hydrogen peroxide with UV radiation. The alkaline compounds and temperature increase caused the saponification of fats whereas H₂O₂ and UV radiation formed peroxide systems. Such treatment resulted in microcracks on the plastic surface.

Polypropylene has two phases: (i) isotactic, i.e., pseudocrystalline, and (ii) atactic, i.e., amorphous. The amorphous phase is less resistant to etching, hence, the etching proceeds along the grain boundary of pseudocrystals, creating microcracks which makes anchoring of the metallic layer possible.

Sensitization is based on the adsorption of certain substances that oxidize in the next process. Salts of tin (bivalent) are well-known sensitizers. After sensitization it is important to rinse the material in order to prevent contamination and destruction of the activator bath.

Activation involves the oxidation of the sensitizer and starts the nucleation of metallic particles on the plastic surface. Palladium chloride is often used as activator. The reaction of activation is as follows:



A careful washing in running water is the last step of pretreatment followed by nickel metallization.

Chemical deposition of a metallic layer is based on the reduction of the metal from its salt. The composition of the bath for chemical nickel plating was: NiCl₂ · 6H₂O (30 g/l), NaH₂PO₂ · H₂O (12 g/l), CH₃COONa (10 g/l), with a pH of 5.8 to 6.0; the temperature ranged from 40 to 50 °C.

This electroless deposition proceeds catalytically, i.e., nickel reduction takes place only through contact with a suitable catalyst. The catalyst for this process is solely nickel. After formation of the initial nickel nuclei, the reaction proceeds spontaneously by autocatalysis.

The fabrication of the nickel electrode carrier is completed by nickel electro-deposition (to thicken the nickel layer). Electrochemical nickel plating was carried out in a typical Watt's bath.

Fabrication of the nickel electrode

The parameters of the nickel electrode depend on the metallizing process of polypropylene as well as on the choice of the method for introducing the active material, i.e., Ni(OH)_2 . It is possible to introduce the active material into the carrier by the following methods:

- (i) thermal decomposition of nickelous nitrate;
- (ii) filling of carrier pores by $\text{Ni(NO}_3)_2$ solution under vacuum, followed by cathodic polarization in hot alkali, and
- (iii) electrochemically according to Kandler [9].

The first two methods are quite complicated and time-consuming. The third method is technologically simple, quick, cheap and it allows uniform introduction of active material. We chose the third method because of these advantages. The metallized polypropylene acts as a cathode in an acid electrolyte. The electrolyte consists of metallic ions which are deposited on the carrier as nickelous hydroxide and of ions with a more positive redox potential than that of nickel ions.

The composition of the bath is as follows: $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (200 g/l); $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10 g/l); NaF (0.5 g/l); wetting agent (0.75 g/l), with a pH of 3.0 to 3.5; the current density was 2.0 A /dm²; the room temperature was maintained at 25 °C.

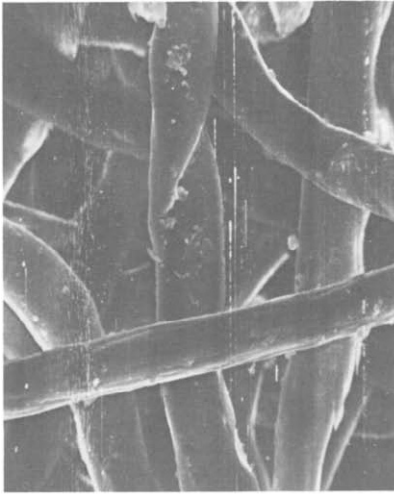
During electrolysis, the pH values in the interior of the carrier and in the bulk of the electrolyte differ significantly. Consumption of hydrogen ions in the carrier pores proceeds more quickly than diffusion from the bulk to the boundary phase, hence, the carrier pores have an alkaline environment. As a result, nickelous hydroxide is deposited in the pores of carrier but not in the bulk.

Figure 1(a)–(d) shows SEM micrographs of PP(I) fabric before and after metallization and insertion of active Ni(OH)_2 .

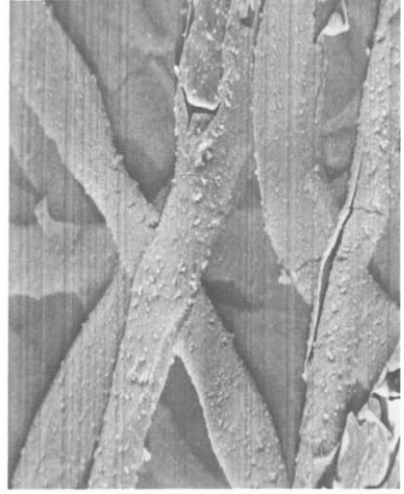
Table 1 presents the parameters of nickel-metallized carrier and after filling by the active material.

TABLE 1
Parameters of carriers

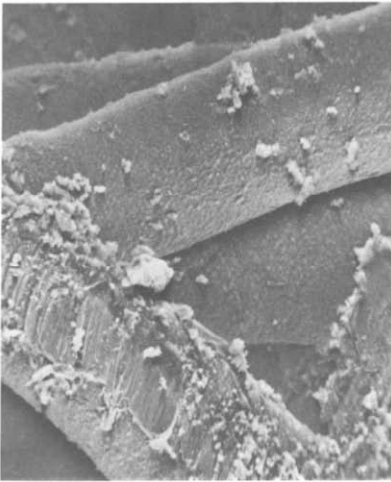
Symbol of polypropylene fabrics	Quantity of nickel (g/cm ³)	Thickness of nickel layer (μm)	Quantity of Ni(OH)_2 (g/cm ³)	Thickness of Ni(OH)_2 (μm)
I (1)	1.83	1.51	4.11	6.24
I (2)	1.80	1.48	4.07	6.16
I (3)	1.78	1.46	3.76	5.70
II (1)	0.84	1.51	1.84	6.07
II (2)	0.82	1.46	1.85	6.10
II (3)	0.87	1.56	1.92	6.35



(a)



(b)



(c)



(d)

Fig. 1. SEM micrographs of PP(I) fibre material: (a) raw; (b) chemically nickel metallized; (c) nickel electroplated, and (d) filled with NiOOH; magnification $\times 1000$.

Electrical investigations

Nickel electrodes were placed in a cell filled with 30% KOH solution. For the potential measurements a zinc reference electrode of constant rest potential was used. Thereby, the capacity of the nickel electrode was estimated. Positive electrodes were charged at 0.25 A for 20 h up to 200% of the theoretical capacity. Then, they were discharged at different rates $C/2.5$, $C/5.0$ and $C/10$. From the theoretical and practical capacities the degree of utilization of the active material was calculated. They are shown in Table 2.

TABLE 2
Parameters of electrical capacity for nickel electrodes

Electrode carriers	Theoretical capacity ^a (Ah)	Practical capacity (Ah)			Utilization of Ni(OH) ₂ (%)		
		10 h	5 h	2.5 h	10 h	5 h	2.5 h
I (1)	2.37	0.98	0.95	0.90	41	40	38
I (2)	2.34	1.05	1.00	1.00	45	43	43
I (3)	2.16	0.98	0.95	0.90	45	44	42
II (1)	2.45	1.40	1.30	1.23	57	53	50
II (2)	2.46	1.35	1.25	1.20	55	51	49
II (3)	2.55	1.48	1.45	1.24	58	57	49

^aDue to the hydration of nickel hydroxide the real theoretical capacity is significantly smaller.

The utilization of the active mass was better for fabric marked II (60%) than for fabric type I (45%). The better utilization of active mass in the case of fabric II can be explained in terms of a smaller degree of packing, hence, diffusion of electrolyte and electrode reactions proceeded more easily. Agglomeration of the active material in the carrier also exerts an influence on this utilization. Increase in current density causes a decrease in practical electrode capacity, hence, the degree of material utilization.

Conclusions

The following conclusions can be drawn from this study:

- (i) Proper pretreatment of polypropylene fibre material enables good electrical parameters of the carrier to be obtained.
- (ii) Relatively low degree of utilization of Ni(OH)₂ for PP(I) is caused by its structure and uneven distribution of active material on the fibres of the carrier.
- (iii) Good utilization of the nickel electrode with the carrier PP(II) is due to the low packing of this carrier (10%).
- (iv) Further improvement in nickel electrode performance is possible.

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