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AN EXPERIMENTAL INVESTIGATION ON CORROSION RATE OF Mg ELECTRODE USING AN EQCN AND IMPROVEMENT IN ANTI CORROSION RATE OF Mg ELECTRODE BY SURFACE COATING

D. H. LEE[a], C. H. PARK[a*], C. S. KIM[a,b]
[a]*Department of Bionanosystem Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea*
[b]*Division of Mechanical Design Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea*

Magnesium is essential constituent in human metabolism and is naturally found in bone tissue. The fracture toughness of magnesium is greater than ceramic biomaterials such as hydroxyapatite, furthermore elastic modulus and compressive yield strength of magnesium are closer to those of natural bone in comparison to other commonly used metallic implants. However, the major obstacle of Mg-based biomaterials has low corrosion resistance. In this study the surface of magnesium is coated with poly carpolactone (PCL) by two methods: by dipping magnesium in PCL solution and by electrospining to enhance the corrosion resistance. Magnesium coated by dipping in polymer solution shows more resistance towards corrosion than coated by electrospining. The corrosion rate for pure magnesium, electrospun coated and dipping coated magnesium is measured by Electronic Quarts Crystal Nanobalance (EQCN) and found to be 3.7ng, 0.6ng, 0.3ng per second respectively for 500 second.

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1. Introduction

In recent years, vascular stents[1-2] is recognizing as a universal technology for coronary artery and drug is coated on or drug-implanted into stents[3-5]. Furthermore, biodegradable stents[6] which dissolve or can be completely absorbed into blood vessels is growing as a next generation stent since it is aimed to prevent a foreign body reaction from blood vessels without any help of consuming drugs.[7] In particular, magnesium stents are a promising material among many materials since it has not only biodegradable properties but also sufficient strength as the use of implants.[8-10] However, when this material is used for stents, magnesium particles disturbs the flow of blood vessels due to the rapid rate of degradation rather than absorption, and also it is not possible to keep in the blood vessels for appropriate time due to the rapid absorptions.

Thus, many researchers proposed the surface treatment and coating techniques in order to slow the degradation of magnesium, but the research on its quantitative measurements has been barely done. EQCN is a device that is able to see a mass change of the metal ion on the electrode surfaces, which is through the changes in oscillation frequencies.[11-12]

In this study, we verified the real-time elution mechanism for magnesium using **EQCN** and to slowdown degradation rate we measured the change quantitatively after treating the magnesium surface.

From the process, we can be aware of magnesium absorption time in body and derive a method of an accurate surface treatment accordingly.

[*]Corresponding authors: biochan@jbnu.ac.kr

2. Experiment

2.1 EQCN

When an external stress or voltage is applied to a quartz crystal disc consisting silicon and oxygen atoms, piezoelectric effect proportional to polarization against the applied stress occurs and consequently converse piezoelectric effect occurs therefore the structure of a quartz crystal is proportionally deformed against the applied voltage. Based on these conditions, the quartz crystal will vibrate at resonant frequency when it forms electrodes and is applied by AC voltage on both sides of the disc. And then, one of the both-side electrodes is applied for the working electrode in which chemical and physical changes occur, and Quartz Crystal Nanobalance is one of the devices which is able to obtain the information for the movement of materials according to chemical and physical changes during the process of adhesion and deposition on the working-electrode surface. The shape of Quartz Crystal for the electrode is generally a disc or rectangular, and (Fig.1)AT-Cut(35° 15“ against the y-z sides) is mainly used, which is not sensitive to changes in surrounding temperature as well as is able to vibrate in a stable state.

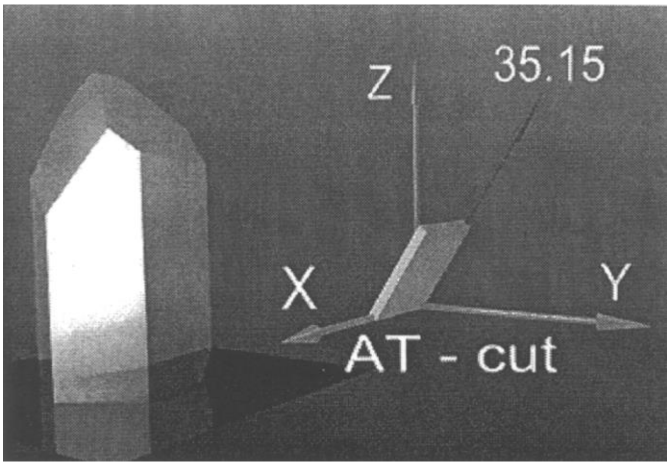

Fig.1 AT-cut diagram of Quartz crystal

The difference between resonance frequency and real frequency which is due to mass transfer depends on the Sauerbrey equation.

$$\Delta f = -2\ \Delta mn\ f_0^2 / (A\sqrt{(m_q\ r_q)})$$

f_0: Natural frequency of Quartz crystal electrode
n: Overtone number
A: Area of thin film
m_q: shear form modulus(=2.947x10^{11} g cm^{-1} s^{-2})
r_q: Density of Quartz crystal electrode (=2.648 g cm^{-3})

Therefore, changes in a oscillation frequency(Δf) is represented as a proportional constant Cf which is the unique values when Quartz Crystal is produced, and it can be simply expressed by mass change(Δm) and the proportional constant.

$$\Delta f = -\ Cf\ \Delta m$$
(Cf : Proportional factor)

EQCN is the machine which is able to measure adsorption and desorption of any material through frequency changing.

2.2 Method

We used Electrodes that are deposited with magnesium and coated Bio absorbent polymer on it.

The methods of coating were electrospinning and dipping. pasting the paper as shown in Fig.2(b) is to coated only on the measurement site of the electrode prior to the coating process.

PCL fiber were coated on it by electrospinning.

Coated electrodes are shown in Fig.2.

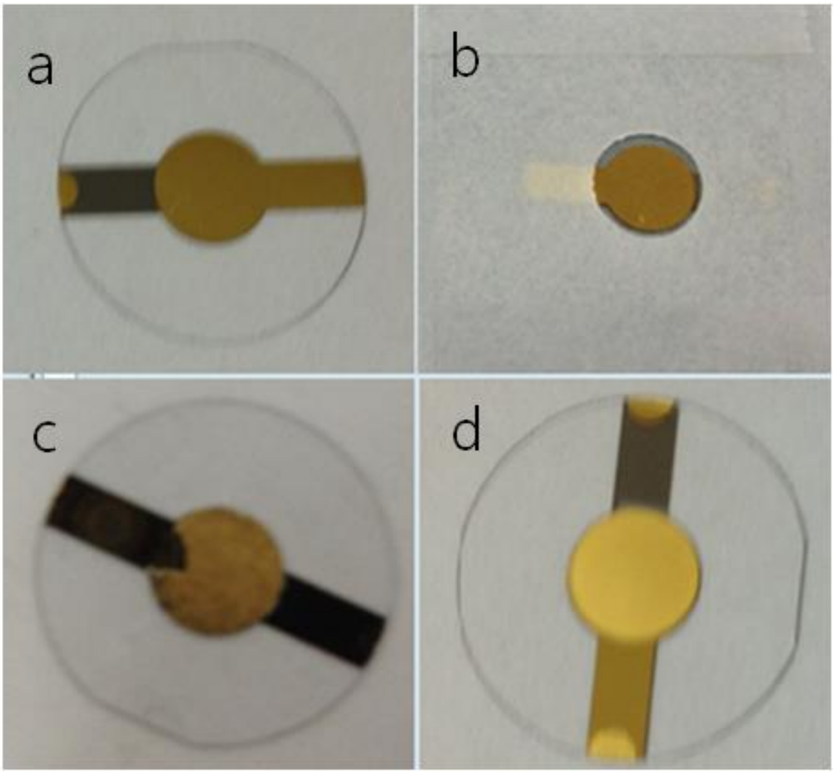

Fig.2 Pure Mg based-electrode (a), Preparation of sample for PCL coating (b), PCL electrospun coated Mg based- electrode(c), PCL dipping coated Mg based-electrode

Electrospinning is used for coating polymers on Quartz electrode.

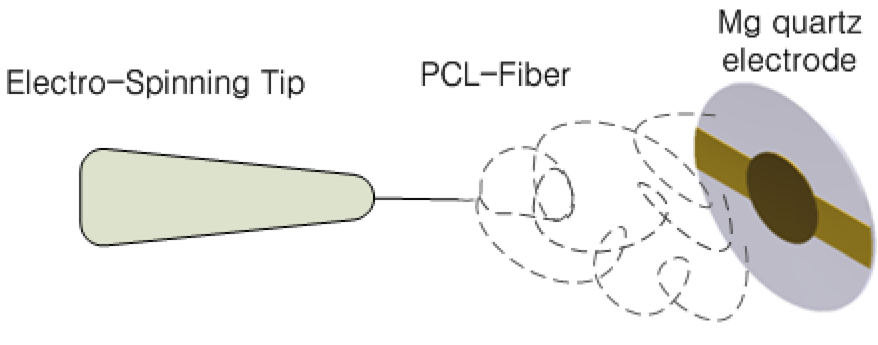

Fig.3 PCL fiber coating on Mg electrode

In this study the amount of D-F (difference Frequency) change over time was measured to verify the real-time Mg corrosion mechanism. The real-time mechanism for pure Mg and surface treated Mg (PCL dipping coated Mg and PCL electrospun fiber coated Mg) were compared. Experimentally, the reference electrode and the working electrode was measured in the frequency difference after mounting Cr/Au/Mg electrode in the L-tube and injecting 2mL of each solution (distilled water, NaCl).

2.3 Performance test of the EQCN

Performance of the EQCN was evaluated by Au frequency in distilled water and NaCl

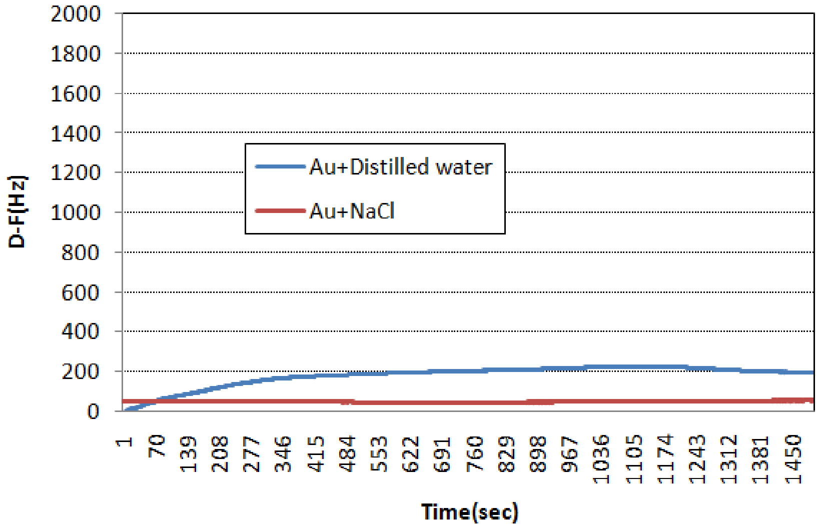

Fig. 4 Performance test frequency

2.4 Mass change measurement of magnesium in distilled water

2mL of the distilled water was taken in the L-tube and change in mass of magnesium was measured by QCN. We found that the mass of magnesium changes over time is proportional with respect to frequency.

1Hz frequency of change has an amount of 1ng change. Fig.5 shows the variation of D-F (Hz) with time for pure magnesium electrode in distilled water. Thus it is possible to obtain the graph for weight change of magnesium in distilled water,

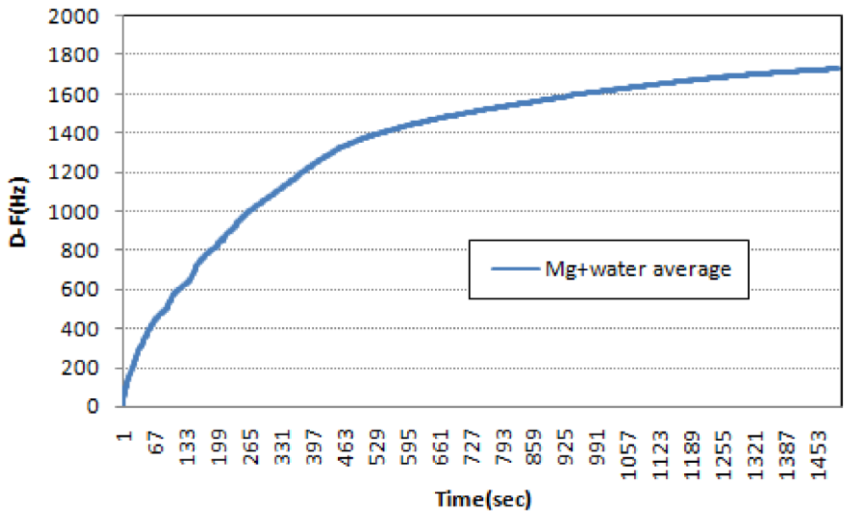

Fig. 5 Variation of D-F frequency with time for magnesium electrode in distilled water

From Fig.5, the mass of Mg electrode is rapidly corroded in the interval from 0 to 500 seconds in the distilled water. After 500 seconds, it has relatively it changes gradually. During 1500 seconds, the frequency was changed to around 1750, and it can be converted to 1750ng which represents the mass changes of Mg electrode.

2.5 Mass change measurement of magnesium in NaCl solution

We used NaCl solution for our experiment as it has similar pH to human body fluids. As in previous section, 2mL of NaCl was taken in the tube and the mass loss of Mg was measured during the same time interval. The graph for weight change of Mg electrode in NaCl solution is shown in Fig. 6

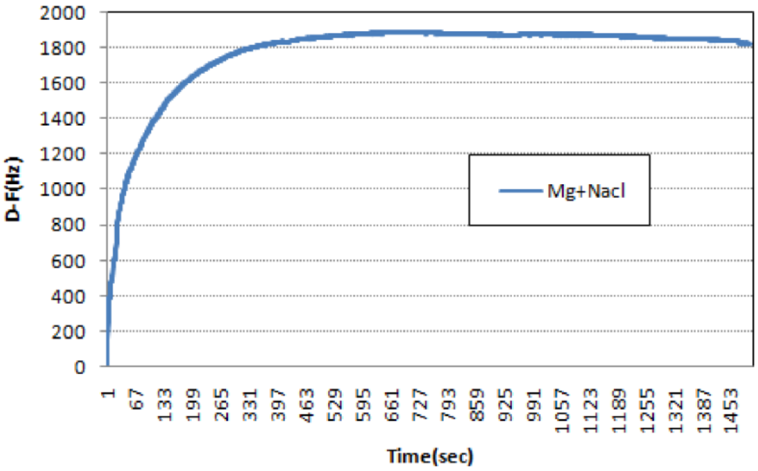

Fig.6 Variation of D_F frequency of magnesium electrode with time in NaCl solution

It has been found that pure Magnesium electrode corroded in a fast rate (within 400 seconds) indicating that the magnesium dissolves in a faster rate in the pH environment such as human body fluids in comparison to distilled water.

2.6 Mass change measurement of PCL dipping coated magnesium in NaCl solution

The change in weight of PCL dipping coated magnesium was measured using QCN. And then the change in weight was measured after injecting 2mL of NaCl solution.
It is shown in Fig.7, the mass change in magnesium treated by Dipping PCL coating.

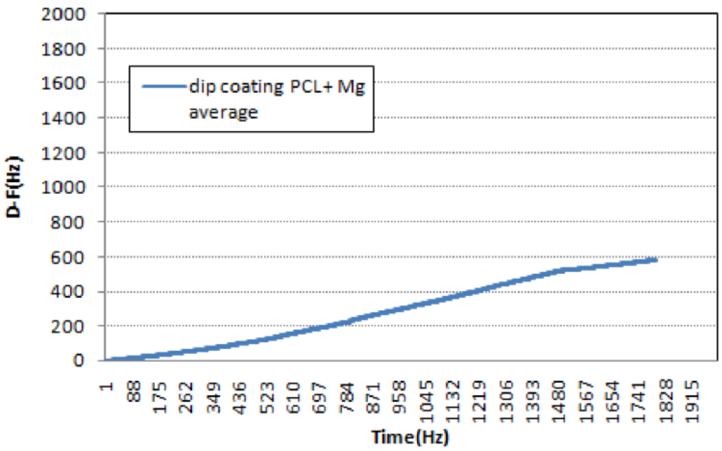

Fig.7 Variation frequency graph of PCL dip coated magnesium in NaCl solution

When we compare the PCL dipping coated magnesium(Fig 7) with the non-coated magnesium (Fig 7), it is clearly observed that the magnesium with Dipping PCL coating dissolved remarkably in slower rate. The reason for this phenomena may be predicted as after the since dipping coating layer on the surface of magnesium comes in contact with the solution first and Mg dissolves which slowdown the rate of corrosion. It has been observed that nearly 600ng of variation during 1500 seconds.

2.7 Mass change measurement of PCL electrospun coated magnesium in NaCl solution

The change in weight of PCL electrospun coated magnesium was measured using QCN. And then the change in weight was measured after injecting 2mL of NaCl solution.

It is shown in Fig.8, the mass change in magnesium treated by electrospun PCL coating.

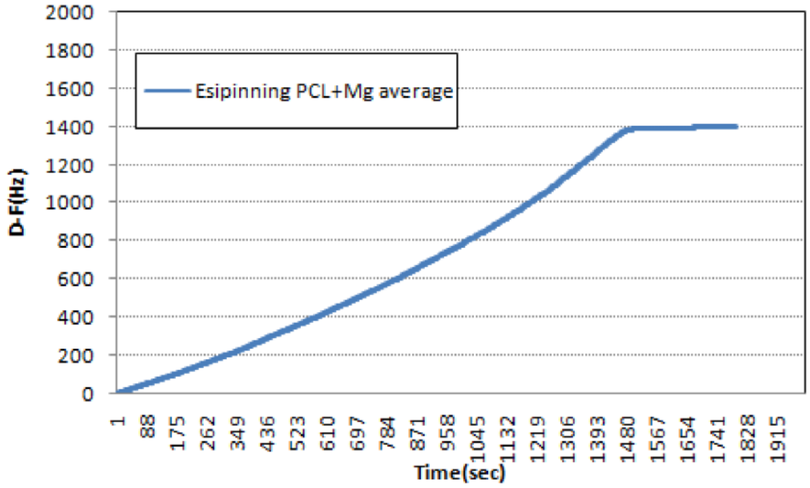

Fig.8 Variation frequency graph of PCL electrospun coated magnesium in NaCl solution

When compared to the Fig.6, it is seen that the elution rate is faster. The solution is simultaneously in contact with the PLC coating layer and Mg surface since the coating with electrospun is a fiber structure. The coating layer and magnesium layer dissolve at the same time.

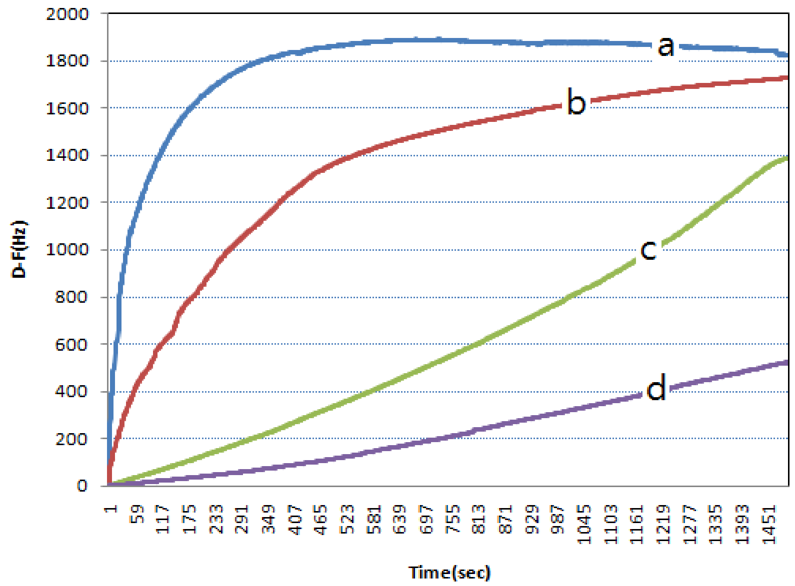

Fig .9 Pure Mg-based electrode in NaCl solution (a), Pure Mg-based electrode in distilled water (b), PCL electrospun coated on Mg based-electrode in NaCl(c), PCL dipping coated on Mg based-electrode in NaCl(d)

3. Conclusion

In this study, the corrosion rate of magnesium is measured quantitatively by using EQCN equipment. Corrosion rate of magnesium is slowdown by polymer coating. The real-time mass change in mass of magnesium was measured before and after surface coating with PCL. The experiment is conducted to measure the mass of magnesium changes in the water, it was found that the frequency changes approximately 1750Hz corresponding to 1750ng of changes in weight of magnesium at 1500 seconds. From the Fig.8, magnesium leach at a fast pace, and it is show around 2.8ng of the variation per second from 0 to 500 seconds. When the experiment was conducted in a PH environment equal to human body fluids, the frequency change of approximately 1900Hz corresponding to 1900ng in weight at 1500 seconds. From the Fig. 9 magnesium was eluted at a fast pace and the corrosion rate was shown 3.7ng per second for 0-500 seconds. The faster elution rate of magnesium in water compared to NaCl solution indicates magnesium has faster reaction rate in human body fluid.

Dipping coated magnesium is found to be eluted at a much slower rate. PCL coat on the surface of magnesium blocks the contact of the magnesium with aqueous solution and magnesium dissolves only after PCL disolve. The frequency change was approximately 600Hz which corresponds to 600ng in weight in 1500 seconds. The corrosion rate was found to be 0.3ng per second for 0-500 seconds.

Electrospun coated magnesium eluted at a slower rate than dipping coating. Electrospun fiber has interconnected pores, so aqueous solution simultaneously comes in contact with magnesium and electrospun fiber dissolving magnesium and fiber simultaneously. In 1500 seconds, the frequency changes of approximately 1400Hz corresponding to 1400ng in weight. The corrosion rate was shown about 0.9ng per second. In conclusion, the corrosion resistance of magnesium is greatly enhanced by coating with polymer.

Acknowledgements

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