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Stress-Induced Polarization of CNT-Mixed Cement Paste under Cyclic Loading and Moisture Variation: Mechanisms and Electrical Characteristics

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A B S T R A C T

In recent years, the deterioration of infrastructure built during Japan' s rapid economic growth has become a major issue, highlighting the need for efficient and sustainable maintenance strategies. To address this, self-diagnostic and sensing technologies for structural health monitoring have gained attention. Among various approaches, functional materials utilizing the electrical and mechanical properties of carbon nanotubes (CNTs) are promising. CNTs can form conductive networks within cementitious materials, imparting a self-sensing capability. This study investigates carbon nanotube-mixed cement paste (CNTCPs) to clarify how changes in electrical conductivity affect stress-induced polarization. Electrical impedance spectroscopy was conducted to assess frequency-domain conductivity variations, and cyclic loading tests were performed under varying moisture and material age conditions.

Results show that a periodic voltage response is preserved across all formulations, and the voltage amplitude peaks at a 2 wt.% CNT dosage. Furthermore, a high moisture content or advanced material age diminishes the voltage response, which is governed by the electrochemical time constants (τ=RC) identified in the impedance plots. These insights provide critical guidelines for optimizing the stress-induced polarization characteristics and design of self-sensing cementitious composites.

Keywords: Self-Sensing Materials, Carbon Nanotubes, Stress-induced polarization, Interfacial Polarization, Streaming Potential

1. Introduction

For the establishment of efficient and sustainable maintenance strategies, the development of functional materials that leverage the unique electrical properties of carbon nanotubes (CNTs) [1] is promising and has attracted significant attention. CNTs possess excellent electrical conductivity and mechanical properties [2][3]. They are capable of detecting subtle strains and physical changes in electrical signals. Therefore, by dispersing CNTs within cementitious materials, it is possible to impart self-sensing capabilities throughout the entire structure.

The piezoelectric effect is a phenomenon in which an electric voltage is generated when mechanical stress is applied to a crystalline structure. Typical piezoelectric materials are lead zirconate titanate (PZT) and quartz. In contrast, a cement paste matrix inherently lacks a non-centrosymmetric crystalline structure that could exhibit the true piezoelectricity. Nevertheless, phenomena in which cement paste exhibits transient voltage responses to external forces have been reported [4]. The phenomena eventually result from the simultaneous manifestation of multiple stress-induced polarization mechanisms within the cement paste matrix, causing responses that resemble piezoelectric materials. Specifically, it is presumed that the generation of voltage signals arises from the complex interplay of electrochemical mechanisms such as interfacial polarization, modulation of electric double layers, and the generation of streaming potentials. These behaviors analogous to the piezoelectric effect, are here defined as the pseudo-piezoelectric effect.

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Importantly, the majority of existing studies on CNT-modified cementitious materials focus on piezoresistivity [5][6], where external damage or strain is monitored through changes in electrical resistance under a continuous external power supply. In contrast, research targeting the pseudo-piezoelectric effect, particularly self-driven voltage generation, remains limited, yet it holds substantial potential for developing autonomous, external-power-free sensors for structural health monitoring.

In this preliminary study, CNTs are incorporated into a cement paste matrix using a pre-dispersed solution supplied by a commercial manufacturer to investigate the fundamental characteristics of stress-induced polarization in the resulting CNT-mixed cement paste (hereinafter referred to as CNTCP).

This paper serves as an initial investigation to qualitatively clarify how the incorporation of CNTs influences the pseudo-piezoelectric behavior of the matrix under cyclic loading, with a particular focus on the qualitative mechanisms of charge behavior. To understand the underlying mechanism without overcomplicating the numerical parameters, the electrochemical time constant (τ=RC) is introduced as a conceptual bridge. By analyzing the relationship between the time constant obtained from frequency-domain impedance measurements and the time-domain voltage responses under different material ages and moisture conditions, the study evaluates how the conductive network formed by CNTs and the interfacial properties between CNTs and the matrix are involved in the generation, accumulation, and transport processes of stress-induced polarization, while more advanced quantitative trade-offs and microstructural evaluations under extended loading ranges are positioned as a subsequent phase of this research.

2. Overview of Experiments and Specimen

Table 1 presents the mix proportions of the CNTCPs. To investigate the changes in pseudo-piezoelectric properties with CNT contents, the water-to-cement ratio (W/C) is fixed as 25%. This low water-to-cement ratio was intentionally selected to prevent bleeding and subsequent material segregation, thereby ensuring the structural homogeneity of the matrix. Minimizing bleeding is critical for maintaining a uniform spatial distribution of CNTs and securing a stable baseline for the multi-path conductive network composed of both the pore solution and the CNT pathways, which facilitates sensitive and reproducible electrical measurements.

CNT contents were set at four levels, using the weight percentage of CNT to water (CNT/W). Because CNTs exhibit high agglomeration tendencies, it is well known that direct mixing of CNTs into cement paste matrix does not introduce sufficient dispersion. Therefore, a preprocessing step to ensure uniform dispersion of CNTs is essential. Specimens were prepared using CNT-dispersed mixing water obtained from a commercial supplier. For the 2 wt.% CNT content, a predispersed solution that had undergone ultrasonic dispersion treatments during the manufacturer's production process was utilized. The 1 wt.% CNT content was prepared by diluting this treated 2 wt.% solution with water. In contrast, for the 4 wt.% CNT content, the pre-dispersed water was supplied by the manufacturer without any ultrasonic processing during its production and was used directly as received.

The specimens used for impedance measurements were prepared by casting the CNTCP into a 55 × 55 × 40 mm plastic mold, in which electrode plates were affixed to the inner surfaces using adhesive. For four CNT content levels (0, 1, 2, and 4 wt.%), three specimens were prepared for the dried condition and three for the saturated condition (totaling six specimens per level). Regarding the environmental conditioning prior to the measurements, the saturated specimens were cured in water at a constant temperature of 20° C. For the dried specimens, owing to the material limitations of the plastic molds which preclude the use of organic solvents, a vacuum drying treatment was continuously applied from three days before the measurement until the day of testing, without implementing any preparatory acetone immersion.

Impedance measurements were conducted by connecting

Table 1 Mix proportions

Tested Specimens	[wt.%]			[kg/m^3]			
	W/C	CNT/W	Ad/C	W		C	Ad
				Tap water	CNT sol.		
CNT0	25	0	0.5	660	0	2643	13.2
CNT1		1		330	330		
CNT2		2		0	660		
CNT4		4		0	660		

W: Water, C: Cement (3.16 g/cm^3), CNT: Carbon nanotube (BET: 158 m^2/g), CNT sol.: Carbon nanotube solution (CNT purity: 93 %), Ad: High-performance AE water-reducing agent (Polycarboxylic acid ether type)

the electrodes attached to the specimens with the measurement device, applying an alternating current of 10 mA. The measurement frequency ranged from 3 MHz to 0.1 Hz, with the sweep mode from the high-frequency side to the low-frequency side. Measurements were conducted on 14 and 28 days of material age elapsed, respectively.

The specimens used for evaluating the pseudo-piezoelectric properties were cylindrical measuring 50 mm in diameter and 100 mm in height. The saturated specimens were maintained under water curing at a constant temperature of 20°C until the loading test. Conversely, the dried specimens underwent a rigorous solvent-replacement drying process: four days before the loading test, the specimens were immersed in acetone for 24 hours, followed by a continuous vacuum drying treatment from three days before the test until the moment of loading. Under both dried and saturated conditions, three specimens were prepared for the four CNT content levels. To evaluate the responses against mechanical stimuli, repeated loading tests were conducted on the specimens at the ages of 14 and 28 days.

The measurement setup for the voltage response was configured as follows: copper plates with attached lead wires were placed on the top and bottom ends of the cylindrical specimen to serve as electrodes. Furthermore, insulation plates were inserted above and below these copper plates to isolate the specimen and electrode system electrically from the universal testing machine.

The cyclic compressive loading range was set between a minimum load of 1 kN and a maximum load of 5 kN. The minimum load of 1 kN was maintained during the cyclic testing to prevent any separation or loss of contact between the specimen ends and the copper plate electrodes, thereby ensuring stable and continuous electrical connectivity. This relatively low maximum load of 5 kN (corresponding to an approximate compressive stress of 2.55 MPa) was intentionally selected as a non-destructive preliminary evaluation to minimize the occurrence of structural microcracking or irreversible damage in the cement paste matrix, allowing for a focused investigation into the reversible electrochemical polarization behavior and the qualitative mechanism of the pseudo-piezoelectric effect. Within this range, ten cycles of repeated loading were applied at a loading rate of 8 kN/min.

3.Results and Discussion

3.1Impedance characteristics

Figure 1 (a) shows the Bode plot of the impedance magnitude, while Fig. 1 (b) represents the Bode plot of the phase angle under the dried condition at 14 days of material age.

From Fig. 1 (a), it is observed that the overall impedance in the range of 100 Hz to 10 kHz tends to decrease with the increase in CNT content from 0 wt.% to 2 wt.%. This fact could be attributed to the function of CNTs as conductive fillers, which may facilitate the formation of additional conductive pathways alongside the inherent pore solution within the cement matrix. It is noted that the CNT4 specimen exhibits a minor deviation from this hierarchical trend in the high-frequency range; this subtle inversion is not considered a measurement error but could be interpreted as a reflection of local microstructural heterogeneity or altered network connectivity naturally arising at such a high concentration level.

Further, although the corresponding graphical data for 28 days of material age are omitted here for brevity, the overall impedance at this advanced age was higher than that at 14 days of age across all CNT content levels. This consistent trend is presumably due to the progress of the hydration reaction over time. As unhydrated cement particles react, the resulting densification of the pore structure potentially leads to a restriction of ionic transport pathways and a reconfiguration of the networks formed by the pore solution and CNTs.

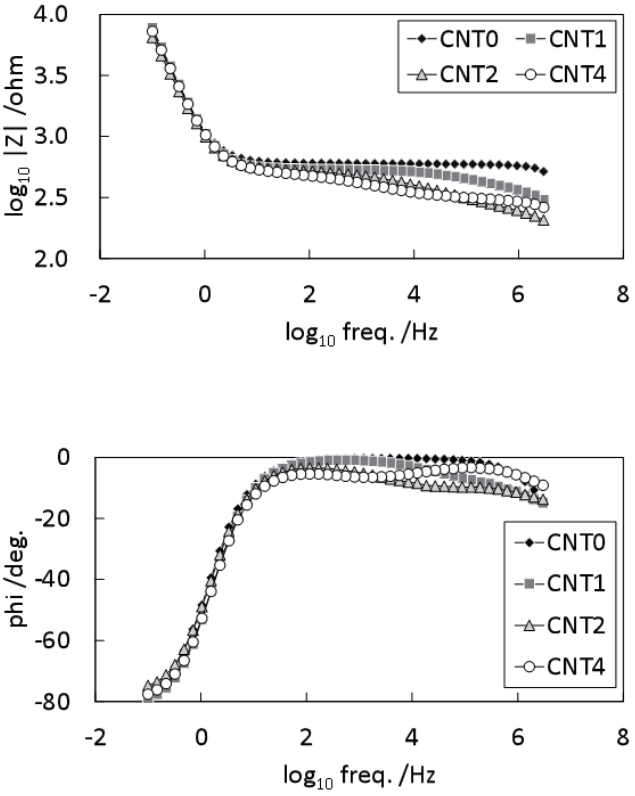


Fig. 1 Bode plots under dried condition at 14 days of material age: (a) impedance magnitude, and (b) phase angle.

From Fig. 1 (b), at all CNT content levels, the phase angles approach approximately − 80° in the low-frequency range (0.1–10 Hz) suggesting that the capacitive component dominates the impedance response in this range. In contrast, in the mid-to-high-frequency range (10 Hz–10 kHz), the phase angle shifts toward 0° , implying that the resistive feature becomes the primary governing factor of the impedance characteristics. These results indicate that a significant phase lag occurs in the low-frequency range, which could reasonably suggest the presence of distinct charge accumulation and interfacial polarization processes.

To further analyze these electrochemical processes, Fig. 2 shows the Nyquist plot of the impedance. An examination of the overall spectral profiles reveals a systematic structural evolution in the internal impedance characteristics depending on the CNT dosage. Specifically, across all CNT content levels, the semicircular arcs on the low-frequency side are observed to almost overlap with one another, suggesting that the primary time constants (τ=RC) governing the lower-frequency domain remain largely unchanged under the same moisture state. In contrast, regarding the responses in the higher-frequency region, the semicircular arc of the CNT0 specimen is positioned furthest to the right (indicating a larger real impedance component). With the increase in CNT dosage, this high-frequency arc systematically shifts toward the left side, concurrently increasing the number of detectable arcs for the CNT2 and CNT4 specimens. This spectral evolution suggests a progressive enhancement of the high-frequency alternating current transport, which could be closely linked to the alteration of individual electrochemical time constants introduced by the internal CNT networks.

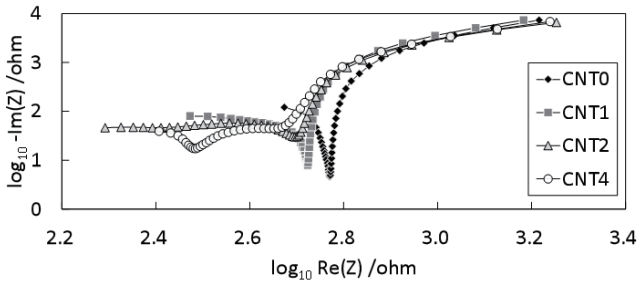


Fig. 2 Nyquist plots under dried condition at 14 days of material age.

For the CNT0 and CNT1 specimens, the spectral responses across the measured frequency range are characterized by a combination of two interconnected semicircular arcs, which can be interpreted as representing two distinct primary electrochemical time constants within the system. In the CNT2 specimens, a flattened or collapsed semicircular response is observed on the high-frequency side, which could be attributed to the proximity and subsequent overlapping of the time constants associated with the cement matrix and the newly formed CNT-matrix interfaces. In contrast, the CNT4 specimens display a distinct resolved response consisting of three separate semicircular arcs. This separation suggests that at higher concentrations, the electrical features of the intensive CNT networks may alter the respective resistance and capacitance, shifting their characteristic time constant away from that of the matrix and allowing it to appear as an independent spectral component. Concurrently, as the CNT content increases, the entire Nyquist profile systematically shifts toward the lower impedance zone (the left side of the real axis). These results suggest that the semicircular responses observed in the plots correspond to the microscopic resistive and capacitive elements formed at the internal interfaces, specifically, the interfaces between adjacent CNTs or between the CNTs and the cement matrix. As the CNT content increases, these interfacial responses become more distinct within the spectrum, suggesting that the introduction of CNT networks introduces additional capacitive boundaries that potentially participate in the high-frequency alternating current transport within the material.

3.2Pseudo-piezoelectric voltage responses

3.2.1 Influence of moisture conditions

Fig. 3 presents the synchronized time-series plots of the structural strains and pseudo-piezoelectric voltage responses of the CNT0 specimen to isolate and evaluate the intrinsic influence of moisture conditions on the matrix baseline, free from the complex electrical effects of CNT networks. The changes in pseudo-piezoelectric responses due to moisture conditions are discussed below, focusing exclusively on the specimens at 14 days of age.

Under dried conditions (Fig. 3 (a)), the CNT0 specimen exhibits a periodic and stable voltage response synchronized with the strain variations. This baseline behavior suggests that, under dried conditions, the high internal resistance prevents the rapid dissipation or neutralization of stress-induced charges, thereby allowing effective charge accumulation at the electrode–material interface. This phenomenon can also be interpreted as potentially resulting from the formation and release of electric double layers (EDLs) [7]. Furthermore, a subtle phase lag is observed between the mechanical load and the voltage peak, which could be linked to the long electrochemical time constant (τ=RC) under dry conditions. However, it is also possible that multiple stress-induced polarization mechanisms, such as the flexoelectric effect, interfacial polarization or charge migration within the microscopic structure, are simultaneously contributing to the observed response. Further detailed classification of these stress-induced polarization mechanisms should be elucidated through charge transport processes in future investigations.

In contrast, under saturated conditions (Fig. 3 (b)), despite the compressive strain being comparable to that under the dried condition, the voltage response is significantly diminished in amplitude, and its periodic characteristics disappear. In general, the application of stress induces moisture movement within the pore structure, and this movement likely causes ionic migration, which theoretically generates a streaming potential [8]. However, under saturated conditions, the continuous presence of free water filling the capillary pores reduces the baseline electrical resistance of the matrix. Consequently, the electrochemical time constant becomes excessively short, leading to an almost instantaneous dissipation of any stress-induced potential. Therefore, it is presumed that the transient ionic charges originating from the moisture movement leak or neutralize rapidly before effective polarization can be maintained at the boundaries, eventually suppressing the stable periodic voltage response.

Based on these results, it is suggested that the presence of moisture within the pore structure plays a critical role in controlling the stability of the pseudo-piezoelectric response, wherein a high moisture content dynamically accelerates

charge relaxation via decreased internal resistance and short-circuited time constants.

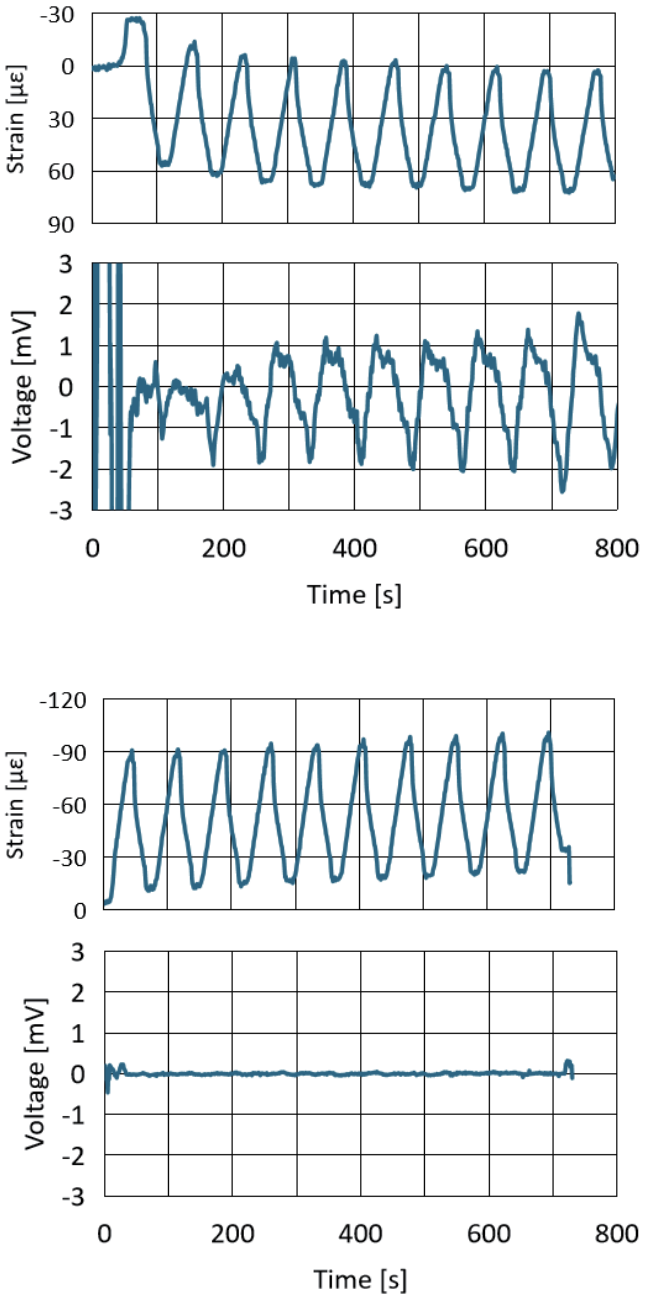


Fig. 3 Synchronized time-series plots of mechanical and voltage responses demonstrating the influence of moisture conditions for CNT0 specimens at 14 days of material age: (a) dried condition, and (b) saturated condition.

3.2.2 Influence of material age

To investigate the effect of material age of the cement matrix, Figure 4 shows the pseudo-piezoelectric responses with respect to material age of the CNT0 specimen. These are the results of specimens in the dried condition, because, in the saturated condition, the influence of moisture is so predominant that discerning the effects of the material matrix becomes difficult.

At 14 days of age (Figure 4 (a)), a voltage response is clearly observed. In contrast, at 28 days of age (Figure 4 (b)), the response becomes unstable and exhibits reduced periodicity. This trend is presumed to be closely associated with pore structural factors.

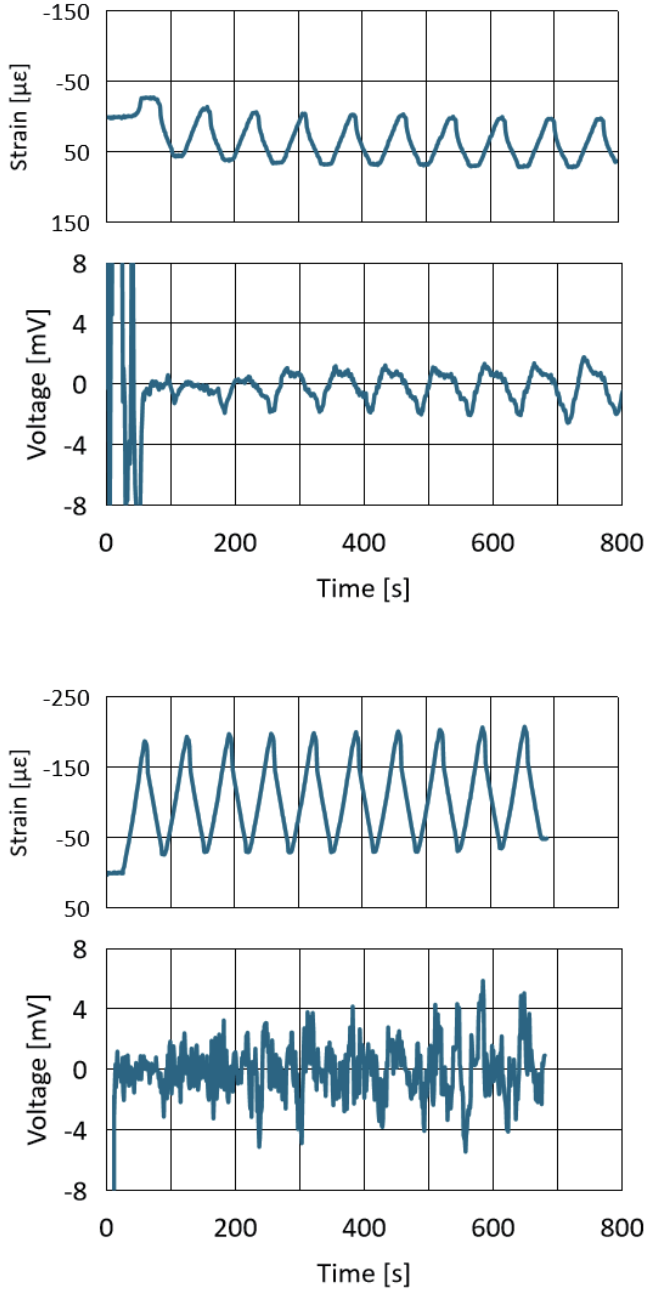


Fig. 4 Synchronized time-series plots of mechanical and voltage responses demonstrating the influence of material age for CNT0 specimens under dried condition: (a) 14 days of material age (replotted from Fig. 3(a) with axes adjusted for comparative analysis), and (b) 28 days of material age.

In the specimen at 14 days of age, the hydration reaction is not yet complete, leaving a substantial number of unreacted cement particles and capillary pores within the matrix. This

pore structure potentially functions as a site for moisture retention as well as for the polarization and accumulation of local charges. Even after the drying treatment, the formation of EDL and the generation of a streaming potential could remain through the residual moisture within the micro-pores. As a result, periodic voltage fluctuations in response to applied stress are observed.

In contrast, in the specimen aged 28 days, the cement hydration has further progressed, leading to a densification of the matrix and a reduction in pore volume. Due to this densification, the local charge accumulation sites are not only lost, but the amount of moisture retained within the matrix could be significantly reduced.

Thus, in the dried condition, the progress of material age could negatively affect the stability and clear manifestation of the pseudo-piezoelectric response. This suggests that the manifestation of the pseudo-piezoelectric response is supported by the pore structure and the small amount of moisture retained within it. It emphasizes the significance of structural changes induced by material aging on polarization characteristics.

3.2.3 Influence of CNT contents

In Fig. 5, the influence of the CNT content is given. Importantly, a clear periodic voltage response synchronized with the cyclic loading is observed across all specimens,

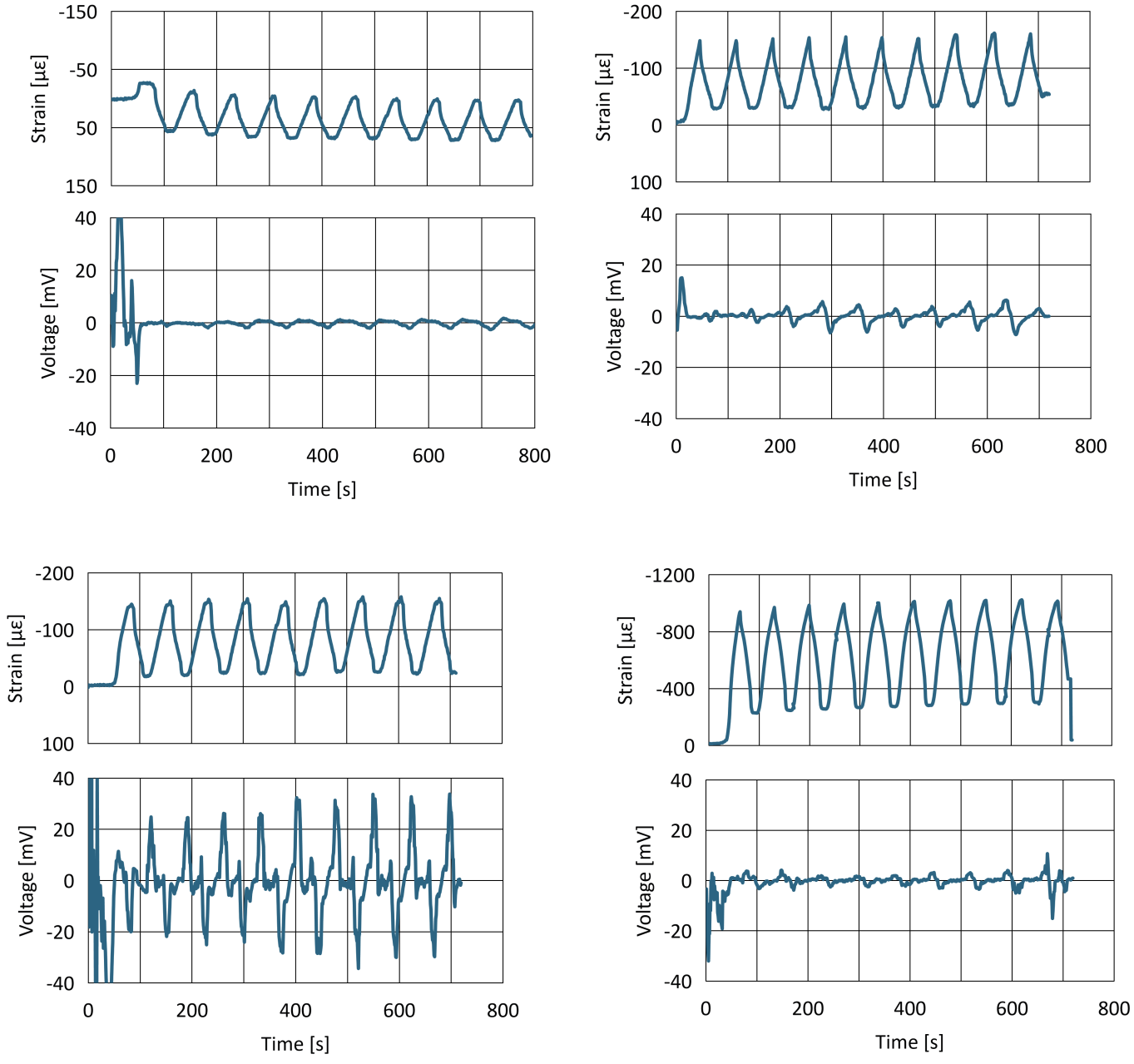


Fig. 5 Synchronized time-series plots of mechanical and voltage responses demonstrating the influence of CNT content for specimens under dried condition at 14 days of material age: (a) CNT0 (replotted from Fig. 3(a) with axes adjusted for comparative analysis), (b) CNT1, (c) CNT2, and (d) CNT4 (with the strain axis scale modified independently).

demonstrating that the stress-induced polarization characteristics are preserved throughout the tested dosage range.

The CNT0 specimen (Fig. 5 (a)) exhibits the smallest voltage amplitude with a sluggish onset. With the introduction of CNTs, the voltage output increases in the CNT1 specimen (Fig. 5 (b)), while the CNT4 specimen (Fig. 5 (d)) displays an amplitude comparable to that of CNT1. Most notably, the CNT2 specimen (Fig. 5 (c)) demonstrates the highest voltage output amplitude among all formulations, indicating that a 2 wt.% dosage optimizes the magnitude of stress-induced polarization and subsequent charge migration within the matrix. Furthermore, the total mechanical strain amplitude systematically increases with higher CNT dosages, as visibly reflected in the expanded scale required for the CNT4 specimen (Fig. 5 (d)), which suggests that the inclusion of CNT networks potentially alters the deformability of the matrix.

This variation in voltage magnitude can be reasonably linked to the frequency-domain electrical characteristics discussed in Section 3.1. The shift of the high-frequency semicircular arcs toward the left side (lower real impedance) in the Nyquist plots (Fig. 2) directly reflects the formation of additional conductive pathways and altered interfacial resistance by CNT incorporation. The enhanced charge migration capability facilitated by the CNT network and its surface wettability [9] is considered to increase the total generated potential, reaching a maximum at 2 wt.%. However, at an excessive dosage such as 4 wt.%, the complex interfacial structure, evidenced by the emergence of multiple resolved RC components in Fig. 2, as well as the potentially formed short-circuiting pathways, may dynamically accelerate charge relaxation (shortening the local time constants). This accelerated dissipation likely counteracts the polarization process, causing the voltage amplitude of the CNT4 specimen to decrease back to a level comparable to the CNT1 specimen.

Thus, the appropriate incorporation of CNTs plays a crucial role in promoting the polarization response within cementitious materials, enhancing the manifestation of pseudo-piezoelectric responses. Particularly in the CNT2 specimen, a favorable balance between conductive pathways and interfacial structure is achieved, resulting in superior voltage generation amplitude. On the other hand, excessive addition of CNTs (as in CNT4) could lead to charge diffusion and immediate dissipation due to increased interfacial complexity and short-circuited time constants, potentially limiting the peak output magnitude. Therefore, the maximization of pseudo-piezoelectricity requires both the optimization of CNT content and the control of interfacial structure.

4.Summary and Conclusion

(1)It is suggested that the pseudo-piezoelectric response of CNTCPs is governed by the moisture condition and resulting electrochemical relaxation processes under applied stress. Under the dried condition, the small amount of moisture retained within the fine pore structure, in equilibrium with the ambient testing environment, potentially serves as a site for stable polarization, enabling a distinct periodic voltage response. Conversely, under the saturated condition, the continuous presence of free water drastically lowers the internal electrical resistance, which remarkably shortens the electrochemical time constant (τ=RC) and leads to the immediate dissipation of stress-induced potential.

(2)CNTs play a critical role in optimizing stress-induced polarization amplitude and charge migration within the matrix. First, their electrical conductivity facilitates the formation of a conductive network. Second, the introduction of CNTs tend to increase the total generated potential, reaching a maximum amplitude at a 2 wt.% dosage (CNT2). This peak response is presumed to be achieved through a favorable balance between enhanced charge migration paths and interfacial polarization, which is also accompanied by an increase in total strain amplitude with higher CNT contents.

(3)However, excessive CNT content (such as 4 wt.%) increases interfacial complexity, as reflected by the emergence of multiple resolved RC components in the high-frequency region of the Nyquist plots. These capacitive elements and short-circuiting conductive pathways may dynamically accelerate charge relaxation, causing the generated charges to immediately dissipate and consequently lowering the voltage amplitude back to a level comparable to that of the 1 wt.% specimen. In the case of the absence of CNTs (CNT0), the conductive pathways with CNTs are not formed, which restricts the charge transport required to rapidly align transient potentials, leading to a weak output with a sluggish onset.

CRediT authorship contribution statement:

Tatsuya Hirayama: Methodology, Carrying out the experiments, Writing-original draft

Tomoko Fukuyama: Conceptualization, Supervision, Writing-review & editing

Declaration of Competing Interest

This manuscript is original and has not been published nor under consideration for publication elsewhere. We have no conflict of interest to be disclosed.

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