Improved critical current densities and compressive strength in porous superconducting structures containing calcium

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Abstract. Templated control of crystallization by biopolymers is a new technique in the synthesis of high temperature superconducting phases. By controlling the way YBa₂Cu₃O₇-δ (Y123) materials crystallize and are organized in three dimensions, the critical current density can be improved. In this work, we present the results of doping superconducting sponges with calcium ions, which result in higher critical current densities (Jc) and improved compressive strength compared to that of commercially available Y123, in spite of minor reductions in Tc. Y123 synthesis using the biopolymer dextran achieves not only an extremely effective oxygenation of the superconductor but also an in situ template-directing of the crystal morphology producing high Jc, homogeneous superconducting structures with nano-scale crystallinity.

1. Introduction
To further increase the suitability of high-temperature superconductors for high current density applications, it is important that the critical current density be improved. Critical current density (Jc) in these materials is adversely affected by crystallite grain boundaries [1-3] and as a result, control of crystallization is actively researched [4,5]. Achieving this control, either through epitaxial growth of thin films or melt-texturing of bulks often involves complex and sensitive syntheses, unlike the simple and benign approaches to crystallographic control that are characteristic of biomimetic materials chemistry [6-8]. We have recently demonstrated that such a biomimetic approach to the sol-gel synthesis of the superconductor YBa₂Cu₃O₇-δ (Y123) results in an order of magnitude improvement in Jc over that of a commercially available, high purity Y123 powder [9]. Sol-gel techniques are of increasing interest, offering reduced costs and improved throughput when compared to solid-state syntheses, albeit with no active control over crystal growth, resulting in materials having poor crystallinity and inferior physical properties. Our method of biotemplated crystallization [9] has distinct advantages over non-controlled crystallization; calcination in air of the dextran/superconductor precursor sol achieves discrete crystallinity of the superconducting phase as the dextran foams, thereby sparging the rapidly oxidizing synthesis mixture and controlling overall macro-morphology. This creates a material which has an open, porous architecture allowing for effective admission of...
cryogens. Here we report that the incorporation of calcium cations into the synthetic protocol leads to a significantly improved $J_c$ compared to that observed in a commercially available Y123 material. In addition, we show that mechanical strength is improved by the addition of only a small amount of the cationic species.

2. Experimental

Dextran (a complex branched polysaccharide comprised of straight chain $\alpha_{1,6}$ glycosidic and a majority of $\alpha_{1,3}$ branches) was obtained from Fluka, nitrates of yttrium, barium, copper and calcium were all obtained from Aldrich (99.99%). In a typical synthesis, sponges were prepared by the addition of dextran (20g, $M_r = 70,000$) to a superconductor precursor solution (10 ml, approx. 0.1M). The precursor solution was prepared by the dissolution of Y(NO$_3$)$_3$$\cdot$6 H$_2$O (1.915g, 0.05M), Ba(NO$_3$)$_2$ (2.613g, 0.1M) and Cu(NO$_3$)$_2$$\cdot$2.5 H$_2$O (3.489g, 0.15M) in 100 ml of H$_2$O. Dextran and superconductor precursor solution were mixed together in a crucible to form a light blue, viscous paste and left for one day at room temperature to harden. The resulting paste was then heated to a temperature of 920ºC at a ramp rate of 10ºC/min in a Carbolite furnace and held at that temperature for two hours. After this time, the material was allowed to cool back to room temperature in the furnace at a rate of approximately 2ºC/min. Calcium doped Y123 sponges were prepared in the same manner as above, with the addition of Ca(NO$_3$)$_2$$\cdot$4 H$_2$O to the superconductor precursor solution. The concentration of the cationic dopant was varied from 0.4 mM to 0.2 M. Calcination was performed on calcium doped samples as described above. Samples for SEM (JEOL JSM 6330F, 30kV) were prepared by mounting on aluminium stubs and sputter coating with platinum (Agar high-resolution Pt/Pd sputter coater) prior to observation. Powder x-ray diffraction (XRD) was carried out using a Bruker D8 Advance powder diffractometer (CuK$_\alpha$ radiation, 1.54056 Å; 2$\theta$ values 12º to 55º, step interval 0.02º). Compressive strength testing was undertaken using an Imada HV-500N rig, fitted with a DPS-50R digital force gauge. SQUID magnetometry was carried out using a Quantum Design Magnetic Property Measurement System equipped with a 5 T superconducting magnet. The measured data was not corrected for demagnetisation effects. Field cooled (FC) and zero field cooled (ZFC) data were extremely similar, i.e. the magnetisation is highly reversible, implying weak bulk pinning. A high critical current density of 1.8 kA cm$^{-2}$ at 77 K and 1 T field is obtained, rising to 1.1 MA cm$^{-2}$ at 10 K, 1 T (Figure 2a), which can be attributed to surface pinning of the porous structure, as well as its small crystallite size. XRD shows strong peaks corresponding to the lattice planes of Y123 (Figure 4a). Conversely, a commercially available Y123 powder (Aldrich 99.9% — average particle size 5 µm) was found to have a $T_c$ of 92 K and a critical current density of 0.04 kA cm$^{-2}$ at 77K, 1T and 0.02 MA cm$^{-2}$ at 10K, 1T, much lower than the dextran templated Y123 material.

3. Results and Discussion

A typical Y123 dextran-templated sponge is shown in Figure 1a. The sponge has a macroporous, open architecture with the consequence that it is mechanically weak. Compressive strength of this material was found to be less than 1.5 kPa which is accounted for by the lack of crystallinity. Transmission electron microscope (TEM) imaging confirms that the fine structure of the Y123 sponge consists of a gel-like composition with a typical strut size of around 60 nm (Figure 1b). SQUID magnetometry has shown that this material is superconducting, with an onset critical temperature ($T_c$) of 90 K (Figure 2b). In this sample, the field cooled (FC) data and the zero field cooled (ZFC) data are extremely similar, i.e. the magnetisation is highly reversible, implying weak bulk pinning. A high critical current density of 1.8 kA cm$^{-2}$ at 77 K and 1 T field is obtained, rising to 1.1 MA cm$^{-2}$ at 10 K, 1 T (Figure 2a), which can be attributed to surface pinning of the porous structure, as well as its small crystallite size. XRD shows strong peaks corresponding to the lattice planes of Y123 (Figure 4a). Conversely, a commercially available Y123 powder (Aldrich 99.9% — average particle size 5 µm) was found to have a $T_c$ of 92 K and a critical current density of 0.04 kA cm$^{-2}$ at 77K, 1T and 0.02 MA cm$^{-2}$ at 10K, 1T, much lower than the dextran templated Y123 material.
This can be attributed to the large crystallite size and possibly uncontrolled crystallite intergrowth during synthesis, giving rise to critical current-reducing large-angle grain boundaries.

Figure 1 – Electron microscope images of dextran-templated YBCO materials. In (a) SEM shows a highly-porous reticulated structure. In (b) TEM imaging shows the structure comprises approximately 60 nm width gel-like crystallites. Scale bar in (a) is 100 µm, in (b) 100 nm.

Figure 2 - SQUID magnetometry showing critical current density ($J_c$) and critical temperature ($T_c$) of dextran-templated YBCO materials.

Calcium has been used previously in the synthesis of Y123, to improve the phase purity [10], to increase the $T_c$ [11] and as a method of improving $J_c$ by reducing negative charge accumulation at grain boundary dislocations [12]. High-resolution SEM (Figure 3) showed that the addition of calcium to the precursor solution resulted in a crystalline material with an open, reticulated structure. With well defined 200 nm sized crystallites, these sponges were noticeably more structurally stable than the undoped sponges. Compressive testing confirmed this, with the compressive strength of these sponges now 4.74 kPa. This value did not vary appreciably across the range of dopant levels investigated. XRD confirmed that the Y123 phase was retained in this material and that crystallographically was indistinguishable from the dextran only sponge (Figure 4b). SQUID magnetometry revealed that the $T_c$ for this material varied according to the amount of dopant present, from 88 K with 0.4 mM Ca$^{2+}$ (Figure 5b), through 85 K with 4 mM Ca$^{2+}$ (Figure 5d), to 80 K at 0.2 M Ca$^{2+}$ (Figure 5f). This progressive suppression of $T_c$ (viz. 90 K in the undoped Y123 sponge sample)
is consistent with the introduction of non-superconducting species into the material; the lowest suppression being seen in samples with the lowest amount of doping. Critical current densities did not vary appreciably across the range of dopant concentrations, although a slight reduction is observed with increasing dopant concentration. At 10 K and 1 T field, the $J_c$ for calcium-doped sponges is 0.32 MA cm$^{-2}$ for 0.4 mM doping (Figure 5a), 0.26 MA cm$^{-2}$ for 4 mM doping (Figure 5c) and 0.24 MA cm$^{-2}$ for 0.2 M doping (Figure 5e). These values for $J_c$ compare favourably with the commercially available Y123 powder which has a $J_c$ of 0.02 MA cm$^{-2}$ at 10K, 1T and are comparable to values for $J_c$ observed previously for Ag$^+$ and Na$^+$ doped Y123 sponges [9]. An increased splitting of the FC and ZFC curves compared to the undoped Y123 sponges implies an improved flux line pinning as a result of the incorporation of calcium.

Figure 3 – SEM image showing a calcium-doped dextran-templated YBCO material. Scale bar is 10 µm.

Figure 4 – XRD patterns of dextran-templated YBCO materials (a) undoped and (b) doped with calcium.
Figure 5 - SQUID magnetometry showing critical current densities ($J_c$) and critical temperatures ($T_c$) of various porous superconducting structures. In a) and b), a calcium-doped (0.4 mM) dextran templated YBCO, in c) and d), a calcium-doped (4 mM) dextran templated YBCO, in e) and f), a calcium-doped (0.2 M) dextran templated YBCO.

4. Conclusions
We have demonstrated that by performing an in air calcination of calcium doped Y123 in the presence of the polysaccharide dextran, we have created a highly porous, fine grained superconductor in which the critical current density is improved over that observed in a commercially available material. The doped superconducting sponges in particular are able to be handled with no loss of structural integrity due to their improved resistivity to compressive strength, which may render them technologically useful.

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