



## Hierarchically porous carbon–zirconium carbide spheres as potentially reusable transmutation targets



Nicholas Scales<sup>a</sup>, Jun Chen<sup>b</sup>, Tracey L. Hanley<sup>a</sup>, Daniel P. Riley<sup>a</sup>, Gregory R. Lumpkin<sup>a</sup>, Vittorio Luca<sup>c,\*</sup>

<sup>a</sup> Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, New South Wales 2232, Australia

<sup>b</sup> Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, Australian Institute of Innovative Materials, University of Wollongong, Innovation Campus, North Wollongong, New South Wales 2522, Australia

<sup>c</sup> Comisión Nacional de Energía Atómica, Centro Atómico Constituyentes, Av. General, Paz 1499, 1650 San Martín, Provincia de Buenos Aires, Argentina

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### ABSTRACT

The preparation of hierarchically porous phase-pure carbon–zirconium carbide spheres with surface areas upwards of 70 m<sup>2</sup>/g and diameters in the 1–2 μm range has been achieved. The zirconium carbide beads were prepared through carbothermal reduction of polyacrylonitrile–zirconium composites prepared via three different routes including infiltration of a zirconium precursor into preformed polyacrylonitrile (PAN) beads and two one-pot co-precipitation methods. Depending on the route used to prepare the composites, relatively high surface area phase-pure zirconium carbides with the radial macroporous internal structure of the PAN template could be prepared. The adsorption of the elements U, Mo, Cs and Sr by the zirconium carbide beads was studied as a function of pH in the range 1–13 and target element concentrations of 0.025 mmol/L. The as-prepared hierarchical zirconium carbide beads demonstrated almost quantitative uptake of Mo below pH 4 with uptake decreasing to close to zero and above pH 10.5. On the other hand, U uptake was negligible below pH 4 and became quantitative in the range 4–12. Cesium was not extracted to any significant extent in the pH range studied and Sr only to a limited extent above pH 10. The engineered hierarchical porosities, neutron transparency, thermal stability and anticipated chemical stability of the present zirconium carbide spheres makes them promising candidates as reusable transmutation targets for Minor Actinide incineration.

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### 1. Introduction

Non-oxide ceramics such as zirconium carbide (ZrC) and silicon carbide (SiC) are high refractory ceramics with good thermo-mechanical properties. Of the two, ZrC is particularly advantageous for certain applications as it has a higher melting point (3400 °C), hardness, fracture toughness and strength. It is also a good thermal and electrical conductor. These properties make ZrC especially desirable in many nuclear applications. ZrC has been studied as a potential material for ceramic coated fuels and has shown excellent resistance to neutron irradiation performing better than SiC [1–4].

Due to the low neutron cross-section of both of these carbides as well as their inherent stability they can also be considered as transmutation hosts. Transmutation refers to the ability to transform one type of atom into another by changing its nuclear structure. This can be accomplished by bombarding the atoms of interest with neutrons either in a nuclear reactor or in an accelerator driven fission-system. In the context of irradiated nuclear fuel, transmutation can for instance, convert Pu and other radiotoxic and long-lived radionuclides into radionuclides with more favourable characteristics, viz shorter half-lives [5]. A large international research effort has been underway for many years with the objective of separating highly radiotoxic nuclides into separate fractions, recycling those with high energy value, and dealing with the others independently [6,7]. Among these radionuclides, the Minor Actinides (MAs) Np, Am and Cm are the most significant contributors to the long-term radiotoxicity of spent fuel. If these

\* Corresponding author.

E-mail address: [vluca@cnea.gov.ar](mailto:vluca@cnea.gov.ar) (V. Luca).

elements are extracted, the time taken for the radiotoxicity of spent fuel to return to the same level as the starting U ore, could be reduced from hundreds of thousands of years, to mere hundreds of years.

The variety of parameters to be considered in MA incineration and design of targets and fuels, including core physics, chemical stability, radiation tolerance and thermal conductivity, have already been reviewed in great detail [5]. So far, a promising assortment of candidate materials for use as targets and fuels (including the so-called Inert Matrix Fuels (IMFs)) in the incineration of MAs, have been described and their performances under different irradiation conditions elucidated. These include actinide metal-containing alloys and composites, oxides, nitrides, carbides, MgO, MgAl<sub>2</sub>O<sub>4</sub> (spinel), yttrium-stabilised ZrO<sub>2</sub> (YSZ) and Y<sub>3</sub>Al<sub>2</sub>O<sub>5</sub> (yttrium aluminium garnet or YAG) [8–18]. This list is by no means exhaustive. Generally these materials incorporate MAs into the host matrix either as part of a solid-solution or interdispersed as a separate phase. One drawback of most of these refractory ceramic compacts and monoliths is that they are fully dense and therefore cannot be readily recycled. This technology might be improved by development of a reusable target or IMF with accessible porosity onto whose interior surface target radionuclides could be deposited prior to neutron irradiation. Deposition could be achieved by infiltration and/or precipitation, or better still, adsorption processes. Notably, an infiltration approach has already been applied to the synthesis of (presumably non-recyclable) actinide-loaded fuel kernels from non-radioactive and porous MgAl<sub>2</sub>O<sub>4</sub> [19] and YSZ spheres pre-formed by sol–gel method [20,21]. Stripping of the less long-lived fission products post-irradiation from this proposed porous composite matrix would in theory permit recycling of the porous target, greatly minimising total waste volumes and therefore reducing costs associated with long-term storage. Moreover, it stands to reason that a porous target may also mitigate the effects of He generation (bubble/void formation and swelling) and thereby outperform its fully dense counterpart with respect to physical stability. The general features of such a support material would ideally include 1) high chemical and radiation stability, 2) ease of incorporation of MAs, 3) high neutron transparency and 4) good thermal conductivity.

However, for such a material to be viable for the said purpose, it would need to be easily prepared and would have to possess suitable morphology, porosity and adsorption properties such that loading with MAs could be achieved by some convenient means. Since ZrC has excellent thermomechanical and thermoelectrical properties and is under consideration as an IMF for the transmutation of MAs [22], we would consider hierarchically porous ZrC spheres to be ideal for this purpose.

Traditionally, preparation of ZrC involves carbothermal reduction of a zirconium precursor (Zr or ZrO<sub>2</sub>) using graphite as the reductant at temperatures above 1800 °C. However recently, sol–gel and other methods that produce molecular-scale mixing of the precursors have shown that ZrC can be prepared at much lower temperatures, sometimes as low as 900 °C [23]. The tangible benefit of these latter methods is that fabrication of ZrC-based materials can be achieved with common laboratory equipment making synthesis of ZrC-based spheres highly feasible.

The aim of the present work is the synthesis and characterisation of porous ZrC spheres for potential application as reusable transmutation targets or IMFs for the incineration of MAs or other long-lived by-products of conventional nuclear power generation. To this end, we have used three different methods to produce composites beads of polyacrylonitrile (PAN) and Zr precursors and have subjected the resulting monolithic materials to carbothermal reduction at the lowest temperatures possible in order to form the desired ZrC phase. PAN beads formed through a gelation process,

are a promising template structure as they typically possess an hierarchical and radial pore structure well-suited to dynamic or flow-through applications, potentially providing a convenient means to loading with MAs and desorption of their fission products.

## 2. Experimental

### 2.1. Chemicals

All chemicals were used as received without further purification. Anhydrous dimethyl sulfoxide (DMSO) (99.9%), zirconium (IV) propoxide (70 wt% solution in 1-propanol), Pluronic F-127, anhydrous ethanol (>99.5%), ZrCl<sub>4</sub> (>99.5%), Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (>99.5%), CsNO<sub>3</sub> (99.999%) and Sr(NO<sub>3</sub>)<sub>2</sub> (99.995%) were obtained from Sigma Aldrich. UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>99%, metals basis) was obtained in house and its purity determined by ICP-MS. Technical grade polyacrylonitrile (PAN) powder was sourced from Yongyi Chemicals, Jiangsu, China. Analytical grade 25 wt% aqueous ammonia, analytical grade 50 wt% aqueous sodium hydroxide and trace metal analytical grade 69% nitric acid were sourced from Merck, Australia. The 3.5 mol% H<sub>2</sub> in Ar gas mix was sourced from Coregas, Australia. Milli-Q<sup>®</sup> high purity water (18.2 MΩ cm) was sourced via a Millipore system.

### 2.2. Nomenclature

Synthesised materials were designated as ZrAC-x, ZrHC-x and ZrAl-x representing materials prepared by alkoxide co-precipitation, halide co-precipitation and alkoxide infiltration, respectively. The value of x represents the Zr content with a value of 1 being the lowest Zr/C ratio and 4 being the highest. For example the first member of the alkoxide infiltrated PAN series is ZrAl-1. PAN bead samples (no Zr content) stabilised at 240 °C and heated to 1350 °C were designated as PAN-240 and PAN-1350, respectively.

### 2.3. Synthesis

#### 2.3.1. 4 wt% PAN/DMSO precursor solution

A 4 wt% solution of PAN in DMSO was prepared by stirring a mixture of PAN powder and anhydrous DMSO at 50–60 °C in a water bath for up to 24 h under nitrogen on a Schlenk line. Aside from keeping the solution under a flow of nitrogen during dissolution and subsampling, no other steps were taken to exclude air and moisture. The result was a viscous golden solution.

#### 2.3.2. Alkoxide co-precipitation route

To warm 4 wt% PAN/DMSO precursor solutions, zirconium (IV) propoxide and Pluronic F-127 were added in the open air. Dissolution was achieved with stirring under a flow of nitrogen. The mass ratios of DMSO/PAN to zirconium (IV) propoxide to Pluronic F-127 were 1:0.11:0.011; 1:0.32:0.011; 1:0.53:0.011 and 1:0.74:0.011.

Using an in-house droplet generator the Zr-containing precursor solution was added dropwise to a stirred bath (4 L of deionised water plus 0.5 mL of aqueous 10 wt% F-127 solution), resulting in coagulation of PAN beads. The beads were thoroughly washed to remove surfactant and DMSO then dried to constant weight at low temperature (<35 °C).

#### 2.3.3. Halide co-precipitation route

A fresh subsample of anhydrous ZrCl<sub>4</sub> was taken from a nitrogen glove box and then handled thereafter in the open air. To each of 0.75, 1.25, 1.75 and 2.25 g of ZrCl<sub>4</sub> respectively, 20 mL of freshly prepared 4 wt% PAN solution in DMSO was added. It proved necessary to add the solution quickly to quench heat evolved by the exothermic reaction between the components, otherwise

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