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Enhanced thermoelectric effect of cement composite by addition of metallic oxide nanopowders for energy harvesting in buildings

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HIGHLIGHTS

- Metallic oxide nanopowders were incorporated in the cement composite.
- This cement composite exhibited enhanced Seebeck coefficient.
- The introduced interfaces and enhanced DOS contributed to enhanced Seebeck coefficient.
- The composite has potential application in energy conservation in buildings.

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ABSTRACT

In this paper, metallic oxide nanopowders were incorporated in cement matrix to increase the thermoelectric effect of cement composites. It can be seen from the result that the Seebeck coefficient of these composites increased steadily with metallic oxide content. And the Seebeck coefficients of these composites were measured to be higher than 1000 μV/°C, which were about 10 times higher than that of fiber reinforced cement composites indicated earlier. The increased surface density of the electronic state near the Fermi energy level of the nanostructured metallic oxide is very possibly responsible for the enhanced Seebeck coefficient of the cement composites. The high Seebeck coefficient of this kind of cement composite is important for the potential application in energy harvesting and air-conditioning system of future buildings.

1. Introduction

Thermoelectric effect, providing a method for converting thermal energy to electrical energy, is expected to play an important role in dealing with energy shortage. For example, thermoelectric cooling technologies are gaining more interest in the field of energy conservation in buildings [1,2]. In the former study of thermoelectric cooling technologies, thermoelectric devices made of traditional thermoelectric materials such as Bi_2Te_3 were installed on the wall and window [3]. But if the concrete wall possesses thermoelectric characteristics itself, the application of its thermoelectric effect will be more effective and convenient for energy harvesting and refrigerating. The concrete materials which possess thermoelectric effect for energy harvesting are characterized by zero energy consumption, environmentally friendly and low converting coefficient, so the benefits and drawbacks are clear.

Thermoelectric effect in cement based materials was firstly reported by Sun et al. [4,5]. The reported material was made of cement paste, short carbon fibers and a disperser. And carbon fibers contributed the majority of the total thermoelectric effect in the composite. Almost at the same time, Wen and Chung researched the thermoelectric effect of carbon/steel fiber reinforced cement composites systematically. It was found that the Seebeck coefficient was about 5.5 and 68.0 μV/°C for carbon and steel fiber reinforced cement composites with a fiber content of 1.0% by mass of cement respectively [6,7]. In addition, they pointed out the origin of the thermoelectric behavior of carbon/steel fiber reinforced cement paste [8,9].

But the absolute thermoelectric power has to be increased greatly before its application in energy harvesting, so more attention was paid to increase the thermoelectric effect of cement composite since then. Substituting ordinary polyacrylonitrile fibers with bromine-intercalated carbon fibers, Wen and Chung

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increased the Seebeck coefficient of carbon fiber reinforced cement composite from 5.5 to 21.2 μV/°C [10]. Zuo et al. increased the Seebeck coefficient to 23.5 μV/°C by incorporating carbon nanotubes to carbon fiber reinforced cement composite [11]. Demirel and Yazicioglu obtained absolute Seebeck coefficient up to 127 μV/°C from carbon fiber reinforced lightweight concrete with silica fume inside [12]. And Wei et al. obtained Seebeck coefficient up to 100.28 μV/°C by incorporating 5.0% Bi_2O_3 microparticles by mass of cement in the cement matrix [13]. However, these obtained Seebeck coefficients are not high enough for their potential use in ambient energy harvesting, coolers or structural health monitoring [14–16]. To increase the Seebeck coefficient of cement composites by order of magnitude, incorporating new thermoelectric component may be an effective method.

Historically, the Seebeck effect was discovered early in the 19th century. In the 1950s, the field of thermoelectric advanced rapidly when more and more heavily doped semiconductors exhibited good thermoelectric effects. However, this field regained much attention until 1990s, when new research directions were found to develop the next generation of thermoelectric materials. Two different research approaches were proposed: one using new families of advanced bulk thermoelectric materials [17–21], and the other using low-dimensional materials systems [22–24]. As a result of this guide, Hochbaum et al. verified silicon nanowires as a kind of effective thermoelectric materials [25], and Song et al. found the Seebeck coefficient of MnO_2 nanopowder was higher than 20,000 μV/°C [26]. Transition metal oxides are gaining increasing attention for their thermoelectric properties due to their high temperature stability, tunable electronic and phone transport properties and well established synthesis techniques [27]. Based on the aforementioned promising properties, low-dimensional transition metal oxide was chosen as thermoelectric component to increase the thermoelectric effect of cement composites in this paper.

In this study, the nanostructured ZnO and Fe_2O_3 powder are incorporated in cement composites. It shows that the introduction of ZnO and Fe_2O_3 powder can significantly influence the Seebeck coefficient of cement composites. The giant Seebeck coefficient of higher than 1000 μV/°C is obtained by incorporating a little metallic oxide nanopowders in the cement composites. Moreover, the enhancement mechanism is discussed in detail and the potential application of the composites in energy harvesting of future buildings is indicated.

2. Materials and methods

2.1. Cement paste specimens

Portland cement (P) was used in conformance with Standard EN 197-1(2000), and the composition and properties of available cement and silica fume are described in Table 1. ZnO and α-Fe_2O_3 powder were purchased from Macklin Biochemical Co., Ltd, Shanghai. The as-received ZnO powder was 50 ± 10 nm in diameter and spherical Fe_2O_3 was 30 ± 5 nm in diameter.

The dosage of silicon fume was fixed 15% by mass of cement, and the water/cement ratio was fixed 0.46. The dosage of ZnO and Fe_2O_3 nanoparticles into cement composites were 1.0, 2.0, 3.0, 4.0 or 5.0 wt% by mass of cement. The cement composites were prepared following the standard mixing procedure (using a Perrier planetary mixer) which consists of the following steps: mixing the dry components at low speed (60 rpm) for 30 s; joining the required quantity of kneading water and mixing at low speed for 30 s; scraping down the sides of the mixer bowl for about 30 s and mixing at low speed for 30 s. After mixing, the specimens were cast in steel molds with a size of 40 × 40 × 160 mm^3 and compacted with a vibrating table. After casting, the specimens were cured at 20 ± 1 °C and 90 ± 5% humidity for 24 h, and then demolded. After demolding, the specimens were cured under standard curing conditions for 14 days. Before the test of Seebeck coefficient, thermal conductivity and electrical conductivity, samples were dried at 105 °C for 24 h and then cooled at room temperature to remove the moisture inside, under which treatment the heat transportation could be more uniform.

2.2. Characterizations of the ZnO and α-Fe_2O_3 nanoparticles

The ZnO and α-Fe_2O_3 nanoparticles in this work were identified by X-ray diffraction (XRD). XRD pattern measurements were carried out by a Ultima IV diffractometer (Japan) using the Cu Kα (k = 1.5418 Å, tube voltage: 40 kV, tube current: 40 mA) at room temperature. XRD pattern scanned within the range of 2θ from 10° to 80°, with a step width of 0.02° and an acquisition time of 0.01 s per step. The crystalline phases were identified with the corresponding JCPDS diffraction data cards. The particle sizes and morphologies of the nanoparticles were analyzed using a scanning electron microscope (SEM) (Tabletop Microscope, S3400, HITACHI, Japan).

2.3. Electrical conductivity, thermal conductivity and Seebeck coefficient measurements

The electrical conductivity of the cement paste specimen with the size of 40 × 40 × 160 mm^3 was measured using the four-probe method, as illustrated in Fig. 1 [28]. The electrical conductivity measurement involving the use of current contacts (A and D) in the form of copper wire adhered by silver paste and voltage contacts (B and C) in the form of copper electrodes. Two Fluke B15 multimeters were used to test the current flowing through the specimen and the voltage between the two copper electrodes. According to the definition of electrical conductivity of a specimen, σ can be calculated by the following equation:

$$\sigma = \frac{1}{\rho} = \frac{L}{S}\frac{I}{V} \tag{1}$$

where σ and ρ are the electrical conductivity and resistivity of the specimen, respectively; I and V are the tested current and voltage values; L and S are the length and cross-sectional area of the specimen.

The thermal conductivity of the cement paste specimen with the size of 300 × 300 × 20 mm^3 was measured using a steady-state conductivity tester (DRH-300, China), as shown in Fig. 2. Prior to conducting the test, all specimens were dried in an oven at 105 °C for 24 h and then cooled to room temperature to remove the moisture inside. The specimen was placed between the cold plate and hot plate, and the temperature difference between the two sides was controlled by the heating and cooling system. The temperature value of the cold plate and hot plate was set as 20 °C and 70 °C respectively. Thus the thermal conductivity of the cement paste specimen can be calculated by the formula as follows:

$$\kappa = \frac{I \cdot U \cdot d}{S \cdot \Delta T} \tag{2}$$

where κ is the thermal conductivity of the specimen, I and U are the current and voltage of the heatmeter, respectively; d, S and ΔT are the thickness, cross-sectional area and temperature difference between the two sides of the specimen.

The schematic of the apparatus for measuring thermoelectric voltage around room temperature was shown in Fig. 3. Two ends of the hydrated cement composite samples were covered with a copper sheet. Heat was applied through one side (40 × 40 mm^2) to the other side of the specimen by a platelet resistance heater.

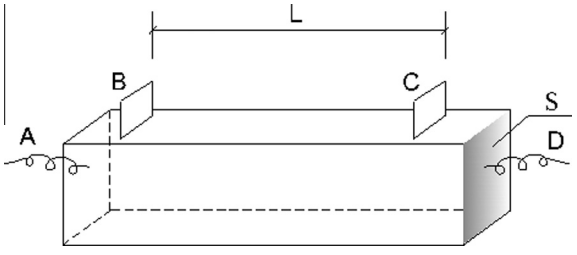

Fig. 1. Cement paste specimen for electrical conductivity measurements.

Table 1
Compositions and properties of Portland cement (P) and silica fume (S).

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	TiO_2	Density (g/cm^3)	Specific surface (m^2/kg)
P	21.42	5.63	2.70	63.32	1.91	3.43	0.68	0.29	3.12	346
S	95.80	1.76	0.10	0.40	0.52	–	0.87	–	2.46	19,000