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Electrodeposition of Nanostructure Materials

Souad A. M. Al-Bat'hi

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Abstract

We are conducting a multi-disciplinary research work that involves development of nanostructured thin films of semiconductors for different applications. Nanotechnology is widely considered to constitute the basis of the next technological revolution, following on from the first Industrial Revolution, which began around 1750 with the introduction of the steam engine and steelmaking. Nanotechnology is defined as the design, characterization, production, and application of materials, devices and systems by controlling shape and size of the nanoscale. The nanoscale itself is at present considered to cover the range from 1 to 100 nm. All samples prepared in thin film forms and the characterization revealed their nanostructure. The major exploitation of thin films has been in microelectronics, there are numerous and growing applications in communications, optical electronics, coatings of all kinds, and in energy generation. A great many sophisticated analytical instruments and techniques, largely developed to characterize thin films, have already become indispensable in virtually every scientific endeavor irrespective of discipline. Among all these techniques, electrodeposition is the most suitable technique for nanostructured thin films from aqueous solution served as samples under investigation. The electrodeposition of metallic layers from aqueous solution is based on the discharge of metal ions present in the electrolyte at a cathodic surface (the substrate or component.) The metal ions accept an electron from the electrically conducting material at the solid- electrolyte interface and then deposit as metal atoms onto the surface. The electrons necessary for this to occur are either supplied from an externally applied potential source or are surrendered by a reducing agent present in solution (electroless reduction). The metal ions themselves derive either from metal salts added to solution, or by the anodic dissolution of the so-called sacrificial anodes, made of the same metal that is to be deposited at the cathode.

Keywords: Electrodeposition, nanomaterials, thin films, nanotechnology

1. Introduction

Materials with grain size less than 100 nm are classified as nanostructure materials [1, 2]. Due to the ultra-small building units and high surface/volume ratio, these materials exhibit special properties, such as mechanical, optical, electronic, and magnetic properties [3]. In nanostructure materials, all size-related effects can be integrated by controlling the sizes of the constituent components [4]. For instance, nanostructure metals and ceramics can have improved mechanical properties compared to conventional metals and ceramics. Besides, nanostructure materials are capable of being sintered at much lower temperatures than conventional powders, enabling the full densification of these materials at relatively lower temperatures. Technological applications of semiconductor nanostructure materials in optoelectronic devices such as photodiodes and quantum dotes semiconductors are owed to the size-related effects, particularly quantum size effects caused by the spatial confinement of delocalized electrons in confined grain sizes [5]. Nanostructure materials magnetic applications are fabrication of devices with massive magnetoresistance (GMR) effects, to read data on computer hard drives by magnetic heads, and development of magnetic refrigerators by replacing compressed ozone-chlorofluorocarbons by solid magnets as refrigerants [6]. Nanostructured metals seem to be a candidate for new catalytic applications [7].

Fundamental advances in energy conversion and storage which are full of vigor in meeting outfaces of some environmental phenomena such as global warming and impact of fossil fuels are held by new materials, particularly nanomaterials, which present unique properties as electrodes and electrolytes in many applications such as lithium batteries, solar cells, fuel cells, and supercapacitors [8].

There are several techniques that can be used to develop thin films of metals and semiconductors in both micro- and nano-structures. Some of these techniques are: sol-gel process [9], chemical deposition method [10], hydrothermal method [11], pyrolysis method [12], chemical vapor deposition (CVD) [13], and electrodeposition method [14]. In Table 1, we summarize some previous studies on general concepts of nanostructure materials, their properties, and their methods of preparation. This chapter will be concerned particularly with the electrodeposition technique. Figure 1 shows thin films deposition techniques.

Materials may undergo some changes in physical properties when changing state from microstructure to a nanostructure. High surface/volume ratio and particles' transfer to a domain with dominant quantum effects are two main factors in characteristics' change. An increase in surface/volume ratio results in the dominance of surface atoms' behavior compared with internal atoms. This factor affects both the particle's properties and its interaction with the other materials. Vast surface of the nanoparticle leads to specific features such as mechanical, chemical, and thermal properties.

Nanoparticles are the basic structural blocks in nanotechnology. They are the starting point in producing nanostructure materials and tools. The production of nanoparticle is an important factor in the development of research in nanoengineering and nanoscience.

Different types of nanoparticles are prepared by using precursors in solid, liquid, and gaseous phases in the production and arrangement of nanomaterials. Based on their chemical reactivity or physical compression, these materials align the nanostructures as structural blocks side-by-side.
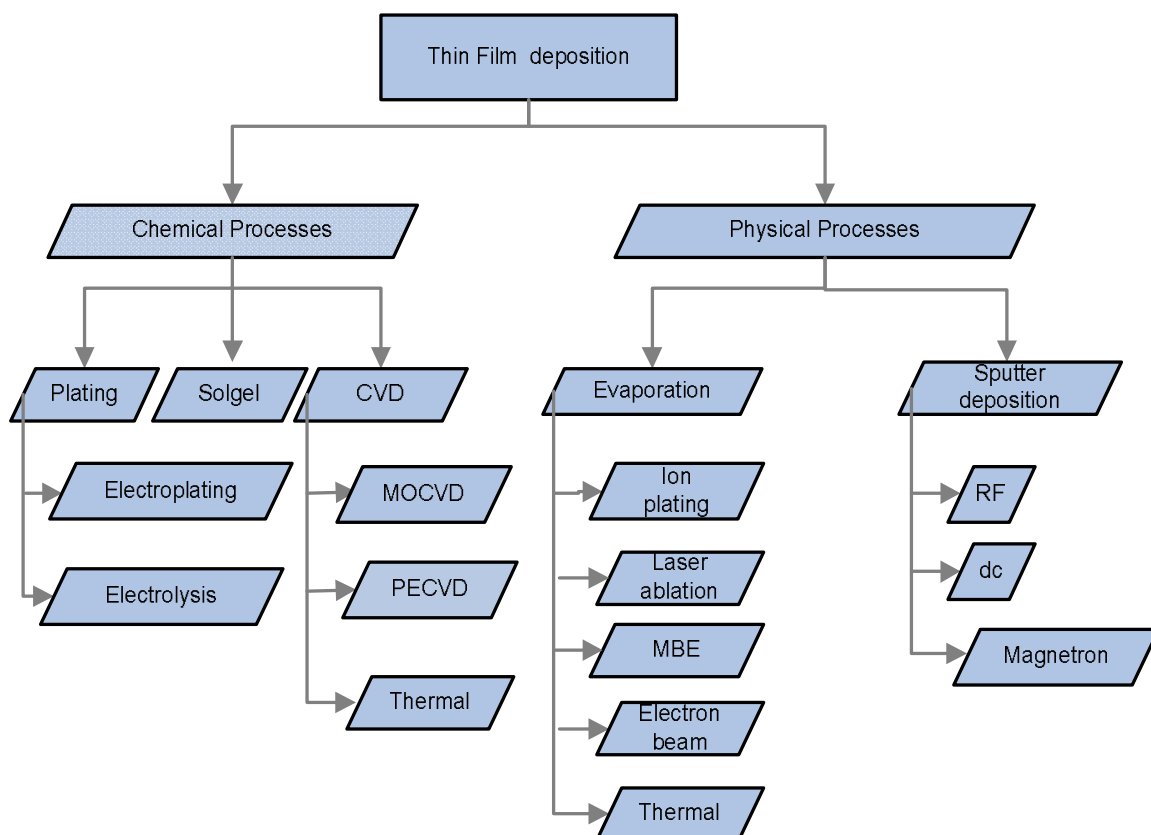

Figure 1. Thin film deposition techniques [Souad A., (2007)] [15].

	Title	Description	Reference
1.	Electrodeposition of Copper Oxide Nanoparticles on Precasted Carbon Nanoparticles Film for Electrochemical Investigation of anti-HIV Drug Nevirapine	A novel medical application is developed for the analysis of the anti-HIV drug, nevirapine (NEV), based on electrodeposition of CuO/CNP nanoparticles. The modified electrode (sensor) has shown a good response, which makes it suitable for the determination of NEV in	Saeed, S. et al., Electroanalysis. DOI: 10.1002/elan. 201500027,2015, WILEY-VCH [16]

Title	Description	Reference
	real samples of human blood serum.	
2. Electrochemical Synthesis of Mesoporous CoPt Nanowires for Methanol Oxidation	Thin films CoPt nanowires have been successfully synthesized by electrodeposition technique. Electrodeposition helps easy synthesis of mesoporous materials useful for catalytic applications without any agent's employment. The mesoporous CoPt nanowires have shown enhanced catalytic behavior for methanol oxidation reaction in acidic medium. Because of the catalytic activity and cost reduction, these nanowires can be a potential alternative for methanol fuel cells.	Albert S. et al., Nanomaterials (2014), 4(2), 189-202 [17]
3. Nanostructured Solids From Nano-Glasses to Quantum Transistors Materials Assembled from Atom Clusters	A review provides a discussion of method of preparation, structure and properties of nano structured solids that consist of totally crystalline, totally amorphous, and partially amorphous components.	H. Gleiter, Th. Schimmel, H. Hahn, Nano Today.. (2014) 9, 17-68 [18]
4. Nanocarbon-Based Electrochemical Systems for Sensing, Electrocatalysis, and Energy Storage	A review provides comparison between carbon nanofibers, carbon nanotubes, and graphene; the three types of carbon nanostructure materials which have been focused on.	Xianwen et al., Nano Today. (2014) 9, 405-432 [19]
5. Electrodeposition of Polypyrrole/ Reduced Graphene Oxide/Iron Oxide Nanocomposite as Supercapacitor Electrode Material	Nanocomposite polymer thin films prepared by electrodeposition technique have shown an enhanced electrochemical stability and exhibit excellent specific capacitance (F/gm)	Eeu Y. C. et al., Hindawi Publishing Corporation J Nanomater. Volume 2013, (2013), Article ID 653890 [20]

	Title	Description	Reference
6.	ZnxCd1-x (O) Thin Film Nanorods for PV Applications	A hexagonal nanorods thin film of ZnxCd1-x (O) were electrodeposited on ITO substrate and is used as working electrode in photovoltaic cells to generate electricity from solar energy by absorbing sun light.	Umer M. and, Souad. A., Int J Nano Sci Technol. (2013) 1, (3), April, 09-16 [21]
7.	Electrodeposition of Platinum and Ruthenium Nanoparticles in Multiwalled Carbon Nanotube-Nafion Nanocomposite for Methanol Electrooxidation	A 10-15 nm diameter of PtRu nanoparticle have been electrodeposited within nanocomposite (MWCNT-Nafion). cyclic voltammetry is used to investigate the electrocatalytic activity toward the methanol electrooxidation at three different nanocomposite electrodes.	Yu-Huei H. and Yu Chen T., J Nanomater. Volume 2009 (2009) [22]
8.	Electrodeposition of One-Dimensional Nanostructures	Electrodeposition technique is successfully used to synthesize 1D nanostructure materials with and without temples and a comparison between the two approaches is well discussed.	Guangwei S., Lixuan M., and Wensheng S., Recent Patents Nanotechnol. (2009), 3,182-191 [23]
9.	Characterization of Electrodeposited Zn (Se, Te) Thin Films/Polymer (PEO–Chitosan Blend) Junction for Solar Cells Applications	The work has focused on the possibility of using Zn (Te, Se) semiconductors with PEO-chitosan blend polymer electrolytes for PV applications. The methods to produce the semiconductors (electrodeposition) and polymer electrolyte (solution casting) are suitable and cheap. The economy of the processes involved such as the electrodeposition method and the solution cast technique, show some	Souad A. (2007), PhD thesis [15]

	Title	Description	Reference
		promise for future large-scale production.	
10.	Ionic Liquids as Green Electrolytes for the Electrodeposition of Nanomaterials	Air and water as ionic liquids attract the attention of researchers due to their amazing physical properties, particularly in electrodeposition of nanocrystalline metals. Copper and aluminum can be electrodeposited in the air and water ionic liquids on solid electrodes and they have shown an adequate electronic conductivity.	S. Zein El Abedin, et al., Green Chem. (2007),, 9, 549-553 [24]

Table 1. Summary of Some Previous Studies on General Concepts of Nanostructure Materials

2. Growth technique of nanomaterials thin films

Nanomaterials are produced by two main technical methods: "bottom-up" and "top-down" techniques. In the bottom-up technique, the substance developed from the bottom (atom by atom, molecule by molecule, or cluster by cluster). Colloid dispersion is produced in this technique. The top-down technique begins with bulk material and progresses toward the ideal state by its designing or abrasion. This technique is similar to the electron beam lithography in which patterns are used. In nanotechnology industry, bottom-up and top-down techniques are playing a considerable role. The major advantage of both techniques is creation of high-purity ultra-small structures. However, using bottom-up method produces improved nano-structures such as less or defect-free, homogeneous and long- and short-term orders, all due to free Gibbs energy decreases resulting in thermal balanced nanomaterials. However, in the top-down technique, mostly the material suffers from an increase in surface defects, since the material is subjected to internal stress [25]. Figure 2 shows a schematic representation of the building up of nanostructures.

3. Electrodeposition technique

Electrochemical deposition, or electrodeposition for short, refers to a film growth process which consists in the formation of a metallic coating onto a base material (substrate) occurring through the electrochemical reduction of metal ions from an electrolyte to achieve the desired electrical and corrosion resistance, reduce wear and friction, improve heat tolerance, and for
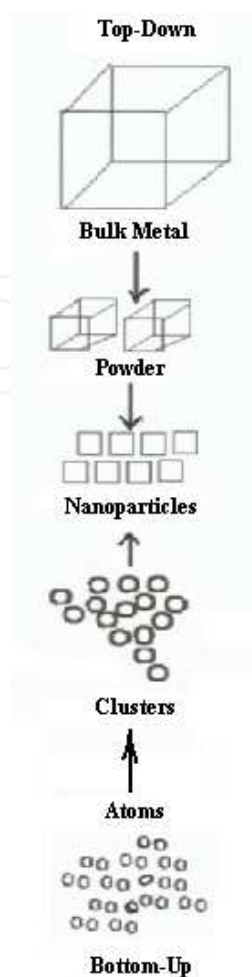
Figure 2. Schematic representation of the building up of nanostructures

decoration. The analogical technology is oftentimes known as electroplating. In addition to the production of metallic coatings, it is also for electrometallurgy in which metals are extracted from their ores or for electroformation where molds to form objects in their final shapes are produced. Mostly, the metallic deposit obtained is crystalline. This process can therefore be called electrocrystallization, a term introduced by russian chemist V. Kistiakovski in the early twentieth century.

The electrolyte contains positive and negative ions. Therefore, it is considered an ionic conductor. To prepare an electrolyte, the desired metal contained in a chemical species liquidized (mostly dissolved in water) to form a molten salt besides different organic and ionic liquids are currently used for particular electroplating processes. To begin electrodeposition, the cathode (working electrode, W.E) immersed in the electrolyte contained in a vessel (cell) along with the anode (counter electrode, C.E). To allow electric current flow in the circuit, the two electrodes are connected to a battery or any other power source. The cathode is connected to the negative terminal of the battery, while the anode is connected to the positive terminal so that the metal ions are reduced to metal atoms, which eventually form the deposit on the

surface. Figure 3 shows a schematic presentation of an electrolytic cell for electroplating or electrodepositing a metal "M" from an aqueous (water) solution of metal salt "MA".
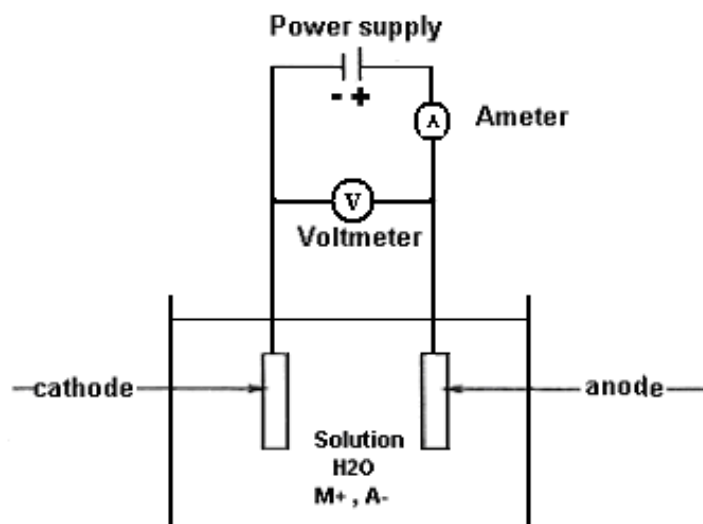

Figure 3. A schematic electrodeposition technique

This type of circuit arrangement directs electrons into a bath from the power supply to the cathode. In the bath, the electric current is carried by the positively charged ions from the anode toward the negatively charged cathode. This enables the metal ions in the bath to migrate toward extra electrons that are located at or near the surface of the cathode. Finally, the metal ions are removed from the solution and are deposited on the surface of the object as a thin layer. The reaction in aqueous medium at the cathode therefore obeys equation 1:

$$M^{+n} + ne^- \rightarrow M \tag{1}$$

where n is the number of electrons involved in the reaction.

The thickness of the electrodeposited layer on the substrate is determined by the time duration of the plating. The longer the object remains in the chemical bath, the thicker the deposited layer is [15].

Lately, electrodeposition has become increasingly popular and is being extensively used by researchers in disparate fields of inquiry. What exactly is causing such an interest? The process itself is deceptively simple, a conductive surface is immersed into an electrolyte containing ions of the material to be deposited and a voltage is applied across this solid/electrolyte interface, resulting in a charge transfer reaction and film deposition. The driving force for this process is the applied potential, a quantity that can be easily and precisely controlled down to the mV and over timescales as short as 1ns. This feature leads to considerable control over the material formation process, its microstructure, and properties. The challenge in developing electrodeposition processes today is not the synthesis of a predefined material, but to strike a

compromise between the ideal conditions used to produce this material and the commercial feasibility of the process. Other often-cited advantages of electrodeposition include the high utilization rate of the raw materials, low energy consumption, low material waste, little capital investment, and ease of implementation. Although the latter two are usually considered an advantage, they are perhaps a double-edged sword, they may in fact encourage quick experimentation, thereby relegating the science to the backstage and undermining the efforts of the community to place this technology on par with vacuum/gas/plasma deposition methods.

New materials and processes are being developed and integrated in microelectronic manu‐ facturing to provide new functionalities, for example, in MEMS, lab-on-a-chip, or microfluidic devices. Polymers and biomaterials are electrodeposited for biomedical applications; metal oxides and compound semiconductors are grown electrochemically for electronic or optoe‐ lectronic applications. Electrodeposition in new electrolytic media such as ionic liquids or supercritical fluids is being strongly pursued with some success. Electrodeposition plays an important role in the development of sustainable energy conversion technologies, both at the portable and on a global scale. In addition, the principles governing the scale-up of electrode‐ position processes are well understood, facilitating the development of large-scale manufac‐ turing processes [15].

3.1. The electrolysis cell

3.1.1. Constituents of the cell

The electrolysis process consists of four parts:

1. The external circuit, with power supply or battery as a source of direct current (dc), that is conveyed to the plating tank, and associated with instruments such as ammeters, voltmeters, and voltage and current regulator to regulate them at appropriate values.

2. The working electrodes or cathodes (the material to be plated). The cathodes are to be immersed in the plating solution so that contact is made with the current source.

3. The plating solution or solution bath.

4. The counter electrodes or anodes (metal or conducting materials being plated which serves merely to complete the circuit).

The electrodeposition cell containing the plating solution or the electrolyte is usually made of plain mild steel (for alkaline solutions) or of lined steel (for acidic solutions). Steel lining could be of rubber, plastics, glass, or even lead [26].
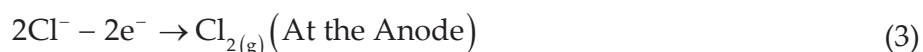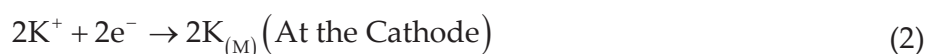
3.1.2. Electrolytes (Solution baths)

The solution bath serves as a source of metal to be deposited, which contains ions of that metal, hence it provides conductivity, a stabilizer to stabilize the solution, for example, against hydrolysis and to stabilize the solution pH when acts as a buffer, regulates the corporal form

of the deposit and helps dissolve the anodes. Finally, modifies properties of either the solution or of the deposit,

Complex ions are formed to stabilize the cation, which becomes much more stable when complexed to some ligand or to metal atoms by coordinate bonding. The concentration of the free (equated) ion is lowered by the presence of the ligand. Complex ions are also formed to hold the equated form at suitably low concentration allowing control of the evenness of plating.

Electrolytes can be defined as substances such as acid, base, and salts, which can conduct electricity in their aqueous solution due to ionization. The ions existing in the electrolyte are responsible for the conduction that results in current or free electrons passing through the wires. When a voltage is applied across the cell, and under the influence of the potential difference, the negatively charged ions migrate to the anode and the positively charged ions migrate to the cathode. The flowing of ions in aqueous solution of an electrolyte is called electrolysis [27]. For electrolysis of KCl in aqueous solution, it must be molten first by heating and elevating its temperature to the melting point. The molten ionic compound will be dissociated by electrolysis process into its elements. The reaction at each electrode is shown in equations 2 and 3:

$$2K^+ + 2e^- \rightarrow 2K_{(M)} \left(\text{At the Cathode} \right) \tag{2}$$

$$2Cl^- - 2e^- \rightarrow Cl_{2(g)} \left(\text{At the Anode} \right) \tag{3}$$

At the cathode, potassium ions are reduced to potassium atoms (metal) by gaining electrons. On the other hand, at the anode, chloride ions are oxidized to chlorine atoms by losing electrons which are combined to form molecules of chlorine gas.

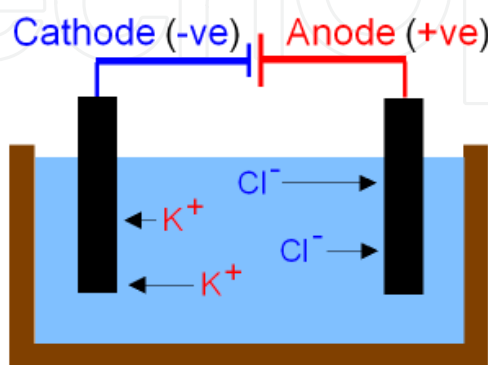The combining of equations 2 and 3 results in the following reaction:

$$2K^+Cl^-_{(l)} \rightarrow 2K_{(s)} + Cl_{2(g)} \left(\text{Overall Reaction} \right) \tag{4}$$

Figure 4. Electrolysis process of potassium chloride [http://www.gcsescience.com][28]

Strong Electrolytes

Some electrolytes such as potassium chloride, sodium hydroxide, and sodium nitrate are completely ionized in their constituent ions (>99%) in solution. These electrolytes are known as strong electrolytes. In other words, strong electrolytes are 100% dissociated in their aqueous solution. Generally, strong acids like sulfuric acid, nitric acid, hydrochloric acid; strong bases like potassium hydroxide salt and many others are strong electrolytes [27]. Salts that are composed of oppositely charged ions held by strong electrostatic forces of attractions are considered strong electrolytes and they dissolve in water, which highly weakens the attraction forces between ions and reduces it by a factor of 80 due to its high dielectric constant of 80. Therefore, it facilitates the free movement of ions that are stabilized by solvation/hydration process with water. Figure 5 demonstrates how sodium and chloride ions are surrounded by water molecules due to ion-dipole interaction.
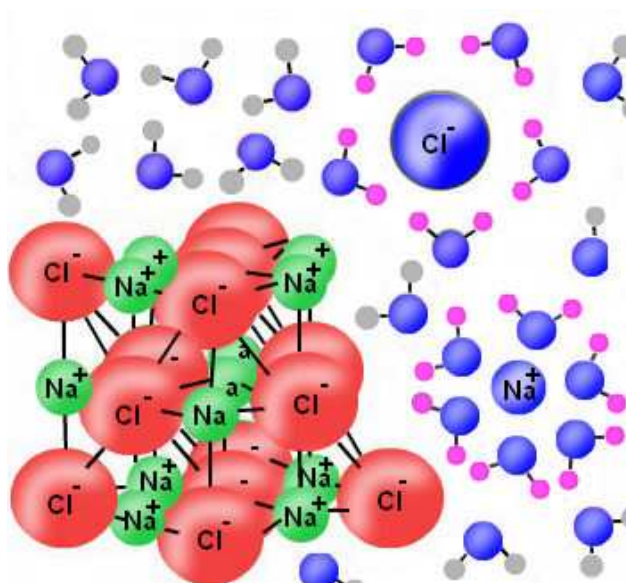

Figure 5. Sodium chloride solvation process

Weak Electrolytes

Some electrolytes are weak. A weak electrolyte is an electrolyte that partially dissociates in solution. In other words, ions and molecules of the electrolyte are both included in the solution. A moderately small percentage of ions (<1%) are given in solution with most of the compound staying in a non-ionic form (>99%) resulting in poorly conducting solutions. Acetic acid, carbonic acid, ammonia, rubidium hydroxide, some organic bases, and many others are considered weak electrolytes [29].

Nonelectrolytes

Substances that do not dissociate into ions in solution (water) are known as nonelectrolytes. These substances include most carbon compounds such as methyl alcohol, ethyl alcohol, glucose, and many others [30].

3.1.3. Electrode potential

When a metal electrode is placed in an ionic solution, ions will be exchanged between the metal and the solution. Ions from the metal enter the solution, and ions from the solution enter the metal lattice. The boundary between the two phases is called the interface. Due to an electron exchange between the electrode and the ions in solution, the interface becomes electrified and a potential difference across the metal-solution interface is generated. This potential difference is called electrode potential.

In case more ions leave than enter the metal electrode, there is an excess of electrons on the metal and hence it acquires negative charge, which attracts positively charged metal ions from the solution and repels negatively charged ions. Therefore, an excess of positive ions in the solution near the metal interface and the solution side acquires opposite (positive) and equal charge. The rate of positive ions leaving the metal electrode slows down due to repulsion with the positive charge at the solution side of the interface and the rate of ions entering the metal electrode accelerates [31]. In a short time, equilibrium between the metal and its ions in the solution is achieved, as shown in Figure 6.

$$\vec{n} = \overset{\backsim}{n} \tag{5}$$

where, $\vec{n}$ denotes the number of positive ions that enter the metal electrode and $\overset{\backsim}{n}$ denotes the number of positive ions that leave the metal electrode.

At equilibrium:

$$q_M = -q_S \tag{6}$$

where, q is the electric charge.

The result of the changing of the interface is the potential difference, $\Delta\Phi$ (M, S), between the potentials of the metal, Φ_M, and the solution, Φ_S:

$$\Delta\Phi(M, S) = \Phi_M - \Phi_S \tag{7}$$

In order to measure the potential difference of an interphase, one must connect it to another one and thus form an electrochemical cell. The potential difference across this electrochemical cell can be measured [32].

The cell shown in Figure 7 may be schematically represented in the following way:

$$Pt, H_2(p = 1)|H^+(a = 1)||Cu^{2+}(a = 1)|Cu|Pt|$$
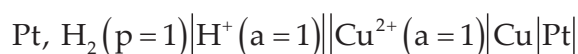
where the electrode at the left side is the hydrogen reference electrode. When the pressure of H_2 p = 1 atm and the activity of H^+ ions a = 1, the hydrogen electrode is called the standard hydrogen electrode (SHE) and its potential is zero by convention. The standard electrode potential of a solution, $E^{\underline{o}}$ (V) is the tendency for a chemical species to be reduced. The more positive the potential, is the more likely it will be reduced [1].

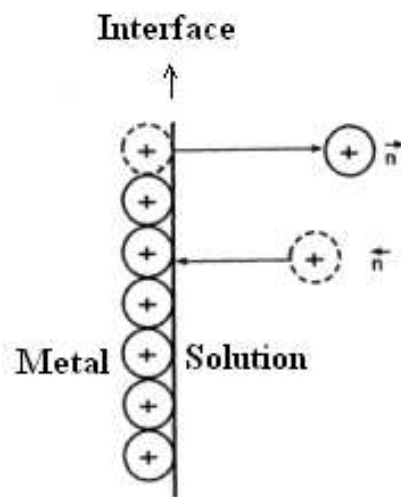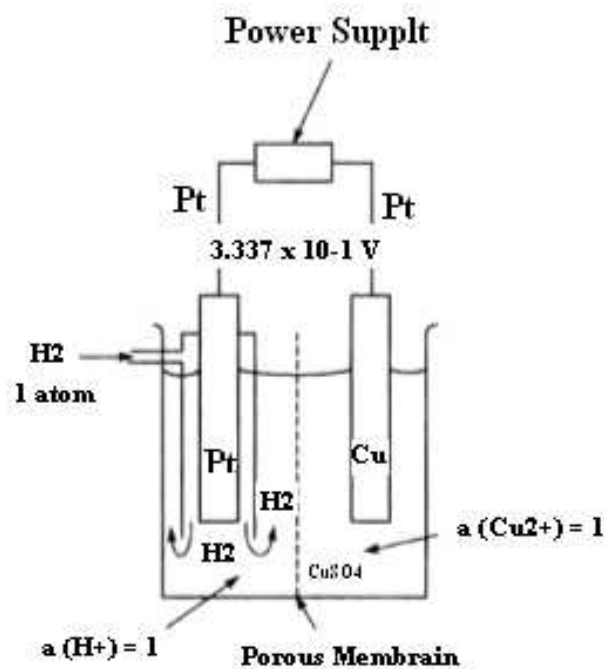**Figure 6.** Formation of metal-solution interface (equilibrium state, $\vec{n}=\bar{n}$)

Figure 7. Relative standard electrode potential E^0 of a Cu/Cu²⁺ electrode

3.1.4. Some electrode reactions

Some acidic and basic solution reductions with their corresponding standard electrode potential E^0 measured at 25ºC are presented. Obviously, the more positive the potential E^0 is, the more likely it will be reduced. However, the potential E^0 of the reference electrode is zero, below which the potential E^0 is increasing negatively, as shown below [33]:

F_2 (g) / F^- (aq)	+2.87
Co^{3+} (aq) / Co^{2+} (aq)	+1.82
Pb^{4+} (aq)/Pb^{2+} (aq)	+1.8
NiO_2 (s) / Ni^{2+} (aq)	+1.7
Au^+ (aq) / Au (s)	+1.68
Ce^{4+} (aq) / Ce^{3+} (aq)	+1.61
MnO_4^- (aq) / Mn^{2+} (aq)	+1.51
Au^{3+} (aq) / Au (s)	+1.5
ClO_3^- (aq) /Cl_2 (g)	+1.47
BrO_3^- / Br^- (aq)	+1.44
Cl_2 (g) / Cl^- (aq)	+1.358
$Cr_2O_7^{2-}$ / Cr^{3+} (aq)	+1.33
$N_2H_5^+$ (aq) / NH_4^+ (aq)	+1.24
MnO_2 (s) / Mn^{2+} (aq)	+1.23
Pt^{2+} (aq) / Pt (s)	+1.2
IO_3^- (aq) / I_2 (aq)	+1.195
ClO_4^- (aq) / ClO_3^- (aq)	+1.19
Br_2 (l) / Br^- (aq)	+1.066
$AuCl_4^-$ / Au (s)	+1
Pb^{2+} (aq) / Pb (s)	+0.987
NO_3^- (aq) / NO (g)	+0.96
NO_3^- (aq) / HNO_2 (aq)	+0.94
Hg^{2+}(aq) / Hg_2^{2+}(aq)	+0.92
Hg^{2+}(aq) / Hg (l)	+0.855
Ag^+(aq) / Ag (s)	+0.7994
Hg_2^{2+}(aq) / Hg (l)	+0.789
Fe^{3+}(aq) / Fe^{2+}(aq)	+0.771
$SbCl_6^-$(aq) / $SbCl_4^-$(aq)	+0.75

$[PtCl_4]^{2-}$ (aq) / Pt (s)	+0.73
O_2 (g) / H_2O_2 (aq)	+0.682
$[PtCl_6]^{2-}$ (aq) / $[PtCl_4]^{2-}$ (aq)	+0.68
H_3AsO_4 (aq) / H_3AsO_3 (aq)	+0.58
I_2 (s) / I^- (aq)	+0.535
TeO_2 (s) / Te (s)	+0.529
Cu^+ (aq) / Cu (s)	+0.521
$[RhCl_6]^{3-}$ (aq) / Rh (s)	+0.44
Cu^{2+} (aq) / Cu (s)	+0.337
$HgCl_2$ (s) / Hg (l)	+0.27
AgCl (s) / Ag (s)	+0.222
SO_4^{2-} (aq) / SO_2 (g)	+0.2
SO_4^{2-} (aq) / H_2SO_3 (g)	+0.17
Cu^{2+} (aq) / Cu^+ (aq)	+0.153
Sn^{4+} (aq) / Sn^{2+} (aq)	+0.15
S(s) / H_2S (aq)	+0.14
H^+ (aq) / H_2 (g) (reference electrode)	0
N_2O (g) / NH_3OH^+ (aq)	-0.05
Pb^{2+} (aq) / Pb(s)	-0.126
Sn^{2+} (aq) / Sn (s)	-0.14
Ni^{2+} (aq) / Ni (s)	-0.25
Co^{2+} (aq) / Co (s)	-0.28
Tl^+ (aq) / Tl (s)	-0.34
Se (s) / H_2Se (aq)	-0.4
Cd^{2+} (aq) / Cd (s)	-0.403
Cr^{3+} (aq) / Cr^{2+} (aq)	-0.41
Fe^{2+} (aq) / Fe (s)	-0.44
CO_2 (g) / $(COOH)_2$ (aq)	-0.49
Ga^{3+} (aq) / Ga (s)	-0.53
Cr^{3+} (aq) / Cr (s)	-0.74
Zn^{2+} (aq) / Zn (s)	-0.763
H_2O (l) / H_2 (g)	-0.8277
Cr^{2+} (aq) / Cr (s)	-0.91
Mn^{2+} (aq) / Mn (s)	-1.18

V^{2+} (aq) / V (s)	-1.18
Zr^{4+} (aq) / Zr (s)	-1.53
Al^{3+} (aq) / Al (s)	-1.66
H_2 (g) / H^- (aq)	-2.25
Mg^{2+} (aq) / Mg (s)	-2.37
Na^+ (aq) / Na (s)	-2.714
Ca^{2+} (aq) / Ca (s)	-2.87
Sr^{2+} (aq) / Sr (s)	-2.89
Ba^{2+} (aq) / Ba (s)	-2.9
Rb^+ (aq) / Rb (s)	-2.925
K^+ (aq) / K (s)	-2.925
Li^+ (aq) / Li (s)	-3.045
OOH^- (aq) / OH^- (aq)	0.88
NH_2HO (aq) / N_2H_4 (aq)	0.74
ClO_3^- (aq) / Cl^- (aq)	0.62
MnO_4^- (aq) / MnO_2 (s)	0.588
MnO_4^- (aq) / MnO_4^{2-} (aq)	0.564
NiO_2 (s) / $Ni(OH)_2$ (s)	0.49
O_2 (g) / OH^- (aq)	0.4
ClO_4^- (aq) / ClO_3^- (aq)	0.36
Ag_2O (s) / Ag (s)	0.34
NO_2^- (aq) / N_2O (g)	0.15
N_2H_4 (aq) / NH_3 (aq)	0.1
$[Co(NH_3)_6]^{3+}$ (aq) / $[Co(NH_3)_6]^{2+}$ (aq)	0.
HgO (s) / Hg (l)	0.0984
NO_3^- (aq) / NO_2^- (aq)	0.01
MnO_2 (s) / $Mn(OH)_2$ (s)	-0.05
CrO_4^{2-} (aq) / $Cr(OH)_3$ (s)	-0.12
$Cu(OH)_2$ (s) / Cu (s)	-0.36
$Fe(OH)_3$ (s) / $Fe(OH)_2$ (s)	-0.56
H_2O / H_2 (g)	-0.8277
NO_3^- (aq) / N_2O_4 (g)	-0.85
$Fe(OH)_2$ (s) / Fe (s)	-0.877
SO_4^{2-} (aq) / SO_3^{2-} (aq)	-0.93

N_2(g) / N_2H_4(aq)	-1.15
$[Zn(OH)_4]^{2-}$(aq) / Zn(s)	-1.22
$Zn(OH)_2$(s) / Zn(s)	-1.245
$Cr(OH)_3$(s) / Cr(s)	-1.3
SiO_3^{2-}(aq) / Si(s)	-1.7

3.2. Electrical relationships

3.2.1. Faraday's law of electrolysis

Michael Faraday (1791–1867) observed that redox reactions occur when electric current passes through electrolyte solutions. When external source supplies electric current to the electrolytic cell, the electrons flow in the cell is in the opposite direction of that in the external circuit. At the cathode, electrons are supplied from the external source, which causes reduction reaction to occur. Similarly, oxidation reaction occurs at the anode since electrons return to the external source from this electrode.

Faraday's law states that the amount of electrochemical reaction occurs at an electrode is proportional to the electric charge Q passing through the cell that is.

$$w = ZQ \tag{8}$$

where w is the product weight, Z is the electrochemical equivalent, the constant of proportionality, Q is the electric charge:

$$Q = It \tag{9}$$

where, I is the current measured by amp (A), and t is the time measured by second (s)

$$w = ZIt \tag{10}$$

One mole of electrons is called one faraday. Faraday constant F is defined as the charge of one mole of electrons. To produce 1 g of reaction product at the electrode, 96,487 C (Faraday constant F) is required, which can be calculated as in Eq. 11:

$$F = N_A e \tag{11}$$

where N_A is Avogadro number, e is the electron charge.

$$1 \text{ Faraday} = 9.64870 \times 10^4 \left(C \text{ mol}^{-1} \right) \tag{12}$$

To produce one mole of hydrogen molecules H_2, two faradays are required since the reduction of $2H^+$ requires two electrons; for one mole of silver, one faraday is required since the reduction of Ag^+ requires one electron; and for one mole of aluminum, three faradays are required since the reduction of Al^{3+} requires three electrons. Generally,

$$w_{eq} = \frac{A_{wt}}{n} \tag{13}$$

where A_{wt} is the atomic weight, n is the number of electrons [32].

If $Q = 1C$, then

$$w_{Q=1} = Z \tag{14}$$

Equation 14 shows that the electrochemical equivalent Z is the weight produced or lost.

Combining Eqs. (8) and (14) produces:

$$w = w_{Q=1}Q \tag{15}$$

Since 96,487 C is required for the deposition of an equivalent of a metal, w_{eq}

$$w_{eq} = 96,487\ Z \tag{16}$$

And

$$Z = w_{Q=1} = \frac{w_{eq}}{96,487} = \frac{w_{eq}}{F} \tag{17}$$

Using Eq. (13):

$$Z = \frac{A_{wt}}{nF} \tag{18}$$

$$w = ZQ = \frac{A_{wt}}{nF}Q \tag{19}$$

3.2.2. Current efficiency

The current efficiency of metal electrodeposition is highly determined by the deposition rate and energy. For instance, in copper electrodeposition the current efficiency decreases with

increasing deposition current density and concentration of acidic solution. However, it is directly proportional with increasing copper concentration, solution flow rate, and solution temperature [34]. Based on Faraday's law, the amount of chemical change at the electrode is proportional to the quantity of electricity passing through the solution. Therefore, the quantity of metal deposited at the cathode or dissolved at the anode is our concern, and the elaborated hydrogen or oxygen at the cathode or the anode, respectively, is considered electrical energy dissipation and process efficiency reduction. Equation (20) is a statement of percentage current efficiency:

$$CE\% = \frac{Act}{Theo} \times 100 \tag{20}$$

where CE is current efficiency, Act is the actually deposited weight, and Theo is the expected deposited weight. Current efficiency when applied to the cathode reaction is called cathode efficiency and current efficiency as applied to the anode reaction is called anode efficiency [26].

3.2.3. Deposit thickness

Michael Faraday has formulated many laws. But the most important law in this regard is the relationship between current, time, and the weight of the deposit metal, represented by the following equation:

$$w = (I.t.A)/(n.F) \tag{21}$$

where, w (g) is the weight of deposit metal, I (C/s) is the current, t (s) is the time, A (g.mol^{-1}) is the atomic weight, n (equivalents.mol^{-1}) is the valence of the dissolved metal in solution and F is Faraday's constant (96,485.309 C/equivalent).

Consider nickel electrodeposition at the cathode, nickel ions will be reduced or deposited as nickel metal.

$$Ni^{2+} + 2e^- \rightarrow Ni \tag{22}$$

If a current of 1 amp is supplied to the cathode for 1 h.

$$w = \frac{(1 \times 3600 \times 58.69)}{(2 \times 96485.309)} = 1.09 \text{ g}$$

Hence, the thickness is:

$$T = \frac{w}{\rho \times a} \tag{23}$$

where T (µm) is the thickness, ρ (gm.cm^{-3}) is the density, and a (cm^2) is the surface area of the deposit.

Combining Eqs., 21 and 23 yields:

$$T = \frac{(I \times t \times A)}{(n \times F \times \rho \times a)} \tag{24}$$

Assume that, the surface area of the Ni deposit is 22.1 cm^2. Thus,

$$T = \frac{(1 \times 3600 \times 58.69 \times 10000)}{(2 \times 96485.309 \times 8.90 \times 22.1)} = 55.67 \ \mu m$$

From the above equation, thickness is proportional inversely with the surface area, provided that, all other parameters in the equation are maintained the same [35].

4. Research and development

Electrodeposited thin films are playing a major role in the development of new materials such as magnetic materials, where electrodeposition reveals strong potential to grow high-quality ultrathin magnetic layers with interesting magnetic properties, and, further, in the study of magnetism on micro- and nano scales [36]. Thermoelectronic devices are another emerging technology that uses electrodeposited materials [37]. J.F.K. Cooper, et al., have successfully grown thin films of ternary alloy of CoNiCu by single-bath electrodeposition techniques using weak and strong electrolytic solutions, whereby the potential can be controlled to grow a wide range of homogeneous films [38]. Nanostructured deposits of the alloys of bismuth, antimony, tellurium, and select other elements have useful thermoelectric properties. One successful fabrication technique is to electrodeposit the materials into nanoscale pores [39]. Electrodeposition is a simple and flexible method for the synthesis of one-dimensional (1D) nanostructures of metals, semiconductors, and polymers in the form of nanowires, nanorods, nanotubes, and nanoribbons that have shown novel physical properties and amazing potential applications in nanodevices [40]. The photovoltaic (PV) conversion of solar energy is one of the most promising renewable energy sources for our future energy needs. Electrodeposition technique was used successfully to synthesize nanostructured electrodes of Zn_xCd_{1-x} (O) on ITO glass substrate with several values of x in an aqueous medium containing Zn^{2+} and Cd^{2+} species for energy generating photovoltaic cell, and the efficiency achieved was 1.6% [21]. Electrodeposition of materials has the potential to change phase of deposits upon heating or cooling. Deposit in the amorphous state at room temperature can change phase to crystalline when annealing at elevated temperatures. The switching between amorphous and crystalline phases is useful for rewritable optical storage and solid-state memory [41]. Wiring of printed circuits and interconnections of multilayer microchips are another developed areas of electrodeposi-

tion for electronic applications. The plated area can be accurately defined by using photoresist. Electroless plating or Autocatalytics permits a conducting layer to be deposited on insulating materials. For connection, a solder thin layer can be deposited [42].

5. Conclusion

Electrodeposition is the application of metallic coatings to metallic or other conductive surfaces by electrochemical processes for the purpose of good appearance, protection, special surface properties, and engineering or mechanical properties. Electrodeposition is a multidisciplinary technique and based on chemistry, physics, chemical and electrical engineering, metallurgy, and probably others. Besides, it retains the aspects of art, in which experience is the only way to learn. No text on electroplating will produce an expert electroplater. There is no substitute for experience and what is somewhat inelegantly termed know-how. The most beautiful feature of electrodeposition technique is that the deposit thickness, deposition temperature, and deposition potential can be relatively controlled.

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