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Development of electroconductive polyacrylonitrile fibers through chemical metallization and galvanisation

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Abstract

The paper describes the modification of PAN fibres with metallic nickel in order to give the fibre electroconductive properties. This is achieved by two consecutively executed processes. The first process is chemical metallization, involving the immersion of the PAN fibres in a bath containing 0.5 mol l^{-1} $NiCl_2$ and 1.5 mol l^{-1} Rongalite at pH = 5.5 and $T = 288$–293 K. Ni(II) is absorbed in the structure of the fibre and adsorbed at the surface through a complex reaction with the cyanide and carboxylic acid groups present in the PAN chemical structure and the Rongalite reduces the adsorbed Ni(II) to metallic Ni. The second process is galvanisation of the Ni-containing PAN surface (the Ni particles present at the surface form a "seed" layer) in an electrolyte bath using an electrolyte with 150 g l^{-1} of $NiSO_4$ at pH 5–6 and room temperature. The resulting fibre showed a specific electrical resistance of the order of 10^{-6} Ω m, which is a promising result.

1. Introduction

The synthesis [1, 2], characterization [3–5] and applications [3–6] of conductive polymers and fibres constitute an important field of research [6].

Electroconductive fibres can be obtained by various methods. Among these are: the synthesis of a conductive fibre similarly to the synthesis of conductive polymers; blending common non-conductive fibres with electroconductive fibres, such as stainless steel or carbon; synthesis of polymers that contain a carbon or metal [7]; the metallization [8–12] of fibres. This last is the method most closely related to the technology described in this paper. Metallization means that metal salts are taken up by a fibre and reduced to their metallic conductive form using a reducing agent. Frequently this process is completed by galvanic surface coating in order to interconnect the initially absorbed metal particles better.

The main applications of electroconductive fibres and textiles are for shielding effects [8] and discharge purposes [13, 14]. In clothing, they act as a faraday cage for human beings and/or equipment, while in carpets they avoid charging of the carpet and/or material that rubs on it.

In a previous paper [15] PAN fibre production was discussed and optimized as a function of the electroconductive, chemical and mechanical properties of the resultant fibre. The chemical metallization of these fibres offers the possibility of obtaining highly conductive fibres: chemical coating is very flexible, being suitable to almost any substrate. Its main advantage is that it gives the PAN fibers high conductivity without significantly altering other properties such as density, flexibility and handling of the substrate. Thanks to these characteristics this type of fibre can easily be processed by means of standard textile technology. For example it can be subjected to additional galvanic metallization. This paper describes both the metallization process parameters and the subsequent galvanic coating procedure.

The purpose of this research is to develop electroconductive fibers in an economically feasible way that allows the production of protective clothing accessible to people in relatively poor countries such as those formerly part of the Soviet Union. The key element here is the possibility of producing these fibers using feedstock available in these countries. Production of such fibers in industrialized countries and/or with feedstock from those countries would make production costs prohibitive. The envisaged applications are mainly in heating and shielding.

This work is the result of a collaborative project between Belgium and Uzbekistan. The availability of Ni and PAN-production plants in Uzbekistan justifies the use of these compounds. However, Ni causes allergic reactions, which is a problem when used in protective clothing. This can be circumvented by coating the Ni-layer with a more precious metal chemically or electrochemically.

2. Experimental

Sodium dithionite, Rongalite ($NaOHCH_2SO_2$), sodium hypophosfite, hydroquinone, hydrazinesulfate, hydroxylamine, ethylene diamine tetra acetic acid (EDTA) and nickel(II)chloride, were obtained from Sigma–Aldrich. Polyacrylonitrile fibres were obtained from the NITRON plant in Uzbekistan and from domestic production on wet-spinning devices. The Ni(II) concentration was determined by titration with EDTA.

For the galvanization of PAN fibres a standard galvanization setup was used, as shown in Figure 1. Two (1, 2) cathodic rollers were used to feed the cables with fibre (3) through the electrolyte solution (4) in the bath (5). Anodes (6) were positioned in the bath in order to be able to apply a potential difference between anode and cathode (roller + cables), resulting in the deposition of Ni on the fibre surface. The composition of the electrolyte solutions used was determined by the purpose of this investigation and is given in Table 1. The capacity of the bath was about 50 l. The fibers and yarns were pulled through the bath at a velocity of about 1 m per minute, resulting in a contact time between fibre and solution of about 2 min.

The following equipment was used for analysis and characterization of the metallized polyacrylonitrile fibres: electronic microscope PEM-100 (Russia), scanning electronic microscope REM-200 (Russia), IR-spectroscope UR-75 (Russia), Rentgen DRON-3M (Russia), optical microscope MBI-6 (Russia), Derivatograf MOM (Hungary), X-ray photo-electron spectroscopy (Perkin Elmer PHI ESCA 5500 system) and Raman spectroscopy (system 1000 dispersive, Renishaw).

For the conductivity of the treated samples the simple fundamentals of a division measurement over a known resistor and an unknown one, being the sample, were applied (Figure 2). A resistor of 1K ohm was used in series with the unknown sample resistance. The applied potential was varied from 1 to 20 V over both resistors from DC to AC and with a change in frequencies for the AC behaviour. The resulting unknown resistance was calculated with the following formula (Equation (1)):

$$R_{\text{unknown}} = \frac{(V_{\text{tot}} - VR_{\text{known}})}{VR_{\text{known}}} \times R_{\text{known}} \tag{1}$$

For the measurement of the resistance, a self-written program in labview, capable of measuring all values at once with a high accuracy and sample rate, was used. The calculated resulting resistance was the same value every time, which shows the typical behaviour of a passive component very similar to a normal resistance. It is also important to note that no capacitive or inductive effects were measured or seen through the whole chain of measurements.

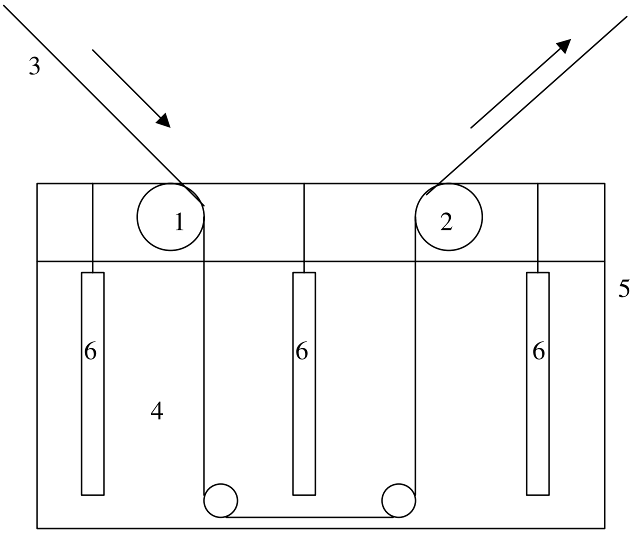

Fig. 1. Scheme of the galvanisation setup with (1, 2) rolling cathodes, (3) chemically metallized yarn, (4) electrolyte solution, (5) galvanisation bath and (6) anodes.

Table 1. Composition of the electrolyte solutions used for the galvanisation of the PAN fibres

Composition (g l^{-1}) and parameters of electrolyte	Electrolyte solution		
	Number 1	Number 2	Number 3
$NiSO_4$	72	145	290
Na_2SO_4	45	45	–
$MgSO_4$	–	27	55
H_3BO_3	22	22	27
NaCl	7	7	4
NaF	–	–	–
pH	5.6–5.8	5.0–5.5	3–5

3. Results and discussion

3.1. *Stability of the reducing agent in aqueous solution*

Prior to stability testing, a preliminary metallization of PAN fibres was performed using different types of reducing agents. The metallization itself was performed in pH = 5.5 solutions containing 0.3 mol l^{-1} of Ni(II) and 0.6 mol l^{-1} of reducing agent. It was found that from sodium hypophosfite, hydroquinone, hydrazinesulfate, hydroxylamine, sodium dithionite and Rongalite, only the last two gave satisfactory results and were able to reduce Ni(II) to its metallic form and so only with these two reducing agents were PAN fibres modified into conductive fibres. Therefore, it is clear that at this stage in our knowledge only sodium dithionite and Rongalite should be used in further investigations.

First, the stability of Rongalite and sodium dithionite in solution was investigated. From the literature it is clear that sodium dithionite is relatively unstable over the entire pH range [16–20]. Our experiment, executed at pH = 5.5, showed that sodium dithionite indeed decomposes relatively fast, while Rongalite remained stable at room temperature. At elevated temperatures (>330 K) Rongalite decomposed very slowly (with a rate of 0.005 mol l^{-1} h^{-1}). Its decomposition rate was independent of the concentrations of Rongalite, which indicates that this rate is only an apparent value. It is assumed that the oxygen uptake rate in the solution determines this apparent rate because oxygen is a compound taking part in the reaction [15] and its limited solubility makes its concentration in solution low.

3.2. *Reduction rate of Ni(II) to metallic Ni in reaction with Rongalite*

In this section of the research, the aim is to investigate the optimal composition of the Ni(II) solution as a function of Ni(II) reduction rate, the total amount of Ni reduced, the fraction of NiS formed and the properties of PAN fibre, such as specific electrical resistance.

In Figure 3 data are shown for the variation of Ni(II) and Rongalite concentrations as a function of time and temperature starting from a constant initial Ni(II) concentration and increasing the initial Rongalite concentration. It should be mentioned that at this point in the research no fibre was immersed in the solution, so the pure kinetic parameters of the reduction reaction of Ni(II) by Rongalite could be studied. Similar experiments were performed with different initial Ni(II) concentrations.

The experiments yielded three significant findings. First, the initial reduction rate (slope of the decreasing Ni(II) curves during the first 15–30 min) is high. In all cases the reaction has finished after about 60 min, independent of the ratio of Rongalite/Ni(II). This is explained by the formation of formaldehyde in the solution as the Rongalite decomposes into formaldehyde and sulfite. Formaldehyde is an inhibitor of the Ni(II) reduction reaction. It is formed by the compound that reduces Ni(II). Therefore this type of inhibition is also called “auto-inhibition”.

Secondly, the Ni(II) reduction rate increases with temperature. In addition, it can be observed that at room temperature it is rather limited and too small for practical use. Higher temperatures should be used in order to obtain higher reduction rates and relatively short production times. The fact that the linear section in the initial decreasing Ni(II) reduction curves shortens with increasing temperature confirms that formaldehyde inhibits further reduction. At elevated temperatures a higher decomposition rate for Rongalite is observed, resulting in higher formaldehyde concentrations in the solution and a larger inhibiting effect. For this reason, the linear part of the initial decrease of the Ni(II) reduction curve is shorter at higher temperatures.

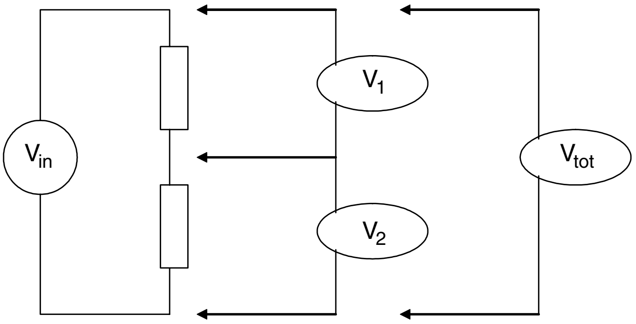

Fig. 2. Electrical circuit for the measurement of the unknown resistance related to the metallized and/or galvanised polyacrylonitrile fibres.

Thirdly, the absolute amount of Ni(II) reduced in the reaction increases with increasing Rongalite concentrations. From the complete set of data it was found that an optimum was obtained for $c_{\mathrm{rongalite}}/c_{\mathrm{Ni(II)}} = 3$ and the optimal value for the absolute concentrations was 0.5 mol l^{-1} of Ni(II) and 1.5 mol l^{-1} of Rongalite. A small ratio is not favourable because of limited Ni(II) in solution, while a ratio higher than 3 results in the formation of too much formaldehyde.

The reaction rate for the reduction of Ni(II) by means of Rongalite correlates with the following equation:

$$c = c_0 + A\frac{B\tau}{1 + B\tau} \tag{2}$$

where c and c_0 are, respectively, the actual and initial Ni(II) concentration in solution, τ is time (s) and A and B are constants. From the data obtained in this set of experiments A and B can be calculated with good correlation coefficients for the first 20 min of the reaction. At larger reaction times the equation no longer expresses the kinetics because of inhibiting influences from formaldehyde. Table 2 shows the results of A and B for different Rongalite/Ni(II) concentration ratios. The value of K is the correlation coefficient for the obtained values of A and B.

Differentiation of Equation (2) yields information about the reaction rate itself:

$$-\frac{dc}{d\tau} = \frac{AB}{(1 - B\tau)^2} \tag{3}$$

This equation was used to calculate the reaction rates as a function of temperature and Rongalite/Ni(II) concentration ratios; Table 3 shows the results for a ratio of 1.5/0.5. The data in this table confirm the previous conclusion that a temperature of about 333 K produces the most economically and technologically acceptable reaction rate and to avoid a large influence of auto-inhibition by formaldehyde, an unfavourable effect that increases with temperature.

3.3. *Ni(II) reduction by means of Rongalite in the presence of PAN fibres*

During the production of cations containing PAN fibres [15] it was found that absorption of Ni(II) in the fibre structure and adsorption at the surface of the fibre through the formation of complexes with cyanide and carboxylic acid groups of the PAN fibre structure were controlled by kinetic parameters. In order to investigate the influence of the active surface of fibre on the kinetics of the interaction of Ni(II) with Rongalite, the following experiment was conducted: the Ni(II) and Rongalite concentrations in solution were subject to titration in the presence both of equivalent amounts of newly formed and thermofixated PAN fibres and also of PAN fibre precursors such as itaconic acid and acrylonitrile. The data are shown in Figures 4 and 5. First, it can be seen that the quantity of Ni(II) in solution is much smaller when PAN fibre or its precursors are present there. This is only to be expected because apart from the reduction of Ni(II) by Rongalite in solution (see Section 3.2 above), chelate formation also occurs between Ni(II) and PAN active groups (cyanide, carboxylic acid), resulting in a decrease in free Ni(II). In addition, the

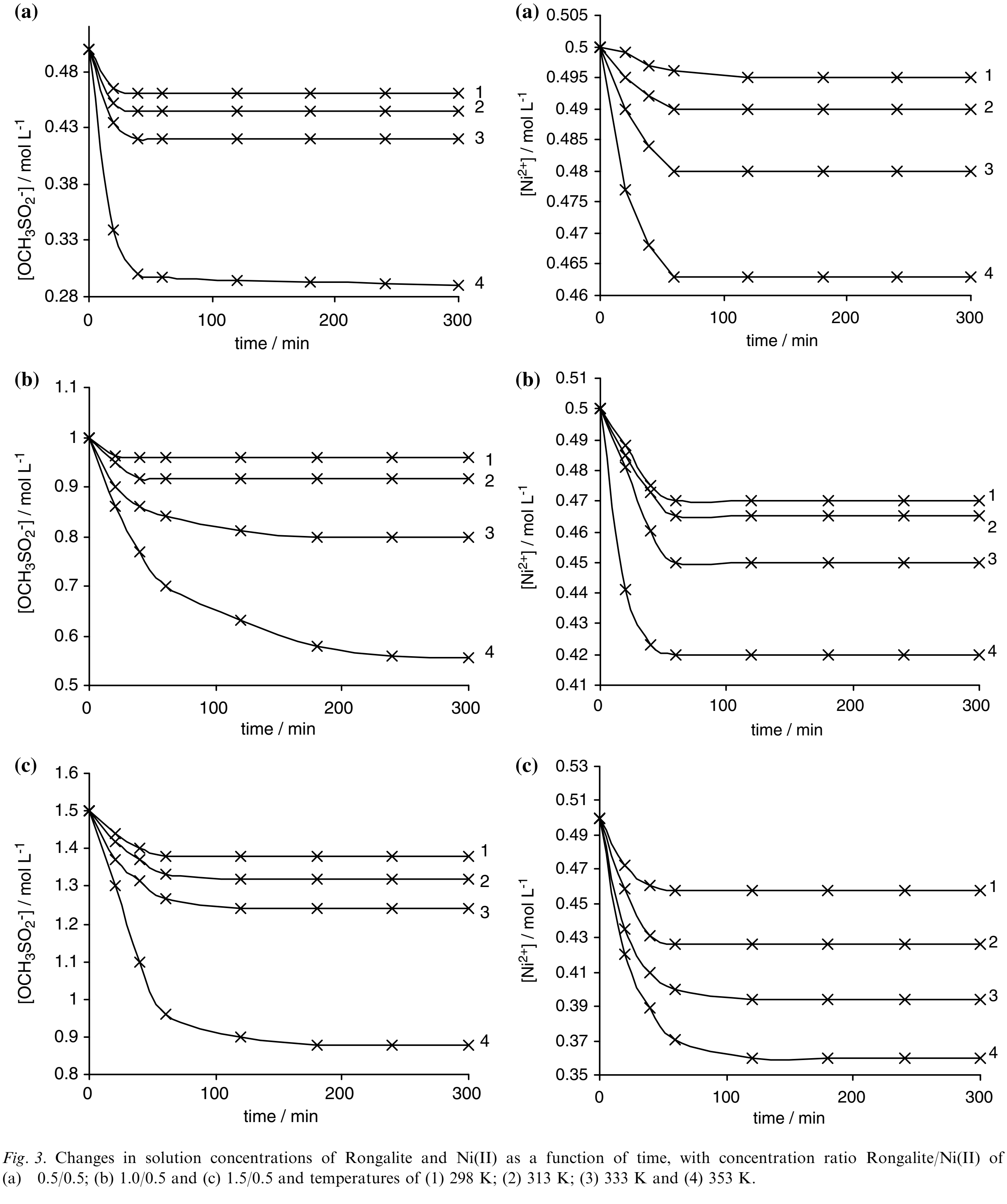

Fig. 3. Changes in solution concentrations of Rongalite and Ni(II) as a function of time, with concentration ratio Rongalite/Ni(II) of (a) 0.5/0.5; (b) 1.0/0.5 and (c) 1.5/0.5 and temperatures of (1) 298 K; (2) 313 K; (3) 333 K and (4) 353 K.

Table 2. Kinetic data for A and B in Equation (2) of the reduction of Ni(II) by Rongalite for different concentration ratios of Rongalite/Ni(II)

c ratio/mol l^{-1}	A 10^2 (mol l^{-1})				B 10^2 (mol l^{-1})				K			
	298 K	313 K	333 K	353 K	298 K	313 K	333 K	353 K	298 K	313 K	333 K	353 K
1.5/0.1	−0.41	−6.65	−9.34	−10.4	8.79	2.85	2.17	2.25	0.999	0.997	0.998	0.998
1.5/0.3	−3.34	−6.61	−8.91	−13.1	3.19	5.80	3.66	3.00	0.996	0.999	0.999	0.998
1.5/0.5	−5.42	−9.00	−11.7	−13.6	5.95	3.14	3.51	3.76	0.998	0.999	0.999	0.999
1.5/0.7	−3.24	−5.13	−11.0	−13.5	4.69	4.20	3.62	2.27	0.995	0.999	0.999	0.999
0.5/0.5	−0.87	−1.01	−2.45	−4.03	3.85	3.22	6.35	5.86	0.994	0.999	0.999	0.999
0.7/0.5	−1.40	−1.81	−4.22	−8.06	8.50	5.12	2.82	6.80	0.999	0.999	0.999	0.999
1.0/0.5	−4.36	−4.83	−5.98	−8.45	2.45	2.98	4.08	8.52	0.995	0.999	0.999	0.999

drop in the concentration of Rongalite is much more pronounced in the presence of PAN fibre and its precursors. As is well known from the literature, Ni(II) complexes formed with cyanide (e.g. $Na_2[Ni(CN)_4]$) are excellent catalysts for the decomposition of Rongalite. Therefore, the formation of complexes between Ni(II) and PAN fibre through cyanide results in the formation of similar complexes and it is these which are responsible for the continuing drop.

Moreover, the drop in Ni(II) concentration is even more pronounced in the presence of the PAN fibres than in equivalent amounts of PAN precursors. Equivalent amounts here means that an equivalent amount of functional groups are dissolved in solution. This difference can be explained by two effects:

- Using precursors, the Ni(II) concentration drops because of the reduction by Rongalite (Section 3.2) and the complex formation with the functional groups of the PAN precursors, followed by reduction.
- Using fibres, the first effect also applies but in addition absorption of Ni(II) in the fibre structure (not only on the surface) occurs. It should also be noted that in the fibre the functional groups are close to each other, which means that complex formations can occur much faster than when PAN precursors are used, especially if the concentration of functional groups in solution is low.

A final observation is that there is a difference in reduction, absorption and adsorption rates of Ni(II) can be observed between newly formed and thermofixated PAN fibres. No explanation was found for this effect but probably the absorption capacity of the thermofixated fibre is reduced resulting in a decrease in the absorption of Ni(II) in the PAN fibre structure.

In a second experiment the kinetics of Ni(II) decrease was followed as a function of time in solutions containing different amounts of newly formed PAN fibre. The results were also calculated using Equations (2) and (3) and an acceptable correlation was found between the two methods (Table 4). From Table 4 it appears that only A is dependent on the amount of fibre present in solution. The value of B is not affected by it. Figure 5 shows the experimental data and the data from the modelling. It can be noted that the kinetics increase when more PAN fibre is present. This is to be expected both because more PAN fibre means a higher capacity to ad- and absorb Ni(II) and also because the concen-

Table 3. Reaction rates for the reduction of Ni(II) by Rongalite in solution at different temperatures using Equation (3)

Temperature (K)	Reaction rate, $V\times 10^4$ (mol l^{-1} min^{-1})
298	6.72
313	10.66
333	14.18
353	16.70

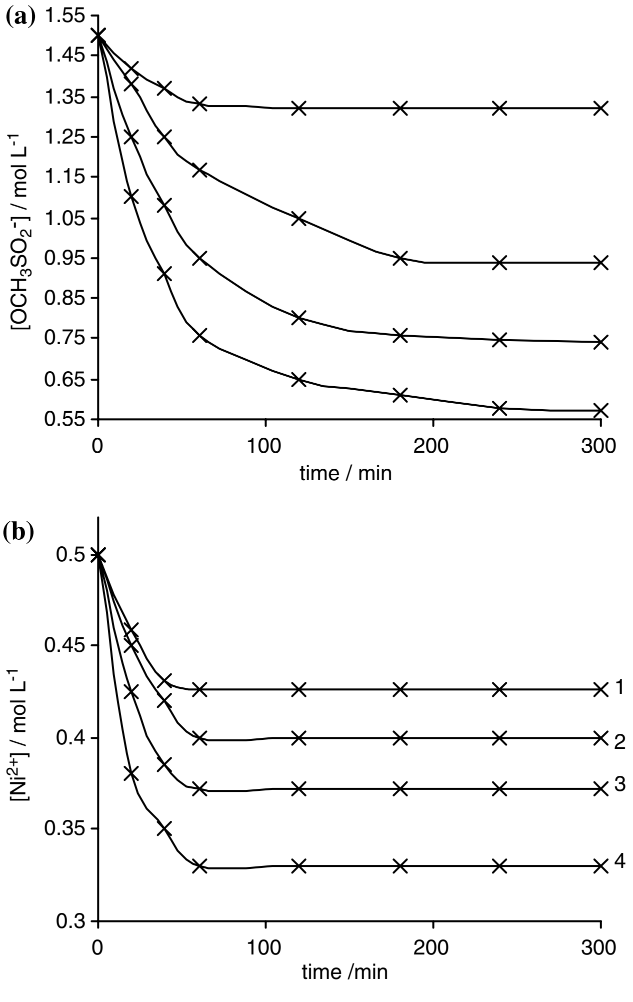

Fig. 4. Changes in solution concentrations of Rongalite and Ni(II) for an initial concentration ratio Rongalite/Ni(II) of 1.5/0.5 as a function of time containing (1) only Ni(II) and Rongalite; (2) thermofixated PAN fibre and (3) newly formed PAN fibre.

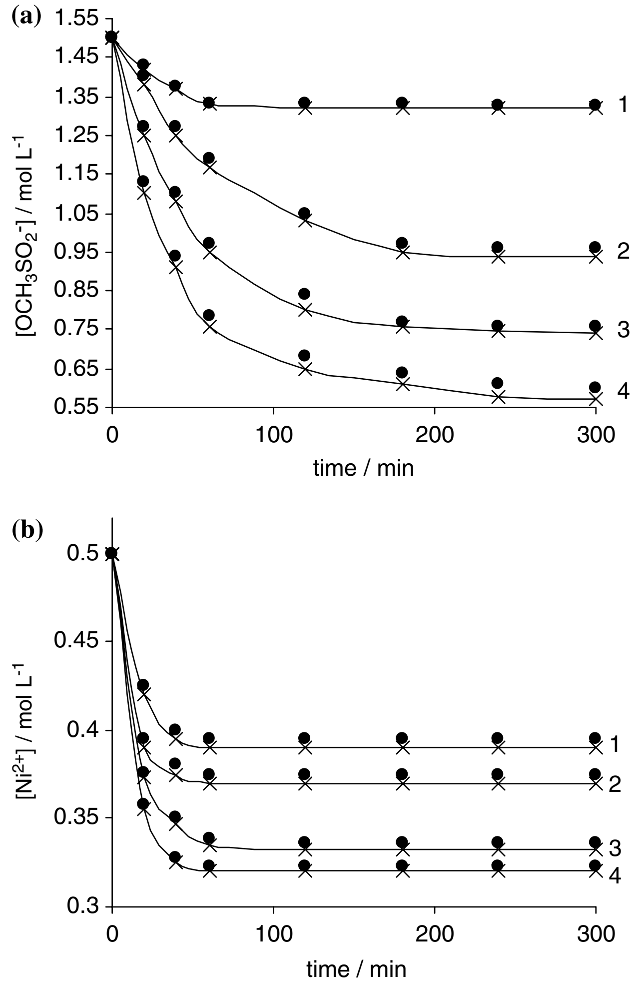

Fig. 5. Changes in solution concentration of Rongalite (a) and Ni(II) (b) for an initial concentration ratio Rongalite/Ni(II) of 1.5/0.5 as a function of time and at 313 K, containing (1) only Ni(II) and Rongalite; (2) 4.6 g l^{-1} newly formed PAN fibre; (3) 20.0 g l^{-1} newly formed PAN fibre; (4) 29.6 g l^{-1} newly formed PAN fibre (×) and equivalent amounts of PAN fibre precursors. Data from the modelling using Equations (2) and (3) are given in "●".

tration of Rongalite drops faster as a result of more catalytic decomposition through interaction with Ni–cyanide complexes.

Several cables of PAN fibres were obtained through an optimised wet-spinning process [20] followed by chemical metallization in a pH = 5.5 solution at 333 K and containing 1.5 mol l^{-1} of Rongalite and 0.5 mol l^{-1} $NiCl_2$ resulting in a specific electrical resistance of $2.5 \times 10^{-4}\,\Omega$m. These fibres contain about 5.5% Ni, consist of about 40 000 elementary fibres and have a weight of 15.3 g m^{-1}. Their specific electrical resistance, although lower than the untreated fibre, is still much higher than for a metallic conductor. However, because of the adsorption capacity of PAN fibres for Ni(II), through their cyanide and carboxylic acid groups, a relatively large fraction of Ni is present at the surface of the fibres. These Ni-centres form a sort of "seed" layer that can be used as a substrate for growing a Ni-layer using an electrodeposition method in a plating bath, a process known as galvanisation. This is described in the following section.

3.4. *Galvanisation of Ni-metallized PAN fibres*

Galvanisation of the metallized fibre will improve its properties as an electrical conductor because of the formation of a continuous metallic coating at its surface. In this respect, the "seed" layer formed during metallization (see Section 3.2) is crucial for a good adhesion between the metal layer and the PAN fibre structure. In galvanisation it is the electrolyte solution used that determines the final properties of the coating and the textile fibre and yarn. The most important properties are surface coverage, continuity and uniformity of the layer, its thickness and homogeneity and specific electrical resistance. The values of these parameters can be determined from the electrical current measured during galvanisation as a function of applied potential difference between anodes and cathodes and by spectroscopic methods showing the structure of the deposited layer. However, the measured current is dependent not only on electrochemical parameters such as the type of electrolyte solution and applied potential, but also on geometrical parameters. In order to keep the latter constant only one electrode setup (see Section 2) was used in this investigation.

A first parameter to be studied is the applied potential difference between anode and cathode. This potential is not necessarily equal to the actual potential difference between the electrodes because ohmic drop effects decrease the tension applied between the electrodes. Examples are anode polarization, tension failure, IR-drop of the electrolyte solution and the specific electrical resistance of the fibres and yarns. This means that relatively high potential differences should be applied (a few volts) in order to obtain an optimal potential difference over the anode and cathode. Figure 6 shows

Table 4. Changes of *A* and *B* as a function of PAN fibre quantity in solution for an initial Rongalite/Ni(II) concentration ratio of 1.5/0.5 at 313 K for 20 min

PAN fibre quantity (g l^{-1})	A 10^2 (mol l^{-1})		B 10^2 (mol l^{-1})		K		$V \times 10^4$ (mol l^{-1} min^{-1})	
	Fibre	Model	Fibre	Model	Fibre	Model	Fibre	Model
4.6	−0.155	−0.164	−0.084	−0.097	0.999	0.999	18.2	18.3
20.0	−0.166	−0.175	0.083	0.106	0.999	0.999	19.5	19.1
29.6	−0.177	−0.180	0.081	0.096	0.999	0.999	21.1	21.2

the evolution of the measured electrical current between anode and cathode as a function of time for several applied potential differences in three electrolyte solutions. It can be noted that for applied potential differences smaller than 6 V an increase in the electrical current is detected. For potentials above 6–8 V, an initial increase followed by a decrease is observed.

The increase of current at small applied potentials (<6 V) is caused by the electrodeposition of Ni(II) at the fibre surface resulting in an increase of its conductive properties, so that more electrical current can pass the cable per time unit. After about 15 min it reaches a constant value. At that moment the surface is fully covered (confirmed with XPS analysis) with Ni. Further deposition continues but no longer affects the conductive properties of the deposited layer.

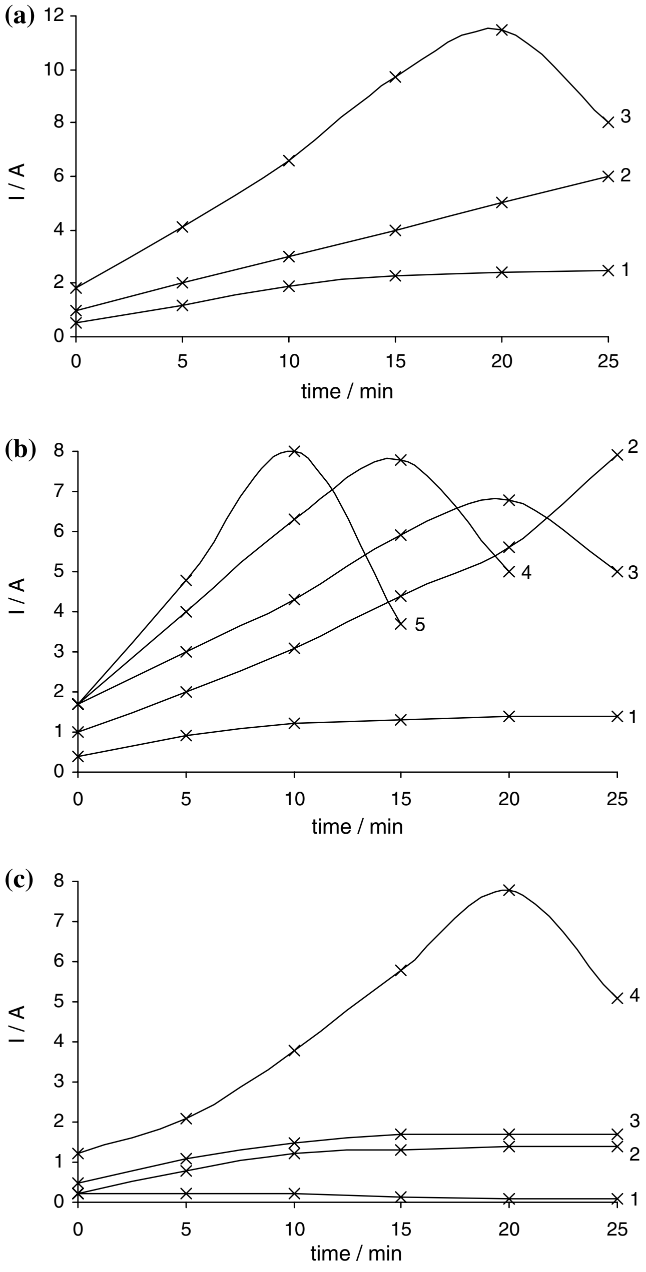

Fig. 6. Current–potential curves recorded in the galvanisation bath shown in Figure 1 during deposition of Ni(II) on metallized PAN fibre surfaces in electrolyte solutions (a) number 1, (b) number 2 and (c) number 3 for applied potential differences of (1) 4 V, (2) 6 V, (3) 8 V, (4) 10 V and (5) 12 V at 298 K.

At higher potential differences the electrical current reaches a maximum. The decrease in electrical current is the result of various effects. It should be kept in mind that applying higher potential differences includes the risk of side reactions such as the decomposition of water with formation of oxygen at the anode and hydrogen at the cathode. These two compounds have a limited solubility in water and thus form oxygen and hydrogen air bubbles at the surface of the anode and the yarn resulting in an increase in the specific resistance of the system. In addition, the reduction of water to hydrogen consumes hydrogen ions in the vicinity of the cathodes, making the pH increase locally at that level and causing precipitation of Ni(II) as $Ni(OH)_2$ at the surface of the cable and cathodes. This effect also increases the specific resistance of the cables because of the deposition of a non-conductive $Ni(OH)_2$ layer. The presence of this compound at the surface of the fibres is confirmed by Raman spectroscopy but only when a maximum is observed in the current–potential curves. That also confirms the fact that at lower applied potentials the decomposition of water does not occur.

Minor differences between the three electrolyte solutions can also be observed. First, electrolyte number 3 only shows a peak maximum in the current–potential curves only at potentials higher than 8 V. This is only to be expected because its pH value is smaller, but it means that this electrolyte solution possesses a higher buffer capacity against consumption of hydrogen ions in the vicinity of the fibre surface, avoiding hydrogen gas formation and $Ni(OH)_2$ precipitation. Secondly, at a potential of 4 V no deposition occurred in electrolyte solution number 3, indicated by no increase in the measured electrical current and confirmed by XPS data. The lower pH also plays an important role in this case. Because of its smaller value the applied potential difference does not overlap with the potential window in which the reduction of Ni(II) occurs. Therefore no deposition is observed.

In an industrial galvanisation line it is not the potential difference applied between anode and cathode that counts but the current that is measured because this current reveals information about how much of the compound is deposited. In industry, therefore, a constant electrical current is applied, not a potential difference. However, care should be taken that the applied current does not cause high potential differences. Otherwise the unfavourable effects of an increase in the specific electrical resistance of the PAN fibres will appear. The need for this precaution was verified in an additional experiment, which found that a current density of about 0.025 A dm^{-2} should be applied at the first cathodic roller (1 in Figure 1). This may seem small but can be explained by the relatively high

Table 5. Relative variations of amount of nickel and specific electrical resistance in individually cut PAN fibre pieces obtained through chemical metallization and galvanisation

Index of electrolyte	K_{Ni} (%)	$K\rho_v$ (%)
Number 1	31.8	66.1
Number 2	20.0	62.3
Number 3	76.0	82.6

resistance of the fibres at the initial stage of the process. At the second cathodic roller (2 in Figure 1) a much greater density of 0.5 A dm^{-2} should be applied because at this roller the electrical resistance of the cables, which causes a large ohmic drop, should be taken into account.

Finally, experiments were performed applying current densities of 0.025 and 0.2 A dm^{-2} at the first (1 in Figure 1) and second (2 in Figure 1) cathodic rollers respectively. Galvanisation time was 12 min, after which the galvanised cables were cut into 100 pieces of each 10 cm each and the variation factors of the contents of nickel in fibre K_{Ni} and of the specific electric resistance of fibre – $K\rho_v$ were determined. The variations between the individual pieces are summarized in Table 5 for the different types of electrolyte solution. This table shows that differences of 60% in specific electrical resistance were obtained. However, this is acceptable as for all the individual pieces a specific electrical resistance of the order of 10^{-6} Ω m was obtained, which reveals good conductive properties. More important is the variation in the amount of Ni deposited. These values clearly show that electrolyte number 2 provides a much better uniformity and homogeneity in the deposited layer than other electrolyte solutions. This can be explained by the fact that the concentration of Ni(II) in electrolyte solution 3 is much too high, resulting in too much Ni(II) deposited in a short time, while for electrolyte solution 1 the concentration of Ni is too small, resulting in a concentration polarization (too large local drop of the concentration) in the vicinity of the cable surface. Additional experiments with shorter galvanisation times revealed that the minimal value for the specific electrical resistance was obtained after about 5 min, about 8 g m^{-1} of Ni having been deposited.

It can therefore be concluded that the galvanisation process should be executed with the following parameters:

- current density of first cathodic roller: 0.025 A dm^{-2},
- current density of second cathodic roller: 0.2 A dm^{-2},
- electrolyte composition: number 2 (Table 1) with $c_{\mathrm{Ni(II)}} = 150$ g l^{-1} and pH = 5,
- temperature: 298 K. This results in PAN fibres with the following properties:
- 23 ± 1 g m^{-1} of weight (after metallization + galvanisation),
- specific electrical resistance $= 5.8 \pm 1.8 \times 10^{-6}$ Ω m.

4. Conclusion

PAN fibres were subjected to chemical metallization using Ni(II) and Rongalite as reducing agents, followed by galvanisation in Ni(II)-containing electrolyte solutions. The methods used were successful in obtaining metallized PAN fibres with promising electroconductive properties. This combination of a relatively simple chemical and electrochemical method has a lot of potential in industry and is economically feasible.

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