# Thermoelectric Characteristics of Graphene and Aluminum Doped Zinc Oxide Nanopowder Enhanced Cement Composite for Low-Temperature Applications

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## **ABSTRACT HEADING**

Thermoelectric (TE) cement composite is a new type of TE material. Unlike ordinary cement, due to the inclusion of additives, TE cement can mutually transform thermal energy into electrical energy. In extreme weather, the large temperature difference between indoor and outdoor can be harvested by TE cement to generate electricity. In moderate weather, given power input, the same material can provide cooling/heating to adjust room temperature and reduce HAVC load. Therefore, TE cement has the energy-saving potential in the application of building enclosures and energy systems. Its ability to convert different forms of energy and use low-grade energy is conducive to the operation of net-zero buildings. In this study, the graphene nanoplatelets and aluminum-doped zinc oxide nanopowder enhanced cement composite, was fabricated. The performance indicator of TE materials includes the dimensionless figure of merit ZT, calculated by Seebeck coefficient, thermal conductivity, and electrical conductivity. These TE properties were measured and calculated by a Physical Property Measurement System at different temperatures. The highest ZT of 15wt.% graphene and 5wt.% AZO enhanced cement composite prepared by the dry method is about 5.93E-5 at 330K.

## INTRODUCTION

Energy crisis and environmental degradation make people pay more attention to the use of renewable energy and lowgrade energy. Hence, thermoelectric (TE) technology becomes a promising research topic. TE technology can convert heat into electricity. In the hot summer, the exterior surface of the city will aggravate the urban heat island effect and have an essential impact on urban energy consumption. Therefore, researchers combine the traditional TE module with the pavement, which not only takes away the heat of the road to cool the surface, but also make use of low-grade energy to generate electricity (Datta et al., 2017; Hasebe et al., 2006; Jiang et al., 2017, 2018; Tahami et al., 2019). On the other hand, TE technology can directly convert electricity into heat absorption and dissipation. TE cooler/heater has been used in building envelope, to provide active cooling or heating for buildings (Ibañez-Puy et al., 2018; Irshad et al., 2015; Khire et al., 2005; Liu et al., 2015). However, the existing studies use commercial TE modules that need to be embedded inside or on the surface of the infrastructure. To improve the integration of the TE system and maximize the use of temperature differences for a better performance of heat transfer, the TE cement composite as building envelope materials has been proposed. The key to improving the performance of TE cement-based enclosure is to develop cement with high TE performance. A unique property of TE materials is the Seebeck coefficient (S), which is the ratio of the output open-circuit voltage ( $\Delta V$ ) to the input temperature difference ( $\Delta T$ ). For TE cement, the choice of additives plays a vital role in its TE properties. In recent years, research began to focus on graphite/graphene and carbon nanotubes as additives. In this study, the graphene and aluminumdoped zinc oxide nanomaterials enhanced cement composite, was fabricated by the dry mixing and compression method and characterized by physical property measurement system.

# METHODOLOGY

This study used Portland cement (Type I) from Buzzi Unicem, USA. The additive used grade-H graphene nanoplatelets (xGnP), with an average particle diameter of 5 µm, purchased from XGSciences, USA. Another additive used the Aluminum (5wt%) doped Zinc Oxide nanoparticles (AZO) with an average diameter of 300 nanometers, from US Research Nanomaterials, USA. One TE cement sample, with the concentration of xGnP around 15wt.% and the concentration of AZO around 5 wt.% was fabricated by the dry mixing and compressing method. In the dry method, the cement powder and additives were mixed without the use of water and dispersant. Then, the homogeneous mixture was placed in a customized cylindrical stainless-steel mold with a metal strip and die block. A Mechanical Test System (MTS) applied the pressure at 50 MPa to the metal strip, which compressed the dry mixture into a cylinder with a diameter of 9.5 mm (3/8 inches) and a height of 5~10 mm. The compact cylinder sample was first put on a saturated (water) sponge for 24 hours to pre-cure, and it was then soaked in a water tank for three days to fully cure the sample in the ambient atmosphere. After curing, the sample was stored in the lab under a constant temperature of 25 °C and relative humidity of 50%.

The Thermal Transport Option (TTO) module in DynaCool® Physical Property Measurement System (PPMS) was adopted to measure TE properties at low temperatures (300-350K), including the Seebeck coefficient, thermal conductivity, and electrical conductivity of the TE cement composite. Figure 1 shows the puck for sample mounting in the TTO module. Two copper plates were bonded at the ends of the cement sample by the silver epoxy EPO-TEK® H20E. The copper plates were tightly connected with two sensors, one heater, and a cold foot by screws. The top-right sensor is used to measure the voltage as well as the hot-side temperature. The sensor at the left bottom is for voltage and cold-side temperature measurement. The heat was imposed on the sample by a heater at the top-left side. It also helps to impose the current to the sample for resistance measurement.



Figure 1 Photographic view of sample mounting.

In this study, the PPMS-TTO measured the thermal conductivity by the steady-state heat conduction method. It monitored the temperature gradient  $(T_h - T_c)$  across the sample given a known heat input through the sample. When the system achieved steady-state, the thermal conductivity could be calculated according to Fourier's Law of heat conduction. At the same time, due to the temperature gradient across the sample, the TE cement composite automatically generated a voltage output. The thermal voltage across the sample was measured simultaneously using a nano voltmeter. The ratio of the voltage output to the temperature gradient, both measured in real-time, was the value of the Seebeck coefficient. After removing the heat and allowing the sample to return to an isothermal state, an AC resistance bridge measured the two-probe electrical conductivity according to Ohm's Law. The sample was initially stabilized at 300K before all measurements were taken. The operating temperature of the sample was increased in increments of 10K up to 350K.

#### **RESULTS AND ANALYSIS**

Two measurements were conducted for the same sample at different times. The average values of the four TE properties under different operating temperatures were plotted in Figure 2. The vertical line shows the estimated system error from the measurement and the modeling (i.e., heat loss compensation). It can be found that the thermal conductivity varies from 1.1 to 1.4 W/mK, and it decreases with the higher temperature. The average value of the two-probe electrical resistivity is about

0.00275 Ohm-m and it also decreases with the higher temperature. A lower resistivity can be obtained by applying the fourprobe measurement. The Seebeck coefficient fluctuates between 15.2 to 22.2  $\mu$ V/K, which is much higher than that of the ordinary cement. This may because adding graphene and AZO nanomaterials brings more carrier scattering and helps improve the electrochemical potential. As a result, the figure of merit, ZT, fluctuates between 2.0E-5 to 4.5E-5. The highest value from one measurement is about 5.93E-5 at 330K.



Figure 2 Thermoelectric properties of GnP-AZO enhanced cement composite: (a) Thermal conductivity, (b) Electrical resistivity, (c) Seebeck coefficient, and (d) Figure of merit ZT.

## CONCLUSION

In this study, the thermoelectric performance of the graphene and AZO enhances cement composite was investigated experimentally. The physical property measurement system was used to simultaneously measure the Seebeck coefficient, thermal conductivity, and electrical conductivity of the samples to study the variation of the figure of merit at different operating temperatures ranging from 300K to 350K. The measured data showed the highest ZT of 15wt.% graphene and 5wt.% AZO enhanced cement composite prepared by the dry method is about 5.93E-5 at 330K. A higher electrical conductivity can be obtained by applying the four-probe measurement additionally. The high ZT of the GnP-AZO enhanced TE cement as compared to carbon-fiber-reinforced cement provides a more possible selection of additives for the future development of TE cement composites. The rigorous characterization method can guide the performance evaluation of TE cement composite.

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