

A review on electrospinning design and nanofibre assemblies



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It is therefore vital for us to understand the various parameters and processes that allow us to fabricate the desired fiber assemblies. Fiber assemblies that can be fabricated include unwoven fiber mesh, aligned fiber mesh, patterned fiber mesh, random three-dimensional structures and sub-micron spring and convoluted fibers. Nevertheless, more studies are required to understand and precisely control the actual mechanics in the formation of various electrospun fibrous assemblies. (Some figures in this article are in color only in the electronic version) 1.

Introduction Since the beginning of this century, researchers all over the world have been re- looking at a century old process (Cooley 1902, Morton 1902) currently known as electroplating. Probably unknown to most researchers for most of the last century, electroplating is able to produce continuous fibers from the submission diameter down to the nanometer diameter. It was not until the mid-1990s with interest in the field of nanotechnology and nanotechnology that researchers started to realize the huge potential of the process in nanofiber production (Dodos and Reenter 1995).

Nanofibers and nanowires with their huge surface area to volume ratio, about a thousand times higher than that of a human hair, have a potential to whom any correspondence should be addressed. The potential to significantly improve current technology and find application in new areas. Applications for nanofibers include microanalysis, tissue scaffolds (Wang et al Bibb, Lie et al 2002), protective clothing, filtration and nanoelectronics (Ramekins et al 2005).

Although there are other methods of fabricating fibers such as phase separation (White et al 1996) and template synthesis (Creativity and Better 1998), few, if any, can match electroplating in terms of its versatility, flexibility and ease of fiber production. At a laboratory level, a typical electroplating set-up only requires a high voltage power supply (up to 30 kV), a syringe, a flat tip needle and a conducting collector. In terms of the flexibility of the process, electroplating is able to fabricate continuous fibers from a huge range of materials.

Of the major classes of materials, electroplating is able to produce fibers of polymers, composites, ROR 0957-4484/06/140089+18\$30. © 2006 IOP Publishing Ltd printed the UK semiconductors and ceramics (Ramekins et al 2005, Hung et al 2003, Chronics 2005). Although the most commonly electroplated material is polymer, ceramic precursors have also been electroplated without the addition of polymers (Son et al 2006, Wang and Santiago-Aviles 2004, Larsen et al 2003).

Thus, it is not surprising that over 500 research papers on electroplating were published in the last decade on various issues such as the fundamentals of electroplating (Human et al 2001, Fen 2002, Yarn et al 2001), electroplating conditions (Krishna et al 2003, Tan et al 2005, Digitize et al 2001 b, Mit-apathy et al 2004) and characterization of fiber for various applications (Shawano and Sung 2002, Ideas et al 2004, Rayon et al 2006). A good summary of the various studies on electroplating, its fibers and their references can be found in the book by Ramekins et al (2005).

Recent research on electrospinning fibers has been on exploring various materials that are electronically, characterization of the fibers and finding new applications for it. However, for the potential of electrospinning fibers to be fully realized, it is important to fabricate various fibrous assemblies, as the fiber arrangement will have a significant affect on the performance of a device. Ordered nano-grooves and assemblies have been shown to influence cell proliferation and morphology (Xx et al 2004). For use as narrower, it is vital that the single narrower can be grown or positioned across specific electrodes.

In application as filtration membrane, a unwoven mesh may be desirable. The ability to form yarn made of knobbier may pave the way for higher performance clothing or woven scaffolds. Due to the size of inferiors, it is difficult to form various assemblies through physical manipulation.

Nevertheless, electroplating is able to fabricate various knobbier assemblies in situ. This gives electroplating an important edge over other larger-scale knobbier production methods. This allows customization of knobbier assemblies to meet the requirement of specific applications such that its performance is enhanced.

In this review, we will concentrate on the different electroplating designs to obtain various knobbier assemblies and other modifications in the set-up. This will allow researchers on various domains to know the array of knobbier assemblies that can be fabricated and their corresponding set-ups. Various concepts, which researchers used to create the knobbier assemblies, will be described to facilitate understanding of the process such that new designs may be created to construct knobbier assemblies to meet specific needs.
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Solution High Voltage power supply Electroplating Jet Collector .

Electroplating fundamentals The formation of inferior assemblies through electroplating is based on the uniaxial stretching of a polymer solution. To understand and appreciate the process that enables the formation of various nanofiber assemblies, the principles of electroplating and the different parameters that affect the process have to be considered.

Unlike conventional fiber spinning methods like dry-spinning and melt-spinning, electroplating makes use of electrostatic forces to stretch the solution as it solidifies. Similar to conventional fiber spinning methods, the drawing of the solution to form the fiber will continue as long as there is enough solution to feed the electroplating jet. Thus without any disruption to the electroplating jet the formation of the fiber will be continuous. For a typical electroplating set-up as shown in figure 1, a solution is first fed through a spinneret.

A high voltage is applied to the solution such that at a critical voltage, typically more than 5 kV, the repulsive force within the charged solution is larger than its surface tension and a jet would erupt from the tip of the spinneret. Although the jet is stable near to the tip of the spinneret, it soon enters a bending instability stage with further stretching of the solution jet under the electrostatic forces in the solution as the solvent evaporates.

Electroplating devices without the use of spinnerets have also been explored by various researchers (Yarn and Susann 2004, Kamala et al 2003).

Generally, a grounded target is used to collect the resultant fibers which are deposited in the form of an unwoven mesh. The parameters to control the

diameter have been discussed in several good references (Ramekins et al 2005, Thereon et al 2004, Mit-apathy et al 2004, Sousaphone et al 2005, Tan et al 2005). A few widely studied parameters include solution viscosity, conductivity, applied voltage, spinneret tip-to-collector distance and humidity.

For example, by reducing the spinneret tip-to-collector distance mesh with inter-connected fibers can be collected (Buck et al 1999), while reducing the solution concentration will reduce the electrospine fiber diameter. Although polymer chain entanglement is an important criterion for fiber formation in polymers (Sheens et al 2005), the viscosity of a solution is a more general parameter since ceramic precursors can also be electrospine despite their low molecular weight (Son et al 2006, Wang and Santiago-Avails 2004).

To achieve various fiber assemblies, there are generally two main methods, one is to control the flight of the electroplating jet through the manipulation of the electric field and the other is to use a dynamic collection device. Nevertheless, by using different static collection devices, it is possible to achieve some form of fiber assemblies. To overcome various limitations of the typical electroplating set-up and to further the performance of the electrospine fibrous mesh, researchers have come out with other modifications to the set-up.

Topical Review Table 1 . List of US patents issued before 1976. Patent issued date 04 February 1902 10 May 1938 19 July 1938 16 May 1939 16 May 1939 06 June 1939 01 August 1939 16 January 1940 29 June 1943 14 December 1943 30 May 1944 18 October 1966 Inventor J F Cooley W J Morton K Hegira

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A Formals C L Norton A Formals A Formals A Formals A Formals A Formals A Formals A Formals E K Cladding A Formals A Formals F W Manning A Formals H L Simons Patent number 692, 631 705, 691 1 1 58, 41 5 58, 416 (Lyons et al 2004, Sanders et al 2005).

Nevertheless, Dalton et al used electrospinning polymer melts to deposit fibers directly on cells to form layered tissue constructs for tissue engineering. This eliminates any chance of introducing toxic solvents into the cell culture when the fibers are deposited (Dalton et al 2006). While there have been patents filed for various electroplating set-ups since the 1980s, it is only in the last decade that academia has been looking into using electroplating to fabricate various nonferrous assemblies. Schematic diagrams of the various electroplating set-ups are shown in table 2.

Various principles behind the fabrication of the nonferrous assemblies will be covered in the following sections. 4. Dynamic mechanical device The ability to create ordered structures has many implications in the performance of a fiber assembly. Cells cultured on aligned knobby scaffolds have been shown to proliferate in the direction of the fiber orientation (Xie et al 2004). Several researchers have shown that it is possible to obtain aligned fibers by using a rotating collector (Matthews et al 2002, Kamala et al 2003, Subramanian et al 2005).

A schematic diagram of the set-up is shown in table 2(A). Matthews et al demonstrated the effect of the rotating speed of a mandrel on the degree of electrospinning collagen fiber alignment. At a speed of less than 500 RPM, a random mix of collagen fibers was collected. However, when the rotating

speed of the mandrel was increased to 4500 RPM (approximately 1.4 m/s at the surface of the mandrel), the collagen fibers showed significant alignment along the axis of rotation. Mechanical testing of the aligned scaffold showed that the peak stress along the principal fiber alignment was 1.5 Amp and the average modulus was 52.3 ± 5.2 Amp, while the peak stress across the principal fiber alignment was 0.71 Amp and the modulus was 26.1 ± 4.0 Amp (Matthews et al 2002). Kim et al (2004) examined the effect of the linear velocity of the rotating mandrel on the crystalline, mechanical properties and alignment of electrospun poly(ethylene terephthalate) (PET). Using wide-angle x-ray diffraction, PET electrospun fibers were found to be more amorphous with increasing mandrel rotation. This is probably due to the rapid solidification and collection of the fibers.

However, the increased linear velocity of the mandrel induced greater alignment of the PET crystals in the fibers. Although the Young modulus, yield stress and tensile stress of the mesh along the PET fiber alignment increased with higher mandrel rotation speed and fiber alignment, the same properties tend to decrease above a linear velocity of 30 m/min. At a linear velocity of 45 m/min, many fibers were dispersed into the air instead of being deposited on the mandrel (Kim et al slower than the linear velocity of the rotating mandrel).

Reported average velocity of the electroplating jet ranged from 2 m/s (Kowalski et al 2005, Sunday et al 2004) to 186 m/s (Smith et al 2005). A separate study by Susann et al using a rotating disc collector demonstrated that at high enough rotation speed, necking of the electrospun fibers was observed (Susann et al 2003). This may account for the reduced mechanical

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properties of the PET mesh collected at high speed ROR 3. History of electroplating For the first inventor of the electroplating process, it is necessary to understand the effect of electrostatics on liquid.

Observation of water behavior under the influence of electrostatics was made as early as the sass (Gray 1731-1732). In the late sass, electrostatics was used to explain the excitation of dielectric liquid under the influence of an electric charge (Alarms 1898). This probably led to the invention of electroplating to produce fibers in the early sass by Cooley and Morton (Cooley 1902, Morton 1902). Early researchers on electroplating showed in-depth knowledge of the process based on the designs that were invented.

In one of the earliest electroplating inventions, Cooley patented a set-up that used auxiliary electrodes to direct the electroplating jet onto a rotating collector. In the sass, Formals came out with several innovative set-ups to produce yarns made out of electroplating fibers including designs that do not require the use of a spinneret (Formals 1934). In fact, many recent electroplating set-ups can be traced back to the patents more than half a century ago such as using multiple spinnerets and using parallel electrodes to produce aligned fibers (Formals AAA, Bibb, ICC, AAA, Bibb).

The list of US patents filed before 1976 is given in table 1. For the fiber industries, one important consideration is the level of fiber production. Electroplating, compared to the popular industrial fiber spinning process, is very slow. Industrial dry spinning has a yarn take-up rate of 200- 1500 m min⁻¹ (Guppy and Katharine 1997) while yarn fabricated from electroplating

has a take-up speed of 30 m min⁻¹ (Kill et al 2005). Thus, before 1990, there was very little research and publications on electroplating (Bandmaster 1971).

Nevertheless, there was some research on the behavior of thin liquid jets in an electric field (Selene 1917, Taylor 1964, 1966, 1969). With melt spinning as the preferred method to produce fibers, efforts were made to electrospin fibers using polymer melts (Larboard and Manley AAA, 1981 b, ICC), but there is currently less research in this, probably due to its difficulty in fabricating fibers with nanometer diameter Table 2. Schematic diagram of various electroplating set-ups for multiple peppiness and to obtain various fibrous assemblies. (Assuming spinneret is given a positive charge unless otherwise stated. Assembly-aligned fibrous mesh A. Rotating drum Advantage Simple set-up Large area of aligned fibers can be fabricated Disadvantage Highly aligned fibrous assemblies are difficult to fabricate Fiber breakage may occur if rotating speed is too high (Matthews et al 2002, Kim et al 2004, B. Parallel electrodes Advantage Simple set-up Highly aligned fibers are easy to obtain Aligned fibers are easily transferable to another substrate Disadvantage Thicker layer of aligned fibers re not possible There is a limit in the length of the aligned fibers (Lie et al 2003) C.

Rotating wire drum collector Advantage Simple set-up Highly aligned fibers are possible Disadvantage Thicker layer of aligned fibers are not possible Fibers may not be aligned throughout the whole assembly (Kate et al 2004)

Rotation D. Drum collector with wire wound on it Advantage Simple set-up

Highly aligned fibers are possible Area of aligned fibers on the wire is

adjustable by varying wire thickness Disadvantage Aligned fibers are

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concentrated on the wire instead of the whole drum (Battier et al 2005) Wire ROR Table 2. Continued.) E.

Rotating tube collector with knife-edge electrodes below Advantage Highly aligned fibers possible Aligned fibers covered the whole tube Thicker layer of aligned fiber deposition is possible Disadvantage Set-up requires a negative electrode to be effective Only possible for small diameter tube (Too et al 2005) Negative high voltage Knife edged blade F. Controlling electroplating Jet using knife-edge electrodes Spinneret with Knife edged blade Advantage Highly aligned fibers possible Able to control the direction of fiber alignment on the tube Thicker layer of aligned fiber deposition is possible

Disadvantage Set-up requires a negative electrode to be effective Only possible for small diameter tube (Too et al 2005) G. Disc collector Advantage Simple set-up Highly aligned fibers are possible Able to fabricate arrayed fibers by attaching a irritable table on the edge of the disc Disadvantage Unable to retain high fiber alignment at the same rotating speed when the deposited fibers are thicker Small area of fiber alignment (Thereon et al 2001, Nina et al 2005, Xx et al 2004) Assembly-? fiber arrays H.

Array of counter-electrodes Advantage Simple set-up Disadvantage Fiber patterning is not consistent throughout the assembly Area of the assembly is limited Thicker fibrous assembly is not possible (Lie et al 2004) ROR Table 2.

(Continued.) I. Rotating drum with sharp pin inside Advantage Large area of arrayed fibers can be fabricated Disadvantage Set-up is complicated Thicker area of arrayed fiber assembly may not be possible (Sunday et al 2004)

Rotation Sharp pin Negative high voltage Translational Assembly-? yarn J.

Blade placed in line Advantage Simple set-up Yarn can be easily removed from the collector Collected yarn is highly aligned Disadvantage Fabricated yarn is of limited length Deposited fibers have to be dipped in water first before yarn is formed (Too and Ramekins 2005) K. Ring collector placed in parallel Advantage Simple set-up Twisted yarn can be fabricated

Disadvantage Fabricated yarn is of limited length One of the rings has to be rotated to twist the fibers that are deposited into yarn (Dalton et al 2005) L.

Yarn collection using water bath Coagulation bath Advantage Simple set-up Long continuous yarn can be fabricated Fibers in the yarn are generally well aligned Disadvantage Yarn collection speed is relatively slow (Smith et al 2005, Kill et al 2005) mix fibers of different materials of desired ratio

Disadvantage Interference between the electroplating jets (Ding et al 2004, Kodiak et al 2005, Thereon et al 2005, Maturity et al 2003, Kit-n et al 2006)

ROR Figure 2. Small diameter electrospinning nonferrous conduit. By Kim et al.

Therefore the mandrel rotation speed and fiber orientation have a direct influence on the material properties of the engineered matrix. The presence of the disoriented fibers collected on the rotating mandrel may be the result of residual charge accumulation on the deposited fibers, which interferes with the alignment of incoming fibers. To achieve greater fiber alignment, a possible way is to reduce the Hattie path of the electroplating jet and to reduce the residual charge accumulation on the rotating mandrel.

Seasick et al used an alternating-current (AC) high voltage supply instead of a typically used direct-current (DC) high voltage supply to charge the solution for electroplating. Polyethylene oxide (POE) collected on a rotating

mandrel showed greater degree of fiber alignment using an AC potential than a DC potential. Using an AC potential to charge the solution may have a dual function. The electroplating Jet from an AC potential may consist of short segments of alternating polarity and this may significantly reduce the chaotic path of the electroplating Jet.

This allows the fibers to be wound onto the rotating mandrel with greater ease and alignment. Given the presence of both positive and negative charges on the surface of the rotating mandrel, there will be a neutralizing effect over the area of the mesh, thus minimizing charge accumulation.