

Mixed ionic-electronic conductivity in yttria-stabilized zirconia/carbon nanotube composites

F. C. Fonseca^{a)} and R. Muccillo

Instituto de Pesquisas Energéticas e Nucleares, São Paulo, SP 05508-000, Brazil

D. Z. de Florio

Universidade Federal do ABC, Santo André, SP 09210-170, Brazil

L. O. Ladeira and A. S. Ferlauto

Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, MG 31270-901, Brazil

(Received 10 August 2007; accepted 14 November 2007; published online 11 December 2007)

The fabrication of yttria stabilized-zirconia/single-wall carbon nanotube (YSZ/SWCNT) composites is reported. Electrical conductivity measurements from 25 to 800 °C revealed that the composites exhibit mixed ionic-electronic conduction. At room temperature, the conductivity increases by 11 orders of magnitude with the addition of SWCNT to the YSZ. At high temperatures (>300 °C), the ionic conduction of the YSZ becomes relevant and a mixed ionic-electronic transport is observed. It is found that the transport can be described by a sum of two parallel contributions: thermally activated ionic conduction from the YSZ and fluctuation-assisted tunneling within the SWCNT network. © 2007 American Institute of Physics. [DOI: 10.1063/1.2821373]

Carbon nanotube (CNT) composites have been attracting a great deal of interest due to the possibility of imparting dramatic changes in the electrical, thermal, and/or mechanical properties of a given material with the addition of small amounts of CNT while preserving the desirable properties of the matrix.¹⁻³ Although most of the studies on ceramic/CNT composites have been directed to the enhancement of the mechanical properties of the ceramic matrix,^{2,4} recently, the electrical properties of ceramic/CNT composites have also come into focus. It was demonstrated that CNT composites with metal oxides, such as alumina and zirconia, present typical percolation behavior⁵⁻⁷ and can achieve high electrical conductivities.⁸ In these studies, the ceramic acts only as an insulating matrix; nevertheless, metal oxides such as the cubic phase of yttria stabilized-zirconia (YSZ) can also exhibit large ionic conduction at high temperatures ($T > 300$ °C). YSZ is the most studied oxygen ion conductor and is largely employed as high-temperature electrolyte.⁹ In this context, YSZ/CNT composites can be envisioned as multifunctional materials, interesting for electrochemical applications, such as sensors and fuel cell electrodes, provided that the operation conditions prevent CNT oxidation ($T < 400$ °C or inert/reducing atmosphere).¹⁰⁻¹²

In this letter, we report preparation and characterization of mixed ionic-electronic conductors based on cubic YSZ/single-wall carbon nanotube (SWCNT) composites. The transport properties of such composites were measured in a wide temperature range and the results demonstrate that their ionic and electronic contributions can be easily tuned by controlling the SWCNT concentration and temperature.

The SWCNTs were produced by arc discharge,¹³ and purified by successive steps of thermal oxidation and hydrochloric acid treatments, resulting in a purity of >96% as determined by thermogravimetric analysis. Composite samples of $\text{ZrO}_2:8 \text{ mol } \% \text{ Y}_2\text{O}_3$ (YSZ)/ x SWCNT, with $0 \leq x \leq 10$ wt %, were prepared by mixing YSZ powder

(Tosoh, average particle size of ~ 100 nm) and the purified SWCNT in ethanol. The YSZ/SWCNT suspension was homogenized in ultrasound for ~ 30 min, followed by ethanol evaporation under stirring. The resulting powder was pressed and sintered at 1400 °C for 1 h under a reducing atmosphere (Ar-H_2), maintained to prevent SWCNT oxidation due to residual oxygen.

Figure 1(a) presents Raman spectra ($\lambda_{\text{laser}} = 514$ nm) corresponding to the purified SWCNT and to the composite with $x = 3$ wt %. The radial-breathing-mode peak at $\sim 185 \text{ cm}^{-1}$ and the G band at $\sim 1590 \text{ cm}^{-1}$ present similar shapes and intensities in both spectra, indicating that the SWCNT have mostly tolerated the sintering treatment. However, the D band at $\sim 1340 \text{ cm}^{-1}$ has a slightly higher relative intensity in the composite spectra, indicating that the SWCNT may have been partially damaged.

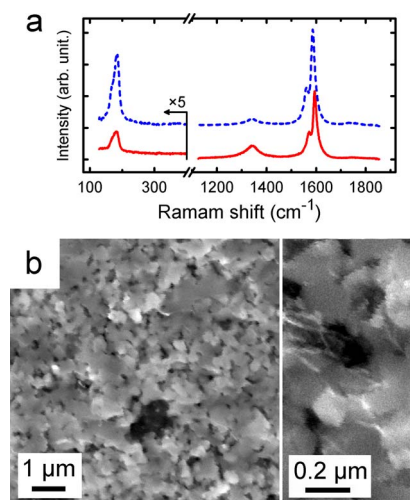


FIG. 1. (Color online) (a) Raman spectra of purified SWCNT (dashed line) and of a typical YSZ/SWCNT composite ($x = 3$ wt %, solid line). (b) SEM micrographs of YSZ/SWCNT composite ($x = 3$ wt %). (Left) Low magnification and (right) high magnification.

^{a)}Electronic mail: cfonseca@ipen.br.

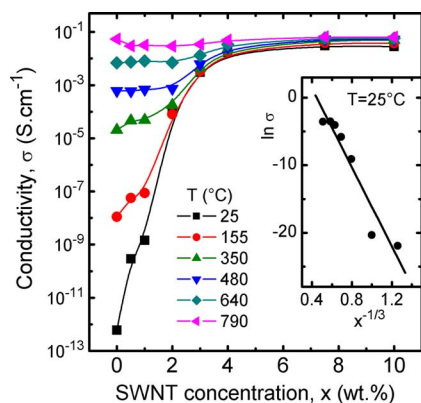


FIG. 2. (Color online) (a) Electrical conductivity (σ) of the composites vs SWCNT concentration (x) measured at different temperatures (the solid lines are guide to the eye). The inset shows the linear dependence of $\log \sigma$ on $x^{-1/3}$ at room temperature.

Figure 1(b) depicts representative scanning electron microscopy (SEM) images of the fractured surface of the sintered composite YSZ/SWCNT ($x=3$ wt %). The YSZ grains can be easily discerned and were found to exhibit an average size of $<1 \mu\text{m}$. These grains form a well connected network and are intercalated by dark regions (also in the submicron range) that probably represent SWCNT bundles. The SWCNT bundles were not easily identified due to resolution limitation of the apparatus but, occasionally, we were able to observe them protruding from the fractured surface, as depicted in the higher magnification image [Fig. 1(b) right]. The observed microstructure is qualitatively similar to those recently presented in $\text{Al}_2\text{O}_3/\text{SWCNT}$ composite prepared by spark plasma sintering, in which SWCNT were found forming bundles along grain boundaries.^{4,14} However, the SEM images indicated that the samples exhibit some porosity, markedly at high SWCNT content. The apparent density values were measured by Arquimedes' method and both the theoretical densities (TDs) and volume fractions were calculated by the mixing rule, using 1.3 and 6.0 g cm^{-3} as density values for SWCNT and YSZ, respectively. Composites with SWCNT content up to 4 wt % have apparent densities of $\sim 90\%$ TD, while for increased x the density is reduced, and samples with $x=10$ wt % have $\sim 60\%$ TD.

The electrical properties of the YSZ/SWCNT composites were measured by impedance spectroscopy for $T=25$ to 800°C under argon flow. The conductivity (σ) was determined from the intercept of the low frequency end (dc limit) of the impedance diagrams with the real axis. For the room temperature measurements of samples with $x < 1$ wt %, σ was estimated by fitting the high-frequency impedance data to a semicircle. The obtained σ values for YSZ are within the range of reported data.⁹ Figure 2(a) shows that the composite electrical conductivity exhibits a strong dependence on the SWCNT content, which is more pronounced at low temperatures. At $T=25^\circ\text{C}$, a clear percolative behavior is observed, with σ increasing by 11 orders of magnitude with increasing SWCNT concentration. In contrast, with increasing temperature the conductivity behavior changes dramatically. At higher T , the ionic transport within the ceramic matrix becomes relevant, and the conductivities of both phases assume comparable values.

The general effective media (GEM) model was used to estimate the percolation threshold (f_c) at different measuring

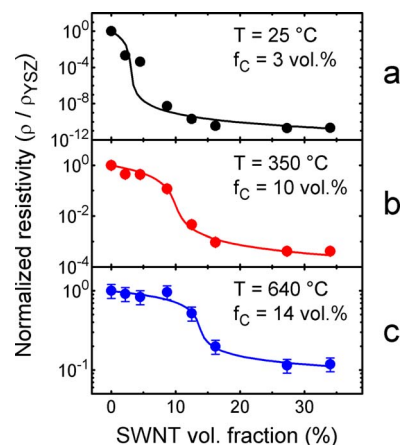


FIG. 3. (Color online) Electrical resistivity (ρ) of the composites normalized by the YSZ value vs SWCNT volume fraction, measured at (a) $T=25^\circ\text{C}$, (b) 350°C , and (c) 640°C . The lines correspond to the best fits of the GEM model. In (a) and (b), the error bars have the same size of symbols.

temperatures.¹⁵ The percolation analysis was done without taking into account the porosity of the specimens. The best fits are shown in Fig. 3 for selected T . At $T=25^\circ\text{C}$, the estimated $f_c \sim 3$ vol % ($x_c \sim 0.7$ wt %) is consistent with the usually observed threshold for ceramic/CNT composites.^{5,6} Such a relatively low f_c suggests that our simple preparation procedure resulted in composites with good CNT dispersion comparable to other ceramic/CNT composites prepared by advanced sintering techniques such as hot pressing or spark plasma sintering.^{2,6} On the other hand, such value is much larger than the one predicted for isolated SWCNT (~ 0.1 vol %). This adds evidence that the SWCNT form bundles that surround the YSZ grains. Based on theoretical calculations of the percolation threshold in CNT composites, the diameter of the bundles can be estimated to be $\sim 30\text{--}50 \text{ nm}$.³ As the temperature increases, the percolation threshold shifts to higher values and was estimated to be ~ 10 and 14 vol % at 350 and 640°C , respectively. One can attribute this behavior to the reduction in the difference between the conductivity of the YSZ and the SWCNT phases, i.e., the appearance of the mixed-phase regime. In this regime, the distinction between the conducting and insulating phases becomes blurred and, as a result, the percolation threshold is shifted to higher SWCNT concentrations. This is an interesting and complex phenomenon that deserves further attention in future studies.

The temperature dependence of the electrical conductivity in the composites can be better observed in the Arrhenius-type plot of Fig. 4(a). For low SWCNT concentrations ($x < 2$ wt %), the characteristic response of YSZ is observed. The oxygen ion transport in YSZ was found to follow the thermally activated Arrhenius type with calculated activation energy $E_a \sim 0.98 \text{ eV}$, in good agreement with reported values.⁹ For intermediate x values ($2\text{--}3$ wt %), the mixed ionic-electronic conduction is clearly demonstrated by the pronounced change in the slope of the $\sigma(T)$ curve at $\sim 350^\circ\text{C}$. In fact, the mixed behavior can be observed in all composites with $x > x_c$, but for increasing SWCNT content the change in the slope is progressively less noticeable and shifted to higher temperatures. It is also worth mention that for composites with SWCNT content well above the percolation threshold ($x \gg x_c$), wherein the SWCNT contribution to the charge transport dominates, the conductivity displays a

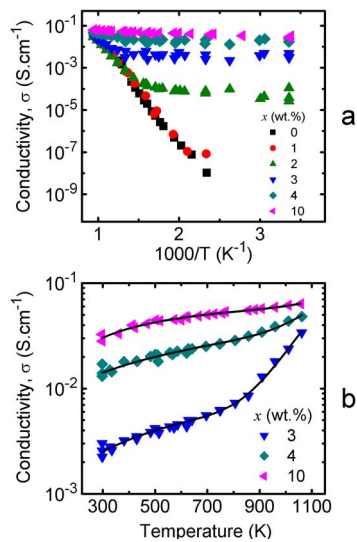


FIG. 4. (Color online) (a) Arrhenius plot of the electrical conductivity (σ) of the composites with different SWCNT concentrations (x). (b) Temperature dependence of σ for SWCNT concentrations above the percolation threshold ($x > x_c$). The lines correspond to fittings based on the parallel model described in Eq. (1).

nonmetallic behavior ($\partial\sigma/\partial T > 0$) within the whole temperature range investigated, and presents activation energy of ~ 30 meV.

The transport behavior of SWCNT samples has been the subject of intense research. It is well known that an individual SWCNT can be either semiconducting or metallic depending on its chirality. In addition, SWCNT in the form of bundles, in macroscopic (bulk) configurations such as aligned films, networks, or within composites, present rich electrical transport characteristics. The resistivities of SWCNT bundles and well-connected networks (buckypaper) present a change in the sign of the conductivity temperature dependence, switching from a metallic behavior ($\partial\sigma/\partial T < 0$) at room temperature to a nonmetallic behavior ($\partial\sigma/\partial T > 0$) as the temperature is reduced.¹⁶ On the other hand, thin networks of SWCNT bundles were recently reported to show a continuous increase of $\sigma(T)$ up to near room temperature.¹⁷ Such behavior is attributed to the difficulty in achieving good metallic pathways throughout the thin network.¹⁷

In general, electron tunneling between adjacent tubes in a percolated network is believed to be the primary charge transport mechanism in CNT composites.³ Such mechanism has been successfully associated with a fluctuation-assisted tunneling model proposed by Sheng.¹⁸ The electrical properties of bulk multiwalled CNT (MWCNT) samples (at high T) and of tetragonal zirconia/MWCNT composites (at low T) can be well described by this model.^{7,19} Similarly, our experimental data were found to be reasonably described by a linear plot of $\log[\sigma(T=25^\circ\text{C})]$ versus $x^{-1/3}$ (see inset in Fig. 2), suggesting that the tunneling-mediated conduction is present in the studied composites.^{7,18}

In this context, the electrical conductivity of the YSZ/SWCNT composites with $x \gg x_c$ can be modeled by a sum of two parallel contributions: the YSZ ionic transport and the fluctuation-assisted tunneling¹⁸ due to the SWCNT percolated network, given by

$$\sigma(T) = A \exp[-E_a/k_B T] + B \exp[-T_C/(T_S + T)], \quad (1)$$

where A and B are preexponential constants, E_a is the activation energy for the ionic transport (fixed at 1 eV), k_B is the Boltzmann constant, and T_C and T_S are the tunneling parameters.¹⁸ This model was used to adjust the $\sigma(T)$ data for $x=3, 4$, and 10 wt %, and the best fits are displayed in Fig. 4(b). The proposed model was found to provide an excellent adjustment of the $\sigma(T)$ curves, indicating that the electrical properties of the samples may be viewed as the sum of the contributions arising from both charge carriers. The obtained values for T_C of sample with $x=10$ wt % can be associated with an activation energy $k_B T_C$ of ~ 35 meV. Such value is within the range of the response of semiconducting SWCNT.¹⁶

In summary, the electrical properties of yttria-stabilized zirconia/single walled carbon nanotube composites were studied in a wide temperature range. The composites present a marked percolative behavior and mixed ionic-electronic conduction. The mixed transport can be clearly established from the temperature dependence of the conductivity, which was successfully described by a model comprising two parallel contributions: thermally activated Arrhenius type from the ceramic matrix and a fluctuation-assisted tunneling from the nanotube network.

The authors acknowledge the Brazilian agency CNPq for financial support (554970/2006-6 and 555173/2005-4) and scholarships. The authors thank S. Oliveira for providing the SWCNT, L. M. Malard and M. A. Pimenta for Raman measurements, and C. S. Moura for some of the SEM measurements.

- ¹E. T. Thostenson, Z. Ren, and T.-W. Chou, *Compos. Sci. Technol.* **61**, 1899 (2001).
- ²E. Flahaut, A. Peigney, Ch. Laurent, Ch. Marlière, F. Chastel, and A. Rousset, *Acta Mater.* **48**, 3803 (2000).
- ³L. Berhan and A. M. Sastry, *Phys. Rev. E* **75**, 041120 (2007).
- ⁴G.-D. Zhan, J. D. Kuntz, J. Wan, and A. K. Mukherjee, *Nat. Mater.* **2**, 15 (2003).
- ⁵S. Rul, F. Lefèvre-schlick, E. Capria, Ch. Laurent, and A. Peigney, *Acta Mater.* **52**, 1061 (2004).
- ⁶K. Ahmad, W. Pan, and S.-L. Shi, *Appl. Phys. Lett.* **89**, 133122 (2006).
- ⁷S.-L. Shi and J. Liang, *J. Appl. Phys.* **101**, 023708 (2007).
- ⁸G.-D. Zhan, J. D. Kuntz, J. E. Garay, and A. K. Mukherjee, *Appl. Phys. Lett.* **83**, 1228 (2003).
- ⁹R. M. Ormerod, *Chem. Soc. Rev.* **32**, 17 (2003).
- ¹⁰A. Thursfield and I. S. Metcalfe, *J. Mater. Chem.* **14**, 2475 (2004).
- ¹¹R. Muccillo, E. N. S. Muccillo, F. C. Fonseca, Y. V. França, T. C. Porfirio, D. Z. de Florio, M. A. Berton, and C. M. Garcia, *J. Power Sources* **156**, 455 (2006).
- ¹²A. S. Ferlauto, D. Z. de Florio, F. C. Fonseca, V. Esposito, E. Traversa, R. Muccillo, and L. O. Ladeira, *Appl. Phys. A: Mater. Sci. Process.* **84**, 271 (2006).
- ¹³S. Iijima and T. Ichihashi, *Nature (London)* **363**, 603 (1993).
- ¹⁴A. L. Vasiliev, R. Poyato, and N. P. Pature, *Scr. Mater.* **56**, 461 (2007).
- ¹⁵D. S. McLachlan, M. Blaszkiewicz, and R. E. Newnham, *J. Am. Ceram. Soc.* **73**, 2187 (1990).
- ¹⁶A. B. Kaiser, G. Dusberg, and S. Roth, *Phys. Rev. B* **57**, 1418 (1998).
- ¹⁷V. Skákalová, A. B. Kaiser, Y.-S. Woo, and S. Roth, *Phys. Rev. B* **74**, 085403 (2006).
- ¹⁸P. Sheng, *Phys. Rev. B* **21**, 2180 (1980).
- ¹⁹H.-L. Zhang, J.-F. Li, B.-P. Zhang, K.-F. Yao, W.-S. Liu, and H. Wang, *Phys. Rev. B* **75**, 205407 (2007).