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Electrical resistance of graphene reinforced cement paste

Farid Sartipi^{1*}; Ali Gharizadeh²; May Gamil²

¹ Institute of Construction Materials, Kingswood, NSW, Australia

² School of Computing Engineering and Mathematics, Western Sydney University, Australia

*Corresponding author: Farid Sartipi, Academic researcher, Institute of Construction Materials, Western Sydney University, Kingswood, Building Z.1.12, NSW, 2747, Australia. E: farid.sartipi@iconsmat.com.au P: (+61)416731647

Abstract

Graphene as an emerging material is compromising outstanding properties in a variety of sectors. In order to facilitate the use of graphene in construction practices, the current paper investigates the electrical resistivity of graphene reinforced cement paste with a perspective to utilized the enhancements. Graphene oxide had been synthesised using electrochemical exfoliation of graphite and replaced by ratios of 1, 3, and 5 to the mass of cement. Anodic and cathodic exfoliation of graphite had shown contrasting results which will be discussed. Bulk electrical conductivity tests had been conducted at 7, 14, and 28 days. It had been observed that the addition of graphene oxide increases the electrical conductivity of samples. At the end, a brief financial review on the Australian market position reveals the possibility of accepting graphene oxide as a new type of supplementary cementitious material.

Keywords

Graphene; Cement; Electrical properties

Introduction

Graphene had attracted many attentions from almost all of the industrial sectors including construction due to its extraordinary mechanical and electrical properties. It a one-layer thick of carbon atoms bonded in sp^2 structure with an exceptional high crystal and electrical quality[1-4]. From the advantageous of using graphene in cement paste is the fact that since graphene has a recorded high thermal conductivity of 3000 W/mK [5] it can facilitate the curing procedure. The mechanism behind the facilitation of curing procedure can be rationalized in such a way that provides a path for the exothermic reaction of cement with water know as hydration. This way, the heat generated during hydration would escape the internal layers much faster in the presence of graphene in the mix. Internal cracking due to the temperature gradient is being avoided as the result.

Generally, the use of carbon nanoparticles in cement composites results in a higher degree of hydration reaction. Carbon nano particles in particular had been investigated as exhibiting an enhancement in the early age strength gain of cement composites. According to the literature review, an average 30% compressive strength improvement had been recorded once carbon nanotubes were added to the cement composites[6, 7].

In terms of solubility, studies report the agglomeration of graphene nanosheets in water due to hydrophobic characteristics[8]. The lack homogenous dispersion of graphene nano platelets would bring workability issues in concrete applications. Noteworthy that graphene oxide platelets, amazingly, compromise different properties in terms of dispersibility in contrast to graphene itself. The hydrophilic properties of GO sheets had shown lubricating effect once added in cement similar to the effect of superplasticizers [9, 10].

Graphite, consisting of stacks of flat graphene sheets and also ribbons of carbon attached is the main source for the mass production of graphene which is also in abundance both in natural and synthesised resources [11, 12]. Currently there are two major production method exist for graphene shown in table 1:

Table 1 Commercial production methods of graphene

Method	Cost of production	Quality of the product
Electrochemical exfoliation	Low – fast production	Low – damage to the honeycomb lattice caused by the oxidation step
Chemical vapour deposition	High – high temperature and expensive substrate	High – Large area graphene platelets gain

Electrochemical exfoliation involves oxidation of graphite sheets in an electrolyte followed by ultrasonic dispersion. Studies show that the amongst the range of electrolytes including HBr, HCl, HNO₃, and H₂SO₄ the sulphuric acid had exhibited a highly efficient exfoliation. Once H₂SO₄ solution was used as an electrolyte, starting off with a low voltage for a few minutes from the beginning of electrolysis would allow the graphite to wet and prepared for proper exfoliation. The voltage applied could be ramped up

after a while to speed up the process. The electrochemical exfoliation of graphite sheets usually yields thick layers of graphene with small surface area. However, the modification of the acidity of the electrolyte and the voltage applied can enhance the quality of the final product [13-16].

Chemical vapour deposition [10] amongst the methods proposed for the production of graphene is known as the most efficient technique which yields the highest ratio of single-layer large-area sheets. The process involves the introduction of gas species in the reactor while heat applies. This is where the hydrocarbon precursors decompose to carbon radicals on the metal substrate surface forming the graphene nanosheets. The metal substrate acts as a catalyst and also provides the base for the deposition mechanism. Ni and Cu are the two major widely used metal substrates in the graphene CVD process[17-19].

Seeking to develop a conductive concrete panel reinforced with graphene particles, this study evaluates the electrical properties of samples made with electrochemically exfoliated graphene. The test includes a measurement on the effect of voltage applied, density of graphite sticks, concentration of acid as electrolyte on the electrical conductivity of cement paste. The results would be beneficial in terms of introducing opportunities for conductive non-destructive health monitoring test on concrete.

Results and discussion

Cathodic graphite exfoliation

This technique refers to the process where graphite sticks are positively charged [20]. The 200 mL of 98% sulphuric acid had been solved in 10 L water in order to decrease the concentration to 2%. This was mostly due to safety considerations. The density of the graphite used for electrochemical exfoliation was recorded as 3250 kg/m³. In the first attempt where 6 V DC current had been connected to the aluminium electrodes no sign of exfoliation had been observed in 30 min. The situation was the same even by increasing the voltage to 12 V. The measures read from the voltmeter one side connected to graphite itself the other to the negative charged aluminium electrode had shown 2-3 V potential differences indicating voltage drop in the acidic electrolyte.

A bit of explanation for the reasons behind the observations can refer to the ion sizes. In the sulphuric acid electrolyte, upon decomposition of the molecules, 2H⁺ and SO₄²⁻ are being produced. Where the graphite is positively charged a larger ion (SO₄⁻) facilitates the intercalation. In simple words, for the dense graphite samples with less openings it is hard to reach between the layers. The cathodic exfoliation in this study were subject to test for 48 hours and only a thin traces of black graphene layers had been observed. It is anticipated that even with longer exfoliation period the quality of the final product would be multi-layer thick GO (graphene oxide) sheets as a low quality result.

Anodic graphite exfoliation

This method, in contrast with cathodic exfoliation, places the negatively charged electrodes on the graphite stick [20]. In another attempt a looser graphite sample in terms of density had

been used with a density of recorded as 2540 kg/m^3 subject to anodic exfoliation starting at the input voltage of 12 V DC in a 2% sulphuric acid with configuration as shown in figure 1.

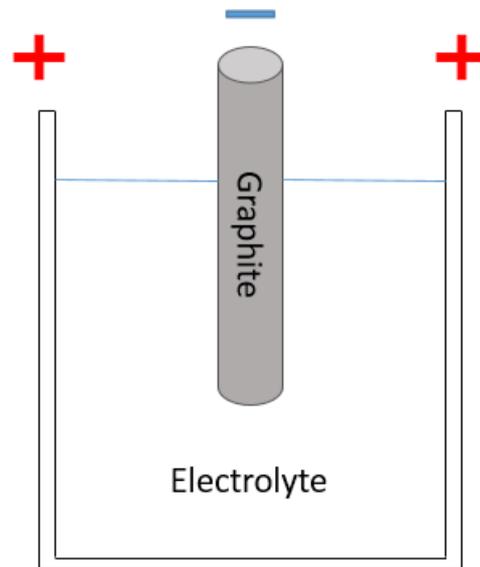


Figure 1 Electrochemical exfoliation apparatus assembled for this study

The graphite stick had exfoliated thoroughly after 24 hours. Using paper filters, the flakes of graphene oxide had been separated from the electrolyte. The filtration process had taken 3 days until dry particles obtained. Reasoning for the success of anodic exfoliation as opposed to cathodic method, Hydrogen ions are much smaller than sulphur ions in terms of size, and they are greater in numbers as each molecule of sulphuric acid decomposes into two hydrogens (2H^+) and one sulphur (SO_4^-). In other word the intercalation of looser graphite sample is much easier with more (in numbers) smaller ions.

One of the mistakes undertaken during the experiments at the beginning stages was the submergence of aluminium holders in the acidic electrolyte. This delays the exfoliation process by considering the level of reactivity of the chemical elements. In such a reactivity series, aluminium stands on top of carbon in terms of yielding a higher reactivity in a corrosive environment.

Cement mix

Graphene oxide after exfoliation had been added to the cement paste with the mix design shown in table 2. The w/c ratio had been kept 0.3 constant in all of the samples to avoid the effect of such on electrical resistance. Graphene oxide had been added to the mix with the ratio of 1%,3%, and 5% to cement. Samples were placed on the vibrator for consolidation purposes for about 30 seconds. Overall, the preparation procedure is in compliance with Australian Standard code: methods of testing concrete [21]. Samples were demoulded after

24 hours of placement and cured in plastics wraps and soaked in water to keep the temperature constant at 22-25°C.

Table 2 Mix proportion of samples

	Cement	Water	GO
S0	600 g	200 g	0 g
S1-G1	600 g	200 g	6 g
S2-G2	600 g	200 g	18 g
S3-G3	600 g	200 g	30 g



Figure 2 From left to right: filter dried graphene oxide - mix portion - cured samples

Electrical resistance

Samples were tested for electrical resistance using the apparatus as shown in figure 2.

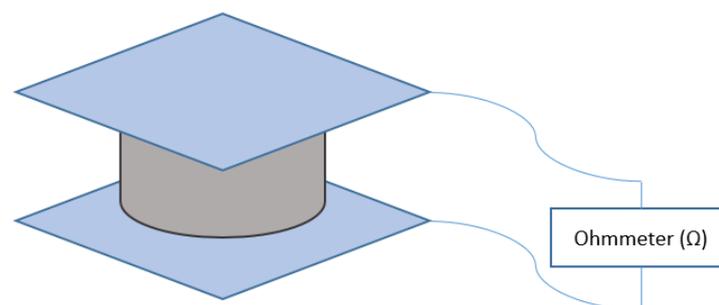


Figure 3 Apparatus used in the measurement of electrical resistance.

Concrete bulk resistivity is measured once two electrodes attached to the two ends of samples. The following equation results in a unified measure for concrete electrical resistivity:

$$\rho = R \frac{A}{l}$$

Where R is the readings from the ohmmeter in the unit of ohm. A is the cross sectional area and l is the length of the samples. Although this method is one of the widely acceptable approaches, it suffers from lack of accuracy due to the presence of metallic contacts which bridges the ohmmeter connection to the samples. The electrical resistivity test had been conducted in compliance with ASTM Standard C1202-10, AASHTO TP 95, and AASHTO Designation: T 358-151.

Each sample had undergone three readings. The electrical resistance of samples had been measured at the ages of 7, 14, and 28 days given the 10 cm average height of the cylindrical cement samples and the cross-sectional area of 19.625 cm².

Table 3 Results of electrical resistance test

	7 days	14 days	28 days
S0	152 Ω.m	210 Ω.m	246 Ω.m
S1-G1	124 Ω.m	142 Ω.m	183 Ω.m
S2-G2	92 Ω.m	122 Ω.m	156 Ω.m
S3-G3	61 Ω.m	88 Ω.m	110 Ω.m

The above table in conjunction with figure 3 are indications of the enhancements in electrical conductivity of concrete samples made with graphene particles. One of the important criteria which also needs to be addressed every time that the electrical conductivity of concrete samples is subject to discussion is the durability index. In our case, as the conductivity increases [11] the corrosiveness of the paste requires attention. Kessler et al. [22] suggest the following range in order to predict the corrosiveness:

- When $\rho \geq 120 \Omega.m$: corrosion is unlikely
- When $120 \Omega.m \geq \rho \geq 80 \Omega.m$: corrosion is possible
- When $80 \Omega.m \geq \rho$: corrosion is fairly certain

Based on that, it is not recommended to reinforce samples containing graphene particles with steel rebars to avoid corrosion. Although lack of steel reinforcement might bring up concerns about the tensile strength of concrete specially for structural purposes, other studies [6, 7] had shown an average of 30% increase in flexural strength of GO reinforced samples which ease the concerns eventually.

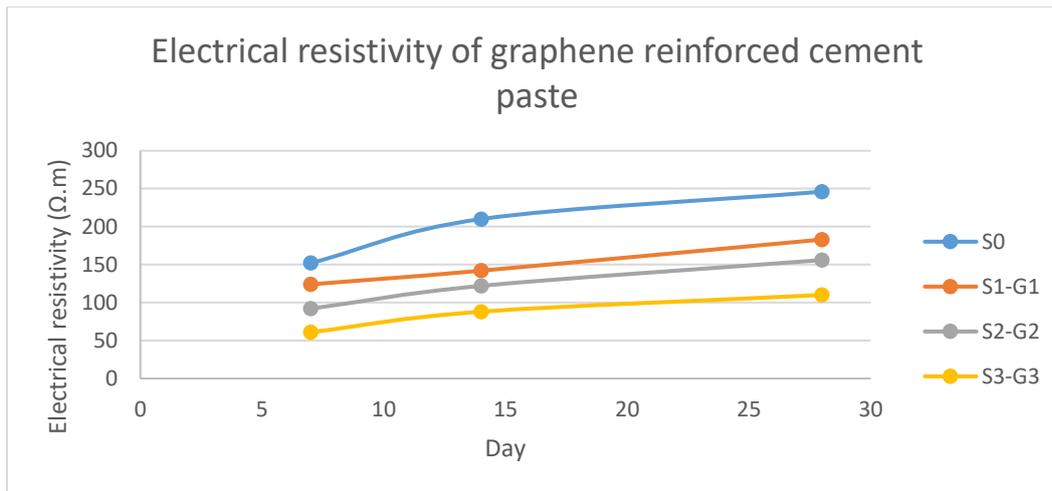


Figure 4 Electrical resistivity measures of samples reinforced with different portion of graphene oxide.

Australian financial market position

As per May 2019, the data from the Australian Securities Exchange (ASX) reports a AUD\$78.8 M market capital for graphene. This is at the same time as the 4 largest builder companies active in the construction industry report a total of AUD\$19 B market capital. The Australian government is encouraging the industry leaning towards a more ecofriendly approach. Cement industry is one of the top ranked industries by carbon emission indices as production of each ton of Portland cement emits the same amount of carbon dioxide in to the atmosphere. The construction industry is leaning towards using Supplementary Cementitious Materials (SCM) in a wider scale in order to reduce the consumption of Portland cement in the benefit of environmental conservation[23]. Having an environmental perspective to the mass production of graphene, this material is more likely to be widely accepted in the Australian construction industry.

Conclusion

The records from the laboratory experiments indicate in order to achieve a high yield exfoliation of graphite sticks into graphene particles, anodic exfoliation must be utilized as long as Aluminium electrodes are used. It is also important to be noted that since the Aluminium chemical reactivity stands on top of the carbon in the relevant series of reactivity, the negative electric carriers must not be submerged in the acidic electrolyte. The electrical resistivity of samples with higher graphene content had been enhanced. This can be seen as an opportunity to innovate concrete samples being able to produce electricity once NP-doped graphene particles were added in the mix.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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