

Brief communication

Effect of an alternating current for crystallization of CaCO_3 on a porous membrane

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Received 25 June 2008; received in revised form 3 October 2008; accepted 27 October 2008
Available online 13 November 2008

Abstract

Calcium carbonate formation on a porous membrane was accelerated by using an alternating current system. A hydrophilic-treated polytetrafluoroethylene (PTFE) porous membrane was utilized for the calcium carbonate formation. The PTFE membrane was interposed with two pairs of glass cells. Calcium chloride and sodium carbonate solutions were filled in each glass cell, and an alternating current of 10 Hz was applied for 30 min. The resulting membrane was characterized in terms of crystal morphology and polymorph using scanning electron microscopy and X-ray diffraction. The major component of the resulting calcium carbonate was spheroidal vaterite, along with rhombohedral calcite. The composition of polymorphs was slight different on the two sides of the membrane. In the absence of the alternating current, only calcite was formed on the membrane. It is considered that the alteration of calcium carbonate formation is regulated by supersaturation, including electric migration, diffusion and electrolysis, during application of the alternating current. The resulting supersaturation was different on the two sides of the membrane, and different quantities of the polymorphs were formed. Taking this result into account, the alternating current catalyzed the development of supersaturation around the membrane, enabling calcium carbonate crystal to be formed.

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Keywords: Alternating current; Calcium carbonate; Vaterite; Calcite; Organic–inorganic hybrid

1. Introduction

Biological mineralization consists of several factors, such as chemical composition of the template, initial nucleation, crystal growth and positioning of the mineral [1]. Organisms have used calcium carbonate mineralization to form precise structures and hierarchical architectures for a variety of biofunctions, along with survival [2]. Although efforts toward the demonstration of mineralization strategies have been increasing recently, many details of the process involved are not yet understood. Many researches have focused on investigating the promoting effect of the combination of insoluble polymers and soluble acidic polymers on crystal nucleation and crystal growth [3–8]. In

contrast, crystal formation in nature is highly regulated and finely tuned at the molecular level. Therefore, a bio-inspired approach has been one of the strategies employed for artificial crystallization [9]. Moreover, the crystallization mechanism has been investigated in terms of nucleation and polymorph selectivity. In particular, crystal nucleation has been modeled with the help of not only surface chemical modification [10,11] but also nanospace regulation [12,13].

Calcium carbonate precipitates in three distinct crystalline forms: calcite, aragonite and vaterite, in the order of decreasing thermodynamic stability [14]. In the literature, the most common calcium carbonate polymorphs, calcite and aragonite, have been precipitated by mixing carbonate solution with calcium ion solution under conditions of regulated temperature and concentration [15]. Another approach for the regulation of calcium carbonate

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polymorphs, the addition of cations such as Li^+ , Mg^{2+} , Fe^{2+} and Ba^{2+} , has also been reported [16–18]. The added cations can adsorb on the crystal facet, promoting anisotropic crystal growth. The transformation of crystal is also crucial for the regulation of the polymorphs [19].

In recent years, we have reported controlled mineralization, such as calcium carbonate and hydroxyapatite formation in a hydrogel using a conventional gel electrophoresis apparatus [20,21]. For calcium carbonate formation, calcium chloride and sodium carbonate aqueous solutions were poured into anode and cathode cells, respectively, and the hydrogel was set in the central region between the anode and cathode cells. By applying a direct current (100 V), calcium (cation) and carbonate (anion) ions migrated into the hydrogel, where ion mixing occurred (Fig. 1A). The electrophoretic approach greatly increased the rate of ion delivery relative to spontaneous diffusion. However, only calcite crystal was formed in the hydrogel. In this process, ions were continuously supplied to the hydrogel from the solution in the cells; therefore, a high ion concentration was retained. Thus, thermodynamically stable calcite formation was achieved. We believe that a suitable process is required for vaterite formation wherein metastable crystal formation will be crucial.

In the present study, an alternating current was utilized for facilitating the ion migration (Fig. 1B). The frequency is freely changeable in the alternating current system. As a template material, a hydrophilic-treated porous membrane was used for calcium carbonate formation and as a mixing environment for the calcium chloride and sodium carbon-

ate solutions. Although the calcium and carbonate ions were separated by the porous membrane, if an alternating current with an appropriate frequency is applied, the calcium and carbonate ions could effectively migrate to the other side through the porous membrane. Moreover, electrolysis was induced in each cell. As shown in Fig. 1B, chloride ions were oxidized to produce chlorine gas (CaCl_2 side), and then the dissolved chlorine gas was converted to hydrochloric acid and perchloric acid. The resulting acids could reduce the pH on the CaCl_2 side. On the other hand, electrolysis of water was only observed on the Na_2CO_3 side. Therefore, the pH of the Na_2CO_3 side was maintained by applying the alternating current. From this experimental design, we discovered that an alternating current system accelerates vaterite and calcite formation on both sides of a porous membrane.

2. Materials and methods

2.1. Calcium carbonate formation on a porous membrane by using alternating current

A hydrophilic-treated polytetrafluoroethylene (PTFE) porous membrane (diameter: 25 mm, thickness: 35 μm) was purchased from ADVANTEC Toyo Kaisha Ltd., Tokyo, Japan. The PTFE membrane was used without any pre-wetting treatment. The average pore size was 0.1 μm , and the void fraction was 71% according to the data sheet from the supplier. The membrane was interposed between glass cells (Shibata Scientific Technology

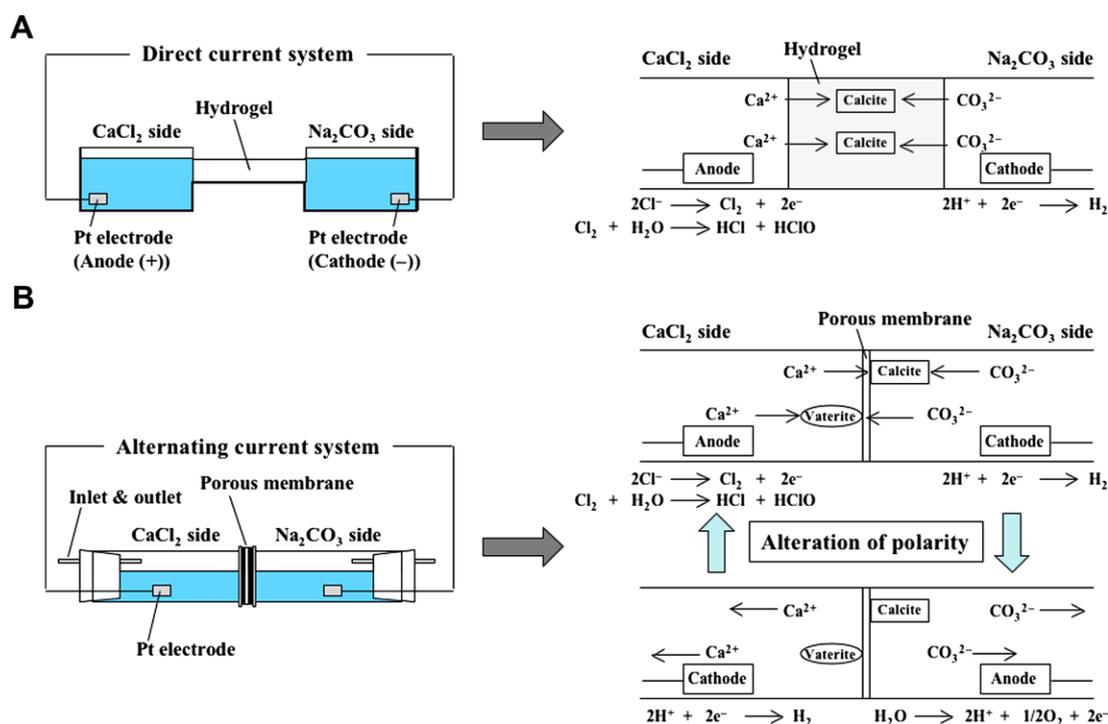


Fig. 1. Schematic illustration of calcium carbonate formation by electrochemical approaches: (A) direct current and (B) alternating current were utilized for the crystallization.

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