

Attempt to Apply Surface-Conductive PAN as a Precursor for aPAN Ionic Electroactive Polymer Gel Fabrication

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Abstract

Chemically activated polyacrylonitrile (aPAN) displays ionic electro-mechanically active polymer properties. Thin, gel-like fibre is a technically feasible form of aPAN, as it quickly shrinks or swells in response to a variation in electrolyte pH, soaking it in. A prerequisite for direct electrical stimulation of aPAN fibres through electrolysis-produced variations in pH is their electrical conductivity, commonly achieved by complex surface modification of already-formulated aPAN. The paper presents an alternative approach involving the exploitation of electro-conducting surface-modified PAN fibres as a precursor for fabrication of aPAN. The electrical conductivity of precursor PAN fibres was achieved by the chemical formation of a copper sulfide complex covering.

Key words: electroactive polymer, artificial muscle, activated polyacrylonitrile, electrical conductivity, sulfide, polymer gel.

Introduction

The idea of “artificial muscles” - materials that mimic the mechanical performance of natural muscle tissue - is practically realised in electroactive polymers (EAPs). EAPs are plastics and polymeric composite materials which change their geometric dimensions significantly (or other mechanical properties, such as viscosity or elasticity) in response to electrical stimuli [1]. EAP gels (named as Ionic Polymer Gels IPG) comprise a sub-family of ionic EAPs. IPGs are hetero-phase material systems encompassing solid, cross-linked and partially dissociated polymer (polyelectrolyte) interpenetrated by interstitial liquid (solvent; usually water), remaining in thermodynamic equilibrium with the polymeric matrix. The special feature of IPG is its substantial reversible volume change in response to pH variations. Placing IPG in the anodic or cathodic region of an electrochemical cell allows to electrically churn out changes in the pH of the gel liquid phase and thus produce its shrinkage or swelling as a result of electrical stimuli. From an application point of view it is highly desirable to induce pH changes directly in the volume of the IPG, possibly by means of electrodes deposited on the surface of the gel or hosted directly in its volume. As the kinetics of the electro-mechanical reaction of IPG is limited mainly by diffusion in the liquid phase, the volume change rate depends - among other factors - on the dimensions of the gel actuator. In practice, this means that the elements of artificial IPG muscles

must be constructed in the form of thin, micrometer-in-diameter fibres [2].

A cross-linked polymer with attached groups of polyacrylic acid (PAA) displaying an anionic poly-electrolytic character is often cited in the literature as a typical IPG. It is produced from polyacrylonitrile (PAN) in a two-phase conversion process called “activation”, proposed by Umemoto [3]. This procedure involves the initial thermal oxidation of PAN, which leads to the creation of a PANox form partially cross-linked by thermally-induced pyridine rings, but still containing a certain amount of non-reactive nitrile -CN groups. The subsequent second stage of the process entails the saponification of PANox in hot aqueous solution of strong alkali, leading to hydrolysis of the remaining -CN groups to carboxylic -COOH groups of the PAA acid and the formation of a so-called activated PAN (aPAN) network of presumed structure, shown in **Figure 1** (see page 30).

The resulting aPAN hydrogel alternates its volume in response to a change in pH: in acidic conditions it shrinks, while in alkaline it swells. It is a result of interactions between -COOH and electrolyte-originated protons and changes in the molecular conformational structure of the aPAN cross-linked network according to the molecular reaction mechanism proposed by Schreyer [4]. As transferring aPAN strands between acidic and alkaline solutions is not technically feasible in practical application, a change of pH is thus produced by means of a reversible electro-chemical reaction. Fibres

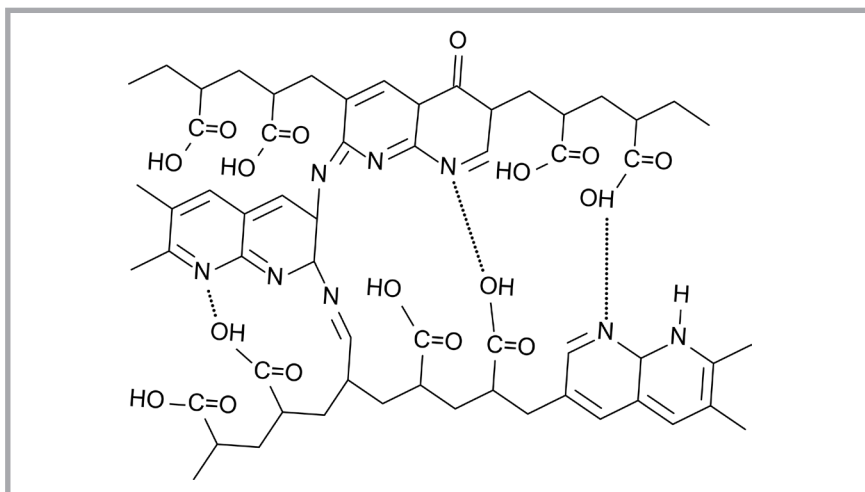


Figure 1. aPAN structure (hypothetical, based on [9]).

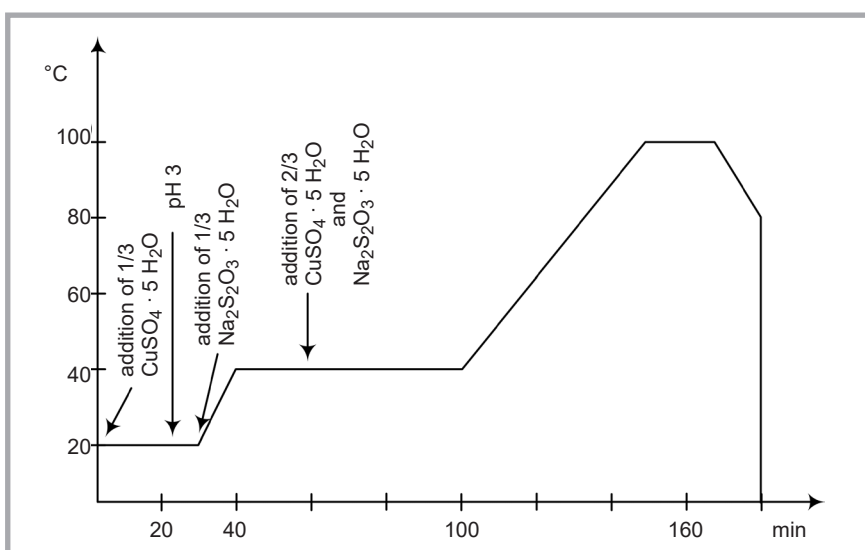


Figure 2. Schematic outline of PAN surface modification process.

of aPAN are located in the direct vicinity of the anode or cathode of the electrolytic cell, where the pH may be electrically varied. However, such an approach is also not perfect as it requires a massive (in relation to aPAN strand dimensions) electrolytic cell and electrodes, which are bulky (e.g. made of metallic mesh) or laborious to make (e.g. by winding a thin Pt wire around aPAN strands). Therefore for a direct electrical stimulation of aPAN fibre its surface must be made to be electro-conductive in order to produce an electrode that stays in intimate contact with the aPAN gel. Such conductivity is achieved either by post-activation chemical metallisation [1] or by making up aPAN composite structures encompassing Ag, polyaniline or polypyrrolle [1]. Hou *et al.* showed that the electrospinning of a PAN solution containing up to 35% of multiwall carbon nanotubes (MWCNT) surface-modified with car-

boxylic groups furnishes PAN-MWCNT composite nanofibres approx. 200 nm in diameter with carbon nanotubes well-aligned along the fibres length [5]. Gonzalez and Walter exploited such an approach to make aPAN fibres electro-conductive by means of carbon nanotubes (MWCNT) and graphite modification. PAN-MWCNT composite nanofibre mats, with significant agglomeration of conductive additive material were successfully produced by electrospinning. However, when subjected to thermal annealing and hydrolysis the integrity of aPAN mats was significantly reduced, producing weak, difficult-to-handle structures not applicable as electrically-activated IPG [6]. An approach to apply activated carbon to compose electrodes and to exploit the electric double layer effect (as exercised in supercapacitors) for actuation in supramolecular nanocomposite ionogel containing UV-photopol-

ymers hydroxyethyl methacrylate interpenetrated with ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate), was recently exploited by Liu *et al.* as a method to produce non-water based IPG applicable for a wide temperature range [7].

Treatments used to establish conductivity in aPAN are thus complicated, multistage, and require toxic, explosive or flammable chemical reagents. Moreover such conductive phases are non-replicable, unstable and weakly bonded with the IPG fibre core. As a result their delamination after a very limited number of electrochemically-induced shrink-swallow cycles is observed, leading to the disappearance of electrically-driven mechanical action.

The paper presents an experimental attempt to reverse the conventional formulation sequence of PAN → aPAN → → conducting aPAN. In such a customized approach, raw PAN fibres were initially made to be surface-conducting and then exploited as a precursor to produce aPAN. A wet xanthate process was adopted to produce surface-conductive PAN by surface modification to form a superficial layer made of copper sulfide complexes bonded to nitrile functional groups of the underlying PAN fibre core. It provided a continuous, highly conductive, robust and strongly PAN fibre-bonded covering resistant to wear and multiple washing. It is a well-established process developed and commercially employed by the Textile Research Institute. Electro-conducting PAN fibres commercially produced this way are known under the brand name Nitril-static (N-S) and are used to manufacture charge dissipative yarns and nonwovens [8]. Surface-conducting PAN precursor with a copper sulfide complex covering was then subjected to the classical chemical activation process, involving thermal oxidation and saponification, transforming firm PAN fibres to gel-like aPAN filaments displaying properties representative of IPG.

Materials and methods

Commercially available PAN fibres (Dralon X 100, Dralon GmbH, Germany) of 20 - 25 μm diameter and 3.3 dtex linear density in the form of 60 mm long staples were used in a wet process leading to the formation of an electro-conducting covering. A proprietary xanthating method developed by the Textile Research Institute (Lodz, Poland) consisted of several

wet treatment steps undertaken in a hot water bath containing:

- 5% w/w $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ and
- 7% w/w $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$

(concentration given in relation to the mass of the fibres processed). The acidity of the reaction bath was kept at pH 3 by the addition of a suitable amount of formic acid. **Figure 2** illustrates the schematically thermal and reactional treatment steps leading to the formation of copper complexes strongly bonded to the PAN surface. Finally the fibres were thoroughly rinsed in distilled water and hot air dried. The above-mentioned xanthating process was also applied in order to reconstitute the electro-conductivity of aPAN gel fibres, which will be discussed later in the text.

In order to obtain aPAN electroactive gel, the PAN precursor fibres were subjected to a traditional two-phase conversion process [4]. First the fibres were thermally oxidised in ambient air at 220 °C for 90 minutes and then slowly cooled down; oxidation process parameters were chosen according to Shreyer [4]. Loose strands of PANox were then bonded into bunches containing a few hundred fibres, for each of which chemo-resistant epoxy resin was used (460 DP, 3M). Bundles of PANox fibres were then subjected to saponification in boiling 1 N aqueous solution of LiOH for 30 minutes. The resulting aPAN gel fibre bundles were finally thoroughly rinsed in distilled water for 30 min.

Microscopic examination and fibre composition analysis was made using an SEM microscope (Hitachi S-3400N, Japan) fitted with an EDS analyser. The reaction of aPAN to pH variation was monitored visually using an optical microscope (MMT 800BT, Microlab, Poland). Measurement of the resistance of individual fibres was carried out using an electrometer (Keithley 6517, USA) working at 10 V test voltage. In order to do that two electrodes made of copper foil adhesive tape (1181, 3M) were affixed to a dielectric substrate and separated by a 10 mm gap. The electrodes were fitted with cable connectors to the electrometer and single polymeric fibres were then attached between electrode pairs using electro-conducting glue (EP77M-F, Masterbond).

■ Results and discussion

The electrical surface conductivity in PAN precursor fibres was related to the continuous copper sulfide Cu_xS_y

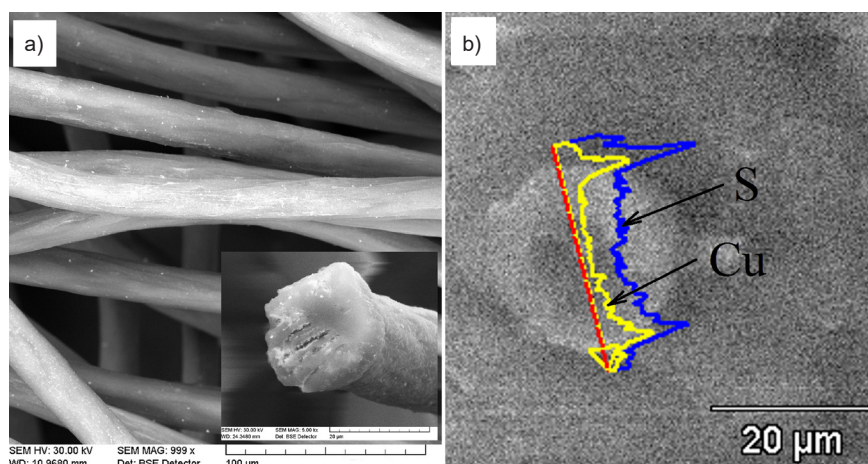


Figure 3. Surface-conducting PAN fibres: a) SEM image, b) EDS-SEM microanalysis of the fibre cross-section.

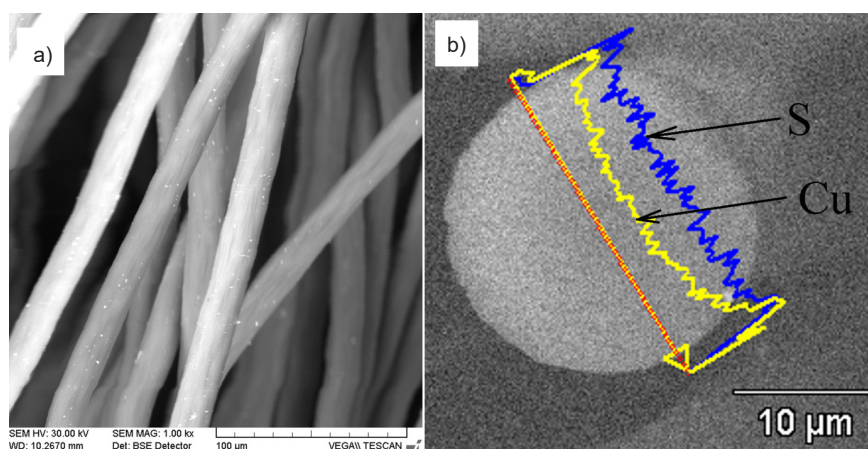


Figure 4. PANox fibres after thermal treatment: a) SEM image, b) EDS-SEM microanalysis of the fibre cross-section.

layer strongly attached to the PAN fibre surface, owing to co-ordinate bonding with PAN nitrile functional groups [9]. Such electro-conductive sulfide cladding displayed both good mechanical endurance and resistance to multiple washing. The as-processed PAN precursor fibres had a distinctive, olive-greenish hue and diameter of approx. 22 µm (**Figure 3.a**). The surface of the PAN precursor fibres was minimally rough (**Figure 3.a** inset) and generally homogeneously, composed of a negligible number of minuscule dust-like protrusions.

EDS-SEM composition microanalysis of the PAN precursor surface revealed C, Cu, S, and O as its main atomic components. The ratio of $\text{Cu}:\text{S} = 1:1$ determined suggested that the main compound present in the superficial section of the fibre was CuS (which may also be responsible for its olive-greenish coloration). The EDS-SEM line composition microanalysis focused on 2 constituents of CuS i.e. Cu and S, and was also carried out

along the cross-section of the fibre (**Figure 3.b**). Low quality SEM image shown in **Figure 3.b** (and also in **Figure 4.b**) was due to the so-called environmental mode used for the EDS-SEM analysis in order that its results not be hindered by the PAN precursor specimen Au metallisation used in the standard SEM mode of operation (the environmental mode uses low pressurization of the SEM chamber and thus residual humidity to disperse electron-beam-generated charges, which, however, results in low quality SEM images fuzzed and blurred due to electron beam dispersion). Such ESD-SEM line analysis indicated, however, that the sulfide covering was not strictly superficial, because the majority of Cu and S atoms were located to a depth of about 2 µm, corresponding to about 20 % of the diameter of the fibres. This fact explains the good adhesion of the conducting layer to PAN fibre and its resistance to wear and wash. The experimentally determined resistance of 1 cm of the PAN precursor fibre was approx. 1 MΩ. As-

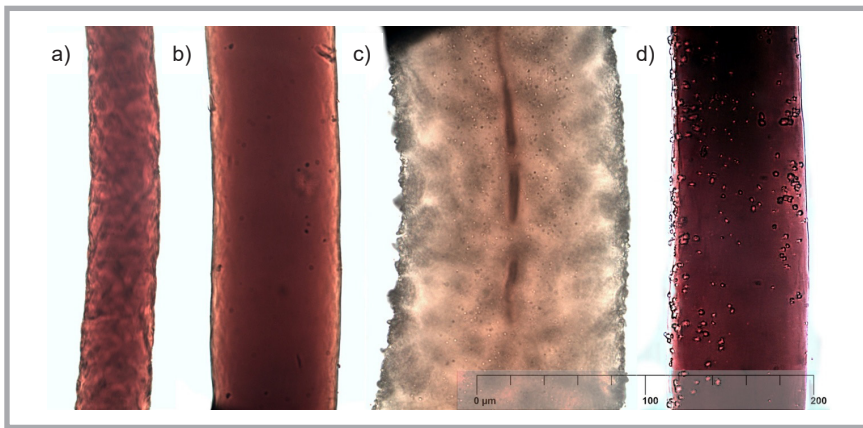


Figure 5. Microphotographs of aPAN fibres at: a) pH 1, b) pH 7, c) and d) pH 14 (explanation in the text).

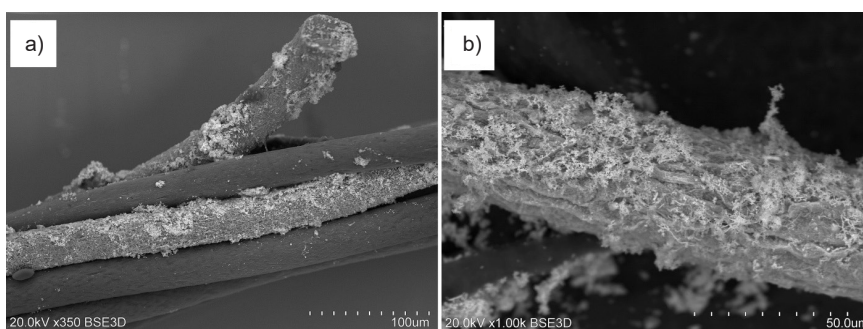


Figure 6. SEM image of aPAN fibres after attempt to reconstitute the surface-conducting sulfide cladding.

suming that the thickness of the sulfide layer was 2 μm , its mean resistivity was approx. 1.2 Ωcm , which stayed in a good agreement with literature data which declared that more than 87% of electro-conducting PAN fibres displayed a resistivity in the range 1 - 5 Ωcm [10].

After the completion of the first phase of the activation process i.e. after thermal oxidation, the PANox fibres become uniformly black. SEM microscopic analysis showed (**Figure 4.a**) that the thickness of the fibres decreased to approx. 18 μm and the microstructure of the oxidized fibre surface was not noticeably distorted. Unfortunately as a result of the oxidation process, fibres lost their initial good electrical conductivity, manifested by a resistance exceeding 1000 M Ω , as experimentally determined for 1 cm long PANox fibres.

EDS-SEM composition analysis made along the oxidized fibre cross section (**Figure 4.b**) indicated evident changes in the distribution of Cu and S in the sub-surface region of the fibre as well as a substantial change in the Cu:S ratio in this area. It suggests that the sulfide layer was partially diffused towards the fibre

core and supposedly some part of the original CuS was also thermally transformed into other Cu-S compounds. Literature sources provide a different CuS transformation temperature: 220 $^{\circ}\text{C}$ [11], 130 - 330 $^{\circ}\text{C}$ [12], 181 - 313 $^{\circ}\text{C}$ [13] and the temperature range cited depends mainly on the way CuS was synthesised. It can therefore be presumed that when the PAN precursor fibres were heated a thermo-chemical transformation of CuS into chalcocite Cu_2S or digenite $\text{Cu}_{1.8}\text{S}$ may have already started at 130 - 180 $^{\circ}\text{C}$. The resulting black colour of the PANox precursor fibres further supports this assumption as chalcocite is a black mineral. As a result of CuS diffusion and transformation into Cu-rich forms, a significant deterioration of electrical conductivity was observed. Chalcocite Cu_2S is substantially more resistive ($5.7 \times 10^5 \Omega/\text{sq}$ [14]) than digenite $\text{Cu}_{1.8}\text{S}$ (346 Ω/sq [14]) and both display p-type semiconducting properties. On the other hand covellite CuS exhibits metallic-like conduction [15] and is characterized by low resistivity (3.6×10^{-6} - $6.3 \times 10^{-7} \Omega\text{m}$ [16]).

Despite the negative result of the first phase of the activation i.e. obtaining

non-conductive PANox fibres, they were subjected to saponification in order to test whether such altered PANox fibres may be correctly saponified to produce the aPAN form, whether sulfide surplus may interfere with the saponification process, and whether it is possible to recreate a sulfide covering on such gel aPAN fibre boundless using the xanthating method. Saponification process parameters, including the use of LiOH, were chosen according to Choe [17]. PANox fibres were bonded together with chemo-resistant glue into boundless prior to saponification because loose PANox fibres tend to form unusable tangles when boiled. As a result of saponification, proper elastic fibres of aPAN were fabricated, which significantly contracted when the pH was reduced from 14 (1 N LiOH) to 7 (distilled water). Strong volumetric variations of gel aPAN fibres caused by a pH shift were clearly evident in microscopic images (**Figure 5**). An increase in pH from 1 to 7 was accompanied by over 180% relative thickness expansion of the fibres from approx. 40 μm (**Figure 5.a**) to approx. 75 μm (**Figure 5.b**). A further increase in pH up to 14 brought about a thickness rise of up to approx. 135 μm (**Figure 5.c**), almost reaching the 330% relative thickness change related to the pH range 1 - 14. Due to the isotropic character of the expansion process, the length change of the fibres was expected to be similar. It was also observed that among the correctly pH-responding aPAN fibres there were some exotic fibres that reacted correctly by compression in acidic conditions but displayed virtually no volumetric change in the pH range 7 - 14 (**Figure 5.d**). However, the reason for this effect was unidentified.

Finally an attempt was made to re-create a sulfide complex layer on aPAN gel fibres using the same procedure as applied to produce the covering on PAN precursor fibres. However, as a result only a certain fraction of aPAN gel fibres was covered with a layer of Cu_xS_y (**Figure 6.a**) and the coating was deposited only along parts of the fibre length. The sulfide layer was not dense and it consisted of porous agglomerates built up on the filament surface (**Figure 6.b**). The re-created coating was therefore completely different in nature from the covering formed on the original PAN precursor fibres, where the sulfide layer was built in the surface and sub-surface part of the fibre and represented its solid section. As the re-formed covering was non-continu-

ous it did not provide a path for electrical current flow, making the aPAN gel fibre non-conductive. The failure in re-creation of the conductive sulfide covering may be identified as related to the minimal amount of -CN functional groups left in the aPAN once the saponification process (turning -CN into -COOH) was terminated. On the other hand, the sulfide formation method required the existence of nitrile groups, which were responsible for creating centers for Cu atom coordination bonding. The areas of aPAN on which the sulfide layer was re-established probably contained residual -CN groups that had not been transformed in -COOH during the course of saponification. Such a flimsy sulfide layer could also have arisen as a result of the precipitation of sulfides from the solution and their physical deposition on the fibre - the spongy structure of the restituted sulfide conglomerates, which was weakly linked to the surface of the fibres, testifying to this assumption. An additional factor which led to the weak coverage of fibres with a properly attached sulfide layer was also related to the necessity to carry out the xanthating process using bundles of aPAN, which seriously hampered the penetration of reagents between individual fibres. As a result, only a minor fraction of fibres was fitted with electrically-conductive surface entities, which translated into the electrical discontinuity of such structures and to the very high electrical surface resistance of aPAN subjected to Cu_xS_y restitution.

Conclusion

It was experimentally shown that electroconductive PAN can be used as a precursor to form proper aPAN gel, responding to a shift in pH from 1 to 14 with a more than 300% relative thickness change. Unfortunately the process of thermal oxidation of the electro-conductive PAN precursor leads to the disappearance of its surface electrical conductivity, associated with the diffusion and thermal transformation of CuS into a less conducting sulfide type. An attempt at restitution of

this layer on aPAN gel fibres was not effective due to the lack of coordination bonding sites, required for the formation of properly bonded CuS. Further experiments need to be performed in search of an effective CuS deposition technique for aPAN gel fibres, which may include the application of dyes which display the capacity of coordinative bonding to metal sulphides [18].

Editorial note

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