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Electrical behavior of cement-based junctions including the pn-junction

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Abstract

Electric current rectification, though not perfect, was attained by using a junction (pn or nn^+) between cement pastes with different extents n- or p-type character. The n-type character was enhanced by using steel fibers as an admixture. The p-type character was enhanced by using carbon fibers as an admixture. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The pn-junction is the junction between a p-type conductor (a conductor with holes as the majority carrier) and an n-type conductor (a conductor with electrons as the majority carrier). The pn-junction is ideally rectifying, i.e., the current–voltage characteristic is such that the current is large when the applied voltage is positive on the p-side relative to the n-side and is small when the applied voltage is positive on the n-side relative to the p-side. The pn-junction is an electronic device that is central to electrical circuitry, due to its importance to diodes and transistors. Akin to the pn-junction is the n–n^+ junction, which is a junction between a weakly n-type conductor and a strongly n-type (i.e., n^+) conductor.

In the field of electrical engineering, a pn-junction is obtained by allowing a p-type semiconductor to contact an n-type semiconductor. These semiconductors are obtained by doping with appropriate impurities that serve as electron donors (for n-type semiconductors) or electron acceptors (for p-type semiconductors).

Cement is inherently n-type, although it is only slightly n-type [1]. Upon addition of a sufficient amount of short carbon fibers (i.e., 1.0% by mass of cement) to cement, a composite that is p-type is obtained [1–4]. Upon addition of short steel fibers to cement, a composite that is strongly n-type is obtained [5]. In other words, the cement matrix contributes to conduction by electrons; carbon fibers contribute to conduction by holes; steel fibers contribute to conduction by electrons.

This paper provides the first study of a cement-based pn-junction, as obtained by separate pouring of different cement mixes side by side. In addition, the current–voltage characteristics of cement junctions made from cement pastes with different extents of n- or p-type character are reported.

Concrete is a structural material. However, functional properties allow concrete to be multifunctional, thereby widening the abilities of a structure. Multifunctionality is particularly important to smart structures. The cement-based pn-junction provides the basic building block for concrete to provide electronic functions, which may potentially be electrical control, electrical signal processing, absorption, and emission of electromagnetic radiation, and electrical energy generation (like solar cells). These electronic functions are distinct from that associated with the sensing of strain, damage, and temperature. The use of cement-based materials for sensing has been previously reported [2–12]. The sensing is mostly through electrical resistance measurement.

Compared to semiconductor junctions (such as those involving silicon), cement junctions are much easier to make — no need of vacuum processing, single crystals or high purity, which are required for semiconductor junctions. Moreover, cement is mechanically rugged compared to semiconductors. However, cement tends to be more resistive electrically than semiconductors, probably due to the lower mobility of the charge carriers.

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2. Experimental methods

The steel fibers used to provide strongly n-type cement paste were made of stainless steel No. 434, as obtained from International Steel Wool (Springfield, OH). The fibers were cut into pieces of length 5 mm prior to use in the cement paste in the amount of 0.5% by mass of cement (i.e., 0.10 vol.%). The properties of the steel fibers are shown in Table 1 of Ref. [5]. The mechanical properties of mortars containing these fibers are described in Ref. [13]. However, no aggregate, whether coarse or fine, was used in this work.

The carbon fibers used to provide p-type cement paste were isotropic pitch based, unsized, and of length ~ 5 mm, as obtained from Ashland Petroleum (Ashland, KY). They were used in the amount of either 0.5% or 0.1% by mass of cement (i.e., either 0.48 or 0.96 vol.% in the case of cement paste with silica fume, and either 0.41 or 0.82 vol.% in the case of cement paste with latex). The fiber properties are shown in Table 1 of Ref. [1]. No aggregate (fine or course) was used. The cement paste with carbon fibers in the amount of 1.0% by mass of cement was p-type, whereas that with carbon fibers in the amount of 0.5% by mass of cement was slightly n-type, as shown by thermoelectric power measurement [1].

The cement used in all cases was portland cement (Type I) from Lafarge (Southfield, MI). Silica fume (Elkem Materials, Pittsburgh, PA, EMS 965) was used in the amount of 15% by mass of cement. The methylcellulose, used in the amount of 0.4% by mass of cement, was Dow Chemical, Midland, MI, Methocel A15-LV. The defoamer (Colloids, Marietta, GA, 1010) used whenever methylcellulose was used was in the amount of 0.13 vol.%. The latex, used in the amount of 20% by mass of cement, was a styrene butadiene copolymer (Dow Chemical, 460NA) with the polymer making up about 48% for the dispersion and with the styrene and butadiene having a mass ratio of 66:34. The latex was used along with an antifoaming agent (Dow Corning, Midland, MI, No. 2410, 0.5% by mass of latex).

A rotary mixer with a flat beater was used for mixing. Methylcellulose (if applicable) was dissolved in water and then the defoamer was added and stirred by hand for about 2 min. Latex (if applicable) was mixed with the antifoam by hand for about 1 min. Then the methylcellulose mixture (if applicable), the latex mixture (if applicable), cement, water, silica fume (if applicable), carbon fibers (if applicable), and steel fibers (if applicable) were mixed in the mixer for 5 min.

A junction between any two types of cement mix was made by pouring the two different mixes into a rectangular mold ($160 \times 40 \times 40$ mm) separately, such that the time between the two pours was 10–15 min. The two mixes were poured into two side-by-side compartments of the mold and the paper (2 mm thick, without oil on it) separating the compartments was removed immediately after the completion of the two pours. Each compartment was roughly half the length of the entire mold.

After pouring into oiled molds, an external electrical vibrator was used to facilitate compaction and decrease the amount of air bubbles. The resulting junction could be seen visually, due to the color difference between the two halves of a sample. The samples were demolded after 1 day and cured in air at room temperature (relative humidity = 100%) for 28 days.

Five types of cement paste were prepared, namely (i) plain cement paste (weakly n-type, consisting of just cement and water), (ii) steel fiber cement paste (strongly n-type, consisting of cement, water, and steel fibers), (iii) carbon-fiber silica-fume cement paste (very weakly n-type, consisting of cement, water, silica fume, methylcellulose, defoamer, and carbon fibers in the amount of 0.5% by mass of cement), (iv) carbon-fiber silica-fume cement paste (p-type, consisting of cement, water, silica fume, methylcellulose, defoamer, and carbon fibers in the amount of 1.0% by mass of cement), and (v) carbon-fiber latex cement paste (very

Table 1
Absolute thermoelectric power (μV/°C)

Cement paste	Volume fraction fibers (%)	μV/°C	Type	References
(i) Plain	0	1.99 ± 0.03	weakly n	[1]
(ii) S_f (0.5*)	0.10	53.3 ± 4.8	strongly n	[5]
(iii) C_f (0.5*) + SF	0.48	0.89 ± 0.09	weakly n	[1]
(iv) C_f (1.0*) + SF	0.95	-0.48 ± 0.11	p	[1]
(v) C_f (0.5*) + L	0.41	1.14 ± 0.05	weakly n	[1]

SF = silica fume; L = latex.

Table 2
Cement junctions

Junction	Pastes involved	Junction type
(a)	(iv) and (ii)	pn
(b)	(iii) and (ii)	nn^+
(c)	(v) and (ii)	nn^+
(d)	(iii) and (i)	nn^+
(e)	(v) and (i)	nn^+

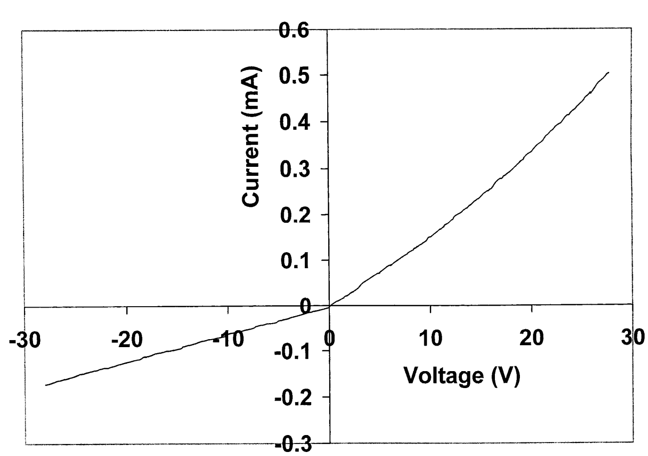

Fig. 1. I–V characteristic of junction (a).

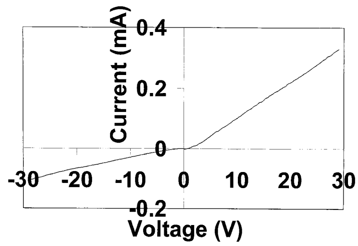

Fig. 2. *I–V* characteristic of junction (b).

weakly n-type, consisting of cement, water, latex, and carbon fibers). The water/cement ratio was 0.45 for pastes (i), (ii), (iii), and (iv), and was 0.25 for paste (v). The absolute thermoelectric power of each paste is shown in Table 1.

Five pairs of cement paste were used to make junctions, as described in Table 2. Six specimens were tested for each pair.

Current–voltage (*I–V*) characteristics were determined by using the two-probe method, with silver paint in conjunction with copper wires for electrical contacts. The two-probe method gave essentially the same result as the four-probe method, due to the high sample resistance. A Keithley 2001 multimeter was used. Each electrical contact was applied around the entire 40×40 mm perimeter of the rectangular specimen. The two contacts were at two parallel cross-sectional planes that were 140 mm apart, such that they were symmetrically positioned with respect to the junction. The voltage was swept from $+30$ to -30 V over a period of 120 s, while the current was measured. The positive end of the indicated voltage was at the first of the two listed pastes in each row in Table 2, as this is the more p-type or less n-type partner. The indicated current was in the direction from the positive end to the negative end of the indicated voltage.

3. Results

Fig. 1 shows the *I–V* characteristic for junction (a), which is a pn-junction. The *I–V* characteristic is non-linear within the positive voltage regime and linear within the

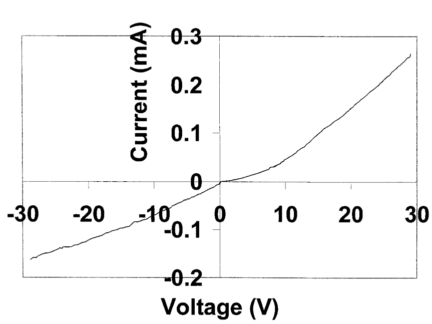

Fig. 3. *I–V* characteristic of junction (c).

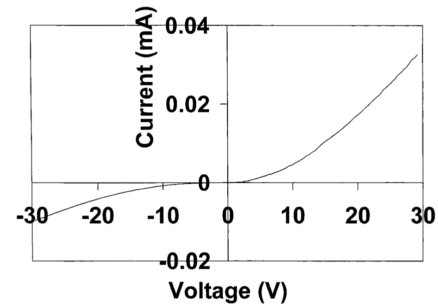

Fig. 4. *I–V* characteristic of junction (d).

negative voltage regime. The slope is much steeper in the positive voltage regime than the negative voltage regime. Thus, the junction is rectifying, though the rectification is not perfect and the *I–V* characteristic differs in shape from that of a conventional pn-junction.

Fig. 2 shows the *I–V* characteristic of junction (b), which is an nn^+-junction. It is similar to that in Fig. 1, except that the slope is less linear in the negative voltage regime and the current is lower at the same voltage. The lower current in Fig. 2 is consistent with the higher resistivity of cement paste (iii) of junction (b) than that of cement paste (iv) of junction (a).

Fig. 3 shows the *I–V* characteristic for junction (c), which is an nn^+-junction with less contrast between the n and n^+ sides than the nn^+-junction of Fig. 2. The junction is essentially not rectifying, though the slope of the *I–V* characteristic is mostly higher in the positive voltage regime than the negative voltage regime. The *I–V* characteristic is non-linear.

Fig. 4 shows the *I–V* characteristic for junction (d), which is an nn^+-junction with even less contrast between the n and n^+ sides than the nn^+-junction of Fig. 3. The junction is rectifying, but the *I–V* characteristic is non-linear, with a shape that differs from that in Fig. 1. The current is very low compared to those in Figs. 1–3, as expected from the absence of fibers in cement paste (i) of junction (d).

Fig. 5 shows the *I–V* characteristic for junction (e), which is an nn^+-junction with less contrast between the n and n^+ sides than any of the other nn^+-junctions mentioned above. Its shape is quite similar to those in Figs. 4 and 2. The current is low, as in Fig. 4.

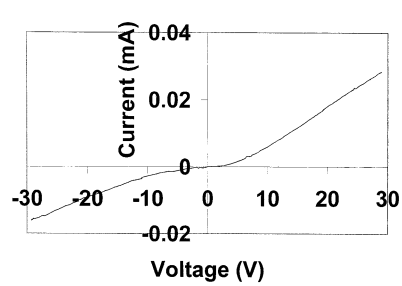

Fig. 5. *I–V* characteristic of junction (e).

Of all the junctions studied, only junction (a) is a pn-junction (Table 2). It gives the best rectification behavior.

4. Discussion

The asymmetry in the $I-V$ characteristic on the two sides of the origin observed in this work for various junctions is in sharp contrast to the symmetry previously observed for a homogeneous piece of cement paste without a junction (Fig. 6) [12]. This symmetry was observed for various paste compositions at various temperatures [12]. Hence, the asymmetry is attributed to the junction itself. The current at the same voltage is higher in Fig. 6 (without a junction) than in Figs. 1–5 (with a junction), due to the contact resistance associated with the junction.

Junctions (a), (b), (d), and (e) are rectifying, though the rectification is not perfect; the magnitude of current is much larger when the voltage is positive than when the voltage is negative. The rectification is attributed to the asymmetric electron flow resulting from the pn or nn^+ junction. Due to the high concentration of electrons in the n or n^+-side, electrons predominantly flow by diffusion from the n-side to the p-side or from the n^+-side to the n-side across the junction. This flow is enhanced by a positive voltage (i.e., forward bias), which lowers the contact potential at the junction. When the voltage is negative (i.e., reverse bias), the contact potential is high, causing the diffusion current to be low. However, electrons are swept from the p-side to the n-side, or from the n-side to the n^+-side under the electric field associated with the high contact potential at the junction, resulting in a drift current in the direction opposite to the diffusion current. The drift current is enhanced by a more negative voltage, but is low due to the low electron concentration in the n-side.

When the junction involves weakly n-type and very weakly n-type cement pastes, as for junctions (d) and (e), the difference between the two pastes is small electrically

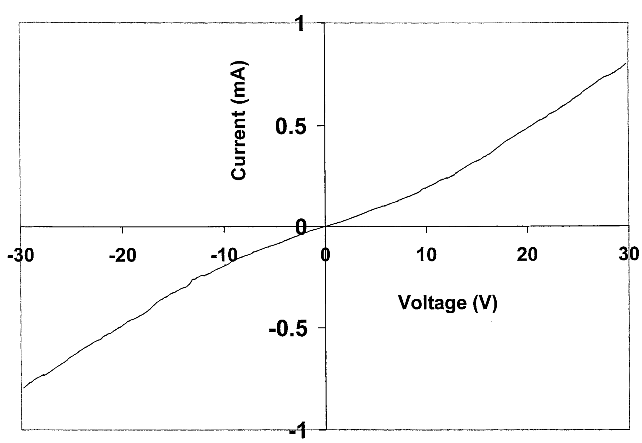

Fig. 6. $I-V$ characteristic of carbon-fiber silica-fume cement paste (no junction) at room temperature [12].

and the junction, though rectifying, has a non-linear $I-V$ characteristic akin to that in the absence of a junction [12]. However, when the junction involves a combination of p- and n-type cement pastes, or a combination of weakly n-type and strongly n-type cement pastes, as for junctions (a) and (b), respectively, the difference between the two pastes is large electrically and the junction has an $I-V$ characteristic that differs greatly from that in the absence of a junction.

At the same voltage, the current is much higher for junctions (a), (b), and (c) than junctions (d) and (e). This is attributed to the strongly n-type character of paste (ii) contributing to the diffusion current.

Junction (b) is more rectifying than junction (c); junction (d) is more rectifying than junction (e). This is due to the involvement of junctions (c) and (e) with latex in the cement paste with carbon fibers and the involvement of junctions (b) and (d) with silica fume in the cement paste with carbon fibers. As shown in Table 1, silica fume (paste (iii)) brings out the p-type influence of carbon fibers more than latex (paste (v)). Furthermore, latex is electrically insulating and its presence at the junction may interfere with the charge transport through the junction.

The piecewise linearity in the $I-V$ characteristic up to $+30$ V in the positive voltage regime in Fig. 2 and down to -30 V in the negative voltage regime in Fig. 1, such that the slope is different between the positive and negative voltage regimes of each $I-V$ characteristic, is in sharp contrast to the linearity (not piecewise, but uniform, with the same slope on both sides of the origin due to ohmic behavior) range of up to $+11$ V and down to -11 V in the case of a homogeneous piece of cement paste without a junction (Fig. 6) [12]. The origin of the piecewise linearity and slope change in the junction case (Figs. 1 and 2) is not completely clear, though it must be due to the effect of the junction on carrier movement.

The effect of moisture content on the electrical resistivity of cement pastes containing electrically conducting short fibers is small, as shown by the small effect of curing age on the electrical resistivity [14]. For example, the resistivity of mortar containing latex and short carbon fibers (1.0% by weight of cement) increases by 4% from a curing age of 1 day to a curing age of 56 days [14]. Thus, the electrical behavior of the junctions involving cement pastes with fibers on both sides is expected to have little dependence on the moisture content. For similar reasons, the influence of the zeta potential on the electrical behavior of these junctions is expected to be small. The junction effect reported in this paper is unrelated to the streaming potential [15], as water movement is not the issue.

5. Conclusion

Electric current rectification, though not perfect, was achieved by using a junction (pn or nn^+) of electrically dissimilar cement pastes, such as those having different concentrations of free electrons (from steel fibers and the cement matrix) or holes (from carbon fibers). The current from the more p-type or less n-type side to the other side of the junction is high when the voltage is positive at the former side. The current is low when the voltage is negative at the former side. The presence of latex in the cement paste degrades the rectifying ability of the junction.

Acknowledgments

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