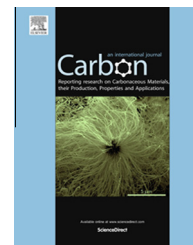


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Robust nanoporous alumina monoliths by atomic layer deposition on low-density carbon-nanotube scaffolds

S.J. Shin ^{a,*}, I.C. Tran ^a, T.M. Willey ^a, T. van Buuren ^a, J. Ilavsky ^b, M.M. Biener ^a,
M.A. Worsley ^a, A.V. Hamza ^a, S.O. Kucheyev ^a

^a Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

^b Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

ARTICLE INFO

Article history:

Received 5 November 2013

Accepted 3 March 2014

Available online 11 March 2014

ABSTRACT

Synthesis of nanoporous alumina monoliths with controlled morphology and density is a challenge. Here, we demonstrate mechanically robust alumina monoliths synthesized by conformal overcoating of graphitic nanoligaments of low-density carbon-nanotube-based aerogels (CNT-CAS) by using atomic layer deposition. Young's modulus of resultant monoliths increases superlinearly with the monolith density with an exponent of ~ 2.4 , defined by the morphology and connectivity of the CNT-CA scaffold. As a result, for a given monolith density, alumina-carbon composites have moduli comparable to those of CNT-CAS and significantly superior to those of pure alumina aerogels reported previously.

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1. Introduction

Aerogels are low-density, open-cell nanoporous materials with typical porosities of $\geq 80\%$. They are made of randomly interconnected high-aspect-ratio nanoligaments of complex geometry that could often be approximated as curved rods, strings of interconnected spherical particles, or thin sheets. With high surface areas, tunable monolith densities, and control over the elemental composition and geometry of ligaments, potential applications of aerogels are numerous [1]. In particular, alumina aerogels [2–9], which are the focus of the present work, are attractive as high-temperature catalysts or catalytic supports, structural ceramics, high-temperature thermal insulators, and adsorptive separators.

However, synthetic routes to monolithic alumina aerogels are currently limited. Two main sol–gel-based approaches to the synthesis of alumina aerogels have been reported. In

the first approach, alumina aerogels have been prepared with alkoxide precursors [3–6]. Due to high reactivity of the alkoxide precursors, synthesis of uniform macroscopic monoliths with this method is difficult. The second approach overcomes this limitation by using aluminum salts ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) instead of the reactive alkoxide precursors. [7] In such salt-derived alumina aerogels, the crystallographic phase and geometry of nanoligaments are controlled by the choice of the precursor salt [7] and by post-synthesis thermal annealing, which causes material dehydration (i.e., conversion of AlOOH into Al_2O_3) and curling of nanoleaflet-like ligaments [8]. Although such alumina aerogels with nanoleaflet-like ligaments have greatly improved mechanical properties compared to the other alumina aerogels reported [8], their stiffness remains inferior to that of more mechanically robust carbon aerogels. In particular, carbon-nanotube-based carbon aerogels (CNT-CAS), recently developed by Worsley

* Corresponding author.

E-mail address: shin5@llnl.gov (S.J. Shin).

<http://dx.doi.org/10.1016/j.carbon.2014.03.006>

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and coworkers [10], are approximately ~ 3 times stiffer than the “robust” salt-derived alumina aerogels with nanoleaflet-shaped ligaments [10,11].

Here, we report a templating method of the synthesis of alumina aerogels by conformally overcoating nanoligaments in low-density CNT-CA scaffolds with alumina using atomic layer deposition (ALD). The resultant nanoporous alumina-carbon composites have mechanical properties significantly superior to those of pure alumina aerogels, with the scaling law of Young's modulus on the monolith density determined by the morphology and connectivity of the starting low-density CNT-CA scaffold.

2. Experimental

Three sets of monolithic CNT-CAs with a CNT loading of 25–50 wt.% and densities of 30, 60, and 125 mg cm⁻³ were prepared as described in detail elsewhere [10]. In brief, purified single-walled CNTs (Carbon Solutions, Inc.) were dispersed in water in a sonication bath. The sol-gel precursors (resorcinol and formaldehyde) and the polymerization catalyst (NaCO₃) were added, and the mixture gelled. Wet gels were washed with acetone, dried with supercritical CO₂, and pyrolyzed at 1050 °C under N₂.

Nanoligaments of as-synthesized CNT-CAs were conformally coated with alumina layers by alternating exposures to trimethyl-aluminum (TMA, which is Al(CH₃)₃) and water precursors in a warm wall ALD reactor (Kurt J. Lesker), as described elsewhere [12,13]. During the deposition, reactor walls and the sample stage were kept at 100 and 125 °C, respectively. The aerogel samples were repeatedly exposed to the following sequence: TMA pulse, Ar purge, H₂O pulse, and Ar purge. The pressure during TMA and H₂O pulses was 0.8 Torr and 1.2 Torr, respectively. Long pump, pulse, and purge cycles (20, 500, and 500 s, respectively) were used for uniform coatings throughout nanoporous monoliths [14].

Monolith densities of resultant carbon-alumina composites were determined based on the initial densities of CNT-CAs and the elemental composition measured by Rutherford backscattering spectrometry (RBS) with a 2 MeV ⁴He ion beam. Selected samples were examined by scanning electron microscopy (SEM) in a JEOL 7401-F microscope operated at 2 kV and by bright-field transmission electron microscopy (TEM) in a FEI TF-20 Tecnai microscope operated at 200 kV. For TEM imaging, CNT-CAs were dispersed on holey carbon grids with an ultrathin (<3 nm) carbon support film. Selected samples were also analyzed by ultra-small angle X-ray scattering (USAXS) with a double-crystal Bonse-Hart instrument at beamline 15ID-D at the Advanced Photon Source, Argonne National Laboratory. The X-ray energy was 16.9 keV. Slit-smear USAXS data were corrected for background scattering, calibrated against a reference sample, and desmeared with Irena software tool suite [15]. Irena suite [15] was also used to fit desmeared scattering profiles with a model assuming scatterer size distributions with carbon cylinder and carbon-core/alumina-shell cylinder form factors for uncoated and alumina-coated CNT-CAs, respectively.

Mechanical properties were studied by indentation in the load-controlled mode in an MTS XP nanoindenter with a flat punch diamond tip with an effective diameter of 62 μm, which is much larger than the size of individual ligaments or pores (<0.1 μm). Before indentation, monoliths were machined with a cylindrical endmill, yielding macroscopically flat surfaces. Both loading and unloading rates were kept constant to maintain an indentation strain rate of 10⁻³ s⁻¹ [16]. Stiffness was characterized by indentation Young's modulus, which was calculated based on the initial slope of the unloading curve according to the Oliver-Pharr method [17]. In Oliver-Pharr calculations, we assumed Poisson's ratios of diamond and aerogels of 0.07 and 0.2, respectively, and a Young's modulus of diamond of 1141 GPa [16,18].

3. Results and discussion

Fig. 1 shows representative SEM and TEM images of uncoated and alumina-coated CNT-CAs. Consistent with previous reports [10], CNT-CAs form a network of ligaments made from CNT bundles decorated and interconnected by carbon layers and nanoparticles. After ALD, ligaments are conformally coated with alumina, resulting in an increase in their average thickness (see TEM images in Fig. 1(d)–(f)), with the foam morphology and ligament connectivity determined by those of the starting CNT-CAs (see SEM images in Fig. 1(a)–(c)). The graphene surface of defect-free CNTs is chemically inert and is expected to exhibit poor nucleation with the deposition of isolated alumina particles instead of conformal layers during alumina ALD [19]. Hence, the conformal coating revealed by TEM images of Fig. 1(d)–(f) suggests that the disordered graphitic carbon coating on CNT bundles of CNT-CA nanoligaments provides nucleation sites for the adsorption of TMA.

Quantitative information about the morphology of CNT-CAs, complementing electron microscopy observations, has been obtained by USAXS, which is one of the most common tools for studying aerogel morphology [1]. Fig. 2 shows representative USAXS profiles for an uncoated CNT-CA and CNT-CAs coated with 20 and 100 ALD cycles of alumina. All three profiles of Fig. 2 are rich in features, reflecting the complex morphology of these aerogels. The profile from the uncoated CNT-CA is the simplest. It exhibits a Guinier knee at a scattering vector q of $\sim 2 \times 10^{-2} \text{ \AA}^{-1}$ and a Porod power-law region with a slope of ~ -4 at $q > 5 \times 10^{-2} \text{ \AA}^{-1}$, reflecting scattering from CNT-CA nanoligaments.

After ALD deposition, Fig. 2 reveals that the overall scattering intensity increases, which could be attributed to larger scattering contrast of alumina.¹ The Guinier knee shifts to lower q , consistent with an increase in the nanoligament width. Several new scattering features associated with the alumina coating appear in the range of $q > 10^{-2} \text{ \AA}^{-1}$ and become more evident with increasing number of ALD cycles. Their oscillatory behavior precludes the use of the standard Guinier or Porod analysis and suggests a uniform distribution of scatterers with a narrow size distribution [20]. Hence, given the cylinder-like shape of nanoligaments revealed by TEM (Fig. 1(d)–(f)), we have used a scattering population

¹ Calculated X-ray scattering contrast of graphite and Al₂O₃ is 314 and $1080 \times 10^{20} \text{ cm}^{-4}$, respectively [15].

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