

CHAPTER 2

LITERATURE REVIEW

2.1 Theories

Calcium phosphate bioceramics such as hydroxyapatite have become a favorable material for implants because of its chemical and structural similarity to the calcium phosphate minerals which present in hard tissue.

Moreover, other forms of calcium phosphate compounds, which are acceptable to be used as implant materials such as dicalcium phosphate dihydrate (DCPD, Brushite) and dicalcium phosphate anhydrous (DCPA, Monetite), also have been used for more than a decade. The reason is that their composition contains Ca and P as main element which is found in human bone.

Table 1 Abbreviations for various nonapatitic calcium phosphates.

Abbreviation	Explanation
CaP	Any calcium orthophosphates.
MCPM	Monocalcium phosphate monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
MCPA	Monocalcium phosphate anhydrous, $\text{Ca}(\text{H}_2\text{PO}_4)_2$
OCP	Octacalcium phosphates, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$
DCPD	Dicalcium phosphate dihydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. Not used as abbreviation for the mineral brushite.
DCPA	Dicalcium phosphate anhydrous, CaHPO_4 . Not used as abbreviation for the mineral monetite.
TetCP	Tetracalcium phosphate, $\text{Ca}_4(\text{PO}_4)_2\text{O}$
β -TCP	β - $\text{Ca}_3(\text{PO}_4)_2$ without structural HPO_4^{2-} or Mg^{2+} ions.
β -TCa-MgP	β - $(\text{Ca},\text{Mg})_3(\text{PO}_4)_2$ without structural HPO_4^{2-} ions.
Mg-whitlockite	β -TCP-like precipitates with structural HPO_4^{2-} and Mg^{2+} ions.
ACP	Amorphous calcium phosphate that gives an X-ray diffraction pattern without discernable peaks from lattice periodicities.
ACa, Mg, CO_3P	As above, but containing Mg^{2+} and CO_3^{2-} (and HCO_3^-) ions.

2.1.1 Calcium phosphate compounds

Calcium phosphate compounds are existing in a wide range of stoichiometry and morphology. Calcium phosphate compounds have been divided into two main groups, nonapatitic calcium phosphates and apatites. Abbreviations for various nonapatitic calcium phosphates are shown in table 1.

Apatites group is definitely different from nonapatite group by its formulas. Apatites have the formula $\text{Ca}_5(\text{PO}_4)_3\text{X}$ where X can be a F^- ion (fluorapatite, FAp), OH^- ion (hydroxyapatite, HAp), or a Cl^- ion (chlorapatite, Clp) for example. Table 2.1 shows the abbreviations for various apatites.

2.1.1.1 Monocalcium phosphate monohydrate (MCPM)

Monocalcium phosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, MCPM) is an important constituent of superphosphate made by the acidulation of rock-phosphate with H_2SO_4 , H_3PO_4 or HNO_3 . MCPA also occurs as an intermediate when rock-phosphate is acidulated with hot fuming HNO_3 or superphosphates are heated to $110\text{-}180^\circ\text{C}$.

2.1.1.2 Dicalcium phosphate dihydrate or Brushite (DCPD)

Dicalcium phosphate dihydrate (synonyms: DCPD, calcium monohydrogen phosphate dihydrate, dibasic calcium phosphate dihydrate, calcium hydrogen orthophosphate 2-hydrate, brushite) has the formula $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. Brushite occurs in small amount as a component of insular and continental rock-phosphate deposits an encrustation on ancient bones. As already known, DCPD can occur as an intermediated in the precipitation of HAp. Moreover, it also has been known for a long time that the ultimate product of DCPD hydrolysis is HAp, but the crystals formed are not pseudomorphs of the starting material.

Table 2.1 Abbreviation for various apatites.

Abbreviation *	Explanation
HAp	Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.
s-HAp	Stoichiometric HAp. Used when emphasis is required that the compound has a chemical composition corresponding to the ideal, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.
ns-HAp	Nonstoichiometric HAp (CO_3 -free). Indicates that the chemical analysis shows (or would show) a departure from that of s-HAp. This may involve lattice H_2O , HPO_4^{2-} , Ca^{2+} ions and/or 2OH^- replaced by O_2 .
Ca-def HAp	A precipitated apatitic calcium phosphate (CO_3 -free) with a Ca/P molar ratio in the range 1.66 to 1.5 or less. Compounds that might contain interlayers of OCP are included.
CaCl_2 -def ClAp	An apatite that departs from the ideal for ClAp, $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ in its calcium and chlorine contents in the molar ratio 1:2. Likewise for FAp.
BCaP	Precipitated basic apatitic calcium phosphate with an uncertain composition which may include CO_3^{2-} or HCO_3^- ions.
A- CO_3 Ap	A-type carbonate apatite, ideally $\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3$.
B- CO_3 Ap	B-type carbonate apatites, i.e. a carbonate containing apatite in which PO_4^{3-} ions are replaced by CO_3^{2-} ions.
AB- CO_3 Ap	Carbonate containing apatite in which both the above substitutions take place.
CO_3 Ap	Any carbonate-containing apatite.

2.1.1.3 Dicalcium phosphate anhydrous or Monettite (DCPA)

Dicalcium phosphate anhydrous (Synonyms: DCPA, anhydrous dicalcium phosphate, dicalcium phosphate, calcium hydrogen orthophosphate, and monettite). DCPA does not appear to occur in dental calculus or other pathological calcification, nor

* The above abbreviations are generalized; thus OAp, FAp and IAp are oxy-, fluor- and iodoapatite respectively. B- CO_3 FAp would be FAp in which some of the PO_4^{3-} ions have been replaced by CO_3^{2-} ions, i.e. francolite. The abbreviations refer to the calcium and phosphate compounds unless indicated otherwise, so that BaVO_4HAp is barium vanadate hydroxyapatite. Solid solutions are indicated by commas between the involved ions. For example, $\text{Ca,BaAsO}_4\text{F,ClAp}$ abbreviates $(\text{Ca,Ba})_{10}(\text{AsO}_4)_6(\text{F,Cl})_2$.

has it been found in normal calcification. However, DCPA has been reported in XRD studies of fracture callus and possibly in bone [37]. By the way, DCPA is less soluble than DCPD under all conditions of normal temperature and pressure because of its slow rate of crystal growth and it is less stable.

2.1.2 Electrochemical method

Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects. A large part of this field study about chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reactions. So far, scientists use many of electrochemical techniques on chemical systems for a variety of reasons. Also the same for manufacturing, they also use electrochemical techniques in order to produce their mass productions. So, electrochemical applications need an understanding of the fundamental principles of electrode reaction and the electrical properties of electrode solution interface.

2.1.2.1 Electrochemical cell and reactions

In electrochemical system, we concerned with the processes and factors that affect the transport of charge across the interface between chemical phases, for example, between an electric conductor (an *electrode*) and an ionic conductor (an *electrolyte*). Therefore, the interface and events when an electric potential is applied and current passes between electrode and electrolyte would be concerned. In the electrode phase, charge is transported through the electrode by the movement of electron and holes. Typical electrode materials include solid metal such Pt and Au, liquid metals such as mercury and amalgams, carbon such as graphite, and semi-conductors such as indium-tin oxide and silicon. In the electrolyte, charge is carried by the movement of ions. The most frequently used electrolytes are liquid solution containing ionic species, such as H^+ , Na^+ , Cl^- , in either water or non-aqueous solvent. To be useful in an electrochemical cell, the solvent/electrolyte system must be of sufficiently low resistance. In the other words, it must be sufficiently conductive for the electrochemical experiment.

In general, less conventional electrolytes include fused salt (molten NaCl-KCl eutectic) and ionically conductive polymers (polyethylene oxide, LiClO_4). Solid electrolytes also exist such as sodium β -alumina, where charge is carried by mobile sodium ions that move between the aluminum oxide sheet.

Generally, a difference in electric potential can be measured between the electrode in an electrochemical cell. Typically, this is done with a high impedance voltmeter. This *cell potential* measured in volts (V), where $1 \text{ V} = 1 \text{ joule/coulomb (J/C)}$, is a measure of the energy available to drive charge externally between the electrodes. It, however, is the collected differences in electric potential between all of the various phases in the cell. From observing and studying, it could be found that the transition in electric potential is crossing from conducting phase to another usually occurs almost entirely at the interface. The sharpness of the transition implied that a very high electric field exists at the interface, and one can expect it to exert effects on the behavior of charge carriers (electrons or ions) in the interfacial region. Thus, the measurement and control of cell potential is one of the most important aspects of experimental electrochemistry.

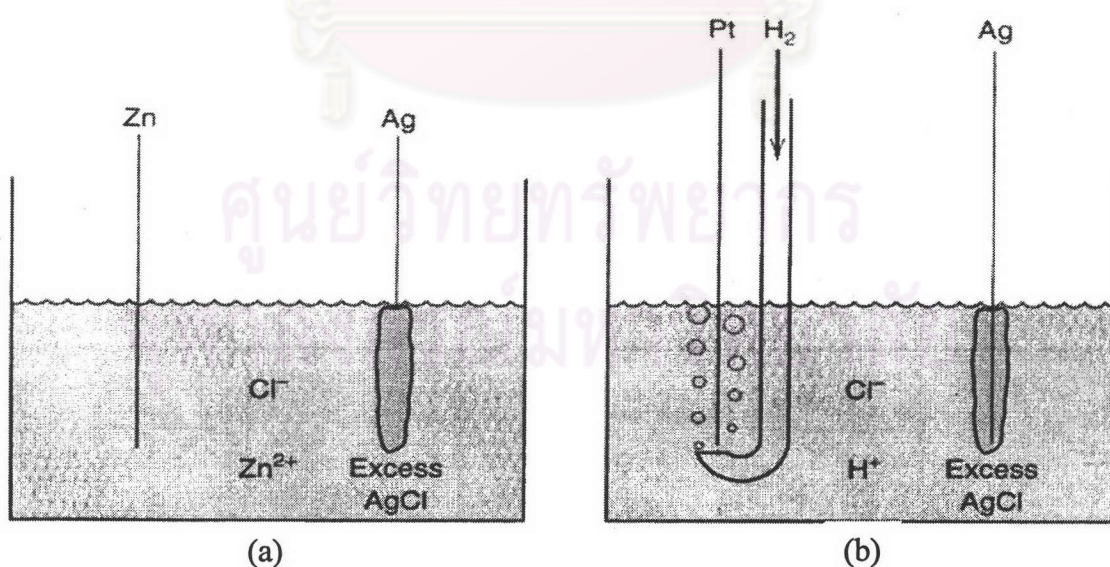
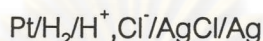


Figure 2.1 Typical electrochemical cells. (a) Zn metal and Ag wire covered with AgCl immersed in a ZnCl_2 solution. (b) Pt wire in a stream of H_2 and Ag wire covered with AgCl in HCl solution.

Anyway, it is useful to make understanding about a notation for expressing the structure of cells. For example, the cell picture in Figure 2.1a is written briefly as

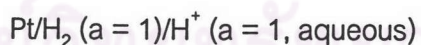


When a gaseous phase is involved, it is written adjacent to its corresponding conducting element. For example, the cell in Figure 2.1b is written schematically as



The overall chemical reaction in a cell is made up of two independent *half-reactions*, which describe the real chemical changes at the two electrodes. Each half reaction responds to the interfacial potential difference at the corresponding electrode. Most of time, the electrode at which the reaction occurs is called the *working electrode*. One standardizes the other half of the cell by using an electrode called a *reference electrode* made up of phases having essentially constant composition.

The internationally accepted primary reference is the *standard hydrogen electrode* (SHE), or *normal hydrogen electrode* (NHE), which has all components at unit activity:



Potentials are often measured and quoted with respect to reference electrode other than the NHE, which is not convenient from an experimental standpoint. A common reference is the *saturated calomel electrode* (SCE) which is



* In this notation, a slash represent a phase boundary, and comma separates two components in the same phase. A double slash, not yet used in this example, represents a phase boundary whose potential is regarded as a negligible component of the over all cell potential.

Another reference electrode is the *silver-silver chloride electrode*,



Since the reference electrode has a constant makeup, its potential is fixed. Therefore, any changes in the cell are ascribable to the working – electrode. It could be say that we observe or control the potential of the working electrode with respect to the reference, and that is equivalent to observing or controlling the energy of the electrons

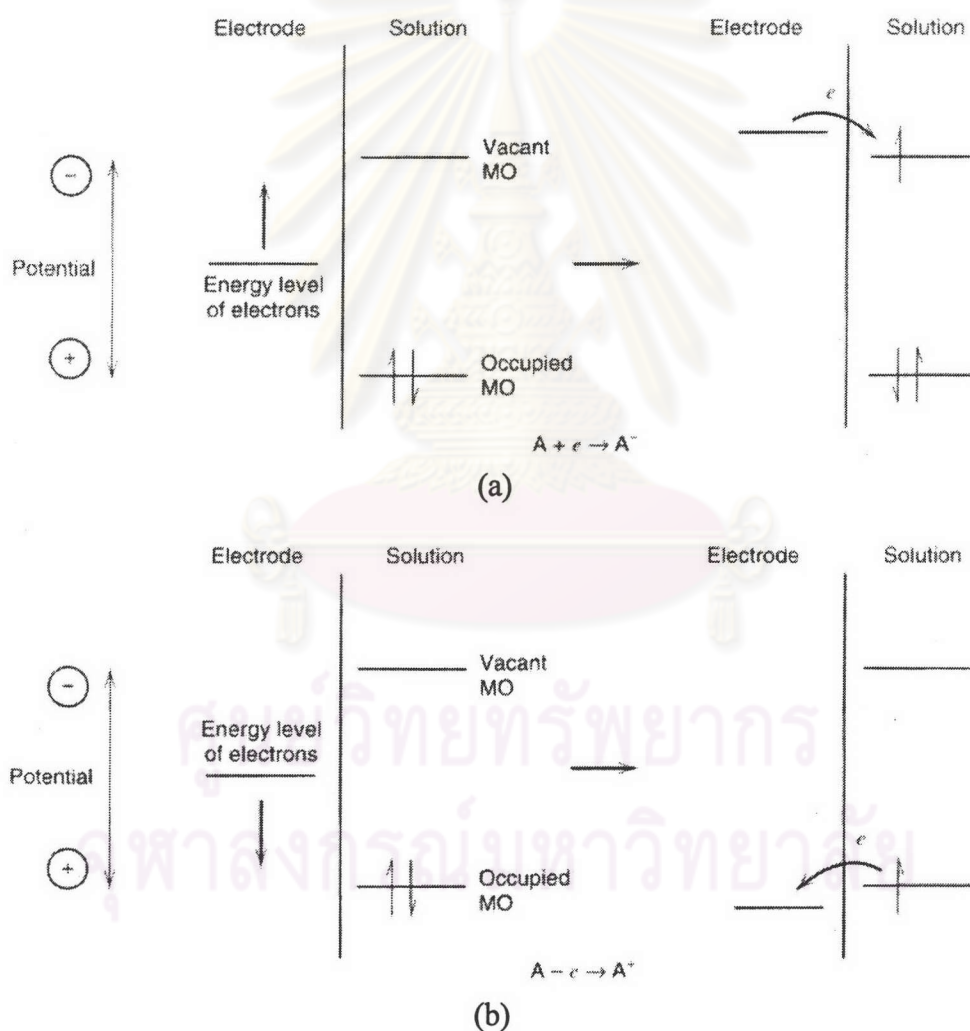


Figure 2.2 Representation of (a) reduction and (b) oxidation process of species, A, in solution. The molecular orbitals (MO) of species A shown are the highest occupied MO and the lowest vacant MO. These correspond in an approximate way to the E^0 's of the A/A^- and A^+/A couples respectively.

with in the working electrode [38-40]. By driving the electrode to more negative potentials – by connecting a battery or power supply to the cell with its negative side attached to the working electrode -, the energy of the electron is raised. They can reach a level high enough to transfer into vacant electronic states on species in the electrolyte. In that case, a flow of electrons from electrode to solution (a *reduction current*) occurs as show in figure 2.2a. Similarly, the energy of the electrons can be lowered by imposing a more positive potential, and at some point electron on solutes in the electrolyte will find a more favorable energy on the electrode and will transfer there. Their flow, from solution to electrode, is an *oxidation current* as show in Figure 2.2b.

2.1.2.2 Faradaic and Nonfaradaic processes

There are two types of processes occurred at the electrode. One is the process in which charges such electrons are transferred across the metal-solution interface. Electron transfer causes oxidation or reduction to occur. Since such reactions are governed by Faraday's law, the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed, they are called *faradaic processes*. Electrodes at which faradaic processes occur are called *charge transfer electrode*. However, processes such as adsorption and desorption can occur, and the structure of the electrode-solution interface can change with changing potential or solution composition. These processes are called *nonfaradaic processes* (charge does not across the interface, external currents can flow transiently when the potential, electrode area, or solution composition changes). **Both faradaic and nonfaradaic processes occur when electrode reactions take place.** Though, the faradaic processes are usually interested in the investigation of an electrode reaction while the nonfaradaic processes must be taken into account in using electrochemical data to obtain information about the charge transfer and associated reactions.

2.1.2.3 Electrochemical cells – types and definitions

Electrochemical cells in which faradaic currents are flowing are classified either *galvanic* or *electrolytic* cells. A galvanic cell is one in which reaction occurs spontaneously at the electrode when they are connected externally by a conductor (Figure 2.3a). These cells are employed in converting chemical energy into electrical energy. Galvanic cells of commercial importance include primary or non-rechargeable cells, secondary or rechargeable cells, and fuel cells. An electrolytic cell is one in which reaction are effected by the imposition of an external voltage greater than the open circuit potential of the cell (Figure 2.3b). These cell are employed to carry out desired chemical reaction by expending electrical energy. Commercial process involving electrolytic cells include electrolytic syntheses, electrorefining, and electroplating. From Figure 2.3, it can be seen that in electrolytic cell, the cathode is negative with respect to the anode; but in a galvanic cell, the cathode is positive with respect to the anode.

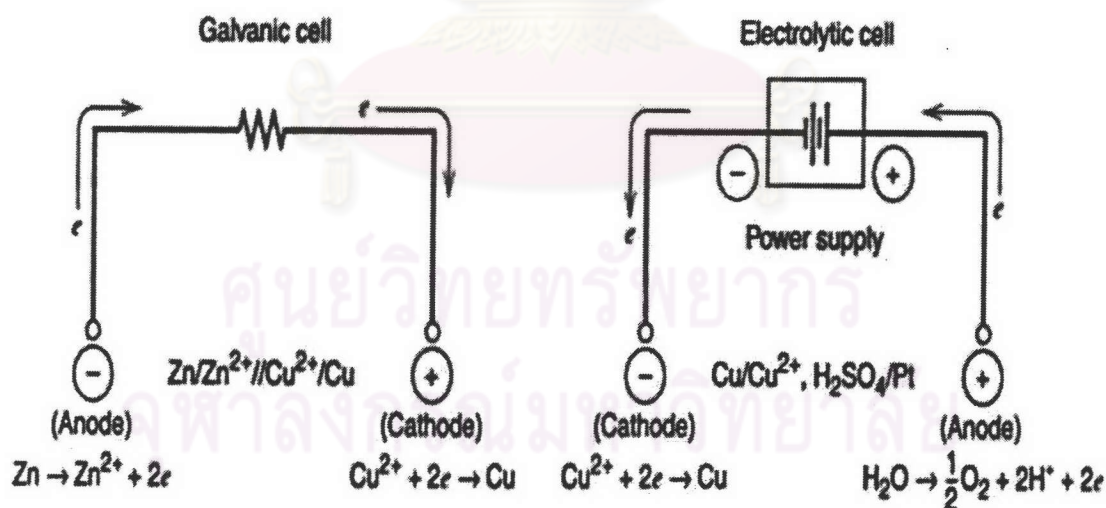


Figure 2.3 (a) Galvanic cell (b) electrolytic cell

Anyway, volume and design of a cell are determined by the type and size of the working electrode and the goal of a certain measurement, which depend on each kind of experiment: Large electrodes require large volumes of the solution (usually, not

necessarily). Fast measurements are best using small electrodes and small cell volumes. However, these are coarse rules and not laws. By the way, electrolytic deposition could be set into two kinds of cells setting. The first one is two electrodes, the other is 3 electrodes system as shown in figure 2.4 and 2.5 respectively.

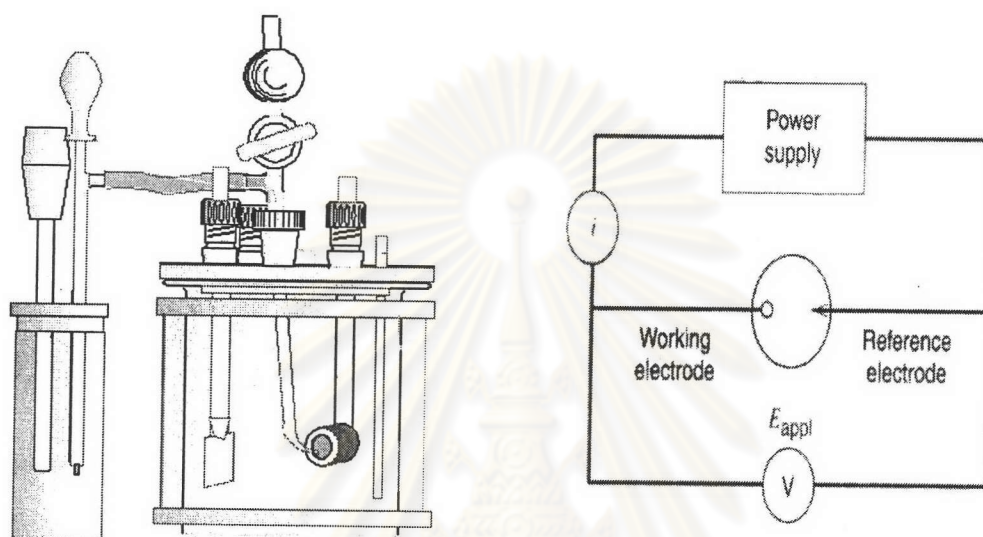


Figure 2.4 An ordinary cells: two electrodes.

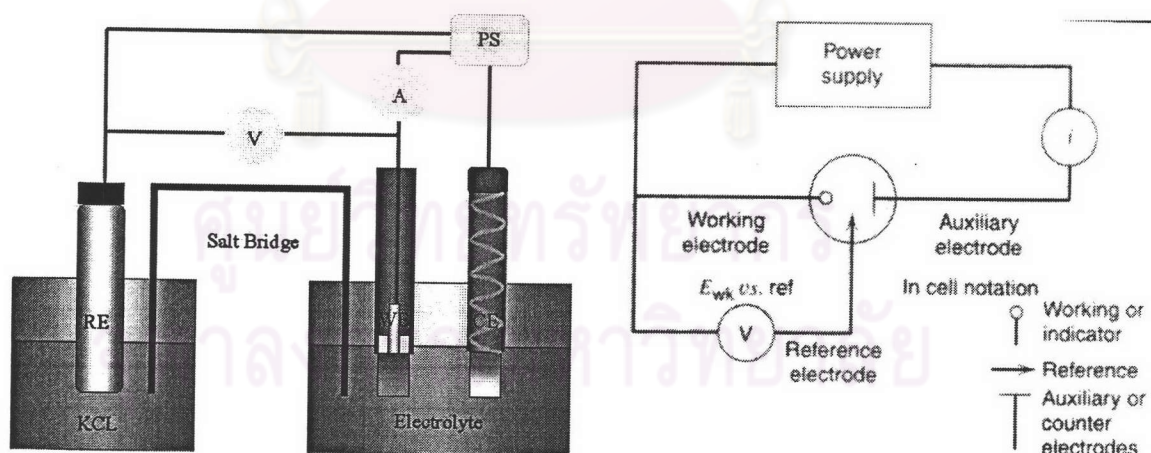


Figure 2.5 An ordinary cells: three electrodes.

The three electrodes system is composed of working electrode, reference electrode and auxiliary or counter electrode as described below:

Working electrodes: If the working electrode itself is subject of an investigation, its geometry usually is not a subject of electrode design. In other words: The size and

shape of the working electrode defines the cell design. Usually, only certain faces of a material are subject of an investigation. A good coating on working electrode must be chemically stable in the given electrolyte, it shall not form any contaminate ions and it shall not release any chemicals into the electrolyte which may influence the measurement.

Reference Electrodes: A reference electrode is a complete half - cell, maintaining a stable potential. Commonly, calomel electrodes (SCE) or silver/silver chloride electrodes (Ag/AgCl) are used. In chloride - containing solutions, a simple silver wire will form a good reference electrode. Depending on the electrolyte, other reference electrodes may be preferred: Hg/HgO electrodes in strongly basic solutions, Hg/HgSO₄ - electrodes in sulphuric acids. All these electrodes are stable as long as "electrode poisons^{*}" are not allowed to enter the reference electrolyte. Special reference electrode systems are required in molten salts. To keep the electrolyte of the reference cell clean, it is usually separated from the cell using a separated reference cell beaker, which is connected by a liquid junction to the cell which contains the working electrode. Frits or gel - electrolytes are used to prevent inter - diffusion of the different electrolytes. However, long bridges have high electric resistance and may affect fast measurements.

Auxiliary or Counter electrodes: The only conditions of the counter electrode is, that is must not dissolve in the electrolytes. Only noble metal and carbon fulfil this condition perfectly. In some cases, corrosion - resistant alloys with large surfaces will meet the requirements, especially if only anodic currents occur at the working electrode. If a large active surface of the CE is required, platinum coated with platinum black will give best results. Also this coating is a process which can be done using the potentiostat, by electrolytic deposition of platinum from a platinum chloride solution. Carbon electrodes form CO₂ when polarised to high anodic potentials. This polarisation is reduced if the CE area is increased, thus decreasing the current density at the CE.

* Inter-diffusion of the different electrolytes.

2.1.2.4 Factors effecting electrode reaction rate and current

The overall electrode reaction, $O + ne \rightleftharpoons R$, composed of a series of steps that cause the conversion of the dissolved oxidized species, O, to a reduced form, R, also in solution as show in Figure 2.6. Generally, the current or electrode reaction rate is governed by the rates of processes such as:

1. Mass transfer, for example O from the bulk solution to the electrode surface.
2. Electron transfer at the electrode surface.
3. Chemical reactions preceding or following the electron transfer. This might be homogeneous processes (protonation or dimerization) or heterogeneous ones (catalytic decomposition) on the electrode surface.
4. Other surface reactions, such as adsorption, desorption, or crystallization (electrodeposition).

The rate constants for some of this processes such electron transfer at the electrode surface or adsorption depend upon the potential.

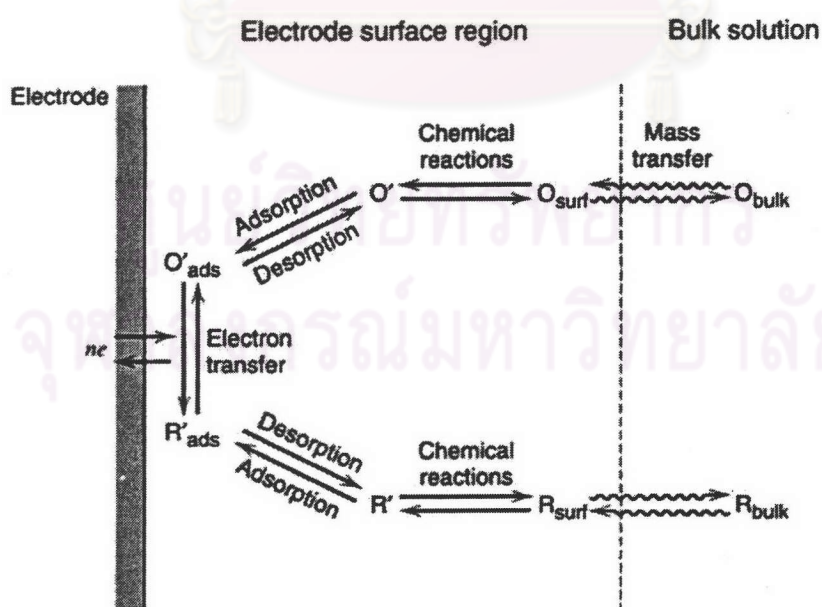


Figure 2.6 Pathway of a general electrode reaction.

2.1.3 Ceramics film using cathodic electrodeposition

Electrodeposition is evolving as an important method in ceramic processing. Two processes for forming ceramic films by cathodic electrodeposition are electrophoretic deposition, in which suspensions of ceramic particles are used, and electrolytic deposition, which is based on the use of salts solutions (figure 2.7). Electrolytic deposition enables the formation of thin ceramic films and nanostructured powders; electrophoretic deposition is an important tool in preparing thick ceramic films and body shaping. Significant interest has recently focused on cathodic electrodeposition, which offers important advantages for various applications [41]; cathodic electrolytic deposition is a new technique in ceramic processing that has been used to produce a variety of ceramic thin films [42]. In this study, however, is mainly study in electrolytic deposition.

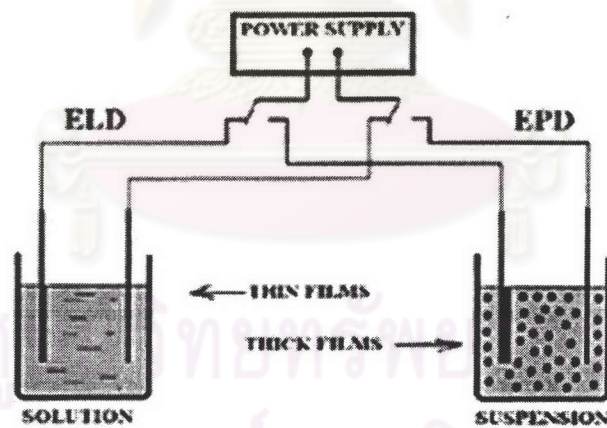


Figure 2.7 A schematic of electrolytic deposition and electrophoretic deposition.

2.1.3.1 Electrolytic deposition of hydroxyapatite

Electrolytic deposition produces ceramic materials and provides their deposition. In the cathodic electrodeposition method, the following reaction are used to generate base at an electrode surface[42-43]:



Electrolytic deposition, however, of HAp has been conducted in the mixed aqueous solution of $\text{Ca}(\text{NO}_3)_2 \bullet 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ for a decade [29,31, 33, 44-45]. It is well known that the local pH within the diffusion layer will be increased by the following two reactions:



Then, the concentration of phosphate acid, HPO_4^{2-} should be effected by the following equilibrium:



Or



When extra OH^- is afforded, HAp can be deposited on the cathodic surface by the following reaction:



Oftenly, HAp that was formed by electrodeposition technique, accompanied with other unstable phases such as DCPD and/or other forms of calcium phosphates.

2.1.4 Biomimetic process

In the field of implant materials studying, it is believed that the essential requirement for an artificial material to bond to living bone is formation of the bone-like apatite layer on its surface.

According to Kim et. al., the bone-like apatite formation on bioactive materials *in vivo* can be produced even in a simulated body fluid (SBF), with ion concentrations nearly equal to those of human blood plasma. In addition, the SBF has been widely used for formation of bone-like apatite on various implants *in vitro*. Unfortunately, the SBF has higher Cl^- ion concentration and lower HCO_3^- ion concentration than those of blood plasma do. So, the above authors believed that the HAp formed in the SBF might be slightly different in its composition and structure from the biological apatite. Therefore, the authors tried to prepared new type of SBF called revised-SBF (R-SBF) which contained ion concentrations, including Cl^- and HCO_3^- , equal to those of human blood plasma (table 2.2) may be much more useful for assessment of bioactivity and production of the bone-like apatite.

Table 2.2 The ion concentrations of SBF and R-SBF compared with human blood plasma.

Ion	Concentration / mM		
	Blood plasma	SBF	R-SBF
Na^+	142.0	142.0	142.0
K^+	5.0	5.0	5.0
Mg^{2+}	1.5	1.5	1.5
Ca^{2+}	2.5	2.5	2.5
Cl^-	103.0	148.8	103.0
HCO_3^-	27.0	4.2	27.0
HPO_4^{2-}	1.0	1.0	1.0
SO_4^{2-}	0.5	0.5	0.5

2.1.5 Additive ions in electrolytic deposition

According to Monma (1993) the additive ions in MCPM solution, which were F^- and NO_3^- (from NaF and $NaNO_3$, respectively), were effective to apatite formation, and enlarged remarkably the formation regions. It was found that the addition of $NaNO_3$ was effective for the depositions of apatite and amorphous calcium phosphate (ACP). These calcium phosphates are thought to be deposited as a result of pH increases in the vicinity of the cathode surface.

From the F^- added solution, the deposition of apatite occurred in a wide ranges of combination of temperature and MCPM concentration, accompanying of the deposition regions of DCPD and particularly DCPA.

2.2 Literature survey

In 1993, Monma[34] studied about the electrochemical deposition of calcium-deficient apatite on a stainless steel substrate. He used 0.02-0.21 mol/dm³ MCPM solutions added with and without $NaNO_3$ and NaF at a cathode current of 6 mA/cm² at 20-90°C. He found that at high MCPM concentration, brushite or monetite was deposited. The addition of $NaNO_3$ and /or NaF was effective for the formation of apatite.

In 1994, Vijayaraghavan and Bensalem[47] studied about electrodeposition of apatite coating on pure titanium and titanium alloys. They used pure Ti and Ti-6Al-4V as substrates and their electrolyte was calcium phosphate tribasic powder dissolved in 1M-NaCl solution with pH 4.4 using 0.1 N-HCl. The experiments were conducted over the range of room temperature to 65°C and range of cathodic potentials of -1100 to -1500 mV. They found that uniform HAp coating were obtained on titanium substrates at 55°C and at cathodic potential of -1300 mV and above. At room temperature and cathodic potential below -1300 mV, brushite was the predominant product.

Ban and Maruno[48] studied in 1995 about calcium phosphate coatings, which were deposited on titanium plate by an electrochemical method in simulated body fluid at 5 – 62°C. Their substrate was a pure titanium plate and their electrolyte was a conventional simulated body fluid. The potential, -2 V, was applied to the working electrode for 5,10, and 30 minutes and 1 and 2 hours. They found that at the temperature lower than 37°C, the films were amorphous calcium phosphate. At the temperature higher than 37°C up to 62°C, the films were contained Mg(OH)₂, CaCO₃ and carbonate apatite of low crystallinity.

In the same year, Ishizawa and Ogino[49] tried to form anodic titanium oxide film containing Ca and P (AOFCP) on titanium substrates. They used calcium phosphate compounds based aqueous solution as electrolyte. The maximum electrolytic voltage that was set in the range of 150-400 V, and the current density was 50 mA/cm². They found that β-GP, β-glycerophosphate disodium salt pentahydrate, and CA, acetate monohydrate, were suitable for the electrolytes to form an AOFCP having an equivalent Ca/P ratio to HAp. Their HAp crystals were precipitated on the AOFCP by a hydrothermal treatment and completely covered the surface.

In 1996, J. Redepenning et. al.[50] studied about deposition of pure brushite coating on high surface area metal substrates (316L stainless steel) by electrolytic preparation; and they used saturated MCPM solution as electrolyte. From their studied, they could form brushite film on 316L stainless steel and being converted to hydroxyapatite by simulated body fluid.

In 1997, Sridhar et. al.[51] tried to form HAp film on 316L stainless steel by electrophoretic deposition. They used HAp powder dissolved in H₃PO₄ and Ca(OH)₂ solutions. The potential was in the range of 20-110 Vcm⁻² with a deposition time for 1 minute. They also used thermal treatment at 300°C for 1 hour. They found that the best condition of which the HAp could deposited was 30 V with a deposition time for 1 minute.

In the next year, Ban and Maruno[52] (1998) studied about calcium phosphates deposited on a pure titanium plate for various loading times under 1.3 and 12.9 mA/cm² in a modified simulated body fluid at 52-92°C. They used mixed solution of 137.8 mM NaCl, 1.67 mM K₂HPO₄ and 2.5 mM CaCl₂•2H₂O buffered with 50 mM [(CH₂OH)₃CNH₂] to pH 7.2. They got OCP as minority coexisted with HAp at higher temperature 72-92°C.

In 1999, Han et. al.[53] formed pure brushite coating on porous Ti6Al4V substrates. They used 0.21M Ca(NO₃)₂•4H₂O and 0.125M NH₄H₂PO₄ solutions as electrolytes. The pH value of the electrolyte was adjusted to 4 by the addition of ammonia. Electrochemical deposition of the coating on Ti6Al4V was accomplished using a potentiostat. The coating process was carried out of 60°C and 1.5 V for 1.5 hour in a conventional electrolytic cell. It was found that the content, Ca/P atomic ratio, grain size and pore size of HAp in coating increase with increasing hydrothermal treatment temperature, and that increasing the pH value can promote brushite to HAp conversion and reduce the grain size of HAp.

In 2000, Manso et. al.[54] also prepared HAp by using A-0.4 M calcium acetate CaAc₂, 0.78 M acetic acid HAc, and B-0.24 M sodium phosphate Na₃PO₄ and 0.8 M NaOH in distilled water. The pH of solution was 9.1. The potential applied in the ranged 2-4 V were applied for 1 hour. They could get a well-crystalline HAp film on titanium films (300 nm thickness) on silicon wafers substrates.

In 2002, Kannan et. al.[55] used aqueous solution comprising calcium chloride dihydrate (CaCl₂•2H₂O) and ammonium dihydrogen phosphate (NH₄H₂PO₄) adjusted to Ca/P ratio of 1.67. These electrolytes were taken as electrolyte for deposition at constant current and temperature at different time duration. Their result showed that the optimum condition was 12 mA current for one hour at 50°C to formed bone-like calcium phosphate films.

In 2003, Sridhar et. al.[56] were studied about electrolytic deposition of hydroxyapatite on 316L stainless steel. They found that the optimum coating parameter were established at 60 V and 3 min, after vacuum sintering at 600°C. They used H_3PO_4 0.3M and $Ca(OH)_2$ 0.1M solutions for chemically synthesis of hydroxyapatite. They got stoichiometric hydroxyapatite as a result after studied under simulated body fluid.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย