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Metallization of Kevlar Fibers with Gold

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Supporting Information


Clean Kevlar Kevlar-Ni (electroless) Kevlar-Ni-Au (electrodeposition)

ABSTRACT: Electrochemical gold plating processes were examined for the metallization of Kevlar yarn. Conventional Sn^{2+}/Pd^{2+} surface activation coupled with electroless Ni deposition rendered the fibers conductive enough to serve as cathodes for electrochemical plating. The resulting coatings were quantified gravimetrically and characterized via adhesion tests together with XRD, SEM, TEM; the coatings effect on fiber strength was also probed. XRD data showed that metallic Pd formed during surface activation whereas amorphous phases and trace amounts of pure Ni metal were plated via the electroless process. Electrodeposition in a thiosulfate bath was the most efficient Au coating process as compared with the analogous electroless procedure, and with electroplating using a commercial cyanide method. Strongly adhering coatings resulted upon metallization with three consecutive electrodepositions, which produced conductive fibers able to sustain power outputs in the range of 1 W. On the other hand, metallization affected the tensile strength of the fiber and defects present in the metal deposits make questionable the effectiveness of the coatings as protective barriers.

KEYWORDS: Kevlar, conductive fiber, electroplating, gold, electrochemical

INTRODUCTION

Polymer metallization is an area of intense activity due to the practical importance of the resulting materials. For instance, metallized polymer films play very significant roles in microelectronics, space and automotive technologies.[1] Metallization imparts useful properties to polymeric components of space vehicles and structures, including protection against degradation processes that can be severe in the harsh environment of low earth orbit.[2] In fact, material erosion together with electrostatic charging are problems that have hindered the realization of space tethers consisting, in the simplest form, of a flexible cable.[3] Tethers have long been considered promising propulsion systems and for specific applications the demands imposed on the physical properties of the flexible cables seem to be met by currently available high strength fibers.[4] Interestingly, an earlier study showed that deposition of μm thick Cu/Ni coatings onto Kevlar fibers, poly(p-phenylene terephthalamide), yielded conductive materials exhibiting good erosion resistance without affecting the mechanical strength of the polymer.[5] Although these results suggested a route for achieving satisfactory tether materials based on the aramid fibers, the methodologies used for metal deposition remain unknown.

Metallized fibers have been of interest to the textile industry because of their practical use in heating and antibacterial garments.[5,6] The appeal for such materials is increasing due to their relevance to textiles that incorporate sensors and/or wearable electronic devices (including processors), energy responsive fabrics and other garment technologies.[7−10] Conducting fibers for electromagnetic shielding have been usually obtained by means of metal vaporization and doping;[11] the former method has also yielded sensors based on metallized Kevlar monofilaments.[12] Electroless metal deposition has been frequently used to treat fibers due to the effectiveness of this procedure in the metallization of plastics.[13] This method has enabled preparation of conductive cotton fibers plated with Cu/Ni and also metallization of PBZT, poly(p-phenylenebenzobisthiazole), fibers with Ag.[14,15] Gold plating on polyacrylonitrile (PAN) fibers has been accomplished at room temperature with an electroless Au(I) thiosulfate bath.[16] Analogous procedures operating at higher temperatures enabled plating of polycarbonate fibers with Au, Cu and Ni.[17] Metallization of aramid fibers has been reported to occur after activating them with a combination of bases and Ag.[18]

Presented here are results from investigation on electrochemical methods for metallization of Kevlar fibers with Au. The aim was to achieve reproducible metallization of aramid yarn because this material exhibits physical properties (such as tensile strength to weight ratio) suitable for some tether applications.[4] Selection of gold seemed logical given that this metal is not affected by the corrosive space environment.[2b] Several electrochemical procedures and an electroless plating process were tested and compared including recently proposed methods that are cyanide-free.[19−21] Au plating was performed on fiber substrates exhibiting low resistivities that were obtained using conventional electroless Ni metallization procedures for plastics.[13] Although sulfite-based electrochemical procedures for gold metallization are also cyanide-free,[19,20] electroless Au deposition in the presence of sulfite ions requires high temperatures.[13] Plating by means of a Au(I) thiosulfate bath was selected given that such system enabled direct comparison at room temperature between electroless and electrochemical

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deposition methods. Au electrodeposition by means of a thiosulfate bath yielded the best results, producing conductive yarns exhibiting significant mass increases and negligible loss of flexibility but the coatings affected the tensile strength of the fibers.

EXPERIMENTAL SECTION

All chemicals were used as received from the manufacturers; deionized water obtained from a Barnstead D7401 purification system was employed to prepare all solutions. KCl, $CHCl_3$, $SnCl_2 \cdot 2H_2O$, NH_4Cl, KOH, and NH_4OH were supplied by Fischer, whereas $NiCl_2 \cdot 6H_2O$, $Na_3Au(S_2O_3)_2 \cdot xH_2O$, and anhydrous citric acid were from Alfa. Hexane, K_2PdCl_4, and $NaH_2PO_2 \cdot H_2O$ were obtained from Aldrich, L-ascorbic acid was from J.T. Baker, CH_3OH was supplied by Aater, and Kevlar 49 yarn was provided by DuPont. Experiments were conducted on samples of Kevlar yarn cut to lengths of 9 and 25 cm, then tied at one end with a knot to prevent the separation of the individual fibers. All Kevlar materials were rigorously cleaned via immersion in an ultrasonic bath containing first CH_3OH, then hexane and finally $CHCl_3$. In each of these steps the polymeric materials were exposed to ultrasound for 10 min and then air-dried. Metallization experiments for electroless coated yarn were performed in water-jacketed glass containers (25 cm in diameter, 15 cm depth), which allowed control of the reaction temperature. Electrochemically coated yarn was metallized in clean open containers (beakers, Petri dish) at room temperature. After every chemical step described below, the resulting fibers were rinsed with deionized water and air-dried. Adhesion of coatings was tested via a 10 min exposure to ultrasound of treated yarn immersed in water to dislodge any metal not firmly bound to the fiber surface. Occasionally, the results were confirmed using the adhesive tape test.[22]

Pretreatment of the fiber surfaces involved first a 1 min immersion of clean fibers in an aqueous solution containing 1 g/L (4.4×10^{-3} M) of $SnCl_2 \cdot 2H_2O$, followed by exposure to a solution containing 2 g/L (1.13×10^{-2} M) of $PdCl_2$ and 0.84 g/L (1.13×10^{-2} M) of KCl for the same amount of time. This two-step process lasted about 5 min. The third pretreatment step consisted of electroless Ni plating, which was conducted by immersing the sensitized Kevlar fibers for 5 min in a nickel bath that contained 30 g/L (0.126 M) $NiCl_2 \cdot 6H_2O$, 60 g/L (0.312 M) citric acid, 10 g/L (9.4×10^{-2} M) $NaH_2PO_2 \cdot H_2O$ and 50 g/L (0.935 M) NH_4Cl. The pH was adjusted to 9−9.4 with a NH_4OH solution (28%) and plating took place at 60 °C. Electrochemical Au metallization occurred via polarization of Ni-coated fibers submersed in an Au bath containing 6.3 g/L (1.29×10^{-2} M) $Na_3Au(S_2O_3)_2 \cdot xH_2O$, 19.8 g/L (0.1 M) sodium L-ascorbate, 15.2 g/L (7.9×10^{-2} M) citric acid and 11.2 g/L (0.2 M) KOH. Also employed was a commercial gold cyanide bath from SMC Inc. (of proprietary composition) that contained 11.8 g/L (4.1×10^{-3} M) $KAu(CN)_2$; diluting this solution by a factor of 10 with water yielded the best results. The fibers functioned as cathodes whereas the anode consisted of a Pt wire mesh and a saturated KCl Ag/AgCl electrode served as the reference. Electrochemical depositions were controlled by means of a BAS CV-27 potentiostat. For comparison, a few experiments were conducted in which Ni-plated fibers were subsequently metallized with an electroless Au deposition procedure described in the literature.[16] In this method the Au bath consisted of a solution with 25.5 g/L (5.2×10^{-2} M) $Na_3Au(S_2O_3)_2 \cdot xH_2O$, 19.8 g/L (0.1 M) sodium L-ascorbate, 15.2 g/L (7.9×10^{-2} M) citric acid and 11.2 g/L (0.2 M) KOH. The reaction was carried out at room temperature and immersion times ranged from 3−30 min.

Coated fibers were characterized in terms of mass gain and conductivity. Mass changes were monitored throughout the coating steps with an analytical balance. The resistance of treated fibers was measured by means of the two-point method using a digital ohm-meter from IET Laboratories model LOM 4000; stretched samples were used to ensure consistency in the analysis. Power output for coated fibers was quantified on an electrochemistry workstation with a modified AFRDE4 Bi-Potentiostat (Pine Instrument Co.) set to galvanostatic mode with the output $I-V$ curves plotted with a BAS X-Y recorder. The current was stepped ~5−10 mA/s while measuring both current passed and voltage dropped across the fiber. An Instron 1122−4400R test machine served to determine the tensile strength of coated and uncoated fibers. Surface morphology was examined with optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For fibers plated with electroless methods, SEM measurements were performed on a Zeiss DSM 940 microscope equipped with an EDS detection system. Specimens were made by immobilizing yarn in plastic pipettes, followed by sectioning the fibers at the pipet tip with a knife and sputter-coating with Au to avoid charging effects. Yarn plated electrochemically was analyzed with a Zeiss EVO 50 VPSEM; these conducting materials needed no additional coating and specimens were prepared by pressing

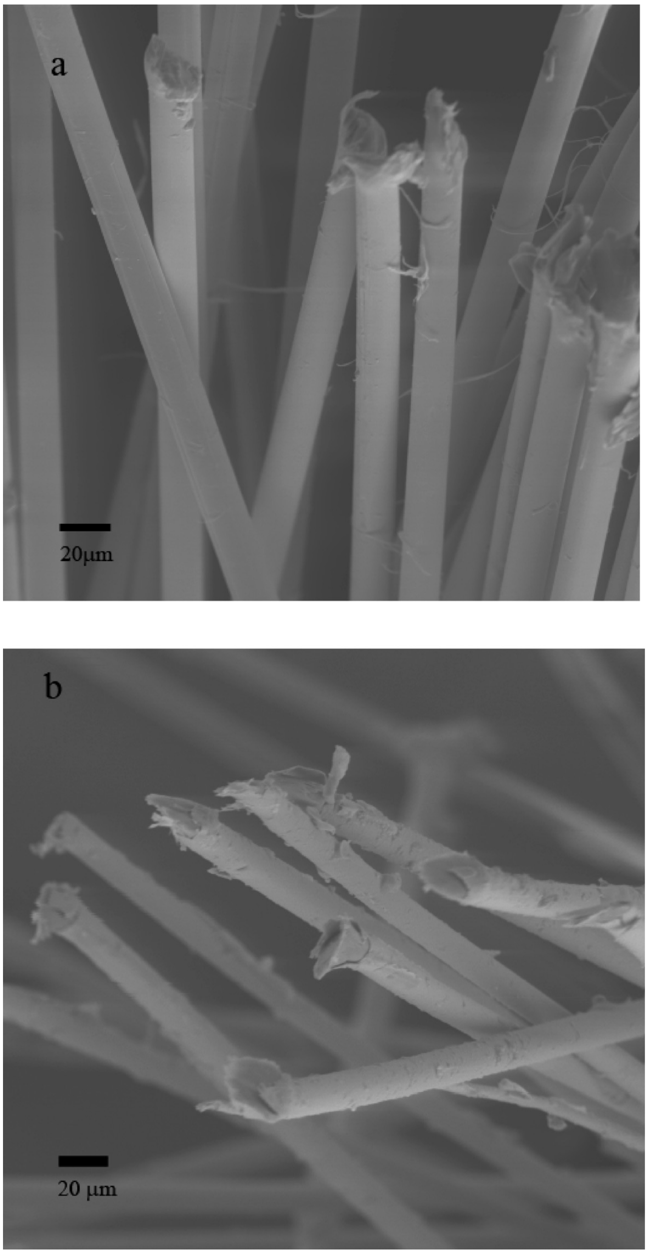

Figure 1. SEM image of (a) clean sectioned Kevlar fibers exhibiting an average fiber diameter of 11.2 μm; (b) sectioned Kevlar fibers coated with a single treatment of electroless Ni plating containing 0.14 g of deposited material per g of fiber.

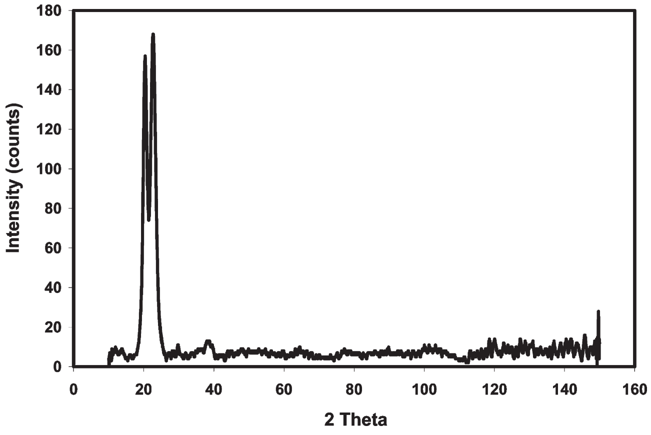

Figure 2. Diffractometer trace of clean Kevlar fibers exposed to Cu K(α) radiation.

metallized fibers onto C-coated tape. TEM analysis was carried out on a Zeiss EM 10CR instrument using 95 nm thick slices of fibers prepared via microtoming. X-ray diffraction (XRD) measurements employed a Bruker Smart APEX CCD diffractometer using a Mo K(α) radiation, $\lambda = 0.071$ nm, or a Rigaku Miniflex instrument using Cu K(α) radiation, $\lambda = 0.154$ nm.

RESULTS AND DISCUSSION

Metal deposition on yarn involves chemical transformations taking place on the fiber surface. Thus, the presence of impurities on the fiber surface was anticipated to affect plating efficiency. Figure 1a) depicts an SEM image of fibers subjected to the cleaning procedure described above, which yielded smoother surfaces free of the contaminants present as irregular objects in the case of "as received" yarn (shown in Figure S1 in the Supporting Information). In addition, the average fiber diameter decreased slightly from 12 to 11.2 μm after the cleaning step. The flattened and deformed fiber top ends resulted from the sectioning procedure used to prepare the samples. Presented in Figure 2 are XRD data obtained after exposing cleaned Kevlar fibers to Cu K(α) radiation. The intense peaks at 2θ values of 20.3 and 22.6 degrees agree well with the signals (20.6 and 22.8) reported previously,[23] which have been assigned to equatorial scattering of X-rays by the fiber material. Considering that the fibers were positioned perpendicular to the radiation beam, the predominance of signals originating from radial scattering of X-rays in our experiments is not surprising.

All metal depositions were performed with rigorously clean fibers to avoid the erratic and inefficient plating that resulted otherwise. Coated samples were selected for characterization and further treatment by examination of color changes since fibers coated with the Ni electroless method displayed a dark-gray coloration, whereas Au coatings were red. Failed experiments were those producing nonuniform plating, or brittleness resulting in flaking of the metal coating. Polymeric materials such as Kevlar are devoid of surface groups able to bind metal ions electrostatically and require pretreatment (surface activation) to create nucleation sites that enable metal attachment.[13] Surface activation is believed to involve binding of Sn(II) ions to the surface of the polymeric material, followed by deposition of Pd particles,

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd \qquad (1)$$

Attempts to quantify gravimetrically the amounts of Sn and Pd present on the fiber surfaces were unsuccessful. Small Pd particles derived from this process are thought to catalyze the electroless Ni deposition since plating was successful only when the fibers were subjected to surface activation. Immersion of surface-pretreated Kevlar yarn into the Ni electroless bath for 5 min induced uniform darkening of the fibers together with evolution of numerous bubbles believed to be H_2 gas.[13] Removal of the bubbles from the fiber surface using glass rods promoted the plating process. Depicted in Figure 1b is an image of the resulting material; the coating is clearly noticeable particularly at the fiber tips. Significant damage to the coatings, including fracturing, was induced by the sectioning procedures employed during preparation of the SEM samples. On average, a single Ni plating step increases the fiber diameter to about 12 μm and the yarn mass by about 14% but larger changes occurred sporadically. Ni together with low amounts of Sn and Pd were detected during EDS measurements conducted on plated fibers. While the coatings appear uniform in Figure 1b, examination of longer fiber segments revealed the presence of uneven deposits and of places on the surface of the polymeric materials that remained uncoated.

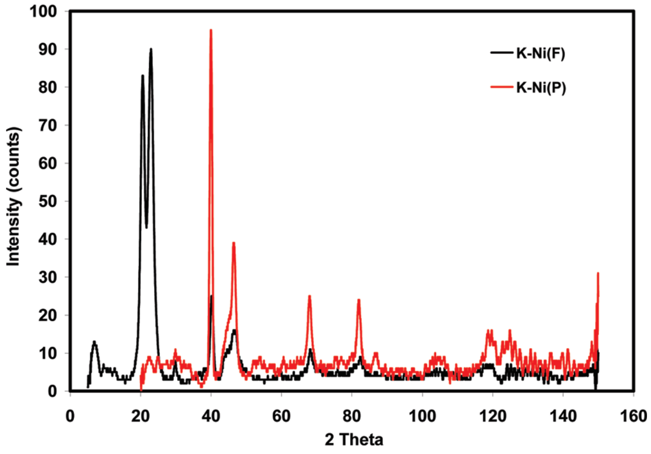

Figure 3. XRD signals obtained with Cu K(α) radiation from samples prepared via exposure of surface activated Kevlar fibers to the electroless Ni bath. K−Ni(F): results from fiber samples; K−Ni(P): data from powdered fibers.

Earlier metallization studies using electroless Ni baths containing hypophosphite ions have reported the formation of mixtures of materials including metallic nickel.[13] For this reason, the nature of the coatings was investigated by means of XRD. Data represented with a continuous line in Figure 3 were obtained from the coated fibers shown in Figure 1b. Apart from the strong fiber signals at lower angles shown in Figure 2, intense reflections at $2\theta = 40$, a doublet signal with maxima at 44.5 and 46.6°, and at 68.2 and 82.1° were detected together with weaker peaks at 86.4, 105.2, 119.7, and 125.2°. The broken line shows a pattern obtained after grinding coated fibers to a fine powder. Essentially the same reflections resulted in both cases, except that the low angle signals due to scattering from the fibers are absent in the pattern of the powder sample. Stronger reflections resulted from the powder because of the larger surface area of this material. The signal centered at 44.5 degrees that is part of the doublet can be interpreted as corresponding to diffractions from the {111} planes of metallic Ni, JCPDF card 4−0850. However, missing are the other anticipated nickel peaks from the {200}, {220}, and {311} crystallographic planes ($2\theta = 51.8$, 76.3, and 92.9°). Given that the signal from {111} planes of fcc Ni are usually strongest (JCPDF card 4−0850), the absence of the anticipated {200},

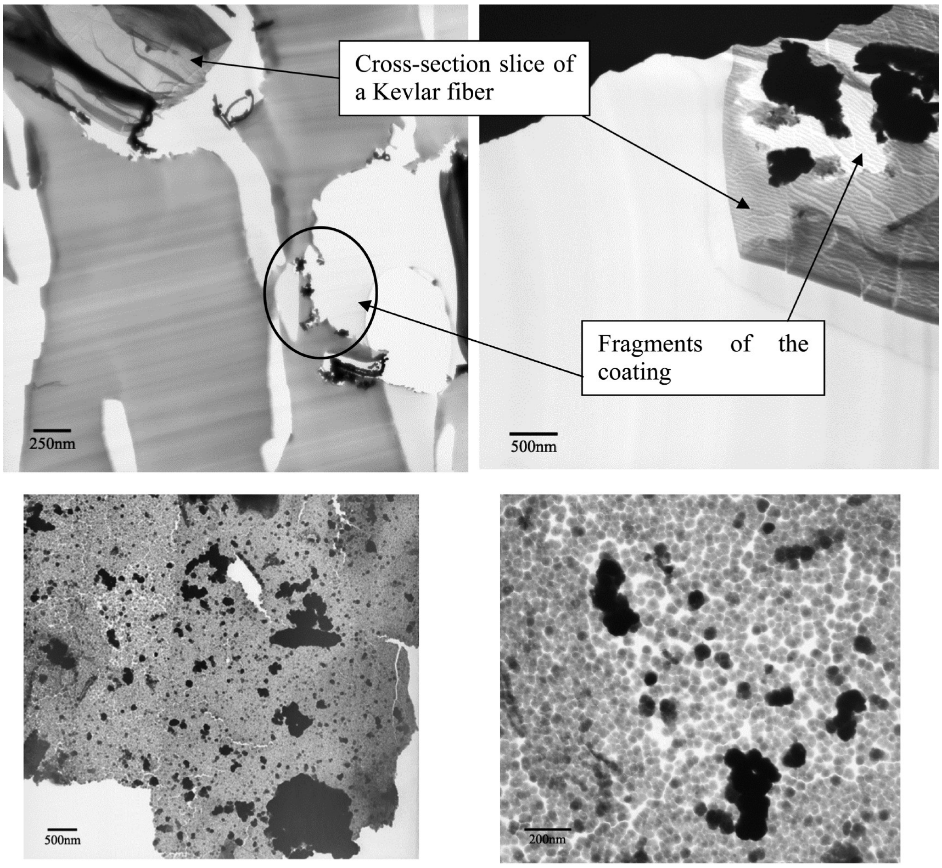

Figure 4. TEM imaging of specimen obtained from Kevlar fibers plated using Ni electroless deposition. Top: slices of cross-sectioned coated fibers; bottom: a segment of the fiber surface imaged at different magnifications.

{220}, and {311} signals is an indication that only small amounts of metallic nickel were deposited on the fibers.

Electroless Ni plating is known to yield some metallic Ni and also amorphous phosphides (Ni_xP_y) that crystallize upon annealing at high temperatures to form Ni_2P, Ni_3P, and $Ni_{12}P_5$.[24−27] Attempts to match the diffraction data of the phosphides with the signals at $2\theta > 35°$ shown in Figure 3 were unsuccessful. However, the data match well the diffractions from metallic Pd located at $2\theta = 40.1, 46.7, 68.1$, and 82.1 degrees arising from the {111}, {200}, {220}, and {311} planes, (JCPDF card 46−1043). Even the weaker signals shown in Figure 3 can be indexed as reflections from the {222}, {400}, {331}, and {420} crystallographic planes of fcc Pd ($2\theta = 86.6, 104.8, 119.3$, and 124.6°). Furthermore, the doublet signal can be identified as composed of reflections from Ni {111} planes at 44.5 degrees and a stronger peak at 46.6 degrees due to diffractions from Pd {200} planes. Detection of metallic Pd confirms the occurrence of reaction 1 and the low intensity of the XRD data is consistent with EDS results indicating that only small amounts of palladium are present on the fiber surfaces. Metallic Ni is clearly a minor product of the electroless process, which yields mainly amorphous materials, presumably Ni_xP_y phases.[24−27] Electroless Ni deposition using a hypophosphite bath has been rationalized in terms of[13]

$$Ni^{2+} + 2H_2PO_2^{-} + 2H_2O \rightarrow Ni + 2H^{+} + 2H_2 + 2HPO_3^{2-} \qquad (2)$$

The results of the present study indicate that reaction 2 fails to accurately represent the overall deposition process since metallic Ni and H_2 are just side products.

TEM images of a microtomed Kevlar fiber coated via the Ni electroless deposition method are presented in the top panels of Figure 4. The images mainly show light regions corresponding to the thin sliced polymeric material. Also noticed were some dark irregular objects originating from the fiber surface, which correspond to deposited materials denser than the polymeric matrix that are not penetrated by the electron beam. Powder samples derived from the plated fibers occasionally contained surface segments of the plated fibers that were suitable for TEM imaging. Presented in the bottom panels of Figure 4 are images from a surface fragment of a plated fiber measuring several μm. Large irregular objects with dimensions between 0.1 and 1 μm were present together with numerous nearly spherical particles characterized by an average diameter of about 50 nm. Given the XRD results presented above, the particles are, most probably, composed of amorphous Ni_xP_y phases.

Yarn treated with the electroless Ni bath were the starting point of attempts to plate Au on Kevlar fibers. This strategy was adopted because efforts to coat fibers pretreated just with the Sn^{2+}/Pd^{2+} surface activation step were unsuccessful. Only fibers with mass increase of at least 14% from the electroless Ni process were found to be suitable as substrates for subsequent Au plating experiments. Initially tested was the room-temperature electroless method based on $Na_3Au(S_2O_3)_2$ and L-ascorbate

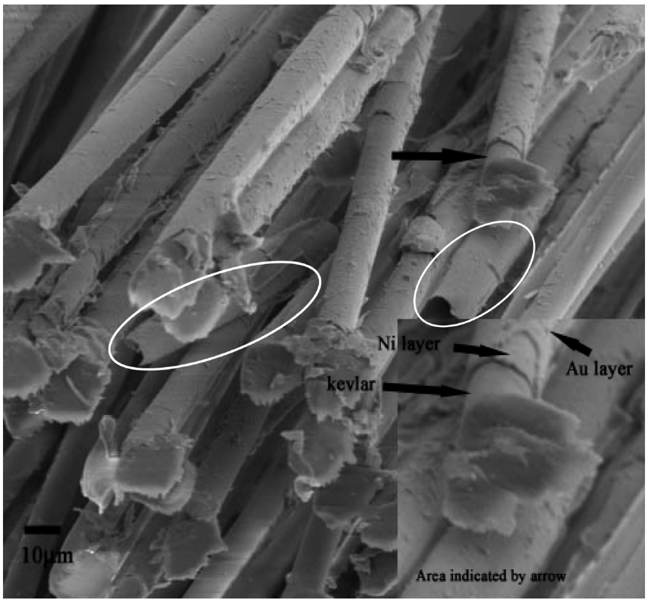

Figure 5. SEM image of sectioned Kevlar fibers first coated with the electroless Ni bath, followed by treatment with the Au(I) thiosulfate electroless method yielding 0.64 g of total coated material per g Kevlar. Ellipses highlight hollow metal coatings. Inset: close-up of the area that includes the fiber tip highlighted by an arrow in the main image.

ions as the reducing agents. Reduction of Au(I) ions by ascorbate ions on surface deposits generated by the electroless Ni bath can be represented by the reaction,

$$2\mathrm{Au}(\mathrm{S_2O_3})_2{}^{3-} + \mathrm{C_6H_7O_6}^- \rightarrow 2\mathrm{Au} + \mathrm{C_6H_5O_6}^- + 4\mathrm{S_2O_3}^{2-} + 2\mathrm{H}^+ \qquad (3)$$

One reason for selecting this approach is that electroless Au coating by means of the thiosulfate bath was reported to require only 3 min of immersion time in the case of PAN fibers pretreated with an electroless Ni process similar to the one used here.[16] Another reason is that electrochemical experiments described below employed the same thiosulfate bath.

Presented in Figure 5 is a SEM image obtained after sectioning fibers that were plated with the Au electroless method following the electroless Ni step. After such treatment the average fiber diameter was 13.5 μm, which is a substantial change when compared to that (11.2 μm) of the clean, noncoated material. The mass increased on average by about 44% as compared with that measured after the electroless Ni treatment. As illustrated in the image, sectioning of the samples induced significant damage including fracturing of segments of the coating. Separation of the metal coating from the substrate occurred in some cases, resulting in hollow metallic tubes highlighted by the ellipses. Analogous observations were made in an investigation that employed similar electroless plating baths to grow metal tubes using fibers as sacrificial templates.[17] The inset in Figure 5 displays a magnified view of the fiber highlighted by an arrow in the main image. Two overlaying layers are clearly detected on the fiber surface; EDS measurements confirmed that Ni was the main component of the bottom layer whereas the top layer consisted of Au. In contrast, coatings consisting of a single layer were obtained previously upon metallizing PAN fibers with consecutive electroless Ni and Au plating methods very similar to those employed in the present study.[16]

XRD measurements on fibers exposed sequentially to Ni and Au electroless plating yielded the low angle signals typical of the Kevlar materials in conjunction with strong reflections from metallic (fcc) Au and a weaker diffraction signal from metallic Ni. These results together with a diffractometer trace obtained from uncoated fibers are presented in Figure S2 in the Supporting Information. Although the golden color of the resulting yarn appeared fairly uniform under visual inspection, SEM examination revealed that the electroless Au plating method frequently yielded uneven coatings as well as fiber sections that remained uncoated. Furthermore, in contrast to the observations made with PAN fibers,[16] electroless Au deposition onto Kevlar yarn was not easily reproducible since immersion times that varied between 5 to 30 min were required in order to achieve a constant golden coloration of the coatings. In view of these reproducibility shortcomings, the electroless Au plating method was deemed unsatisfactory and was not explored further.

Electrochemical experiments were performed on yarn plated with the Ni electroless method given that attempts to electroplate Au onto fibers treated only with the $\mathrm{Sn}^{2+}/\mathrm{Pd}^{2+}$ surface activation step were unsuccessful. This result is not surprising since the very high resistivity of fibers after the surface activation procedure made them unsuitable as electrodes. In contrast, fibers coated with a single electroless Ni deposition exhibited a typical resistivity ≤ 30 ohm/cm, which enabled them to serve as cathodes. Initial experiments with such fibers served to characterize the reaction parameters for Au electrodeposition with both the thiosulfate and cyanide systems described in the Experimental Section. The optimum deposition parameters were identified empirically and correspond to a potential of −0.6 V vs Ag/AgCl for the $\mathrm{Au}(\mathrm{S_2O_3})_2{}^{3-}$ system and −1.09 V vs Ag/AgCl for the $\mathrm{Au}(\mathrm{CN})_2{}^-$ system. Electrodepositions were performed at those potentials, and in both systems the average current was coincidentally about −2.5 mA despite the fiber electrode areas varying considerably. In the NHE scale these potential values correspond to −0.401 and −0.891 V and are significantly more negative than the standard potentials, 0.153 and −0.595 V, respectively.[19] Such potential differences may result from the high fiber resistance, reactant concentrations lower than those of the standard states and overpotentials necessary for a fast deposition. Given the variations and uncertainty in the electrode surface areas, the efficiencies of the electrochemical processes were not determined and the rates of deposition could not be accurately ascertained.

Electrochemical reduction of gold ions to atoms on a conductive surface acting as the cathode can be represented in a simplistic fashion by reaction 4

$$\mathrm{Au}(\mathrm{S_2O_3})_2{}^{3-} + \mathrm{e}^- \rightarrow \mathrm{Au} + 2\mathrm{S_2O_3}^{2-} \qquad (4)$$

As anticipated, the net current output increased during Au coating process in both systems because the deposited gold lowered the resistance of the fibrous material and facilitated further metal plating. Plating times in the range of 3−5 min produced uniform substrate coloration in the case of the thiosulfate electrochemical system. Although the thiosulfate bath contains L-ascorbate ions able to reduce the Au(I) complexes thermally, the contribution of this process to Au plating during electrochemical experiments is considered to be minor since metal deposition occurs in most cases significantly faster via reaction 4 than through reaction 3. The cyanide electrodeposition method required 1 h to yield strongly adhering and dense

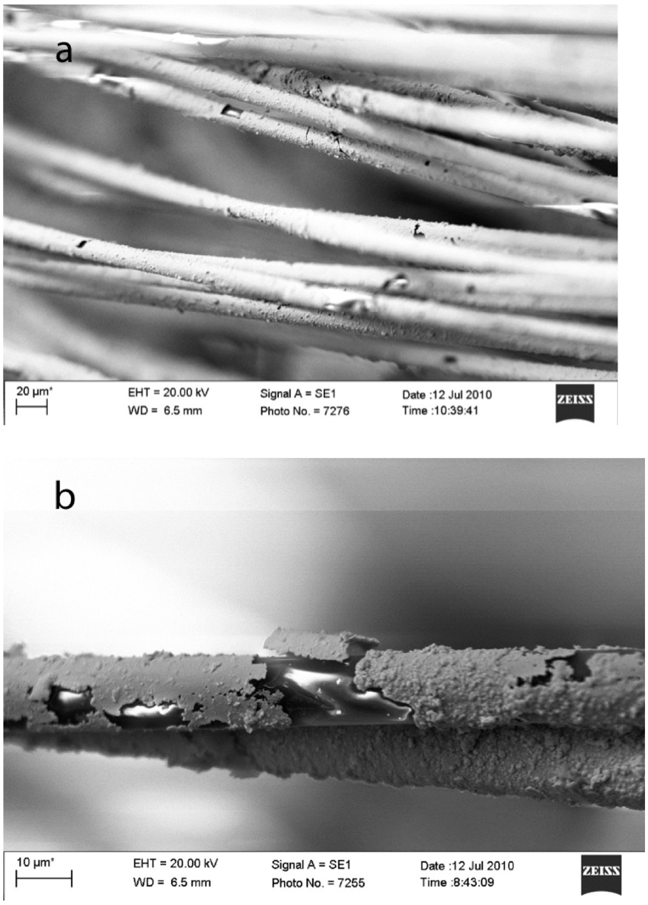

Figure 6. SEM image at (a) low and (b) higher magnification of Kevlar fibers first coated in the Ni electroless bath, then exposed to ultrasound in H_2O and electroplated with Au via the thiosulfate procedure.

coatings (average diameter = 12.9 μm) but the extent of fiber surface left uncoated was markedly higher. Both electrochemical procedures produced coatings more uniform that those generated with electroless Au deposition. However, the thiosulfate electroplating procedure was selected for further optimization because this method avoided handling of fairly toxic solutions and was most effective in terms of coating efficiency and reaction times.

An important property of metallized fibers is robustness of the coatings, which was probed via exposure of the coated yarn to ultrasound in H_2O. Depicted in Figure 6 are SEM images obtained at increasing magnifications of fibers first treated with the Ni electroless bath, followed by exposure to ultrasound and then coated with Au using the thiosulfate electrochemical procedure. Figure 6a shows a low magnification overview of a group of fibers treated in such a fashion. Electroplating induced a large increase in average fiber diameter to 15.9 μm as compared with that (12 μm) obtained after coating with the electroless Ni bath. Most of the plated material seems uniform but coating defects exist including uncoated areas and fractures, which are less numerous on fibers not subjected to the ultrasound test. Presented in Figure 6b is a close-up image centered on a fiber displaying a coating fracture and several areas where the metal deposit is missing. At this magnification the surface roughness of the coating is evident in the form of granules. The coating appears as a uniform, single film, which contrasts with the layered structure of deposits formed when both metallization steps used electroless procedures (see Figure 5). As mentioned earlier, consecutive Ni and Au electroless platings on PAN fibers also yielded single-layer coatings.[16] This result was explained by assuming that deposited Au diffused to some extent into the initially plated nickel material. A similar phenomenon may occur during Au electrodeposition onto Kevlar yarn, where the resulting coatings were 10 times thicker than those plated on PAN fibers.

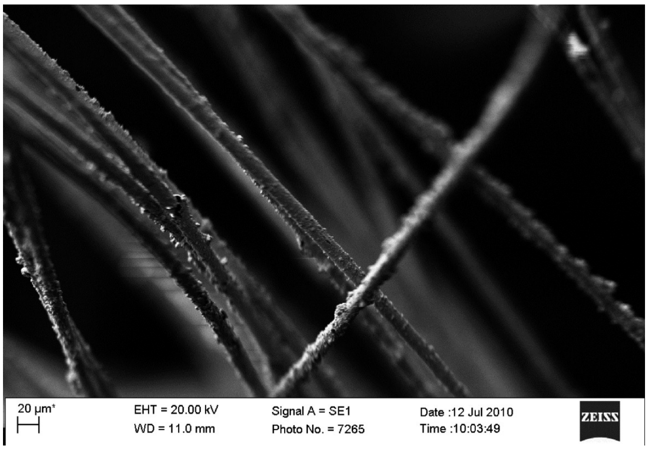

Figure 7. High-magnification SEM image displaying coatings on Kevlar fibers treated three times with the electroless Ni method, then coated three times with Au via electrodeposition. The coating contained 1.03 g of Ni/Ni_xP_y and 3.68 g of Au per g of fiber.

Exposed sections of the polymer surface are frequently noticed in Figure 6a), indicating that segments of the Ni electroless coating were stripped from the fibers by the ultrasound. Dislodgment of weakly adhering Ni/Ni_xP_y deposits left bare areas on the fiber surface where electrodeposition of Au was not possible. Coating fractures were less frequent and probably originated from ultrasound-induced rupturing of defect regions in the Ni/Ni_xP_y coatings. Obviously, the subsequent Au electrodeposition step was unable to close the fractures. An interesting observation was that Au metallization on yarn not exposed to ultrasound started simultaneously on numerous places and extended via overlap of the growing coating. In contrast, Au electrodeposition after the ultrasound exposure started at the yarn end connected to the external electrical circuit and propagated along the fiber axes. This means that disruption of the Ni/Ni_xP_y deposits by the ultrasonic waves decreased the electron mobility in the yarn, inhibiting simultaneous reduction of gold ions along the fibers. TEM measurements from slices obtained via microtoming fibers that were subjected to the ultrasound test yielded images very similar to those displayed on the top panels of Figure 4. An unusual observation was the presence of numerous nanometer-sized particles inside the fibers. Because particles were found within the polymer backbone only after the electroplating step was performed, an obvious interpretation is that they consist of Au but their formation mechanism remains unknown.

Further experiments showed that the adhesion problems could be solved through application of multiple electroless Ni plating steps, each also involving a surface sensitization step. Adhesion of the coatings improved considerably when three consecutive electroless Ni depositions were carried out prior to three successive Au electrochemical platings. Coatings derived from this procedure were no longer affected by ultrasound waves or by the adhesive tape test. Nearly constant total mass increases

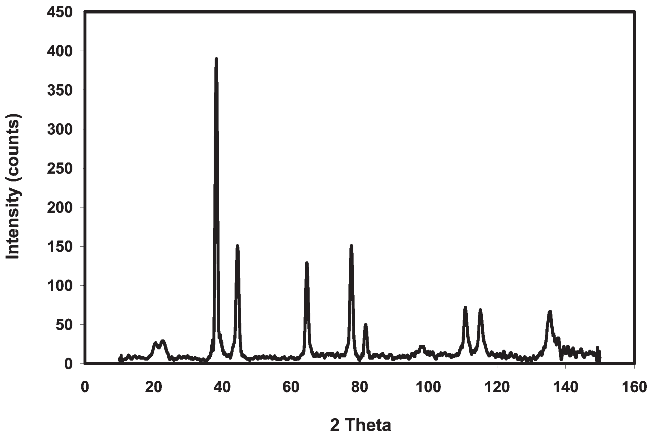

Figure 8. XRD pattern obtained with Cu K(α) of Kevlar fibers coated three times via electroless Ni deposition followed by three electrochemical Au plating steps.

of about 100% resulted when surface activated Kevlar fibers were subjected to three electroless Ni coating steps, yet the contribution of each individual plating step was not equivalent. On the other hand, mass changes resulting from Au plating varied somewhat linearly with the number of deposition steps and increases between 150 and 180% resulted after three coatings. Surface activation of the fibers between successive Au plating steps qualitatively appeared to improve the rate of the subsequent electrochemical deposition. Displayed in Figure 7 is a high magnification SEM image of fibers plated with the multiple deposition method. The resulting fibers exhibit an average diameter of 17.5 μm and numerous grains with sizes between 1 and 10 μm protruded from the coatings. The larger Au crystallites found in the case of the Kevlar fibers may be a consequence of plating on curved surfaces since multiple gold electrodepositions on flat substrates were reported to also generate smaller Au grains.[28,29] The multiple step deposition procedure employed in the present study suppressed significantly coating defects, particularly the occurrence of places on the fiber surface that remained free of coating. However, fractures in the coating were not entirely eliminated.

Figure 8 depicts a diffraction pattern obtained from fibers plated three times with the electroless Ni method followed by three gold electrodepositions. Signals at 2θ angles of 38.3, 44.6, 64.8, 77.8, 82, 98.8, 111, 115.5, and 135.7° were detected, which can be indexed as diffractions from the {111}, {200}, {220}, {311}, {222}, {400}, {331}, {420}, and {422} lattice planes of fcc Au (JCPDF card 4−0784). Despite the fact that the multistep plating method yielded large amounts of coated nickel materials, and that EDS measurements confirmed the presence of this element on the fiber surfaces, diffractions corresponding to fcc Ni were not observed. These results support the conclusion that the electroless Ni process mainly produced amorphous Ni_xP_y phases. Given the large amounts of gold plated on the fiber surfaces and the small Pd concentrations present in the coatings, any diffractions corresponding to palladium were obscured by the much more intense Au peaks. Only weak scattering signals originating from the fibers are observed at low angles in Figure 7, probably because of partial shielding of Kevlar from the X-rays by the thick coatings.

Compiled in Table 1 are results of mass increases and resulting conductivities from fibers coated via different procedures; the first two entries pertain to samples prepared via three consecutive electroless Ni plating steps combined with three successive electrochemical depositions using the thiosulfate procedure. Included are results obtained from fibers exposed one time to the electroless Ni bath and then coated via a single Au plating step consisting of electrodeposition with either the thiosulfate procedure or the cyanide method, entries three and four, respectively. Treatment of the fibers multiple times with the electroless Ni procedure resulted in large mass increases (60−120%), which in turn, increased the efficiency of electrochemical Au plating by means of the thiosulfate method. The fact that the measured Au mass increases correlated with the number of electrodeposition steps suggests that depletion of $Au(S_2O_3)_2^{3-}$ ions within the bulk of the solution may play a role during plating. This interpretation is consistent with the lower mass gain detected when the yarn length doubled, as is evident from entries 1 and 2 in Table 1. Increases in percent mass from the electrodeposition steps refer to the masses measured after and before Au plating. On the other hand, the mass percent increases from the electroless process resulted from the difference between plated and nonplated fibers. Consequently, the mass increases resulting from the Au deposition process are much larger than those derived from the electroless treatment. An exception occurred for fibers subjected to the ultrasound test, which experienced anomalously high plating during the Ni electroless step, yielding very similar increases of mass in both electroless and electrochemical platings.

Table 1. Conductivity and Mass Change for Metallized Fibers

treatment	no. of depositions of Ni and Au	Δmass Ni (%)	Δmass Au (%)	conductivity (S cm^{-1})
K−Ni−$Au(S_2O_3)_2^{3-}$	3 and 3	102.5	181.5	[a]NT: 3.07; TW: 6.02
K−Ni−$Au(S_2O_3)_2^{3-}$	3 and 3	103	149	[b]NT: 1.19; TW: 3.17
[c]K−Ni−$Au(S_2O_3)_2^{3-}$	1 and 1	110	49.5	[a]NT: 0.75; TW: 2.4
K−Ni−$Au(CN)_2^-$	1 and 1	14	100	[a]NT: 0.86; TW: 1.17

[a] NT = fibers not twisted; TW = twisted fibers, fiber length =9 cm. [b] Metallized fibers of a length of 25 cm. [c] Fibers sonicated for 10 min after electroless Ni coating, then electroplated with Au.

Resistivity measurements were performed on twisted and nontwisted metalized yarn; as shown in Table 1, the conductivity increased by a factor of 3.6 after twisting the fibers. Twisting of coated fibers is known to increase their conductivity,[14] which is rationalized on the basis that a higher number of contact points between fibers exist in twisted yarn. This leads to additional conductive pathways for electrons to migrate that are not available in nontwisted fibers. Another general correlation is that raising the mass of deposited Au increased the fiber conductivity. Comparison of entries 3 and 4 in Table 1 indicate that Au coating of Kevlar fibers via a cyanide method yielded conductivities similar to that obtained by means of the thiosulfate procedure. Considering that the latter treatment is faster and safer, utilization of the cyanide method offers no significant advantage. Illustrated in Figure 9 are results from experiments that probed the ability of metallized Kevlar fibers to sustain electrical currents utilizing freestanding, nontwisted yarn. To improve electrical contact, yarn sections were wrapped in narrow strips of Al foil and clamped to connectors linked to the current source. This arrangement allowed determinations of power output at variable distances along the yarn. The data presented in Figure 9a

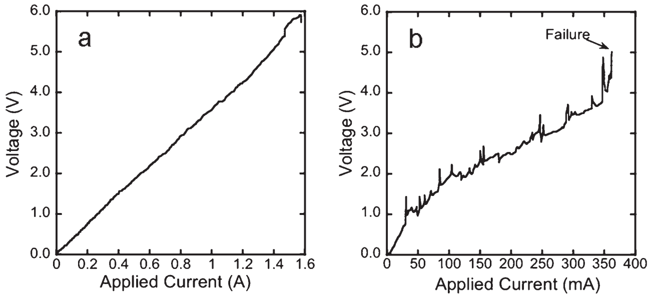

Figure 9. Plots of voltage versus current obtained for a 9 cm Kevlar yarn treated three times with the electroless Ni method, then coated three times with Au via electrodeposition. (a) Results from measurements over a yarn distance of 3.2 cm; (b) a point failure at 1.8 W for a distance along the yarn of 6.5 cm.

Table 2. Tensile Strength Measurements for Metallized Fibers

sample type	no. of depositions of Ni and Au	average maximum load (cN)	C.V.% (average maximum load)[a]	% change in fiber strength
clean Kevlar		31.5	5.2	0.0
K−Ni	1	28.5	23.3	10.6
$K-Ni-Au(S_2O_3)_2^{3-}$	3 and 3	23.0	33.9	26.9
$K-Ni-Au(CN)_2^{-}$	1 and 1	22.7	14.4	27.8

[a] C. V. = coefficient of variance, measures the deviation in the determined maximum load.

demonstrated that over a yarn distance of 3.2 cm no limitation in the passage of current existed up to a power output of 9 W (the maximum value that can be determined by the instrument). As illustrated in Figure 9b, numerous spikes attributed to breakage of individual filaments were observed when the measurements were performed over a yarn distance of 6.5 cm. A catastrophic failure was detected at 1.8 W, at which time the fiber showed obvious burn marks at one point along the current path. Systematic determinations showed that, on average, the Au metallized Kevlar fibers were able to sustain a power output of 1 W.

Compared in Table 2 are tensile strength results determined from individual Kevlar monofilaments that are the components of the metallized materials. A single electroless Ni plating step induces of modest decrease of 10% in the strength of the filaments, but an additional electrochemical Au plating step with the cyanide method induces a larger decrease of about 28%. Metallization of the yarn with three consecutive electroless Ni platings and three successive Au electrochemical depositions resulted in a similar (27%) decrease in the strength of the monofilaments. Obviously, Au coatings affect the fiber strength in a fashion more pronounced than Ni and also negatively influence the reproducibility of the experiments.

Metallization of Kevlar fibers involving surface activation initiated by strong bases in dimethyl sulfoxide has been reported to yield coatings that have no negative effect on the fiber tensile strength.[18] Furthermore, the resulting coated materials were claimed to exhibit the same conductivities as those of the pure metals employed in the coatings. Although the coatings derived from the present study affected the strength of the fiber and exhibited lower conductivities, their preparation was free of the reproducibility issues that seem to plague methods involving surface activation with bases. The conductivity values reported here for Au electrodeposited Kevlar fibers (NT = 1.02 S/cm, TW = 3.65 S/cm) are as good or better than those of Cu coated cotton fibers (∼1 S/cm) obtained using electroless plating techniques.[14] As anticipated, no changes in the properties of Au plated Kevlar fibers were detected after storing them under air for two years, which contrasts with the conductivity decreases experienced by the Cu coatings due to their reactivity toward O_2. Also, the Au coatings seem to exert no significant deterioration of the fiber flexibility but data from specific tests are needed to quantify this observation. Utilization of the metallized fibers as materials for space tethers seems questionable given their limited conductivity together with the presence of defects in the coatings. The decrease in tensile strength of the resulting Kevlar materials will not hinder possible practical uses of the metalized fibers in areas such as textiles. Although the expense of Au electrodeposition may be prohibitive for textile applications, electroplating Cu or Ag may yield affordable metallic conductive coatings.

The tested electroless Ni and Au deposition methods exhibited reproducibility problems in terms of achieving uniform metallization. Part of this problem is related to the reduced (laboratory) scale of the experiments because the reactions were carried out in relatively small containers with respect to the length of the fibers that were coated. Sporadic contacts between the fiber surfaces are unavoidable under such conditions, and probably contribute to the reproducibility problems, as has been reported before.[16] Despite the fact that the electroless Ni deposition failed to produce metallic nickel on the fiber surfaces, the resulting coatings (probably amorphous Ni_xP_y) aided the subsequent electrochemical Au deposition. However, plating of such Ni compounds on the fiber surfaces may inherently yield nonuniform coatings, negatively affecting the uniformity of the subsequent Au deposition. Another concern related to the electroless Ni-phosphite baths is the evolution of H_2 gas as a byproduct of the deposition process. Since H_2 is believed to form within the coatings as well, evolution of this gas inevitably leaves behind voids in the plated material and also between substrate and coated layer.[27] Further efforts should be devoted to achieving uniform metallic Ni coatings by means of deposition processes that are free of these problems.

CONCLUSIONS

Gold electrodeposition procedures were superior as compared to electroless methods in terms of reproducibility, and yielded higher mass gains, better adhesion and lower resistance. Inconsistencies encountered during Au deposition onto the surface of Kevlar fibers are likely results of problems associated with the initial Ni coating treatment and not with the electrodeposition method. Utilization of alternative electroless Ni deposition methods that produce coatings of metallic Ni is anticipated to improve the plating procedure. Although the metallization method presented here is somewhat laborious, the coated Kevlar fibers seem capable of sustaining power outputs of about 1 W and may be useful in applications involving "smart" textiles.

ASSOCIATED CONTENT

Supporting Information. Figure S1 shows an SEM image of the "as-received Kevlar fibers prior of been subjected to the cleaning procedure. Displayed in Figure S2 is an XRD pattern of clean fibers treated first with the electroless Ni plating procedure followed by metallization with the electroless Au method. This material is available free of charge via the Internet at http://pubs.acs.org.

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