

Effect of substrate pre-coating on adhesion of sintered nickel plaques for electrode application in rechargeable batteries

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Abstract

The battery industry sees a need to improve the adhesion strength between porous nickel plaques and substrates in sintered nickel electrodes in order to reduce the use of nickel and to achieve higher battery capacity. In this paper we report on the use of a thin buffer layer to enhance plaque/substrate adhesion. In particular, we have attempted to improve adhesion performance of conventional sintered plaques produced from filamentary Ni powders (INCO-255, particle size 2.2–2.8 μm) through the introduction of a thin, intermediate layer made of finer Ni powders (INCO Type 110 and INCO Type 210, particle size 0.8–1.5 μm and 0.5–1.0 μm , respectively). The process consists of two steps. First, a buffer layer was applied from a slurry containing the finer Ni powders. After drying, the substrate was coated again with a slurry containing standard Type 255 powder. A vertical coating apparatus with periodically contacting blades was designed to produce thin, uniform buffer layers with low surface density (1–10 mg cm^{-2}). For adhesion testing, a tensile strength test specimen holder was modified to ensure planar loading of the interface. Significantly enhanced bonding between the plaque and substrate was observed due to the introduction of the buffer layer. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Porous nickel structures produced by sintering INCO Type 255 filamentary nickel powder on nickel-plated perforated steel sheets are called nickel plaques and are widely used in the fabrication of electrodes for nickel-based rechargeable batteries [1–4]. Although pasted or foam electrode technology has been employed more recently by many nickel based battery manufacturers due to their shorter production cycle and lower capital requirement, sintered nickel electrodes are still the choice of electrode technology for battery applications demanding high power and reliability, along with long cycle and calendar life, such as batteries for aerospace and railway applications, power tools, and some portable elec-

tronics. In addition to its higher cost, the high nickel content and the difficulty in completely filling the fine small pores with active material, sintered nickel electrodes usually exhibit lower specific battery capacity than foamed or pasted ones. The battery industry is therefore seeking to reduce the cost of sinter electrodes while retaining their positive merits. One possible approach is increasing the porosity of the sintered nickel plaque into which $\text{Ni}(\text{OH})_2$ is chemically impregnated to form the final electrode. In a recent paper we have reported an improved method for processing sintered plaques that leads to increased porosity at a given strength level [11]. However, an additional issue is the weakened bonding of the porous nickel structure to the perforated substrate, which could potentially cause problems in the electrode fabrication process and also jeopardize electrode service life. The objective of the present work is to explore methods of enhancing plaque adhesive strength as a means to manufacture high porosity sintered nickel plaques.

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The mechanical strength of the nickel plaque and its bonding strength to the substrate are both critical to the reliability of batteries in service as well as to the reduction of rejection rate during the electrode manufacturing process. First, the Ni plaque has to survive severe chemical, thermal, and mechanical cycles during the repeated chemical impregnation process for filling of its pores with active mass. Any breakage of the plaque or de-bonding from the substrate at this stage leads to failure and rejection of the electrode. Battery electrodes are then subjected to a demanding chemical environment (e.g. KOH), cyclic distortion associated with charge/discharge processes and thermal fluctuations. Currently the porous plaques are pasted or coated onto nickel-plated perforated steel sheets in order to enhance the lateral strength. Thus the overall mechanical performance of the electrodes depends mostly on adhesion between the plaque and the substrate.

A conventional slurry-based process is widely used for the fabrication of tape-like porous nickel compacts (as is well described elsewhere [1,5–11]). Briefly, a slurry is prepared by mixing filamentary Ni powder in an aqueous solution containing a binder such as hydroxypropyl methyl-cellulose (HPMC) (Fig. 1). The substrate is then coated on both sides with the slurry and dried producing a green part. Finally the green part is fired at 700 to 1050 °C for up to one hour in a reducing atmosphere to produce the final sintered plaque ready for chemical impregnation and electrode fabrication.

Generally the as-sintered plaques have a volume about one third that of the starting slurry as illustrated schematically in Fig. 1. Such a large compaction during drying and sintering builds in mechanical stresses thought to be tri-axial in nature. The structural gradients and stresses perpendicular to the surface of the substrate are negligible because it is a thin (<1 mm) layer. However the stresses acting in the plane of the substrate can result in bending, mechanical degradation and cracking of the coatings even during drying and sintering, as well as in service.

Many technological parameters need to be under precise control to achieve reasonable reproducibility of the structural, mechanical and electrical properties of the plaques. Therefore, it is evident that the formation of a high quality interface between the porous nickel and the substrate, resulting in sufficient adhesion, is a rather complicated task. Moreover, the stochastic nature of the contacts within the plaque and between plaque and substrate make this difficult to reproduce consistently.

In spite of the worldwide production and application of rechargeable batteries there are very few reports [1–11] offering details of the fabrication process or characterization of the adhesion properties of these materials. This is due in large part to the proprietary nature of processing research and the highly competitive market for batteries. This project therefore attempts to contribute to the development of the coating technology by offering a systematic approach to the measurement of plaque-substrate adhesion and its application in developing strongly adhered coatings. In particular

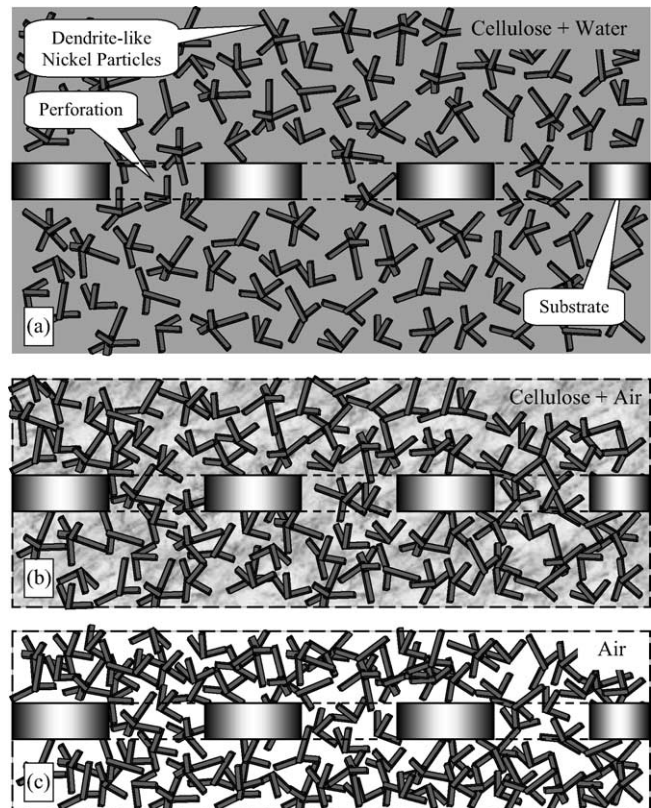


Fig. 1. Three phases in the processing of porous nickel plaques: (a) a perforated substrate is coated with a uniform (constant thickness) layer of fluid slurry (high-viscosity paste) containing individual nickel particles in a solution of cellulose in water, (b) dried plaque (nickel particles are still not chemically bonded to each other or to the substrate, instead temporary attachment is achieved through bonding to methyl cellulose molecules, and (c) sintered porous nickel plaque (nickel particles are bonded chemically and form a continuous porous network bonded to the substrate).

we have attempted to improve plaque adhesion by means of pre-coating the substrate with a slurry containing a finer Ni powder (following the suggestion of Ettl [1997]). The hypothesis is that the finer Ni powder is easier to sinter and may lead to greater contact density with the substrate, resulting in strengthened bonding between the substrate and the plaque. We also hypothesize that the bulk powder slurry that is then deposited over the pre-coated layer penetrates into it and offers a strong bond at the interface between the pre-coating layer and functional porous plaque as well.

2. Tape casting

An ordinary slurry based procedure widely used for the fabrication of the tape-like porous nickel compacts in industry was selected for the study of the coating process and adhesive properties of the resulting coupled (plaque/substrate) structures. The slurries were produced from filamentary nickel powders (Table 1) supplied by INCO Ltd. (types 255, 110, and 210) and partially described in Refs. [4–8,11].

Table 1
Nickel powders produced by chemical vapor decomposition

Powder	Average particle size (Fisher sub-sieve size) (μm)	Density (g cm^{-3})
110	0.8–1.5	0.90–2.30
210	0.5–1.0	<0.5
210H	0.2–0.5	<0.60
255	2.2–2.8	0.50–0.65
255-1	2.1–2.2	0.4
255-2	2.1–2.2	0.3

2.1. Substrates

Commercially available (electrolytically) nickel-coated perforated steel substrates about $70\ \mu\text{m}$ in total thickness were used to assemble the adhesive joints and to carry out measurements of the adhesive properties. The perforations of the substrate were about 1 mm in diameter, ordered in a regular hexagonal network (Fig. 2). Perforated substrates are generally used in the industrial production of the electrodes due to the enhanced mechanical linkage of the plaques to the substrate they provide [12] as seen in Fig. 2 (right,

above). In this case cohesive co-bonding of layers pasted on opposite sides of the substrate through the orifices is also responsible for overall adhesion of the plaque to the substrate. In most cases the contribution of this cohesive bonding is considerably greater than that due to any adhesive bonding formed between the porous nickel structure and the substrate.

2.2. Slurry preparation

The slurries were prepared by rotary or manual mixing of the corresponding Ni powder (Table 1) with an aqueous solution containing 4.1 wt.% hydroxypropyl methylcellulose (HPMC). Thereafter, these slurries were degassed for 2–20 min using a laboratory compressor. We found that partial dehydration of the fluids also occurred at this stage due to the low-pressure environment and the corresponding increase of water evaporation from the slurry surface. Therefore some loss of weight and a decrease in temperature were detected after this treatment. The as-produced fluids were then used for the tape casting, as described in following subsections.

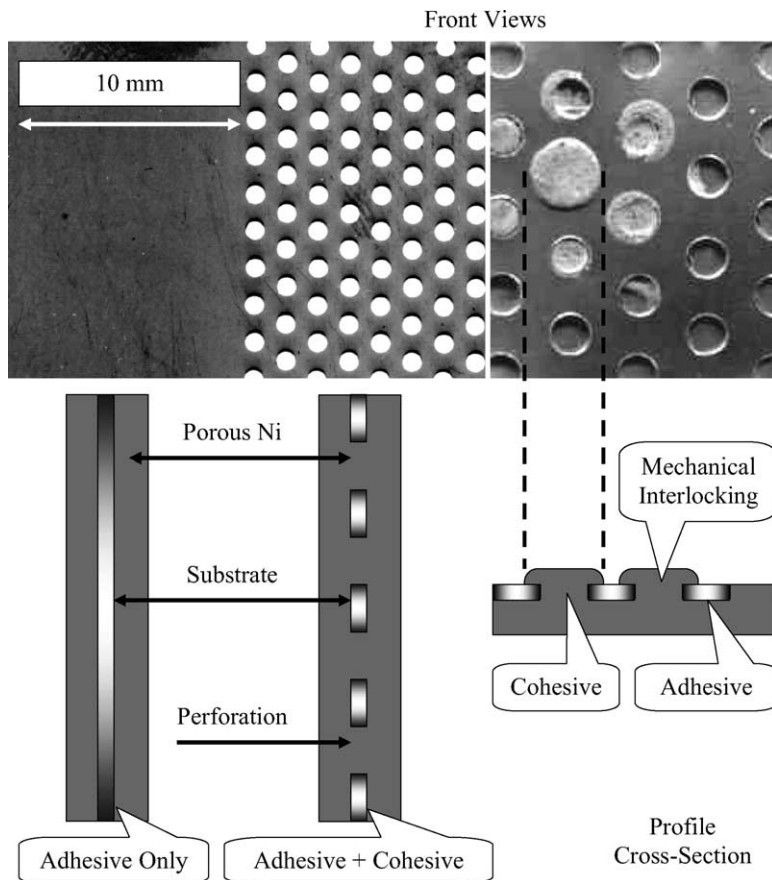


Fig. 2. View of a typical substrate (left, above) containing continuous solid and discontinuous perforated fields. Perforated substrates are generally used in industrial tape casting. Right picture illustrates mechanical interlocking of the plaque via its penetration through the perforation. Schematic of the plaques produced on different (perforated and non-perforated) substrates (left, below) demonstrates enhancement of effective (measurable) adhesion of the plaques due to perforation of the substrate. This enhancement results when cohesive bonding between porous plaques pasted on opposite sides of the substrate is stronger than adhesive bonding between the plaque and the substrate.

Final dehydration of as-pasted plaques was achieved through drying of the specimens at room temperature (24–25 °C) for 24 h or at 70–150 °C for 20–40 min. In order to decrease the number of variables in the study, the nickel/4.1%–HPMC-solution weight ratio was fixed at 3:10 or 5:10 for the slurries used for the preparation of the final plaques using INCO-255 powder or its low density fractions that are referred to as batch 255-1 and batch 255-2 below. However the composition of the slurries used for pre-coating with fine nickel powders was varied over a wide range in order to enable optimization of the process.

2.3. Pre-coating of substrates: vertical tape casting with periodically contacting blades

Double-sided coating of the substrates with a relatively thin layer of low-density powders was almost impossible using a conventional horizontal or vertical tape casting apparatus and a flat Doctor Blade. Control of the slurry loading and thickness uniformity of the pre-coating layers was exceptionally difficult because of uncontrollable deformation of the thin and therefore bendable substrate under the fluid slurry (Fig. 3). Using a narrow gap Doctor Blade (Fig. 3, below), even negligible deformation of the substrate in the vertical direction (from the point of view projected in Fig. 3) results in an easily detected non-uniformity of the thickness distribution or even some discontinuity of the coating.

Instead, a simple laboratory scale apparatus was developed which enabled the production of relatively large, uniform, double-sided nickel powder coatings. This is shown in Figs. 4 and 5. According to the procedure described here, the substrate was first coated with a relatively thick and non-uniform layer by immersion and then pulled from a bath filled with the slurry (Fig. 4). Thereafter, the undesirable portion of the slurry was removed from the surface by passing the substrate through a die formed with two parallel blades.

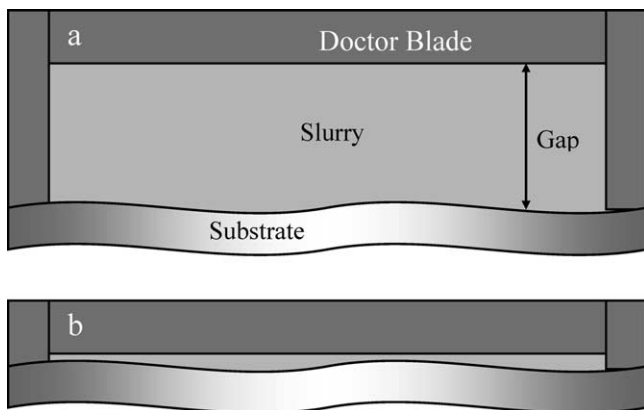


Fig. 3. Effect of local displacement of the substrate (20–50 μm) due to bending on the thickness uniformity of the slurry coating produced using Doctor Blade tape casting. (a) In the case of a thick layer (about 1000 μm) the bending does not affect the uniformity very much (2–5%). (b) However, in the case of a thin layer (50–100 μm) such a variation can lead to excessive non-uniformity of film thickness.

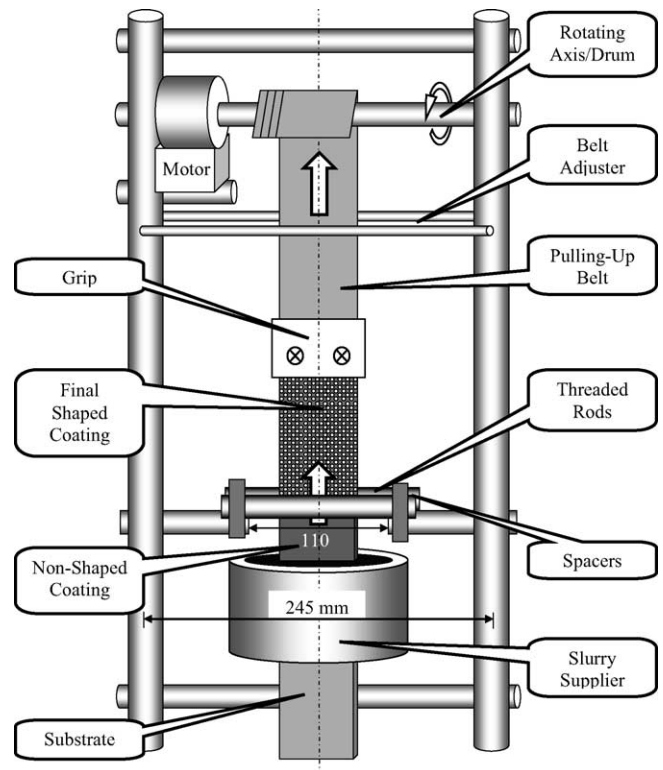


Fig. 4. Schematic illustration of the vertical tape casting apparatus with periodically contacting blades. Pre-coating layers were produced via passage of a perforated substrate in through two stages: (1) inlet and outlet of the slurry supplied bath (preliminary non-shaped coating with fluid nickel-containing slurry), and (2) between a pair of threaded rods limiting upward mass transfer and allowing uniform dispersion of the slurry along surface of the substrate (see also Fig. 5 for details).

These blades had a periodically oscillating surface that allowed support and protection of the substrate from uncontrolled bending (Fig. 5) and resulted in a uniform upward mass transfer of the slurry attached to the substrate. The “blades” that controlled final thickness of the pre-coating layers were made from identical fully threaded cylindrical rods (Fig. 5). The thickness and nickel loading of the final layer (Figs. 4 and 5) were easily controllable by selection of appropriate dimensions of the threads and inter-blade distance.

Generally the cross-sectional area of the space between the rods and the substrate was constant through the full width of the substrate leading to a uniform thickness distribution along the horizontal axis. Moreover, equal loading on both sides of the substrate with the slurry was established due to the symmetry of the set up (Fig. 5) and the symmetry of acting forces responsible for re-distribution of the slurry. The slurry flow was adjusted by appropriate selection of: (i) the difference between major and minor diameters of the threaded rods; (ii) the shape of the threads; and (iii) the distance from one peak of the thread to the next (“the pitch”). Displacement of the substrate between the die-forming rods was achieved by a motor-operated drive (Fig. 4) and through wrapping of the easily bendable polyethylene belt onto a rotating drum. The

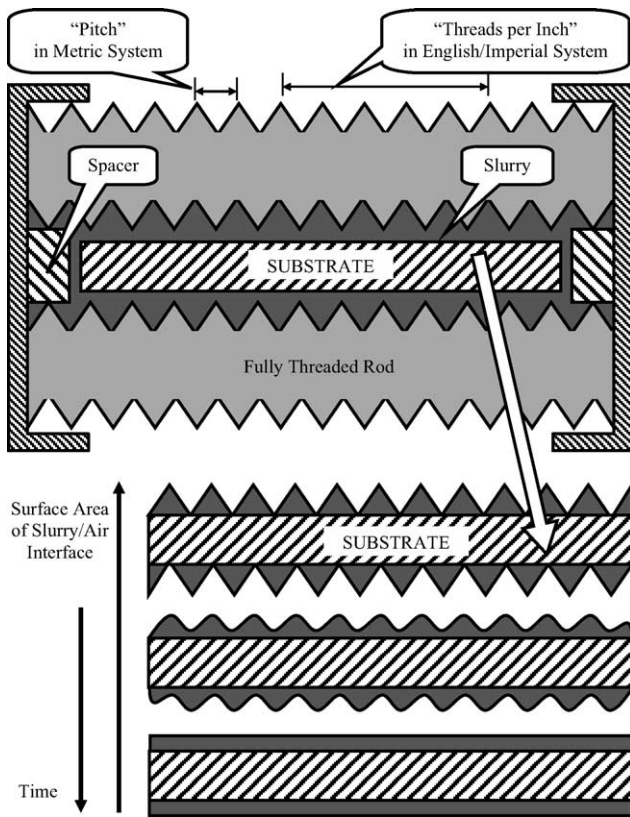


Fig. 5. Schematic top view of periodically contacting blades for vertical double-sided tape casting (above) and evolution of slurry coating (below). Immediately after coating the layers almost copy the shape of the threaded rods. Very shortly thereafter, the fluid coating is smoothed spontaneously due to surface tension.

resulting linear casting speed was controlled by the rotation rate of the drum and was varied from 25 to 100 cm min^{-1} which corresponds well to the speed range applied in the battery industry.

Table 2

Composition of selected slurries, dimensions of the substrates, and surface density of the coatings measured directly after drying the plaques at 110–120 °C for 15–20 min (Density-1) and those calculated by subtracting of corresponding amount of HPMC that could be burned out lately at sintering stage (Density-2)

No.	Ni	Ni-110 (g)	4.1%-HPMC (g)	Ni/4.1 wt. ratio	Width (cm)	Length (cm)	Area (cm^2)	Density-1 (mg cm^{-2})	Density-2 (mg cm^{-2})
236	110	26.05	45.03	0.5785	10.2	41	836.4	7.99	7.46
236A	110	26.05	45.03	0.5785	6.5	41	533	7.88	7.36
239	110	25.01	45.08	0.5548	10.2	41.1	838.4	7.24	6.74
239A	110	25.01	45.08	0.5548	6.5	41.1	534.3	7.34	6.83
245	110	11.01	44	0.2502	10.2	41.4	844.6	2.66	2.23
245A	110	11.01	44	0.2502	6.5	41.5	539.5	2.61	2.3
246	110	12	44.03	0.2725	10.2	41.2	840.5	3.31	2.94
246A	110	12	44.03	0.2725	6.5	41.2	535.6	3.32	2.96
254	210	6.02	50.03	0.1203	10.2	41.4	844.6	2.46	1.84
254A	210	6.02	50.03	0.1203	6.5	41.4	538.2	2.53	1.88
255	210	9.01	50.08	0.1799	10.2	41.2	840.5	3.78	3.08
255A	210	9.01	50.08	0.1799	6.5	41.2	535.6	3.88	3.16
259	210	16.51	55.03	0.3	10.2	42	856.8	5.32	4.68
259A	210	16.51	55.03	0.3	6.5	42	546	5.37	4.72
260	210	16.53	55.12	0.2999	10.2	42.2	860.9	5.96	5.24
260A	210	16.53	55.12	0.2999	6.5	42.2	548.6	5.96	5.24
262	210	18.05	54.01	0.3342	10.2	42.8	873.1	6.61	5.89
262A	210	18.05	54.01	0.3342	6.5	42.8	556.4	6.58	5.86

The shape of the as-pasted slurry as it passed through the die was far from uniform and was wave-like in fact on a scale related to the pitch of the threaded rod (Fig. 5). However it was observed that on the macro-scale (with specimen widths up to 110 mm) the uniformity of the slurry thickness along the surface of the substrate was very high due to the precise periodicity of the threads. In terms of the surface density (loading) discussed later the non-uniformity of the plaques did not exceed 1–3% (Table 2).

Final smoothing of the surface was achieved spontaneously due to the effect of surface tension and fluidity of the slurry (Fig. 5), these being controlled by slurry composition (Fig. 6). The total length of substrate per pass was about 2 m. This enabled the tape-casting of samples measuring up to 110 mm in width and 700 mm in length. The largest specimens discussed in this report were 102 × 428 mm (Table 2).

2.4. Pre-coated layer: surface density

The pre-coated layer produced using fine nickel powders may have lower porosity after sintering for two main reasons. First, a finer powder, such as Type 210 (Table 1) with thinner filaments and lower density, sinters more readily and to fuller density under conditions suitable for sintering the main functional plaque formed from Type 255 powder. In addition, some of the powders used, such as Type 110 (see Table 1), are spherical which enables them to pack to a higher green density. Therefore the thickness and surface density of the pre-coated layer should be minimized so as to maintain a high overall porosity. At the same time this pre-coated “buffer” layer should be thick enough to improve bonding between the substrate and the functional, highly porous nickel plaque. Taking into consideration the design of the apparatus described above (Figs. 4 and 5), the control of the thickness (and surface density) of the pre-coated layer can be easily

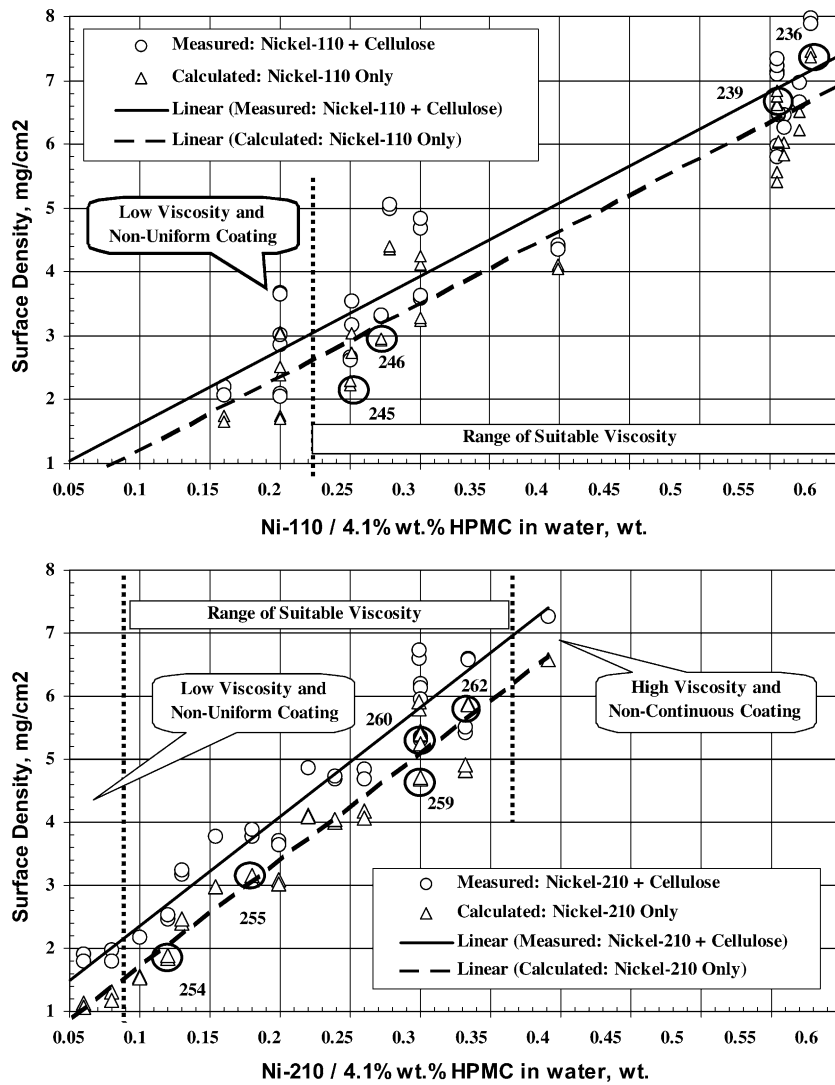


Fig. 6. Surface density vs. slurry composition for the as dried pre-coating plaques produced by vertical tape casting with periodically contacting blades (Fig. 5). Bold circles represent the specimens listed in Table 2. Calculated data (referred as Density-2 in Table 2) were obtained by subtracting the weight of the cellulose burned out during sintering. Ranges of slurry compositions suitable for preparation of high-quality continuous and uniform pre-coating layers are outlined by the vertical dotted lines. Different ranges for two fine powders (referenced as 110 and 210 in Table 1) demonstrate the effect of particle structure on performance of the slurry during plaque pasting.

achieved by adjustment of the gap between the threaded rods and/or modification of the slurry composition (Fig. 6).

After preliminary experiments and corresponding optimization 10–24 threaded steel rods¹ were chosen for the dies. In the experiments discussed here we used identical dies made with the minimum gap width (gap between protuberances of the threads) that allowed passage of the substrates (70–100 μm thick). The as pre-coated specimens were dried at 65–110 $^{\circ}\text{C}$ for several hours.

According to the results summarized in Table 2 for the plaques produced using INCO-110 and INCO-210 fine powders as buffer layers even small variations of the slurry composition allowed fabrication of coatings with the densities

ranging from 1 to 10 mg cm^{-2} . Thus, quite accurate control of the surface density could be easily achieved using linear dependencies similar to those shown in Fig. 6. The surface density of pre-coating layers was measured using the surface area and weight of the pre-coating fine powder nickel layer without consideration of the weight of the cellulose binder constituent. This is indicated as the “measured data” in Fig. 6. Thereafter more precise values of actual nickel loading were calculated by subtracting the weight of the cellulose (denoted as “calculated data” in Fig. 6), since the binder is burnt out at the later stage of sintering.

2.5. Tape-casting of functional porous plaque

The main (thick) plaques were produced at a casting rate of about 100 cm min^{-1} using a conventional vertical tape cast-

¹ 10–size (nominal/major diameter, 4.826 mm), 24–number of threads per inch.

ing apparatus with a pair of parallel flat Doctor Blades. The slurry was first pasted on the substrate (with or without a pre-coating layer). Thereafter, the substrate was inserted between two stainless steel Doctor Blades and pulled in an upward direction. The uniform thickness of the as-pasted plaques was controlled through the thickness of a pair of stainless steel frames that were utilised to fix the position of the substrate exactly in the middle of the gap formed by both blades. The as-produced layers were then dried at 130–150 °C for about 40 min and the thickness of the plaques was measured to estimate slurry shrinkage (see Fig. 1 for reference).

3. Sintering

The as-coated pieces with both a pre-coating and bulk layer (listed in Table 2) were typically placed in an oxygen-free nitrogen atmosphere (gas flow of 2 l min⁻¹), sometimes enriched with H₂, to achieve reducing conditions in a sealed three-zone horizontal electric furnace. The structures were first kept at a moderate temperature of about 100 °C for 10 min for complete dehydration of the coatings and to avoid additional thermal stresses that may result in damage of the pre-coating/substrate and plaque/pre-coating interfaces during heating. Thereafter the dried specimens were placed into the middle (hottest) part of the furnace and sintered at 950 °C for 10 min or at 1050 °C for 1 min in the same atmosphere. We presume that the final decomposition of the remaining cellulose occurs at the beginning of this step. Samples were cooled to about 100 °C and held for a further 10 min to reduce the effect of thermal shock. Porosity of the as sintered plaques was 89.7–91.6.

4. Tensile strength adhesion tests

4.1. Bonding of specimens with epoxy glue

In order to obtain the most correct data characterizing adhesion of the plaque to the substrate it is necessary to perform tensile tests perpendicular to the plane of the substrate. One of the main obstacles in such tests involving porous materials is related to the development of suitable specimen holders and grips. After considerable experimentation, the set-up schematically illustrated in Fig. 7 was found to be appropriate.

As a first stage a sandwich structure similar to that shown in Fig. 7 was produced at room temperature using two part epoxy glues of different viscosity. Following this procedure a set of these sandwiches (usually 6 to 12 nickel coated fragments with dimensions of 20 mm × 20 mm each, together with flat back supporters and front nail-like holders) was placed into an electrically heated oven for complete curing of the epoxy. One of the main disadvantages of the application of epoxy for assembling of the specimens according to Fig. 7 was related to the time-dependent viscosity of epoxy

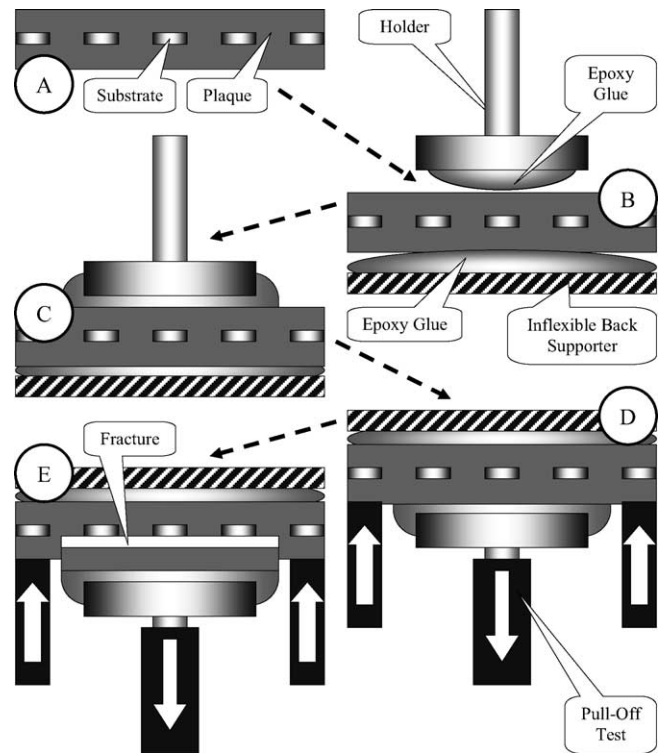


Fig. 7. Schematic illustration of the specimen assembly process using epoxy glue (A–C) and subsequent tensile adhesion test (D,E) using the Instron and Sebastian-Five tester. The holder and back supporters were preliminarily coated with two part epoxy glue and kept for certain period of time to achieve predetermined viscosity of the glue for controllable penetration of the glue into the plaque at the stage of assembling (B,C).

adhesives. Therefore, it was relatively difficult to control viscosity, rate of penetration, and finally rate of curing of the glue in the plaque.

Over-penetration of epoxy through the entire plaque was often observed visually when freshly mixed and highly fluid glue was applied. Such samples demonstrated extraordinary high fracture resistance and their data were rejected. Also mechanical performance of several specimens produced at the same time was very different, and the results of the tests were not reproducible.

An additional disadvantage of the application of epoxy is related to the complete curing and hardening of the glue. It was feared that curing may result in additional stressing of nickel filaments with unavoidable degradation of the mechanical performance of the plaque as a whole.

4.2. Bonding of specimens with hot melt adhesive

In a later stage of the test development (Fig. 8) commercially available thermal glues (also called hot melt adhesives) were tested. It was felt that these temperature sensitive adhesives would be more suitable for gluing porous nickel plaques to the specimen holders. The following advantages were taken into consideration when modifying the procedure (from Figs. 7 and 8): (1) uncomplicated controllability of vis-

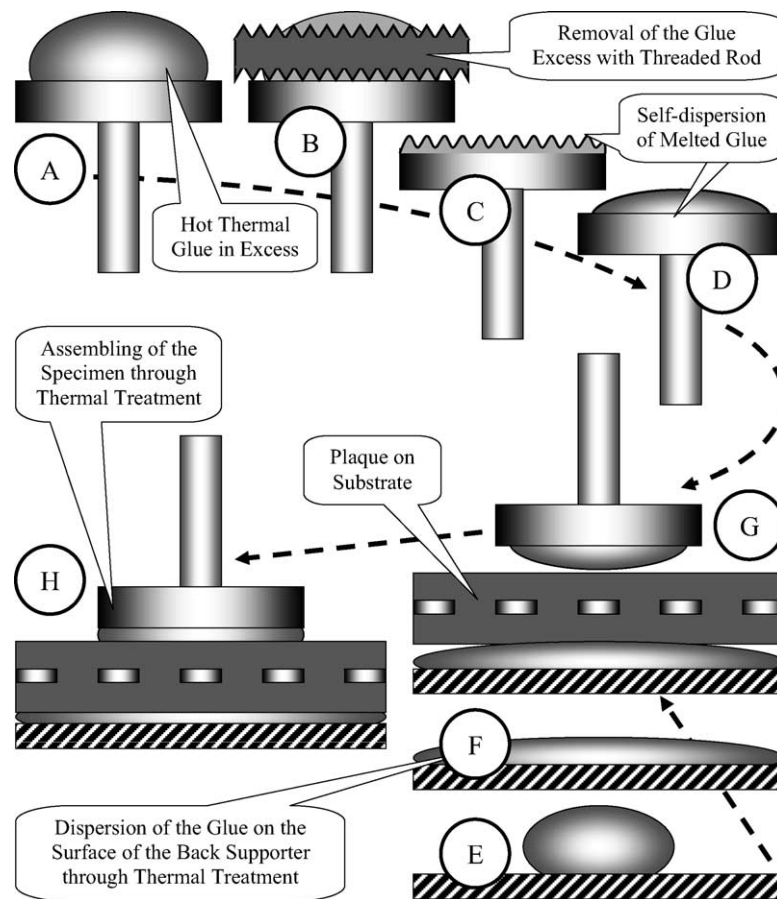


Fig. 8. Schematic illustration of the specimen assembly process using hot melt adhesive. The holder (A–D) and back supporters (E,F) were preliminarily coated with hot melt adhesive and kept at 130 °C for about 60 min. A smooth and reproducible convex shape of the glue coating was achieved due to surface tension and wetting. Thereafter the parts were cooled and the specimens were assembled at room temperature according to (G). The specimens were finally treated again at about 80 °C to control the softening and penetration of the glue into pores of the plaques (H).

ous properties by means of temperature; (2) reversibility of solidification; (3) superior elastic properties that decrease the stress due to glue on the filaments and the whole specimen; and (4) simple cleaning/removal of these glues via re-heating and therefore possible recycling of used parts of the specimen (e.g. metallic nail type holders and back supporters, shown in Fig. 8).

According to the modified processing route illustrated in Fig. 8, removal of excess glue from the nail type holders and flat back supporters was performed using a threaded rod similar to the procedure described earlier for fabrication of the pre-coating layers (In both cases application of threaded rods allowed fabrication of a uniform fluid layer, as follows from a comparison Figs. 5 and 8). Using this process a predetermined thickness of the hot melt adhesive layer was easily achievable leading to reproducible specimen behaviour. Aluminium discs of about 20 mm in diameter and 2 mm thick were used as back supporters. The amount of hot melt glue on the holders and supporters was approximately 10 and 25–30 mg, respectively (see Fig. 8).

In optimizing this process it is important to select the optimal temperature and duration that enables only a moderate

penetration thickness of glue into the specimen. Excessive temperature and/or duration resulted in over penetration of the glue into the plaque resulting in bonding of the glue to substrate. The hot melt adhesive specimens discussed in this report (Fig. 8) were treated at 130 °C for 60 min for preliminary coating of the holders and buck supporters and at 82 °C for 60 min for assembling of the specimen.

Some of the plaques were tested using specimens produced using both epoxy and hot melt adhesive. Correlation of the average data obtained from both sets of measurements was reasonably acceptable. The difference between both did not exceed 30% of the average value. Considering the scatter in the results that will be illustrated in following subsections, the data obtained by each technique seems to be acceptable.

4.3. Pull-off test

Typically tensile grips used for testing materials are fixed to the rigid base of the pulling mechanism. Adhesion tests are very sensitive to any shear loading however. Moreover, the low strength of these porous structures makes it nearly impossible to achieve a degree of alignment sufficient to

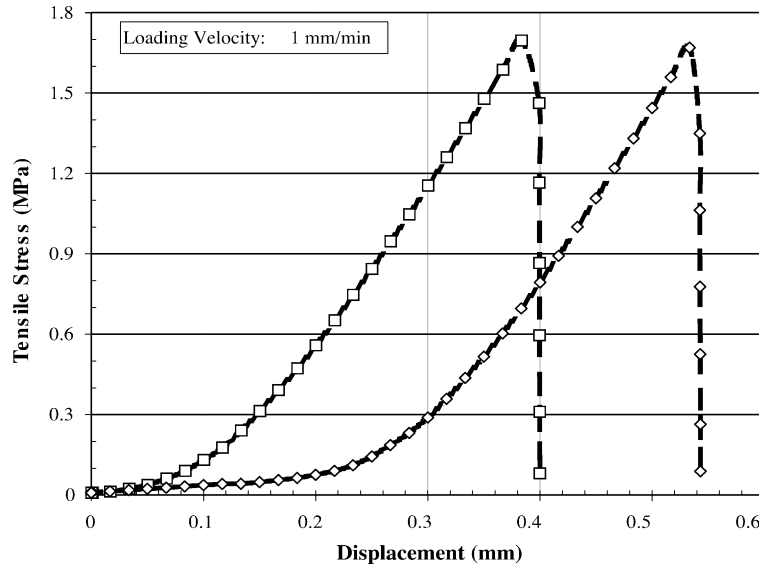


Fig. 9. Tensile stress vs. displacement data for the samples produced from standard 255 Powder (see Table 1) with fine powder buffer layers (Instron tester).

eliminate shear stresses that would result in peeling and/or acting of rotational forces on the specimens. Therefore, the specimens were designed so as to remove lateral forces as far as possible. The load/displacement data recording (Fig. 9) and one-step fracture strength measurement (Fig. 10) were

performed using an Instron and Sebastian-Five tensile apparatus, respectively.

It is evident that the spatial distribution of the stresses acting on all parts of the pull-off specimen is not uniform. This distribution is quite complicated even for an ideal geometry

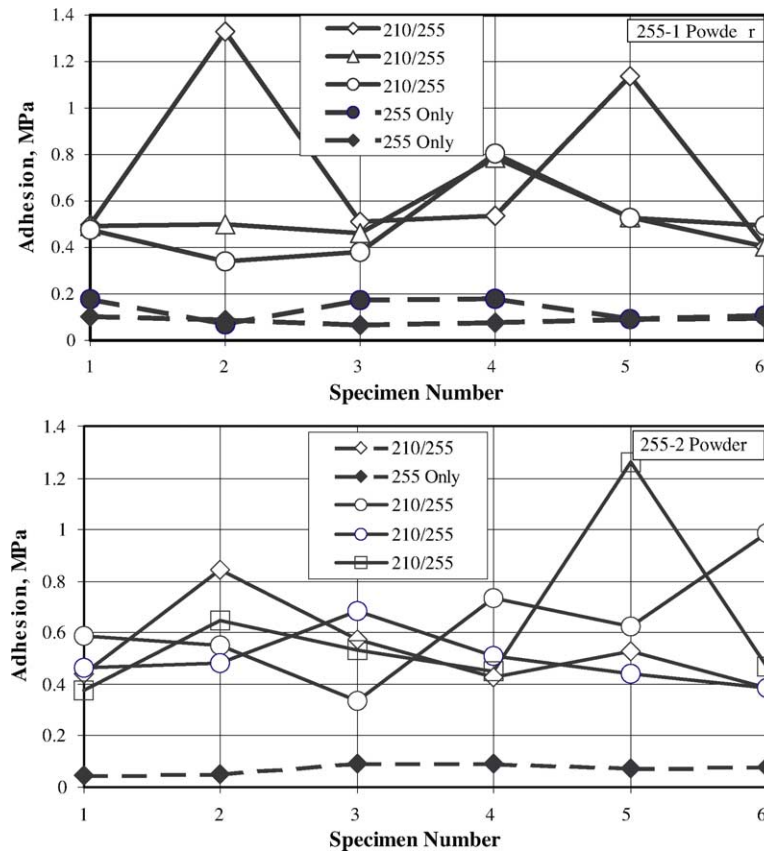


Fig. 10. Adhesion test results for the plaques produced from 255-1 and 255-2 powders (see Table 1) without and with 210 powder buffer layer (Sebastian tester).

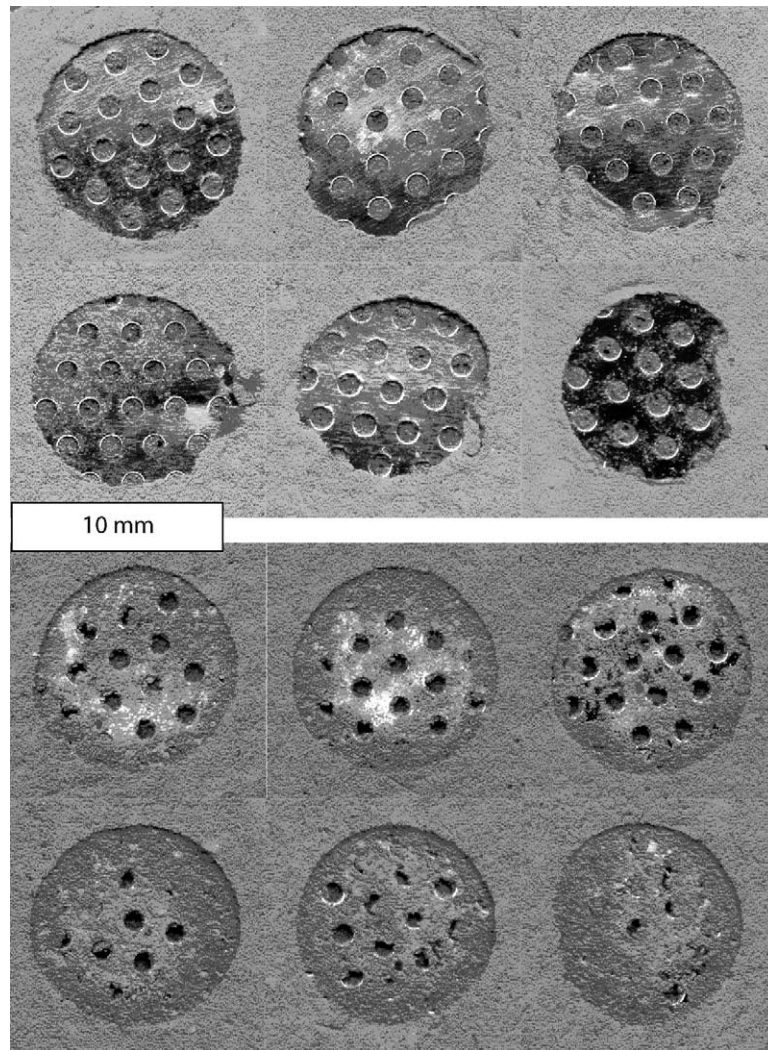


Fig. 11. Fractography of the specimens produced on a plain substrate (above) and on a pre-coated (210 powder) substrate (below). The substrate surface is clearly visible in specimens produced on plain substrates (above). On the other hand, a considerable amount of the powder is observed on the fracture surfaces of the specimens pre-coated with fine nickel powder.

of tested material, pulling apparatus, and acting forces. Considering specimens similar to those illustrated in Figs. 7 and 8, the stresses are minimum in the central part of the bonding interface [13]. This non-uniform distribution leads to the generation of peeling forces acting on the peripheral part of the nail-like specimen holder (Figs. 7 and 8). Finally bending of the specimens is often observed.

Thus, the test results given here may not fully represent the actual strength of the bond between the plaque and the substrate, and may not correspond well to similar data obtained by other test techniques. However, the main purpose of this study was to demonstrate the positive relative effect of introducing pre-coating buffer layers on the adhesion performance of the resulting plaques. All adhesion test specimens were prepared with the same dimensions and in identical conditions independently of the pasting procedure. Therefore, the results reported here can be used for comparison

of mechanical performance of the plaques produced using different pasting routines (with and without fine-powder pre-coating).

Instron tensile testing was used at the preliminary stage only. The purpose of these experiments was the step-by-step visualization of loading and the history of the specimen response. Typical results obtained for the plaques with comparatively high adhesion performance are shown in Fig. 9.

Later in the project the Sebastian-Five tester was chosen as the most favourable test system due to its simplicity and wide application in the battery industry. The basis for this test is shown schematically in Fig. 7. Briefly, during the measurement the nail-like holder is pulled downwards (Fig. 7D) until the specimen fails. This is detected by a sharp decrease in load. The maximum load during the test is detected digitally from the load cell. The results for a series of tests are given in Fig. 10.

4.4. Effect of Buffer layer on the adhesion of 255 powder plaques

Hundreds of the layered specimens with and without a pre-coating layer were tested using the Sebastian tester (see Fig. 10). The experimental data demonstrate a considerable degree of scatter in the failure stress that makes interpretation of the results difficult. Optimization of both coating procedures for pre-coating as well as for the bulk plaque coating (and more careful reproduction of all steps and operations at the stage of the specimen preparation according to Figs. 7 and 8) resulted in somewhat better reproducibility of the measurement data. Nevertheless the results of some of the measurements exceeded the average values very much. Particularly, this could be associated with over-penetration of the glue into porous plaques resulting in accidental bonding of the glue to the substrate.

Fig. 10 offers a typical example of the results obtained when adhesion properties were measured on the plaques produced from low-density fractions of 255 Type powder. Two powders (Lots No. 255-1 and No. 255-2 in Table 1) with apparent or bulk density of 0.4 and 0.3, respectively were tested by means of pasting of the corresponding slurries onto plain and pre-coated substrates. As can be seen from Fig. 10, the data obtained for both types of powder (255-1 and 255-2) were very similar from the point of view of the general effect of pre-coating layer on adhesion strength.

The results given in Fig. 10 show a clear and dramatic effect of the pre-coating layer on adhesion performance. The adhesive strength for the plaques produced without a pre-coating was consistently less than 0.2 MPa with an average strength of about 0.1 MPa. On the other hand the substrates pre-coated with 210 powder had strengths that were always in excess of 0.3 MPa with an average value

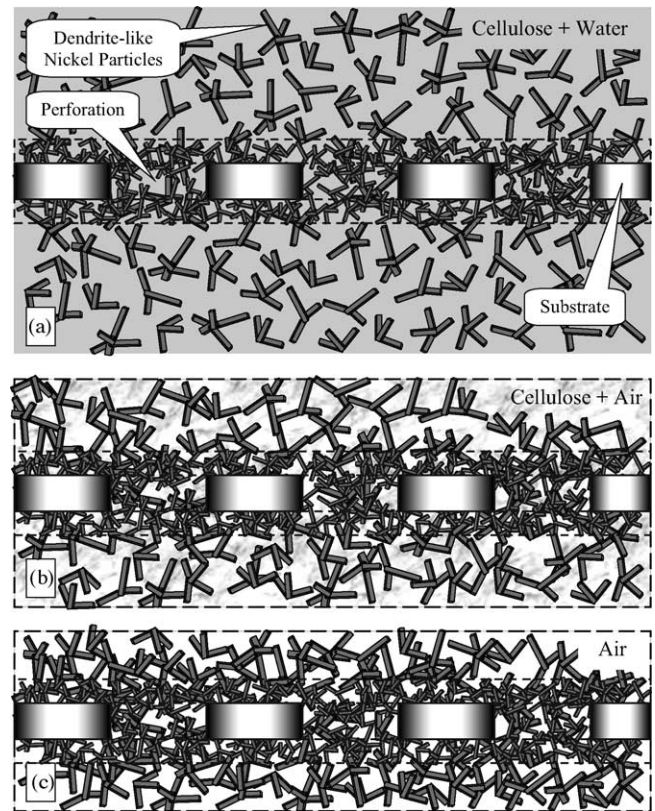


Fig. 12. Schematic illustration of microstructure development in plaques produced with a fine powder buffer layer.

of 0.5 MPa. Thus overall the use of the pre-coating layer increases the adhesion strength by about a factor of 5, indicating a very positive effect of pre-coating on adhesion strength.

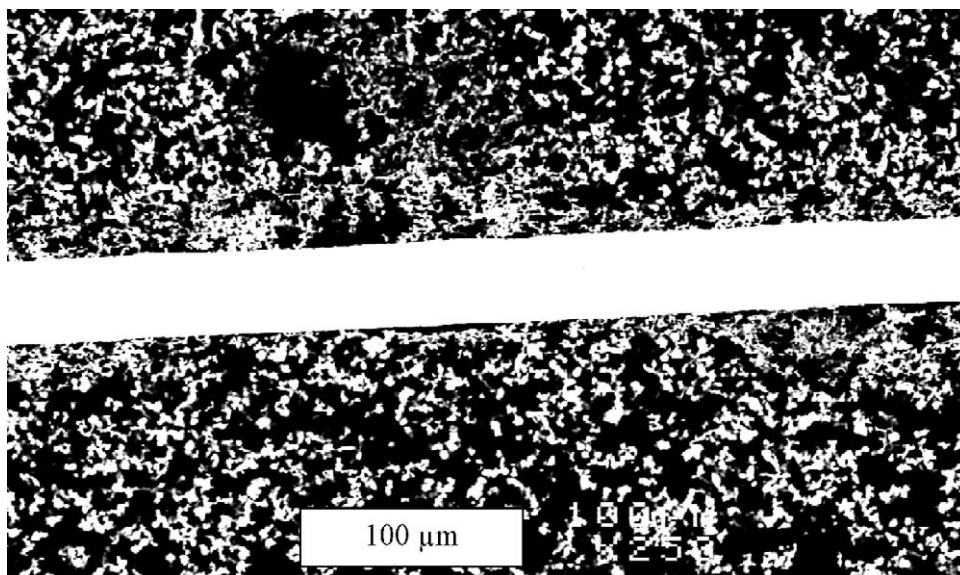


Fig. 13. Scanning electron microscope (SEM) view of the cross-section of the plaque produced on a pre-coated substrate. A higher density layer is noticeable on the vicinity of the surface of the substrate (white band running through the centre of the micrograph).

4.5. Fracture interface

Together with fracture strength data, fractography provides additional proof of the beneficial effect of a buffer layer. The micrographs of the fracture interfaces (Fig. 11) for samples produced on a plain substrate and on a 210 powder pre-coated substrate, respectively illustrate quite different mechanisms of fracture. Notably the diameter of the fracture interface was about 10 mm and varied slightly ($\pm 10\%$) depending on specimen.

In the case of conventional plaque sintered on a plain substrate, the fracture interface was found at the substrate surface, as shown in Fig. 11 (above), i.e. this surface was visible through all fracture interfaces. This illustrates that the bonding between the nickel plaque and the substrate represents the weakest link in the specimen (Fig. 7C).

On the other hand in the case of sintered plaque produced on a pre-coated substrate, the surface of the substrate was almost completely covered with coating (pre-coating) after fracture (Fig. 11, below). This provides direct evidence of the enhanced adhesion between the plaque and the substrate, such that adhesion to the substrate is no longer the controlling feature in these plaques.

We note that the porosity of the pre-coating layer produced from fine 210 powder should be lower than that of the main layer because interaction between fine nickel particles of 210 powder was more intensive due to increased surface area. The high surface area of the 210 particles resulted in greater sintering of the pre-coating layer. This effect is illustrated in Figs. 12 and 13 where a cross-section of sintered nickel plaque produced using pre-coated substrate is shown.

5. Summary

- (1) A vertical tape casting process with periodically contacting blades and corresponding accessories has been designed, produced, and studied. Thin and uniform buffer layers containing fine Ni powder (INCO-110 and INCO-210) with surface density ranging from 1 to 10 mg cm⁻² were successfully pre-coated on perforated substrates using this apparatus. Reproducibility of the results with respect to the surface density of the coatings produced using the same starting slurry and accessories was reasonably high (3%).
- (2) The double-sided vertical tape casting process with flat Doctor Blades was applied to the pre-coated substrates to produce the main porous nickel plaque.
- (3) Tensile strength test results from a collection of over 100 specimens show a clear positive effect of fine powder pre-coating on the adhesion properties of the plaque.
- (4) For all the specimens produced with pre-coating of the substrate, fracture occurred in the plaque but not on the

substrate/plaque interface. This indicated that adhesion was reproducibly improved and the bonding between the plaque and the substrate is no longer the weakest point.

- (5) Thus, a positive effect of this pre-coating procedure on the final adhesive performance of the plaques has been confirmed. The additional pre-coating process adds an additional step to existing production lines, thus increasing costs. However, the technique may allow for development and use of higher porosity plaques that lead to greater cost savings and benefits in terms of higher electrode capacity. In addition, this process may find applications where reliability of the device is exceptionally important (e.g. aerospace equipment).

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