

DEVELOPMENT OF NANOFIBROUS TARGET MATERIALS FOR SHORT-LIVED ISOTOPE PRODUCTION

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

August 2018

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Abstract

For over a decade, refractory metals and carbide powder materials have been used to produce radioactive ion beams (RIB) using the isotope separation online method at the ISAC facility at TRIUMF. A continuous 500 MeV proton beam generated from the world's largest cyclotron is used to bombard the target materials to produce exotic isotopes. Particularly, short-lived isotopes are of high degree of interest in many disciplines including medicine, but only limited quantities are available due to the nuclear decay during the time associated with the diffusion and effusion of the species to migrate from the target materials to the ion source. The target materials are required to operate at high temperature to promote the release of the species; therefore, sintering of the grains is promoted, which results in lengthening of the diffusion paths for the isotopes causing the reduction of RIB yields. A possible way to improve the intensities of RIBs is by incorporating nanoparticle materials into nanofibres to increase the release efficiencies. In this study, nanometric SiC fibre target materials are fabricated by electrospinning. Upon a high-temperature heat treatment process, the organic carrier converts into a carbon fibre backbone that immobilizes the SiC target material with controlled nanometric grain size and reduced sintering dynamics. The weight composition of the final product is determined to be 60% SiC and 40% carbon nanofibre. The nanofibres were pressed into discs to achieve a combination of highly dense ($1.1\text{-}1.2\text{ g/cm}^3$) and porous (56-54% total porosity) target materials, preserving the fibre morphology. The nano-SiC fibrous target material will be tested in September 2018 to evaluate the RIB yields explicitly for the short-lived isotopes at several milliseconds such as ^{22}Al (91.1 ms), ^{20}Mg (90.8 ms), ^{21}Mg (122 ms), and ^{20}Na (447.9 ms).

Lay Summary

Since the first discovery of a radioactive elements, expanding the chart of nuclide has been essential for the fundamental of nuclear physic research and for many other disciplines including medicine. One common method to produce radioactive ion beams is using the Isotope Separation On-line technique in which target materials are irradiated with a proton driver beams. The common materials for isotope production targets are refractory materials which combine short diffusion paths and high temperature resistively needed to promote the release efficiencies. However, the inevitable sintering process has a negative impact for short-lived isotopes due to grain growth and removal of pores, thus reducing the release efficiencies. Fabrication of nanofibrous target materials is a promising way to improve the RIB intensities for such high demand short-lived radioisotopes. Nano-SiC fibres have been successfully developed and are able to be operated at high temperature with the preservation of the nanostructures.

Preface

The present work was conducted in the Advanced Fibrous Materials Laboratory at the University of British Columbia and in the ISAC Chemistry Laboratory at TRIUMF. My supervisors, Dr. F. Ko (UBC), Dr. A. Gottberg (TRIUMF), and Dr. P. Bricault (TRIUMF retiree) were involved and assisted me to complete the present thesis.

In Chapter 3, the ISAC target fabrication was based on the original work conducted by Dr. M. Dombisky and Ms. V. Hanemaayer. I am responsible for optimizing the target material processes for mass production to be used in the ISAC facility. Furthermore, I conducted the experiment on the sintering effect of ZrC target material and provided the SEM images.

In Chapter 4, the fabrication of SiO₂/PAN nanocomposite fibres was developed by Dr. L. Wan. The electrospinning of PAN solution was performed and optimized by Dr. A. Bahi. I was responsible for the thermal treatment process and provided the data on the fibre density and shrinkage. Dr. L. Wan and I performed the fabrication of α -SiC/PAN nanofibres. The SEM, EDS and XRD experiments were performed with the help from Dr. L. Wan. I conducted the experiments on the instability of α -SiC at high-temperature treatment under vacuum and replaced it with β -SiC. XRD data confirming the silicon coating on the Evaporator-2 viewport window was performed at UBC Chemistry X-ray crystallography facility with the help from Ms. A. Lam.

In Chapter 5, the dynamic light scattering particle size analysis and thermal conductivity measurements were performed with the help from Dr. S. Soltanian.

In Chapter 6, thermogravimetric analysis data was performed with the help from Dr. M. Cho. STEM/EDS data analysis was performed at SFU 4D lab with the help from Dr. X. Zhang. I

acquired the XRD data at the EM Lab at UBC and SEM images at the ISAC-SEM laboratory at TRIUMF. All the data were generated and compiled by myself, and I wrote the entire thesis.

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List of Symbols

ρ_{theo}	theoretical density
ρ_{tot}	total density
m.p	melting point
np	nanoparticles
$t_{1/2}$	half-live
wt%	weight percentage

List of Abbreviations

Be	Berry numbers
BF	bright field
CERN	The European Organization for Nuclear Research
C-PAN	carbon from carbonized polyacrylonitrile
CRC	Cyclotron Resource Centre
DLS	dynamic light scattering
DMF	dimethyl formamide
EDS	energy dispersive X-ray spectroscopy
EPICS	experimental physics and industrial control system
EtOH	ethanol
FEBIAD	forced electron beam induced arc discharge
FWHM	full width at half-maximum
GANIL	Grand Accélérateur National d'Ions Lourds
HAADF	high-angle dark field
HCl	hydrochloric acid
HP	high power
HRIBF	Holifield Radioactive Ion Beam Facility
HR-TEM	high-resolution transmission electron microscope
IF	in-flight
IR	infrared
ISAC	Isotope Separation and Acceleration facility at TRIUMF
ISOL	Isotope separation on-line
ISOLDE	Isotope Mass Separator On-line facility at CERN

LP	low power
MWCNT	multi-walled carbon nanotubes
NMF	N-methylformamide
O.D	outer diameter
OM	optical microscope
PAN	polyacrylonitrile
PDF	powder diffraction file
RIB	radioactive ion beam
RVCF	reticulated-vitreous-carbon foam
SDS	sodium dodecyl sulfate
SE	secondary electron
SEM	scanning electron microscopy
SF	stacking fault
STEM	scanning transmission electron microscopy
TEOS	tetraethyl orthosilicate
TGA	thermogravimetric analysis
TRIUMF	Canada's national particle accelerator centre
ULA	ultra-low viscosity adapter
XRD	X-ray diffraction

Acknowledgements

Firstly, I would like to express my sincere gratitude to my supervisors Dr. Frank Ko, and Dr. Alex Gottberg for their guidance, encouragement and gracious support throughout the course of my work, for their expertise in the field that motivated me to continue my work in this area, and for their faith in me at every stage of this research. I will forever be thankful to my former supervisor Dr. Pierre Bricault for providing great advice many times during my career at TRIUMF.

I also wish to thank Dr. Oliver Kester, Dr. Friedhelm Ames, Dr. Peter Kunz, Dr. Lia Merminga, and Dr. Marik Dombisky for believing in my research capabilities and for sharing their research philosophy.

My special thanks are extended to the AFML members Dr. Addie Bahi, and Dr. Lynn Wan, Dr. Taeski Chae, Dr. Li Ting, and Dr. Heejae Yang for their help and support. I also wish to acknowledge the technical help provided by Aaron Schmidt and Jacob Kabel for setting up the SEM instrument at TRIUMF.

I would like to acknowledge the financial support for this project by TRIUMF via a contribution agreement with the National Research Council of Canada.

Above all, special thanks are owed to my wife Sijia for her unfailing love, support and understanding for my pursuit of a master's degree while she was pregnant. Since our son's birth, I have watched her turn into a mother so quickly and skillfully. She has battled through endless sleepless nights to make sure our son Ethan is fed and loved, and made the completion of this thesis possible.

Dedicated to the memory of my beloved parents

Chapter 1 Introduction

1.1 Background of ISOL facilities

More than 3000 radioactive isotopes have been discovered so far; however, only from half of these isotopes detailed information is known [1]. Almost all the stable or near-stable long half-life nuclides have been well identified, either due to their natural or artificial abundance. As illustrated in Figure 1-1 of the nuclide chart, the black squares represent the stable isotopes of the elements in the periodic table. Far away from the region of stability, however, these short-lived isotopes which do not exist naturally on earth, are available only in limited quantities and focus a high degree of interest in many disciplines, including medicine.

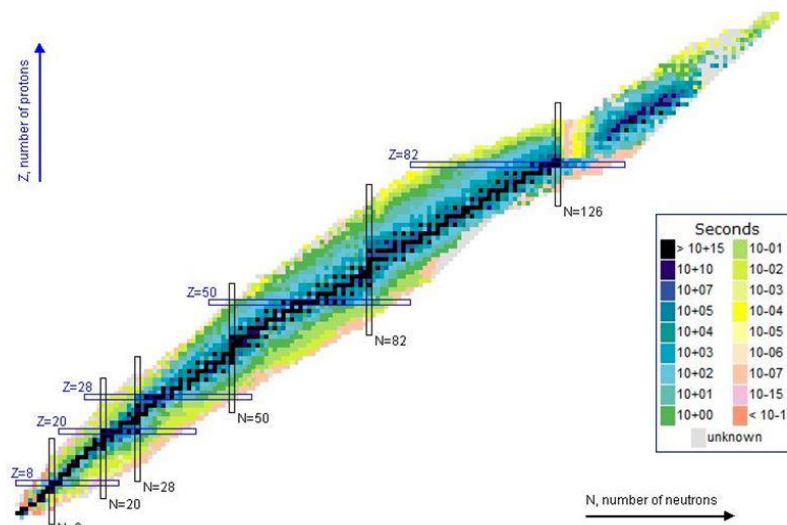


Figure 1-1: The chart of nuclides [2]. The insert shows the color scheme for the different half-lives (in seconds) of the isotopes.

The two common techniques to produce exotic isotopes (half-lives less than 1 minute) are the In-Flight (IF) separation, and the Isotope Separation On-line (ISOL) techniques [3] [4]. Both methods essentially transport isotopes from irradiated materials to experimental stations where the nuclear properties can be studied. The major differences between the IF and ISOL methods are the primary driver beam, the target, and the resulting properties of the selected isotope beam.

In the ISOL method, at least one accelerator system is usually required: A high-energy light-ion driver beam accelerator. A combination with a post-accelerator is often used to achieve different energies of the radioactive ion beams (RIBs). The driver beam is used to bombard thick target materials that are kept at high temperature. An abundance of radioactive nuclides is produced by spallation, fragmentation and fission processes; then these isotopes thermally diffuse out from the target material. An ion source is usually coupled close to the crucible or the target container to extract the RIBs which then extracted and accelerated to the desired energies [5]. A schematic of an ISOL system is illustrated in Figure 1-2.

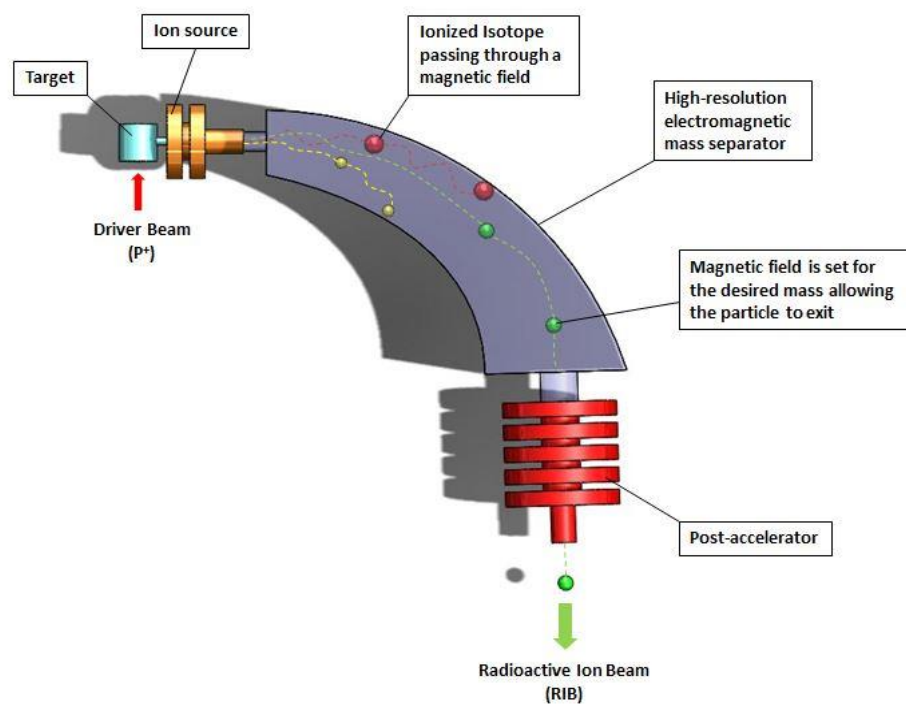


Figure 1-2: A schematic of an ISOL system.

1.1.1 TRIUMF-ISAC facility

In the early 1970s, TRIUMF, Canada's national laboratory for nuclear and particle research located in Vancouver, built the world's largest cyclotron to produce high energy protons. The 500-MeV cyclotron can accelerate protons up to 75% of the speed of light and provide beam intensities of up to 100 μA per beamline. Four transport beam lines connect to the cyclotron which allow to deliver the accelerated proton beams to different experimental areas simultaneously. One of these beamlines is used for exotic isotope production in the Isotope Separation and Acceleration facility (ISAC), as shown in Figure 1-3 (highlighted ISAC-I in orange and ISAC-II in red). This state-of-the-art facility uses the ISOL technique which consists of a primary proton driver beam, a target and ion source, a high-resolution mass separator, and

an ion beam transport system to produce a variety of radioactive ion beams for a broad range of scientific disciplines including nuclear astrophysics, molecular and materials science.

Depending on the desired elements, a particular ionization principle such as surface ionization, resonant laser ionization or FEBIAD (forced electron beam induced arc discharge) ionization is chosen and the respective ion source is closely coupled to the target container to provide good quality, high intensity RIBs.

In 1998, the first RIB was produced at the ISAC facility using CaO target pellets [6]. A surface ionization source was used to successfully deliver ^{37}K with a lifetime of 1.2 seconds to an experiment. Ion source research and development program is paramount at the TRIUMF-ISAC facility to improve the purity, intensity and availability of the RIBs [5] [7], but this subject is not covered in this work. This thesis describes a possible way of improving targets by using nanometric materials.

BEAM LINES AND EXPERIMENTAL FACILITIES

September 2015

ISAC-I
ISAC-II
ARIEL

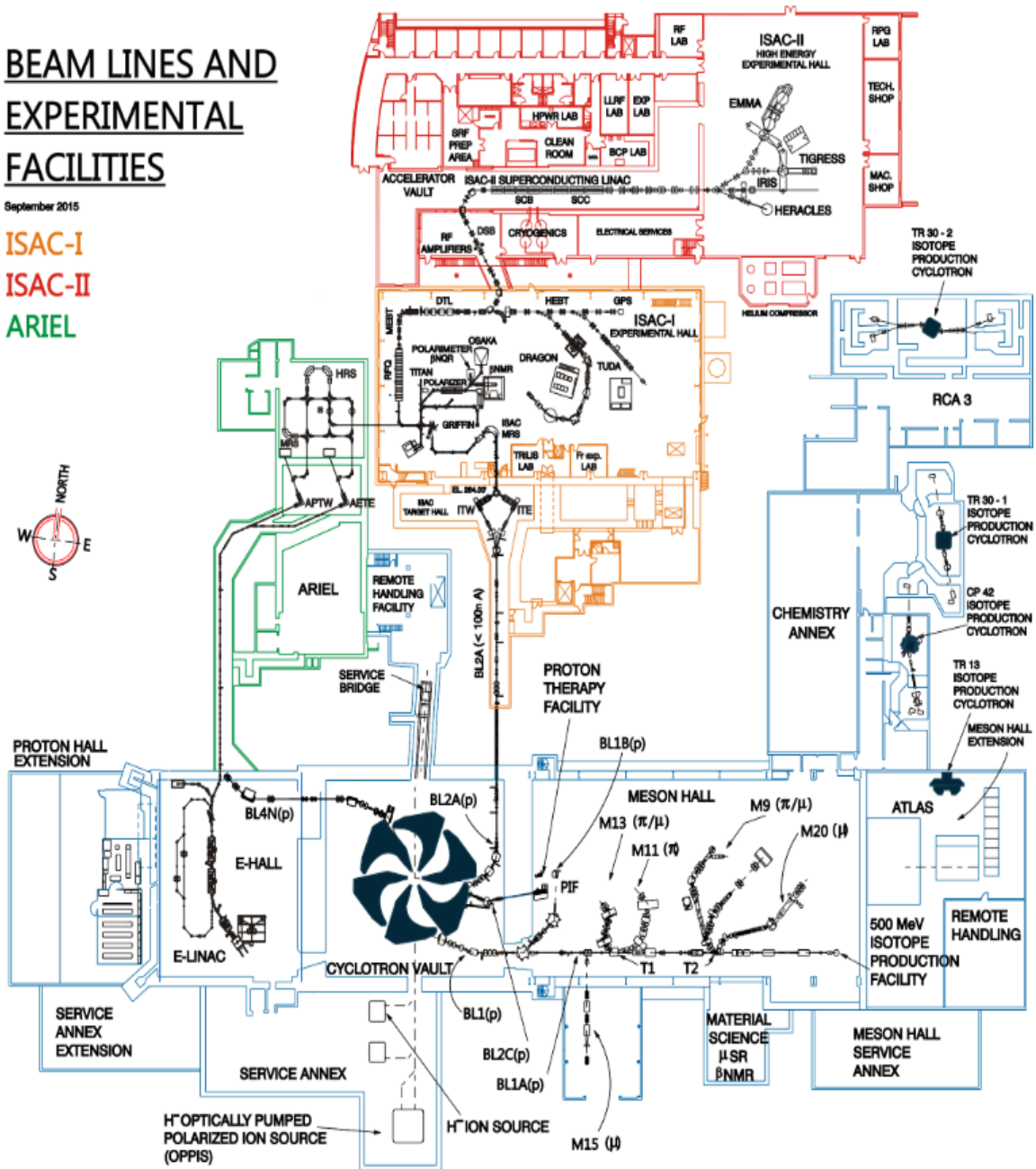


Figure 1-3: Overview of beam lines and experimental facilities at TRIUMF; highlights are the ISAC-I (orange), ISAC-II (red), and ARIEL (green) facilities. [Drawing by TRIUMF]

1.1.2 International framework

The ISOLDE facility at CERN (The European Organization for Nuclear Research) has been in operation since 1967 to produce low-energy RIBs. About twenty years later, the CRC (Cyclotron Resource Centre) facility in Louvain-la-Neuve, Belgium also started producing RIBs using the ISOL method. At that time, CRC was able to produce and deliver ^{13}N and ^{19}Ne with intensities of 4×10^8 and 2×10^9 ions/s, respectively [8]. Moreover, HRIBF (Holifield Radioactive Ion Beam Facility) at Oak Ridge National Laboratory operated for 50 years to provide high-quality beams of 200 rare isotopes. It is worth mentioning that the HRIBF target group was actively involved in materials research and development particularly in high porous targets to improve short-lived RIB intensities (see section 1.3); however, the laboratory was placed in shutdown status in 2012.

Today, the major ISOL facilities in the world to provide a large variety of RIBs include GANIL (the Grand Accélérateur National d'Ions Lourds) SPIRAL (Système de Production d'Ions Radioactifs en Ligne) in France, and FRIB (Facility for Rare Isotope Beams) in USA. The world-renowned ISOL facilities are summarized in Table 1-1.

The growing interest in research using exotic RIBs led to the future ARIEL (Advanced Rare Isotope Laboratory, Figure 1-3 highlighted in green) at TRIUMF. ARIEL will transform TRIUMF into a multi-user facility that will provide up to three simultaneous beams [9].

Facility	Location	Accelerated Driver Beam *	Main RIBs available
CRC	Louvain-La-Neuve Belgium	Cyclotron: p 30 MeV, 200 μ A	Low masses, (e.g., ^{13}N , ^{19}Ne)
HRIBF	Oak Ridge, USA	Cyclotron: p, d, α 50-100 MeV, 10-20 μ A	Large variety including fission fragments
ISOLDE	CERN, Geneva	PS booster: p 1.4 GeV, 2 μ A	Large variety including fission fragments
SPIRAL	Ganil Caen, France	Double cyclotrons: d, n	He, Ne, Ar, Kr, N, O, F
GSI	Darmstadt, Germany	Synchrotron 2 GeV	Large variety including fission fragments
RARF RIKEN	Tokyo, Japan	Ring cyclotron	H to Bi
TRIUMF- ISAC	Vancouver, Canada	Cyclotron: p 500 MeV	Large variety including fission fragments

* P = proton , d = deuterium, α = helium

Table 1-1: ISOL facilities around the world.

1.2 Radioactive ion beam productions at ISAC

The desired radioactive nuclei which are to be post-accelerated as RIBs are produced by proton irradiation of thick targets. In order to produce the particular isotopes through spallation, fragmentation or fission reactions, the atomic mass of the target must be greater than the one of the desired species. A variety of target materials have been developed and produced at ISAC and cover a broad range of elements. The common targets are refractory metals (e.g. Ta, Nb) and ceramic composites (e.g. SiC, TiC, ZrC, NiO, UO₂, UC_x) [10]. The RIB production rate, however, is limited by several factors including radioactive decay, the cross-section for nuclear reactions, primary beam intensity and target thickness. These factors will be discussed in more details in Chapter 3.

Uranium-based targets are of particular interest since they can be used to produce neutron-rich isotopes. Only recently, ISAC is able to produce and deliver RIBs such as Fr and Ac beams by the use of UC_x target which can be bombarded with up to 10 μ A proton beam (the current license to irradiate actinide targets) [11]. The RIB intensity distribution over the nuclear chart as reported in the ISAC Yield Database is shown in Figure 1-4. Some of the recent yield measurements of the short-lived isotopes are listed in Table 1-2. Presently, the half-life limit for the isotopes which can be delivered at the ISAC facility is several milliseconds.

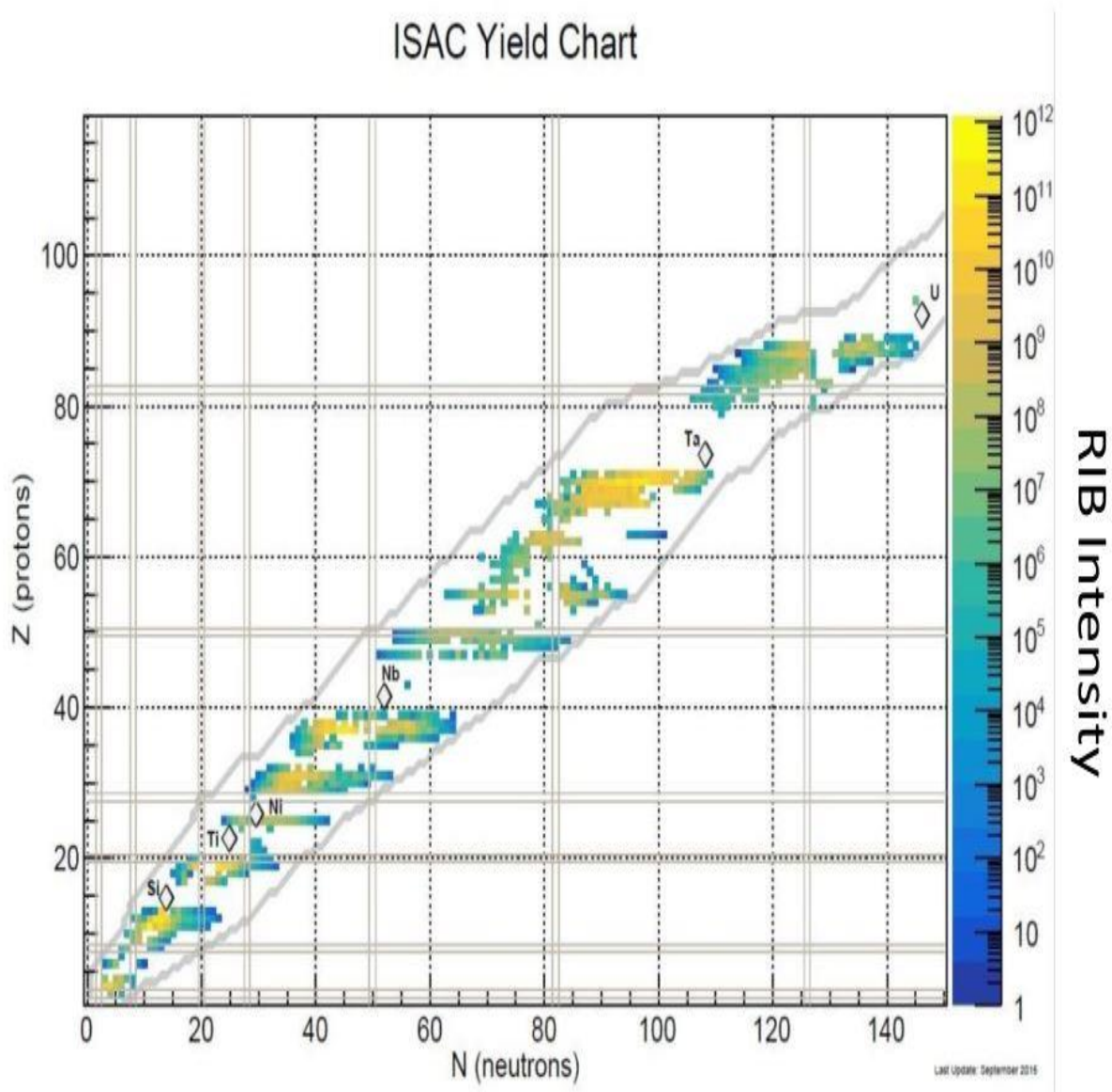


Figure 1-4: ISAC yield chart with RIB intensities [last update 2016, data from ISAC RIB-group]. The diamond markers indicate the refractory target nuclei which give rise to the regions where some of these isotopes are not accessible due to their non-volatile chemical properties.

Isotope	Half-life (s)	Target Material	Target Nucleus	Target Thickness (mmol/cm ²)	P+ current (μA)	*Production rate (1/s)	**Yield (1/s)
¹¹ Li	0.0088	Ta	Ta	130	60	3.0 x 10 ⁷	3.3 x 10 ⁴
¹¹ Be	13.8	Ta	Ta	130	50	1.0 x 10 ⁹	4.0 x 10 ⁶
¹³ N	0.00996	NiO	O	200	15	6.3 x 10 ¹⁰	1.3 x 10 ³
²⁰ Na	0.4479	SiC	Si	430	70	1.6 x 10 ¹¹	6.9 x 10 ⁷
²¹ Na	22.5	SiC	Si	430	60	1.1 x 10 ¹²	1.9 x 10 ⁸
²² Al	0.059	SiC	Si	430	70	7.5 x 10 ⁷	N/A
²³ Al	0.47	SiC	Si	430	65	2.6 x 10 ⁹	3.6 x 10 ²
²⁰ Mg	0.093	SiC	Si	430	70	2.5 x 10 ⁸	5.0 x 10 ⁴
²¹ Mg	0.122	SiC	Si	430	70	1.3 x 10 ¹⁰	1.6 x 10 ⁶
³⁴ Mg	0.02	UC _x	U	46	9.8	1.2 x 10 ⁹	2.7 x 10 ³
²¹⁴ Fr	0.005	UC _x	U	46	9.8	2.8 x 10 ⁸	1.9x 10 ⁶
²¹⁴ Fr	0.005	UO ₂	U	46	9.8	2.8 x 10 ⁸	N/A
²²² Ac	5.0	UO ₂	U	46	9.8	1.0 x 10 ¹⁰	4.7 x 10 ²

* Based on simulation method GEANT4

** Average value

Table 1-2: Recent yield measurements of selected short-lived Isotopes produced from Ta, O, Si, and U target nuclei.

1.3 Research objectives

One of the major challenges for ISAC is to provide consistently intense, short-lived RIBs to the users. Often the intensities of short-lived isotopes generated by the ISOL technique are limited by the nuclear decay during the diffusion and effusion of the species to migrate from the target materials to the ion source.

Typically, the targets are made of refractory metals or carbide powder composite materials with a grain size of several μm . The idea of using refractory powder materials is to combine short diffusion paths and high temperature to promote fast release of products [12]. However, grain growth through sintering also occurs, thus lengthening of the diffusion paths for the isotopes. As a result, most short-lived isotopes decay inside the material matrix before having enough time to diffuse out to the surface (see Table 1-2, column 7 and 8 for the RIB production versus yield intensities). In most cases, the decrease in yields of isotope can be observed after a few days of operation. While reducing the particle size and increasing the open porosity can improve the release efficiency for the short-lived RIBs, sintering rates are often greater as grain size reduces; fabrication of such target material remains a great challenge. In fact, the ISOLDE group was the first to utilize graphite cloth (fibre diameter $\sim 20 \mu\text{m}$) and rayon felt by impregnating in a suspension to produce porous targets to enhance the release of short-lived isotopes [12][13]. One problem with targets of this type is that low amounts of target material get absorbed by the fibres, resulting in low isotope production [14]. Commercially available metal oxide fibres, such as Al_2O_3 and HfO_2 (manufactured by Zircar Corporation) with fibre diameters in a few μm have also been tested at HRIBF and showed promising results especially for ^{17}F ($t_{1/2} = 64.8 \text{ s}$) production [15]. However, oxide-based targets show a fast sintering and can only accept low power levels of proton beam due to low thermal conductivities and large self-diffusion coefficients. Generally, refractory metal backing foils such as Nb are required for heat dissipation [16]. Furthermore, composite of UC_2 on micrometric reticulated-vitreous-carbon foam (RVCF) targets for the production of neutron-rich isotopes were developed at HRIBF by using the infiltration coating method [17][18]. RVCF, a product of ERG Aerospace, is a highly permeable and low-density carbon fibre with a diameter $\sim 100 \mu\text{m}$ that can enhance the isotope

release efficiency and provide stability during operation. Target materials coated on RVCF, however, are still subjected to sintering effects.

The main goal of this thesis is the development of nanofibrous ISOL target materials that address the challenges mentioned above. The concept of design is to use the electrospinning technique to form nanofibres, and these fibres will serve as carriers and sintering inhibitors of the RIB target materials that are dispersed in the nanofibre network. The electrospun nanofibrous materials will be used directly as RIB target material to reduce and stabilize the diffusion pathway in the target material grains. Although uranium is of major interest for the ISAC target development, non-actinide materials will be used for the subject of this investigation as proof-of-principle. Since SiC is a common ISAC target with a significant amount of measured yield data, co-electrospun nanofibrous SiC will be investigated. The obtained samples will be in pellet or disc form; these samples will be characterized by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) to investigate their surface morphology, fibre diameter, grain size and chemical composition. Scanning topography electron microscope (STEM) will be conducted to observe any structural changes and particle distribution as a function of position in the nanofibres. Density, porosity, thermal conductivity, mass loss and shrinkage of the pellets will be carefully characterized after thermal treatment. Furthermore, X-ray diffraction (XRD) will be used to identify the final phase and assemblage of crystallographic characteristics.

Chapter 2 Introduction to Nanofibre Technology

Although the concepts of nanotechnology were first introduced in 1959, it was not widely known until the late 20th century [19]. Today, nanotechnology defines the subjects of science and engineering on materials, structures, and devices which at least one dimension is at the nanometer scale (10^{-9} m) [20]. According to Health Canada, nanometer scale describes the size range between 1 to 100 nm [21]; however, materials in fibre form with a diameter below 1 μ m are typically recognized as nanofibres [22]. Nevertheless, when particles are created with dimensions at the nanometer scale, the chemical and physical properties of the materials change significantly from those bulk materials. With a diameter of less than 500 nm, typical polymer nanofibres can have a surface area to mass ratio as large as 10,000 m²/kg, 500 times that of a human hair [22]. Thus, these advanced properties make nanofibres an excellent candidate for many industrial applications, including ISOL targets for radioactive ion beam productions.

There is a variety of techniques to process polymer nanofibres including drawing [23], self-assembly [24], template synthesis [25], and electrospinning [26]. Most processes take a relatively extended period of time to produce nanofibres in macroscopic amounts [27].

Electrospinning seems to be a promising method to provide not only an easy and convenient process for producing an ultra-fine fibre with a diameter less than 500 nm but also a method for possible mass production.

2.1 Electrospinning process

Although electrospinning systems are increasingly becoming popular these days, the technique was first patented by W. J Morton in the US in 1902 with surprisingly little attention [28]. Then in 1937, A. Formhals filed a US patent on the method and apparatus for spinning. It was only in 1970, Baumgarten utilized the electrostatic spinning apparatus to produce ultra-fine acrylic fibres with diameters in the range of 0.05 to 1.1 μm [29]. This process is now widely known as electrospinning which involves the application of an electric field between a capillary tip and a grounded collector.

A conical shaped polymer droplet known as a Taylor cone is observed at the capillary tip during the processes from which a jet of charged particles is emitted above a threshold voltage. With the right concentration of polymer solution, a whipping motion of continuous fibre is formed, and finally, the nonwoven mat is collected on the grounded surface as shown in Figure 2-1. The key role in reducing the fibre diameter to nanometer scale is governed by rapid evaporation of the solvent during the whipping motion of the fibre elongation process [30].

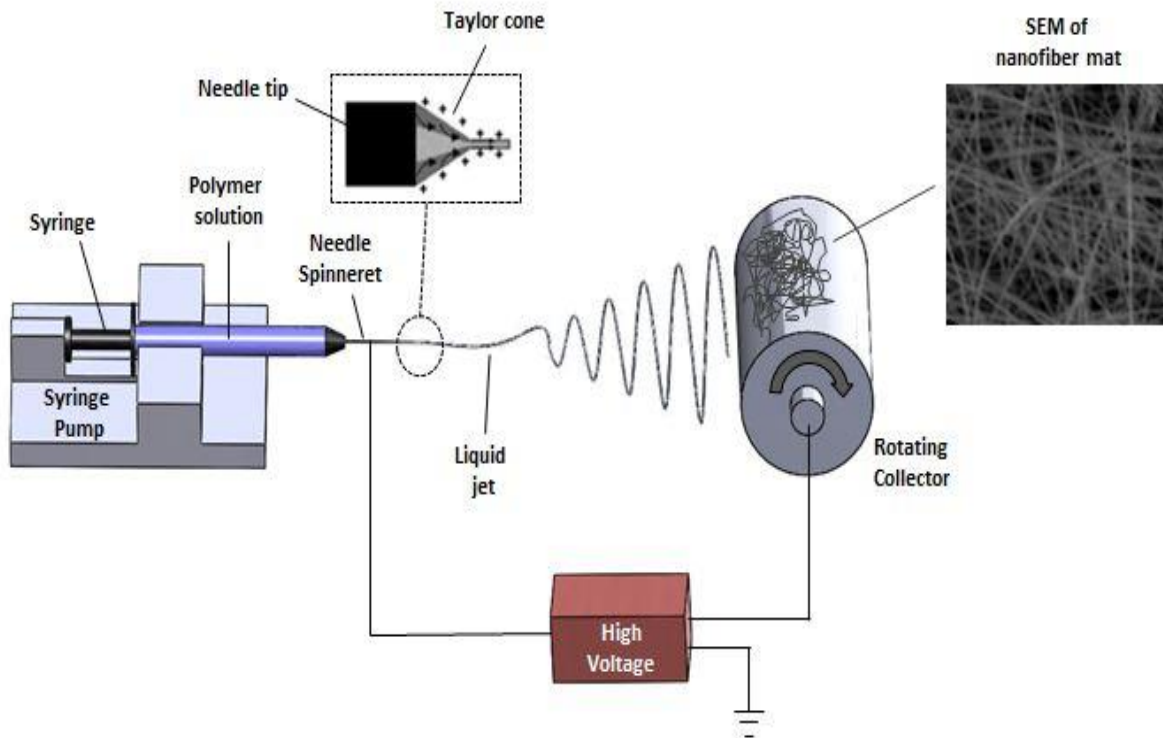


Figure 2-1: Essential components of an electrospinning setup.

2.2 Processing parameters

There are many parameters that can affect the formation of fibre from the polymer solution during the electrospinning process. These factors can be grouped into spinning dope solution, processing, and ambient as shown in Table 2-1. Each of those parameters can significantly affect the fibre morphology and diameter. By properly controlling the parameters, electrospun fibres with desired morphologies and diameters can be achieved.

Spinning Dope Solution	Processing	Ambient
Viscosity (molecular weight, concentration)	Voltage	Humidity
Surface tension	Flow rate	Temperature
Electrical conductivity	Needle Tip to collector distance	Pressure
Dielectric constant	Needle gauge	

Table 2-1: Factors affecting the electrospinning process

2.2.1 Spinning dope solution

In general, all polymers can be electrospun into nanofibres providing that the polymer molecular weight is sufficiently high and the solvent can be evaporated in time during the electrospinning process. Many studies have shown that the spinning dope concentration is one of the most significant parameters [31], [32]. Since the viscosity is directly proportional to the polymer concentration, higher viscosity results in a larger fibre diameter [29]. If the concentration is too low, polymeric micro particles will be obtained as jets break up into droplets [27], [33]–[35]. Surface tension and solution viscosity can also be optimized by changing the mass ratio of solvent to polymer to obtain the desired fibre diameter [36]. Addition of salts such as NaCl, LiCl, and $MgCl_2$ can improve the electrical conductivity of the spinning dope solution to obtain finer fibres and fewer beads [37]–[39].

A general dependency was found that the solution properties and fibre formation are related to the Berry numbers (Be), which follows the equation (2.1):

$$Be = [\eta]c \quad (2.1)$$

where,

$[\eta]$ = intrinsic viscosity of the solution

c = concentration of the solution

The intrinsic viscosity can be calculated using the Mark-Houwink-Sakurada as described in [40]. Typically, Be above 1 and below 2.7, fibre diameters between 100 – 500 nm are expected to form. Be between 2.7 and 3.6, fibres diameters between 1700 – 2800 nm are usually formed, and above 3.6, fiber diameter can be larger than 3000 nm [41] [42].

2.2.2 Processing

The applied voltage is another crucial factor within the electrospinning process. To obtain charged jets emitted from the Taylor Cone, the applied voltage must be higher than the threshold voltage. By controlling the Taylor Cone, the diameter of the electrospun nanofibres is adjustable [39], [40]. This cone was described by Geoffrey Ingram Taylor who derived the condition for the critical voltage as formulated in the following empirical equation (2.2); the factor 0.09 is inserted to give the prediction in kilovolts [45]:

$$V_c^2 = 4 \frac{H^2}{L^2} \left[\ln \frac{2L}{R} - \frac{3}{2} \right] (0.117\pi\gamma R) (0.09) \quad (2.2)$$

where,

V_c : Critical voltage for the jet formation (kV),

H : Distance between the capillary and ground collector (cm),

L : Length of the capillary (cm),

R : Radius of capillary (cm),

γ : Surface tension of the solution (dyn/cm)

Furthermore, low flow rates of solution and sufficient distances between needle tip and collector are recommended to achieve ultra-fine fibres [43]. Decreasing the orifice diameter can also reduce the fibre diameter; however, this will increase surface tension, thus higher voltage is usually required [46]. Also, a model has been created to solve the equations of motion for the jet to control fibre diameters as a function of material properties (i.e., conductivity, dynamic viscosity, surface tension) and operating characteristics (i.e., flow rate, applied electric field) as described in [47].

2.2.3 Ambient Conditions

Humidity, temperature, and pressure can affect the fibre diameter and morphology. Some studies have demonstrated that at high humidity, solvent evaporation reduces pore formation at the fibre surface [48]. However, at low humidity, volatile solvents dry out rapidly resulting in

clogging of the needle tip. In fact, the variety of humidity can affect the surface morphologies of electrospun fibres. At elevated temperatures, uniform finer fibres can be produced [39].

Chapter 3 Review of Literature

In order to resolve the intensity issues for short-lived isotopes at the ISAC facility, it is important to explore the general dependencies of the ISOL system. Also, understanding the conventional method of target material fabrication and the operating conditions helps to develop a full picture of the results before each approach to design of experiments can be properly layout.

3.1 RIB intensity (I_{RIB})

The following equation can express the intensity of a radioactive ion beam, I_{RIB} (1/s):

$$I_{RIB} = (\sigma_{prod} \cdot N_{target} \cdot I_{beam}) \cdot \epsilon_{tot} \quad (3.1)$$

where,

σ_{prod} : Cross-section (cm^2) of a characteristic area of a nuclear reaction
causing the production of the desired isotope;

N_{target} : Number of atoms per surface area (cm^{-2});

I_{beam} : Primary driver beam intensity (1/s of p^+);

ϵ_{tot} : Total efficiency;

To maximize the isotope production yield, the quantity of target material (N) and the intensity of the driver beam (I) can be increased. However, these factors are limited and often result in reductions of total efficiency (see section 3.2).

The total efficiency is a series product of partial efficiencies which account for all processes after the nuclear reaction to the acceleration of the RIB to the experimental station; this can be formulated as followed:

$$\epsilon_{tot} = \epsilon_{acc} \cdot \epsilon_{sep} \cdot \epsilon_{ion} \cdot \epsilon_{rel} \quad (3.2)$$

where the partial efficiencies can be expressed as,

ϵ_{acc} : Acceleration;

ϵ_{sep} : Electromagnetic mass separation & transport;

ϵ_{ion} : Ionization;

ϵ_{rel} : Release from the target material;

Typically, the product of $\epsilon_{acc} \cdot \epsilon_{sep}$ can range between 10% to 100%, and ϵ_{ion} from 0.1% to 90%; however, the produced isotopes release efficiency from the target material can be as low as 10^{-6} [10] (also see Table 1-2 for some recent ISAC yield measurements).

An intensive study of short-lived isotopes release from refractory powder materials with particle sizes varying from 10 to 100 μm was performed in the early 1970s at CERN-ISOLDE [12], and a general dependency was found where the release efficiency follows the expression:

$$\epsilon_{rel} \sim \sqrt{\frac{D}{\lambda r^2}} \quad (3.3)$$

where,

D: Diffusion coefficient;

λ : Isotope's decay constant;

r: Particle radius of the target material grain (assuming spherical particles);

The diffusion coefficient (D) and the sticking time (τ) of the isotopes are governed by the Arrhenius relationship as expressed in equations (3.4) and (3.5). For the RIB release rate, the temperature is a major factor that influences the isotope diffusion and effusive-flow characteristics.

$$D = D_0 e^{-\Delta E/kT} \quad (cm^2/s) \quad (3.4)$$

$$\tau = \tau_0 e^{\Delta H_a/kT} \quad (s) \quad (3.5)$$

Consider a solid-state diffusion as in the case for ISAC target materials, D is dependent on the activation energy (E) which is required to mobilize the atoms or vacancies from site to site, and on the temperature (T) of the target. ΔE is determined experimentally by measuring the target temperature dependence of D on T with such methods as described in [17], [18]. For diffusion in porous media, the sticking and surface collisions of isotopes on pore surfaces lead to a slowdown of the release process. The sticking characteristic depends on the elements; for example, Ar and Kr have very short sticking times, whereas Ni sticks to surfaces and τ depends on T [49]. The impact of the particle radius stated in equation (3.3) is the primary motivation for nanoparticle refractory ISOL target material development aiming to improve the release of short-lived isotopes as discussed in this thesis.

3.2 Target container designs

The target materials for RIB production are loaded into a container made of tantalum. The purpose of using tantalum is its remarkable refractory characteristic having a melting point above 3000 °C, good weldability and machinability for easy fabrication. The container is a round cylindrical tube with 19 cm length and 18 mm inner diameter as shown in Figure 3-1. Another tantalum transfer tube with inner diameter of 3 mm is welded to the center of the target container perpendicular to the proton beam axis to allow the produced isotopes to migrate into the ionizer.

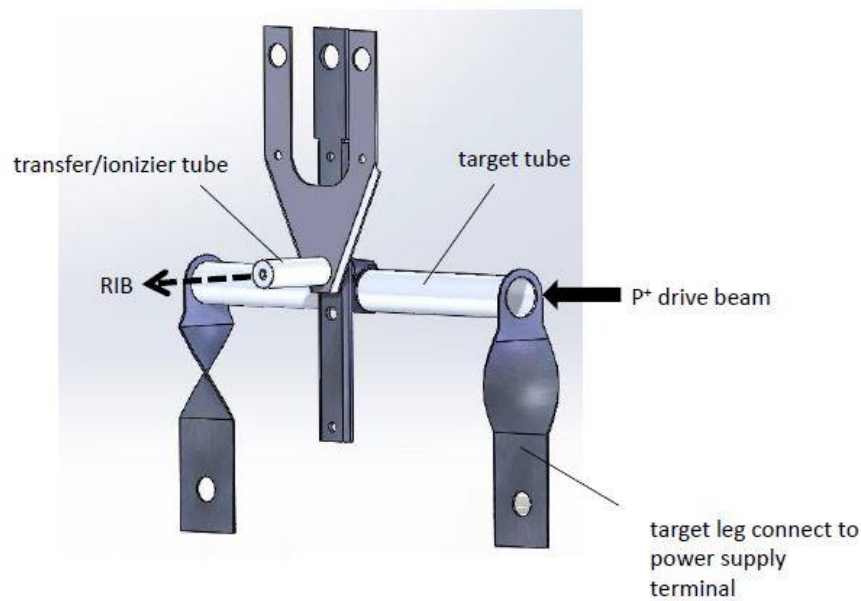


Figure 3-1: A 3D SolidWorks model of a target container with the sketch of RIB release out from the transfer tube as the proton beam enters the target tube and bombards the materials.

[Drawing by TRIUMF]

The overall target container temperature is constantly maintained by Joule heating; the operating temperature can be as high as 2000 °C to enhance the diffusion and effusion of the product nuclide out of the target [50]. However, the proton beam current is limited by the types of target materials that are being used to produce the desired isotopes. When the high-power proton beam bombards the target, the core temperature of the material rises instantly. If the proton power density is too high, the materials disintegrate or vaporize, resulting in the destruction of the target or the ion source. The effective heat transfer depends on the thermal conductivity and emissivity of the target material.

To balance the target temperature, the heat deposited in the materials from the proton beam, and the isotope production, two types of target containers have been developed. The low-power (LP) container was the first design to withstand the proton beam intensities up to 50 μA on Nb or Ta targets, and up to 20 μA on a SiC target [51]. The high-power (HP) container consists of fins installed onto the Ta tube to aid heat dissipation, can sustain proton beam intensities up to 100 μA . The first HP-Nb target was operated in 2009 with 99 μA of proton beam [50]. Figure 3-2 shows both the LP and HP target containers.

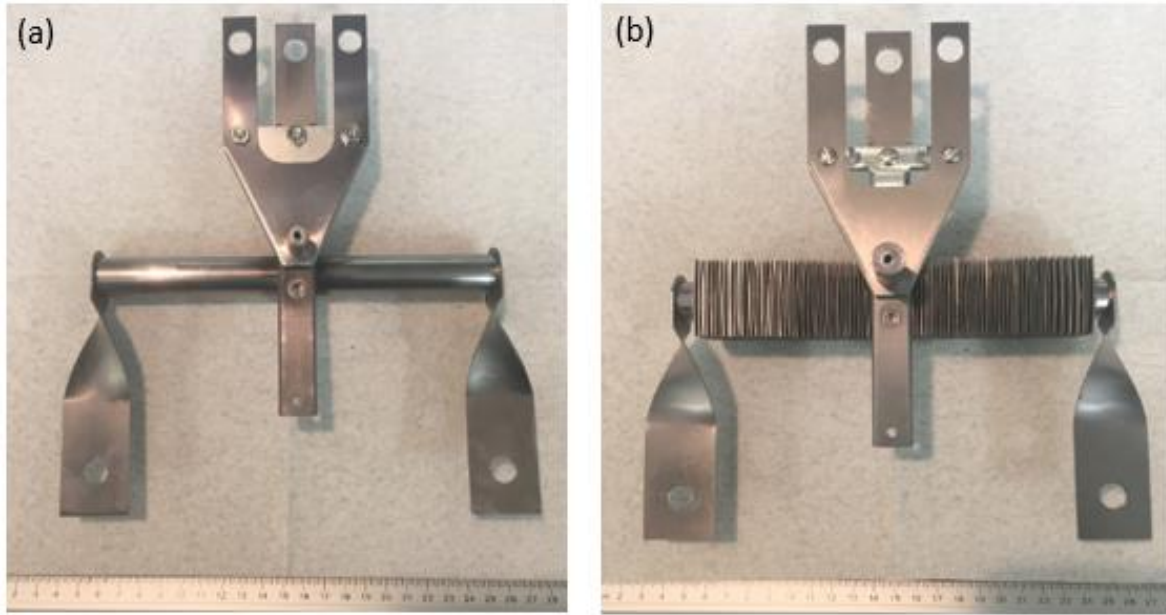


Figure 3-2: (a) LP-target and (b) HP-target equipped with fins for heat dissipation.

3.3 ISAC target materials

The target materials should be able to sustain temperatures as high as possible but below its melting, sublimation or dissociation point. Typically, the target is kept between 1500 °C and 2000 °C under high vacuum to promote the diffusion and desorption processes for the volatile species to extract out from the material to the transfer tube. In order to maintain the functionality of the ion source, the vapor pressure of the hot target material must not exceed 10^{-6} mbar [52]. Furthermore, the target material has to be able to dissipate the heat from the proton beam and be stable over several weeks of operation. Table 3-1, columns 2 – 5 summarizes some maximum temperatures and proton beam currents at which the targets can be operated without exceeding the vapor pressure limit. The target specifications are summarized in Table 3-1, columns 6 – 9.

Chemical composition	Melting Point ¹ (°C)	Vapour pressure ² at 2000°C (mbar)	Maximum operating temperature ³ (°C)	Target container & Max proton beam intensity (μA)	Target length (cm)	Target bulk density (g/cm ³)	Element for isotope production	Element thickness (mmol/cm ²)
Ta	3020	1.6 x 10 ⁻⁸	2300	LP, 50 HP, 99	3.4	14.6	Ta	130
Nb	2469	5.0 x 10 ⁻⁶	2000	LP, 50 HP, 99	4.5	2.4	Nb	120
UC _x	2500	< 10 ⁻⁶	1900	LP, 10 HP, n/a	7.5	2.6	U	46
ZrC	3400	< 10 ⁻⁶	1900	LP, 50 HP, 75	13	3.0	Zr	130
ThO ₂	3390	< 10 ⁻⁶	<2000	LP, 10 HP, n/a	4	2.7	Th	40
SiC	2730	exceed limit	1800 ^a	LP, 20 HP, 60	17	2.4	Si	430
NiO	1955	exceed limit	1100 ^b	LP, n/a HP, 15	9	2.1	O	200

1. For pure materials. When deposited onto C, metallic foils, or Ta target containers, the thermal properties change.

2. The upper limit pressure for operating the ISAC Ion sources is 10⁻⁶ mbar.

3. Carbides targets are limited to below 2000°C due to corrosion of the Ta container.

a. Evaporation of Si above 1800°C.

b. NiO reacts with the Ta container forming low-melting alloy.

LP = Low-power container

HP = High-power container

Table 3-1: Physical properties and specifications of ISAC targets. [Data from ISAC RIB group]

3.4 ISAC target fabrication

3.4.1 Metal foil targets

Refractory metal targets such as Ta and Nb are commonly used at ISAC which can accommodate proton beam intensities of up to 100 μA. Ta or Nb targets usually consists of about 400 to 500 foils, each foil 2 μm thick and 19 mm diameter. The foils are cut into D-shape with a laser cutter and stacked together in a target container as shown in Figure 3-3. The foil

thickness, target length, and shape have been developed to optimize the speed of diffusion and effusion processes [53].

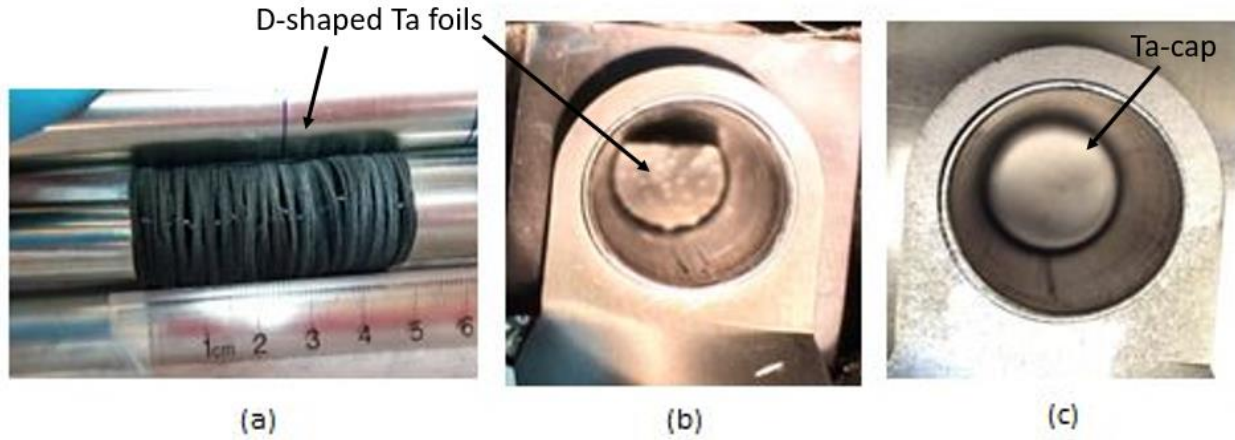


Figure 3-3: An example of a Ta target material production. (a) The cut-out D-shaped Ta foils are packed together into a thick target and loaded into a container (b), and (c) both ends of the target container are then sealed with Ta-caps.

3.4.2 Ceramic targets

In general, powder-based target materials possess poor intrinsic thermal conductivities due to their porous structures. In order to accommodate high-power proton beam, the slip casting technique was used to produce thin ceramic targets that can withstand beam intensities up to 70 μA [53] [54]. The process involves milling the raw material powders (e.g., SiC, TiC, ZrC, UC_2 , ThO, UO_2 , NiO) to grain sizes of several μm . The refined powder plus additives (organic binders, plasticizers, and surfactants) are carefully mixed with a milling machine. The slurry compositions are then slip-casted onto a backing foil to form a thin layer cast upon drying at room temperature. Graphite sheets of 0.13 mm thickness, are used as backing foils for carbide-

based materials to enhance heat conduction from the target material into Ta enclosed cylinder.

For ThO and NiO targets, pure Nb and Ni sheets serve as backing foils, respectively.

The casted foils are cut into D-shape and loaded into a tantalum container for the heating process under vacuum to remove the organic compounds and densify the materials. The overall process is illustrated in Figure 3-4. For the carbide-based targets, prior to loading the discs, a coating of a sintered layer of TaC on the inside of the container is required to prevent high-temperature chemical reactions with the Ta container [55].

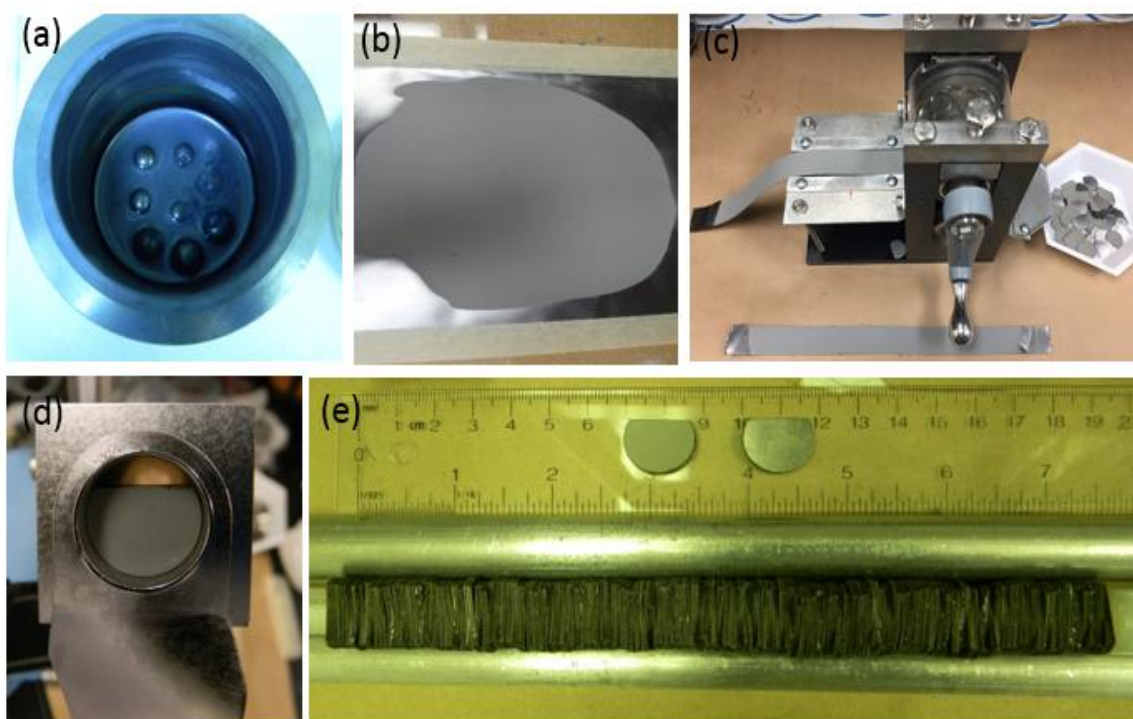


Figure 3-4: An example of a SiC ceramic target material production: (a) Raw powders are milled in a metal jar consists of milling balls to form slurry compounds, and slip-casted on a flat surface (b). (c) The dried green cast is cut out into D-shaped discs ready to be loaded into a Ta container (d). (e) A typical SiC target consists of 480 discs with each disc about 0.32 mm thick.

3.5 Target sintering effects

The fabrication of a ceramic ISAC targets involves a heating process which takes place in a high-temperature vacuum furnace to allow the burnout of organic compounds, stabilize the material and prevent undesired out-gassing during operation. However, the high-temperature heating treatment also leads to target sintering which causes grain growth and removal of pores resulting in lengthening the diffusion pathway as shown in Figure 3-5, in the example of ZrC target material. Similar sintering effects are observed for the conventional SiC target, see Figure 4-16.

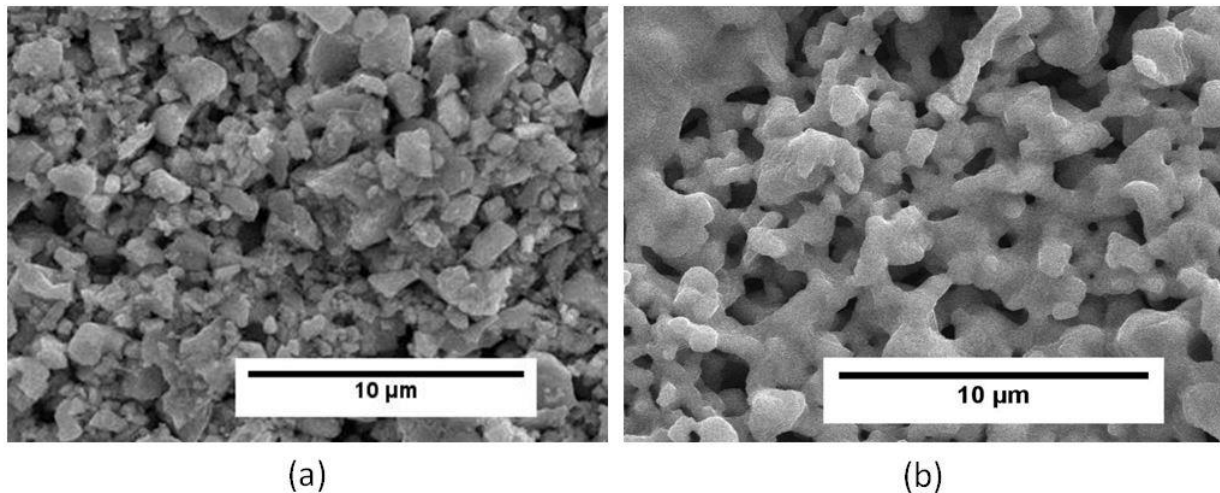


Figure 3-5: An example of sintering of ZrC target material: (a) Green target with a grain size of 1 – 5 μm after milling, (b) heat-treated target at 2000 $^{\circ}\text{C}$ under vacuum showing sintered particles.

The sintering process has the most severe negative impact especially for short-lived isotopes since the intensities are limited by the decay time associated with the diffusion and effusion of the species to migrate from the target materials to the ion source. As a rule of thumb, when a

powder is heated to more than half its melting point, sintering takes place [12]. The sintering rate depends on the initial particle dimension, morphology, impurity, self-diffusion coefficient, and temperature. The heating is supplied not only from the Joule heating of the target container, but also partly by the incident proton beam depositing energy inside of the materials. In fact, the decrease of exotic short-lived RIBs (e.g., $^{31-33}\text{Ar}$ beams) produced from a micrometric CaO target (m.p. 2572 °C) has been reported at ISOLDE as the result of sintering at high operation temperature (>1050 °C) [13]. A major development at ISOLDE is the nanometric CaO powder target which yielded the unexpected high release of Ar isotopes even at room temperature operation [56]. The enhanced release rates are primarily due to porous nanomaterials. However, for operating temperatures higher than 1000 °C, a significant increase in sintering kinetics of the nanometric CaO resulting in a reduction of surface area was reported [57].

Several attempts have been made to increase the isotope yields by reducing the grain size and to prevent sintering through coating foam like structures such as carbon meshes [58]. A recent development in target fabrication at TRIUMF was using the spraying method. The selected material was mixed into a slurry and sprayed on a backing foil to produce porous and uniform thickness layer NiO targets [59]. As a result, the sintering process was found to reduce significantly; however, the isotope production could also reduce due to the relatively low density of the target material. Recently, the use of carbon black or carbon nanotubes was investigated as a sintering inhibitor for carbide targets where the carbon source not only reduces the contact points of the target materials to reduce the diffusion pathway but also allows the target to operate at much higher temperature for fast release [60].

3.6 Silicon for isotope production

Silicon based refractory compounds come in many different forms such as SiC, Si₃N₄, and MoSi₂ for a wide variety of applications including high temperature ceramic catalyst supports, engine parts, and heating elements. The element silicon is mainly used as a semiconductor for computer devices and microelectronic industries, but it is also commonly used as an ISOL target in the form of SiC compound for RIB production. Si has three naturally occurring isotopes: ²⁸Si (92.23%), ²⁹Si (4.67%), ³⁰Si (3.10%) [2]. In theory, the combined production cross-sections (σ) of these three isotopes can produce isotopes with atomic mass less than 30 through spallation reactions. Short-lived isotopes such as ²²Al, ²⁰⁻²¹Mg, and ²⁰Na at several milliseconds, as shown in Figure 3-6, can be produced with conventional ISAC SiC ceramic disc targets; however, the intensities are known to be poor and unstable due to target sintering. With the nanofibrous SiC target, an initial test will be performed at the ISAC facility to determine the release efficiency for these short-lived isotopes.

For the proposed online test-method, the fabricated SiC nanofibre material will be loaded into a LP-surface ion source target container with a maximum operating temperature of 1500 °C under high vacuum ($<10^{-6}$ mbar). Prior to loading the material, the inside of the target container will be coated with a thin layer of TaC and heat treated at 1800 °C under vacuum; this will prevent the corrosion of the Ta container at high temperature. The target will be bombarded with gradually increasing proton beam intensity ($\leq 100 \mu\text{A}$). For each proton intensity, yield measurements of Al, Mg, Na isotopes as a function of target temperature will be evaluated to determine the release efficiency. Heating and proton beam intensity will be increased until a degradation of yield due to sintering or SiC decomposition can be observed.

Online irradiation tests of the nano-SiC target at ISAC have been approved and scheduled for September 25 to October 1, 2018. This is a major investment in the project at an average rate for beam time of CND \$30,000 per day.



Figure 3-6: The chart of nuclides taken from [2] showing the three stable Si isotopes (solid-line red box) and the short-lived Al, Mg, Na isotopes (dashed-line red box) to be investigated for the yield efficiency from the nanofibrous SiC target material.

Chapter 4 Preliminary Experiments

The goal of this preliminary work is to investigate if electrospun SiC can be used as a target material at ISAC, and to understand the processing and handling of nanofibres. To achieve the aims of this work, several approaches for the SiC nanocomposite fibres will be evaluated based on the radio isotope yield under photon irradiation and quality of the composite fibres. The methods are summarized below:

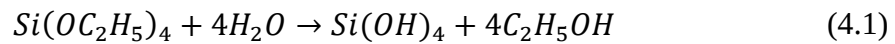
- i) Post sol-gel coating and In-situ electrospinning: Carbon precursor polymer solution is electrospun to form nanofibres. These fibres are then coated with SiO₂ nanoparticle through the sol-gel process before thermal reduction to form SiC nanoparticle coated carbon nanofibres. In addition, the silicon oxide precursor is mixed directly with a carbon precursor polymer to form electrospinning dope. The spinning dope is then converted to nanofibres through electrospinning before thermal reduction to form composite SiC/carbon nanofibres.
- ii) Direct co-electrospinning: The polymer solution with dispersed SiC particles is directly electrospun to form the composite nanofibres.

As for the polymer solution mentioned above, polyacrylonitrile (PAN) will be used as carbon precursor material for electrospinning and served as the sintering inhibitor for SiC nanoparticles. All the as-spun fibres will be thermally stabilized by removing the polymeric elements and oxygen before carbonizing the nanofibre matrix through further heat treatment at high temperature under vacuum.

The obtained nanocomposite fibres will be characterized by scanning electron microscopy (SEM) equipped with the energy dispersive X-ray spectroscopy (EDS) to investigate their surface morphology, fibre diameter, grain size and chemical composition. X-ray diffraction (XRD) will be used to identify the final phases and their crystallographic features. The vacuum level in the furnace chamber will be analyzed through the heating process, and the samples will be measured and weighted in all heating conditions.

4.1 Fabrication of SiO₂/PAN nanocomposite fibres

Silica nanoparticles were synthesized by using the sol-gel process, a common method for the fabrication of metal oxides [61] [62]. The sol-gel reaction involves hydrolyzes of a liquid alkoxide precursor, such as Si(OR)₄, where R is CH₃, C₂H₅, or C₃H₇ by mixing with water. Silica colloidal particles can be synthesized by mixing tetraethyl orthosilicate (TEOS) and distilled water in the molar ratio of TEOS:H₂O, 1:4 to form silicate acid as shown in equation (4.1). The hydrated silica tetrahedral undergoes a condensation reaction, forming Si-O-Si bonds; eventually, a SiO₂ network is produced by releasing water from the reaction as shown in equation (4.2).



The PAN nanofibres were produced by using the electrospinning process; the fibre mat was then dipped into the SiO₂ gel solution, followed by heat treatment. The overall process is summarized in Figure 4-1.

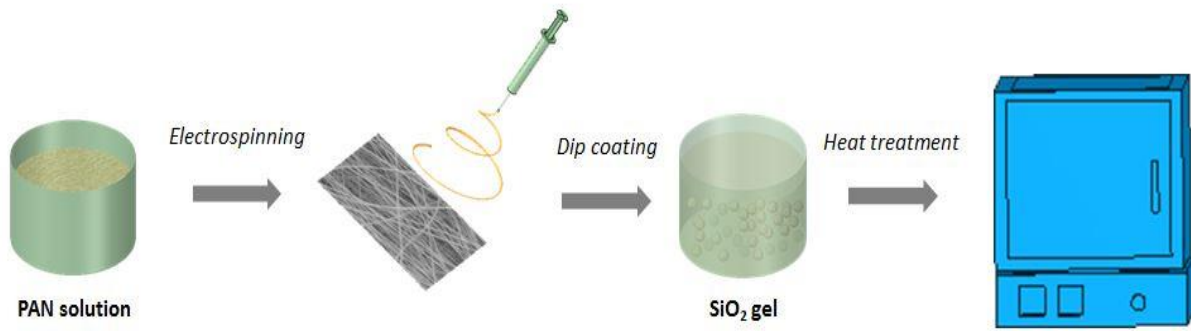


Figure 4-1: Post sol-gel coating process of SiO₂/PAN nanocomposite fibres.

With PAN as a carbon precursor, high-temperature heating under vacuum was performed to determine the possibility of the formation of silicon carbide or metallic silicon. The possible reactions of the carbothermic reduction of silica are shown in equations (4.3) and (4.4).



4.1.1 Raw materials

Tetraethyl orthosilicate (TEOS; $\text{Si}(\text{OC}_2\text{H}_5)_4$, Cat #: 333859) as a silicon precursor, and hydrochloric acid (HCl, Cat #: 320331) as the catalyst were purchased from Sigma-Aldrich. Ethanol ($\text{C}_2\text{H}_6\text{O}$, Cat#: AC615090010) as a mutual solvent was purchased from Fisher Scientific. Polyacrylonitrile (PAN; $(\text{C}_3\text{H}_3\text{N})_n$, $M_w = 150,000$, Cat #: 1056) as carbon source, was purchased from Scientific Polymer Products, Inc. The organic solvent dimethyl formamide (DMF, Cat #: 68-12-2) from Fisher Scientific, was used to dissolve PAN for preparation of the electrospinning dope solution.

4.1.2 Synthesis of nanoparticle silica sol-gel

3.2 ml of EtOH was first added to 3.0 ml of TEOS and gently stirred for a few minutes. 3.9 ml of distilled H_2O was then added to the TEOS solution with continuous magnetic stirring at 60 °C. At this stage, the solution was immiscible. However, by adding about two drops of HCl to keep the pH at around 1.6, the solution was well mixed as shown in Figure 4-2.

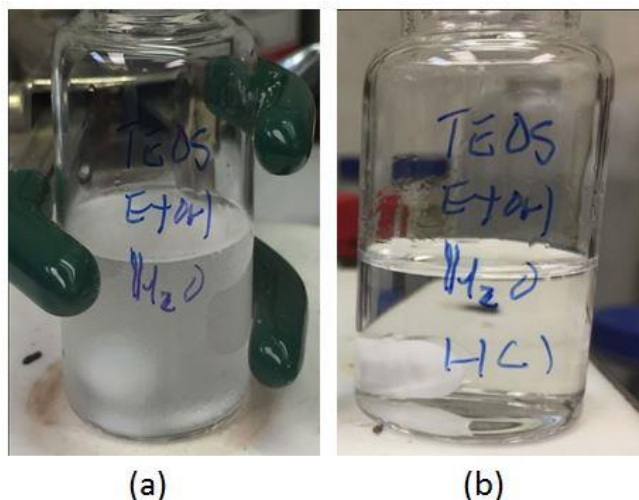


Figure 4-2: Synthesis of SiO₂ sol-gel: (a) Immiscible solution of TEOS/EtOH/H₂O. (b) Miscible solution after a few drops of HCl.

The solution was removed from heat but effectively stirred continuously. The mechanical mixing of the colloidal silica solution prevented precipitation. Thus the solution can be used for coating the PAN nanofibre homogeneously. The silica sol-gel compositions are showed in Table 4-1.

Reagent	Amount	Number of moles
TEOS	3.0 ml	0.0134
EtOH	3.2 ml	0.0536
Distilled H ₂ O	3.9 ml	0.2144
HCl	2 drops	

Table 4-1: Silica sol-gel chemical reagent compositions, (solution pH ~1.6).

4.1.3 Preparation of PAN solution

10% of PAN solution was prepared by dissolving 1 g of PAN in 9.5 ml of DMF. The solution was prepared on a magnetic stirring hot plate at 60 °C. The PAN polymer was completely dissolved in DMF after 3 hours. The solution was removed from heat and continuously stirred until it reached room temperature.

4.1.4 Electrospinning of PAN solution

To conduct electrospinning, the 10% PAN solution was transferred to a 10-ml disposable syringe with a 22 gauge (0.71 mm O.D., black color-code) needle. The solution was electrospun to fabricate nanofibres by using the electrospinning apparatus (NEU-2, Kato Tech. Co. Ltd., Japan) shown in Figure 4-3.

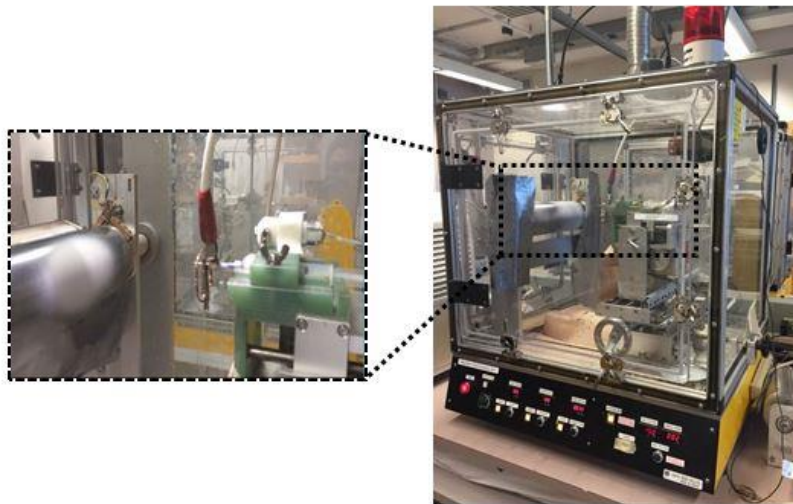


Figure 4-3: Electrospinning unit for the fabrication of PAN fibres.

A voltage of 15 kV was applied to the needle tip, and the syringe pump was set at a rate of 0.03 mm/min. To collect the electrospun fibres, the grounded drum was covered with a thin graphite foil (0.025 mm thick, purchased from Ceramaterials) to avoid any metal cross-contamination such as aluminum. The drum rotated at a rate of 1 m/min, and the transverse speed of the syringe stage was set at 1 cm/min. The spinning distance between the needle tip and the drum was maintained at 15 cm during the electrospinning process.

The as-spun PAN nanofibre was then dipped in the sol-gel solution for several minutes as shown in Figure 4-4, and the coated fibre mat was let dry in air for one day before proceeding with the heat treatment.

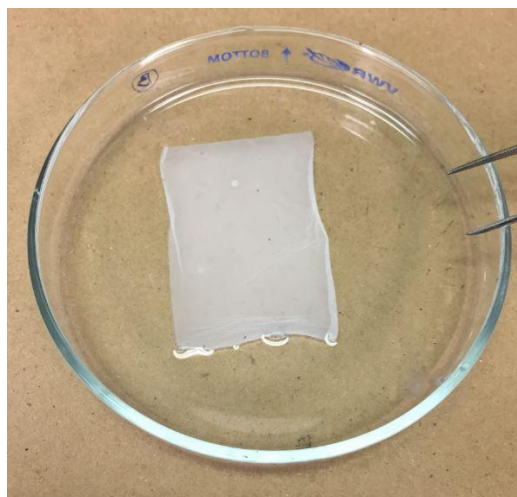


Figure 4-4: PAN nanofibre dipped in the SiO₂ sol-gel solution.

4.1.5 Thermal treatment process

The as-spun PAN nanofibre coated with SiO₂ gel was treated under three stages of heat treatment in order to remove polymeric elements and to do pyrolysis of long-chain carbon fibre composites

with the silicon matrix. In the stabilization stage, the sample was heated in a furnace (Barnstead Thermolyne 48000) at 250 °C for 1 hour in air with a ramping temperature rate of 1 °C/min; this allowed the thermoplastic PAN to convert in a non-plastic ladder structure compound [32]. After the sample was cooled to room temperature, it was further carbonized at 900 °C in an argon atmosphere at a ramping rate of 5 °C/min and held at the temperature for 1 hour. The sample was cooled again to room temperature before it was heated to 1600 °C for 5 days under vacuum in the Evaporator-2, a high temperature vacuum furnace for target material processing at TRIUMF, with the pressure maintained in the order of 10^{-6} mbar. The overall heating process is shown in Figure 4-5.

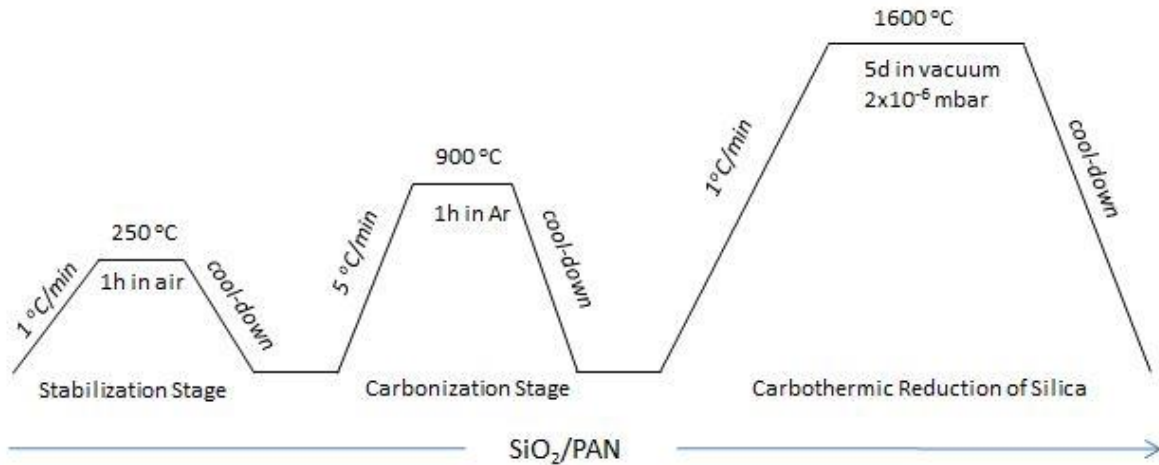


Figure 4-5: Heating process of SiO₂/PAN nanofibre.

For the high-temperature treatment in vacuum, the sample was loaded into a Ta-container, previously coated with TaC and sintered before the crucible was installed into the chamber as shown in Figure 4-6. The container was wrapped around with a thin layer (0.025 mm thick) of Ta-foil to improve the heat distribution. The temperature of the container was maintained by

joule heating, and it was closely monitored using the OMEGA iR2 ultra-high performance 2-color ratio fibre optic infrared temperature measurement system with the emissivity calibrated for Ta. Type-C thermocouples were welded to the Ta-container for an extra set of measurements.

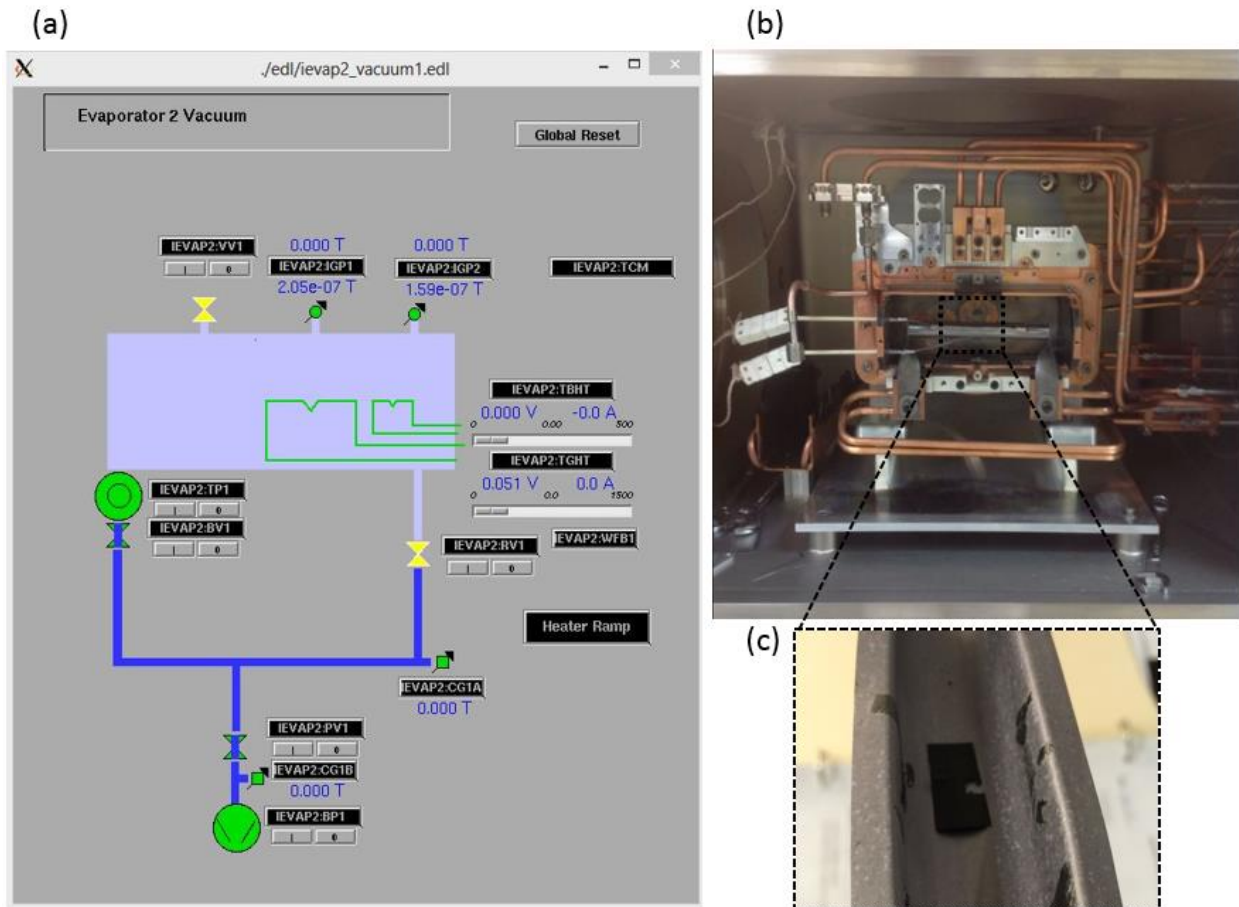


Figure 4-6: High-temperature high-vacuum furnace (Evaporator-2) built in-house at TRIUMF. The system is operated using the EPICS control system (a). (b) Inside the vacuum chamber, a Ta-container is installed onto the power supply terminals. (c) The nanofibre sample is placed inside the Ta-container, previously coated and sintered with TaC.

4.1.6 Results and discussion

A preliminary study of the PAN nanofibre coated with the SiO₂ nanoparticle through the sol-gel process was carried out by analyzing samples using scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM/EDS, Hitachi S-3000, Japan). After SEM-EDS analysis on the carbonized sample at 900 °C in Ar, the same sample was re-analyzed after heat-treated at 1600 °C under vacuum.

Scanning Electron Microscopy (SEM) Analysis:

With the detector set for the secondary electron (SE) signals, the surface morphology of the nanofibre mats was examined at an acceleration voltage between 10 to 15 kV. The SEM images of the as-spun and heat treated nanofibre mats are shown in Figure 4-7. The pristine PAN nanofibres coated with the SiO₂ sol-gel were uniform and bead-free; the average diameter was found to be around 480 nm. However, shrinkage of the fibres was observed after the sample was heated at 900 °C under Ar atmosphere; the average fibre diameter reduced to around 180 nm. After the high-temperature treatment at 1600 °C under vacuum, the nanofibres exhibited severe abrupt shrinkage leading to rupture and disintegration of the fibres as shown in Figure 4-8.

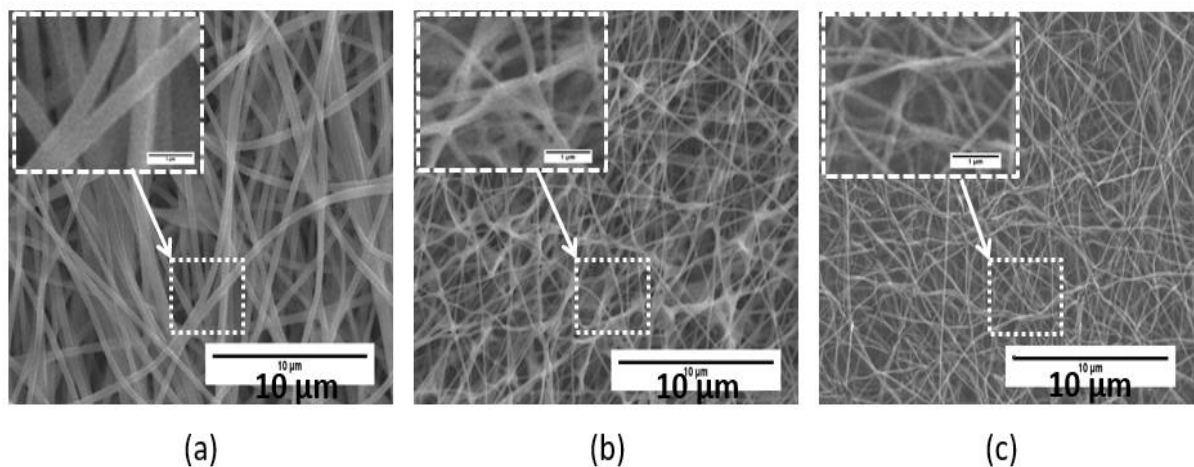


Figure 4-7: Effect of heat treatment on the morphology of electrospun PAN nanofibres coated with SiO₂ sol-gel solution. SEM images of (a) as-spun fibres, (b) carbonized fibres at 900 °C in Ar, (c) high-temperature treatment at 1600 °C under vacuum. The insets show the close-up images, scale-bar of 1 µm.

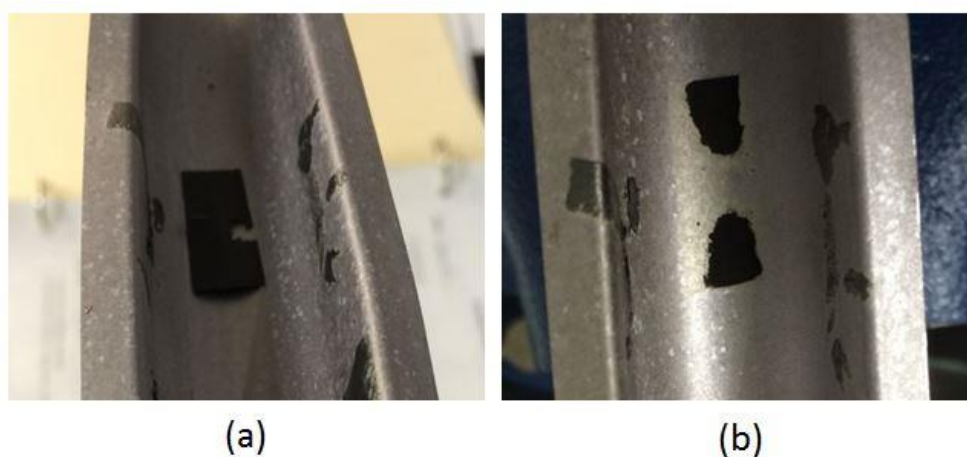


Figure 4-8: Optical photographs of PAN nanofibre mat coated with SiO₂ (a) before high-temperature treatment, and (b) after 1600 °C under vacuum.

Energy Dispersive X-ray Spectroscopy (EDS) Analysis:

The EDS spectra were taken with a primary electron beam energy of 20 keV. When analyzing the composition of the fibre mats, no coating was used on the sample to avoid any signal interference since the elements of interest were C, O, and Si.

By using the X-ray mapping, the composition fluctuation across the selected area shown in Figure 4-7 b and c of the insets, indicated that the nanofibres contained no silicon after the sample was heated at 1600 °C under vacuum. X-ray spot analysis was also carried out on several locations of the fibre mats, and the results were identical. Figure 4-9 shows the EDS spectra collected from a spot before and after high-temperature treatments under vacuum. The strobe peak at 0 keV signal in the EDS spectra was caused by the electronic noise of the EDS detector.

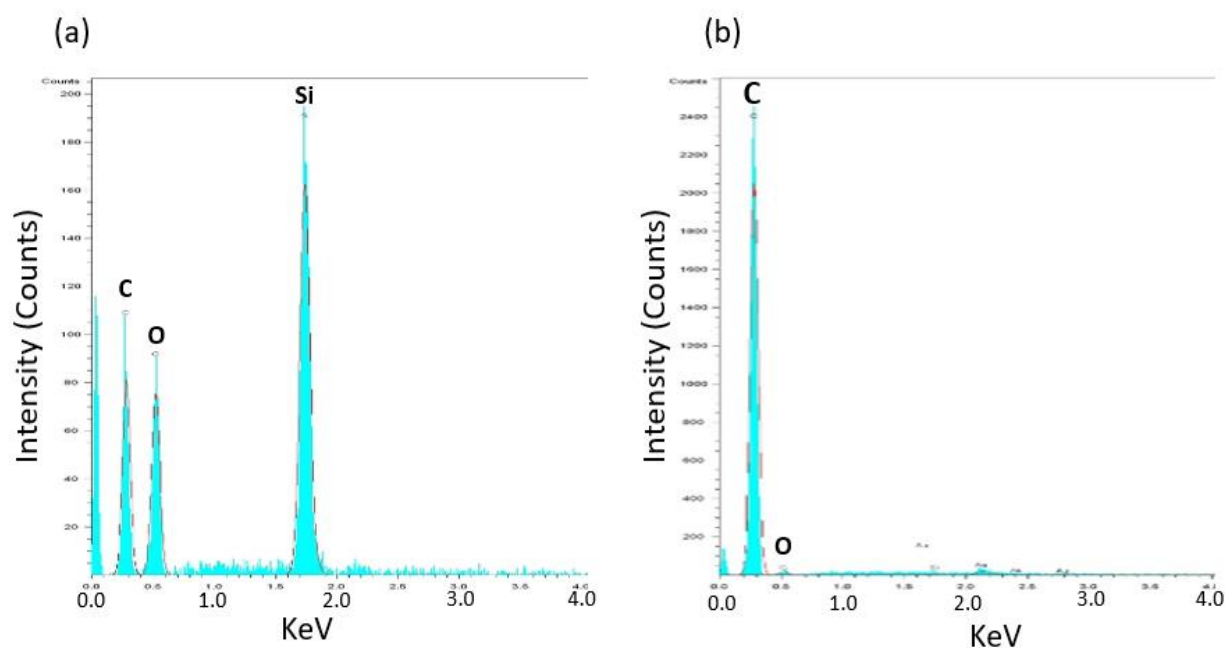


Figure 4-9: EDS spectra of PAN nanofibre coated with SiO₂: (a) Carbonized at 900 °C under Ar, (b) heat treated at 1600 °C under vacuum. *(Ignore the strobe peak at 0 keV signal)*

Vacuum levels during the high-temperature treatments:

To illustrate the results of the outgassing behavior of the PAN/SiO₂ nanofibre sample (previously heated to 900 °C under Ar), Figure 4-10 shows the pressure in the vacuum chamber as a function of the Joule-heating power. The chamber was pumped down to about 1×10^{-6} before the heating process was initiated. As the temperature was ramping up from 25 °C at a rate of 1 °C/min, the pressure increased rapidly and reached the order of 10^{-5} mbar. On the basis of already reported thermogravimetric studies, the peaks around 300 °C can be attributed to dehydrogenation reactions and release of volatiles such as H₂O, CO, CO₂, CH₄, NH₃ and HCN [63].

Carbonization of PAN began at around 900 °C, and the heating up to 1200 °C led to further gas evolution of CO which could be attributed to complete carbonization of PAN nanofibres.

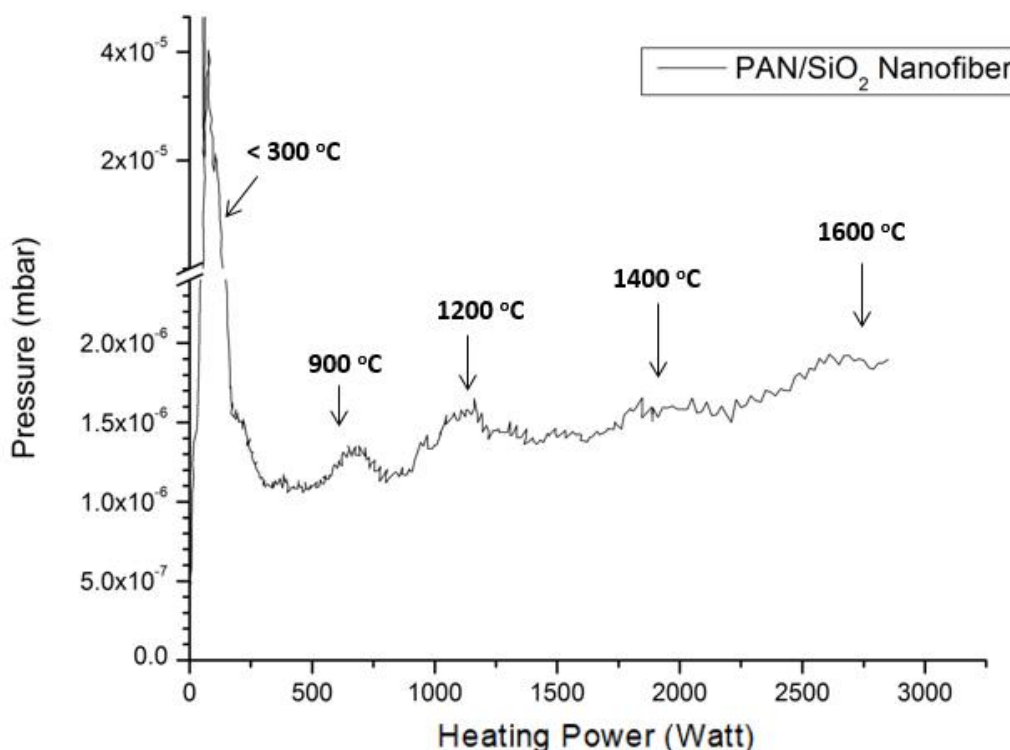
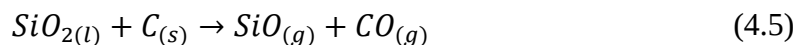


Figure 4-10: Vacuum levels during the high-temperature treatment of a PAN/SiO₂ nanofibre mat.

As the temperature continued to ramp up to 1600 °C, the pressure steadily increased; the gas release was likely from the evaporation of SiO₂. The reaction occurred in the vacuum system at high temperature could be explained by the following equation (4.5).



Under vacuum atmosphere, liquid silica could occur below the theoretical melting point of 1713 °C. The liquid phase diffused to the carbonized PAN fibre and led to the formation of silicon monoxide (SiO) gas. The increase in pressure with increasing temperature above 1400 °C was most definitely related to the evolution of SiO and CO gases. Due to the difficulty in measuring the vapor pressure of SiO, various results have been reported in the literature [64]. Nonetheless, it is entirely possible that the volatile SiO gas could have removed from the nanofibres and condensed on the surrounding cold surfaces before it could further reduce to SiC. Evidently, the EDS result in Figure 4-9 (b) reveals the absence of silicon in the nanofibre mat.

A similar experiment was carried out by mixing TEOS to PAN polymer solution in DMF in a weight ratio of 7:3, and the concentration of PAN in DMF was set to 10% as in the above experiment. The spinning dope solution was successfully electrospun into nanofibres. However, after the heat treatment at 1600 °C under vacuum for several days, no silicon was present in the carbonized nanofibres; the results were confirmed by EDS analysis similar to the spectra shown in Figure 4-9.

Many studies have shown that in small laboratory furnaces under Ar atmosphere, the temperature for the carbothermic reduction of SiO₂ ranges from 1500 to 2000 °C [65]–[67]. The synthesis temperature to form SiC from SiO₂ and carbon mixtures usually begins around 1500 °C; the

predominated product is β -SiC, which is stable up to 2100 °C before completely transforming to α -SiC at 2400 °C [67]. However, this preliminary work has shown that the transformation of SiO₂ or TEOS as silicon precursor to SiC was unfavorable under vacuum. It is also worth mentioning that in order to satisfy the required conditions for ISAC targets, the materials should be able to withstand high temperatures under vacuum with pressure not exceeding 10⁻⁶ mbar.

On the positive aspect, the PAN nanofibres were successfully carbonized, and thermally conditioned at 1600 °C under vacuum. The nanofibre network was maintained with the desired fibre diameter. Incorporation of SiC to PAN nanofibres will be investigated in section 4.2.

4.2 Fabrication of α -SiC/PAN nanofibre

For this experiment, the PAN polymer solution dispersed with SiC particles was directly electrospun to fabricate the composite nanofibre. The main advantage of the direct co-electrospinning method is the known SiC crystal structure and size incorporated in the PAN nanofibre. α -SiC micro particle size powder, conventionally used for fabricating the ISAC SiC ceramic target, was mixed directly with PAN polymer solution. The mass ratios of α -SiC to PAN were decided based on the spinnability of the dope solution and the electrospun nanofibre morphologies. The α -SiC/PAN nanofibres were produced by using the electrospinning process, followed by heat treatments to determine the stability of the structure under a high-temperature vacuum environment. The overall process is summarized in Figure 4-11.

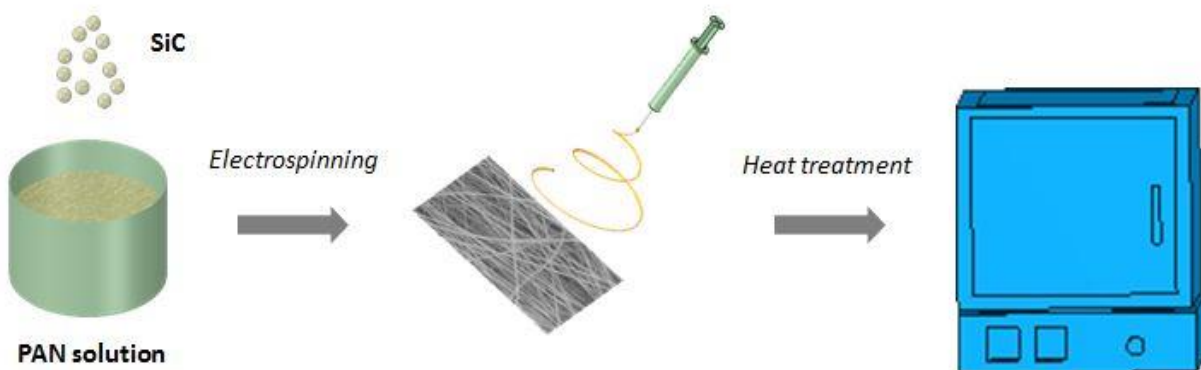


Figure 4-11: Direct co-electrospinning process of SiC/PAN composite nanofibres.

4.2.1 Raw materials

Silicon carbide (α -SiC; 1 μm , Cat #: S-2022) as a silicon precursor was purchased from Materion Advanced Materials. Polyacrylonitrile (PAN; $(\text{C}_3\text{H}_3\text{N})_n$, $M_w = 150,000$, Cat #: 1056) as carbon source, was purchased from Scientific Polymer Products, Inc. Sodium dodecyl sulfate (SDS; Cat #: 811034) as a surfactant, was purchased from MP Biomedicals. Organic solvent dimethyl formamide (DMF, Cat #: 68-12-2) from Fisher Scientific, was used to dissolve PAN and mix with SiC for preparation of the electrospinning dope solution.

4.2.2 Preparation of α -SiC/PAN spinning dope solution

Two samples were prepared for comparison with the mass ratios of SiC and PAN of 1:1 and 1:4. These samples were referred to as α -SiC/PAN-1 and α -SiC/PAN-2, respectively. The concentrations of PAN solution in DMF were 12% for α -SiC/PAN-1 and 9% for α -SiC/PAN-2.

The compositions of both samples are shown in Table 4-2. Both sample solutions were vigorously mixed using a vortex mixer and followed by ultrasonication (Qsonica -700 W, equipped with a horn for the indirect sonication). Ultrasonic energy was employed for 90 min in pulsing mode (10 sec on, 10 sec off) for an effective sonication time of 45 min. The solutions were removed from the sonicator and placed on a magnetic stirring hot plate at 60 °C. After 48 hours, the solutions were removed from heat and continuously stirred until they reached room temperature.

	α-SiC (g)	PAN (g)	DMF (g)	SDS (g)
α -SiC/PAN-1	1.2	1.2	8.8	0.12
α -SiC/PAN-2	0.23	0.90	9.1	0.023

Table 4-2: Compositions of α -SiC/PAN spinning dope solutions.

4.2.3 Electrospinning of α -SiC/PAN solution

Each sample solution was scheduled to undergo the electrospinning process at a given time using the electrospinning system (NEU-1, Kato Tech. Co. Ltd., Japan) as shown in Figure 4-3. Prior to conducting the process, each solution underwent ultra-sonication for 30 min. All other parameters are as introduced in Chapter 4.1.4.

4.2.4 Thermal treatment process

Discs with a diameter of 18 mm were punched out from the obtained α -SiC/PAN-1 and -2 nanofibre mats collected on the graphite backing sheet. The samples were stabilized at 250 °C in a furnace (Barnstead Thermolyne 48000) for 1 hour in air with a ramping temperature rate of 1 °C/min. The fibrous discs were then cooled to room temperature before they were heat treated in a high vacuum furnace. Prior to initiate the furnace heating power, all the parameters are as introduced in Chapter 4.1.5.

For sample α -SiC/PAN-1, three high-temperature treatment schedules were performed to determine the composition and the stability of the fibre mats at different heating stages. The sample was heated to 1200 °C at a ramping rate of 1°C/min and held for 4 hours before initiating the cooling process. The sample was then removed from the vacuum furnace for examinations. The processes were repeated at 1400 °C and 1600 °C, but for each heat treatment, the temperature was held for four days. For sample α -SiC/PAN-2, the temperature was ramped up directly to reach 1600 °C at a rate of 1 °C/min; the desired temperature was held for four days before cooling to room temperature. The overall heating process is summarized in Figure 4-12.

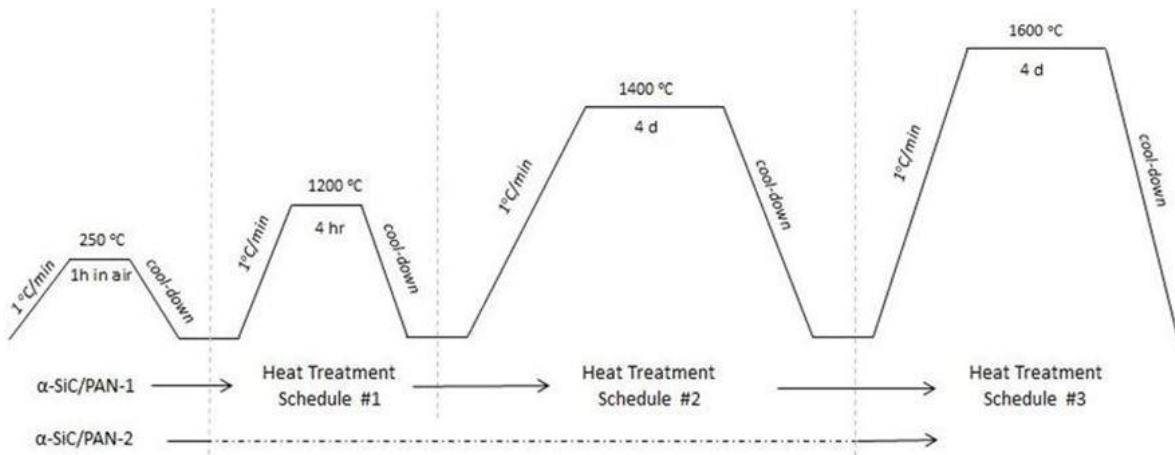


Figure 4-12: Heating processes of α -SiC/PAN-1 and -2 nanofibre samples.

4.2.5 Results and discussion

α -SiC with a particle size of 1 μm was chosen for this preliminary experiment as this powder has been used for ISAC targets routinely. Solutions of α -SiC in PAN/DMF were prepared at mass ratios, SiC to PAN of 1:1 for α -SiC/PAN-1 with 12% PAN concentration, and 1:4 for α -SiC/PAN-2 with 9% PAN concentration. The dispersed SiC particles in PAN polymer were successfully electrospun into nonwoven fibrous mats; however, the needles clogged multiple times during the electrospinning for α -SiC/PAN-1 solution due to its high concentration and viscosity. By keeping the relative humidity between 23-30%, and the temperature around 30 $^{\circ}\text{C}$ during the electrospinning process, no clogging of the needle was observed; however, maintaining such environmental conditions remained a challenge at this current stage. α -SiC/PAN-2 solution was electrospun with no needle clogging due to its lower concentrations of SiC and PAN.

Figure 4-13 shows the optical photographs of α -SiC/PAN-1 fibrous discs. No shrinkage of the fibrous disc was observed after the thermal stabilization at 250 $^{\circ}\text{C}$ in air; the diameter of the disc remained at 18 mm as that of the graphite backing foil. Heating the samples for several days under vacuum to 1400 $^{\circ}\text{C}$ causes shrinkage of the fibre mats as the exposure of the graphite backing foil was observed in Figure 4-13 (b). Further heat treatment at 1600 $^{\circ}\text{C}$ resulted in thermal shear stress leading to deformation of the nanofibre mats, thus slightly lateral expansion and damage was observed in Figure 4-13 (c). Moreover, the sample became brittle and easily fractured during handling; hence measuring the physical dimensions of the discs was inconclusive.

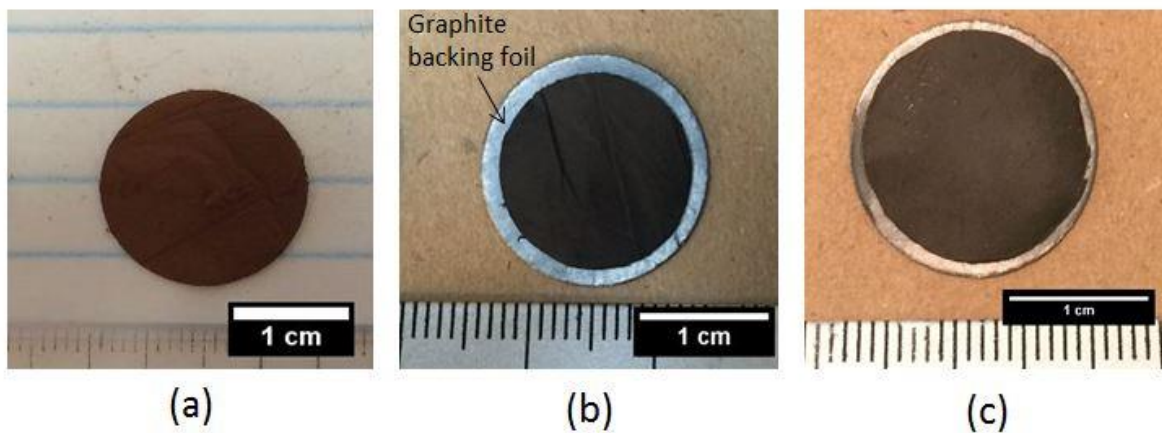


Figure 4-13: Optical photographs of α -SiC/PAN-1 discs with graphite backing foils: (a) stabilized at 250 °C in air, (b) 1400 °C and (c) 1600 °C in vacuum for 4 days, respectively.

Detailed characterizations of the α -SiC/PAN -1 and -2 nanofibre mats were carried out by using electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM/EDS, Hitachi S-3000, Japan). The phases and crystallographic features of the samples were monitored by X-ray diffractometer (XRD; Rigaku Multiflex, Japan). Moreover, the vacuum levels during the high-temperature treatments were carefully analyzed, and the samples were weighed in all heat treatment conditions to determine mass losses.

Scanning Electron Microscopy (SEM) Analysis:

The α -SiC/PAN-1 and -2 fibres were heat treated at different temperatures, and the morphological appearances of the as-spun samples were investigated from the scanning electron

micrographs as shown in Figure 4-14 and Figure 4-15. The surface morphology of the composite nanofibres is smooth at low SiC concentration and rougher at high concentration.

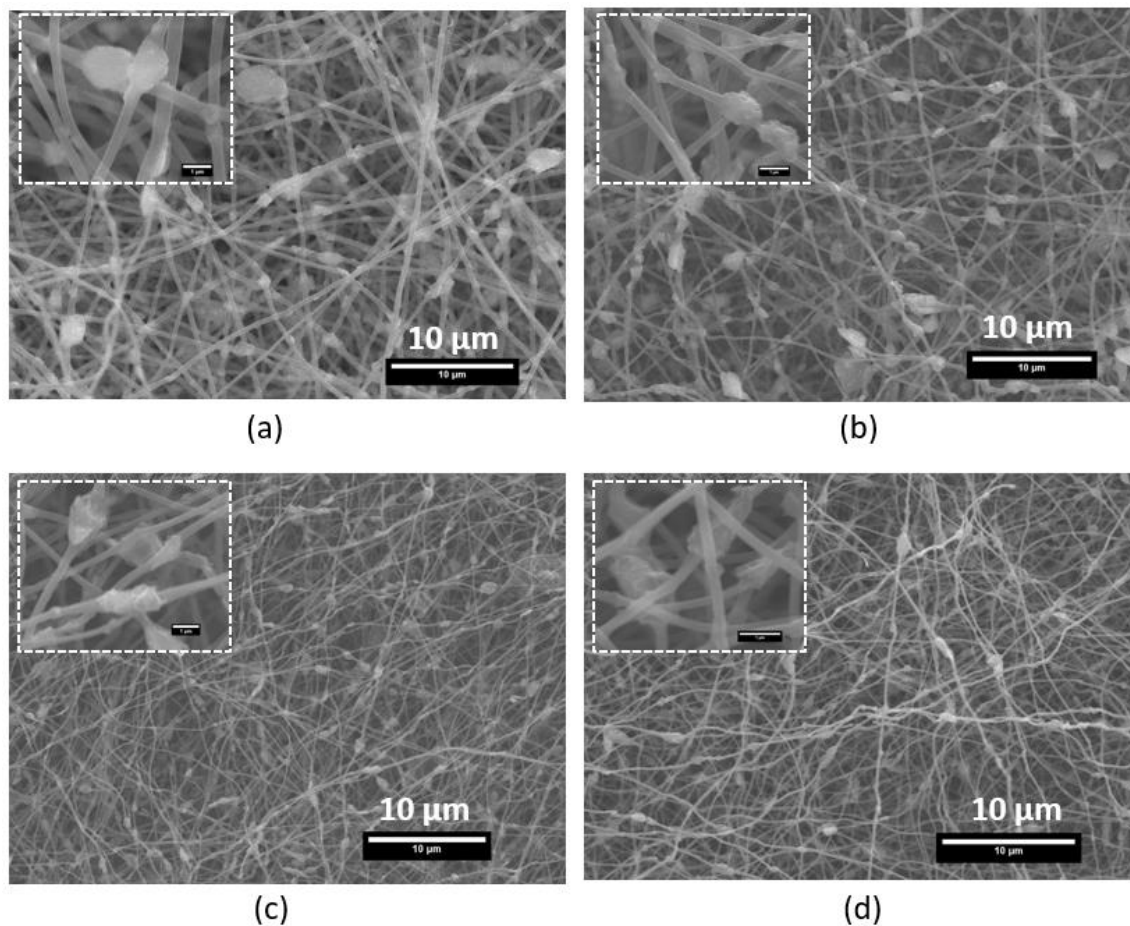


Figure 4-14: SEM images of α -SiC/PAN-1: (a) Before high-temperature treatment, heat treated under vacuum at (b) 1200 °C, (c) 1400 °C, and (d) 1600 °C, respectively. The inserts are the close-up SEM images, scale-bar at 1 μ m.

The as-spun fibres obtained from α -SiC/PAN-1 were found to have more agglomerated SiC particles than those from α -SiC/PAN-2. Nonetheless, both pristine composite nanofibre samples were visible in the SEM photographs, Figure 4-14 (a) and Figure 4-15 (a), have SiC particles

with a size of about 1 μm at least partially entrained or embedded within the electrospun PAN nanofibres. The fibres for both samples shrunk during the heat treatment process; the diameter of the carbonized PAN nanofibre reduced significantly as temperature increased from 1200 $^{\circ}\text{C}$ to 1600 $^{\circ}\text{C}$ as shown in Figure 4-14 (b-d) and Figure 4-15 (b).

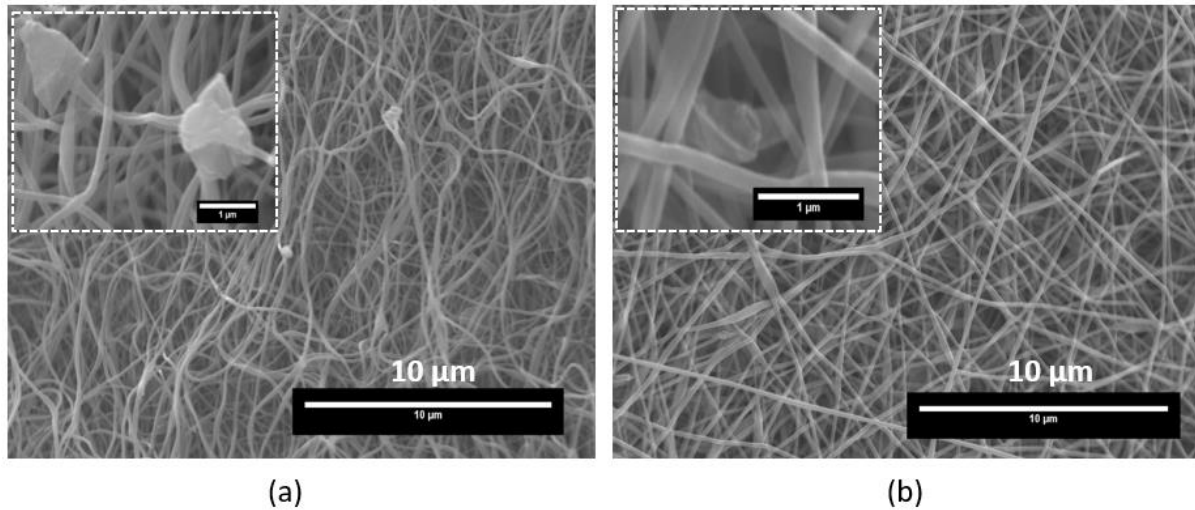


Figure 4-15: SEM images of α -SiC/PAN-2: (a) Before high-temperature treatment, (b) heat treated under vacuum at 1800 $^{\circ}\text{C}$ for four days. The inserts are the close-up SEM images, scale-bar at 1 μm .

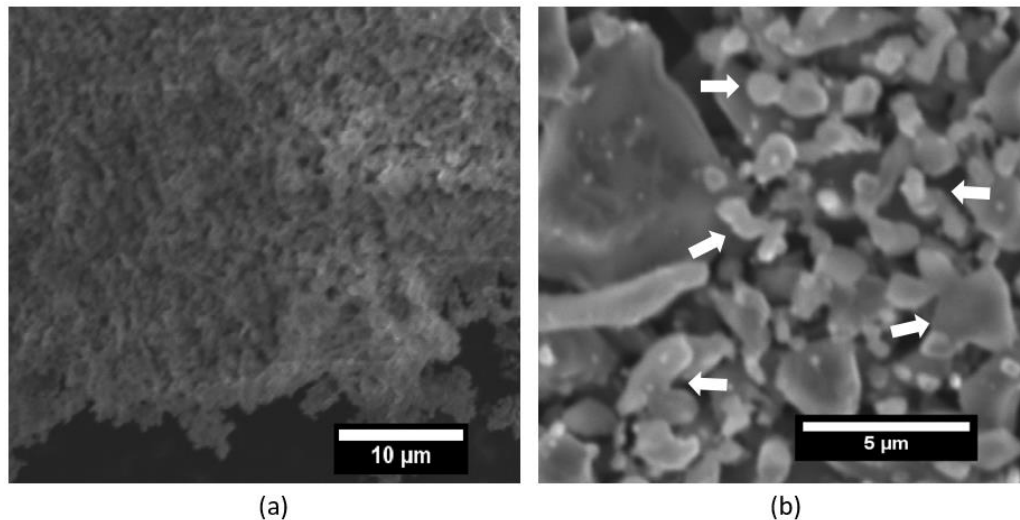


Figure 4-16: SEM images of the ISAC conventional SiC target: (a) 1 μm grain size precursor powder, (b) sintered at 1400 $^{\circ}\text{C}$, arrows showing examples of the grain growth.

Generally, the sintering effect of SiC begins at around 1400 $^{\circ}\text{C}$ resulting in grain growth shown in Figure 4-16 (b), thus a negative impact on characteristics for short-lived isotopes can be expected. In comparison, the embedded SiC particles separated by the nanofibres reduced the number of contact points when the sintering temperature was reached. Figure 4-14 (c) shows that the SiC particles underwent individual sintering at temperature of 1400 $^{\circ}\text{C}$ and maintained their open structure as the carbonized nanofibre prevented them from fusing together.

Energy Dispersive X-ray Spectroscopy (EDS) & X-ray Diffraction Analysis:

The EDS spectra were taken with primary electron beam energy of 20 keV to evaluate the SiC composite PAN matrix nanofibres. When analyzing the composition of the fibre mats, no coating was used on the sample to avoid any signal interference. X-ray qualitative spot analysis was carried out on several locations of the fibre mats for samples α -SiC/PAN-1 and -2 after each heat treatment.

With the aid of EDS results, the phase transformations of PAN and α -SiC during heat treatment schedules #1 and #2 were monitored using an X-ray diffractometer (XRD; Rigaku Multiflex, Japan) with $\text{CuK}\alpha$ radiation at 40 kV and 20 mA. Monochromatic graphite crystal was used to filter out other continuous X-rays and $k\beta$ emissions. A more advanced XRD diffractometer (XRD, Bruker D8 Advance, Germany) with a Cu source at 40 kV and 40 mA was used to analyze the final phase composition of the samples after heat treatment schedule #3. A nickel filter was used to eliminate Cu $k\beta$ emissions. The divergence and scattering slits were set to 1 mm and 8 mm, respectively.

The EDS spectrum from Figure 4-17 (a) confirms the presence of the major elements of Si, C, N, and O in the PAN matrix for α -SiC/PAN-1 and -2 samples after thermal stabilized at 250 °C in air; S was detected possibly an impurity from the graphite backing foil (300 ppm of sulfur content expected as per the supplier Cera Materials). The XRD diffraction pattern in Figure 4-17 (b) reveals reflexes caused by the aromatic structure of oxidized PAN at around $2\theta = 26^\circ$ and 55° . The (101) (102) and (103) reflexes as shown in the inset of Figure 4-17 (b) correspond to the diffraction pattern of SiC.

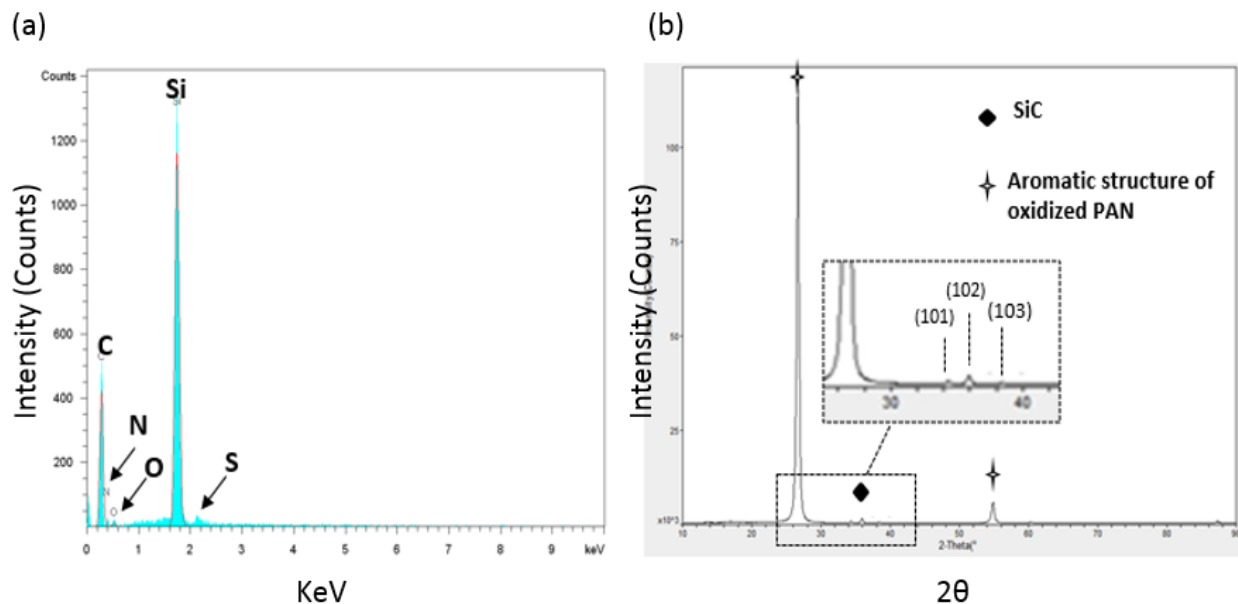


Figure 4-17: (a) EDX spectrum and (b) XRD diffractogram for α -SiC/PAN samples after thermal stabilization at 250 °C in air. Both α -SiC/PAN-1 and -2 samples show similar results.

After the heat treatments schedule #1 and #2, the presence of Si was confirmed from α -SiC/PAN-1, and the absence of N after 1200 °C indicated that the PAN fibre was fully carbonized as shown in Figure 4-18 (a). The XRD diffractogram as illustrated in Figure 4-18 (b) reveals the α -SiC crystalline structure, which matched PDF #29-1131. A broad peak at $2\theta = 26^\circ$ corresponds to amorphous carbon from carbonized PAN.

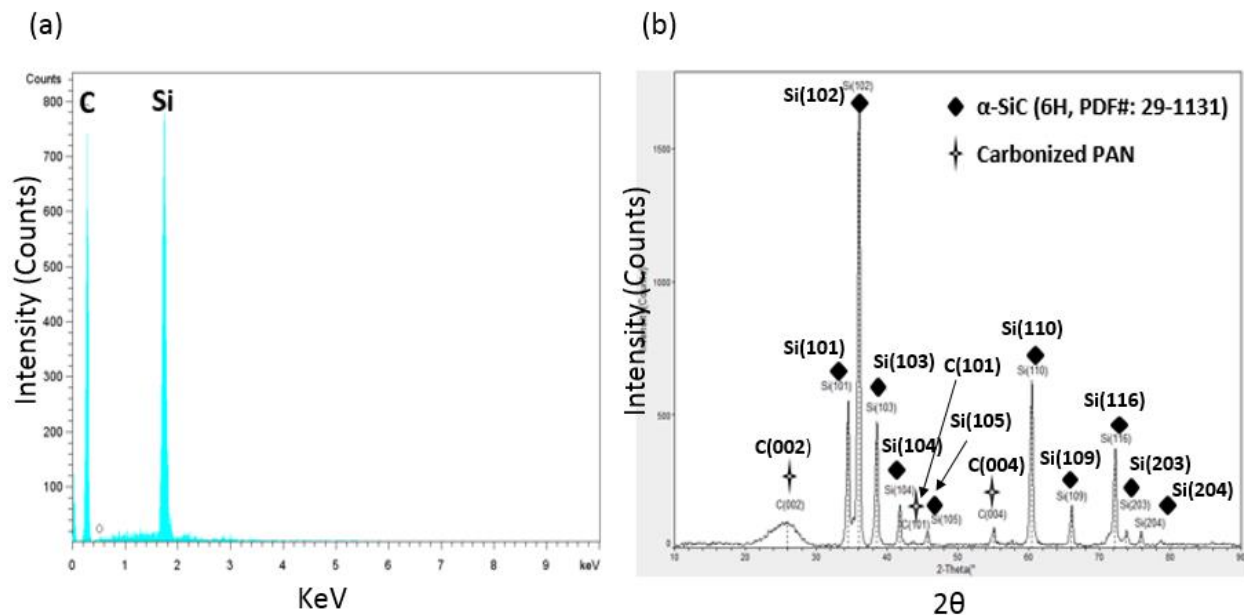


Figure 4-18: (a) EDX spectrum and (b) XRD diffractogram for α -SiC/PAN-1 after heat treatments; the results are similar to heat treatments schedule #1 and #2.

The characteristic Si K- α X-rays at 1.74 KeV for both samples were found to be absent after the heat treatment schedule-3 as shown in Figure 4-19 (a). Evidently, Figure 4-19 (b) shows only the diffraction pattern for amorphous carbon. It may be assumed that at an elevated temperature near 1600 °C in a high vacuum environment, phase transformation into α -SiC occurs and leads to dissociation and sublimation of silicon. As a consequence, gaseous silicon diffused out from the carbon nanofibre and precipitated on any cool surfaces in the vacuum chamber.

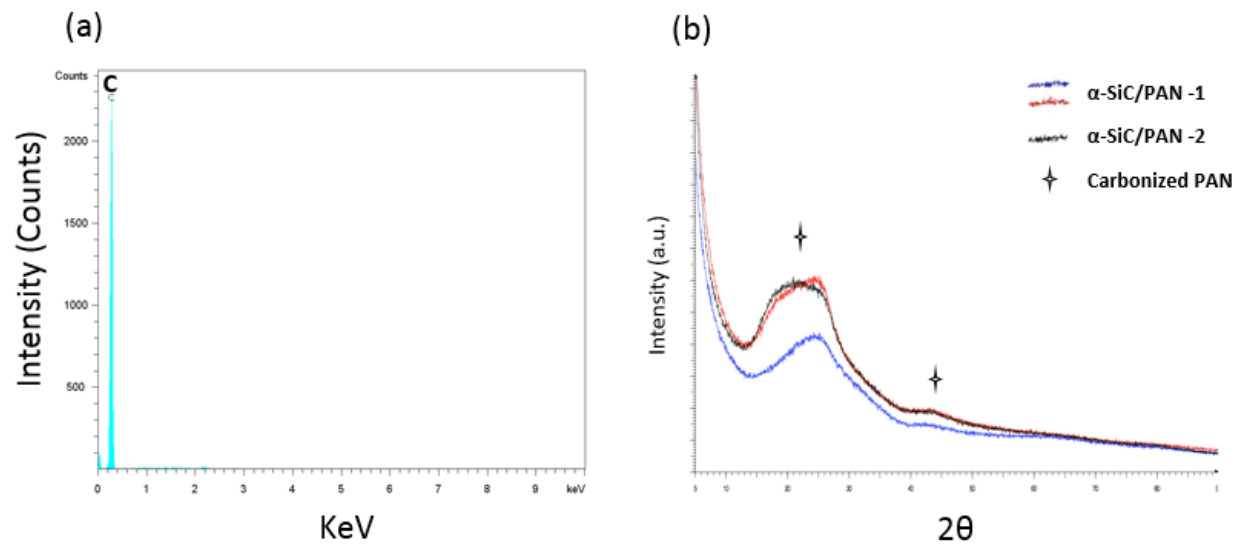


Figure 4-19: (a) EDX spectrum and (b) XRD diffractogram for α -SiC/PAN-1 and -2 after heat treatments schedule #3.

In fact, the extraction of Si from the conventional ceramic α -SiC ISAC target material has been observed during the heat treatment process under vacuum. The side view port window of the vacuum furnace was found to be coated with silicon at sample temperatures above 1400 °C, as shown in Figure 4-20. The XRD pattern, in Figure 4-21, revealed the gray and metallic lustrous substance to be silicon which matches PDF #27-1402.

It is important to mention that any volatile material condensation, if not properly thermal conditioned to the desired operating temperature for online isotope production, may cause the deposit of material between the target transfer tube and the extraction electrode resulting in undesired electrical contacts and failure of the ion extraction system. Moreover, the loss of Si in the target material due to evaporation results in the reduction of isotope production rates and leads to a decrease in beam intensities.



Figure 4-20: Silicon coating on the side viewport window of the vacuum furnace during the heating process of the conventional ceramic α -SiC ISAC target material.

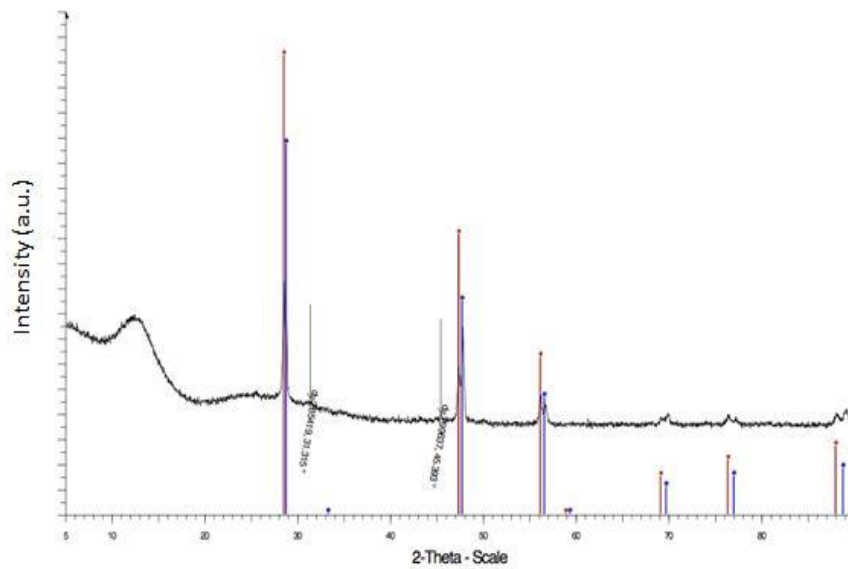


Figure 4-21: XRD pattern of the coating material on the side viewport window of the vacuum furnace showing all characteristic crystalline silicon reflexes, which match PDF #27-1402.

It is worth noting that SiC exhibits more than 250 polytypes, which are based on the tetrahedral coordination of carbon and silicon, where the layer stacking sequence causes differences in physical properties [68]. Under high vacuum, evaporation of silicon near 1400 °C from α -variant SiC (i.e., 2H, 4H or 6H hexagonal polytype) which led to undesired outgassing as mentioned above. Other than the α -variant SiC, the only possible cubic polytype is 3C-SiC or β -SiC with three-bilayer stackings. Under all conditions, β -SiC is stable at a high temperature up to 2200 °C [67]. For that reason, the raw ceramic powder was replaced by micrometric particle β -SiC for use in the conventional ISAC SiC target. A major improvement was achieved in terms of the thermal stability at high temperature under vacuum; however, sintering of the particles remains an issue as shown in Figure 4-16.

Vacuum Levels and Mass Losses during the High-Temperature Treatments:

To illustrate the results of the outgassing behavior for the α -SiC/PAN nanofibre samples, Figure 4-22 and Figure 4-23 show the pressure in the vacuum furnace as a function of the Joule-heating power.

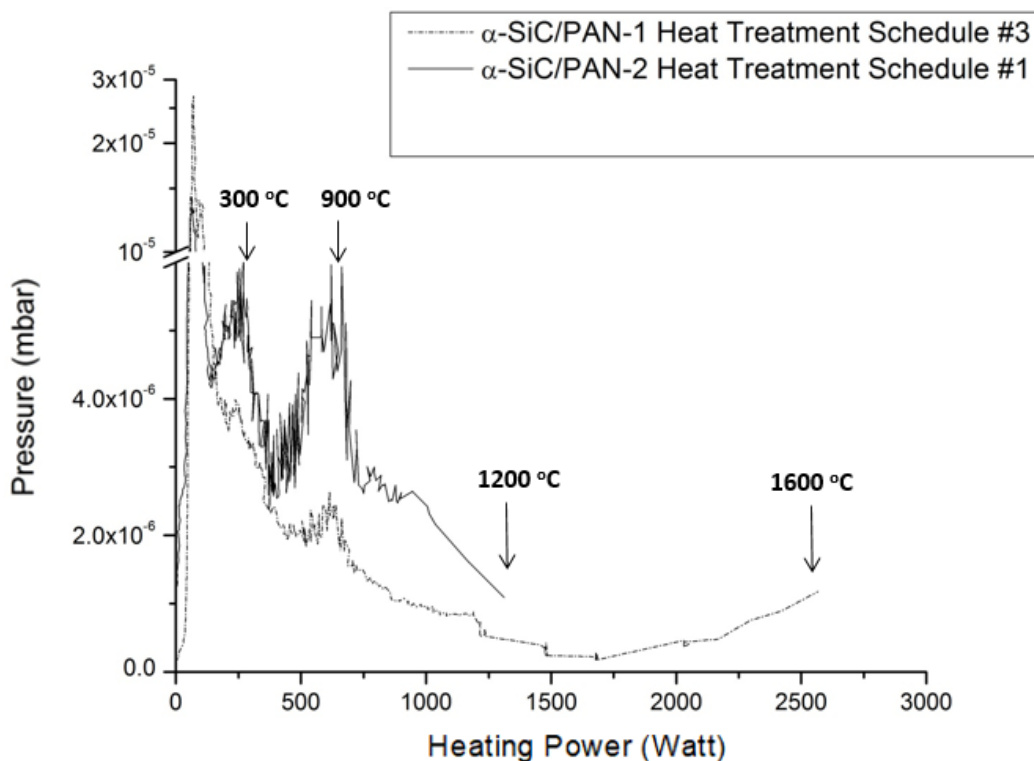


Figure 4-22: Vacuum levels during the heat-treatment Schedule #1 for α -SiC/PAN -1, and Schedule #3 for α -SiC/PAN -2.

Before the heating process was initiated, the vacuum chamber was pumped down to 10^{-7} mbar. Heat treatment schedule #1 was initially carried out for α -SiC/PAN-1 nanofibre to reach 1200 °C. As the temperature was ramped up from 25 °C at a rate of 1 °C/min, the pressure increased rapidly and reached the 10^{-5} mbar. The vacuum excursion at 300 °C was associated with dehydration reactions and release of volatiles such as H_2O , CO , CO_2 , CH_4 , NH_3 , and HCN from PAN polymer. More outgassing at 900 °C was observed which could be attributed to the carbonization of PAN nanofibres, which is in good agreement with the EDS and XRD results shown in Figure 4-18.

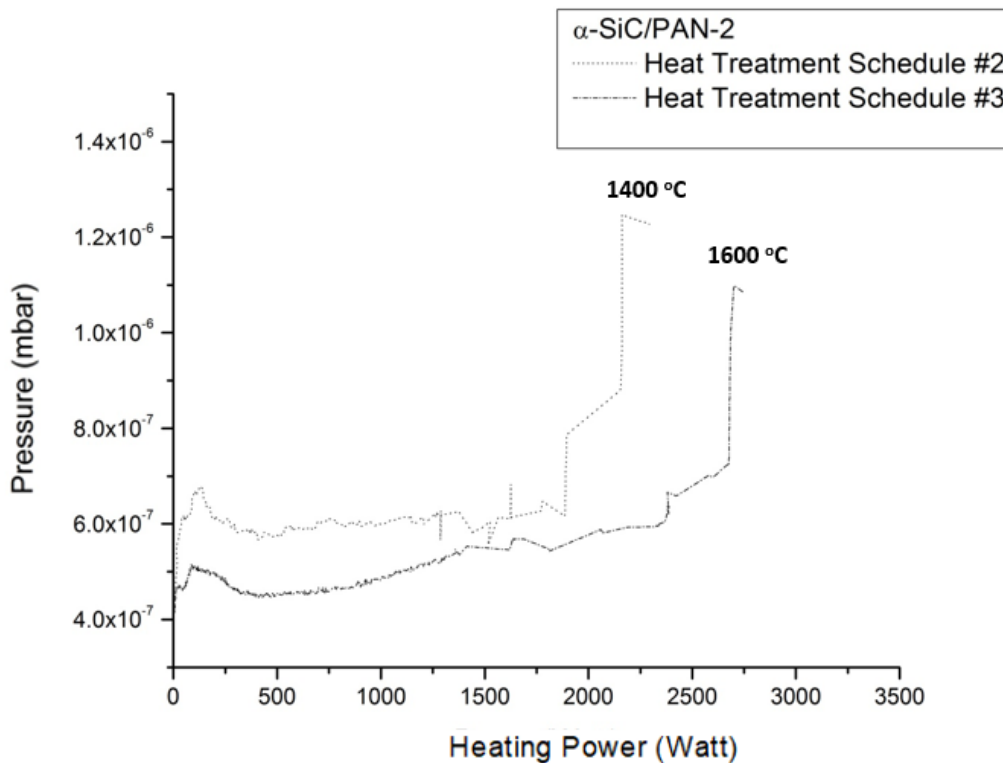


Figure 4-23: Vacuum levels during the heat-treatment Schedule #2 and #3 for α -SiC/PAN -1.

Moreover, the evolution of weight loss of the α -SiC/PAN nanofibres was measured as a function of temperature as shown in Figure 4-24. Based on many reported thermogravimetric studies, a mass loss between 30 – 40 % for fully carbonized for PAN is commonly expected [63][69]; this pattern for temperatures up to 1200 °C was similar for the α -SiC/PAN-1 sample as it underwent the heat treatment schedule #1. Heat treatment schedules #2 and #3 resulted in a further vacuum excursion related to SiC dissociation leading to sublimation of Si. The assessment of the total weight loss is in good agreement with the EDX and XRD results shown in Figure 4-19, which correspond to the loss of Si content at 1600 °C.

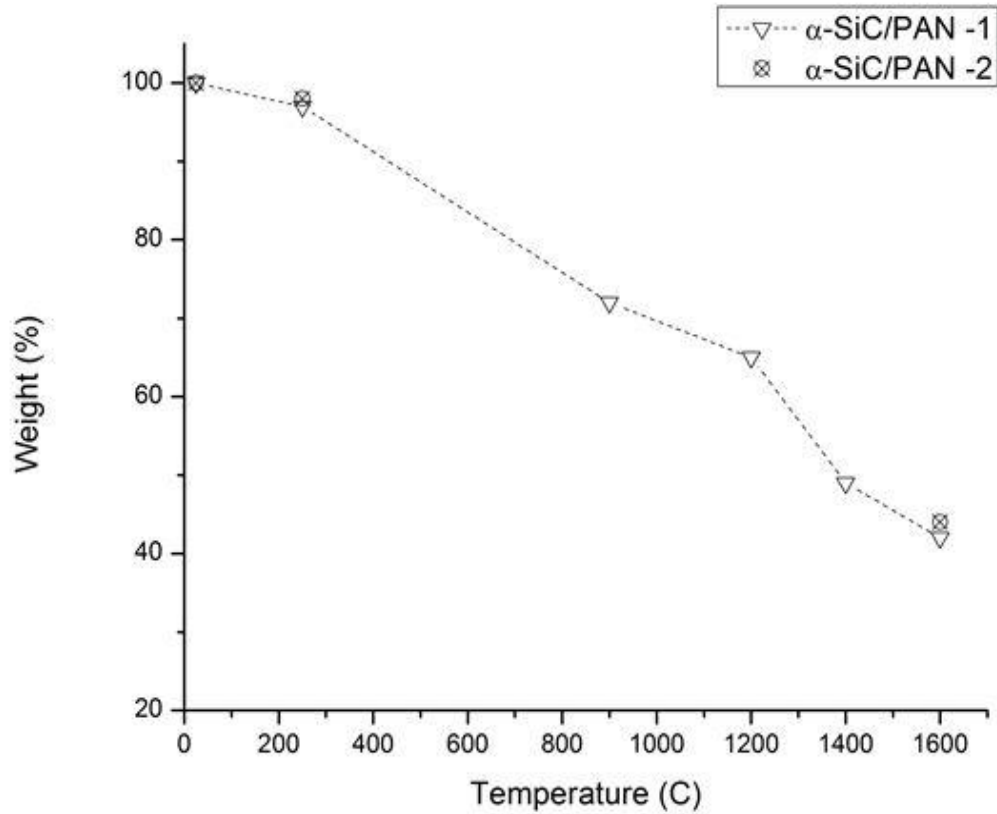


Figure 4-24: Measurement of the weight as a function of temperature for α -SiC/PAN-1 and -2 nanofibre samples.

As the α -SiC/PAN-2 sample underwent heat treatment schedule #3, the pressure excursion during the carbonization process behaved similarly, and the vacuum pressure began to drop until the heating power went beyond 1500 W, see Figure 4-22. A continued rise in vacuum pressure to the order of 10^{-6} mbar was detected as the temperature approached 1600 °C. Figure 4-24 shows the final weight percentage which matched the result obtained for α -SiC/PAN -1.

4.3 Remarks

The research reported in the preliminary experiments has investigated the feasibility of producing SiC target materials for ISAC using the electrospinning process. For the first time, SiC particles were successfully embedded in the PAN nanofibre using the novel direct co-electrospinning process. SiC particle suspensions in 10% PAN provided a spinnable solution and yielded a fibre diameter of less than 500 nm. Although the sintering process was reduced dramatically, a higher concentration of Si with nanometric particle size is the most desirable for the production of exotic short-lived isotopes. In the next chapters, the development of nanoparticle (np) SiC fibrous target materials will be presented.

Chapter 5 Dispersion of Nano-SiC in Non-Aqueous Suspensions

A common phenomenon in ultrafine particles is the formation of agglomerates to submicron particles mainly due to van der Waal forces [70]–[72]. The agglomerated particles strongly affect many properties of bulk powders such as chemical activities and the quality of the electrospun fibres for use in ISAC. Furthermore, nanoparticles are subjected to clustering or sintering during pyrolysis, resulting in larger particle size [73]. The initial stage of sintering is well known to happen inside the aggregated or agglomerated powders leading to the decrease in porosity and lengthening in the diffusion pathway for the isotopes [57]. Use of ultrasonication enables dispersion of aggregates to primary particle sizes [74]. To obtain SiC nanoparticles suspensions in liquid media for the electrospinning dope, dispersion and deagglomeration of particle solutions by direct and indirect sonication methods were investigated.

5.1 Materials and methodology

β -silicon carbide nanoparticles (np-SiC, US Research Nanomaterials, Inc., Cat #: US2028) has been studied as a precursor to produce a nanomatrix RIB target material composite. The np-SiC raw powder was purchased in the form of nanoparticles with an average size of 50 nm. Due to its high surface energy, the nanoparticles as supplied are intensely agglomerated and coagulated to micrometer-size. Sodium dodecyl sulfate (SDS; Cat #: 811034) as a surfactant, was purchased from MP Biomedicals. Organic solvent dimethyl formamide (DMF, Cat #: 68-12-2) from Fisher Scientific is used to suspend np-SiC.

Dispersion of np-SiC suspensions is performed using two types of ultrasonication setup: Direct sonication with a microtip probe (Qsonica, part #: 4420, tip diameter: 6.4 mm, vibration amplitude: 200 μ m) and indirect sonication with a horn (Qsonica part #: 431C2, diameter of horn: 63.5 mm). The ultrasonic generator for the dispersion of nanoparticles is Qsonica-700W (USA, frequency: 20 kHz; generating power: 700 W). For the direct sonication, the microtip probe is introduced directly into the solution, and the suspension container is immersed in a cooling bath during ultrasonication process to limit the temperature variations below 50 °C to minimize solvent evaporation. Except for a small opening for the probe, the container is covered with an aluminum foil to reduce the evaporative loss and concentration change of the solution. The temperatures of the solution and the probe are monitored with a Fluke IR Thermal Imager (model Ti25). For the indirect sonication, the sealed container with suspension is immersed into the horn-cup containing a cooling bath through which ultrasonic waves are propagated from the horn. The temperature of the ultrasonic water bath is monitored with a conventional thermometer. Both sonication types are shown in Figure 5-1.

The ultrasonic generator is set to provide pulses with a 100% amplitude and a sequence of 10 sec on and 10 sec off for an effective process time of 30 min. To correct for suspension volume, the ultrasound energy density [kJ/mL] is chosen as effective parameter.

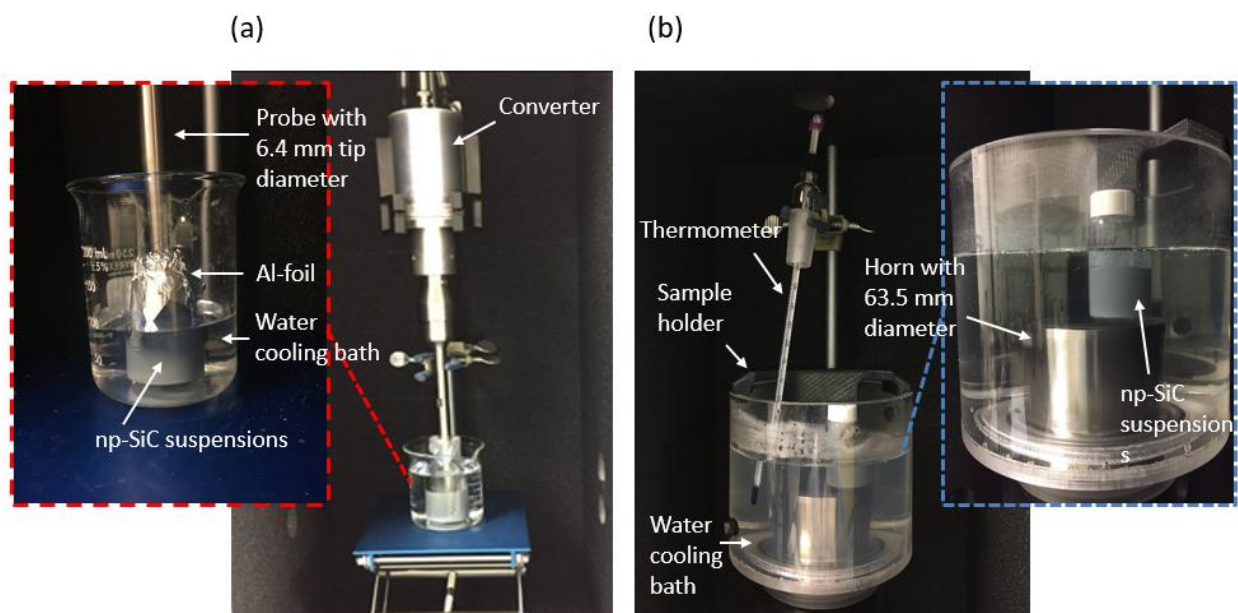


Figure 5-1: Setup of the sonication dispersion of np-SiC suspensions: (a) The probe-type (direct sonication), (b) the horn-type (indirect sonication).

10 g solution consisting of 1 g np-SiC and 0.1 g SDS in DMF are mixed in a 20-ml glass vial for 1 min using a vortex mixing device (Vortex-Genie 2, Scientific Industries, Inc. USA). Sample 1 (ID: P_np-SiC_1) and sample 2 (ID: H_np-SiC_2) are treated with the direct probe-type and the indirect horn-type sonication, respectively. Every 3 min in-between the process time, the suspension is taken to measure the particle size distribution. In addition, 1 g of PAN is added to each sample 3 (ID: P_np-SiC/PAN_3) and sample 4 (ID: H_np-SiC_4); the viscosities of the solutions are investigated as a function of energy input from the ultrasonication. Sample 5 (ID: X_np-SiC_Ref) is prepared with no ultrasonic treatment as a control. Samples 6 and 7 (ID: X_P_10%-PAN_Ref and X_H_10%-PAN_Ref) are prepared as controls for investigating the viscosity of PAN/DMF solution under the influence of ultrasonication. The compositions and sonication-type of all the samples are summarized in Table 5-1.

Sample ID	np-SiC (g)	SDS (g)	DMF (g)	PAN (g)	Sonication Setup
P_np-SiC_1	1.00	0.01	8.99	-	Probe
H_np-SiC_2	1.00	0.01	8.99	-	Horn
P_np-SiC/PAN_3	1.00	0.01	8.99	1.00	Probe
H_np-SiC/PAN_4	1.00	0.01	8.99	1.00	Horn
X_np-SiC_Ref	1.00	0.01	8.99	-	None
X_P_10%-PAN_Ref	-	-	9.00	1.00	Probe
X_H_10%-PAN_Ref	-	-	9.00	1.00	Horn

Table 5-1: Summary of nanoparticle SiC suspensions and reference solutions.

5.2 Characterization of the np-SiC suspension

5.2.1 Optical microscope (OM) analysis

A small amount of np-SiC raw powder was sprinkled on two microscope slides, and a pinch of SDS surfactant is added to one of the samples. On each slide, a drop (approximately 0.1 ml) of DMF solvent is added and mixed with a glass rod. The samples are viewed using a Nikon optical microscope (Eclipse LV100) equipped with a Nikon digital camera (DS-Fi1), to capture images with the data processor controller software. An OM numerical aperture of 0.4 is used, and the images are captured at 200X magnification.

5.2.2 Dynamic light scattering (DLS) particle size distribution

DLS is used to measure the size distribution of np-SiC using a NanoBrook Omni Particle Analyzer (Brookhaven Instruments, USA). Each sample is diluted to 0.01 wt% with DMF to make up 10 g solution. The diluted sample is pipetted into a standard glass cuvette (10 mm path, $V = 3.5$ ml) to about 80% full. A plastic cuvette must not be used since it dissolves in DMF solvent resulting in erroneous measurements. Refractive indices of 1.428 and 2.653 are used for DMF and β -SiC, respectively, and the scattering angle is fixed at 90° . The data collection time per sample is set to 2 min with a wait-time of 5 min before taking the next measurement.

5.2.3 Viscosity measurements

The viscosity of the various samples is measured as a function of energy density applied from the ultrasonicator. Viscosity is measured using a DV-E viscometer (Brookfield, USA) with a ULA low-volume spindle rotating at 50 RPM at a constant temperature of 25°C .

5.3 Results and discussion

Nanopowders often form agglomerates 10 – 20 times larger than the primary nanoparticle [75]. For SiC, there is an oxygen-rich layer on its surface which is commonly introduced during the synthesis process [76]. Moisture exposure is expected when handling the SiC nanoparticles, so surface formation of silanols is an inevitable process [77]. When the SiC nanopowders are wetted with DMF solvent, the silanol layers effectively hydrolyze the solvent to form N-

methylformamide (NMF) and react with OH^- to form Si-O^- with negative charges at the surface of the SiC powder particles [77]. The surface charges promote Brownian flocculation immediately leading to the undesired aggregation to micron-sized particles as shown in Figure 5-2.

Adding sodium dodecyl sulfate (SDS) surfactant effectively reduces the surface tension and Brownian motion, resulting in the formation of stable colloid suspensions as shown in Figure 5-3. Depending on the nature of the counterions, it can be assumed that SDS molecules interacted with np-SiC mainly by their hydrophobic tails due to the negative charges on the particle surface [78]. As a result, this creates an electrostatic repulsion environment between the np-SiC surface and SDS. No Zetasizer analysis is available to study the influence of electric potential near the silicon surface on the adsorption of SDS. Therefore, it is necessary to analyze the effects of ultrasonication on np-SiC colloid particle size and the viscosity of the PAN polymer matrix solution.

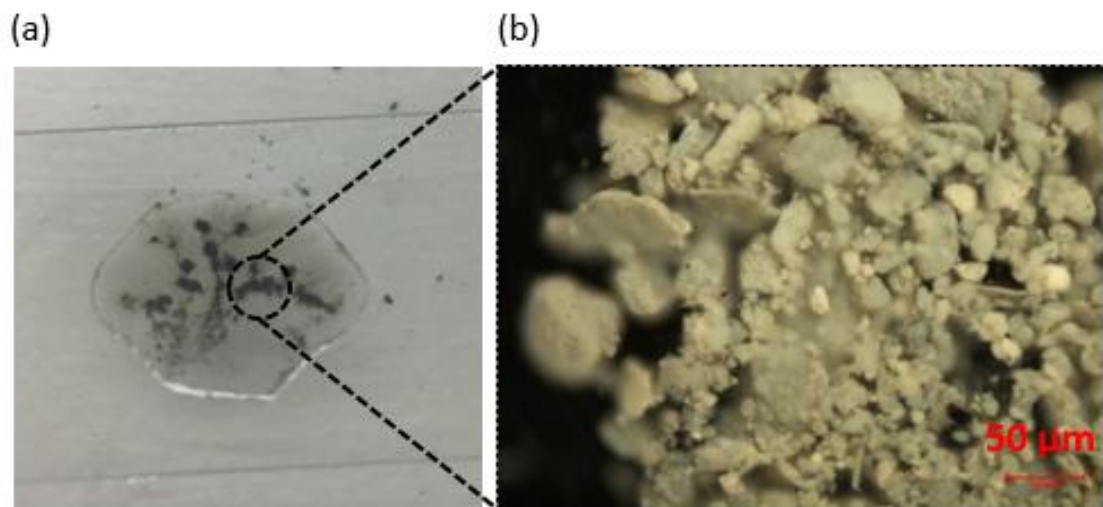


Figure 5-2: Wetting behavior of np-SiC and DMF leading to particle aggregation: (a) Photograph, (b) OM image taken at 200X magnification.

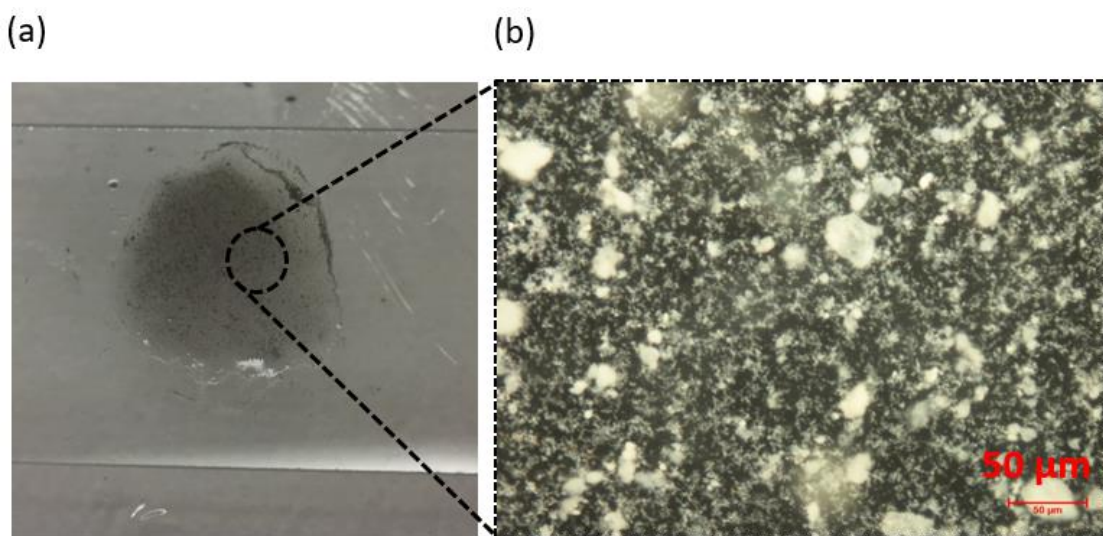


Figure 5-3: Formation of np-SiC colloid suspensions in DMF with the aid of SDS surfactant: (a) Photograph, (b) OM image taken at 200X magnification.

Ultrasonication is particularly advantageous as it generates mechanical forces to disperse the np-SiC colloid suspensions without the need to use chemical dispersants. The nanoparticle aggregation state is measured as a function of sonication energy density semi-quantitatively using dynamic light scattering (DLS) to determine apparent average particle size. The results are shown in Figure 5-4. The effective particle size for sample 1 (ID: P_np-SiC-1) treated with the probe-type direct sonication has been found to decrease dramatically to about 320 nm with an applied energy density of 6.4 kJ/mL (more information about the measurements can be found in Appendix A1). In comparison, over 50 kJ/mL of energy density has been applied to sample 2 (ID: H_np-SiC-2) treated with the horn-type indirect sonication which merely dispersed the agglomerated np-SiC presumably due to power losses in the physical barriers (i.e., water bath and sample container). In addition, DLS measurements are re-taken after the samples have been stabilized for 72 hours, and the particle size distribution results are shown in Figure 5-5. This data is useful for understanding if the np-SiC remained de-agglomerate and suspend at a given time to allow the conduction of the electrospinning process.

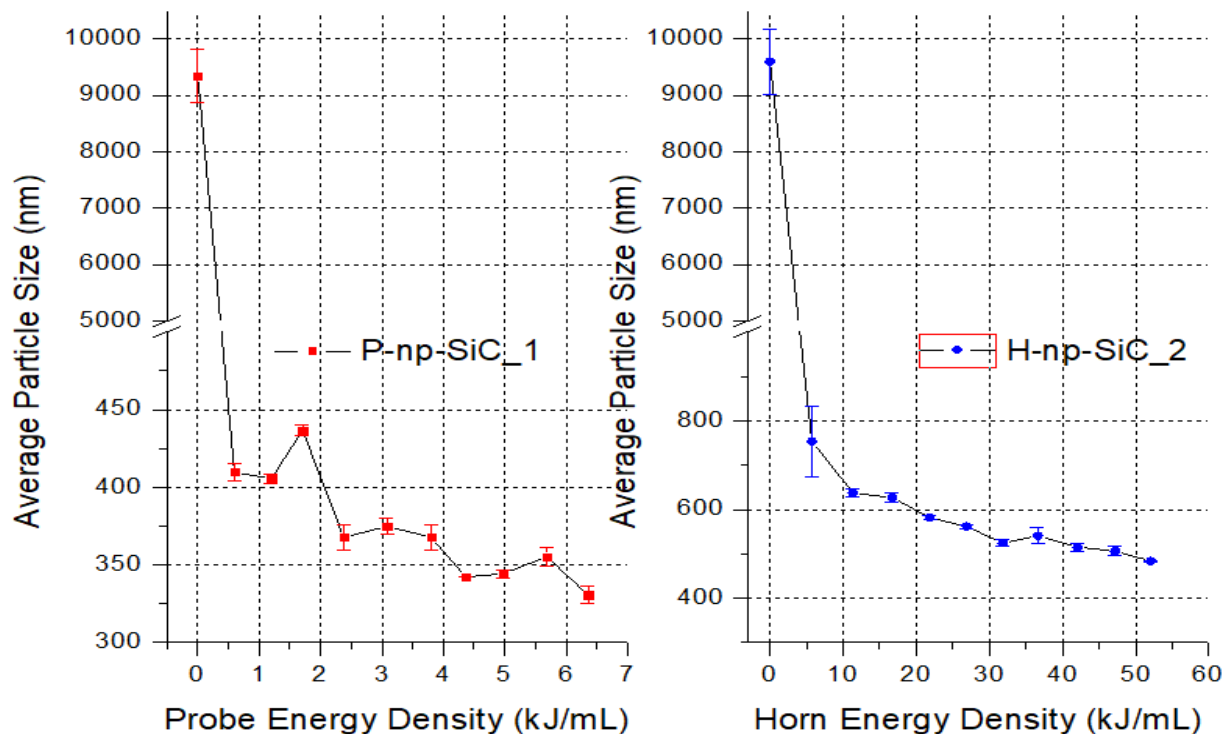


Figure 5-4: Dynamic light scattering (DLS) particle sizes as a function of sonication energy density for the np-SiC suspensions treated with the probe-type (direct) and horn-types (indirect) sonication.

Although the DLS technique provides a quick and non-destructive method to understand average particle size, it should be noted that DLS possesses some limitations which must be overcome. For example, the sample must be very diluted; a concentration of 0.01 wt% np-SiC is required to obtain reproducible data. This limits the determination of aggregations in highly concentrated electrospinning dope solutions. While characterization of nanoparticle suspensions can be challenging, the DLS data helps to explain the underlying dispersion mechanism of the probe and horn setup ultrasonication at least on a qualitative level. The actual particle size of np-SiC

will be characterized in more details in Chapter 6 after the particles are immobilized in the electrospun fibres.

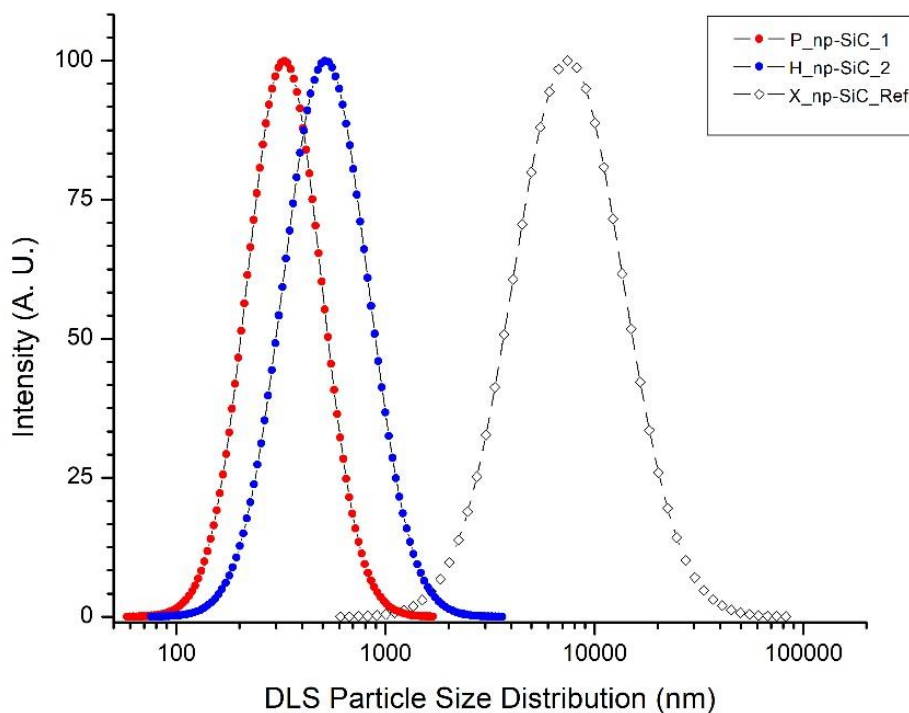


Figure 5-5: DLS particle size distribution based on intensity measurements for samples treated with probe and horn sonication energy densities of 6.4 kJ/mL and 52 kJ/mL, respectively, and a reference sample with no ultrasonic disruption for comparison. DLS measurements are taken after samples have been stabilized for 72 hours.

The probe sonication has proven to be most effective in dispersing nanoparticles; however intense heat and solvent cavitation are generated which causes polymer chain elongation and degradation [79]. Probe sonication is efficiently performed for 30 min with 10 sec on and 10 sec

off, raising the temperatures of the probe and the solution to over 52 °C and 44 °C, respectively. The thermal mapping images are presented in Figure 5-6. Furthermore, during the implosion of the cavitation bubble, the temperature can exceed the average solution temperature locally [79].

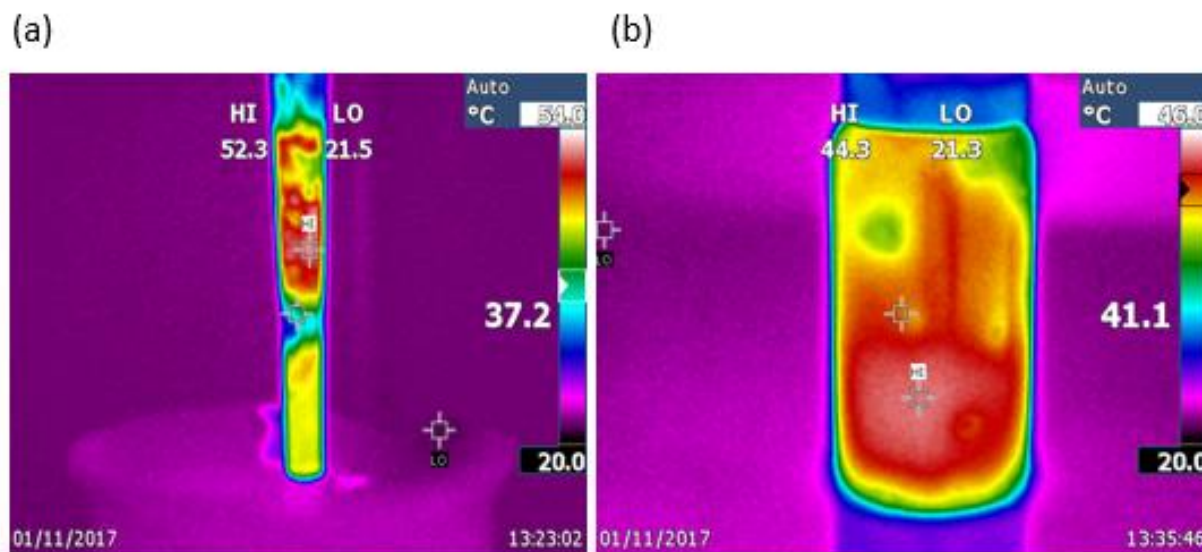


Figure 5-6: Fluke thermal mapping images for the probe and np-SiC suspension during the direct ultrasonication.

Evidently, degradation of PAN polymer resulting in significant reduction of viscosity has been observed for the samples treated with probe sonication as shown in Figure 5-7. The viscosity measured at 25 °C for sample P_np-SiC/PAN_3 decreases rapidly by over 75% to 320 cP in the first 9 min of effective probe sonication with 1.7 kJ/ml of dispersion energy density.

Furthermore, the 10% PAN control samples treated with the probe and horn-type sonication are subjected to the electrospinning process with similar settings as described in section 4.1.4 to determine the fibre quality. Experimental data were well correlated with beaded electrospun fibres for low viscosity polymer as shown in Figure 5-8 (a).

Destruction of the PAN polymeric structure under the action of mechanical stress and temperature generated from the horn-type indirect ultrasonication, sample H_np-SiC/PAN_4 is not pronounced. The temperatures of the water bath and the solution are maintained at around 40 °C for the complete 30 min sonication process. The viscosity decreases by about 8%, which is within the 1000 to 1500 cP range for non-beaded electrospun fibres. Bead-free electrospun fibres were produced as shown in Figure 5-8 (b), similar to the non-sonicated solution.

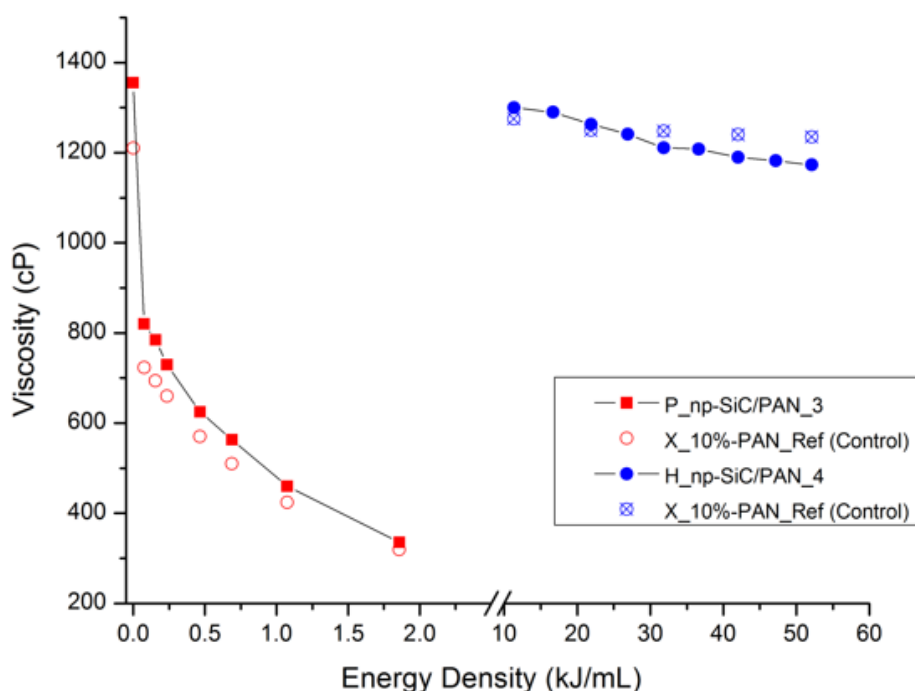


Figure 5-7: Viscosity of the np-SiC suspensions in PAN solution influenced by the ultrasonication.

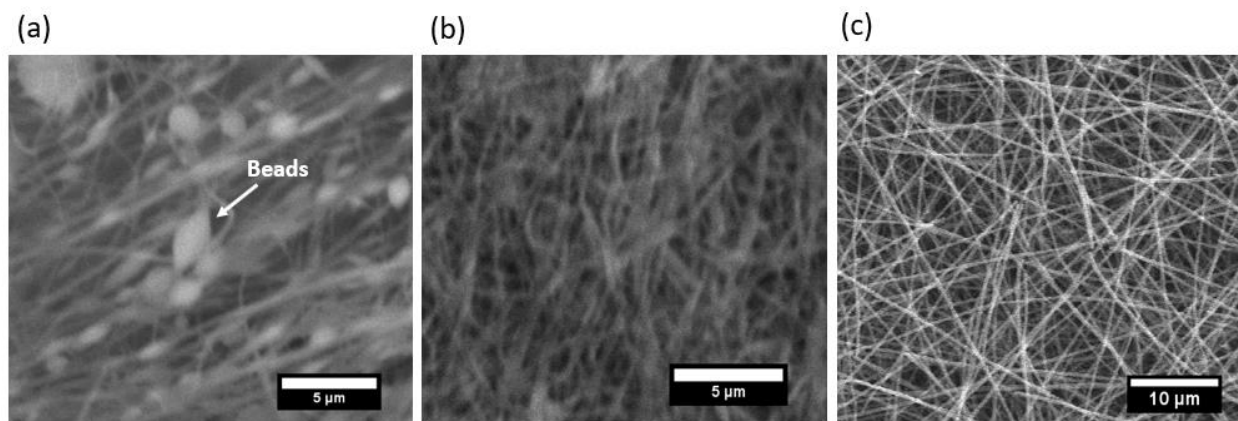


Figure 5-8: SEM images of the electrospun 10% PAN fibres: Spinning dope treated with (a) the probe-type ultrasonication showing the formation of beads, (b) the horn-type ultrasonication showing bead-free fibres, (c) non-sonicated solution.

5.4 Remarks

The experimental results show that the probe-type ultrasonication enhances dispersion of np-SiC in the medium of DMF/SDS leading to improve the stability of the nanoparticle suspension. However, there is a trade-off between improving dispersion and damaging the PAN polymer. Thus the np-SiC spinning dope must not be treated with the probe sonication after PAN polymer is added. It is worth noting that the quality of the np-SiC nanofibres depends primarily upon the process of preparing the final stage of the spinning dope. Once the np-SiC suspension solution is electrospun, the nanoparticles are fixed and immobilize in the nanofibres. Details on the np-SiC fibre fabrication process will be discussed in Chapter 6.

Chapter 6 Electrospun Nanofibrous ISOL Target Materials

The first ISAC SiC target consisted of micron-sized grains was pressed into pellets with a diameter of about 16 mm. The target was operated at a maximum temperature of 1650 °C but with proton beam limited to 15 μ A due to the low heat transfer mechanism inherent in the pressed pellet targets [55]. For that reason, thin ceramic SiC discs with graphite backing foil have been developed to enhance the heat transfer capabilities; the fabrication process is discussed in section 3.4. Consequently, the maximum operational proton beam current has been extended to 45 μ A. However, sintering of the target materials is an inevitable process leading to negative effects on the release efficiency of short-lived isotopes as discussed in section 3.5.

A fully optimized ISOL target is most challenging because a high yield isotope production involves maximized packing density of target atoms, while the release efficiency, especially for short-lived isotopes, involves a large number of open pores in the material to enhance the diffusion process. In fact, a combination of highly dense and porous target material is not achievable as these properties are inversely proportional. To optimize the isotope production rate and the release time of the products, a multiple disks or pellets fibrous target has been proposed. The bulk density, porosity, and fibre morphology of the compressed np-SiC fibrous have been investigated as a function of the applied press pressure. Shrinkage of the SiC composite nanofibre has been previously observed and is reported in section 4.2. Therefore, the pellets have been fabricated with a diameter of 17.5 mm to fit inside the target container; the area shrinkage is determined after the heat treatment. The heat-treated target fibrous pellet should be large enough to cover the center proton beam 7 mm in diameter as illustrated in Figure 6-1. Furthermore, the discs should be in contact with the container at their bottom which could provide at least some heat transfer through conduction, in addition to radiation between the disc

rim and the inner surface of the target container. Similar to the conventional ISAC targets, thin graphite backing foils packed in between the fibrous discs could be used to enhance the heat transfer capabilities. It is important to mention that ISAC is designed for high-power proton beam interaction with materials. Although low-density fibrous composite targets may possess poor through-plane thermal conductivity to dissipate heat from proton radiation, the nanofibre network possesses a radiation-based intra-material heat transfer mechanism for protons to travel, thereby permitting the use of higher power driver beams, as investigated in [17].

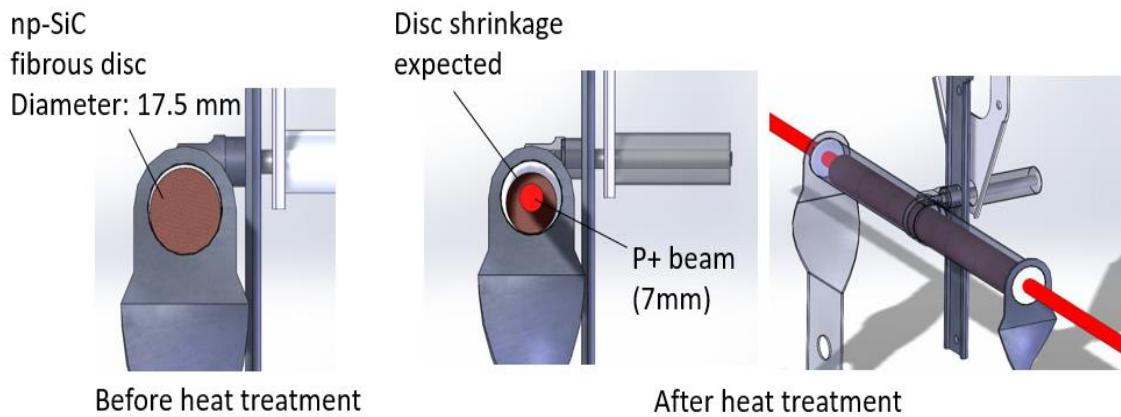


Figure 6-1: Illustration of the np-fibrous compressed disc in a target before and after the heat treatment.

6.1 Materials and methodology

6.1.1 Fabrication of np-SiC/PAN nanofibres

A two-step method has been employed to prepare the np-SiC spinning dope solution:

1. 1 g of SiC nanoparticles is dispersed in a medium of DMF (1 g) / SDS (0.1 g) using the Qsonica-700W (USA, frequency: 20 kHz; generating power: 700 W) ultrasonicator. For comparison, two sets of np-SiC suspension samples (ID: P_np-SiC-1 and H_np-SiC-2, as listed in Table 5-1) are produced using the probe and horn-type ultrasonication with the same settings as described in Chapter 5.1.
2. 1 g of PAN polymer is added to each dispersed suspension solution and prepared on a magnetic stirring hot plate. After the polymer has been completely dissolved, the solution is removed from heat and continuously stirred. Once it has reached room temperature, the solution is ready for electrospinning. No ultrasonication treatment is applied at this stage as it would degrade the PAN polymer leading to formation of beads as shown in Figure 5-8 (a). Additionally, 10% PAN in DMF has been prepared as a control sample (ID: 10%_PAN-Ref).

Electrospinning has been performed as described in Chapter 4.2, except with a syringe equipped with a 18-gauge (1.20 mm O.D., pink color-code) needle to prevent clogging of the orifice.

6.1.2 Direct casting of np-SiC

In addition to the formation of np-SiC fibres, the spinning solution of sample P_np-SiC-1 has subjected to a direct-casting method to investigate the ceramic nanosuspensions and evaluate the resulting np-SiC particle agglomeration upon solution casting. The suspensions are poured into a 10-ml high form ceramic crucible (Coorstek, item# 60104) and let dry in room temperature before heat treatment. This sample is labeled as DC_np-SiC.

6.1.3 Formation of np-SiC fibrous pellets and thermal treatment process

Prior to the heat treatment, the obtained P_np-SiC-1, H_np-SiC-2, and 10%_PAN-Ref samples are peeled off from the aluminum foils and folded up into multilayers nonwoven nanofibre mats. The heat treatment has been performed in a similar method as sample α -SiC/PAN-2, illustrated in Figure 4-12. The samples have been subjected to a two-step heat treatment:

1. The as-spun fibres are thermally stabilized at 250 °C in a furnace (Barnstead Thermolyne 48000) for 2 hours in air with a ramping temperature rate of 1 °C/min. After 1 hour of heating, the samples are carefully turned over with a pair of long forceps to ensure even heating.
2. The thermally stabilized samples are subjected to high temperature in vacuum at 1600 °C (Figure 4-6) for 5 days at a heating rate of 1 °C/min. The vacuum level has been stabilized at below 1×10^{-6} mbar to ensure completion of out-gassing before the cooling process is initiated at the same rate. In addition, selected samples are exposed at 1800 °C to determine the chemical structure and stability of np-SiC at higher temperature.

After the completion of the step-1 thermal stabilization process, the samples are cut into small pieces and loaded into an evacuable pellet die (Specac, USA). A 25-ton manual hydraulic press (Atlas Specac, USA) is used to compress at different pressures (100, 200, 400, and 600 MPa) into pellets to investigate the bulk densities and porosities. About 0.35 g of each sample is used to compress the thermally stabilized nanofibre mats into a pellet. At least three pellets have been produced for each type of sample. The compressed samples are then subjected to the step-2 high-temperature treatment under vacuum. The overall compressed-nanofibre fabrication process are demonstrated in Figure 6-2.



Figure 6-2: Photographs of np-SiC/PAN composite nanofibre mats: (a) As-spun, (b) thermally stabilized (250 °C, in air), (c) high-temperature treated pellets (top) /discs (bottom).

Furthermore, the obtained directed-casting sample DC_np-SiC is subjected to a similar 2-step heat treatment process. The thermally stabilized sample is compressed at 600 MPa to form pellets followed by the high-temperature treatment to investigate the degree of sintering. In addition, the precursor np-SiC powders consisting of 0.25 g (sample ID: Raw_np-SiC) has been heated under vacuum to investigate the sintering behavior and thermal stability. The results are

compared between all the acquired samples mentioned above. In Table 6-1, an overview of the prepared samples subjected to the compression and high thermal treatments is summarized.

	Compressed Pressure & High Temperature treatments (5d, under vacuum)										
	MPa	0		100		200		400		600	
Samples	°C	1600	1800	1600	1800	1600	1800	1600	1800	1600	1800
P_np-SiC-1		✓	✓	✓	✓	✓		✓		✓	
H_np-SiC-2		✓		✓		✓		✓		✓	
10%_PAN-Ref				✓	✓						
DC_np-SiC										✓	
Raw_np-SiC		✓	✓								

Table 6-1: Overview of the prepared samples subjected to compression and high-temperature treatments. (MPa = Megapascal, i.e. 0 MPa = no compression applied; °C = temperature in Celsius; ✓ = check mark indicates the completion of a process)

6.2 Structural and thermal analysis

6.2.1 Optical microscope (OM)

The formation of nanofibres has been monitored with an optical microscope (Nikon, Eclipse LV100). The as-spun nanofibres are collected on a piece of microscope glass slide. To avoid electrical discharge at the spinneret tip, the glass slide has been securely taped to a wooden stick as a holder and inserted into the electrospinning device near the grounded drum. Before opening the electrospinning system chamber door to collect the nanofibres, the exhaust fan is switched on at full speed as nanofibres has been ejected together with the solvent vapors.

6.2.2 Scanning electron microscopy (SEM)

The fibre morphology has been observed using a scanning electron microscope (SEM, Hitachi S-450, Japan); the accelerating voltage was set between 10 to 15 kV. The average fibre diameter is measured from the SEM images with the aid of the image analysis software (ImageJ 1.50i).

6.2.3 Scanning transmission electron microscopy (STEM)

The high temperature treated samples are prepared for scanning and high-resolution transmission electron microscope (S/HR-TEM, FEI Tecnai Osiris, USA) equipped with energy dispersive X-ray spectroscopy (EDS) for the particle size distribution and elemental analysis. The compressed fibrous samples P_{np}-SiC₁ and H_{np}-SiC₂ are prepared by grinding them into a fine powder using an agate mortar and pestle set, then suspended in isopropanol. A drop of the sample solution is added to a lacey-carbon coated copper grid (Ted Pella, Prod #01811) and let dry in air. High-angle dark field (HAADF) and bright field (BF) STEM images are acquired at 200 kV to investigate the fibre morphology and the location of the silicon nanoparticles.

6.2.4 X-ray diffraction (XRD)

Crystalline phases of np-SiC powders and fibre samples have been studied by means of an X-ray diffractometer (XRD, Rigaku MultiFlex, Japan) with a CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 40kV and 20 mA. The heat treated fibrous pellets have been ground into fine powder with a mortar and pestle then filled into a well of the glass plate. The samples are scanned from 2θ of 10° to 90° at a rate of $1^\circ / \text{min}$. Therefore, the crystallite size is estimated by XRD through the

full width at half-maximum (FWHM) of the (111) Bragg peak, governed by the Scherrer equation, (6.1).

$$\Phi = \frac{K\lambda}{\beta \cos \theta} \quad (6.1)$$

where Φ is the crystallite size, K is the Scherrer constant to account for the particle shape (0.94 for the assumption of spherical crystals with cubic symmetry), β is the full width at half maximum intensity, and θ is the Bragg angle.

6.2.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) has been performed to evaluate the thermal behavior of the npSiC/PAN fibres using a microbalance (TGA Q500, Camcor). The samples are placed in a metal platinum pan, with a mass of 6 to 7 mg. The samples are heated from ambient temperature up to a maximum of 1000 °C, at a heating rate of 5 °C/min under argon atmosphere.

Subsequently, the samples are heated in a vacuum furnace (at TRIUMF) to 1600 °C and 1800 °C to measure the mass of np-SiC deposited in the carbonized PAN fibre.

6.2.6 Density and porosity

As for the investigation of porosity of compressed fibrous np-SiC samples after thermal treatment, an estimate of the total porosity in the sample can be derived from the following equation:

$$P_{tot} = 1 - \rho_{bulk}/\rho_{theo} \quad (6.2)$$

where the bulk density (ρ_{bulk}) was calculated from the weight and the volume of each disc after thermal treatment. The theoretical density (ρ_{theo}) value of 2.55 g/cm³ is derived from the weighted average of the densities of bulk np-SiC (3.22 g/cm³, US Research Nanomaterials, Inc., SDS), and carbonized PAN (1.6 g/cm³) [80]. The wt% composition is determined by comparing the mass loss of pure 10% PAN and of np-SiC/PAN composite fibres after thermal treatments.

6.2.7 Thermal properties

A transient plane source (TPS 3500, Thermtest, USA) technique has been used to measure the thermal properties (i.e., thermal conductivity, thermal diffusivity, and specific heat) of np-SiC compressed fibrous composites with a hot disk sensor (spiral nickel metal, sensor #7280). The spiral sensor, fitted in an insulating material (Kapton) acts as a heat source and a resistance thermometer to measure the amount of heat per unit time and unit area which conducted through a plate of unit thickness [81]. To conduct the measurements, the hot disk is sandwiched between two pellet samples, each with a thickness of 6 mm and a diameter of 12.5 mm as illustrated in Figure 6-3. A compressive load of 10 N is applied to the samples, and 200 resistance points are recorded within a pre-set time of 60 s.

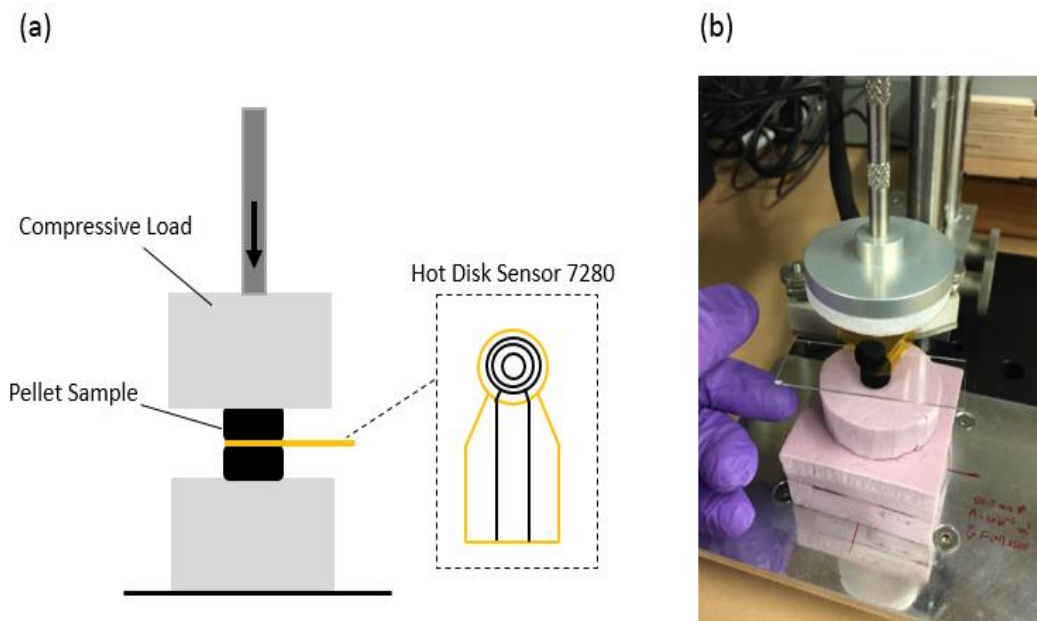


Figure 6-3: (a) Sketch and (b) photo of a TPS-Hot disk setup for measuring the thermal transport properties of a np-SiC fibrous pellet.

6.3 Result and discussion

An optical microscope has been utilized for preliminary examinations of np-SiC nanofibres during the electrospinning process. Although it is not possible to observe nanostructures due to the limiting resolution of about 200 nm, the OM technique has provided a quick and direct analysis of the fibre morphologies. The obtained OM images show that all the fibres have a rough surface, suggesting the incorporation of SiC nanoparticles. The as-spun fibres produced from the spinning dope sample P_np-SiC-1 appear to have the fibre surface homogeneously covered with nanoparticles as shown in Figure 6-4 (a). In comparison, fibres produced from sample H_np-SiC-2 have distinctive beads which appear to be agglomerated nanoparticles as shown in Figure 6-4 (b).

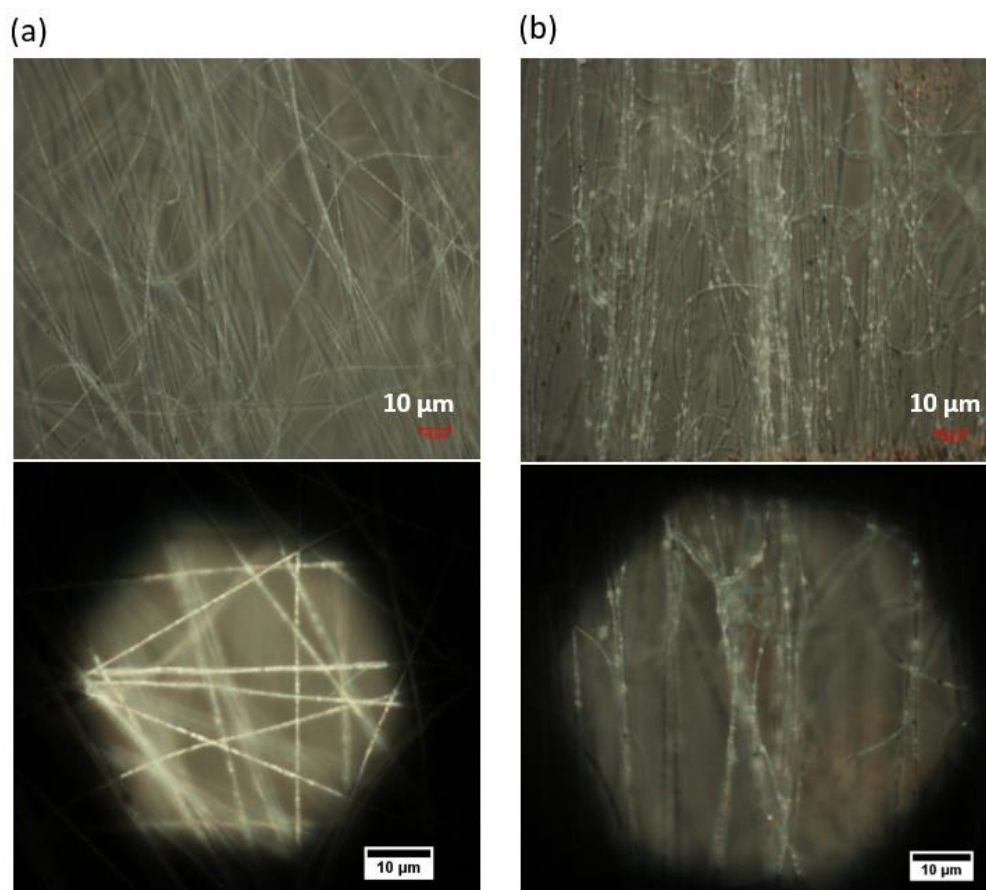


Figure 6-4: Optical images of as-spun np-SiC nanofibres produced from spinning dope solutions: (a) P_np-SiC-1, and (b) H_np-SiC-2.

During the 30 h of each electrospinning process, it is observed that clogging of the tip of the needle with H_np-SiC-2 solution hindered the continuous fibre formation. This suggests that clustering of np-SiC is dominated by the larger particles, eventually blocking the flow of the PAN polymer through the orifice. A series of clusters of different sizes and shapes caused by the agglomeration of particles affects the sedimentation rate, as investigated in [82]. Thus, the dispersing performance of the sample solutions P_np-SiC-1 and H_np-SiC-2 are evaluated by observing the settling behavior of their suspensions on a relevant timescale. Figure 6-5 shows

the optical images of the suspensions after standing for 72 h; a 10%-PAN clear yellow solution is provided as a reference. Evidently, visible sedimentation occurred for the H_np-SiC-2 sample with a continuous growth of the clear yellow top layer and a lower gray np-SiC suspension, whereas less visible sedimentation or flocculation is observed for P_np-SiC-1 sample. The highly stable suspensions of P_np-SiC-1 is in good agreement with the observation on continuous fibre formation with no needle clogging during the electrospinning process. However, a low yield of fibre production measured at about 0.03 g/h remains a great challenge at this stage of the development. It is worth noting that similar setups with multiple syringes can be employed with the Kato Tech electrospinning unit to multiply the productivity but other problems such as jet repulsion and deterioration of fibre quality may arise; further investigations are required.

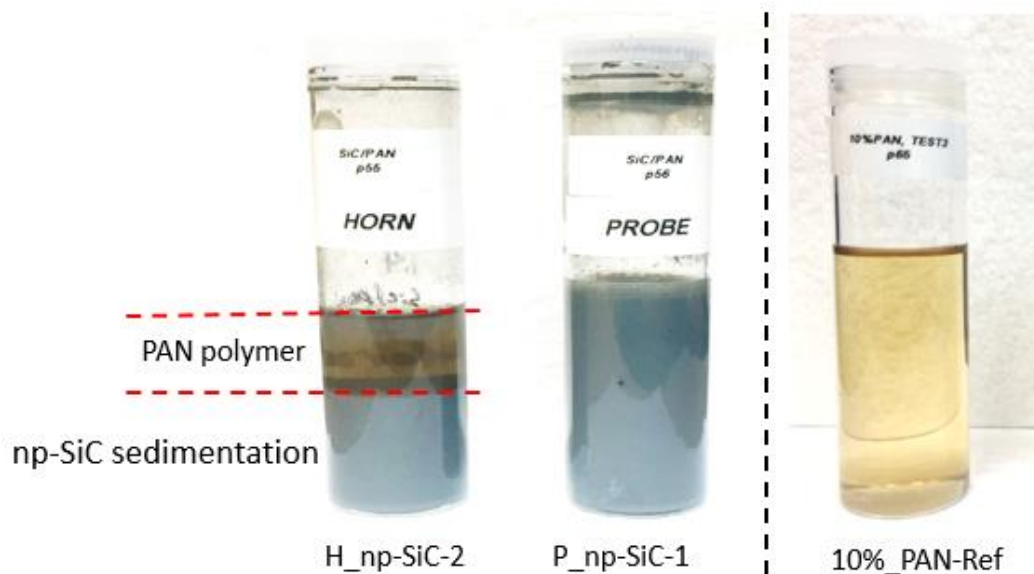


Figure 6-5: Optical images of the P_np-SiC-1 and H_np-SiC-2 suspensions after standing for 72

h.

SEM was employed to characterize the morphology and structure of thermally stabilized fibres after high-temperature treatment. At least 30 individual measurements have been made for samples P_np-SiC_1 and H_np-SiC_2 after the high-temperature treatment at 1600 °C to determine the mean fibre diameters and standard deviations. Figure 6-6 (a) and (b) show typical SEM images of electro spun np-SiC fibres of sample P_np-SiC-1 and H_np-SiC-2, respectively. Notably, the fibres obtained from P_np-SiC-1 sample maintains uniform in morphology with nanoparticles that seemingly look well distributed, whereas larger particles formed by agglomeration of np-SiC is observed from H_np-SiC-2 sample.

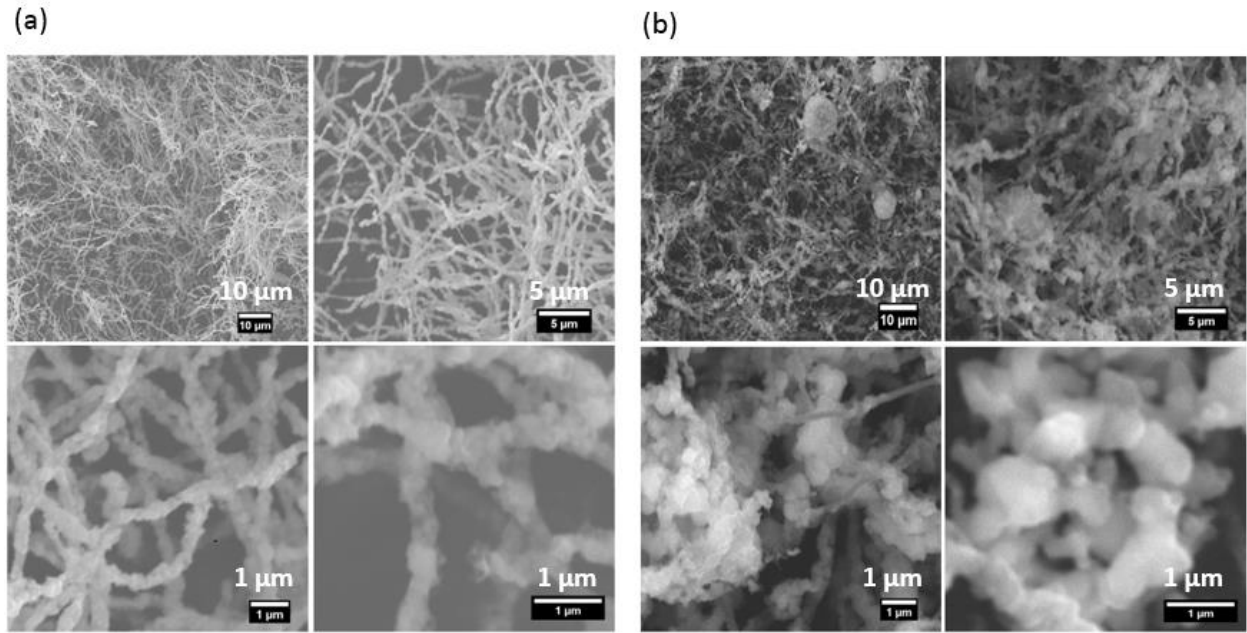


Figure 6-6: SEM images of heat treated uncompressed np-SiC fibres of samples (a) P_np-SiC-1 and (b) H_np-SiC-2. The temperature was maintained at 1600 °C under vacuum (10^{-6} mbar) for

5 days.

The fibres have large variations in the diameter distribution between P_np-SiC-1 and H_np-SiC-2 samples as illustrated in Figure 6-7. The average diameters of 385 ± 9 nm and 918 ± 37 nm have been measured for P_np-SiC-1 and H_np-SiC-2 samples, respectively. Although fibre diameters less than 250 nm are successfully electrospun from both spinning dope solutions, H_np-SiC-2 sample has no visible nanoparticles on several fibre surface fragments, an example is shown in Figure 6-8 (b).

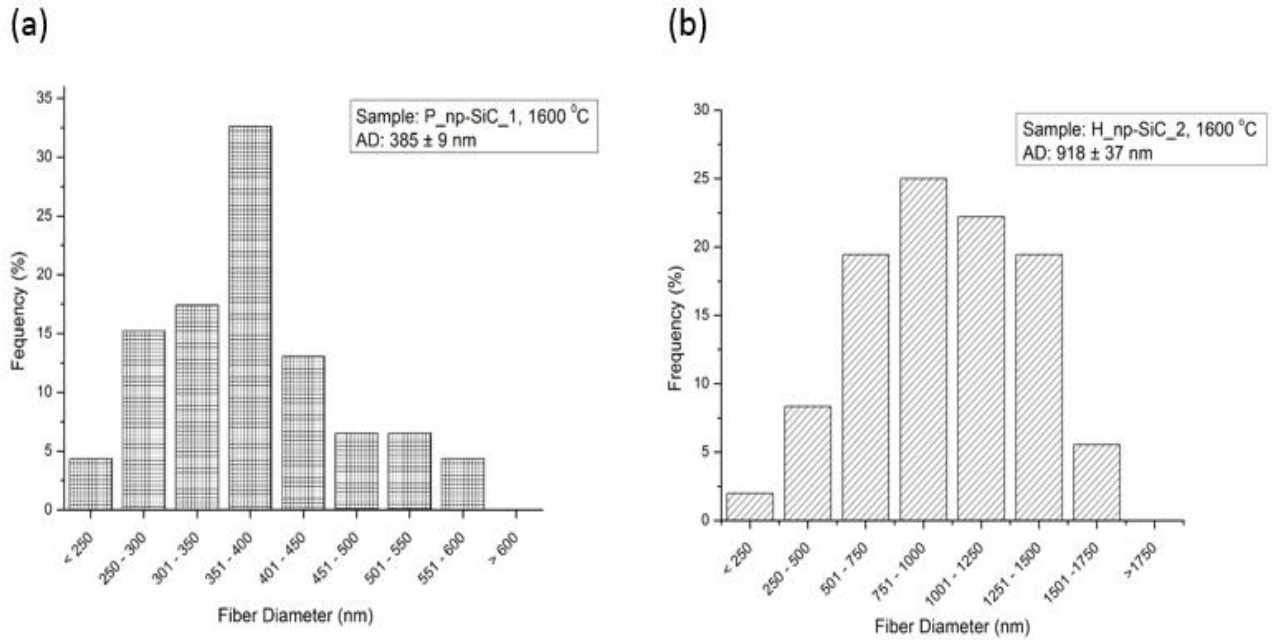


Figure 6-7: Fibre diameter of electrospun (a) P_np-SiC_1 and (b) H_np-SiC-2 samples after high-temperature treatment under vacuum.

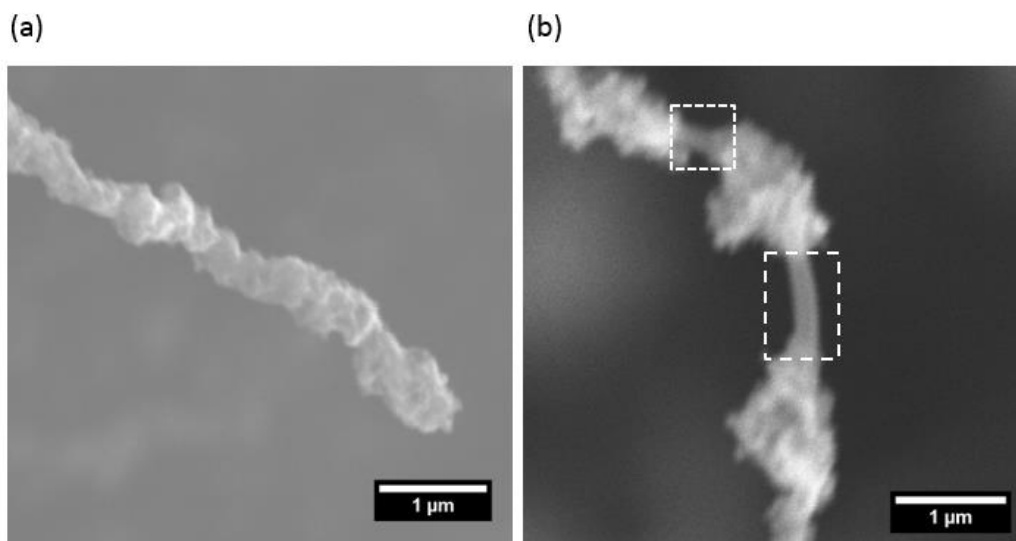


Figure 6-8: SEM images of single nanofibres obtained from electrospun (a) P_np-SiC_1 and (b) H_np-SiC-2 with the white-dash boxes indicating the absence of nanoparticles on the fibre surface.

Further characterization of the np-SiC/carbonized PAN composite fibres has been performed by using STEM operated in bright-field (BF) and high angle dark field (HAADF) modes equipped with EDS elemental mapping. Figure 6-9 presents typical black/white STEM tomograms and color-coded EDS mapping images obtained from P_np-SiC-1 and H_np-SiC-2 samples treated at 1600 °C under vacuum. The STEM/EDS mapping images in Figure 6-9 (a) show various locations of silicon particles (in red/pink) of sample P_np-SiC-1 partially entrained or embed but fairly well distributed within the carbon nanofibre (in green). The EDS line for Si across the fibre obtained from the P_np-SiC-1 sample shown in Figure 6-10 (a-b) suggests that the nanofibres are formed by the closely packed SiC nanoparticles with several of nanometers distance apart. It is worth noting the limitations of TEM such that overlapping particles are difficult to resolve [83].

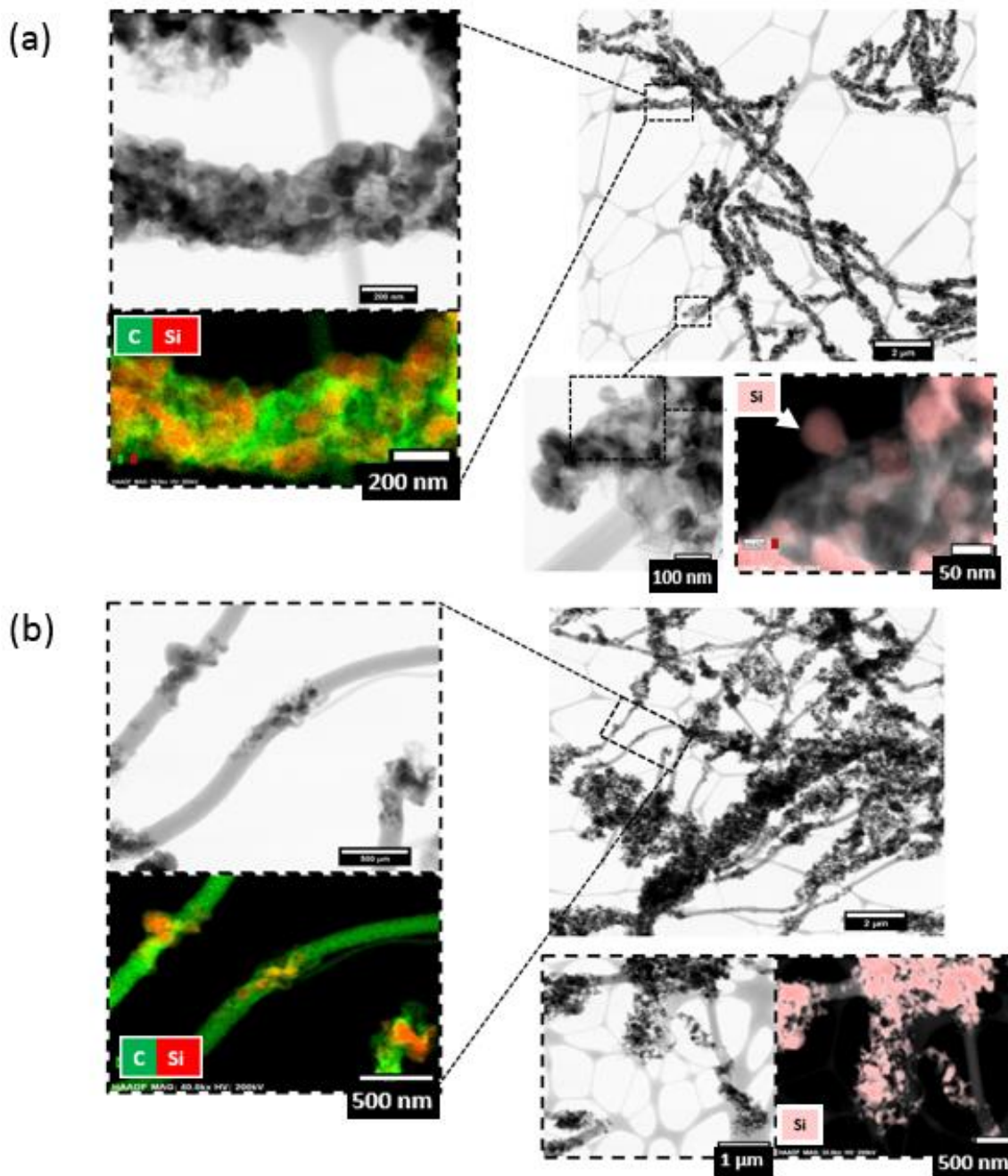


Figure 6-9: STEM tomograms (black/white) and corresponding elemental mapping for Si (red/pink) and C (green) acquired from the high-temperature treated (1600 °C under vacuum) nanofibres (a) P_{np}-SiC-1, and (b) H_{np}-SiC-2.

The accompanied EDS spectrum as presented in Figure 6-10 (c) reveals the chemical composition consisting mainly of Si and C with trace amounts of O from the absorbed oxygen when the fibres are exposed in air (the Cu signals are an artifact caused by the TEM grid).

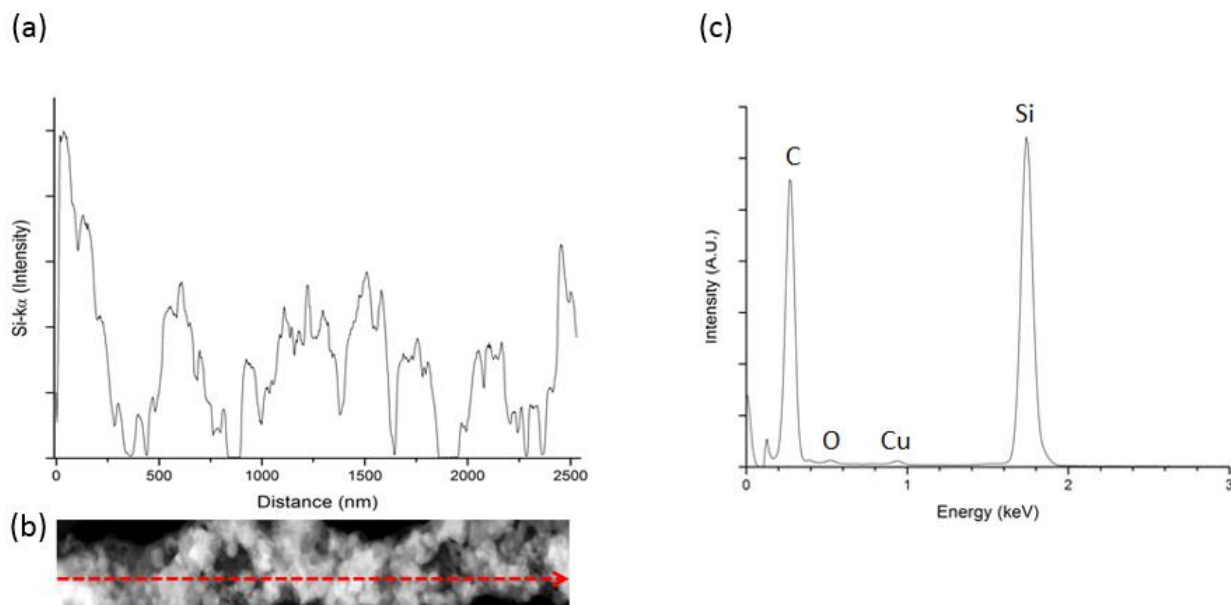


Figure 6-10: EDS under STEM acquired from P_{np}-SiC-1 treated at 1600 °C under vacuum: (a) a plot of Si-K α intensity as a function of distance, (b) TEM image of a selected fibre for the EDS line scan, (c) the accompanied EDS spectrum integrated over the fibres revealing the chemical compositions.

On the other hand, the H_{np}-SiC-2 sample appears to contain a significant fraction of pure carbon fibres in the vicinity that does not carry any silicon containing particles as shown in Figure 6-9 (b). A large number of SiC nanoparticles are seemingly agglomerating during the fibre formation, and each agglomerate contains hundreds of np-SiC entrapped in the carbon

nanofibres. At high-temperature treatments, the agglomerated particles sinter, hence an increase in the grain size.

Under normal circumstances, grain growth of β -SiC by surface diffusion can readily occur without the need of additives as the temperature increases [84]. Concerning the sintering of np-SiC, close observations inside the fibre under higher magnifications of TEM acquired from P_np-SiC-1 sample treated at 1600 °C are shown in Figure 6-11 (a). The image reveals that particles that are separated by the carbon fibre backbone with sizes between 45 – 65 nm are preserved, which suggests the nanoparticles are successfully immobilized in nanofibres with carbonized PAN acting as a sintering inhibitor or preventing particle size growth to certain limits during high-temperature treatments. Fringe patterns have been used to observe the crystallization of np-SiC at 1600 °C as presented in Figure 6-11 (b), a representative HRTEM image recorded from the area marked 1 in Figure 6-11 (a) confirming the coexistence of the SiC (marked 2) and graphite (marked 3) phases. The fringes disclosing the single-crystalline nanoparticle with d-spacing of 0.25 nm and 0.34 nm correspond to the (111) plane of 3C-SiC and the (002) plane of graphite, respectively. Figure 6-11 (c) is the representative XRD pattern acquired from the heat treated P_np-SiC-1 sample with Bragg peaks well matching the phase of 3C-SiC (PDF#: 29-1129). The peak marked with S.F. can be attributed to stacking faults in 3C-SiC structure as previously reported in [85], which correspond to the black stripes in the grains as presented in Figure 6-11 (a). The peak near $2\theta = 41.4^\circ$ was also previously reported as the stacking fault; the intensity of the peak profile at this region would become sharper with an increase of the sintering temperature as the stacking fault density decreases, and hence, an increase in the grain sizes [86].

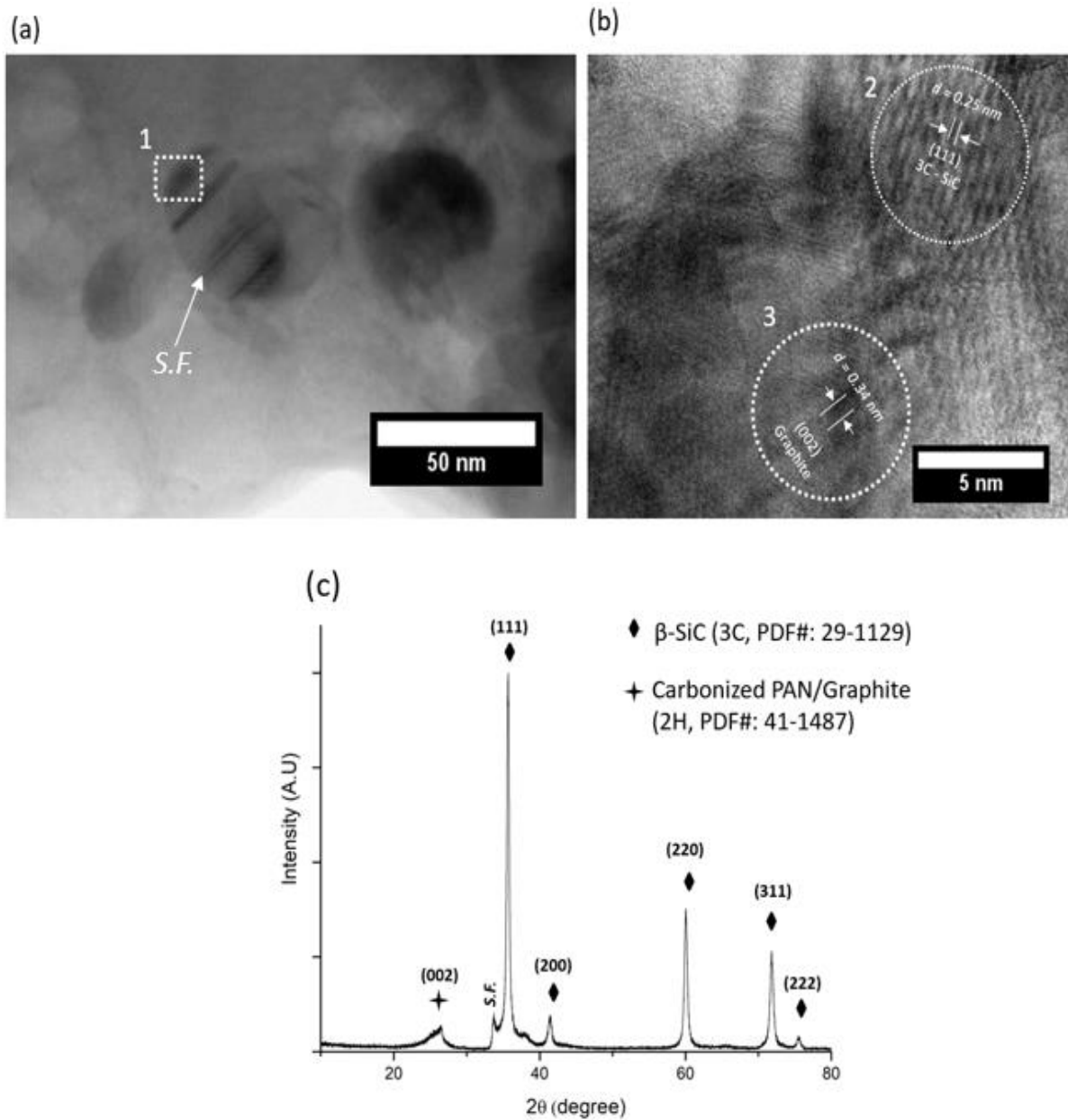


Figure 6-11: (a) High-magnification of TEM bright-field image, and (b) the corresponding HR-TEM image of P_{np}-SiC-1 sample heated at 1600 °C. (c) A representative XRD pattern acquired from the heat treated P_{np}-SiC-1 sample.

To unambiguously provide the evidence of SiC nanostructure preservation in the carbon nanofibres at a high temperature, samples P_np-SiC-1, Raw_np-SiC and DC_np-SiC were treated at 1600 °C and 1800 °C under vacuum for 5 days. Unlike the XRD patterns reported in [85],[86], the peaks near $2\theta = 33.5^\circ$ and 41.4° as shown in Figure 6-12 remain at their relatively low-intensity for the P_np-SiC-1 sample heated at a various temperature, which suggests that the degree of sintering of np-SiC may not be very severe. In addition, a noticeable sharpening of the (002) peak at $2\theta = 26.4^\circ$ confirms the carbonized PAN, which well matches the phase for the crystalline structure of 2H-graphite (PDF#: 41-1487).

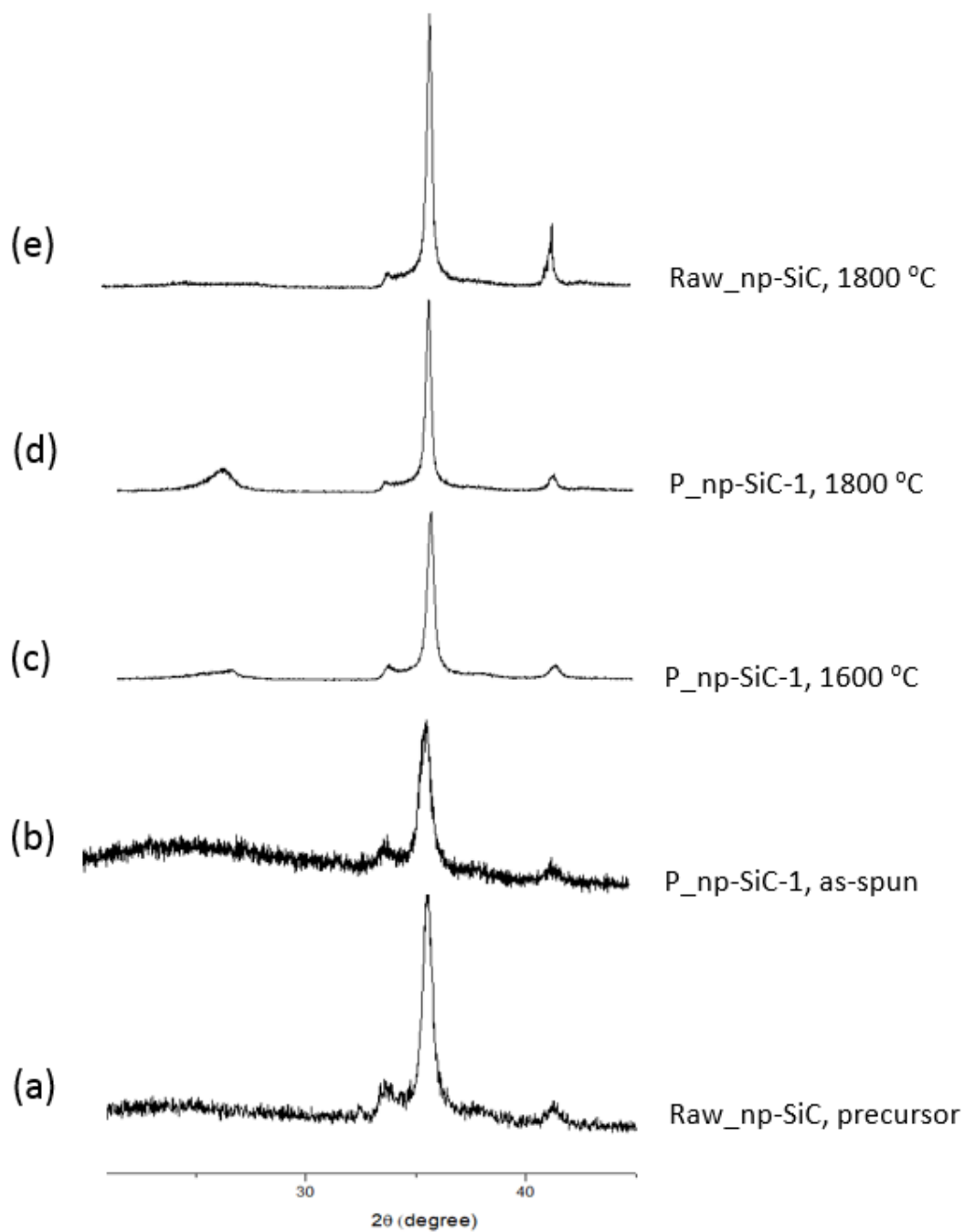


Figure 6-12: XRD patterns of the (a) precursor Raw_np-SiC and (b) as-spun P_np-SiC-1 before sintering, (c – d) after sintering under vacuum for 5 days.

No BET analyzer was available to study the sintering kinetics which could quantitatively study the reduction of specific surface area as the sintering temperature increases [57]. However, the crystallite size of np-SiC is estimated using the acquired XRD data and calculated according to equation (6.1). The plot in Figure 6-13 shows the crystal size of np-SiC enlarging as the temperature ramped up, which suggests that a net sintering effect has taken place within a particle consisting of several different crystallites. The incorporation of SiC particles in the electrospun fibres for sample P_np-SiC-1 preserved the nanoparticle size even when a sintering temperature above 1600 °C has been reached as shown in Figure 6-9 (a) and Figure 6-11 (b).

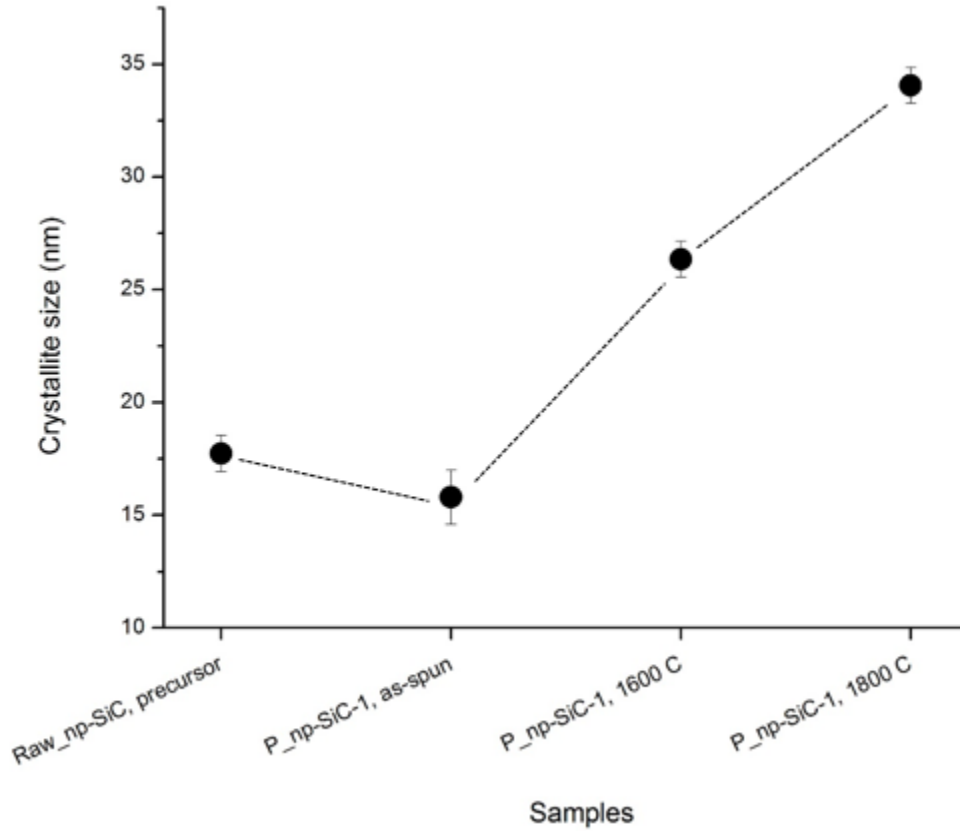


Figure 6-13: Crystallite size of various heat treated SiC nanoparticles estimated by XRD using the Scherrer's formula (6.1).

When comparing heat treated samples Raw_np-SiC to DC_np-SiC, progressive changes in grain shape, pore shape, and pore size are observed. Figure 6-14 (a) shows the typical SEM image of Raw_np-SiC after sintered at 1600 °C under vacuum; the inset image represents a higher magnification area in which grain contact (marked 1), neck formation (marked 2), neck growth (marked 3), and resulting grain growth (marked 4) are identified as mechanism of grain growth of np-SiC. For sample DC_np-SiC prepared with the direct slip-casting technique, segregation of different particle size during sedimentation prompted to a high packing density. Thus, upon heating the sample, sintering of the np-SiC resulting in grain growth and removal of pores is observed under SEM as shown in Figure 6-14 (b).

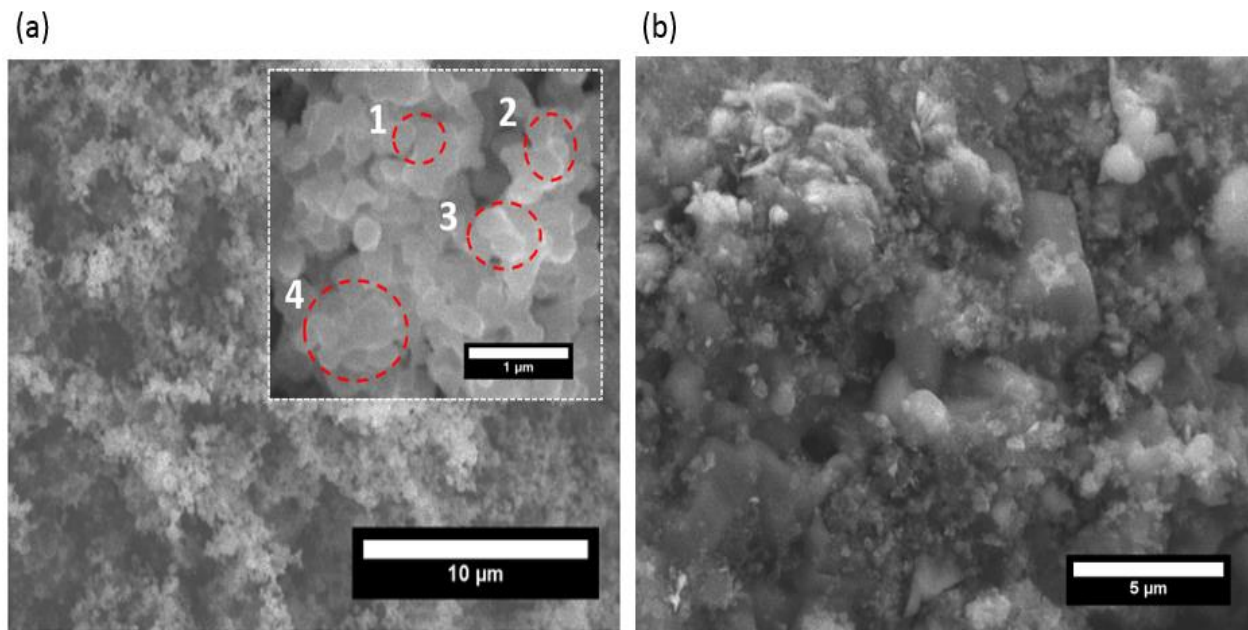


Figure 6-14: SEM images of samples (a) Raw_np-SiC (the insert shows the higher magnification area), and (b) DC_np-SiC after sintered at 1600 °C under vacuum. Both samples show the real grain of np-SiC from sintering.

Several tests are carried out to optimize the characteristics of the np-SiC fibrous pellets. The green pellet is successfully tailored to a diameter of 17.5 mm to fit in the ISAC target container. Upon heating to 1600 °C under vacuum for 5 days, the surface area of the pellet shrinks to 22% which resulted in a diameter of 15.5 mm to provide sufficient area for proton beam bombardment. Figure 6-15 shows the plot of variation in densities and porosities as a function of applied pressure on a pellet (more information about the results can be found in Appendix A3).

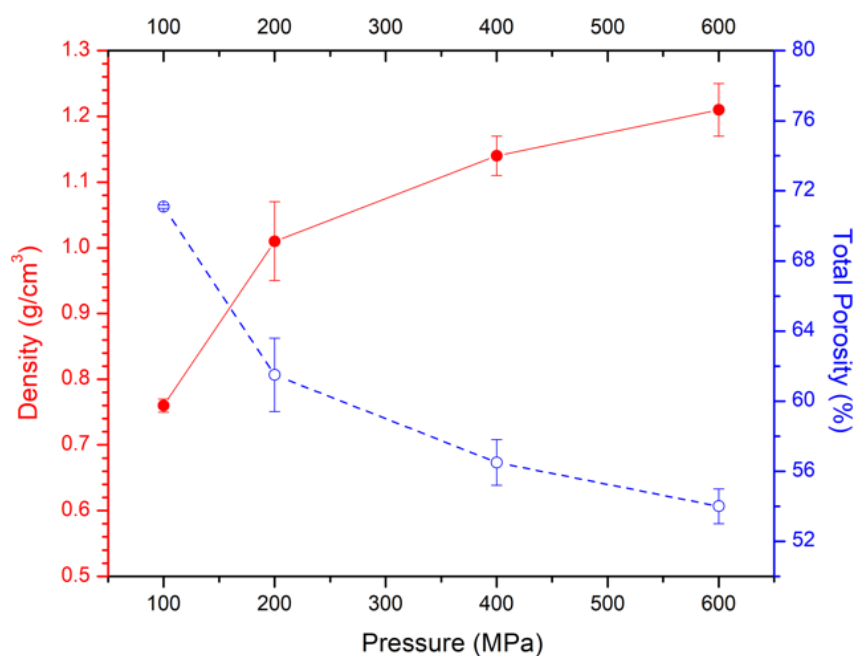


Figure 6-15: Variation of densities and porosities of heat treated np-SiC fibrous pellets after exposure to 1600 °C under vacuum for 5 days.

The SEM observation reveals the random fibre network and open porosity were preserved after the composite fibre mats of P_np-SiC-1 are compressed into pellets as shown in Figure 6-16. As a trade-off between high density for high isotope production rates and reduction of porosity

which would reduce the release characteristics, a hydraulic press of 400 MPa can be applied on the thermally stabilized np-SiC fibre mats to obtain test pellets for the ISAC target material; the thickness of the pellet can be tailored according to the desired specification.

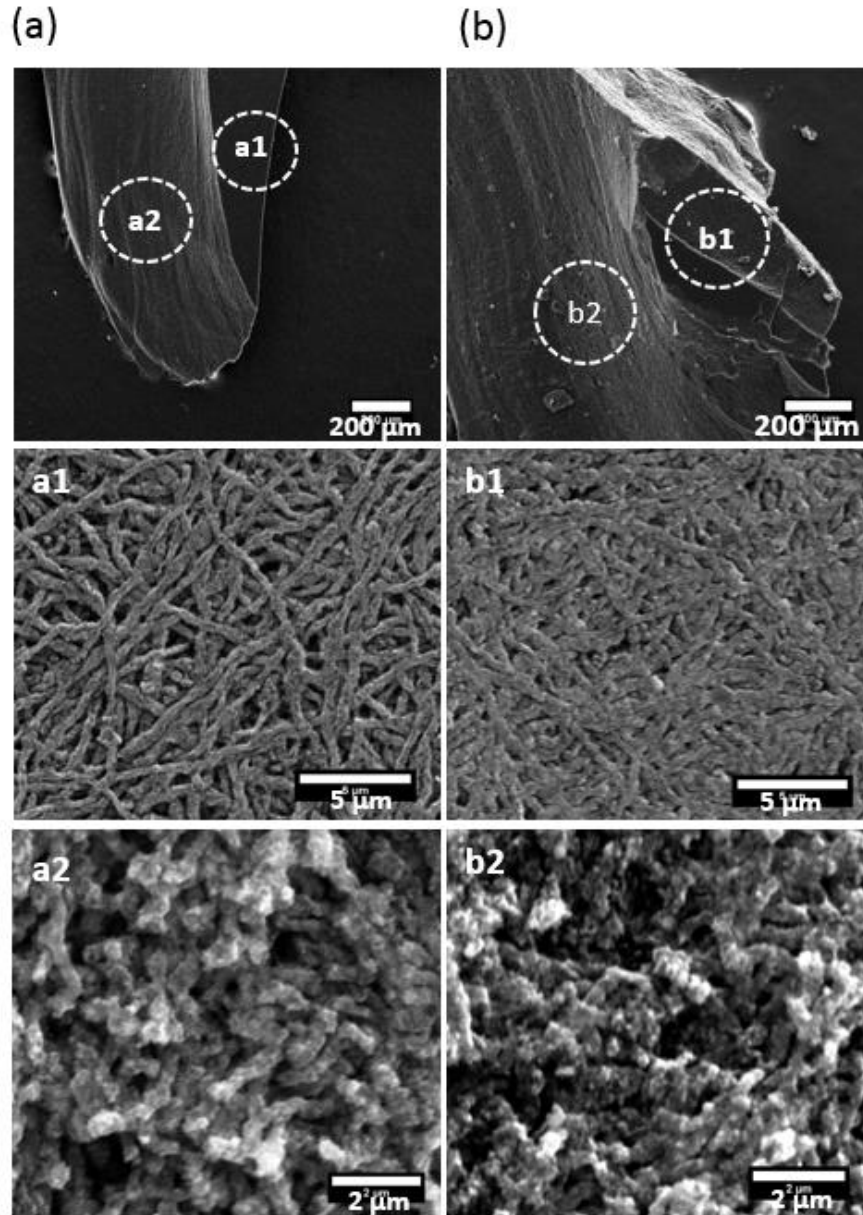


Figure 6-16: SEM images of the 1600 °C heat-treated pellets of sample P_np-SiC-1 with (a) 400 MPa, and (b) 600 MPa. The marked regions (a1, b1) and (a2, b2) represent the inner surface layers and the cross-section areas of the pellets, respectively.

To illustrate the results of the outgassing behavior for the fibrous pellets, Figure 6-17 shows the the pressure in the vacuum chamber as a function of the Joule-heating power. The vacuum chamber is pumped down to 10^{-6} mbar before the heating process is initiated. By comparing the vacuum outgassing behavior to α -SiC/PAN-2 (see Figure 4-22 & Figure 4-23) as discussed in the preliminary experiments, the pressure for P_{np}-SiC-1 sample gradually decreases above 1200 °C and eventually stabilized in the order of 10^{-6} mbar as the temperature approaches 1600 °C. Unlike in the case of the α -SiC/PAN-2 sample, the evaporation point of Si is not observed, which suggests that β -SiC nanoparticles incorporated in nanofibres have not converted to a different crystallographic phase and are stable at least up to 1600 °C under vacuum.

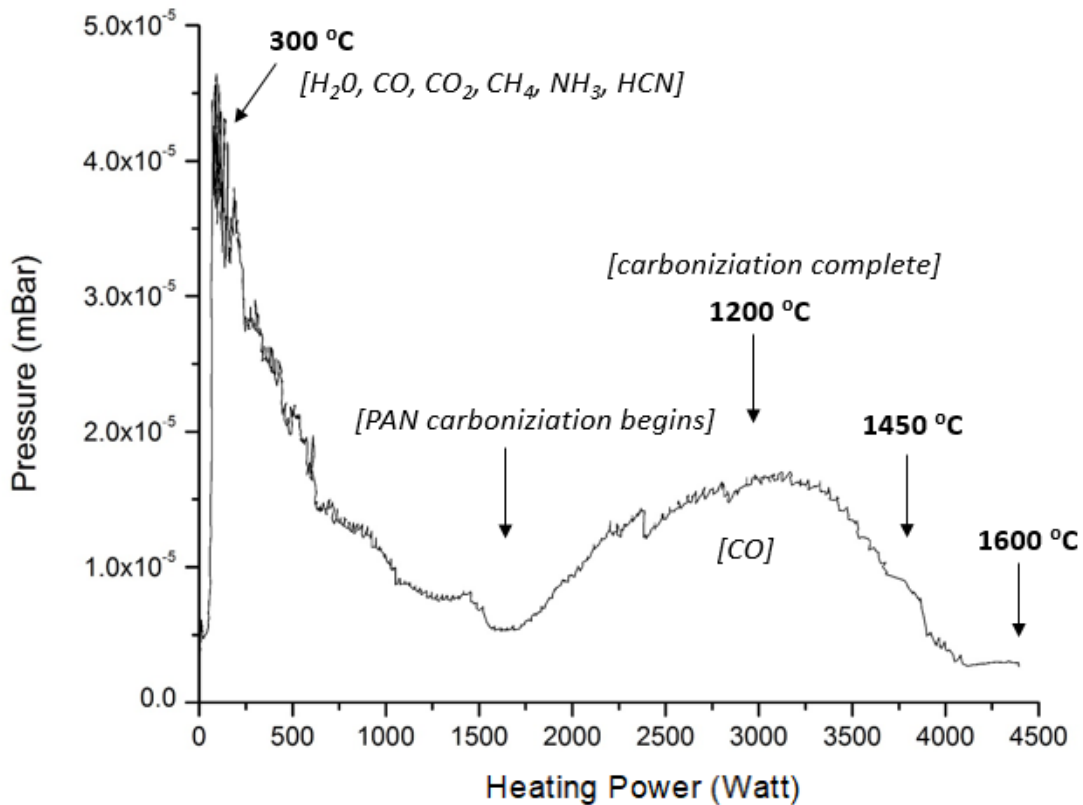


Figure 6-17: Vacuum levels during the heat-treatment of P_{np}-SiC-1.

Moreover, the mass of the pellets P_np-SiC-1 and 10%_PAN_Ref before and after heat treatments are measured to compute the percentage of np-SiC present in the nanofibre. Figure 6-18 shows the plot of weight loss for P_np-SiC-1 against 10%_PAN-Ref as a function of temperature; the weight compositions are determined to be 60% SiC and 40% carbon fibres (C-PAN) for 1600 °C heat treatment under vacuum (details of the calculations can be found in Appendix A2 and A4). However, significant weight loss for sample P_np-SiC-1 is measured at 1800 °C which is most probably triggered by Si sublimation compared to the mass of sample, which 10%_PAN-Ref remains relatively unchanged. Figure 6-19 (a) shows a rise in vacuum level as the temperature approaches 1800 °C. Evidently, upon cooling the furnace and venting the chamber, it is observed that an area of tantalum foil covered above the sample as a heat shield becomes brittle and easily fractured as illustrated in Figure 6-19 (b); no such damage is developed for heat treatment at 1600 °C. Furthermore, dark patches evolves near the pellet rim where it contacted the crucible as shown in the inset photograph of Figure 6-19 (b). This suggests an early sign of graphitization from carbonized PAN which is in good agreement with the XRD results showing the sharpening of the (002) peak ($2\theta = 26.4^\circ$) at 1800 °C heat treatment as shown in Figure 6-12. Furthermore, the through-plane thermal conductivity is measured to be 0.4 W/mK. However, the in-plane thermal conductivity (not measured) can be higher by a factor of 400 for a carbon nanofibre mat, as investigated in [87], thus a high proton beam powder may be permitted and is subject to testing online at TRIUMF-ISAC.

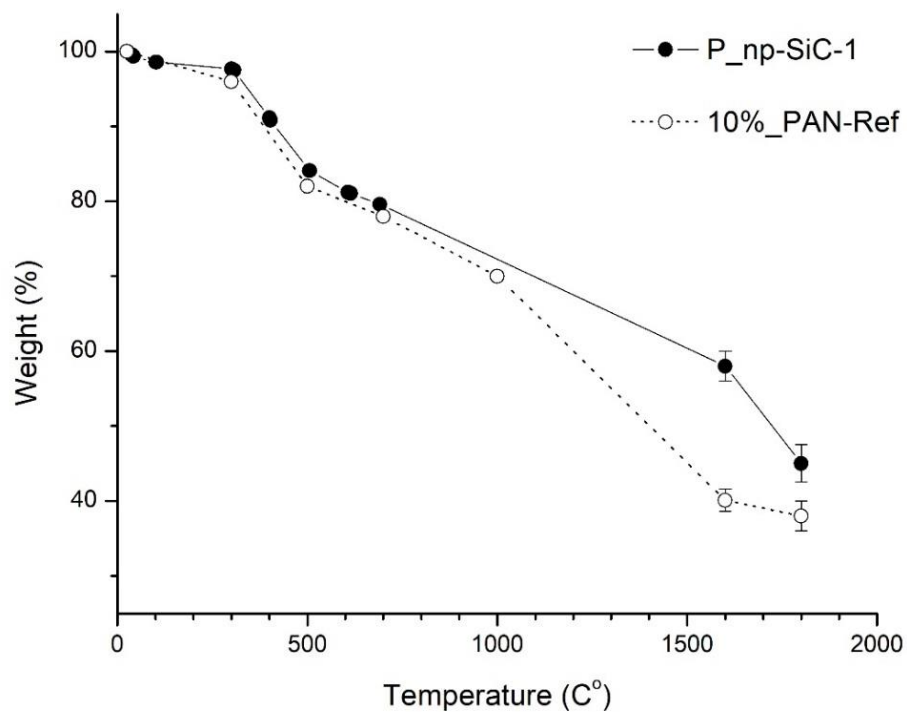
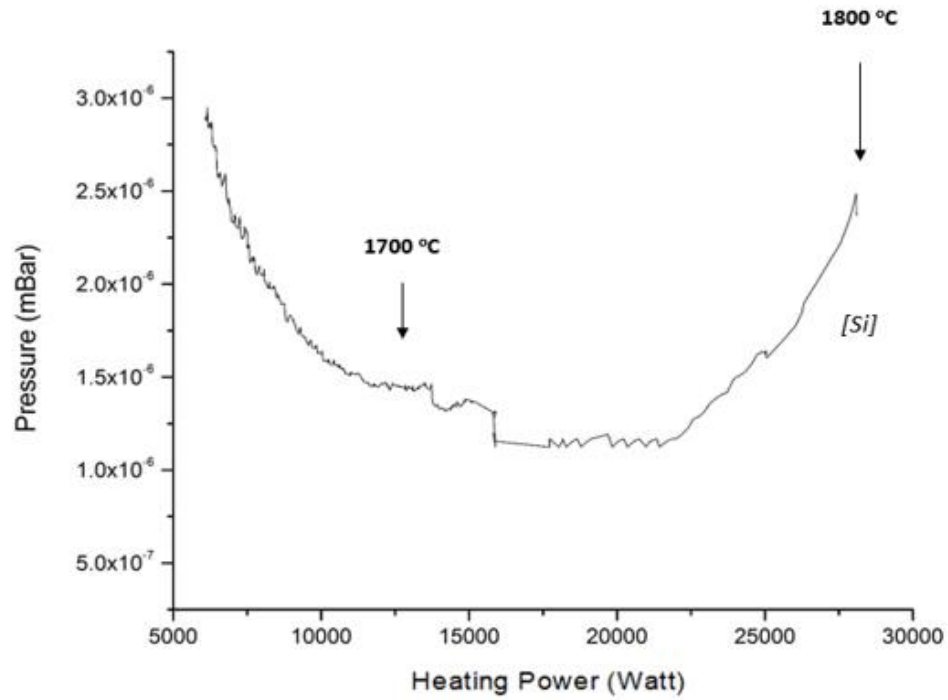


Figure 6-18: Measurement of the weight loss for sample P_np-SiC-1 against 10%_PAN_Ref as a function of temperature to determine the weight % of np-SiC present in the nanofibre. (Measurements from 25 – 1000 °C are acquired from TGA. Above 1000 °C, the measurements are acquired from the high tempeature vacuum furnace.)

(a)



(b)

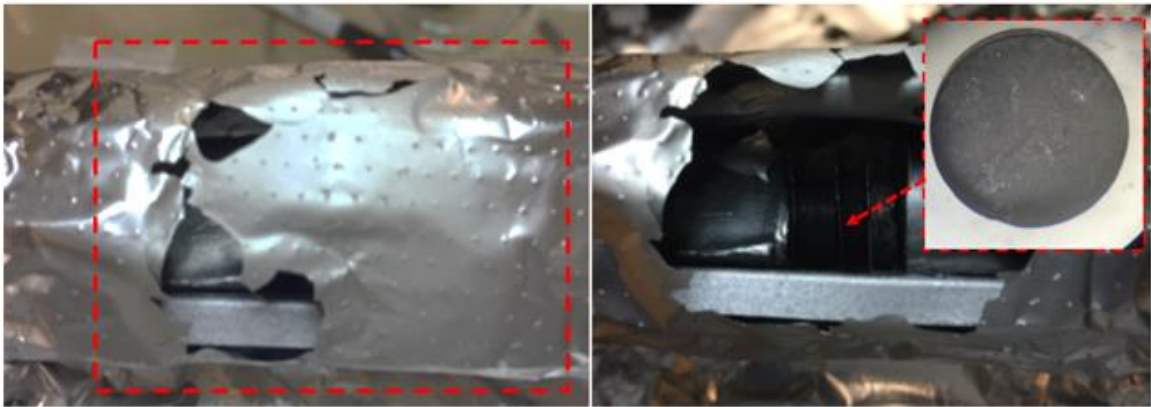


Figure 6-19: (a) Vacuum levels monitored during heat-treatment from 1600 °C to 1800 °C for P_{np}-SiC-1 sample. (b) Thermal reaction damage to the tantalum heat shield at 1800 °C; the inset shows the P_{np}-SiC-1 pellet.

Chapter 7 Conclusion and Future Work

For many years, researchers have drawn attention to reduce particle sizes in ISOL target materials. When stabilized in certain ways, refractory nanoparticles combine short diffusion paths and high-temperature characteristics, overall enhancing the release of short-lived isotopes. However, nanoparticles are prone to clustering and accelerated sintering at elevated temperature, resulting in even larger particle size and reduction of the release efficiencies of RIB. For the first time, SiC nanoparticles suspended in PAN solution were successfully spun into composite nanofibres using a novel direct co-electrospinning process. Direct sonication with a microtip probe has been adapted to improve dispersion of SiC aggregates to native particle size in suspensions for the preparation of the spinning dope. Jets of charged particles during electrospinning aid to further separate and immobilize individual np-SiC into nanofibre mats with average fibre diameter of 395 ± 9 nm. Upon high-temperature treatment under vacuum, PAN successfully converts into a carbon fibre backbone that aids to reduce the sintering dynamics considerably; SiC nanoparticles with sizes 45 – 65 nm are conserved over 5 days at 1600 °C. The weight composition of the final material is 60% SiC and 40% carbon nanofibre. The nanofibres are pressed into pellets to achieve an optimum of density and open porosity of the target materials with the fibre morphology remarkably well preserved. 150 pellets (each 1 mm thick, 15.5 mm diameter) have been fully carbonized yielding a total mass of 26.5 g of fibrous target materials (16 g SiC/10.5 g carbon nanofibres), as shown in Figure 7-1. Its isotope release properties will be tested online in September 2018 at TRIUMF-ISAC.

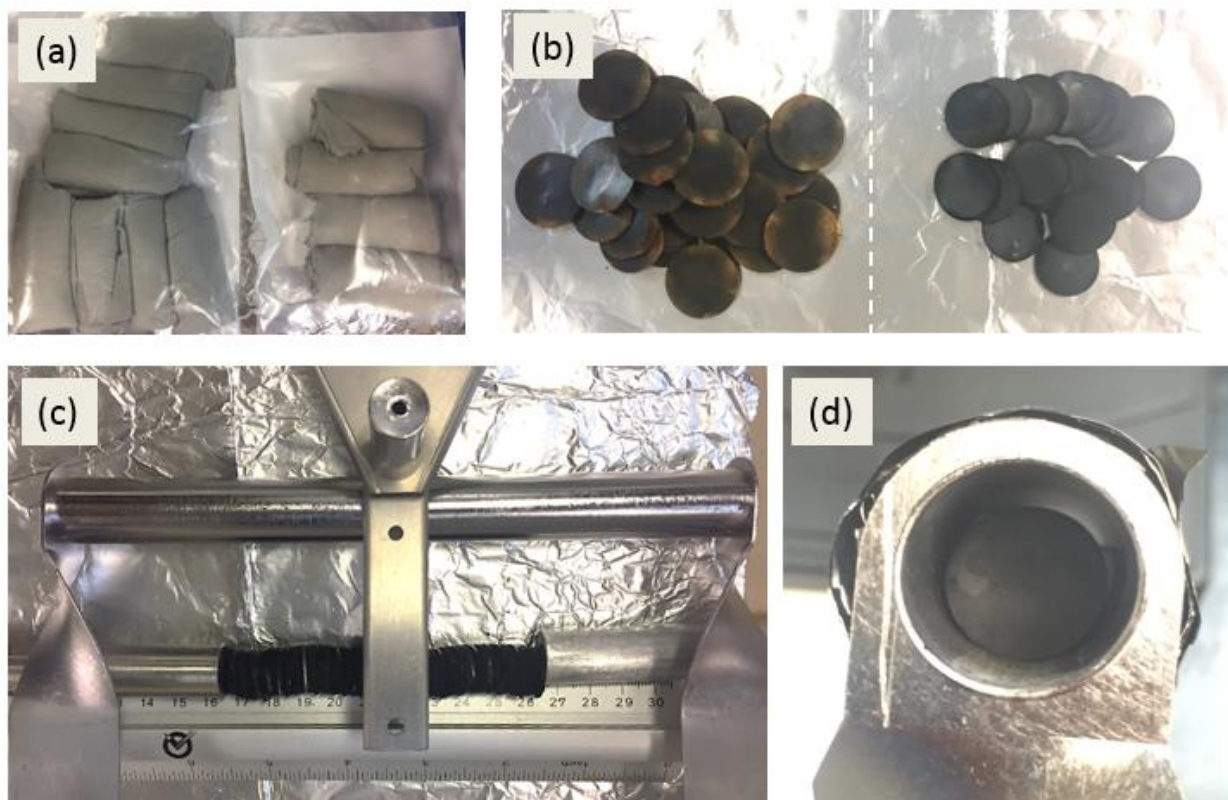


Figure 7-1: (a) As-spun np-SiC/PAN fibre mats, (b) pressed np-SiC discs (left = thermal stabilized at 250 °C in air, right = heat treated at 1600 °C in vacuum), (c) 150 fully carbonized SiC nanofibrous discs ready to be loaded into the Ta target container, (d) sideview of the discs with 15.5 mm diameter inside of the Ta target heater.

Presently, the use of the conventional needle electrospinning technique with the ability to produce nanofibres on a large scale for ISAC target production is still of great challenge; the as-spun fibre yield rate is 0.03 g/hr (for each 10 ml-syringe). To improve the throughput, the use of needleless electrospinning (Elmarco's NS LAB) with np-SiC spinning dope has been investigated preliminarily. The production rate has increased 40 fold. Fibre morphology and nanoparticles distribution of these samples are to be studied and optimized.

The fundamental building blocks of nanofibres network incorporated with np-SiC inspired us to engineer a variety of fibrous target materials, especially uranium carbide (UC_x), a non-commercially available product, for neutron-rich isotope production. A common method to prepare uranium UC_x is by carbothermal reduction. A possible method to produce nano-UC_x fibrous targets is similar to the co-electrospinning method developed in this thesis. The spinning dope can be prepared by introducing MWCNT as a carbon source to the nanoparticle UO₂/PAN suspensions. Handling radioactive material such as uranium requires precautions and a radiological controlled area. The ISAC radiochemistry laboratory may supply a suitable environment where research can be safely conducted for translating the nanofibre synthesis methodology to UC_x target material.

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Appendix

A1. Details of np-SiC suspensions DLS measurements

 Summary Statistics Report						
Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6a - 1	416.13	0.176	9.8	479.2	99.21	1.309E-08
Sample 6a - 2	407.39	0.200	9.9	480.5	100.00	1.337E-08
Sample 6a - 3	405.77	0.131	8.9	479.5	100.00	1.342E-08
Mean:	409.76	0.169	9.5	479.7	99.74	1.329E-08
Std Err:	3.22	0.020	0.3	0.4	0.26	1.037E-10
Std Dev:	5.57	0.035	0.5	0.7	0.45	1.796E-10
Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6b - 1	403.17	0.173	9.4	449.1	99.02	1.351E-08
Sample 6b - 2	404.70	0.190	8.1	450.9	100.00	1.346E-08
Sample 6b - 3	408.74	0.144	9.4	447.4	98.23	1.332E-08
Mean:	405.54	0.169	9.0	449.1	99.08	1.343E-08
Std Err:	1.66	0.014	0.4	1.0	0.51	5.491E-11
Std Dev:	2.88	0.023	0.7	1.8	0.89	9.511E-11
Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6c - 1	439.25	0.185	9.0	414.6	100.00	1.240E-08
Sample 6c - 3	437.83	0.227	9.9	425.4	98.43	1.244E-08
Sample 6c - 4	433.13	0.167	9.5	426.9	99.21	1.257E-08
Mean:	436.74	0.193	9.5	422.3	99.21	1.247E-08
Std Err:	1.85	0.018	0.2	3.9	0.45	5.296E-11
Std Dev:	3.20	0.031	0.4	6.7	0.79	9.173E-11

Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6d - 1	369.51	0.204	9.9	514.0	99.21	1.474E-08
Sample 6d - 2	359.04	0.154	8.1	513.6	99.21	1.517E-08
Sample 6d - 3	374.64	0.199	8.5	519.2	98.43	1.454E-08
Mean:	367.73	0.185	8.8	515.6	98.95	1.481E-08
Std Err:	4.59	0.016	0.6	1.8	0.26	1.862E-10
Std Dev:	7.95	0.027	1.0	3.1	0.45	3.226E-10
Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6e - 1	367.55	0.178	7.1	532.7	97.65	1.482E-08
Sample 6e - 2	377.30	0.159	6.0	522.0	99.21	1.443E-08
Sample 6e - 3	370.82	0.194	8.4	522.9	100.00	1.469E-08
Sample 6e - 4	378.87	0.159	7.8	545.2	99.20	1.437E-08
Sample 6e - 5	379.79	0.185	5.0	537.0	100.00	1.434E-08
Mean:	374.87	0.175	6.9	532.0	99.21	1.453E-08
Std Err:	2.41	0.007	0.6	4.4	0.43	9.400E-11
Std Dev:	5.39	0.016	1.4	9.8	0.96	2.102E-10
Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6f - 1	369.51	0.204	9.9	514.0	99.21	1.474E-08
Sample 6f - 2	359.04	0.154	8.1	513.6	99.21	1.517E-08
Sample 6f - 3	374.64	0.199	8.5	519.2	98.43	1.454E-08
Mean:	367.73	0.185	8.8	515.6	98.95	1.481E-08
Std Err:	4.59	0.016	0.6	1.8	0.26	1.862E-10
Std Dev:	7.95	0.027	1.0	3.1	0.45	3.226E-10

Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6g - 1	342.45	0.174	9.4	494.2	98.23	1.590E-08
Sample 6g - 2	342.08	0.145	9.8	496.4	99.40	1.592E-08
Sample 6g - 3	342.09	0.166	8.9	497.2	98.43	1.592E-08
Mean:	342.21	0.162	9.4	495.9	98.69	1.591E-08
Std Err:	0.12	0.009	0.3	0.9	0.36	5.595E-12
Std Dev:	0.21	0.015	0.4	1.6	0.63	9.691E-12

Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6h - 1	346.43	0.173	7.0	506.0	100.00	1.572E-08
Sample 6h - 2	341.58	0.135	8.3	505.1	99.21	1.594E-08
Sample 6h - 3	345.30	0.153	9.2	506.2	99.21	1.577E-08
Mean:	344.44	0.154	8.2	505.8	99.48	1.581E-08
Std Err:	1.47	0.011	0.6	0.3	0.26	6.754E-11
Std Dev:	2.54	0.019	1.1	0.6	0.45	1.170E-10

Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6i - 1	328.03	0.124	8.8	490.9	98.62	1.660E-08
Sample 6i - 2	338.95	0.179	8.1	496.2	98.43	1.607E-08
Sample 6i - 3	339.05	0.156	9.9	494.1	100.00	1.606E-08
Mean:	335.35	0.153	8.9	493.7	99.02	1.624E-08
Std Err:	3.66	0.016	0.5	1.5	0.49	1.792E-10
Std Dev:	6.34	0.028	0.9	2.7	0.86	3.103E-10

Sample ID	Eff. Diam. (nm)	Polydispersity	Baseline Index	Count Rate (kcps)	Data Retained (%)	Diffusion Coeff. (cm ² /s)
Sample 6j - 1	327.15	0.168	8.7	492.6	99.02	1.665E-08
Sample 6j - 2	327.98	0.183	8.9	487.8	97.64	1.660E-08
Sample 6j - 3	337.19	0.146	9.3	483.1	97.45	1.615E-08
Mean:	330.77	0.166	9.0	487.9	98.04	1.647E-08
Std Err:	3.22	0.011	0.2	2.8	0.49	1.587E-10
Std Dev:	5.57	0.018	0.3	4.8	0.86	2.748E-10

A2. Details of control samples mass loss measurements

Sample set	250 °C (in air)	1600 °C (in vacuum)		1800 °C (in vacuum)	
	Mass (g)	Mass (g)	Mass loss (%)	Mass (g)	Mass loss (%)
10%-PAN-Ref_1	0.361	0.149	59	0.145	60
10%_PAN-Ref_2	0.353	0.136	62	0.128	64
10%_PAN-Ref_3	0.366	0.148	60	0.133	62
Average wt% C from PAN		40% ± 1%		38% ± 2%	

A3. Details of compressed np-SiC samples measurements at various temperature treatments

Sample Set	Compression Pressure (MPa)	Heat Treatments (°C)	Mass (g)	Mass Loss (%)	Thickness (cm)	Diameter (cm)	Area (cm ²)	Area shrinkage (%)	Bulk Density (g/cm ³)	Est. Total Porosity (%)
P_np-SiC-1_1	100	250	1.01	0	0.81	1.31	1.37	0	0.90	-
		1600	0.57	43	0.74	1.14	1.02	25	0.76	71
		1800	0.45	55	0.69	1.12	0.99	28	0.66	75
P_np-SiC-1_2	100	250	0.35	0	0.28	1.30	1.37	0	0.91	-
		1600	0.21	40	0.27	1.14	1.02	25	0.76	71
		1800	0.16	54	0.23	1.13	1.00	27	0.69	74
P_np-SiC-1_3	100	250	0.42	0	0.34	1.30	1.37	0	0.90	-
		1600	0.24	43	0.31	1.14	1.02	25	0.76	71
		1800	0.19	55	0.31	1.13	1.00	27	0.61	77
P_np-SiC-1_4	200	250	1.00	0	0.60	1.31	1.35	0	1.23	-
		1600	0.56	45	0.51	1.14	1.01	25	1.08	59
P_np-SiC-1_5	200	250	0.33	0	0.20	1.30	1.37	0	1.21	-
		1600	0.19	42	0.19	1.14	1.02	25	0.98	63
P_np-SiC-1_6	200	250	0.38	0	0.23	1.30	1.37	0	1.21	-
		1600	0.22	42	0.22	1.14	1.02	25	0.98	63

Sample Set	Compression Pressure (MPa)	Heat Treatments (°C)	Mass (g)	Mass Loss (%)	Thickness (cm)	Diameter (cm)	Area (cm ²)	Area shrinkage (%)	Bulk Density (g/cm ³)	Est. Total Porosity (%)
P_np-SiC-1_7	400	250	0.35	0	0.11	1.77	2.46	0	1.29	-
		1600	0.21	41	0.09	1.55	1.89	23	1.17	55
P_np-SiC-1_8	400	250	0.35	0	0.11	1.77	2.46	0	1.29	-
		1600	0.20	44	0.09	1.55	1.89	23	1.11	58
P_np-SiC-1_9	400	250	0.38	0	0.12	1.77	2.46	0	1.29	-
		1600	0.22	42	0.10	1.55	1.89	23	1.14	57
P_np-SiC-1_10	600	250	0.36	0	0.11	1.77	2.44	0	1.36	-
		1600	0.21	43	0.09	1.55	1.88	24	1.22	54
P_np-SiC-1_11	600	250	0.36	0	0.11	1.76	2.44	0	1.32	-
		1600	0.21	43	0.09	1.55	1.89	22	1.17	56
P_np-SiC-1_12	600	250	0.33	0	0.10	1.77	2.46	0	1.34	-
		1600	0.19	42	0.08	1.55	1.89	23	1.24	53

A4. Details of compressed np-SiC sample total porosity calculations

SiC	3.21 g/cm ³
Carbonized PAN (C-PAN)	1.75 g/cm ³
Wt% Composition	
SiC	60%
C-PAN	40%
Theoretical density (ρ_{theo})	2.63 g/cm ³

$$\rho_{theo} = \left(3.21 \frac{g}{cm^3} \right) * 0.6 + \left(1.75 \frac{g}{cm^3} \right) * 0.4$$

$$P_{tot} = 1 - \rho_{bulk} / \rho_{theo}$$

where,

P_{tot} = Estimated total porosity (%)

ρ_{bulk} = Bulk Density (g/cm³)