

# 비전통핵생성 이론 관점에서 탄산칼슘의 반응경로에 대한 시간분해 분극 및 탈분극 추적

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Time-resolved polarization and depolarization tracking on reaction pathway of calcium carbonates in a view of non-classical nucleation theory

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**Abstract:** The formation characteristics of calcium carbonates are closely related to the durability and mechanical properties of cement-based materials. In this regard, a deep understanding of the reaction pathway of calcium carbonates is critical. Recently, non-classical nucleation theory was summarized and it was presumed that prenucleation clusters are present. The formation of the prenucleation cluster at undersaturated condition ( $\approx 0.1 \text{ ml}$ ) in the present study was investigated via electrical characteristics of an electrolytic solution. Calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were used as starting materials to supply calcium and carbonate sources, respectively. Furthermore, the reaction pathway of calcium carbonates was investigated by time-resolved polarization and depolarization characteristics of the electrolytic solution. The time-resolved polarization and depolarization tests were conducted by switching polarity with an interval of 20 seconds for 1 hr and by measuring the variation of electrical resistance. It can be inferred from the results obtained in the present study that the reactive constituent for the formation of calcium carbonates was mostly consumed in the period possibly associated with the prenucleation and the reaction pathways may be governed by the monomer-addition mechanism.

**키 워 드:** 비전통 핵생성 이론, 핵생성이전단계 클러스터, 분극현상, 탈분극현상

**Key Words:** Non-classical nucleation theory, Prenucleation cluster, Polarization, Depolarization

## 1. Introduction

The formation and the addition of calcium carbonates are closely related to cement-based materials. Calcium carbonates have been used in the field of construction materials. The addition of calcium carbonates could promote the hydration characteristics of cement-based materials, and modify the microstructure (Kakali et al., 2000; Dweck et al., 2000; De Weerd et al., 2007). Meanwhile, the formation of calcium carbonates in cement-based materials could occur during the service life, owing to the carbonation reaction of residual calcium sources and decalcification of calcium silicate hydrates (Johannesson et al., 2001). The carbonation reaction in the cementitious matrix could lead to the reduction in the alkalinity and thereby corrode reinforcing bars in concretes (Gonzalez et al., 1980). While, the carbonation reaction of cement-based materials results in the mineralization of carbon dioxide in

cement-based materials (Zhang et al., 2017). Thus, the investigation of the reaction pathways of calcium carbonates provides essential knowledge for better use of the materials and reaction characteristics.

The reaction process of calcium carbonates is quite complex. The theory related to the reaction pathways has divided into two groups. Conventionally, classical nucleation theory (CNT) proposed by Becker and Döring in the 1930s has been accepted (Becker and Döring 1935). Nuclei in the theory are formed at the supersaturated condition and move to the nucleation process and growth of crystals (Gibbs, 1879). Non-classical nucleation theory was summarized by Gabauer et al. (Gabauer et al., 2008). The critical difference between CNT and NCNT is the presence of prenucleation clusters before the formation of nuclei (Gabauer et al. 2008). Gabauer et al. experimentally verified the presence of a

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matter being presumed as liquid-like ionic polymers and named prenucleation cluster (Gabauer et al. 2008). Afterward, the studies on the prenucleation clusters have been extensively conducted by researchers via time-resolved raman, X-ray diffraction, small angle X-ray scattering, and dynamic light scattering techniques (Wang et al., 2012; Maruyama et al., 2015; Mohammed et al., 2019; Kellermeier et al., 2012).

In the present study, the formation of the prenucleation cluster at undersaturated condition ( $\approx 0.1 \text{ ml}$ ) was investigated via electrical characteristics of an electrolytic solution. Calcium chloride dihydrate and sodium carbonate were used as starting materials to supply calcium and carbonate sources, respectively. Furthermore, the reaction pathway was investigated by time-resolved polarization and depolarization characteristics of the electrolytic solution.

## 2. Experimental program

### 2.1 Raw materials

Calcium chloride dihydrate ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) (Sigma Aldrich, analytical grade) were used as starting materials. The concentration of the starting materials was fixed at  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ . The ultrapure water (Milli Q, resistivity:  $18.2 \text{ M}\Omega \cdot \text{cm}$ ) was used to dissolve the starting materials.

### 2.2 Methods

The starting materials were dissolved in ultrapure water of 500 ml and stirred at 300 rpm for 5 minutes, respectively. Each solution was sealed with paraffin film (parafilm M, Pechiney plastic packaging CO. IL, USA) to prevent the effect of carbon dioxide dissolved from the atmosphere.

Figure 1 shows the experimental setup to measure the electrical resistance of the electrolytic solution. The glass reactor has a capacity of 1 L, and copper electrodes (30 mm  $\times$  90 mm  $\times$  1.0 mm) with a distance of 10 mm were inserted into the cover of the glass reactor to measure the electrical resistance of the electrolytic solution. The electrodes were linked to a data acquisition unit (Agilent

34970A, Agilent Technologies) to measure the electrical resistance of the mixed solution. Sodium carbonate solution in the test was firstly poured and the calcium chloride dihydrate solution was then mixed. The mixed solution was magnetically stirred at 100 rpm to ensure homogeneity of the solution. The beaker was also sealed with the cover within 10 seconds and the electrical resistance of the solution was immediately recorded for 5 hrs.

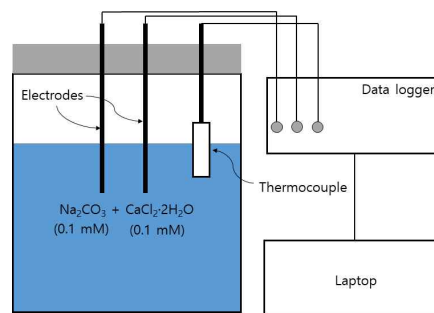


Figure 1. Experimental set up for measurement of electrical resistance variation with time.

For the polarization and depolarization tests, the identical setup to the measurement of electrical resistance was used. The polarity during the test was switched with an interval of 20 seconds for 1 hr to measure the variation of electrical resistance induced by polarization and depolarization effects.

## 3. Result and discussion

Figure 2 shows the electrical resistance variation of the electrolytic solution during the precipitation of calcium carbonates. The curve during the precipitation process can be divided into three regions as shown in Fig. 2. It was observed that the electrical resistance in Zone I slightly increased compared to Zone II. Referring to the previous study conducted by Hamdia et al., the result indicated that polarization effect and the formation of prenucleation clusters mainly contributed to the increase in the resistance simultaneously of Zone I (Hamdia et al., 2019). The polarization effect is the phenomenon that oppositely charged ions are accumulated on the electrode when exposed to an electric field and thereby increased electrical resistance over time (Kim et

al., 2019). That is, the polarization affects the increase in the electrical resistance of Zone I, since an electric field was generated by DC current for measuring electrical resistance. Prenucleation clusters were reported as a thermodynamically stable matter in previous studies, meaning that the number of ionic charge carriers affecting the electrical resistance of the electrolytic solution was reduced as forming the clusters (Avaro et al., 2020). The period of Zone I in the present study was approximately for 20 minutes.

The electrical resistance in Zone II dramatically increased until 2 hrs of the reaction period. The increase in the electrical resistance could be mostly led by the precipitation of calcium carbonates (Hamdia et al., 2019). The precipitation of calcium carbonates could significantly reduce the ionic charge carriers. As aforementioned, prenucleation clusters with a size of approximately 20 nm in non-classical nucleation theory are firstly formed and transferred nuclei through the aggregation of clusters (Gebauer et al., 2018). The nuclei afterward were densified and undergo the crystal growth process (Gebauer et al., 2018). It is generally known that the crystal size of calcite, which is the most stable variety of calcium carbonates, is approximately 5  $\mu\text{m}$  (Folk, 1974). That is, the formation and the crystal growth of calcium carbonates probably consumed a large amount of calcium and carbonate ions, which in turn led to the significant increase in the electrical resistance.

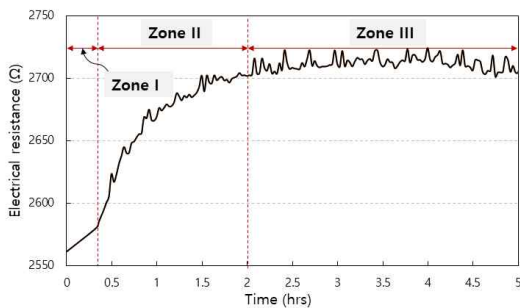


Figure 2. Electrical resistance variation of electrolytic solution ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$ ) during precipitation of calcium carbonates.

The electrical resistance in Zone III was stabilized. The result indicated that the reaction process for the precipitation of calcium carbonates in Zone II was mostly completed and reached an equilibrium state at Zone III. It can be also inferred from the results that the accumulation of ionic charge carriers including sodium and chloride ions due to polarization effect was also stabilized.

Figure 3 shows the representative polarization and depolarization curve of the electrolytic solution (Cao et al., 2004). The electrical resistance of electrolytic solutions increases during the polarization process, since oppositely charged ions are accumulated on electrodes when applying DC current (Kim et al., 2019). The depolarization effect occurs when the reverse electric field is applied. The reversibility of accumulated ionic charge carriers on electrodes at the moment of depolarization in response to the reverse electric field abruptly reduces the electrical resistance of an electrolytic solution (Cao et al., 2004).

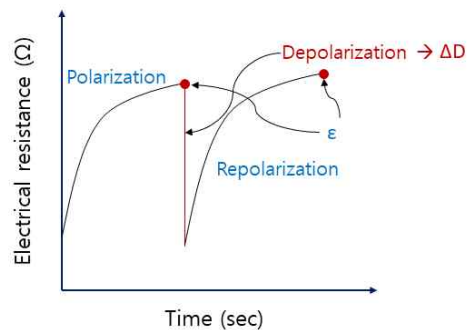


Figure 3. Representative polarization and depolarization curve of electrolytic solution under cyclic tests (Cao et al., 2004).

Figure 4 shows the electrical resistance variation due to cycles of polarization and depolarization effects. The value of an increased resistance ( $\epsilon$ ) due to the polarization effect at each cycle in the test steadily reduced during cyclic tests. In particular, the reduction of  $\epsilon$  was clearly observed until 20 minutes and then mitigated.

Figure 5 shows the variation of electrical resistance ( $\Delta D$ ) induced by depolarization effect at each cycle. The value of  $\Delta D$  at each cycle

was steadily reduced for 1hr. The absolute values of the slope of the regression curve within 20 minutes and after 20 minutes were 0.15 and 0.0551, respectively, as shown in Fig. 5(a) and (b). That is, the reduction in the  $\Delta D$  within 20 minutes was greater than that in the  $\Delta D$  after 20 minutes.

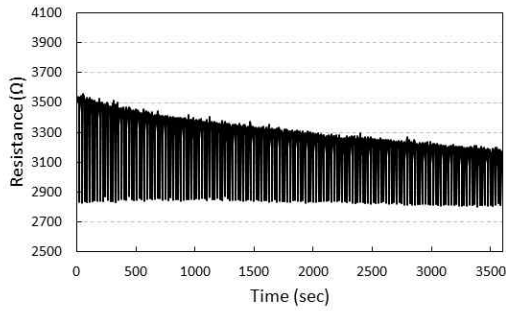
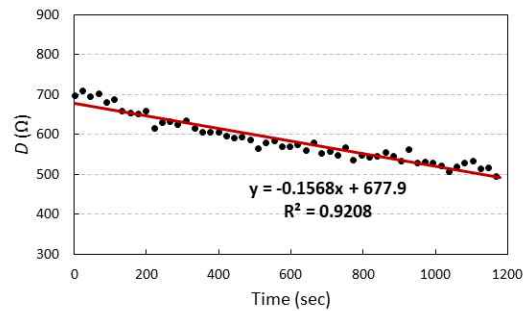


Figure 4. Electrical resistance variation during cycle test of polarization and depolarization

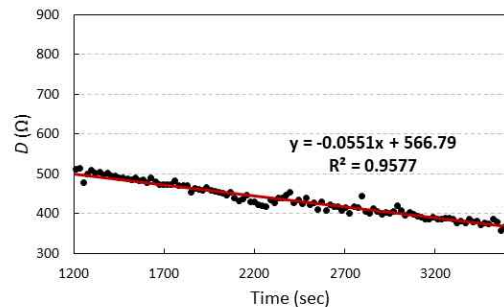
There are generally three layers such as a solid layer, hydrolysis layer, and diffuse layer in electrolytic solution with calcium, chloride, sodium, and carbonate ions (Prus et al., 2019). The solid layer initially consists of nucleation of amorphous calcium carbonates or prenucleation clusters on electrodes, while the hydrolysis layer present next to the solid layer consists of  $H_2O^+$  and  $OH^-$ , and Helmholtz planes including  $Na^+$ ,  $Cl^-$ ,  $HCO_3^-$  and  $Ca^{2+}$  (Prus et al., 2019). The diffuse layer present farthest from the solid layer consists of the ions of starting materials, of which species can be varied with pH values of the solution. That is, the variation of  $\epsilon$  and  $\Delta D$  are mostly governed by free ionic charge carriers included in Helmholtz planes and diffused layer. The free ionic charge carriers significantly affect the polarization and depolarization characteristics of electrolytic solution (Bücker et al., 2019). Thus, the clear reduction of each value within 20 minutes possibly indicated that the formation of prenucleation clusters reduced the contents of free ionic charge carriers such as calcium and carbonate ions, thereby reducing  $\epsilon$  and  $\Delta D$  values. Liu et al. stated that the dominant reaction pathway of growth of amorphous calcium carbonates (ACC) was governed by the monomer-addition mechanism (Liu et al., 2010). That is, ACC in the present study might be

formed by adding monomers consisting of prenucleation clusters with a certain size, indicating that free ionic constituents ( $Ca^{2+}$  and  $CO_3^{2-}$ ) for the formation of calcium carbonates probably were mostly consumed at the stage. Consequently, the reduction of  $\epsilon$  and  $\Delta D$  within 20 minutes was greater than that of  $\epsilon$  and  $\Delta D$  after 20 minutes.

Overall, the relatively slight increase in the electrical resistance Zone I indicated that the prenucleation clusters could partially act as a charge carrier. The formation of calcium carbonates significantly reduced the number of prenucleation clusters, thereby leading to the dramatic increase in the electrical resistivity in Zone II. The obtained results well support the previous studies on the monomer-addition mechanism of calcium carbonates growth (Liu et al., 2012; Chao et al., 2014). In this context, the change in the values of  $\epsilon$  and  $\Delta D$  after 20 minutes was mitigated, since the values might be mainly affected by the variation of free ionic charge carriers. However, a further study is needed to deeply investigate electrical characteristics of prenucleation clusters of calcium carbonates.



(a)



(b)

**Figure 5. Variation of electrical resistance ( $\Delta D$ ) induced by depolarization at each cycle in the range (a) 0 – 20 minutes and (b) 20 minutes – 1hr**

#### 4. Concluding remarks

The formation characteristics of calcium carbonates are closely related to the durability and mechanical properties of cement-based materials. The prenucleation characteristics of calcium carbonates were investigated via polarization and depolarization effects of an electrolytic solution. The finding drawn in the present study can be summarized as follows.

(1) The increase in the electrical resistance of an electrolytic solution with calcium chloride dihydrate and sodium carbonate before 20 minutes was relatively smaller than that in the electrical resistance of the solution after 20 minutes. The results indicated that the formation of prenucleation clusters in the solution probably occurred within 20 minutes.

(2) The values of  $\epsilon$  and  $\Delta D$  induced by polarization and depolarization effects of electrolytic solution before 20 minutes were smaller than those of  $\epsilon$  and  $\Delta D$  after 20 minutes. The results indicated that the free ionic constituents of the solution dominantly reduced within 20 minutes.

(3) It can be inferred from the obtained results in the present study that the formation of prenucleation clusters consuming the free ionic constituents may be mostly completed within 20 minutes, and the reaction pathway for the formation of calcium carbonates may be governed by the monomer-addition mechanism.

The obtained results in this study may provide new insight into the prenucleation, nucleation and growth conditions of calcium carbonates, and the utilization of carbonation reaction in cement-based materials.

#### 감사의 글

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