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## Porous Zr<sub>2</sub>SC-carbon composite microspheres: Possible radiation tolerant sorbents and transmutation hosts for technetium-99

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## Porous Zr<sub>2</sub>SC-carbon composite microspheres: Possible radiation tolerant sorbents and transmutation hosts for technetium-99

### Abstract

The preparation, characteristics and adsorption properties of novel porous carbon-ceramic composite microspheres are presented. The composites were synthesised by a simple ion exchange process involving the cationic Zr tetramer and commonly-available macroporous sulphonated polystyrene-divinylbenzene cation exchange resins, with subsequent carbothermal reduction at 1350 °C. The materials were extensively characterised with respect to composition, chemical structure and porosity. Carbothermal reduction of the Zr-loaded templates resulted in formation of crystallites of the MAX phase zirconium sulphide carbide (Zr<sub>2</sub>SC) embedded within a highly microporous carbon framework with a macroporous secondary structure inherited from the resin template. Despite the high BET surface areas of the Zr<sub>2</sub>SC-carbon composite microspheres (in some cases, greater than 600 m<sup>2</sup> g<sup>-1</sup>), they are extremely mechanically robust. The microspheres displayed high adsorption selectivity for oxoanions relative to cationic solution species, including perhenate (ReO<sub>4</sub><sup>-</sup>), a pertechnetate (TcO<sub>4</sub><sup>-</sup>) surrogate. Accumulation of ReO<sub>4</sub><sup>-</sup> on the Zr<sub>2</sub>SC particles was unequivocally demonstrated by elemental mapping. Such materials are potential candidates as combined <sup>99</sup>Tc sorbents and reusable transmutation hosts.

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1 **Porous Zr<sub>2</sub>SC-carbon composite microspheres: possible radiation**  
2 **tolerant sorbents and transmutation hosts for technetium-99**

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14

15 **Abstract**

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17 composite microspheres are presented. The composites were synthesised by a simple ion  
18 exchange process involving the cationic Zr tetramer and commonly-available macroporous  
19 sulphonated polystyrene-divinylbenzene cation exchange resins, with subsequent  
20 carbothermal reduction at 1350 °C. The materials were extensively characterised with respect  
21 to composition, chemical structure and porosity. Carbothermal reduction of the Zr-loaded  
22 templates resulted in formation of crystallites of the MAX phase zirconium sulphide carbide  
23 (Zr<sub>2</sub>SC) embedded within a highly microporous carbon framework with a macroporous

24 secondary structure inherited from the resin template. Despite the high BET surface areas of  
25 the Zr<sub>2</sub>SC-carbon composite microspheres (in some cases, greater than 600 m<sup>2</sup> g<sup>-1</sup>), they are  
26 extremely mechanically robust. The microspheres displayed high adsorption selectivity for  
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28 (TcO<sub>4</sub><sup>-</sup>) surrogate. Accumulation of ReO<sub>4</sub><sup>-</sup> on the Zr<sub>2</sub>SC particles was unequivocally  
29 demonstrated by elemental mapping. Such materials are potential candidates as combined  
30 <sup>99</sup>Tc sorbents and reusable transmutation hosts.

31 **Keywords:** technetium; adsorption; MAX phase; carbonization; ion exchange resin

32

## 33 **1 Introduction**

34 Nuclear power generation has produced as by-products, large inventories of fissile and  
35 burnable extremely long-lived isotopes of the transuranic elements (Np, Pu, Am and Cm) as  
36 well as long-lived fission products, including, but not limited to, <sup>99</sup>Tc, <sup>93</sup>Zr, <sup>135</sup>Cs, <sup>107</sup>Pd and  
37 <sup>129</sup>I [1, 2]. The above mentioned transuranics together are responsible for long-term decay  
38 heat generation and radiotoxicity. Along with waste partitioning, one means of reducing  
39 waste volume and long-term radiotoxicity that has been receiving serious consideration, is  
40 transmutation via neutron irradiation, in order to convert long-lived radionuclides into much  
41 shorter-lived ones. With respect to the latter initiative, the Gen IV International Forum has  
42 selected next-generation reactor types for further R&D, with a goal of a closed nuclear fuel  
43 cycle incorporating total actinide burn-up [3]. The irradiation matrix is often conceived as a  
44 radiation-tolerant ceramic phase incorporating the Minor Actinides (Np, Am, Cm) in a solid  
45 solution or mixture in the form of a fully-dense monolith, *viz.*, Inert Matrix Fuel (IMF). The  
46 demands on a host matrix in terms of materials properties can best be described as extreme

47 and include very high melting point, thermal conductivity, chemical and radiation stability as  
48 well as low neutron cross-section. Candidate host matrices include oxide, nitride and carbide  
49 ceramics, as well as other mineral-based structures such as  $Y_3Al_2O_5$  (yttrium aluminium  
50 garnet or YAG) and spinel ( $MgSi_2O_4$ ) [4]. For instance in the ECRIX-H experiment utilising  
51 an Am-containing MgO matrix, a transmutation rate of 95% was achieved following  
52 irradiation in the Phénix reactor with 29% fast flux for 318 effective full power days [5].  
53 Nevertheless many technical challenges need to be overcome before Minor Actinide  
54 transmutation can be implemented. Of the long-lived fission products, the transmutation of  
55  $^{99}Tc$ , ( $^{99}Tc + n \rightarrow ^{100}Ru + \beta^-$ ) is generally considered technically feasible, although it has  
56 received much less attention [1, 6]. The current work attempts to address target materials for  
57 the transmutation of  $^{99}Tc$ .

58 Conventional IMFs are dense single- or two-phase monolithic materials. A single phase  
59 system would consist of the radionuclide to be transmuted being incorporated substitutionally  
60 within the crystal structure of a ceramic phase. In two-phase systems such as ceramic-ceramic  
61 (cercer) or ceramic-metallic (cermet) composites the radionuclide is incorporated within a  
62 separate phase. For instance, the ECRIX matrices are cercers since they initially consist of  
63  $AmO_{1.62}$  particles dispersed in MgO [5]. However, most nuclear fuels have limited burn-up  
64 capabilities, and only a fraction (say up to 30%) of the transuranics can be burned before the  
65 fuel reaches its damage limits and needs to be reprocessed and refabricated. Therefore  
66 reprocessability is an important criterion in determining the utility of a transmutation matrix  
67 or fuel. In contrast, wastefrom matrices for the immobilization of transuranics are required be  
68 extremely insoluble under a wide range of potential geological conditions.

69 As an alternative to fully-dense transmutation targets, the dissolution of which might be  
70 difficult, we suggested in our previous work that the aforementioned candidate host materials

71 prepared in suitable porous forms could be the basis for radiation-tolerant and reusable  
72 targets, but with generation of less solid waste [7]. Porous monoliths would have several  
73 potential advantages. First, fission gas generation would be less likely to cause swelling and  
74 cracking since the gas could easily be accommodated within pores. Second, high energy  
75 fragments resulting from neutronic reactions would always reside near pores. Third, the  
76 reactants and products could be introduced and removed by simple solid-liquid phase  
77 adsorption and desorption, respectively; and if the materials were prepared in granular forms,  
78 could readily lend themselves to column chromatography. Such materials might also find  
79 application in the production of nuclear medicines, wherein the easy recycling of costly  
80 isotopically-enriched target elements would be desirable to minimise production costs. To  
81 this end, we had produced carbon-zirconium carbide composite porous monoliths based on a  
82 porous polyacrylonitrile (PAN) sphere template, with demonstrated reversible adsorption of  
83 Mo. As one member of the aforementioned candidate transmutation matrices, zirconium  
84 carbide ( $ZrC_{1-x}$ ) possesses excellent thermal conductivity, radiation tolerance and thermal  
85 stability [8].

86 Sorbents for  $^{99}Tc$  have generally included diverse materials such activated carbon, natural  
87 minerals, synthetic inorganics and ion exchange resins [9-22]. Metal-Organic Frameworks  
88 (MOFs) have also been highlighted for their potential for  $^{99}Tc$  removal and sequestration [23-  
89 26]. There have been few examples of porous granular materials for  $^{99}Tc$  capture and  
90 especially ones well-suited to demanding radiation environments [27]. However, recently Shu  
91 and co-workers reported ion-imprinted inorganic-based magnetic microspheres exhibiting  
92 selectivity for  $ReO_4^-$  ( $^{99}TcO_4^-$  surrogate) even in moderately acidic conditions [28].

93 The  $M_{n+1}AX_n$  (MAX) phases are a relatively new family of layered, machinable, ternary  
94 carbides and nitrides; where M is an early transition metal; A is one of the elements in groups

95 13–16; and  $X$  is C and/or N [29, 30]. Due to their oxidation resistance and other properties  
96 there has been considerable interest in their potential as nuclear structural materials. They are  
97 normally prepared at high temperatures under reducing conditions and are usually obtained as  
98 dense monoliths of little use as adsorbents. However, it has been demonstrated that  
99 exfoliation of the MAX phases can yield two-dimensional MXenes (analogous to graphene)  
100 with cation intercalation properties [31, 32]. In this work, we report new porous composites  
101 containing the  $Zr_2SC$  MAX phase, which were fabricated by a straightforward ion exchange-  
102 based procedure promoting intimate contact between cationic Zr and polymeric organic  
103 cation exchange resins. The latter serve as both porous structural templates and reactive  
104 carbon sources, for *in situ* carbide formation via carbothermal reduction. Although metal-  
105 loaded ion exchange resins have been employed as precursors for a diverse range of carbon  
106 composites with ceramics and metals [33-44], to date this synthetic strategy has only been  
107 applied to produce carbides of U and Si [45, 46].

108 The objective of the current work was to produce novel porous microspheres, which could  
109 conceivably be utilised as radiation-tolerant sorbents for the selective capture of  $^{99}Tc$  and its  
110 subsequent transmutation. We detail the synthesis of these materials; determine their  
111 compositions as well as their chemical and physical structural characteristics; and investigate  
112 their adsorption properties.

113

## 114 **2 Experimental**

### 115 **2.1 Materials**

116 All chemical reagents including strong cation exchange resins were used as received without  
117 further purification. Dowex<sup>®</sup> DR-2030 H, Amberlyst<sup>®</sup> 15 H, Dowex<sup>®</sup> 50WX2 H and  
118 Amberlite<sup>®</sup> IR120 H and ZrOCl<sub>2</sub>.8H<sub>2</sub>O (98%) were sourced from Sigma Aldrich, Australia.  
119 Duolite<sup>®</sup> C 255 H was obtained from Dia-prosim Limited, UK, while NaReO<sub>4</sub> (99.9%) was  
120 obtained from Strem Chemicals, USA. Trace metal analytical grade 69% HNO<sub>3</sub> was sourced  
121 from Seastar Chemicals Inc, Canada and Merck, Australia; and analytical grade 50 wt%  
122 NaOH solution was procured from Fluka Chemicals, Australia. A custom multi-element  
123 standard (2% HNO<sub>3</sub> matrix, > 99.96% purity) was supplied by High Purity Standards, USA.  
124 This solution was 10 mg L<sup>-1</sup> with respect to each element and included Al, As, Ba, Be, B, Cd,  
125 Ca, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ga, Ho, Fe, La, Pb, Lu, Mg, Mn, Nd, Ni, P, K, Pr,  
126 Re, Rb, Sm, Se, Na, Sr, Tl, Tm, U, V, Yb and Zn. Instrument-grade air and 3.5 mol% H<sub>2</sub> in  
127 Ar gas mix were both produced by Coregas, Australia. Milli-Q<sup>®</sup> water (18.2 MΩ.cm) was  
128 used in all experiments.

### 129 **2.2 Synthesis**

#### 130 **2.2.1 Nomenclature**

131 Zirconium-loaded resins were named ZrCX-1 to -5 to indicate the substrates used; these  
132 were: macroporous resins Dowex<sup>®</sup> DR-2030 and Amberlyst<sup>®</sup> 15 (ZrCX-1 and -2,  
133 respectively) and gel resins Dowex<sup>®</sup> 50WX2, Amberlite<sup>®</sup> IR-120 and Duolite<sup>®</sup> C255 (ZrCX-



134 3 to -5, respectively). Substrates were all sulphonated polystyrene-divinylbenzene strong  
135 cation exchange resins (more specifications are given in Table S1).

### 136 **2.2.2 Zr adsorption**

137 Resins were loaded with aqueous  $\text{ZrOCl}_2$  solutions using a batch contact time of one day and  
138 mild agitation provided by a platform shaker (IKA, Germany). Macroporous resins were  
139 loaded with volume-to-mass ratio (V/m) of  $50 \text{ mL g}^{-1}$  and  $0.042 \text{ mol L}^{-1}$   $\text{ZrOCl}_2$ , while for  
140 gel resins, V/m of  $1 \text{ mL g}^{-1}$  and  $2.8 \text{ mol L}^{-1}$   $\text{ZrOCl}_2$  were used. Loaded resins were collected  
141 under suction, washed with Milli-Q<sup>®</sup> water and leached for one day to remove un-adsorbed  
142 Zr. The leached resins were re-rinsed, air-dried overnight under suction and vacuum-dried  
143 overnight at  $60 \text{ }^\circ\text{C}$  (Thermo Electron, Germany).

### 144 **2.2.3 Thermal treatment**

145 Detailed conditions for carbothermal reduction were described in our previous work [7].  
146 Briefly, the samples were heated in a graphite boat with lid in an alumina tube furnace under  
147 a flow of 3.5 mol%  $\text{H}_2$  in Ar mix and 24 hour residence time at any specified temperature.  
148 Heat treatment at  $1350 \text{ }^\circ\text{C}$ , being the maximum temperature achievable by the tube furnace,  
149 was the standard procedure. Sample codes denote the  $1350 \text{ }^\circ\text{C}$ -heated materials, unless  
150 explicitly stated otherwise.

### 151 **2.3 Characterisation**

152 Thermogravimetric analysis (TGA) of samples (vacuum-dried overnight at  $100 \text{ }^\circ\text{C}$ ) was  
153 conducted with a Seiko Instruments Inc. EXSTAR6000 thermal analyser under instrument air  
154 carrier. Optical images were obtained with a Wild M400 optical microscope. Secondary

155 electron images of microsphere fractured surfaces (2–3 nm Pt coated) were acquired with a  
156 Zeiss Ultra Plus Scanning Electron Microscope (SEM). Scanning Transmission Electron  
157 Microscopy (STEM) images and Energy Dispersive Spectroscopy (EDS) spectra were  
158 acquired using a JEOL 2200FS operated at 200 keV. STEM specimens consisted of crushed  
159 grains mixed with ethanol and dispersed on holey carbon films supported on TEM Cu mesh  
160 grids. Nitrogen adsorption-desorption isotherms of samples (vacuum-degassed at 150 °C)  
161 were acquired at 77 K (–196 °C) on a Micromeritics ASAP 2020 instrument. Mercury  
162 intrusion profiles were obtained with a Micromeritics Autosorb IV 9520 Mercury  
163 Porosimeter. Total surface areas were calculated with the Brunauer-Emmett-Teller (BET)  
164 equation; micropore and external surface areas using a t-plot method; and pore size  
165 distributions with a Density Functional Theory (DFT), N<sub>2</sub> on carbon slit pore model. Powder  
166 X-Ray Diffraction (XRD) patterns were acquired with a PANalytical X’pert Pro X-Ray  
167 Diffractometer using Cu weighted K $\alpha$  radiation 1.5406 / 1.5444 Å 2:1, a step size of 0.0334  
168 °2 $\theta$  and an effective scan step time of 624.965 s. Rietveld Analysis of Zr<sub>2</sub>SC was performed  
169 using Rietica software (Version 2.1), employing a Newton-Raphson refinement strategy.  
170 Profile fitting was conducted with a pseudo-Voigt function, while backgrounds were fitted  
171 with a fifth order polynomial function. For Neutron Activation Analysis (NAA), neutron  
172 irradiation was conducted at the OPAL Research Reactor, Lucas Heights, Australia, in a  
173 thermal neutron flux of  $2.2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$  for five minutes. Gamma spectra were acquired  
174 using high purity Ge gamma detectors (P-type, 25% relative efficiency). Standardisation was  
175 achieved using the  $k_0$ -method and certified gold wires standards [47]. Microanalysis of O  
176 content was performed using a routine inert gas fusion method and employing a LECO  
177 TCH600 instrument. All samples for NAA and O microanalysis were first vacuum-dried  
178 overnight at 100 °C and vials backfilled with N<sub>2</sub>. Raman spectra were collected using a  
179 Renishaw inVia Raman spectrometer equipped with a Peltier-cooled CCD detector and set up

180 with either argon (514 nm) or HeCd (325 nm) laser excitation. The carbon in-plane crystallite  
181 size was calculated using a general expression (Eq. 1) taking into account the laser  
182 wavelength:

$$L_a = (2.4 \times 10^{-10}) \lambda_{laser}^4 \left( \frac{I_D}{I_G} \right)^{-1} \quad (1)$$

183 where  $L_a$  is the in-plane crystallite size (nm),  $\lambda_{laser}$  is the laser wavelength (nm),  $I_D$  is the D  
184 peak intensity and  $I_G$  is the G peak intensity [48]. Individual whole microspheres were  
185 mechanically tested between two metal flats (load cell and stationary surface) using an  
186 Instron 5967 instrument with 500 N load cell, employing a compression rate of 0.01 mm  
187  $\text{min}^{-1}$ .

## 188 **2.4 Adsorption studies**

### 189 **2.4.1 Solution preparation**

190 For a pH 2 elemental selectivity profile, a 0.1  $\text{mg L}^{-1}$  cocktail (with respect to each element)  
191 was produced by diluting a multi-element custom standard 100-fold into pH 2.5 nitric acid  
192 solution, with pH adjustment carried out by addition of aqueous  $\text{HNO}_3$ , employing magnetic  
193 stirring.

194 For pH dependence studies, a solution 10  $\text{mg L}^{-1}$  with respect to Re was produced by  
195 dissolution of  $\text{NaReO}_4$  in Milli-Q<sup>®</sup> water. With vigorous magnetic stirring, this was pH  
196 adjusted with aqueous  $\text{HNO}_3$  or  $\text{NaOH}$  solutions to produce subsamples of various pH values.  
197 Each solution was aged for a day and its final pH measured.

198 For Re capacity measurements, STEM-EDS studies of Re loading and temperature  
199 dependence, a 25  $\text{mg L}^{-1}$  Re solution was produced by dissolution of  $\text{NaReO}_4$  in Milli-Q<sup>®</sup>

200 water, with adjustment to pH 5 with dilute aqueous HNO<sub>3</sub> and employing magnetic stirring.  
201 Aged overnight, the pH change was negligible. For kinetics and reuse, 1 mg L<sup>-1</sup> (pH 5) and  
202 10 mg L<sup>-1</sup> (pH 3) Re solutions, respectively, were prepared similarly.

#### 203 **2.4.2 Contact experiments**

204 Batch contact was conducted at about 20 °C with gentle agitation provided by a platform  
205 shaker (IKA, Germany), except for temperature dependence measurements, which were  
206 performed in a temperature-controlled shaker oven (WTC Binder, Germany).

207 The pH 2 selectivity survey was performed in triplicate at volume-to-mass ratio (*V/m*) of 200  
208 mL g<sup>-1</sup> with a contact time of one day. Supernatants were filtered through hydrophilic 0.45  
209 µm syringe filters (Sartorius). Measurements of pH dependence were performed similarly,  
210 but with a contact time of three days.

211 For capacity measurements, single solid portions were contacted for four days, with *V/m*  
212 varied between 50 and 1000 mL g<sup>-1</sup>. Subsampling of supernatants was conducted by pipette.  
213 Re-loading of pre-ground STEM-EDS specimen was executed similarly, but with *V/m* of  
214 2000 mL g<sup>-1</sup>.

215 Kinetics measurements were performed in triplicate at *V/m* of 200 mL g<sup>-1</sup>, with time varied  
216 between 15 minutes and four days. Supernatants were subsampled by pipette.

217 For reuse studies, adsorption-desorption cycling was effected by changes in HNO<sub>3</sub>  
218 concentration. A single solid portion was contacted with 10 mg L<sup>-1</sup> Re solution (pH 3) at *V/m*  
219 of 200 mL g<sup>-1</sup> for four days, with subsampling by pipette. The remaining supernatant was  
220 removed and replaced with HNO<sub>3</sub> solution (pH 0), with subsequent contact for four days,  
221 followed by subsampling by pipette. This procedure was repeated for two full cycles.

222 Between cycles, the solid material was washed and then leached ( $V/m$  of 5000 mL  $g^{-1}$ ) with  
223 Milli-Q<sup>®</sup> water for three days, to remove residual  $HNO_3$ .  
224 Temperature dependence studies were carried out in triplicate with contact at  $V/m$  of 200 mL  
225  $g^{-1}$  for four days, sequentially at 30, 40 and 50 °C, respectively. Supernatants were removed  
226 by pipette and cooled to room temperature prior to dilution for ICP-MS analysis.  
227 Elemental analyses of supernatants and stocks were performed on an Agilent 7900 ICP Mass  
228 Spectrometer. Values of % extraction were calculated using Eq. 2:

$$\% \text{ extraction} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

229 and uptakes were calculated with Eq. 3 and 4:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (3)$$

$$q_t = \frac{(C_i - C_t)V}{m} \quad (4)$$

230 where  $C_i$  is initial concentration ( $mg L^{-1}$ ),  $C_e$  is equilibrium concentration ( $mg L^{-1}$ ),  $C_t$  is  
231 concentration ( $mg L^{-1}$ ) at time  $t$ ,  $q_e$  is the equilibrium amount adsorbed ( $mg g^{-1}$ ),  $q_t$  is the  
232 amount adsorbed ( $mg g^{-1}$ ) at time  $t$ ,  $V$  is volume (L) and  $m$  is mass of sorbent (g). Triplicates  
233 were averaged and errors estimated from two sample standard deviations of each triplicate  
234 set.

### 235 **2.4.3 Model fitting and calculations**

236 Details of standard calculations for fitting adsorption models, as well as thermodynamic  
237 calculations, are given in Supplementary Material.

238

## 239 **3 Results and Discussion**

### 240 **3.1 Loading of resins**

241 The Zr uptake of the various cation exchange resins exhibited considerable variation. While  
242 the macroporous resins (ZrCX-1 and -2 precursors) were readily saturated with dilute  $\text{ZrOCl}_2$   
243 solution ( $0.042 \text{ mol L}^{-1}$ ) (Table S2), loading of the gel resins (ZrCX-3 to -5 precursors) was  
244 only satisfactorily achieved with concentrated solutions ( $2.8 \text{ mol L}^{-1}$ ). From TGA of the  
245 loaded resins (Fig. S1), the refractory residues (presumed to be  $\text{ZrO}_2$ ) were calculated to  
246 verify successful loading with Zr. For ZrCX-1 to -5, these were 24.3, 25.0, 28.5, 10.6 and  
247 10.4 wt%, respectively.

248

### 249 **3.2 Effect of thermal treatment**

250 Carbothermal reduction products of the Zr-loaded resins at  $1350 \text{ }^\circ\text{C}$  were typically lustrous  
251 black and highly spherical microspheres. A typical example, ZrCX-1, is presented in Fig. 1  
252 (images of all materials are supplied in Fig. S2). Upon heating, the specimens exhibited  
253 noticeable shrinkage compared to the precursors. The measured BET surface areas for ZrCX-  
254 1 to -5 were 609, 626, 401, 7.1 and  $7.5 \text{ m}^2 \text{ g}^{-1}$ , respectively. Thus, high Zr content seemed to  
255 have a positive influence on surface area; the three loaded resins with much higher Zr content  
256 (ZrCX-1 to -3) gave very high BET surface areas.

### 257 3.3 Composition and chemical structure

258 Elemental compositions of the thermally-treated microspheres were determined mainly using  
259 NAA and supplemented with O microanalysis (Table 1). From NAA, the main constituents  
260 were Zr, S, Hf and Na, with the remainder presumed to be mainly C and O. Traces of Cl, Mg,  
261 Al, V, Mn, Co and Cs were also found (data not shown). The trends in measured Zr  
262 concentrations agreed well with those seen earlier in the TGA of unheated Zr-loaded resins.  
263 The presence of Hf was anticipated as it is a common impurity in Zr, due to the difficulty in  
264 separating these two elements. The source of Na content was uncertain, however it could  
265 indicate that the starting resins were prepared in their Na forms and converted to H forms  
266 later on. Considerable O content (4.19–12.7%) was also found. The O in the Zr-loaded  
267 precursors originated from both sulphonate ( $-\text{SO}_3\text{H}$ ) and zirconyl ( $[\text{Zr}_4(\text{OH})_8]^{8+}$ ) moieties; the  
268 naked polymer frameworks do not contain it. The compositional remainders (42–75.5 wt%),  
269 were inferred to be mainly C, making up the porous frameworks and the majority component  
270 in four out of the five materials.

271 Powder XRD patterns for ZrCX-1 to -5 are presented in Fig. 2a. Despite initial expectations  
272 of producing ZrC, the three high surface area materials, ZrCX-1 to -3, showed the same  
273 distinct reflections of a crystalline phase identified as the MAX phase zirconium sulphide  
274 carbide ( $\text{Zr}_2\text{SC}$ ) [29, 30]. The  $\text{Zr}_2\text{SC}$  phase is known to have a  $\text{P6}_3/\text{mmc}$  (hexagonal) space  
275 group [30]. The other two materials displayed broad irregular shaped bumps which were  
276 interpreted as amorphous content or very short-range order. Using Rietveld Analysis,  
277 attempts were made at fitting a hexagonal structure model to the data. Fitting background  
278 functions proved challenging due to the high background. Use of a beam knife did not  
279 improve this situation (data not shown) and it was concluded that the backgrounds was due to  
280 amorphous content. Despite this difficulty, peak positions were accurately fitted and lattice

281 parameters calculated. The a and c cell dimensions ( $\text{\AA}$ ) for  $\text{Zr}_2\text{SC}$  in ZrCX-1 to -3 were,  
282 respectively:  $3.416 \pm 0.002$ ,  $12.143 \pm 0.007$ ;  $3.417 \pm 0.004$ ,  $12.150 \pm 0.014$ ; and  $3.423 \pm$   
283  $0.013$ ,  $12.16 \pm 0.04$ . These agreed well with previously reported values for this particular  
284 MAX phase (summarised in Table S3) [49-57]. Interestingly, the Zr-to-S molar ratios  
285 calculated from the compositional data above, ranged from 0.9 to 1.3; less than the 2:1  
286 proportions expected from the  $\text{Zr}_2\text{SC}$  formula. The Zr-to-C molar ratios ranged from about  
287 0.02 to 0.1, indicating that C was in vast excess. However, given the close agreement in  
288 lattice dimensions to prior examples, a deviation in stoichiometry of the MAX phase seems  
289 unlikely.

290 The carbon phases of ZrCX-1 to -3 were characterised by Raman Spectroscopy. Visible and  
291 UV excitation Raman spectra for ZrCX-1 are shown (Fig. 2b); those of the other two  
292 materials were highly similar and are given in Fig. S3. First, the absence of a discernible T  
293 peak ( $\sim 1060 \text{ cm}^{-1}$ ) in the 325 nm (UV excitation) spectrum demonstrated that  $\text{sp}^3$ -hybridised  
294 carbon content was insignificant. The G peak ( $\sim 1600 \text{ cm}^{-1}$ ) was unambiguous evidence of a  
295 ringed  $\text{sp}^2$  carbon structure. Furthermore, the G peak did not disperse (that is, change of peak  
296 position as a function of laser excitation frequency), but only the D peak dispersed; this is  
297 seen only in ordered carbons such as graphite, nanocrystalline graphite and glass-like carbon  
298 [58]. Thus the carbon component of the composites appears to consist of a well-ordered  
299 ringed  $\text{sp}^2$  carbon structure, with relatively few defects.

300 The 2D (overtone) peak provides information about stacking order of  $\text{sp}^2$  carbon sheets. In  
301 highly-graphitised carbon, a fine structure is observed [48]. This was absent in the 2D peak of  
302 the 514 nm spectrum of ZrCX-1, which instead showed a single smooth symmetrical peak.  
303 This was thus evidence of disordered stacking or turbostraticity of the carbon sheets similar



304 to the so-called non-graphitic carbons [59]. An equally valid interpretation would be that the  
305 sheets were randomly positioned in space, relative to one other.

306 Summarising, while there was evidence of an ordered ringed  $sp^2$  graphene-like motif in  
307 ZrCX-1, the carbon matrix exhibited a disordered three-dimensional structure.

### 308 **3.4 Porosity**

309 The internal pore structures of the materials were investigated with SEM. In the two  
310 macroporous resin-derived materials, ZrCX-1 and -2 (Fig. 3a-d), no large macropores (i.e.  
311 pores of the order of tens to hundreds of micrometres in diameter) could be observed. At  
312 higher magnification, irregular coral-shaped polymer structures were observed in both  
313 materials, surrounded by sub-micrometre macropores. Smaller gaps between adjacent  
314 branches could be interpreted as mesopores. The gel resin-derived microspheres, ZrCX-3 to -  
315 5 (Fig. 3e-j), were also lacking in large macropores, but somewhat smoother surface textures  
316 were observed at higher magnification. Thus, these latter materials did not have the small  
317 meso- and macropore architectures of the macroporous resin-derived microspheres. While  
318 some evident loose surface fragments were noted in two of the images, these were probably  
319 artefacts of the sample preparation.

320 The high surface area materials ZrCX-1 to -3 were examined by Nitrogen Porosimetry.  
321 Adsorption-desorption isotherms of these materials are presented in Fig. 4a. All three Zr-  
322 loaded resins developed considerable microporosity on heating, manifested as low relative  
323 pressure branches characteristic of the Type I adsorption isotherm [60]. However, the  
324 unloaded parent resins (Dowex<sup>®</sup> DR-2030, Amberlyst<sup>®</sup> 15 and Dowex<sup>®</sup> 50WX2,  
325 respectively) upon similar heating, gave much lower surface areas of 25, 59 and  $< 1 \text{ m}^2 \text{ g}^{-1}$ ,  
326 respectively. This implied that the inorganic portion played a role in the development of

327 microporosity and also that volatilisation of carbonaceous material could be ruled out as a  
328 cause. The two macroporous resin-derived materials retained considerable  
329 mesoporous/macroporous character of their parents, in contrast to the gel resin, which  
330 collapsed on heating to yield a non-porous product whose surface area was too low to  
331 accurately measure.

332 While the gel resin-derived ZrCX-3 exhibited a pure Type I isotherm, in ZrCX-1 and ZrCX-2  
333 Type IV hysteresis loops were also observed, indicative of mesoporosity [60]. The hystereses  
334 displayed reasonably flat plateaux, suggesting complete mesopore filling and the absence of  
335 substantial macropore and/or external surface areas which would be manifested as Type II-  
336 shaped features at relative pressures approaching unity [60]. The DFT pore size distributions  
337 for ZrCX-1 to -3 (Fig. 4b), confirmed a mixture of micro- and large mesopores for both  
338 ZrCX-1 and ZrCX-2 and only micropores for ZrCX-3. The former type of hierarchical  
339 porosity would be highly desirable in order to facilitate mass transport.

340 Mercury Intrusion Porosimetry of whole microspheres was also undertaken (Fig. S4), but was  
341 largely uninformative with respect to macropores. Apart from intrusion of interstitial  
342 porosity, only mesopore openings were revealed; this thus demonstrated that the microsphere  
343 surfaces were mesoporous.

### 344 **3.5 Mechanical testing**

345 Compressive strength testing of ZrCX-1 to -5 microspheres was conducted. Material ZrCX-1  
346 was exceedingly robust with an average failure point of 38.3 N and sample standard deviation  
347 of 6.3 N (n = 10). The microspheres shattered upon failure. A representative profile is given  
348 in Fig. S5. The smaller-sized ZrCX-3 behaved similarly, with an average failure point of 24.7  
349 N and sample standard deviation of 4.8 N (n = 10). The two low surface area materials also

350 proved to be mechanically strong and exhibited similar-shaped profiles, but also wide-  
351 ranging variation in mechanical strength. ZrCX-4 yielded an average failure point of 26.0 N  
352 and sample standard deviation of 19.0 N ( $n = 12$ ), while ZrCX-5, the most robust of the  
353 series, gave an average failure point of 109.7 N and sample standard deviation of 62.3 N ( $n =$   
354 10). However, the compression behaviour for material ZrCX-2 ( $n = 11$ ) was not reproducible  
355 with respect to profile shapes or failure points (data not shown), probably on account of the  
356 significant proportion of irregular-shaped microsphere fragments. Based on the brittle (albeit  
357 strong) overall nature of the materials and earlier presented Raman data, we would suggest  
358 that the carbon frameworks are probably akin to glass-like carbon.

359 Considering that a typical ZrCX-1 microsphere weighed approximately 0.1 mg, it follows  
360 that the same could withstand a compressive force equivalent to approximately 40 million  
361 times its own weight (assuming  $g$  of  $9.81 \text{ m s}^{-2}$ ). Therefore, mechanical strength should be no  
362 limitation for deployment in separation applications, such as in columns, batch contact or  
363 fluidised beds. In comparison, Drisko and co-workers produced fairly robust hierarchically  
364 porous zirconium titanium oxide beads which could withstand up to 0.57 N [61].

### 365 **3.6 Structural evolution with temperature**

366 Based on its combination of favourable properties including multi-scale porosity, high  
367 surface area and mechanical strength, ZrCX-1 was selected for the further study of its  
368 structural evolution with temperature (Fig. 5). From XRD data, a crystalline phase identified  
369 as tetragonal  $\text{ZrO}_2$  ( $\text{tZrO}_2$ ) had formed by 450 °C, which generally grew in intensity with  
370 increasing temperature (Fig. S6a). By 1150 °C, the peak intensity of  $\text{tZrO}_2$  had diminished  
371 somewhat and from around 1250 °C, the hexagonal MAX phase  $\text{Zr}_2\text{SC}$  appeared which had  
372 increased in intensity by 1350 °C (Fig 5a).

373 Surface area changes were monitored from 350–1350 °C (Fig. 5b; the complete set of  
374 associated adsorption-desorption isotherms are given in Fig. S6b and c). The low external  
375 surface areas for all temperatures confirmed that most of the BET surface area was associated  
376 with micropore content. While it would be tempting to attribute microporosity to the  
377 interstices between crystallites, or between crystallites and the carbon phase, the surface area  
378 changes did not always correlate with the appearance or disappearance of the crystalline  
379 phases. As examples, at 950 °C a large drop in surface area was seen even though no new  
380 crystalline phase had appeared; and at the intermediate stage of 1150 °C, surface area  
381 increased dramatically despite the absence of a well-defined crystalline phase. Instead, we  
382 postulate that surface area increases were due to the reaction of volatile oxygen with carbon  
383 *in situ* and/or voids left in the carbon phase by reaction with the inorganic phases.  
384 Conversely, surface area losses were due to consolidation of groups of smaller pores to form  
385 larger ones. One might consider this a form of activation, although any O-containing  
386 functionalities generated on the carbon surface would likely be removed by the reducing and  
387 carburising conditions.

388 Calculation of carbon in-plane crystallite size,  $L_a$ , for 550 – 1350 °C (Fig. 5c) revealed an  
389 almost linear downward relationship with temperature. Intuitively, one might expect  
390 carbonisation to give the opposite result, that is, coalescence of carbon domains, for example,  
391 as displayed by polyacrylonitrile [62]. These observations, however, are consistent with  
392 reactive carbon removal (postulated above) giving rise to increasingly tenuous connections  
393 between carbon domains and statistically, the semblance of smaller average crystallite sizes.

394 Taken together, these characterisation data support a hypothesis of micropore generation  
395 within the carbon phase. By extension, this explanation probably also accounts for the high

396 surface areas of the other two MAX phase-containing materials; and the low surfaces of the  
397 two materials, ZrCX-4 and -5, in which the Zr<sub>2</sub>SC phase did not form.

398

### 399 **3.7 Adsorption properties**

400 The adsorption properties of ZrCX-1 were scoped for a large suite of 41 elements at pH 2  
401 (please refer to § 2.1 Materials for the full list). The material showed significant extraction  
402 only of oxospecies-forming elements, As ( $94 \pm 4\%$ ), Se ( $93 \pm 4\%$ ), Re ( $87 \pm 7\%$ ) and P (>  
403 95%), with no discernible cation adsorption. Both Se and Re exist under these conditions of  
404 pH and concentration as oxoanions, although interestingly, As(V) and P(V) are found  
405 predominantly as the neutral species, arsenic acid (H<sub>3</sub>AsO<sub>4</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>)  
406 [63, 64].

407 The adsorption of Re prompted us to consider <sup>99</sup>Tc as a credible adsorbate, given the close  
408 similarity in chemistry between these two elements. Existing as the mononuclear tetrahedral  
409 anionic species, perrhenate (ReO<sub>4</sub><sup>-</sup>), Re is analogous to its cousin in Group 7, one period  
410 above, Tc, which exists as pertechnetate (TcO<sub>4</sub><sup>-</sup>) [64]. Thus, it is often regarded as a  
411 surrogate to predict likely affinity for Tc. The adsorption of ReO<sub>4</sub><sup>-</sup> as a function of pH was  
412 further investigated for both ZrCX-1 as well as a carbon blank produced by heat-treating the  
413 Dowex<sup>®</sup> DR-2030 parent resin in the same way ( $S.A._{BET} = 25 \text{ m}^2 \text{ g}^{-1}$ ) (Fig. 6a). Material  
414 ZrCX-1 showed nearly quantitative extraction of ReO<sub>4</sub><sup>-</sup> over the range of pH 3–10.5. By way  
415 of comparison, the carbon blank only showed weak affinity, with discernible adsorption only  
416 over the range of pH 1–5 and a maximum extraction of *ca.* 20% at pH 3. The adsorption  
417 capacity of ZrCX-1 for ReO<sub>4</sub><sup>-</sup> at pH 5 was also assessed (Fig. 6b). Isotherm model  
418 parameters obtained from fitting to the experimental data are presented in Table 2. The

419 Freundlich model was a poor fit, with significant non-linearity evident in the data. The  
420 Langmuir model fit, however, was considerably better. The calculated value of  $q_{\max}$   
421 (adsorption capacity) for the latter model was a modest  $13.85 \text{ mg g}^{-1}$  (*ca.*  $0.074 \text{ mmol g}^{-1}$ ),  
422 which visually accorded well with the plotted isotherm data. Capacity of the carbon blank  
423 was also surveyed at pH 5 for comparison and showed no measurable adsorption, in  
424 agreement with the pH dependence discussed above. Since the high carbon micropore surface  
425 area of ZrCX-1 was obviously underutilised, one avenue for increasing adsorption capacity  
426 could be to activate this carbon surface by sulphonation; load additional Zr; and repeat  
427 carbothermal reduction treatment.

428 The Re adsorption kinetics of ZrCX-1 were investigated (Fig. 6c). Fit parameters for the  
429 pseudo-second-order model are presented in Table 3. Overall, the pseudo-second-order model  
430 proved to be reasonable fit to the data. The kinetics were found to be relatively slow, with  
431 equilibrium only reached in 48–72 hours. Measured uptake at 24 hours was *ca.* 96% of  $q_e$ .  
432 These results can probably be attributed to a lack of large macropores which would facilitate  
433 fast intraparticle diffusion.

434 Measurements of temperature dependence of Re adsorption onto ZrCX-1 were undertaken to  
435 quantify the associated thermodynamic parameters (Table 4). Increasing temperature had the  
436 effect of reducing the  $K_d$  value (Fig. S8). Large negative values of  $\Delta H^\circ$  (enthalpy) and  $\Delta G^\circ$   
437 (Gibbs free energy) were calculated, clearly implying that the adsorption was an exothermic  
438 and spontaneous process. The negative value of  $\Delta S^\circ$  (entropy) would indicate ordering at the  
439 solid surface.

440 One might find the preceding fairly convincing evidence for the  $\text{Zr}_2\text{SC}$  phase supplying the  
441 majority of adsorption sites. However, efforts were made to corroborate this directly by way  
442 of microstructural chemical analysis. Elemental mapping of a portion of the Re-loaded ZrCX-

443 1 material was undertaken using STEM-EDS (Fig. 7). The bright field image of ZrCX-1 (Fig.  
444 6a) exhibited dark inorganic particles suspended on the lighter-shaded carbon phase.  
445 Mapping of Zr, S, O and Re elemental distributions (Fig. 7b–e, respectively) demonstrated  
446 that these four elements were mainly associated with one another. Thus, this unequivocally  
447 demonstrated that  $\text{ReO}_4^-$  accumulates upon the  $\text{Zr}_2\text{SC}$  aggregates/particles, with no  
448 significant adsorption on the carbon phase. With reference to the earlier bulk compositional  
449 data, these results also suggest that O and excess S are not associated with the carbon phase;  
450 and in addition to the  $\text{Zr}_2\text{SC}$  itself, may be part of a secondary inorganic phase. Due to the  
451 very small scale of the STEM specimen, however, it cannot be ruled out that there are  
452 pockets of unreacted material within the bulk of the material, rendered inaccessible to the  
453 carbothermal treatment by shrinkage of the resin precursor during heating. It is also possible  
454 that some O is dissolved within the  $\text{Zr}_2\text{SC}$  lattice. This latter explanation is plausible, given  
455 that other studies have shown that very high temperatures are required to completely remove  
456 dissolved O from ZrC and HfC powders [65].

457 The adsorption results presented above, certainly do contrast with most previous studies of  
458 MXenes, which typically show cation extraction; adsorption of alkali metals, alkaline earth  
459 metals, Pb as well as U, have all been demonstrated [66-68]. It should be noted, however, that  
460 Ying and co-workers reported affinity of  $\text{Ti}_3\text{C}_2\text{T}_x$  ( $T = \text{OH}$  or  $\text{F}$ ) for  $\text{Cr}_2\text{O}_7^{2-}$ , seemingly  
461 attributable to protonated surface hydroxyl groups [69]. We postulate two mechanisms for Re  
462 adsorption, which are not necessarily mutually exclusive. The first is a surface electrostatic  
463 model involving attraction by regions of negative charge on high-electronegative O bound to  
464 the adsorbate, to regions of positive charge on the carbide surface. This is a strong  
465 hypothesis, as it should universally explain adsorption of neutral, anionic and cationic  
466 oxospecies. We have also, in fact, observed the adsorption of cationic  $\text{UO}_2^{2+}$  above pH 3, as  
467 well as neutral and anionic Mo species ( $\text{H}_2\text{MoO}_4$ ,  $\text{HMoO}_4^-$  and  $\text{MoO}_4^{2-}$ ) (Fig. S7). In a

468 second scenario, it is conceivable that the “A layer” S terminating at the solid-liquid interface  
469 is oxidised and anion-exchangeable by adsorbate molecules. If this second hypothesis is  
470 applicable to any degree, one should expect a concomitant release of S into the surrounded  
471 solution.

472 There have been relatively few studies on the neutron irradiation stability of MAX phases  
473 [70-77]. Some phases such as the well-studied  $\text{Ti}_3\text{SiC}_2$  and  $\text{Ti}_3\text{AlC}_2$  appear to be reasonably  
474 tolerant and may be candidate nuclear structural materials. There would seem to be evidence  
475 supporting the role of the A layer in accommodating antisite defects, thus aiding in damage  
476 recovery over amorphisation [71, 77]. The antisite formation energies are in turn, influenced  
477 by the bonding overlap in the MX layer [71, 73]. The specific performance of  $\text{Zr}_2\text{SC}$  in these  
478 respects is unknown. A further consideration is that the cited studies focus on changes to  
479 mechanical properties; as to what influence structural damage (if any) might have on the  
480 surface chemistry and observed adsorption properties is a question that remains to be  
481 answered. Nonetheless, these previous investigations do hold some promise for the durability  
482 of the  $\text{ZrCX-1}$  sorbent, subjected to irradiation.

483 The reusability of  $\text{ZrCX-1}$  was studied two complete adsorption-desorption cycles by varying  
484 the  $\text{HNO}_3$  concentration of the contact solution. For cycle one, 96% adsorption was observed  
485 and 76% desorption; for cycle 2, 96% adsorption and 89% desorption. These preliminary  
486 results show that the  $\text{ReO}_4^-$  adsorption is in principle reversible, although additional work  
487 will be needed to establish optimal conditions.

488



## 489 **4 Conclusions**

490 The synthesis of new mechanically robust and highly porous microsphere composites of  
491 carbon and the hexagonal MAX phase  $Zr_2SC$ , based on a non-laborious procedure involving  
492 the carbothermal reduction of Zr-loaded common strong cation exchange resins has been  
493 demonstrated. The Zr loadings achieved varied among the resins and appeared to be an  
494 important factor in the development of high surface areas and formation of  $Zr_2SC$ , which  
495 were observed in one gel resin-derived and both macroporous resin-derived materials. Cell  
496 dimensions of this phase determined by Rietveld Method agreed well with prior published  
497 examples. It was concluded based on Raman data that the carbon phase consisted of ordered  
498 carbon sheets with disordered stacking or random orientation in space. Porosity was  
499 investigated in the three high surface area  $Zr_2SC$ -containing materials using SEM and  
500 Nitrogen Porosimetry. All had developed microporosity, while the two macroporous-resin  
501 derived materials additionally contained mesopores and small macropores originating from  
502 their substrate resins.

503 Of the three  $Zr_2SC$ -containing materials, ZrCX-1 was chosen for further study based on its  
504 combination of favourable properties including high surface area, mechanical strength and  
505 multi-scale porosity. For ZrCX-1, trends in crystallisation, surface area and carbon in-plane  
506 crystallite size as a function of temperature, together supported a hypothesis of micropore  
507 formation occurring within the carbon phase due to reactive carbon removal. This carbon  
508 phase is ostensibly a relative of glass-like carbon. This hypothesised mechanism probably also  
509 accounts for the high surface areas of the other two MAX-phase materials in the series.

510 Investigation of ZrCX-1 for adsorption selectivity at pH 2, showed affinity for oxospecies-  
511 forming elements, including As, Se, Re and P. Both neutral and anionic species were shown  
512 to adsorb, suggesting that an electrostatic interaction must play at least some role. Re was

513 then used as a surrogate in studies designed to anticipate the performance in extraction of  
514  $^{99}\text{Tc}$ , a long-lived fission product in High Level Waste (HLW). Nearly quantitative extraction  
515 over the range of pH 3–10.5 was demonstrated, with over 90% extraction observed from pH  
516 2. Elemental mapping employing TEM-EDS confirmed the role of the  $\text{Zr}_2\text{SC}$  MAX phase in  
517 the adsorption of  $\text{ReO}_4^-$ . The Langmuir model provided a superior fit to adsorption isotherm  
518 data at pH 5, yielding a  $q_{\text{max}}$  constant (Langmuir adsorption capacity) of  $13.85 \text{ mg g}^{-1}$ . A  
519 suggestion for further optimising this characteristic was offered. Likewise, adsorption  
520 kinetics for ZrCX-1 were modelled by pseudo-second-order model and found to be relatively  
521 slow (equilibrium reached in 48–72 hours), suggesting future opportunities for optimisation  
522 of pore architecture. Thermodynamic measurements demonstrated that the adsorption process  
523 was spontaneous and exothermic. The adsorption was also shown to be reversible, indicating  
524 the possibility for recycling of the matrix.

525 Given the simplicity of their syntheses and porous granular natures affording potential use in  
526 a chromatographic column, one might envisage one application being the deployment of the  
527 materials for the direct selective extraction of  $^{99}\text{Tc}$  from HLW and subsequent transmutation  
528 with thermal neutrons. For instance, the microspheres could be packed into a column within a  
529 Zr-alloyed housing, for convenient loading of  $^{99}\text{Tc}$ , neutron irradiation and post-irradiation  
530 elution of products. The microspheres are rigid and not subject to swelling effects, unlike  
531 polymeric ion exchange resins and are not likely to be damaged by fission gas build-up.  
532 Although radiation tolerance is anticipated, this will need to be evaluated for the  $\text{Zr}_2\text{SC}$  phase  
533 to properly gauge practical lifespan in a real recycling scenario. That is to say, while prior  
534 radiation damage studies of other MAX phases indicate good general stability for this class of  
535 materials, the specific performance of the  $\text{Zr}_2\text{SC}$  MAX phase in high thermal neutron fluxes  
536 would need to be addressed if it is to be considered for this application. This is a question we  
537 are working towards answering.

538

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552

## 553 **Figures captions**

554

555 Fig. 1. Optical microscopy image of ZrCX-1.

556 Fig. 2. (a) Powder XRD patterns. Key: h, hexagonal Zr<sub>2</sub>SC; and (b) Raman spectra of ZrCX-  
557 1, representative of ZrCX-1 to -3.

558 Fig. 3. SEM images of internal fractured microsphere surfaces at 1,000 and 50,000 ×  
559 magnification. (a) and (b) ZrCX-1; (c) and (d) ZrCX-2; (e) and (f) ZrCX-3; (g) and (h) ZrCX-  
560 4; and (i) and (j) ZrCX-5.

561 Fig. 4. Nitrogen Porosimetry data. (a) adsorption-desorption isotherms; and (b) pore size  
562 distributions.

563 Fig. 5. Structural evolution of ZrCX-1 with temperature. (a) Powder XRD patterns. Key: t,  
564 tetragonal ZrO<sub>2</sub>; h, hexagonal Zr<sub>2</sub>SC; (b) micropore, external and BET surface areas; and (c)  
565 in-plane carbon crystallite sizes.

566 Fig. 6. Adsorption data. (a) pH dependence for ReO<sub>4</sub><sup>-</sup> adsorption onto ZrCX-1 and a carbon  
567 blank; (b) isotherm data for ReO<sub>4</sub><sup>-</sup> adsorption onto ZrCX-1 at pH 5 with fitted Langmuir and  
568 Freundlich models; and (c) kinetics data for ReO<sub>4</sub><sup>-</sup> adsorption onto ZrCX-1 at pH 5 with  
569 pseudo-second-order model fit.

570 Fig. 7. STEM studies of Re-loaded ZrCX-1. (a) Bright field image; and corresponding  
571 STEM-EDS elemental maps (b–e) of Zr, S, O and Re distributions.

572

## 573 **Tables**

574 Table 1. Elemental compositions of ZrCX-1 to -5.

<i>Material</i>	<i>Zr (wt%)</i>	<i>S (wt%)</i>	<i>O (wt%)</i>	<i>Hf (wt%)</i>	<i>Na (wt%)</i>	<i>Balance (wt%)</i>
ZrCX-1	26 ± 2	6.9 ± 0.5	9.9 ± 0.2	0.58 ± 0.04	0.0043 ± 0.0003	57 ± 2
ZrCX-2	26 ± 2	8.0 ± 0.6	10.2 ± 0.2	0.57 ± 0.04	0.0051 ± 0.0004	55 ± 2
ZrCX-3	32 ± 2	12.2 ± 0.9	12.7 ± 0.3	0.75 ± 0.05	0.0179 ± 0.0013	42 ± 3

ZrCX-4	11.4 ± 0.8	8.6 ± 0.7	4.19 ± 0.08	0.27 ± 0.02	0.060 ± 0.004	75.5 ± 1.5
ZrCX-5	12.3 ± 0.9	9.6 ± 0.8	4.48 ± 0.09	0.29 ± 0.02	0.40 ± 0.03	73.0 ± 1.7

575

576

577 Table 2. Isotherm model fit parameters for  $\text{ReO}_4^-$  adsorption onto ZrCX-1 at pH 5.

<i>Model</i>	$q_{\text{max}} (\text{mg g}^{-1})$	$b (\text{L mg}^{-1})$	$n$	$K_f (\text{mg g}^{-1})$	$R^2$
Langmuir	13.85	1.59			0.993
Freundlich			2.97	6.56	0.949

578

579

580

581 Table 3. Kinetic model fit parameters for  $\text{ReO}_4^-$  adsorption onto ZrCX-1 at pH 5.

<i>Model</i>	$q_e (\text{mg g}^{-1})$	$k_2 (\text{g mg}^{-1} \text{h}^{-1})$	$R^2$
Pseudo-second-order	0.200	2.36	0.999

582

583

584 Table 4. Thermodynamic parameters for  $\text{ReO}_4^-$  adsorption onto ZrCX-1 at pH 5.

$\Delta S^\circ (\text{J K}^{-1} \text{mol}^{-1})$	$\Delta H^\circ (\text{kJ mol}^{-1})$	Temperature ( $^\circ\text{C}$ )	$\Delta G^\circ (\text{kJ mol}^{-1})$
-109.0	-57.07	30	-24.01

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40 -22.92

50 -21.83

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797 **Figures captions**

798 Fig. 1. Optical microscopy image of ZrCX-1.

799 Fig. 2. (a) Powder XRD patterns. Key: h, hexagonal Zr<sub>2</sub>SC; and (b) Raman spectra of ZrCX-  
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801 Fig. 3. (a) and (b) SEM images of ZrCX-1 and ZrCX-2 internal fractured surfaces at lower  
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804 Fig. 4. Structural evolution of ZrCX-1 with temperature. (a) Powder XRD patterns. Key: t,  
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807 Fig. 5. Adsorption data. (a) Adsorption pH dependence for ReO<sub>4</sub><sup>-</sup> adsorption onto ZrCX-1  
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810 Fig. 6. STEM studies of Re-loaded ZrCX-1. (a) Bright field image; and corresponding  
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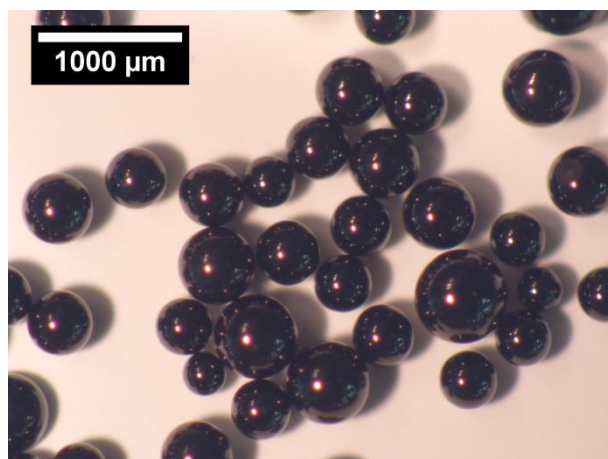
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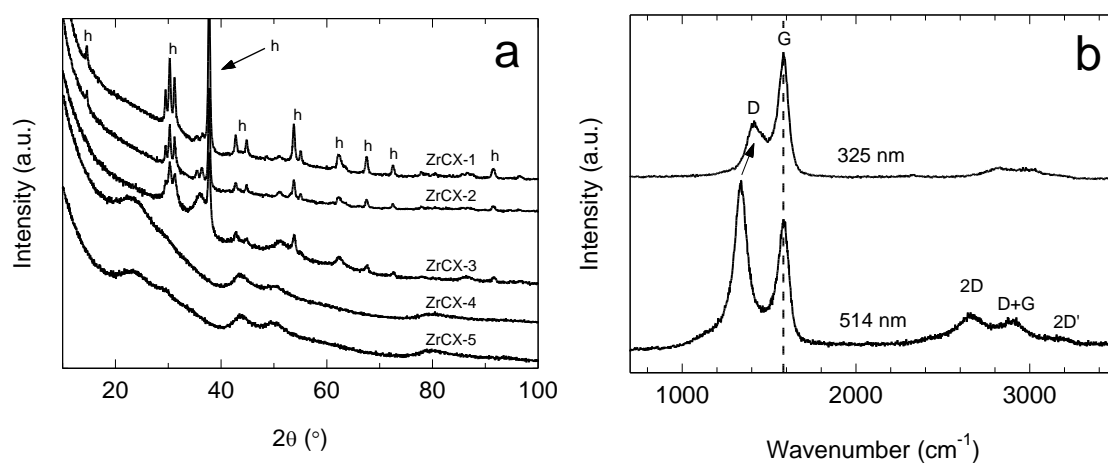
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Fig. 1. Optical microscopy image of ZrCX-1.

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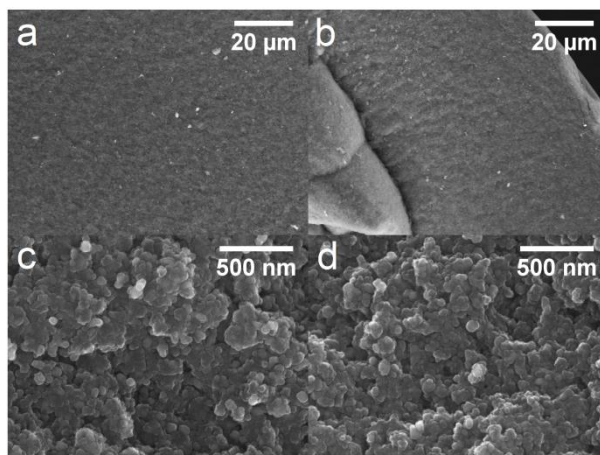
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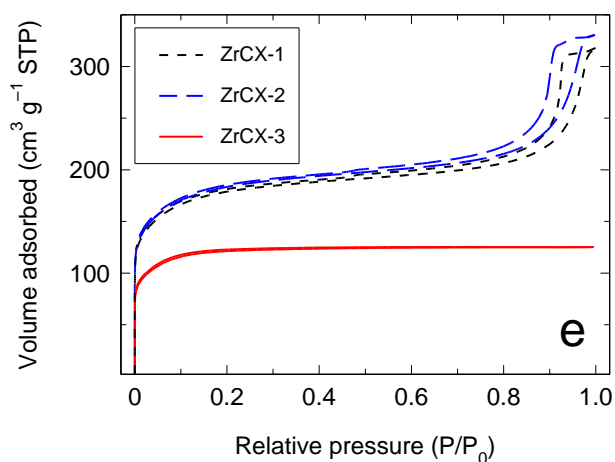
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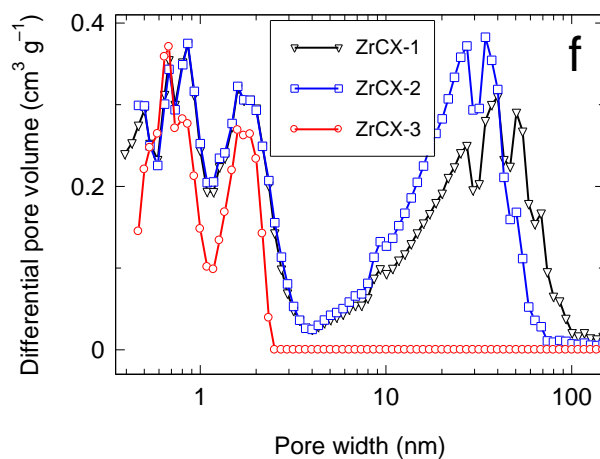
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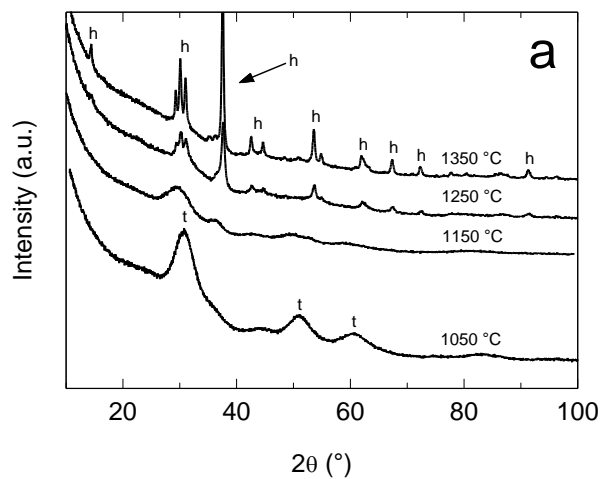
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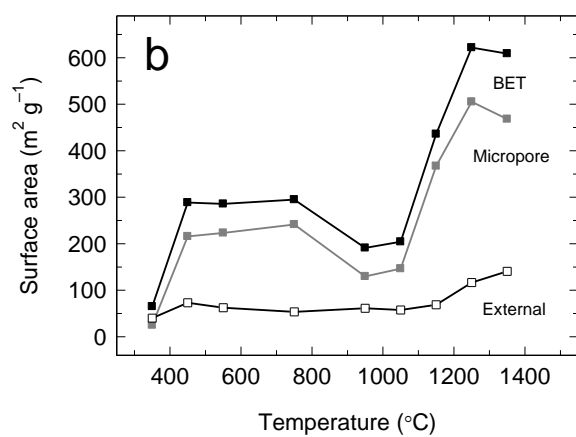
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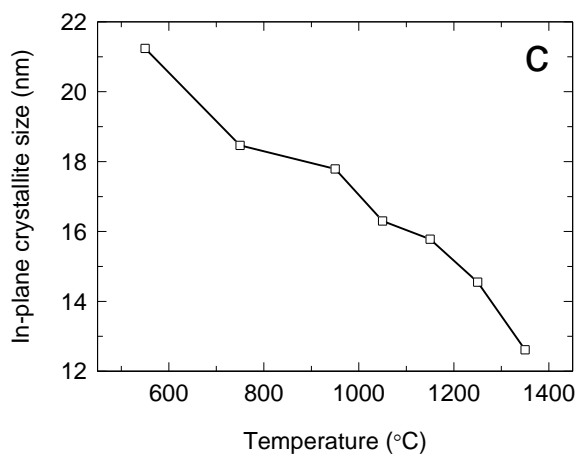
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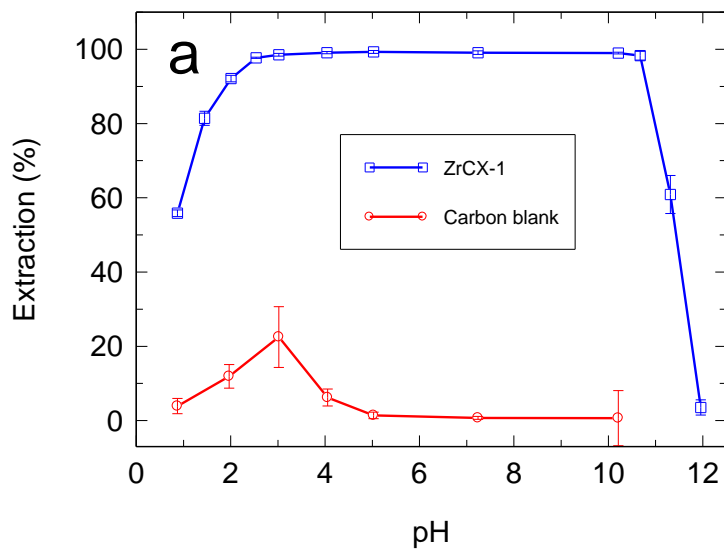
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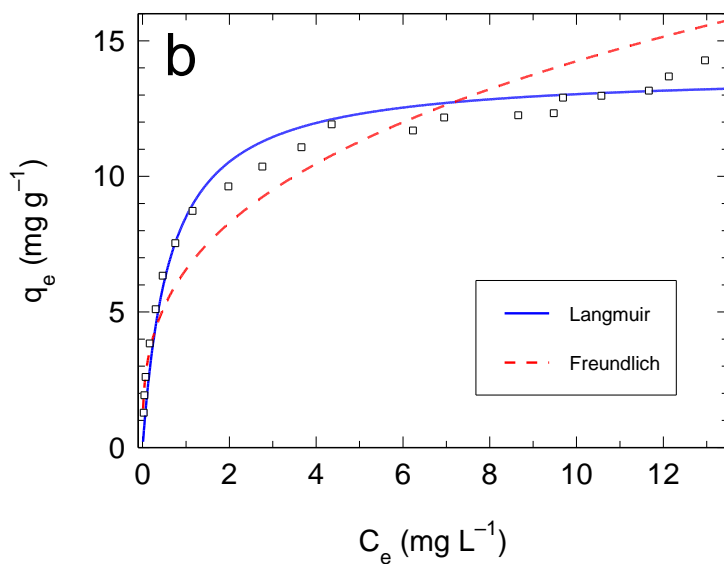
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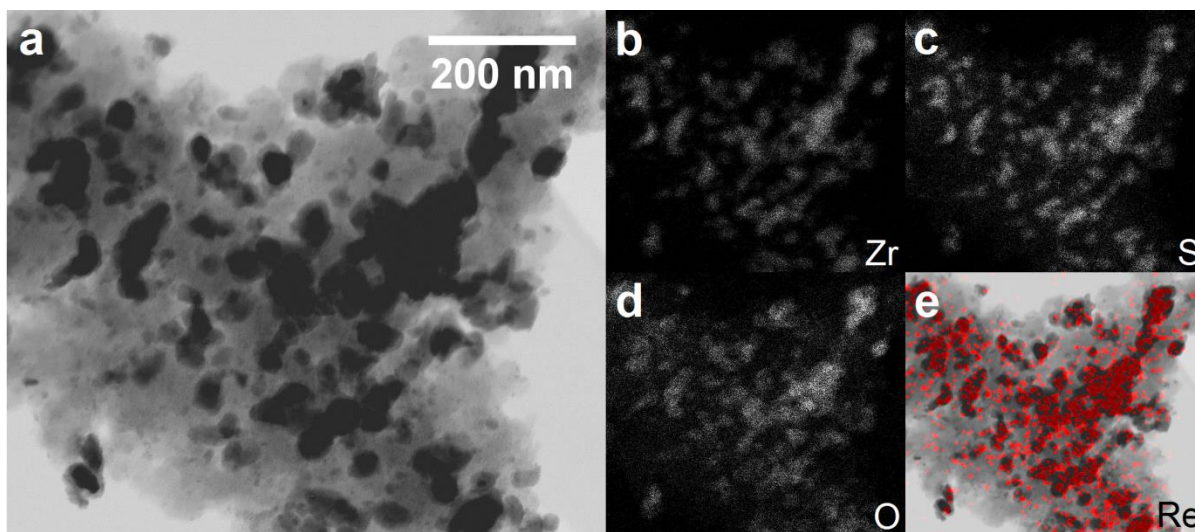
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