

Fabrication of yttria-stabilized zirconia nanofibers by electrospinning

Abdul-Majeed Azad*

Department of Chemical and Environmental Engineering, The University of Toledo, 3052 Nitschke Hall, Toledo, OH 43606-3390, USA

Received 8 March 2005; accepted 29 July 2005

Available online 18 August 2005

Abstract

The technique of electrospinning was employed to fabricate uniform 1-D inorganic–organic composite nanofibers from alcoholic solutions containing polyvinyl pyrrolidone (PVP) and suitable aqueous precursors of yttrium and zirconium ions. Upon firing and sintering under carefully pre-selected time-temperature profiles, yttria-stabilized zirconia nanofibers retaining the original morphological features observed in the as-spun composition were obtained. X-ray diffraction was used to identify the crystalline fate of the final product. Analytical tools such as Raman spectroscopy and scanning electron microscopy (SEM) were employed to elucidate the pathway of ceramic phase formation and the systematic evolution of morphological features in the spun and the processed fibers. Several millimeters long, uniform YSZ nanofibers of high phase purity could be fabricated.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Nanofibers; Electroceramics; YSZ; Electrospinning

1. Introduction

One aspect of current interest and great relevance to the fundamental understanding of the behavior of materials is the role of dimensionality and size on their optical, chemical and mechanical properties for application in a wide range of devices [1]. In this regard, one-dimensional systems with nanoscale attributes are being synthesized and studied in great details. One-dimensional materials or structures are those which exhibit at least one dimension less than 100 nm; average thickness of human hair is ~50,000 nm. For instance, polymer nanofibers are used as selective gas separation membranes, filters, biomedical materials (drug carriers and wound dressings), protective clothing, space mirrors, and precursor platforms or scaffolds for the nanotube/ nanowire synthesis. Owing to the nanoscale features and peculiar shapes, one-dimensional systems exhibit novel physical and chemical properties that can be exploited in optics, catalysis and data storage devices. Thus, they become model systems to study and correlate the theoretical explanations that are still in progress. Such

behavior is almost nonexistent in the bulk material where the particle size is in the micron level. There is growing interest in introducing such attributes in nano-sized inorganic materials as well. The most obvious advantage of doing so is the possibility of their application as quantum dots in a host of devices, such as MEMs, lab-on-a-chip sensors/detectors, structural elements in artificial organs and arteries, reinforced composites, micro solar cell electrodes, micro fuel cells and photocatalysts (splitting of water and in the deactivation of chemical and biological weapons), to name a few.

There is convincing experimental and theoretical evidence that suggests fundamentally new material behavior in nanostructured systems that cannot be predicted by simple scaling laws. For instance, while conductivity enhancement by several orders of magnitude is seen in some nanocrystalline metal oxides, enhanced photocatalytic and photovoltaic activity is evident in other oxides with nanostructural features [2–5]. Hence, there is a window of opportunity to develop nanoarchitected ceramics for achieving high performance gas sensors, photocatalysts, photovoltaics and many other interesting devices.

A novel technique for fabricating 1-D structures is electrospinning. The technique of electrospinning uses

* Tel.: +1 419 530 8103.

E-mail address: aazad@eng.utoledo.edu.

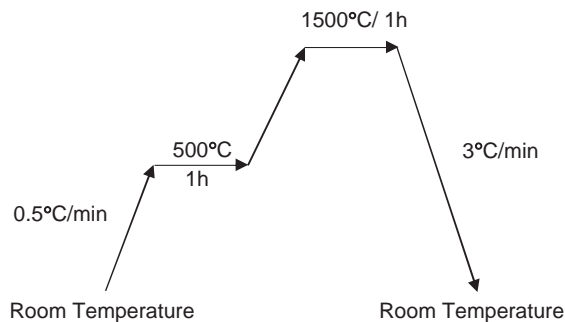


Fig. 1. Firing schedule for the YSZ-PVP polycer composite.

external electrical forces to produce novel polymeric fibers of diameters in the range of 3 to 1000 nm, depending upon the strength of the applied voltage between a drop of the precursor solution (or melt) and the collecting surface. Electrospinning is said to occur when the electrical forces at the surface of the drop overcome the surface tension. When this happens, the solution or melt is ejected as an electrically charged jet and shoots towards the oppositely charged electrode. Upon reaching the collector surface it gets neutralized and collects as dry nanofibers. Electrospinning is a rather old, relatively unknown but simple, convenient and inexpensive method. The first patent was issued more than 70 years ago [6]. During the past few years, however, it has seen a revival [7–13]. The possibility of extending the concept to ceramic systems has opened a new era in nanoscale research during the past couple of years [14–17]. It is possible to synthesize these 1-dimensional nanofibers in pure form, or as suitable ceramic-polymer composites. It is also envisaged that by controlling the jet orifice, one can control and tailor the wall thickness and the internal diameter of the resulting nanofibrillar structures.

In this communication, we report the fabrication of a key ceramic component of relevance to fuel cells, viz., 8 mol% yttria-stabilized zirconia (8YSZ) in nanofibrillar structure. The target composition was first electrospun in the form of polymer-ceramic (*‘polycer’*) composite which were subsequently processed to yield the desired ceramic composition. The transformation of *polycer* to ceramic was followed and the final product was verified by Raman, XRD and SEM-EDS techniques.

2. Experimental procedure

2.1. Preparation of the ceramic precursor solutions

High purity zirconyl chloride, $ZrOCl_2$ (99.99%) was procured from Millennium Chemicals, Australia, while yttrium nitrate, $Y(NO_3)_3 \cdot 6 H_2O$ (99.995%) from Alfa-Aesar, MA, USA, was used as the precursors for the synthesis of the YSZ fibers. The choice of these precursors was based on their appreciable and ready solubility in water. Adequate amount of zirconyl chloride and yttrium nitrate powders were accurately weighed and separately dissolved in minimum volume of de-ionized water by gentle stirring until clear. Subsequently, the two solutions were mixed together and stirred for additional 2 h for effective ionic level mixing and homogenization. The weight calculations were made so as to give 50 mL of a 0.01 M stock solution containing Y^{3+} and Zr^{4+} ions corresponding to the 8 mole% yttria-stabilized zirconia (8 YSZ) solid solution.

2.2. Preparation of the polymeric precursor solutions

Granular polyvinyl pyrrolidone (PVP, average molecular weight $\sim 3 \times 10^6$, Alfa-Aesar, MA, USA) was used as the polymeric component of all the composites fabricated in this study. The polymeric solution was made by dissolving the PVP granular powder in reagent grade ethanol (Fisher Chemicals, PA, USA) under constant and vigorous stirring to give 15 wt.% PVP solution. This concentration was arrived at and selected after several preliminary iterations with respect to the desired viscosity of the inorganic–organic composite solutions were carried out. Due to pronounced volatility of ethanol during and after the preparation, the PVP solution was prepared only when electrospinning was to be carried out; PVP solutions tended to dry out and leave a stiff gel in the container upon prolonged storage.

2.3. Spinning of the fibers

For the electrospinning experiments, equal volumes of the precursor solutions (YSZ and PVP) were added to a beaker and thoroughly mixed with the aid of a magnetic

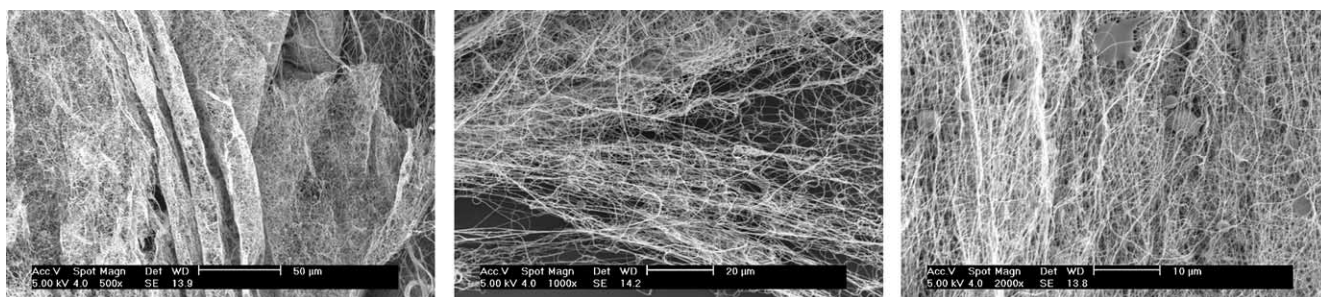


Fig. 2. Morphological features of the as-spun $ZrOCl_2$ -PVP fibers. (Flow rate: 0.05 ml/h; applied voltage: 12 kV. Magnification bar, L to R: 50, 20 and 10 μ m.)

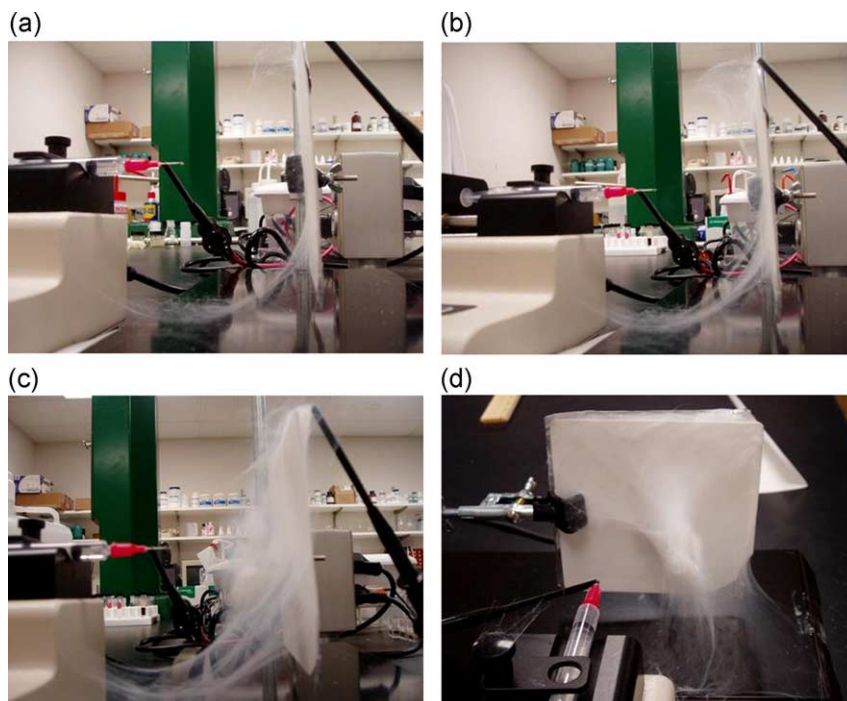


Fig. 3. Photographic timeline of the progress of the electrospinning process and fiber growth in the case of 1 : 1 aqueous YSZ-ethanolic PVP solution (flow rate: 0.03 ml/h; applied voltage: 12–15 kV); shots were taken after (a) 26, (b) 50, (c) 103 and (c) 104 min from the start of the spinning process.

stirrer to form a homogeneous viscous solution. After mixing, this solution was drawn into a 5 ml capacity Benton-Dickenson clinical syringe (VWR International, IL, USA). Precision-tip 1 or 1 1/2 inch long stainless steel needles from EFD Inc., RI, USA (23 or 25 gauge) were attached to the syringe which was mounted on a programmable syringe pump (KDS-100). The syringe and needle make and type, flow rate, and amount to dispense were entered in the syringe pump memory through the front panel.

The pump could be operated either in horizontal or vertical configuration and no difference was noted in the quality of the fibers thus produced. The preferred orientation of the syringe pump in this work was horizontal. An indigenously made DC power supply (30 kV max) with the high voltage system from Ultra Volt (FL, USA) and a circuit design originally developed at NASA Glenn Research Center [18] was used for the electrospinning of fibers.

One terminal of the power supply was connected to the needle while the other was connected to the collector plate. The collector plate was grounded.

Several different types of collector plates were used. A simple collector plate was made by layering several thicknesses of aluminum foil into approximately a 4 × 4 inch square. For the ease of sample handling and subsequently processing, ceramic dishes/plates were used to collect the fibers. In the case of ceramic dishes, a small 1 × 1 square inch of aluminum foil was attached to the back of the dish with double-sides tape and the electrode was hooked to the foil. This allowed the fibers to be collected directly onto the ceramic plate. Using the high voltage power supply, 12–15 kV was applied between the needle and the collector plate in order to initiate the electrospinning. After the voltage was turned on, the syringe pump was started. The voltage was tweaked precisely until the fibers began to form steadily and collect on the collector plate facing the syringe,

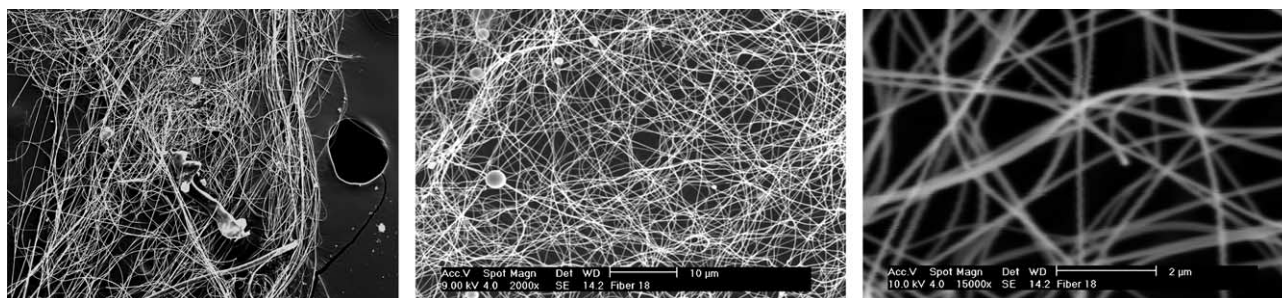


Fig. 4. Scanning electron micrographs of the YSZ-PVP fibers at different magnification. Identical morphological features of individual fibers with large aspect ratio can also be easily seen.

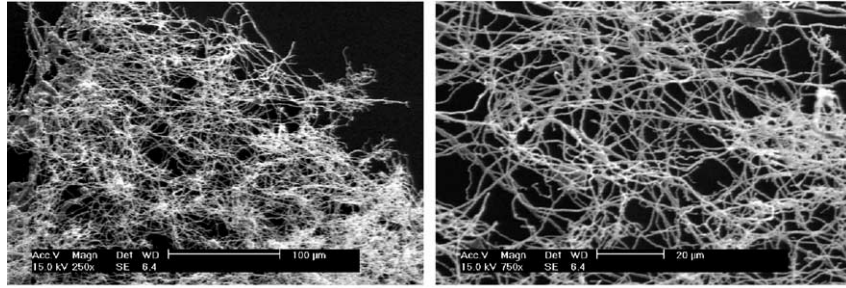


Fig. 5. Electron micrographs of the calcined YSZ fibers. The fibrillar features of the parent composite are retained in the fired ceramic after the polymer has been removed.

placed about 3 inches away from the tip of the needle. Typically, 1 ml of the solution was spun at a time, with a flow rate between 0.03–0.12 ml/h. Thus, an individual run lasted about 8 to 33 h with short intermittent interruptions of the run for periodic cleaning of the clogged needle from time to time.

After spinning was complete, small fraction of the fibers collected on ceramic plates were separated for characterization by Raman and SEM techniques. The ceramic dish with the remaining fibers was directly placed in a PID-controlled programmable box furnace and fired to remove the polymeric component and to form the desired ceramic.

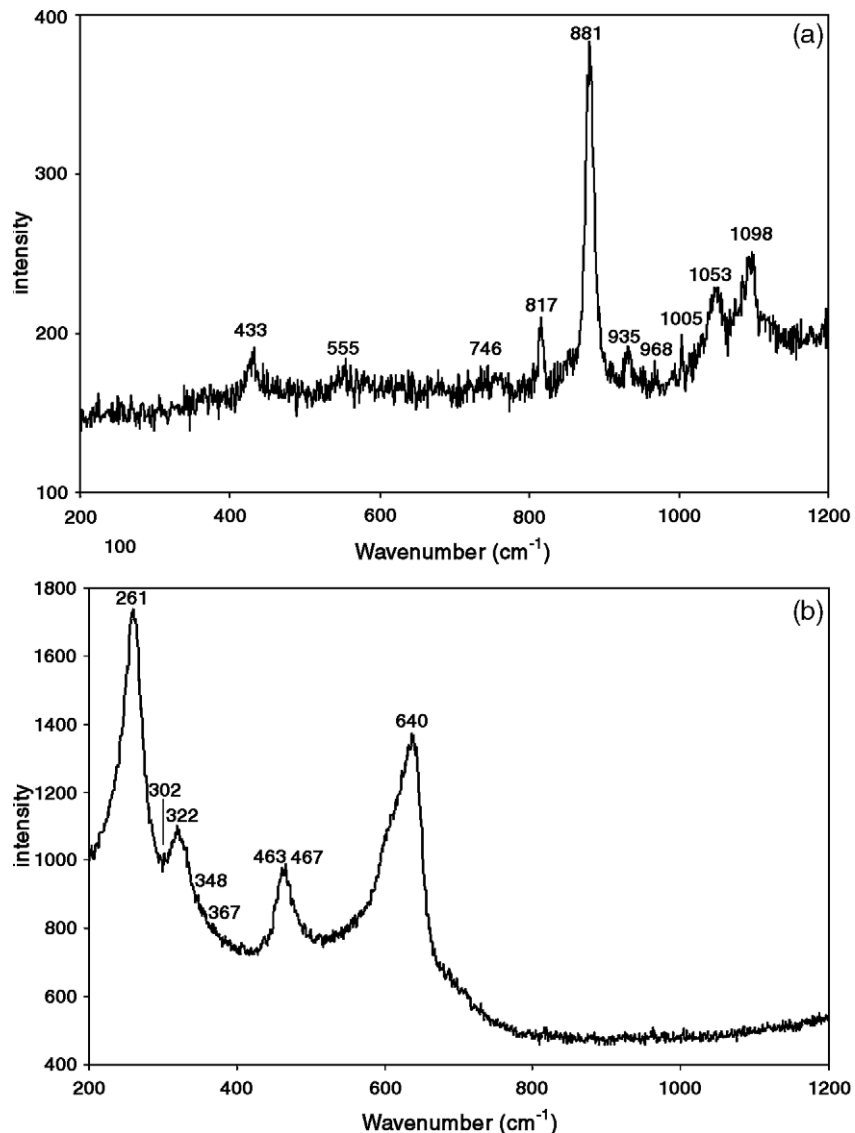


Fig. 6. Raman spectra of the ethanolic solution of PVP (a) and YSZ-PVP (b) composite fibers after they were fired at 1500 °C/1 h.

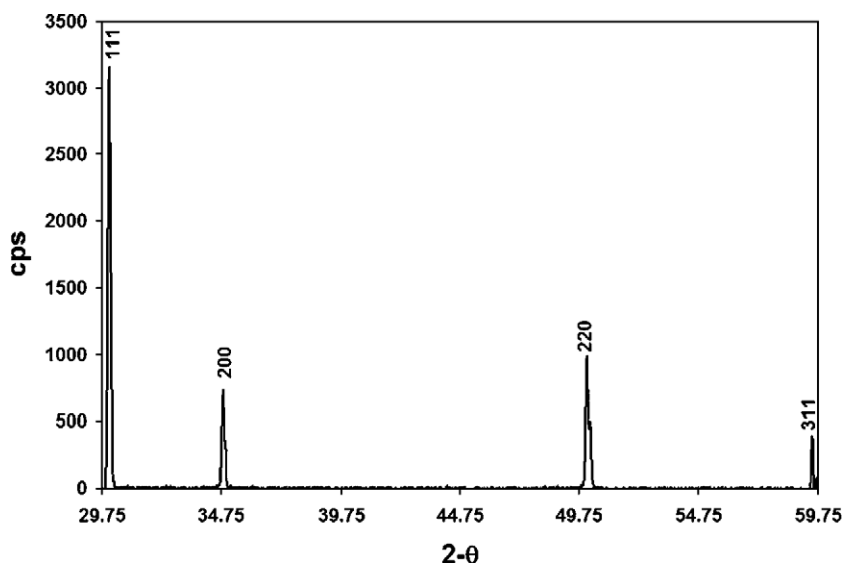


Fig. 7. X-ray diffraction signature of electrospun 8 mol% Y_2O_3 -stabilized ZrO_2 fibers heated at 1500 °C/1 h in air.

In the case of 8 YSZ, fibers were fired up to 1500 °C for 1 h in two stages according to the schedule shown in Fig. 1. The small heating rates were chosen so as to ensure the removal of organic components without destroying the nanofibrillar morphological features in the end products and also to avoid the disintegration of the ceramic fibers; as such, ceramics exhibit rather poor thermal shock resistance, even in bulk. After the furnace was cooled, samples were collected for characterization by various analytical techniques.

3. Results and discussion

In order to test the feasibility of making ceramic fibers by this technique, prior to the electrospinning of the YSZ polycer composites, first a 5 wt.% aqueous solution of zirconyl chloride was mixed with 15 wt.% HMWPVP in equal volumes, homogenized and spun. Fig. 2 shows the scanning electron micrographs of the $ZrOCl_2$ -PVP composite fibers collected on a ceramic plate. Several inches long fibers with uniform diameter were formed.

Fig. 3 shows the progress of the spinning process in real-time and the increase in the amount of the YSZ-PVP composite fibers formed.

The scanning electron micrographs of the as-electrospun composite fibers from the YSZ-PVP solution are shown in Fig. 4.

The fibrillar attributes observed in the as-spun YSZ-PVP composite were virtually retained in the samples that were fired at 1500 °C for 1 h and furnace cooled, as per the heating schedule shown in Fig. 1. This is evident in the SEM pictures shown in Fig. 5.

Fig. 6 shows the comparative Raman spectra (LabRam, Jobin-Yvon Horiba Inc., using 633 nm excitation laser; wave number range: 200 to 4000 cm^{-1}) of PVP in ethanol and the fired YSZ-PVP composite, respectively. The Raman shifts at ~745, 880 and 1053 cm^{-1} in Fig. 6a belong to ethanol [19].

As can be seen, there is no trace of the polymer remnant in the fired sample. The slightly displaced Raman lines at 260, 322, 463/467 and 640 cm^{-1} represent zirconia that contains Y_2O_3 phase, whose mild signatures at 302, 348 and 367 cm^{-1} [20–22] can also be observed in the Raman spectrum shown in Fig. 6b. The shift in the Raman lines from those for pure ZrO_2 and Y_2O_3 phases is a

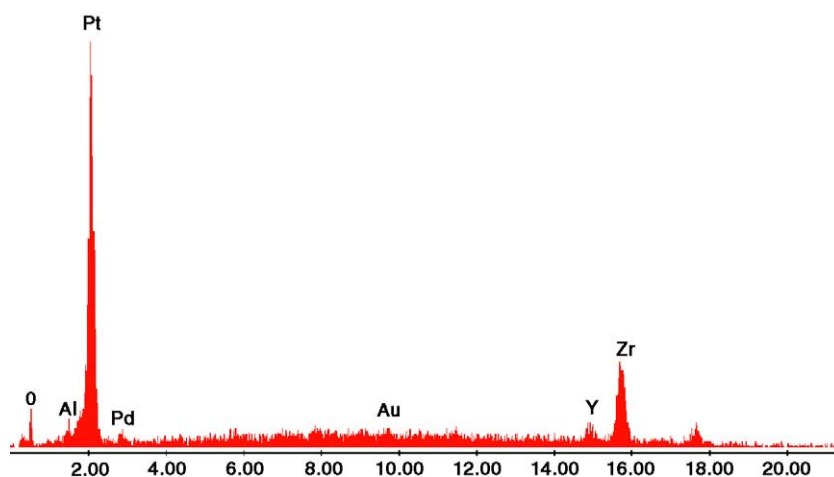


Fig. 8. EDS pattern in the fired YSZ ceramic sample.

manifestation of the incorporation of the latter in the zirconia lattice and the stabilization of the former. It is also worth pointing out that the bands at 368 and 540 cm^{-1} , characteristic of monoclinic zirconia phase [23] are totally absent.

The formation of crystalline YSZ phase in the YSZ-PVP composite fired at 1500 °C/1 h is corroborated by the XRD signature collected at room temperature, using a Scintag XDS-2000 diffractometer with monochromatic $\text{CuK}\alpha$ radiations and Ni filter at a scan rate of 1° (2- θ)/min. The X-ray diffraction is shown in Fig. 7, which excellently matches the JCPDS-ICDD card #30-1468 for the cubic solid solution 8 YSZ.

The energy dispersive spectrum (EDS) collected on the fired YSZ sample (whose microstructure is illustrated in Fig. 5) distinctly identifies Zr and Y as the elemental component in the fiber and is shown in Fig. 8. The peaks belonging to Pt and Pd come from the alloy paste used for coating the calcined samples for SEM viewing.

4. Conclusions

The technique of electrospinning has been successfully employed to fabricate several inches long 1-D ceramic fibers consisting of phase pure yttria-stabilized zirconia from a polymeric solution containing appropriate metal cations in the desired mole ratios. The polymeric component aided in obtaining the required viscosity of the base mixture. The structural and microstructural artifacts of the resulting fibers were investigated by Raman, SEM-EDS and XRD techniques.

Acknowledgments

Thanks are due to Thomas Jacob of Electronics Laboratory in the College of Engineering for assembling the power supply used in the electrospinning experiments. The financial support provided by the University of Toledo's Office of Research in the form of a University Research and Awards Fellowship (URAF) grant was

pivotal for the initiation of this work and is gratefully acknowledged.

References

- [1] Y. Xia, P. Yang, *Adv. Mater.* 15 (2003) 351.
- [2] P. Knauth, H.L. Tuller, *J. Appl. Phys.* 85 (1999) 897.
- [3] I. Kosacki, T. Suzuki, V. Petrovsky, H.U. Anderson, *Solid State Ionics* 136 (2000) 1225.
- [4] Z. Zuo, J. Ye, K. Sayama, H. Arakawa, *Nature* 414 (2001) 625.
- [5] C.D. Grant, A.M. Schwartzberg, G.P. Smestad, J. Kowalik, L.M. Tolbert, J.Z. Zhang, *J. Electroanal. Chem.* 522 (2002) 40.
- [6] A. Formahls, US Patent 1875504 (1934).
- [7] D.H. Reneker, I. Chun, *Nanotechnology* 7 (1996) 216.
- [8] J. Doshi, G. Srinivasan, D.H. Reneker, *Polym. News* 20 (1995) 206.
- [9] I. Chun, Fine fibers spun by electrospinning process from polymer solutions and polymer melts. Ph.D. Dissertation, University of Akron, OH, (1995).
- [10] D.H. Reneker, A.L. Yarin, H. Fong, S. Koombhongse, *J. Appl. Phys.* 87 (2000) 4531.
- [11] C.T. Laurencin, F.K. Frank, US Patent 6689166 (2004).
- [12] A.G. MacDiarmid, W.E. Jones Jr., I.D. Norris, J. Gao, A.T. Johnson Jr., N.J. Pinto, J. Hone, B. Han, F.K. Ko, H. Okuzaki, M. Llaguno, *Synth. Met.* 119 (2001) 27.
- [13] R. Kessick, J. Fenn, G. Tepper, *Polymer* 45 (2004) 2981.
- [14] D. Li, Y. Xia, *Nano Lett.* 3 (2003) 555.
- [15] D. Li, Y. Xia, *Adv. Mater.* 16 (2004) 1151.
- [16] S. Choi, B. Chu, S.G. Lee, S.W. Lee, S.S. Im, S.H. Kim, J.K. Park, *J. Sol-Gel Sci. Technol.* 30 (2004) 215.
- [17] H. Guan, C. Shao, Y. Liu, N. Yu, X. Yang, *Solid State Commun.* 131 (2004) 107.
- [18] D.J. Eichenberg, NASA Glenn Research Center, Cleveland, OH (private communication); <http://www.nasatech.com/Briefs/Nov03/LEW17190.html>.
- [19] S. Sivakesava, J. Irudayaraj, A. Demirci, *J. Ind. Microbiol. Biotech.* 26 (2001) 185.
- [20] J. Moon, H. Choi, Y. Kim, C. Lee, *J. Mater. Sci. Lett.* 20 (2001) 1611.
- [21] A. Sekulic, K. Furic, A. Tonejc, A.M. Tonejc, M. Stubićar, *J. Mater. Sci. Lett.* 16 (1997) 260.
- [22] A. Hartmanova, I. Thurzo, M. Jergel, J. Bartos, F. Kadlec, V. Zelezny, D. Tunega, F. Kundracik, S. Chromik, M. Brunel, *J. Mater. Sci.* 33 (1998) 969.
- [23] C. Li, M. Li, *J. Raman Spectrosc.* 33 (2002) 301.