Application of Impedance Spectroscopy to Cement-Based Materials : Hydration of Calcium Phosphate Bone Cements

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ABSTRACT

Impedance spectroscopy was applied to the initial hydration of calcium phosphate bone cements in order to investigate the electrical/dielectric properties. Hydration or equivalently setting was monitored as a function of the amount of water and initial powder characteristics. Higher amounts of water produced more open microstructures, leading to higher conductivity and enhanced dielectric constant. The effects of the initial characteristics in the powder were investigated using bone cement powder prepared with and without granulation. Granulated powder exhibited a significant change in resistance and produced a higher dielectric constant than those of conventional powder. Through a simplified modeling, the effects of thickness in reaction products and pore sizes were estimated by the frequency-dependent impedance measurements. Furthermore, impedance spectroscopy was proven to be a highly reliable tool for evaluating the continuous change in pore structure occurring in calcium phosphate bone cements.

Key words : Calcium phosphate bone cements, Hydration, Impedance spectroscopy, Electrical/Dielectric properties

1. Introduction

C alcium Phosphate Bone Cements (CPBC) have been recognized as replacement materials for bone repair in surgical applications. The bone cements for medical applications should possess the following biocompatible requirements: nontoxicity, mechanical stability, full resorbability in human bodies, and easy control in final shaping at ambient conditions.[1] The CPBCs incorportate the various compositions, e.g., β-tricalcium phosphate (β-TCP), α-tricalcium phosphate (α-TCP), and tetracalcium phosphate (TECP). Depending on the type of the major components, the setting times, compressive strength, and reaction products vary significantly.[2-4] The hydration in CPBCs involves the continuous reaction through exposure to an environment in which the corresponding microstructure does not remain unchanged. The evolving microstructure has a significant effect on the mechanical properties, compressive strength, and the electrical/dielectric properties. Researchers have attempted to understand the hydration in cement-based materials through the use of various techniques: mercury intrusion porosimetry, scanning electron microscopy, Brunauer-Emmett-Teller (BET) methods, hardness tests, etc. The above-mentioned analysis techniques have poor reproducibility in monitoring the key features of the hydration process due to the destructive characteristics in the sample preparation and analysis steps. Impedance spectros-

copy has been proposed to evaluate the hydration in Portland cements as a nondestructive tool which does not involve any intentional interruption in the continuous setting.[5-10]

Impedance Spectroscopy (IS) is a powerful technique to investigate the electrical/dielectric properties in nonconductive materials. The exemplary systems incorporate a wide range of materials, e.g., grain boundary controlled electroceramics, solid oxide fuel cells, corrosion in metallic systems, and cement-based materials. Frequency-dependent impedance spectroscopy has the function of separating bulk-based responses from electrode-related phenomena by using the simultaneous evaluation of the electrical and dielectric information. The depression analysis in Nyquist plots ($-Z_{imag}$ vs. Z_{real}) can provide information concerning the inhomogeneity in the microstructural features governing the corresponding bulk information. The electrical/dielectric properties, which occur only through hydration in cement-based materials, have been attributed to ionic conduction between the highly resistive solid phases.[5] The ionic conduction arises due to the dissolution of ionic species in cement phases and the high fraction of the liquid phase, which guarantees the percolation in the conducting paths. The resulting characteristics are assumed to be described by the equivalent circuits made up of resistors and capacitors. The resistance and capacitance changes continuously as a function of hydration time and processing variables. Similarly, the CPBC bone cements contain high concentrations of Ca^{+2}, OH^-, PO_4^{-3}. The ionic conduction can be estimated in the evolving microstructure in CPBCs, using impedance measurements, considering the application of IS

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to hydration in cement-based materials. In particular, the setting kinetics is predominantly fast, unlike that of Ordinary Portland Cements (OPC). However, the CPBCs do not show any kind of nano-scale gel-pores present in OPC. Such rapid kinetics and high fraction of capillary pores filled with ionic solutions are ideal for applying IS in order to investigate the setting phenomena in CPBCs.

The present work focuses on the setting behavior in CPBC, using impedance spectroscopy. The electrical/dielectric information was monitored through *in-situ* impedance measurement in terms of hydration time and processing variables, e.g. amount of water, humidity conditions, and powder preparation methods.

2. Experimental Procedure

The CPBC pastes were prepared by hand-mixing the solid powder with the setting liquid at ambient conditions. The ratio of the liquid to the bone cement powder was maintained between 0.4 and 0.6, considering the workability of the paste. After mixing, the paste was poured directly onto a measurement apparatus of Fig. 1 where two electrodes were fabricated in the form of a tube and rod made of stainless steel. The electrodes were connected to a low-frequency impedance analyzer (HP4192A, Palo-Alto, California). The measurement setup was contained under 100% relative humidity at ambient conditions; the sealed chamber incorporated the vessel filled with the tap water. The impedance spectra were collected as a function of frequency 10 points per decade in the logarithmic manner between 10 MHz and 10 Hz. Standard nulling procedures were employed to remove the inductive and capacitive effects from the leads and measurement apparatus through open and short circuit correction procedures.[5]

In order to understand the hydration phenomena, a simplified model was constructed like that applied to ordinary Portland cement.[1] A schematic diagram of a test fixture is shown in Fig. 2, where the barrier was located between two planar electrodes and the barrier was drilled into three different diameters. Impedance information was collected as a
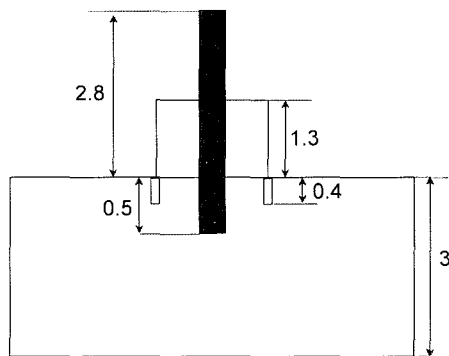
Fig. 1. Experimental setup for impedance measurement in calcium phosphate bone cements which is placed within an sealed container. [unit: cm]
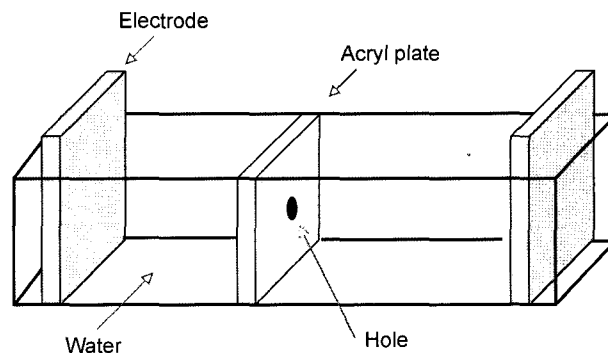
Fig. 2. A simplified model for simulating the impedance behavior in CPBCs.

function of thickness and hole diameter in the barriers. Epoxy was employed as a sealant material for water-proofing in order to prevent water leakage between the barriers and container wall.

3. Results and Discussion

The typical impedance spectra of CPBCs are shown in Fig. 3, and the frequency decreases from left to right. In Fig. 3, impedance spectra were collected as a function of hydration time: the overall impedance changes to the right, indicating high resistance in bulk responses. The impedance spectra are separated into two portions: the high frequency arc is assigned to the bulk-related responses, and the low-frequency portion is estimated to originate from the polarization occurring at the cement/electrode interfaces. The low-frequency arc is a superposition of two electrode arcs since the conventional ac 2-point impedance spectroscopy was applied to the current measurement. The bulk information is affected through a continuously-evolving microstructure: the pore structure contains a highly-conductive solution, and the pore structure becomes more complex, i.e., more tortuous in terms of length and pore size, as the hydration or equivalently setting proceeds. In other words, the self-setting characteristics are reflected in impedance measurement. The pore solution includes high concentrations of hydrated ions such as Ca^{2+}, PO_4^{-3}. OH^-, and HPO_4^{-2}, and the ionic conduction does not perform complete charge transfer between the electrons in electrodes and the ions in pore solutions. Such polarization leads to additional electrode-related features as the low-frequency regime in Fig. 3. Fortunately, impedance spectroscopy allows the separation of the bulk responses with one due to electrodes through the simultaneous monitoring of resistance and capacitance, as evidenced in Fig. 3. Fig. 3(b) exhibits frequency-dependent capacitances: at high frequency, the capacitance is in the range of tens of pF and, thereafter, the capacitance increases up to the range of mF. The discrete difference in capacitance forms the two arcs in the Cole-Cole plot of Fig. 3(a). Based on the experimental information of Fig. 3(a) and (b), an equivalent circuit model is proposed, as shown in
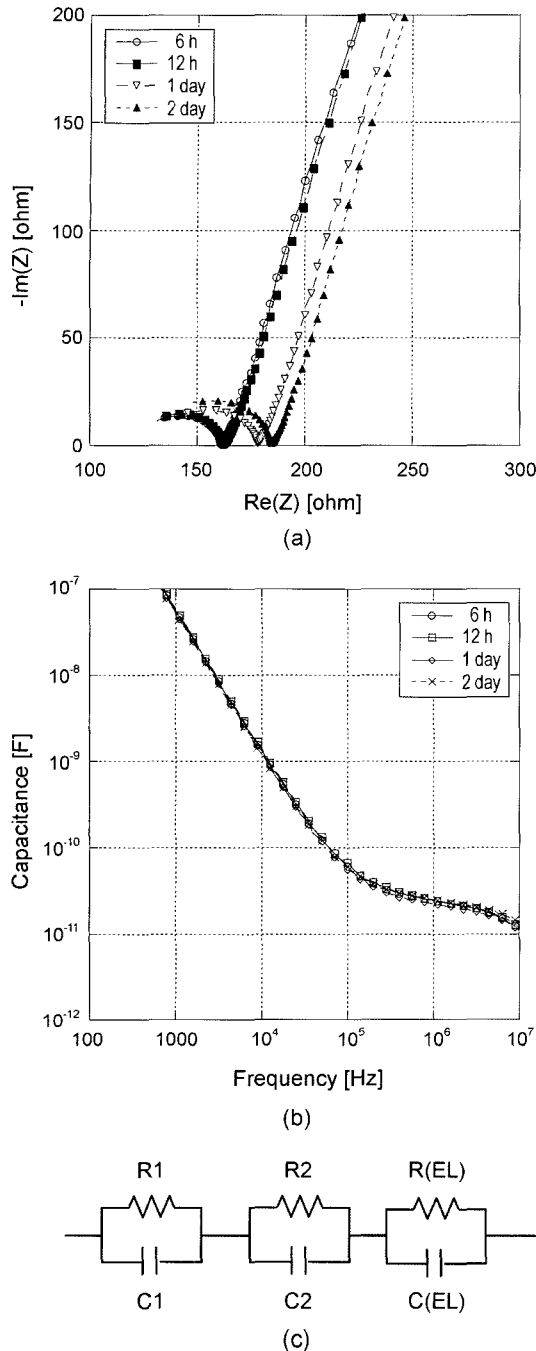
Fig. 3. (a) raw impedance spectra in hydration of CPBCs, (b) capacitance vs. frequency corresponding to Fig. 3(a), and (c) an equivalent circuit model where R1, R2, C1, and C2 are assigned to the bulk responses and R(EL) and C(EL) to the electrode-related components.

Fig. 3(c). The presence of R1 and C1 is not guaranteed at the current stage of work since the measured spectra do not form a complete semi-arc.

The impedance information is significantly dependent on the evolving microstructure whose components are in solid and liquid phases. Each phase is interconnected in three-dimensional format: the 3-3 interconnection is estimated

through the so-called "electrocomposite theory" in the CPBC pastes.[12] The solid component is made up of the initial CPBC cements and the hydration products. The solid phase is highly resistive compared with the liquid phases in the pore solution. Ultimately, the pore solution will dominate the electrical/dielectric response in the hydration in CPBCs. As the hydration continues, the average pore size decreases continuously and the interconnected path in capillary pores becomes narrower and longer. The conduction due to the liquid portion in the microstructure determines the impedance behavior in CPBC-based pastes. The ionic conduction and the changing microstructure can be assumed to be quite similar to that of ordinary Portland cements.[5] The electrical/dielectric properties in both systems are dominated by the amount and size of capillary pores, which can be quantized using the term "tortuosity" (or reciprocally "interconnectivity"). It should be noted that the CPBCs do not involve the gel-pores found in OPCs. The electrical conduction can be described according to the electrocomposite theory.[12] The apparent conductivity is given by

$$\sigma_t = \Sigma\sigma_i\beta_i\phi_i = \sigma_s\beta_s\phi_s + \sigma_o\beta_o\phi_o \tag{1}$$

where σ_t is the apparent conductivity, σ_i the conductivity of phase i, β_i the interconnectivity of phase i, and ϕ_i volume fraction of phase i. The subscripts, s and o are denoted by the solid and liquid phases, respectively. Considering the high resistivity of the solid phase, Eq. (2) is reduced to

$$\sigma_t = \sigma_o\beta_o\phi_o \tag{2}$$

Through the hydration, the effect of the solid phase can be considered to be negligible compared to that of the liquid pore solution. From the impedance spectra, the bulk resistance exhibits information based on the Eq. (2). The longer the hydration time, the higher the resistance. The interactive contribution of the solid and liquid phases is constructed through the conductive ionic flow among insulating solid components (See Fig. 4). Furthermore, higher amounts of the setting liquid retards the setting characteristics, concurring with larger pore sizes. The larger the pore diameter, the smaller the bulk resistance. The high bulk resistance can be ascribed to lower compressive strength since the compressive strength is highly sensitive to the pore structure. Simultaneously, higher amounts of the liquid phase enhance the overall capacitance, qualitatively proportional to the relative ratio of water to cement, as shown in Fig. 4(b).

In actual situations, the CPBCs can be exposed to ambient conditions accidentally or intentionally. The setting in open atmosphere causes the water to vaporize to the surrounding environment: the relative humidity is much lower than 100%, leading to water removal. As the CPBC paste system is exposed to air, the liquid phase is no longer in equilibrium with the atmosphere. The evaporation of H_2O occurs continuously and modifies the microstructural interconnection mediated by the presence of highly conductive pore solutions. Upon exposure to air, the paths in ionic con-
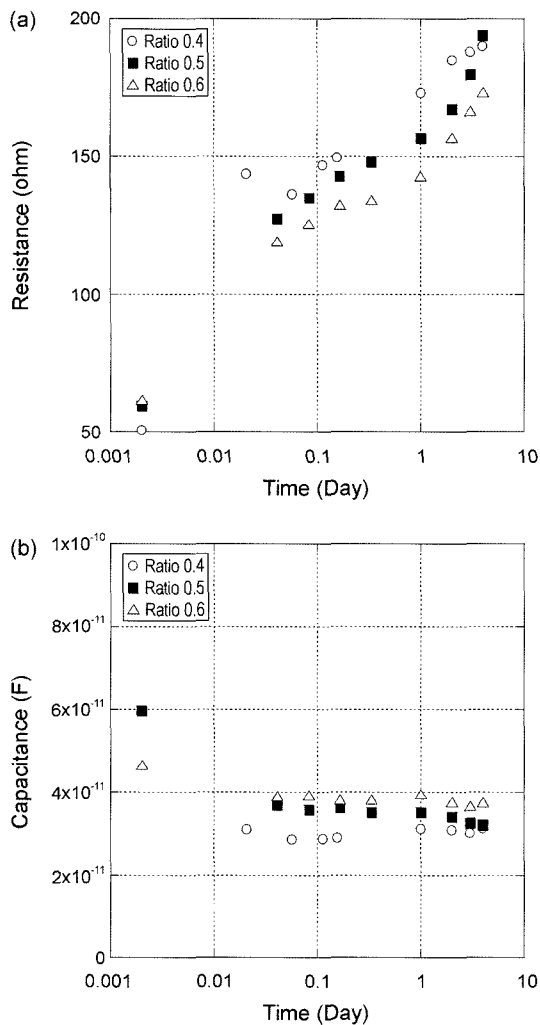
Fig. 4. Effect of the water/cement ratio in CPBCs on the electrical/dielectric properties : (a) resistance and (b) capacitance.
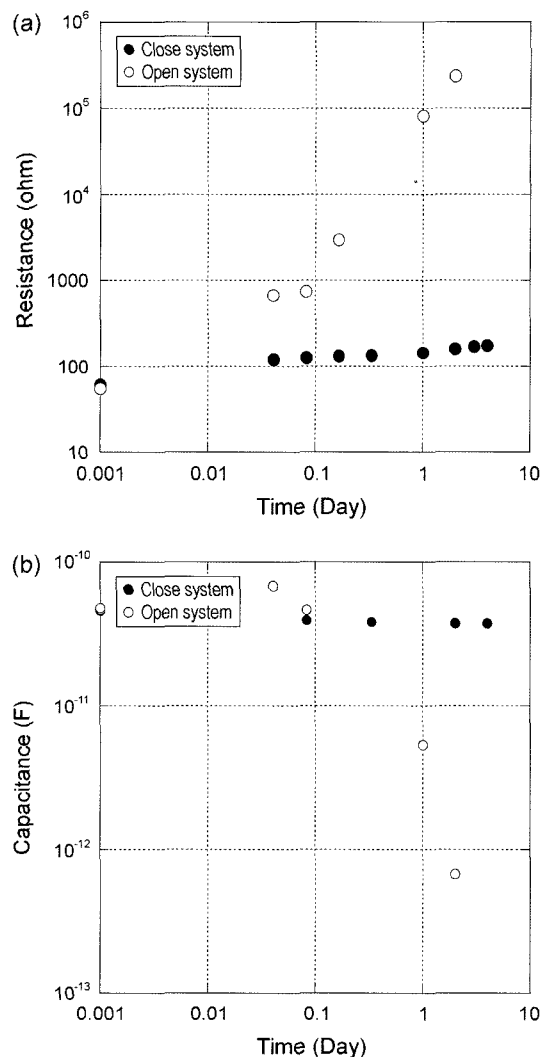

Fig. 5. Effect of hydration environment on the electrical properties as a function of time : (a) resistivity and (b) capacitance for open and closed conditions.

duction are disconnected and the pore solution reduces the fraction of pore volume and retards the formation of reaction products. The combined effects increase the overall resistance significantly, as shown in Fig. 5. The capacitance decreases dramatically compared to that of the closed system after long exposure to air (See Fig. 5(b)).

The initial morphology in the powder was controlled through the application of a granulation process to the calcium phosphate mixture. Conventional powders are subject to uncontrolled and irreproducible agglomerates. The undesired agglomeration modifies paste rheology and hydration in combination with pore structures. The intentional granulation forms controlled agglomerates, typically for facilitating in flowing and filling in molds. The application of granulation provides larger initial size, in addition to enhanced workability in paste form. Fig. 6 shows the impedance spectra measured in two types of powders, i.e., ungranulated and granulated powders. The granular structure in CPBCs increases the resistance rapidly around 0.1 day, i.e.,

2 - 3 h. The concurrent capacitance is more enhanced than that of the conventional CPBC pastes. Both changes appear to be connected to two different modes in pore structures of granulated bone cement pastes: one is assigned to the pores present within the granulated powers and the latter limited to the pores between the granulated powders. The combined contribution is expected to bring about a sudden change in resistance after around 2 - 3 h. The challenging feature in granulated bone cement systems will require further study following the experimental report of this work.

Hydration in cement-based materials is closely related to the formation of reaction products through the consumption of liquid phases. The continuous chemical reaction hinders the effective ionic conduction. Such ion conduction in CPBCs is simulated through a simplified model, as shown Fig. 2: the barrier thickness is assumed to be in the solid phase, and the hole is considered to be an interconnected path in two large capillary pores. The current hydration in
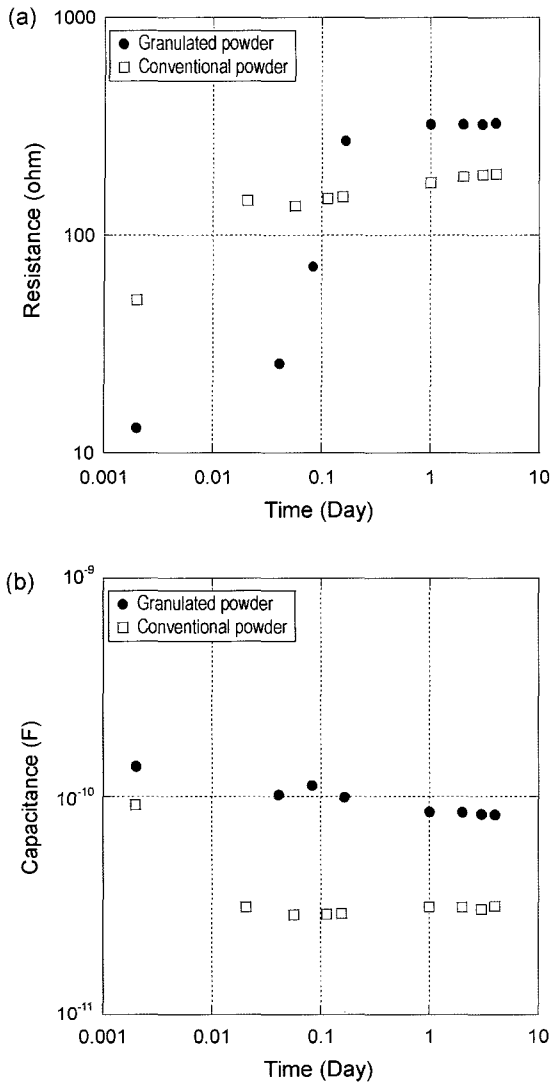
Fig. 6. Effect of initial powder characteristics on the electrical/dielectric properties (a) resistance and (b) capacitance as a function of hydration time.

Fig. 7. Simulated impedance spectra for hydration in CPBCs : (a) Effect of layer thickness on impedance spectra where the hole diameter was fixed to be 1mm. Thin thickness (1.35 mm), medium thickness (1.7 mm), and thick thickness (3 mm) and (b) Effect of hole diameter on impedance spectra where the thickness was fixed to be 1.35 mm. Small diameter (1 mm), medium diameter (3 mm) and large diameter (7 mm).

bone cements concurs with the larger layer thickness and the continuous reduction in pore diameters, as shown in Fig. 2. Fig. 7 shows the effects of the layer thickness and the average hole diameter. As the hydration continues, the reaction products become thicker and the average pore size diameter narrower. The resultant resistance increases as the barrier thickness increases and hole diameters decrease due to the limitation in ionic conduction in the pore solution. (See Fig. 7). Furthermore, thicker and smaller holes produce two arcs in Nyquist plots. The combined effects of the two factors resultantly make the interconnection of the pore solution more tortuous. The simulation is qualitatively in agreement with the experimental trend found in CPBCs.

Depending on the relative amount of Ca, P, O, and H, various types of products are formed. In this study, the essential reaction is related to Monocalcium Phosphate Monohydrate (MCPM) and Dicalcium Phosphate Dehydrate
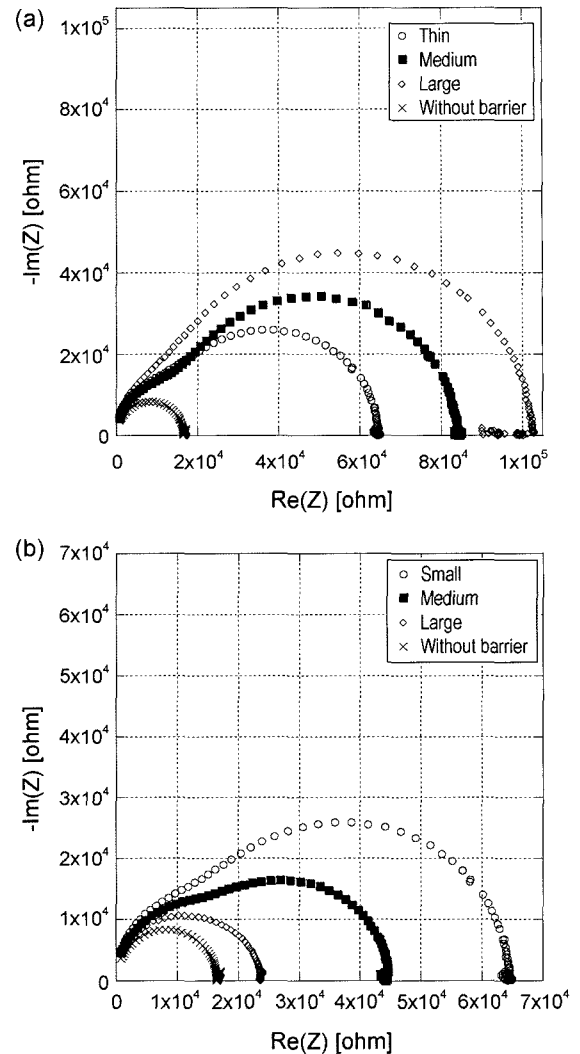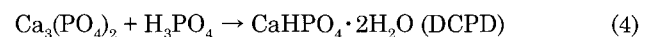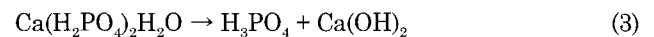
(DCPD). The chemical reactions are as follows:

$$Ca(H_2PO_4)_2H_2O \rightarrow H_3PO_4 + Ca(OH)_2 \tag{3}$$

$$Ca_3(PO_4)_2 + H_3PO_4 \rightarrow CaHPO_4 \cdot 2H_2O \text{ (DCPD)} \tag{4}$$

MCPM is disintegrated into phosphoric acids and calcium hydroxide. The phosphoric acid reacts with calcium phosphate, producing the DCPD and $CaHPO_4 \cdot 2H_2O$. The reaction products modify the pore structure in CPBCs since the DCPD is assumed to form in the initial powder mixture. The higher amount of reaction products decrease the volume fraction of the pore, and, consequentially, the path of pore solution becomes more tortuous in terms of the diameters and effective lengths of percolated liquid components.

The precipitation of DCPD is expected to take needle-like or petal-like features. The formation of reaction products, i.e., DCPD, continuously modifies the interlocking structures. In CPBCs, the cement paste, i.e. a mixture of water and bone cements, is highly sensitive to the moisture content. The minute pore structure is critically dominated by the amount of water and relative humidity, changing the chemistry and detailed pore structure at the solid/pore interfaces, with particular emphasis on the capillary pores within CPBC pastes, approximately in the micron range. Like OPCs, the pore network structure in cement pastes determines the electrical/dielectric properties, in addition to the mechanical properties, i.e., creep and compressive strengths.[4] The current work provides the preliminary data for monitoring the hydration status in calcium phosphate bone cements. The additional information should be added to the electrical/ dielectric characterization, for example, the image analysis in microstructure, mercury intrusion porosimetry, and hardness tests. In this work, impedance spectroscopy has been probed to be a uniquely nondestructive probing tool, unlike the destructive features found in BET measurements, electron microscopy, mercury intrusion porosimetry, implying that preparation procedures cannot maintain the pore structures in hydration.

4. Conclusions

Impedance spectroscopy was proven to be a nondestructive tool for monitoring hydration in calcium phosphate bone cements. In hydration, the amount of water changes the three-dimensional pore structure with emphasis on pore size distribution and interconnectivity. Higher amounts of water lead to higher conductance and higher capacitance, which is confirmed through impedance measurement. Initial characteristics of the powder influence the corresponding microstructure, depending on granulation, and the application of granulation to hydration causes a rapid increase in resistance and higher enhancement in capacitance in the initial stage of setting.

Acknowledgments

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