

Summary of Cement-Based Thermoelectric Materials, Devices and Applications

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Abstract

Cement-Based Thermoelectric Materials (CTEMs) have been a rapidly expanding field in science in the past few years. With traditional cement being a dominant part of global warming and energy consumption, it is important to upgrade such infrastructure to better meet ecological needs. The article “Cement-Based Thermoelectric Materials, Devices and Applications” by Wanqiang Li, Chunyu Du, Lirong Liang, and Guangming Chen covers the current state of CTEM technology. It compares different materials and additives, along with thermoelectric devices and applications for CTEMs. Traditional cement, while a cornerstone of nearly all modern construction, shows low thermal conductivity (k) and high electrical resistance. This low thermal conductivity allows it to hold heat for long periods of time. Constructions exposed to heat for long periods of time, usually due to sunlight, leave large amounts of thermal energy wasted inside the concrete. Use of thermoelectric (TE) materials can help mitigate this, converting this residual heat into electrical energy using the Seebeck effect. This is when a temperature gradient is present within a conductor/semiconductor, in which the transfer of heat generates a TE voltage. When creating a loop with a conductor, the Seebeck effect can be seen. The Seebeck coefficient (S) of a material quantifies the extent to which a material can generate voltage from the effect, and is a way to quantify the magnitude of the Seebeck effect. The formula for S is $S = \lim_{\Delta T \rightarrow 0} \frac{V}{\Delta T}$, where V is the voltage generated by the effect and ΔT is the temperature difference between the two junctions of the conductor. The figure of merit (ZT), which is dimensionless, serves as a measure of a material's TE performance, given by the equation $ZT = \frac{S^2 \sigma}{k} T$ where σ is electrical conductivity, k is thermal conductivity, and T is absolute temperature. This relationship means that high values of S and σ and a low k value would be

ideal for an effective TE material. These values, however, are often interconnected. This means that tradeoffs must be made between S , σ , and k in TE materials must be made to achieve an optimal balance. Through using additives to either change the matrix of concrete's structure, or through uniformly distributed fillers, the thermoelectric properties of concrete can be improved. By heating up one side of a concrete block and keeping the other side cool, electrical energy can be harvested by connecting wires to the hot and cool side of the concrete. The Seebeck effect causes voltage to be created from the movement of charge carriers across the temperature gradient, converting thermal energy to electrical energy. Overall, Li et. al. conclude that CTEM technology has a ways to go before becoming commercially viable in large-scale application. Introduction of certain additives can introduce extra toxicity into the environment. Additionally, the use of thermoelectric fillers makes it much less cost effective. However, with further research and empirical experimentation within the field, CTEMs could become invaluable in urban planning.

Materials & Methods

Since this article is a review of the current state of the CTEM field, no experimentation occurred. As such, the only methodology used by the authors to collect their data was their own research of other papers on the subject.

Analysis

Table 1 Statistics of type of fillers and TE performance of CTEMs**From: Cement-Based Thermoelectric Materials, Devices and Applications**

Species		Matrix	Filler	wt%	WCR	$S(\mu V K^{-1})$	$\sigma(S cm^{-1})$	$k(W m^{-1} K^{-1})$	$PF(\mu W m^{-1} K^{-2})$	ZT	Year	References
	CFs	Cement	—	—	0.35	−2	—	—	—	—	1999	[28]
		Cement	CFs	1.5	0.35	−3.1	—	—	—	—	1999	[28]
		Cement	Br-intercalated CFs	1	0.35	−17	—	—	—	—	2000	[37]
		Cement	CFs	1	0.44	19.73	2×10^{-3}	0.22	7.79×10^{-5}	1.33×10^{-7}	2014	[38]
		Cement	B-doped CFs	5	0.3	—	—	—	0.02	7.24×10^{-6}	2023	[39]
	Graphite and graphene	Cement	Acid treatment CFs	1.2	—	1240	3.25×10^{-3}	0.89	46.60	1.57×10^{-2}	2025	[40]
		Cement	Graphite	1	0.45	17.66	—	—	—	—	2002	[41]
		Cement	EG	5	—	−54.5	24.8	3.21	73.66	6.82×10^{-4}	2018	[42]
		Cement	Graphene	15	—	34	11.68	1.07	1.3	0.44×10^{-3}	2019	[10]
		Cement	rGO	5	—	−23.69	2.01	1.57	0.11	0.23×10^{-4}	2021	[43]
	CNTs	Cement	rGO	0.15	0.4	1859.23	1.9×10^{-3}	—	0.066	—	2022	[17]
		Cement	Acid treatment of EG	10	—	180.5	5.27	1.99	17.10	2.95×10^{-3}	2024	[44]
		Cement	Graphene	0.1	0.057	16.22	0.14	0.658	0.037	—	2025	[45]
		Cement	MWCNTs	1	0.5	−900	1.95×10^{-2}	—	1.58	—	2018	[46]
		Cement	Li ₂ O ₂ -modified MWCNTs	10	—	−73	7×10^{-2}	0.84	0.04	1.75×10^{-5}	2021	[47]
	Metal and metal oxides	Cement	SCWNT	0.5	0.5	1348	15.9	—	2887.70	—	2021	[48]
		Cement	Acid-treatment MWCNTs	5	—	66	0.22	1.13	0.12	0.38×10^{-4}	2022	[49]
		Cement	B-doped CNTs	7	—	−84.8	0.44	1.01	0.14	0.52×10^{-4}	2023	[50]
		Cement	SFs	1	0.35	−68	—	—	—	—	2000	[51]
		Cement	SFs	7.5	—	400.2	0.127	0.13	20.30	0.175	2024	[52]
	Metal oxides	Cement	Nano-ZnO	5	0.46	3300	—	—	—	—	2016	[11]
		Cement	Al-doped ZnO	0.4	0.35	0.19	6.42×10^{-4}	0.6	2.31×10^{-9}	—	2017	[12]
		Cement	MnO ₂	5	0.46	−3085	1.88×10^{-6}	0.72	1.79×10^{-2}	7.60×10^{-7}	2018	[53]
		Cement	Cu ₂ O	5	0.3	−3966	2.68×10^{-6}	0.69	1.79×10^{-2}	1.93×10^{-6}	2022	[54]
		Cement	Graphite-CFs	30 + 0.6	0.3	−52.23	—	—	—	—	2011	[55]
	Compound fillers	Cement	MWCNTs-CFs	0.5 + 0.4	0.46	21.7	—	—	—	—	2015	[14]
		Cement	EG-CFs	5 + 1.2	—	11.59	0.78	—	7.85×10^{-4}	—	2017	[13]
		Cement	EG-CFs	5 + 1.2	—	−9	6.3×10^{-2}	1.97	7.26×10^{-4}	2.22×10^{-7}	2020	[29]
		Cement	EG-CFs	5 + 1.2	—	568	—	3.30	94.30	2.06×10^{-3}	2021	[56]
		Cement	nCB-SWCNTs	0.5 + 0.25	—	4644.2	—	—	1.51×10^4	—	2024	[57]
	Compound carbon-based materials with metal materials	Cement	Fe ₂ O ₃ -CFs	0.5 (total)	0.23	—	—	—	—	3.11×10^{-3}	2016	[15]
		Cement	CFs-Be ₂ Te ₃	0.4 + 0.45	0.46	34.2	—	—	—	1.33×10^{-2}	2020	[58]
		Cement	EG-ZnO	10 + 5	—	−419	12.78	—	224	8.7×10^{-3}	2021	[59]
		Cement	EG-MnO ₂	10 + 5	—	16.74	1.36	2.16	0.04	6.2×10^{-6}	2021	[60]
		Cement	MnO ₂ -CFs	0.8 (total)	0.3	−2880	0.53×10^{-2}	0.67	4.4	2.12×10^{-3}	2021	[61]
		Cement	Bi _{0.5} Sb _{1.5} Te ₃ -CNTs	0.01 (total)	—	40.66	—	—	—	1.2×10^{-2}	2022	[62]
		Cement	EG-NiO	10 + 5	—	50	5.45	7.19	1.3	5.5×10^{-5}	2022	[63]
		Cement	polyaniline-MnO ₂	5 (total)	0.5	−2020	1.5×10^{-4}	—	0.61	—	2022	[64]
		Cement	CFs-Fe ₂ O ₃	5 + 5	0.41	1123	1.4×10^{-3}	0.73	1.76	8.51×10^{-5}	2023	[65]
		Cement	CNTs-SrTiO ₃	1 (total)	0.4	−5500	1.1×10^{-4}	—	1.61×10^{-6}	—	2023	[66]
		Cement	MnO ₂ coated CFs	3.75	—	−2308.9	2.72×10^{-2}	0.63	6.97×10^{-2}	7.73×10^{-3}	2023	[67]
		Concrete	nickel powder-MWCNTs	5 + 0.3	0.25	354.2	0.17	1.32	2148.2	4.9×10^{-7}	2024	[68]
		Cement	Ni-MnO ₂ -CFs	15 (total)	—	873.9	3.42×10^{-2}	0.61	3.42	1.69×10^{-3}	2024	[69]
		Cement	Cu ₂ Se-ZnO-graphene	—	—	10	—	—	2.31×10^{-6}	6.33×10^{-4}	2024	[70]
		Concrete	SFs-MWCNTs	0.3	0.27	488.2	2.6×10^{-3}	1.54	0.62	1.8×10^{-7}	2025	[71]

Table 1. The table above shows the Seebeck Coefficient (S), electrical conductivity (δ), thermal conductivity (k), and figure-of-merit (ZT) of various cement additives.

The Seebeck coefficient of pure cement is quite low, at $-2 \mu\text{V/K}$. However, the water composition of concrete can have drastic effects on its thermoelectrical conductivity. Plain cement paste, without any fillers, can reach a Seebeck coefficient of up to 1.44 mV/K . This is caused by the moisture in the water affecting the porosity of the concrete's structure, which makes transfer of ion carriers more efficient. However, once it dries, the efficiency drastically drops. As such, thermoelectric fillers are highly useful in maintaining thermoelectric output in the long-term in concrete structures. There are two main types of fillers, being carbon-based materials, such as carbon fiber, carbon nanotubes, along with graphite and graphite derivatives. Such derivatives include expanded graphite (EG), graphene, and reduced graphene oxide (rGO). While regular graphite is not as efficient as carbon fiber, and graphene tends to aggregate while in cement leading to uneven distribution, EG and rGO lead to quite high values of figure-of-merit. Carbon nanotubes, however, are the best of the carbon-based structures, with single-walled nanotubes providing the most thermoelectric efficiency. Regarding the metal oxides, nanoparticles of ZnO, MnO₂, and CuO have very high Seebeck coefficients of 3300, -3085, and -3966 $\mu\text{V/K}$ respectively. Although these nanoparticles have large Seebeck coefficients, all three types have minimal effects on the electrical and k of cement. The reasons for this are still unknown, but one explanation is that nano-metal oxides would have to greatly affect the cement structure. Another way to increase the thermoelectrical efficiency of concrete is to change the cement matrix used. Green Concrete (GC) and Autoclaved Aerated Concrete (AAC) are more sustainable than traditional Portland cement, reducing negative ecological

impacts from their development. This is because they use by-products such as fly ash, slag, and metakaolin, which reduces fossil fuel consumption and CO₂ emissions. GC can attain a Seebeck coefficient nearly 30 times as much as unmodified cement. The reason for this is that in the low-dimensional gel structure of the molecules, it increases carrier density and thus encourages electron transport making it much more suitable as a source of electricity. In the creation of CTEM devices, TE devices are the foundation to convert heat into electricity. As of now, there's only 2 main methods for CTEM: dry pressing and wet mixing. To dry press, high pressures are applied to filler and cement powder to compact it which is then procured at a certain temperature and humidity. As a result, the particles from the filler spread out uniformly within the cement as there's no water involved during compaction. However, this method results in internal voids and tiny cracks within the cement. On the other hand, wet mixing utilizes the water absorbing property of cement to bind both the filler and binder. Cement, water and filler are cast into a mold which allows for an easy blend of electrodes and wiring.

At the moment our team is planning to find an efficient way to utilize the heat-absorbing properties of cement to generate electricity. This article would be very beneficial for our research as it can assist in determining different materials to consider for optimization due to different properties including the Seebeck effect and conductivity. In addition to this, the article offers different techniques such as dry pressing and wet mixing and how it affects the thermoelectric performance.

References

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