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The role of electronic and ionic conduction in the electrical conductivity of carbon fiber reinforced cement

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Abstract

Electrical conduction in carbon fiber reinforced cement with a fiber volume fraction below the percolation threshold involves electrons and ions. The fiber affects both the electronic conduction and the ionic conduction. The ozone treatment of the fiber surface helps the ionic conduction. Latex as an admixture helps provide a relatively high ionic conductivity; silica fume as an admixture helps provide a relatively high electronic conductivity. In the dry state (the state of practical importance attained by room temperature drying), electronic conduction is more significant than ionic conduction. In the wet state (water saturated state), ionic conduction dominates. When silica fume is present with the fiber, the fractional electronic contribution in the dry state is 0.99. When latex is present with the fiber, the corresponding value is 0.72–0.78. The ratio of the wet ionic conductivity to the dry ionic conductivity is much increased by fiber surface treatment and is higher when latex rather than silica fume is used. The wet ionic conductivity is much higher than the dry overall conductivity when latex is present, but is lower than or comparable to the dry overall conductivity when silica fume is present; the wet ionic conductivity is lower than the dry overall conductivity when the fiber is not treated and silica fume is present.

Keywords: Carbon composites; Carbon fibers; Electrical (electronic) properties; Transport properties; Dielectric properties

1. Introduction

Cement reinforced with short carbon fiber is of interest due to the enhanced flexural strength, flexural toughness, tensile strength, tensile ductility, electrical conductivity and piezoresistive response and the reduced drying shrinkage provided by the fiber addition [1,2]. The piezoresistive response refers to the reversible change of the electrical resistivity with strain [3–12]. Piezoresistivity allows the composite to serve as a strain sensor, which is useful for weighing, traffic monitoring, border monitoring, building room occupancy monitoring, building security and structural vibration control. In addition, the electrical conductivity allows applications such as electrical grounding, lightning protection, deicing, electromagnetic interference shielding and electrostatic discharge protection. Because of the attractive functional properties, carbon fiber cement–matrix composites are multifunctional structural materials [13]. Due to the fact that the functional properties largely relate to the electrical behavior, it is important to understand the nature of electrical conduction in carbon fiber reinforced cement.

1.1. Electrical conduction in carbon fiber reinforced cement

Cement itself is well known for its ionic conductivity, which is particularly high when the cement contains a substantial amount of free water. However, carbon fiber is an electronic conductor (with the charge carriers being electrons and/or holes [14,15]) rather than an ionic conductor. The charge carriers that are responsible for electrical conduction in carbon fiber reinforced cement have received little prior attention, in spite of the substantial amount of

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prior work on measurement of the electrical conductivity. The prior work has emphasized the percolation phenomenon in relation to the dependence of the conductivity on the fiber volume fraction [16–20].

The dominance of ionic conduction in carbon fiber reinforced cement tends to be assumed by cement scientists, because cement, which is mainly an ionic conductor, is the matrix. However, the thermoelectric behavior of carbon fiber reinforced cement indicates holes as the main carrier [15,21,22]. Furthermore, the p-type character increases upon using bromine intercalated (p-type) carbon fiber in the cement [23]. Due to the controversy over electron/hole conduction and ionic conduction in carbon fiber reinforced cement, this paper is aimed at providing experimental results that enable distinction to be made between ionic conduction and electronic conduction. In this paper, the term "electronic conduction" can refer to conduction by electrons and/or holes.

Whether carbon fiber is present or not in cement, a decrease in the free water content (for example, by drying) increases the electrical resistivity. However, it has negligible effect on the thermoelectric power [22]. This means that the carrier that moves in response to a temperature gradient is electrons/holes rather than ions, though the movement of ions in response to a voltage gradient contributes to the electrical conductivity. Thus, the movement of electrons/holes in response to a voltage gradient should not be neglected.

1.2. Electrical conductivity measurement methodology

The method of electrical conductivity measurement conventionally used in the cement field involves the use of current contacts (i.e., electrical contacts for the passing of current) in the form of an ionic conductor, e.g., water or an aqueous solution, which is applied with a liquid absorbing material such as a sponge or paper towel [24]. Embedded in the absorbing material is a metal, such as stainless steel, which allows connection of the electrical contact to the external circuit. The configuration is illustrated in Fig. 1.

The use of two current contacts (i.e., electrical contacts for the passing of current) and two voltage contacts (i.e., electrical contacts for voltage measurement) constitutes the method known as the four-probe method, as illustrated in Fig. 1. On the other hand, the use of only two contacts, each of which serves both for passing a current and for voltage measurement, is known as the two-probe method. The four-probe method is preferred to the two-probe method, as there is little or no potential drop at voltage contacts that are distinct from the current contacts. In spite of its drawback, the two-probe method is quite commonly used, particularly in AC impedance measurement [25]. In case of the four-probe method, the voltage contacts are conventionally in the form of a metal or an electrically conductive paste (e.g., silver paint, graphite colloid, etc.) that is in contact with the cement-based material. The metal may be embedded in the cement-based material or be on the surface of the cement-based material. In relation to a metal electrical contact that is on the surface, a conductive paste may be applied at the interface between the metal and the cement-based material in order to improve the quality of the electrical contact between the metal and the cement.

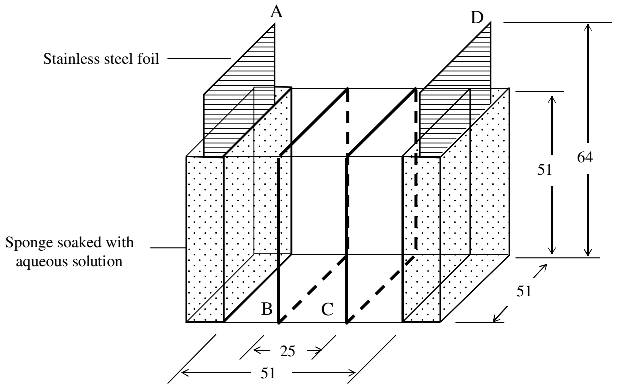

Fig. 1. Configuration of electrical conductivity measurement involving the use of current contacts in the form of an ionic conductor (an aqueous solution in conjunction with a sponge and a stainless steel foil) and voltage contacts in the form of an electronic conductor (silver paint in conjunction with copper wire). The current contacts (51 mm apart) are at two opposite surfaces of the cubic specimen. The voltage contacts (25 mm apart) are at two interior planes that are parallel to these two opposite surfaces. All dimensions are in mm.

Electrical contacts in the form of an ionic conductor do not allow electrons to flow from the metal wire associated with the external electrical circuit to the specimen. As ions cannot flow in a metal, ions cannot flow all the way around the circuit. Hence, ions flow in the specimen while only electrons flow in the external circuit. Thus, the configuration of Fig. 1 allows study of ionic conduction and does not allow study of electronic conduction.

The method of electrical conductivity measurement conventionally used in electrical engineering involves the use of all electrical contacts (both current and voltage contacts) in the form of an electronic conductor (not an ionic conductor), such as a metal or a conductive paste, as illustrated in Figs. 2 and 3 for the four-probe method. The configuration of Fig. 2 or 3 provides an electron circuit, so that electrons can go all the way around the circuit, which includes the specimen and the external metal wire. Ions can still move inside the specimen in response to the voltage gradient, but the ionic movement is more sluggish and more limited than the electron movement. Thus, the configuration of Fig. 2 or 3 allows study of electronic conduction, and, to a lesser degree, ionic conduction.

Although the method of Fig. 1 is conventionally used in cement research, it is not suitable for field implementation. This is because of the evaporation of the water or aqueous solution used for the current contacts. On the other hand, the method of Fig. 2 or 3 is suitable for field implementation. Research on the functional applications mentioned above has been almost all conducted using the method of Fig. 2 or 3.

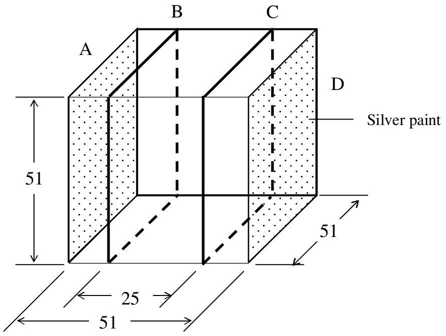

Fig. 2. Configuration of electrical conductivity measurement involving the use of both current and voltage contacts in the form of an electronic conductor (silver paint in conjunction with copper wire). The current contacts (51 mm apart) cover the entirety of two opposite surfaces of the cubic specimen. The voltage contacts (25 mm apart) around the perimeter are at two interior planes that are parallel to these two opposite surfaces. All dimensions are in mm.

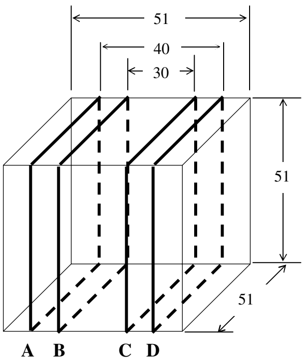

Fig. 3. Configuration of electrical conductivity measurement involving the use of both current and voltage contacts in the form of an electronic conductor (silver paint in conjunction with copper wire). The current contacts (40 mm apart) and the voltage contacts (30 mm apart) are around the perimeter at four interior planes that are parallel to one another. All dimensions are in mm.

Because the method of Fig. 1 and that of Fig. 2 or 3 give information on different aspects of electrical conduction, comparison of results obtained by the two methods is valuable for distinguishing between electronic conduction and ionic conduction. Such a comparison is an avenue (known as the blocking electrode method in the field of mixed ionic electronic conductors [26]) used in this work to probe the mechanism of conduction.

Conductivity measurement can be done under DC or AC condition. In the field of cement research, AC condition is conventionally used [24]. This is because the ions cannot enter the external circuit, so, under DC condition, they gather at one end of the specimen, thus causing electric polarization. The polarization results in a voltage associated with the resulting electric dipole within the specimen. This voltage affects the flow of charges, hence causing the measured resistivity to increase [27,28]. Polarization is much smaller for carbon fiber reinforced cement than for plain cement [28]. This means that ion movement is less significant for the former. Under AC condition, the ions move back and forth as the voltage polarity repeatedly changes, thereby avoiding polarization. Due to the sluggishness of ion movement, polarization takes time to build up under DC condition. Therefore, the use of a short time of electrical measurement (i.e., a short time in which a current is allowed to flow during data acquisition) is another way to avoid the problem of polarization. For practical implementation, DC is simpler and less expensive than AC. Furthermore, the majority of the prior work on carbon fiber reinforced cement uses DC. Thus, this work uses DC and avoids polarization by the use of a short time (1 s) of electrical measurement, as justified below.

In a period of 10 s, polarization results in a 2.5% increase in the measured resistivity in the case of cement paste containing carbon fiber (same type and proportion as in this work) and silica fume (same type and proportion as in this work), and a 5.5% increase in the measured resistivity in the case of cement paste containing carbon fiber (same type and proportion as in this work) and latex (same type and proportion as in this work) [28]. Polarization is more severe when latex is present than when silica fume is present. Nevertheless, for both cases, the effect of polarization for a period of 1 s on the measured resistivity is negligible compared to the resistivity data scatter of around 10% (Table 1), as assessed by measuring three specimens of each type in this work.

1.3. Objective

The objective of this paper is to understand the mechanism of electrical conduction in carbon fiber reinforced cement below the percolation threshold by distinguishing between ionic conduction and electronic conduction through electrical conductivity measurement. To help support the distinction, the conductivity measurement is made for different combinations of fiber surface condition, admixture type, water content, measurement direction and measurement method. The measurement methods are explained in Section 1.2. The other aspects are explained in this section.

The electrical conductivity of carbon fiber reinforced cement increases with increasing fiber volume fraction [16–20]. The volume fraction above which the adjacent fibers touch each other, thereby forming a continuous electrically conductive path, is known as the percolation threshold. The percolation threshold is between 0.5% and 1.0% for carbon fiber reinforced cement without aggregates [20].

For use of carbon fiber reinforced cement as a strain sensor through exploiting the piezoresistive phenomenon, a high electrical conductivity is not required. Therefore, for the purpose of maintaining low cost, high workability and low air void content (which means high compressive strength), a fiber volume fraction below the percolation threshold suffices [1]. However, for use of carbon fiber

Table 1
Measured electrical resistivity (Ω cm) for four compositions of carbon fiber reinforced cement below the percolation threshold

	P	Q	R	S	T	U	V
Untreated fiber, latex	$(1.08 \pm 0.18) \times 10^6$	$(5.89 \pm 0.47) \times 10^4$	$(1.26 \pm 0.19) \times 10^6$	$(7.75 \pm 1.11) \times 10^4$	$(2.97 \pm 0.32) \times 10^5$	$(3.18 \pm 0.35) \times 10^5$	$(6.11 \pm 0.70) \times 10^5$
Treated fiber, latex	$(9.60 \pm 1.24) \times 10^5$	$(3.53 \pm 0.43) \times 10^3$	$(1.14 \pm 0.18) \times 10^6$	$(6.03 \pm 0.94) \times 10^3$	$(2.35 \pm 0.24) \times 10^5$	$(2.50 \pm 0.26) \times 10^5$	$(4.74 \pm 0.49) \times 10^5$
Untreated fiber, silica fume	$(8.43 \pm 1.52) \times 10^5$	$(6.30 \pm 0.77) \times 10^4$	$(9.52 \pm 1.15) \times 10^5$	$(6.80 \pm 0.89) \times 10^4$	$(1.10 \pm 0.13) \times 10^4$	$(1.17 \pm 0.14) \times 10^4$	$(2.50 \pm 0.22) \times 10^4$
Treated fiber, silica fume	$(8.07 \pm 1.13) \times 10^5$	$(4.29 \pm 0.44) \times 10^3$	$(8.79 \pm 1.01) \times 10^5$	$(9.13 \pm 1.19) \times 10^3$	$(0.96 \pm 0.10) \times 10^4$	$(1.01 \pm 0.12) \times 10^4$	$(2.12 \pm 0.17) \times 10^4$

P: dry condition, horizontal measurement direction, configuration of Fig. 1.
Q: wet condition, horizontal measurement direction, configuration of Fig. 1.
R: dry condition, vertical measurement direction, configuration of Fig. 1.
S: wet condition, vertical measurement direction, configuration of Fig. 1.
T: dry condition, horizontal measurement direction, configuration of Fig. 2.
U: dry condition, vertical measurement direction, configuration of Fig. 2.
V: dry condition, horizontal measurement direction, configuration of Fig. 3.

reinforced cement for resistance heating (deicing), a high conductivity is required, so a fiber volume fraction above the percolation threshold is necessary.

Above the percolation threshold, the conduction is dominated by the fibers, due to the electrical connectivity provided by the fibers. Below the percolation threshold, the conduction involves both fibers and cement matrix. Therefore, for the purpose of investigating the relative importance of ionic conduction and electronic conduction, this work addresses carbon fiber reinforced cement with a fiber volume fraction below the percolation threshold.

As water provides ions, ionic conduction becomes more significant as the water content of the cement-based material increases. Therefore, this work includes study of the effect of water content on the mechanism of electrical conduction by addressing the state of being saturated with water (called the wet state) and the state of having been dried at room temperature (called the dry state). The dry state is associated with less free water than the wet state. It is practically more important than the wet state, since structures are seldom saturated with water. The dry state of this work is to be distinguished from the excessively dry state that is obtained by heating, which drives out additional water.

The electrical conductivity of carbon fiber reinforced cement below the percolation threshold increases with increasing degree of fiber dispersion [29]. The degree of dispersion can be improved by the use of admixtures and fiber surface treatment. Silica fume, which is in the form of fine particles of size around 0.1 μm, is a particularly effective admixture for improving the degree of fiber dispersion, due to the fine particles helping to separate the fibers during mixing. The degree of fiber dispersion can also be improved by the use of fiber surface treatments (e.g., ozone treatment, which provides oxygen-containing functional groups on the surface of the fiber [30]) that increase the degree of hydrophilicity of the carbon fiber. As carbon is hydrophobic in nature and water is in the mix, improved hydrophilicity is helpful for increasing the wettability of the fiber by water [30].

The interface between fiber and the cement matrix is also affected by admixtures and fiber surface treatment [31,32]. This interface affects the quality of the electrical contact between the fiber and the cement matrix, thereby affecting the electrical conduction. Polymeric admixtures such as latex [33,34], as used for increasing the toughness and decreasing the water permeability, line the interface, thereby increasing the contact electrical resistivity between fiber and matrix. Ozone treatment of the carbon fiber results in functional groups on the surface of the fiber, thereby also increasing the contact resistivity [30].

Due to the effects of admixtures and fiber surface treatment on the degree of fiber dispersion and on the fiber–matrix interface, this paper includes a study of the effects of admixtures and fiber surface treatment on the mechanism of electrical conduction. The admixtures investigated in this work are silica fume and latex. The fiber surface treatment investigated in this work is ozone treatment.

The short carbon fibers are essentially random in their orientation. However, due to gravity, they have a slight preferred orientation in the horizontal plane during the setting and curing [4]. As a consequence of the preferred orientation, the electrical conductivity is expected to be slightly higher in the horizontal plane than in the vertical direction. This directional dependence reflects the effect of the fibers on the electrical conduction. Therefore, this paper includes a study of this directional dependence.

2. Experimental methods

2.1. Materials

The cement-based materials are cement pastes. In other words, there is no aggregate. Four compositions of carbon fiber reinforced cement are studied, namely (i) paste with untreated carbon fiber (i.e., carbon fiber without surface treatment) and latex, (ii) paste with ozone treated carbon fiber and latex, (iii) paste with untreated carbon fiber and silica fume, and (iv) paste with ozone treated carbon fiber and silica fume.

The carbon fiber is turbostratic carbon made from isotropic pitch. It is unsized and of diameter 15 μm, nominal length 5 mm and electrical resistivity $3.0 \times 10^{-3}\ \Omega$ cm, as obtained from Ashland Petroleum Co. (Ashland, Kentucky). The fiber properties are shown in Table 1 of Ref. [35]. Fibers are in the amount of 0.5% by mass of cement (corresponding to 0.5 vol%).

The ozone treatment of the fibers, as conducted prior to incorporating the fibers in the cement mix, involves drying the fibers at 110 °C in air for 1 h and then surface treating with ozone by exposure to ozone gas (0.6 vol% in oxygen) at 160 °C for 10 min [30].

The cement is Portland cement (Type I) form Lafarge Corp. (Southfield, MI). The water–cement ratio is 0.35 for pastes containing silica fume and is 0.23 for pastes containing latex. Due to the fact that the latex is a dispersion that contains water and about 48% of latex particles, the true water/cement ratio is 0.33 for the case with latex. No aggregate is used. In case that the mix contains silica fume, a water-reducing agent (TAMOL SN, Rohm and Haas, Philadelphia, PA) is used in the amount of 1.0% by mass of cement.

The silica fume (Elkem Materials Inc., Pittsburgh, PA, microsilica, EMS 965) is in the amount of 15% by mass of cement. The methylcellulose (Dow Chemical Corp., Midland, MI, Methocel A15-LV) is in the amount of 0.4% by mass of cement and is used along with the silica fume. The defoamer (Colloids Inc., Marietta, GA, 1010) is in the amount of 0.13 vol% (% of specimen volume) and is used along with the methylcellulose.

The latex is used in the amount of 20% by mass of cement and is a styrene butadiene polymer (Dow Chemical Co., Midland, MI, 460NA) with the polymer making up about 48% of the dispersion and with the styrene and butadiene having a mass ratio of 66:34. The antifoaming agent (Dow Corning Corp., Midland, MI, #2210) used along with the latex is in the amount of 0.5% by mass of cement.

A rotary mixer with a flat beater is used for mixing. Methylcellulose (if applicable) is dissolved in water and then the defoamer is added and stirred by hand for about 2 min. Latex (if applicable) is mixed with the antifoaming agent by hand for about 1 min. Then the methylcellulose solution (if applicable), the latex mixture (if applicable), cement, water, silica fume (if applicable) and fibers are mixed in the mixer for 5 min. After pouring into steel molds of size 51 × 51 × 51 mm (2 × 2 × 2 in.), an external vibrator is used to facilitate compaction and decrease the amount of air bubbles. The specimens are demolded after 24 h and then cured in air at room temperature and a relative humidity of 100% for 28 days.

Specimens in the wet state are obtained by removal from the 100% relative humidity chamber and subjecting the specimens to testing while the specimens are still saturated with water. Specimens in the dry state are obtained by removal from the 100% relative humidity chamber and allowing them to dry in air at room temperature for a few days.

2.2. Testing

DC electrical conductivity measurement is conducted by using the four-probe method and the configurations of Figs. 1–3. Fig. 1 involves current contacts that are in the form of an ionic conductor, whereas Fig. 2 involves current contacts that are in the form of an electronic conductor. In each of Figs. 1–3, the four electrical contacts are labeled A, B, C and D, where A and D are for passing current, while B and C are for voltage measurement. A Keithley 2002 multimeter is used for resistance measurement. For the purpose of avoiding polarization, each resistance measurement was taken within 1 s from the start of current application. The data acquisition at a rate of 1 per s is conducted for at least 10 s, but only the first data point (i.e., that at 1 s) is used. Over the measurement period of typically 10–15 s, the measured resistivity increases very slightly, due to polarization.

The specimens are cubes. In Fig. 1, the two current contacts (labeled A and D) are located at two opposite sides of the cube. Each of the two current contacts is in the form of an aqueous solution containing 0.33 M potassium hydroxide (KOH) and 0.13 M sodium hydroxide (NaOH). The use of this solution is to approach the electrical conductivity of ordinary Portland Cement (OPC) pore solution [25]. The solution is in a sponge with a stainless steel foil (64 × 51 × 51 mm) inserted in the sponge in the plane of the sponge. The two voltage contacts (labeled B and C) are located at two planes that are 25 mm apart and that are both parallel to the abovementioned two opposite sides of the cube. Each of the two voltage contacts is in the form of silver paint in conjunction with copper wire, which is wound around the entire perimeter of the cube.

Fig. 2 is similar to Fig. 1 except that the two current contacts are in the form of silver paint applied on the entirety of each of the two opposite surfaces. Fig. 2 is similar to Fig. 3 except that the two current contacts are applied to the entirety of each of the two opposite surfaces in Fig. 2, whereas they are around the perimeter at two interior planes labeled A and D in Fig. 3. In Fig. 3, the voltage contacts are 30 mm apart, while the current contacts are 40 mm apart. Due to the greater uniformity of the current density in the region between the voltage contacts, the use of current contacts that are on the entire opposite surfaces is expected to give more accurate resistivity results than the use of all perimetric contacts. However, the latter is more suitable for practical implementation. Thus, the latter is the most common configuration in prior work on carbon fiber reinforced cement.

Three specimens were tested for each combination of composition (four compositions), moisture content (two levels of moisture content), measurement method (three methods corresponding to Figs. 1–3) and measurement direction (two directions). The combinations are listed in Table 1. These combinations do not include the case involving the wet condition and the method of Fig. 3. This is because the time (about 1 day or more) required for the silver paint to dry thoroughly in air at room temperature does not allow electrical measurement to be conducted for a specimen in the wet condition.

3. Results and discussion

Table 1 shows the electrical resistivity obtained for various combinations of composition, moisture content (wet and dry conditions), resistivity measurement method (configurations of Figs. 1–3) and resistivity measurement direction (horizontal and vertical directions during setting and curing). Table 2 shows the corresponding values of the electrical conductivity.

As the conductivity for P (dry state) is contributed just by ions, whereas that for T (dry state) is contributed by both ions and electrons, subtraction of P from T gives the electronic contribution in the dry state for the configuration of Fig. 2. This is for the horizontal direction. For the vertical direction, subtraction of R from U gives the electronic contribution. The resulting relative contributions of ionic conduction and electronic conduction to the overall conductivity are shown in Table 3 for both horizontal and vertical directions. For both directions, the electronic contribution is large compared to the ionic contribution for all four compositions of carbon fiber reinforced cement. When silica fume rather than latex is present, the electronic contribution dominates over the ionic contribution. Though the true water/cement ratio is lower for latex (0.33) than silica fume (0.35), the fractional ionic conduction contribution is much higher for latex than silica fume (Table 3). That silica fume enhances the fractional electronic conduction contribution is attributed to the good fiber dispersion, which is known to be helped by the presence of silica fume [29]. It is also known that latex results in poorer fiber dispersion than silica fume [2]. The good fiber dispersion rendered by silica fume makes the fiber more influential in affecting the conductivity, thereby causing the electronic contribution to be more significant to the overall conductivity.

The ratio of wet ionic conductivity to dry ionic conductivity is shown in Table 4, as obtained by dividing the conductivity for Q (wet) by that for P (dry) in case of the horizontal direction and dividing the conductivity for S (wet) by that for R (dry) in case of the vertical direction. The wet ionic conductivity is large compared to the dry ionic conductivity for all four compositions, as shown by the ratio exceeding 1 for all cases. This is consistent with the report that the AC conductivity of cement (without fiber) decreases with the hydration time [25].

The ratio of wet ionic conductivity to dry ionic conductivity is much higher for treated fiber than untreated fiber,

Table 2

Measured electrical conductivity $(\Omega\,\mathrm{cm})^{-1}$ for four compositions of carbon fiber reinforced cement below the percolation threshold

	P	Q	R	S	T	U	V
Untreated fiber, latex	$(9.52 \pm 1.59) \times 10^{-7}$	$(1.71 \pm 0.14) \times 10^{-5}$	$(8.13 \pm 1.23) \times 10^{-7}$	$(1.32 \pm 0.19) \times 10^{-5}$	$(3.41 \pm 0.37) \times 10^{-6}$	$(3.18 \pm 0.35) \times 10^{-6}$	$(1.66 \pm 0.19) \times 10^{-6}$
Treated fiber, latex	$(1.06 \pm 0.14) \times 10^{-6}$	$(2.88 \pm 0.35) \times 10^{-4}$	$(8.99 \pm 1.41) \times 10^{-7}$	$(1.70 \pm 0.26) \times 10^{-4}$	$(4.30 \pm 0.44) \times 10^{-6}$	$(4.04 \pm 0.42) \times 10^{-6}$	$(2.13 \pm 0.22) \times 10^{-6}$
Untreated fiber, silica fume	$(1.23 \pm 0.22) \times 10^{-6}$	$(1.61 \pm 0.20) \times 10^{-5}$	$(1.06 \pm 0.13) \times 10^{-6}$	$(1.50 \pm 0.20) \times 10^{-5}$	$(9.22 \pm 1.09) \times 10^{-5}$	$(8.67 \pm 1.04) \times 10^{-5}$	$(4.04 \pm 0.36) \times 10^{-5}$
Treated fiber, silica fume	$(1.27 \pm 0.18) \times 10^{-6}$	$(2.36 \pm 0.25) \times 10^{-4}$	$(1.16 \pm 0.14) \times 10^{-6}$	$(1.11 \pm 0.15) \times 10^{-4}$	$(1.05 \pm 0.11) \times 10^{-4}$	$(1.00 \pm 0.12) \times 10^{-4}$	$(4.75 \pm 0.38) \times 10^{-5}$

P: dry condition, horizontal measurement direction, configuration of Fig. 1.
Q: wet condition, horizontal measurement direction, configuration of Fig. 1.
R: dry condition, vertical measurement direction, configuration of Fig. 1.
S: wet condition, vertical measurement direction, configuration of Fig. 1.
T: dry condition, horizontal measurement direction, configuration of Fig. 2.
U: dry condition, vertical measurement direction, configuration of Fig. 2.
V: dry condition, horizontal measurement direction, configuration of Fig. 3.

Table 3

Relative contributions of ionic conduction and electronic conduction to the overall electrical conductivity of the dry state (configuration of Fig. 2) for four compositions of carbon fiber reinforced cement below the percolation threshold

	Horizontal[a]		Vertical[b]	
	Fraction ionic	Fraction electronic	Fraction ionic	Fraction electronic
Untreated fiber, latex	0.28	0.72	0.26	0.74
Treated fiber, latex	0.25	0.75	0.22	0.78
Untreated fiber, silica fume	0.013	0.987	0.012	0.988
Treated fiber, silica fume	0.012	0.988	0.012	0.988

[a] Based on the conductivity data in Table 2 for P (ionic contribution) and T (ionic plus electronic contributions).

[b] Based on the conductivity data in Table 2 for R (ionic contribution) and U (ionic plus electronic contributions).

Table 4
Ratio of wet ionic conductivity to dry ionic conductivity for four compositions of carbon fiber reinforced cement below the percolation threshold

	Horizontal[a]	Vertical[b]
Untreated fiber, latex	18.0	16.2
Treated fiber, latex	272	189
Untreated fiber, silica fume	13.1	14.2
Treated fiber, silica fume	186	95.7

[a] Q (wet) divided by P (dry), using the conductivity data in Table 2.
[b] S (wet) divided by R (dry), using the conductivity data in Table 2.

whether silica fume or latex is present (Table 4). This means that the fiber treatment helps ionic conduction, probably because of the interaction of the moving ions with the electric dipoles associated with the surface functional groups imparted by the ozone treatment.

The ratio of wet ionic conductivity to dry ionic conductivity is higher for latex than silica fume, whether the fiber is treated or not (Table 4). This effect of latex is consistent with the report that latex addition (20% by mass of cement, as in this work) to cement increases the relative dielectric constant [37]. In contrast, silica fume addition (15% by mass of cement, as in this work) to cement decreases the relative dielectric constant [37]. The difference between latex and silica fume is particularly large when the fiber is treated (Table 4). This is consistent with the notion (mentioned in the last paragraph) that the fiber treatment helps ionic conduction.

Comparison of Q (wet) and T (dry) for the horizontal direction and of S (wet) and U (dry) for the vertical direction shows that, for the same direction, the ionic conductivity (configuration of Fig. 1) of the wet state is much higher than the electronic conductivity (configuration of Fig. 2) of the dry state when latex is present. However, when silica fume rather than latex is present and the fiber is treated, the conductivity of the wet state (Q and S) is only slightly higher than or comparable to that of the corresponding dry state (T and U respectively). When silica fume is present and the fiber is not treated, the conductivity of the wet state (Q and S) is lower than that of the corresponding dry state (T and U respectively). This effect of silica fume is attributed to the good fiber dispersion [29]. Latex results in poorer fiber dispersion than silica fume [2]. The good fiber dispersion rendered by silica fume makes the fiber more influential in affecting the conductivity, thereby causing the electronic contribution to be more significant to the overall conductivity. A stronger electronic contribution makes the conductivity for T higher. That the electronic contribution is stronger for silica fume than latex is shown in Table 3. The particularly high conductivity for T in the case of silica fume and untreated fiber is probably because the low contact electrical resistivity of the fiber–matrix interface when untreated fiber is used [30] and the good fiber dispersion when silica fume is used [29] making the electronic conduction contribution to T so strong that the conductivity for T (dry state) exceeds that for Q (wet state).

That electronic conduction is much more significant than ionic conduction in the dry state (Table 3) is consistent with the report that holes dominate the Seebeck effect of carbon fiber reinforced cement (dry state) [15,21]. Moreover, it is consistent with the fact that the DC electrical resistivity increases with increasing curing age less significantly for carbon fiber reinforced cement (dry state) than for plain cement (dry state) [36]. It is also consistent with the report that electric polarization is small in carbon fiber reinforced cement (dry state) compared to plain cement (dry state) [28].

The finding that electronic conduction is much more significant than ionic conduction in the dry state for carbon fiber reinforced cement below the percolation threshold (Table 3) implies that electronic conduction is even more significant above the percolation threshold. This is consistent with the report that the relative dielectric constant is decreased as the carbon fiber volume fraction in cement is increased from a value below the percolation threshold to one above the percolation threshold [37]. That electronic conduction dominates above the percolation threshold is because the electrical continuity provided by the fibers above the threshold makes the fibers dominate the conduction and the fibers are an electronic conductor. Therefore, the use of electrical contacts in the form of electronic conductors in practical applications (e.g., strain sensing) that utilize the electrical conductivity of carbon fiber reinforced cement is valid, whether the fiber volume fraction is below or above the percolation threshold.

Ozone treatment seems to decrease the resistivity for all cases in Table 1. This occurs in spite of the increase in fiber–matrix contact resistivity due to the ozone treatment [30]. The resistivity decrease is slight and not totally clear, due to the data scatter involved. It is attributed to an increase in the degree of fiber dispersion [30]. This applies to both cement with silica fume and cement with latex. It applies to ionic conductivity (configuration of Fig. 1) as well as combined electronic and ionic conductivity (configuration of Fig. 2). It applies to both horizontal and vertical directions of measurement. It applies to both dry and wet states, such that the treatment raises the conductivity more for the wet state (Q and S) than the dry state (P, R, T and U), whether latex or silica fume is present. For the wet state, the conductivity is increased by about an order of magnitude due to the treatment. In the dry state, the conductivity is increased only slightly, if at all, by the treatment. The increase in conductivity is because of the increase in hydrophilicity (due to the oxygen-containing functional groups imparted by the ozone treatment) and the consequent increased degree of fiber dispersion, as previously reported [29,30]. That the conductivity increase due to the fiber treatment is more in the wet state than the dry state is attributed to the interaction of the moving ions, which are plentiful in the wet state, with the electric dipoles associated with the functional groups on the fiber surface. In other words, this interaction helps the ionic conduction, thereby increasing the ionic conductivity. Thus, the conductivity measurement technique (whether using the configuration of Fig. 1 or that of Fig. 2) is capable of distinguishing between small differences in the degree of fiber dispersion. These small differences are too subtle to be observed by microscopy, but are revealed by electrical conductivity measurement.

Silica fume (15% by mass of cement) as an admixture gives considerably higher conductivity than latex (20% by mass of cement) for T (dry state, using the configuration of Fig. 2). However, for the same fiber condition (treated or untreated), latex results in an ionic conductivity (Q, wet state, using the configuration of Fig. 1) that is slightly higher, if at all, than silica fume. This effect of latex is consistent with the report that latex addition (20% by mass of cement) to cement increases the relative dielectric constant [37]. That latex results in a relatively low conductivity (T, with the electronic and ionic contributions combined) in carbon fiber reinforced cement is consistent with the report that the electrical resistivity of cement (whether without or with 0.5 vol% carbon fiber) increases with increasing latex/cement ratio [2]. That silica fume results in a relatively high conductivity (T, with the electronic and ionic contributions combined) is consistent with the report that the fractional increase in electronic conductivity due to carbon fiber addition to cement is much higher when silica fume (15% by mass of cement) is present than when latex (20% by mass of cement) is present [2]. That silica fume results in an ionic conductivity (Q) that is slightly lower, if at all, than latex is consistent with the report that silica fume addition (15% by mass of cement) to cement decreases the relative dielectric constant [37]. Electrons cannot readily go through latex, which increases the contact electrical resistivity of the fiber–matrix interface [38], whereas ions possibly can (probably due to the interaction of the ions with the electric dipoles in latex). Thus, to attain a relatively high ionic conductivity (the configuration of Fig. 1), latex may be preferred. However, due to the fact that latex gives only a slight (if any) ionic conductivity increase compared to silica fume, the preference of latex over silica fume for a high ionic conductivity is weak. However, to attain a high conductivity, with the electronic and ionic contributions combined, using the configuration of Fig. 2, silica fume is definitely recommended.

Comparison of Q and S, of P and R, and of T and U shows that the vertical conductivity is slightly lower than the horizontal conductivity. This applies to both wet and dry states, and to the configurations of both Figs. 1 and 2. This is due to the slight preferred orientation of the fibers in the horizontal plane during setting and curing. The preferred orientation is slight. The slightness is expected, since the fibers (nominally 5 mm long) are much shorter than the specimen dimension (51 mm). It has been previously reported that, the smaller is the specimen thickness during setting and curing, the greater is the degree of preferred orientation of the fibers [4]. Although the fibers are an electronic conductor, the fiber preferred orientation similarly affects the ionic conductivity and the electronic conductivity. In particular, the fibers similarly affect the wet and dry states. This means that the fibers affect both the electronic conduction and the ionic conduction.

That the carbon fibers affect the ionic conduction is consistent with the report that carbon fiber addition to cement increases the relative dielectric constant [37] and hastens electric depolarization [27]. This effect of the fibers is probably because of the functional groups on the fiber surface [30]. The electric dipoles associated with the functional groups may interact with the ions that contribute to ionic conduction. In contrast, the addition of steel fiber to cement decreases the relative dielectric constant [37]. Although carbon fiber and steel fiber are both electronic conductors, their surface chemistry is very different.

Comparison of U and V shows that the configuration of Fig. 2 gives conductivity values (Table 2) that are about twice of the corresponding values provided by the configuration of Fig. 3. This is due to the more uniform current density distribution in the part of the specimen between the voltage contacts for Fig. 2. The non-uniformity in the case of the configuration of Fig. 3 is due to the insufficiently large distance (5 mm) between the adjacent current and voltage contacts. Because it takes some distance of electron flow from a surface current contact in order for current to penetrate the specimen fully, this non-uniformity can be alleviated or removed by increasing this distance relative to the thickness of the specimen. Thus, a specimen in the shape of a beam [35] is more suitable than a cubic specimen. The resistivity obtained using the method of Fig. 2 is more accurate than that obtained using the method of Fig. 3. However, Fig. 3 is practically more suitable than Fig. 2, due to the common difficulty of accessing two opposite surfaces of a concrete structural component.

4. Conclusion

Electrical conduction in carbon fiber reinforced cement with a fiber volume fraction below the percolation threshold involves electrons and ions. In the dry state (the state of practical importance attained by room temperature drying), electronic conduction is more significant than ionic conduction, whereas in the wet state (water saturated state), ionic conduction dominates. When silica fume is present with the fiber, the fractional electronic contribution to the dry overall conductivity (with both electronic and ionic contributions), as measured using electrical contacts that are an electronic conductor, is 0.99. When latex is present with the fiber, the contribution is 0.72–0.78. The ratio of the wet ionic conductivity to the dry ionic conductivity (both conductivities measured using electrical contacts in the form of an ionic conductor) is much increased by fiber surface treatment and is higher when latex rather than silica fume is used. The wet ionic conductivity is much higher than the dry overall conductivity when latex is present, but is lower than or comparable to the dry overall conductivity when silica fume is present. In particular, the wet ionic conductivity is lower than the dry overall conductivity when the fiber is not treated and silica fume is present.

Although the fibers are an electronic conductor, they affect both the electronic conduction and the ionic conduction. In particular, the ozone treatment of the fiber surface helps the ionic conduction. Latex as an admixture helps provide a relatively high ionic conductivity, whereas silica fume as an admixture helps provide a relatively high electronic conductivity.

DC electrical conductivity measurement (with the current associated with the measurement applied within a period of only about 1 s), whether using electrical contacts that are ionic conductors or those that are electronic conductors, is capable of distinguishing between small differences in the degree of fiber dispersion, such as that resulting from fiber surface treatment.

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