SAND2013-6065P

Responsive Nanocomposites: Synthesis of Novel Hafnium Carboxylates for the Production of Ceramic Nanowires via Electro/Forcespinning

Daniel T. Yonemoto, Timothy J. Boyle, Thu Q. Doan, Nelson S. Bell

Introduction

The design of materials that respond to changing environmental conditions is a leading-edge materials area that will impact fundamental scientific and mission areas of Sandia. For this project, the responsive materials of interest were nanocomposites. Nanocomposites have come to the forefront of study since very low load levels (< 5 %) of the filler can have a dramatic impact on the matrices final properties. This is due to the increased interfacial interaction of the 1D nanomaterials with the polymeric matrix.

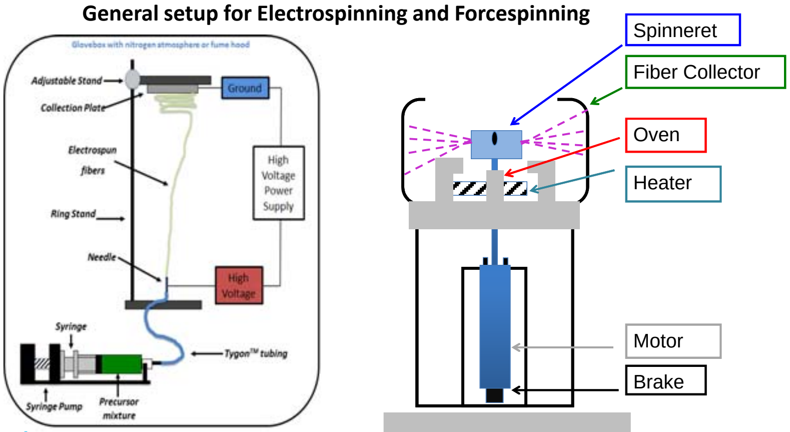
The production of responsive nanocomposites requires the development of fundamental concepts and data to understand the nature and theory of nanomaterials interaction with polymeric materials. This project focuses on the production of ceramic wires to better impact the final characteristics of the polymeric matrix. The production of wires is desired to increase the aspect ratio of the nanomaterial to the polymer and potentially amplify their effects. Once these materials can be produced repeatedly, further investigations will then be needed to determine their effect on the bulk materials.

Nanowire Production Methods

Electrospinning

Electrospinning involves the application of a high electrical field (1-5kV/cm) to a drop of solution pushed through a needle. A general setup is shown in Figure 2.1. The applied high electrical force overcomes the surface energy of the droplet and forms a Taylor cone, which through a whipping motion, forms mats of fibers that possess a high surface area to mass ratio. This method is a simple yet versatile continuous process that can produce fiber diameters in ranges from a few micrometers to 100 nanometers. In order for a continuous fiber to be formed, it is necessary to have a link from drop to drop. Typically this requires the use of a polymer; however, we have shown that simple precursors, such as $[Sn(OR)_2]$ or $[Sn(NR_2)(OR)]_2$ dissolved in polar solvents will work to generate nanomaterials.[1]

General setup for Electrospinning and Forcespinning



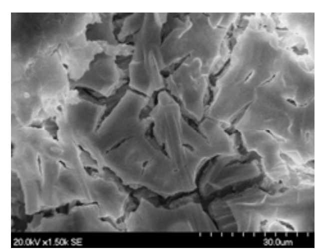
Forcespinning

Another method of interest for the production of ceramic wires is forcespinning. This relatively new method uses centrifugal force and air resistance to spin fibers . It works by filling a reservoir cup with the desired material followed by rotation at high speeds. A set of small holes allow the material to escape and if properly designed the material will form wires. The company 'FiberRio' has made these commercially available and SNL recently obtained it for use in another project. We have investigated the utility of this for production of nanofibers that would be more consistent with higher yields than those noted for ES. Forcespinning, however, does require a lot of material in order to work. Additionally the apparatus is not set up in an inert atmosphere making work with air sensitive materials difficult.

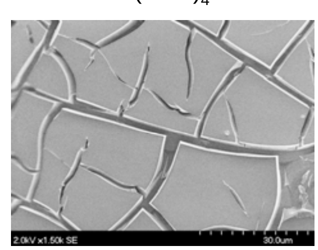
[1]Boyle, T. J., T. Q. Doan, et al. (2012). "Tin(ii) amide/alkoxide coordination compounds for production of Sn-based nanowires for lithium ion battery anode materials." Dalton Transactions.

Forcespinning Results

Forcespinning was also attempted on a variety of compounds to produce nanowires. Unfortunately the SEM images show that our materials sprayed rather than producing the desired wire formations similar to the commercially available components. Further tests are needed to determine the optimal parameters to produce wires using this technology. To the right are SEM images of our sprayed materials.



$Hf(OBu^t)_4$



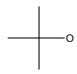
$[Hf(\mu\text{-}OBc)(OBu^t)_3]_2$

Synthesis of Novel Hafnium Carboxylates

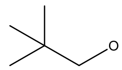
$$Hf(OR)_4 + x\,HORc \xrightarrow{tol} Hf(ORc)_{4-x} + x\,HOR$$

x = 1,2 or 4

OR =



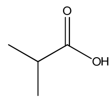
tert-butoxide (OBu^t)



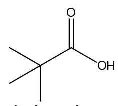
neopentoxide (ONep)

Starting materials were chosen to determine the effects of steric bulk on the final morphologies of the molecular structure and nanomaterial

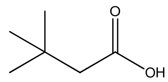
HORc =



isobutyric Acid (HOPc)

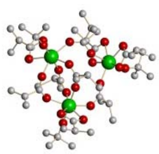


trimethylacetic Acid (HOBc)

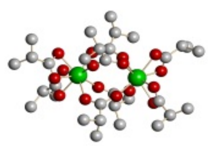


tert-butylacetic Acid (HONc)

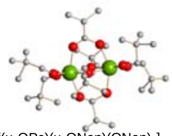
In order to achieve the necessary linkage from drop to drop to form nanowires via electrospinning and forcespinning, carboxy functionalized precursors were utilized. Surprisingly there is very little information available on the structural properties of these compounds. As a result, we undertook the synthesis and characterization of these novel precursors. To do this, commercially available hafnium tert-butoxide and its neopentoxide derivative were reacted on a 1:1, 1:2, and 1:4 ratio with the above carboxylic acid groups. Once mixed, the reactions stirred for 12hours after which crystals were grown of the novel compounds and the appropriate characterization then followed. Below are crystallographic structure plots of various compounds.



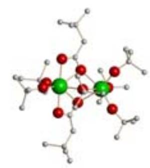
$Hf_3(\mu\text{-}OPc)_5(OPc)_4(OBu^t)_3$



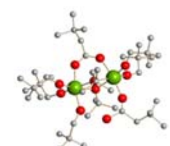
$Hf_2(\mu\text{-}OPc)_4(OPc)_4$



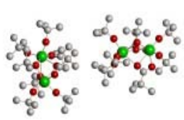
$[Hf(\mu\text{-}OPc)(\mu\text{-}ONep)(ONep)_2]_2$



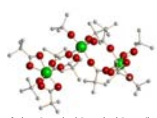
$Hf_2(\mu_c\text{-}ONc)_2(\mu\text{-}OBu^t)(OBu^t)_5$



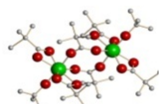
$Hf_2(\mu\text{-}ONc)(\mu\text{-}ONep)_2(HONc)(ONep)_5$



$[Hf_2(\mu_c\text{-}OBc)(\mu\text{-}OBu^t)_2(OBu^t)_5]_2$

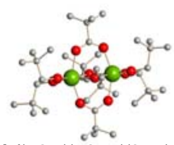


$Hf_3(\mu\text{-}OBc)_4(OBc)_4(OBu^t)_4$

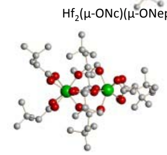


$[Hf(\mu\text{-}OBc)(OBu^t)(OBc)_2]_2$

$Hf_2(\mu\text{-}OBc)_4(OBc)_4$

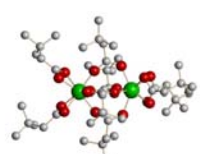


$[Hf(\mu\text{-}OBc)(\mu\text{-}ONep)(ONep)_2]_2$



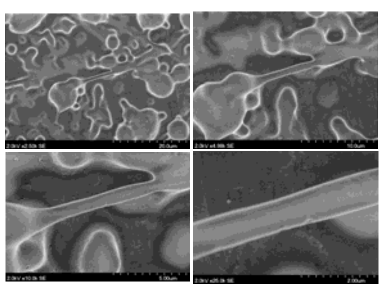
$Hf_2(\mu\text{-}ONc)_4(ONc)_4$

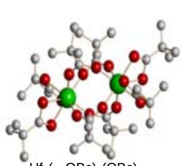
Electrospinning Results



$Hf_2(\mu\text{-}ONc)_4(ONc)_4$

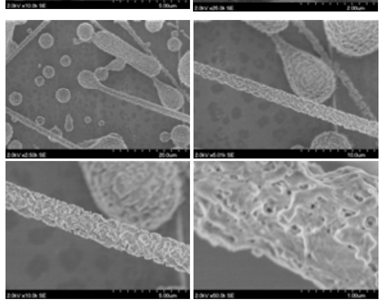
Spun at:
0.2 mmol
10kV
30 μL/min

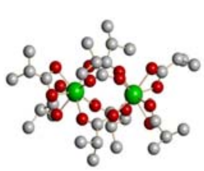




$Hf_2(\mu\text{-}OBc)_4(OBc)_4$

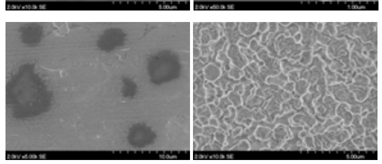
Spun at:
0.2 mmol
10kV
30 μL/min

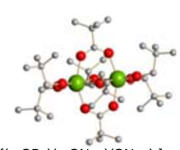




$Hf_2(\mu\text{-}OPc)_4(OPc)_4$

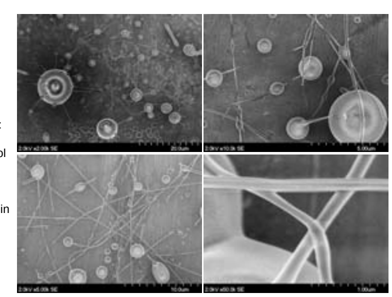
Spun at:
0.2 mmol
10kV
15 μL/min

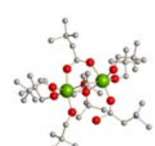




$[Hf(\mu\text{-}OBc)(\mu\text{-}ONep)(ONep)_2]_2$

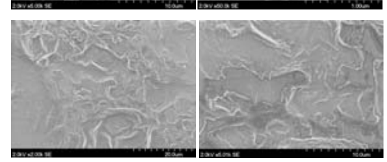
Spun at:
0.2 mmol
10kV
60 μL/min





$Hf_2(\mu\text{-}ONc)(\mu\text{-}ONep)_2(HONc)(ONep)_5$

Spun at:
0.2 mmol
10kV
60 μL/min



SEM imaging of our various fiber mats has shown our ability to make wire and other mixed morphologies. Of particular interest is the grainy wires formed using the hafnium trimethylacetic acid derivative. The pores present in this sample could potentially add to the surface area of our compounds increasing their influence on the bulk material. Further testing is needed to determine if this result is reproducible

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

AML Advanced Materials Laboratory

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NINE