

Electrochemical deposition

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Introduction

Electrochemical deposition (ED) is synthesis method that is used to deposit desired material into surface of other solid material. The chemical reaction takes place on solid-liquid interface and it is achieved by means of electricity. Electrochemical deposition is recognized as convenient fabrication method for complex structures and catalytic surfaces and it have great potential to become unique method in nanotechnology.^[1] Surface energetics and chemical activities of species are fundamental physical properties that are examined in these phenomena. Thus, manipulation and exploitation these properties one can achieve control over the deposition thickness, nucleation, growth and microstructure.

Figure 1 shows schematic illustration of typical electrochemical deposition process. In the figure, working electrode (WE), counter electrode (CE), and reference electrode (RE) are placed into bath (electrolyte) that is aqueous solution of desired deposition ions. Current generator is applied into WE and CE which causes potential difference between electrodes. Current causes ions to move towards electrodes and the deposition occurs when reduction takes place on WE. Reduction requires electron transfer from CE which is achieved via oxidation of ions or neutral molecules. RE is used to monitor potential and current changes during deposition.

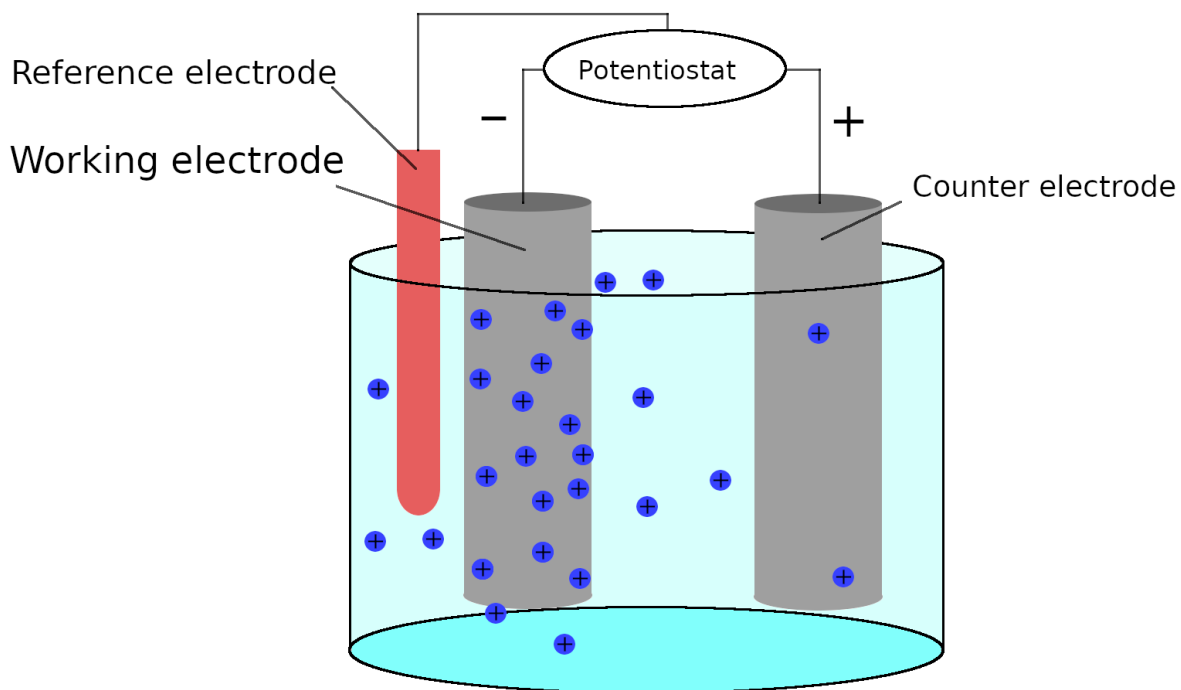


Figure 1. Electrochemical deposition process. Figure: Sami Jääskelä.

Without considering classifications of different ED methods, some features can be recognized in them all. ED requires electricity and selection of process parameters and materials should be taken account when designing the process.^[2] Surface limited redox placement (SLRR), electrochemical deposition redox replacement (EDRR) and electrochemical atomic layer deposition (e-ALD) methods are examples of different types of ED methods. SLRR and EDRR are processes where the deposition occurs first with means of electricity following spontaneous replacement between two metal atoms.^[3] e-ALD is surface limited deposition method where the deposition occurs with underpotential.^[4]

Deposition process

General electrochemical deposition process is achieved with electrochemical cell which constitutes of electrodes, electrolyte and external power supply (Figure 1). Deposition of desired species can be obtained by adjusting potential in working electrode, which can be estimated by Nernst equation:^[5]

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

- E° is potential in standard conditions
- R is gas constant
- T is temperature of reaction

- n is number of electrons in redox reaction
- F is faraday constant
- Q is activity of reducing specie divided by activity of oxidizing specie.

Standard potential can be calculated from tabulated values which are expressed as reduction potential against standard hydrogen electrode (SHE). Activities that are included in Q , can be calculated by multiplying concentration of a species by its activity coefficient. On the other hand, if there is no need for accurate potential value, Q can be approximated using only concentrations. In practice, cell potential is determined by cyclic voltammetry measurement. This is because complexity of redox reaction. Different species and environment affects cell reactions which makes calculations more difficult.

Process parameters

Thickness of deposited layer can be controlled by adjusting the potential on working electrode. In case of surface limited electrochemical deposition the potential is adjusted just below the value where bulk deposition occurs.^[4] This is the case in SLRR and e-ALD methods where deposition process stops after formation of monolayer due to underpotential that is not sufficient for bulk deposition. Underpotential deposition methods provides smooth surfaces that are grown epitaxially.

Electrochemical redox replacement (EDRR) can be used to obtain functional nanoparticles on the surface of an electrode.^[3] Formation of nanoparticles is achieved in higher potentials than SLRR or e-ALD because the goal is to obtain rougher surfaces and thus bulk deposition is desirable. After the deposition of metal layer by means of electricity, spontaneous redox replacement occurs between deposited metal atoms and more noble metal atoms. In the redox replacement step the applied voltage is cut off and open voltage potential is left on for desired time. Electrochemical deposition and redox replacement steps are done multiple times allowing growth of nanoparticles. By adjusting the potential, deposition time, redox replacement time and cycles, constitution and size of nanoparticles can be controlled. Figure 2 shows typical i - V curve that is recorded in EDRR process for solution containing high amount of nickel and dilute amount of platinum.

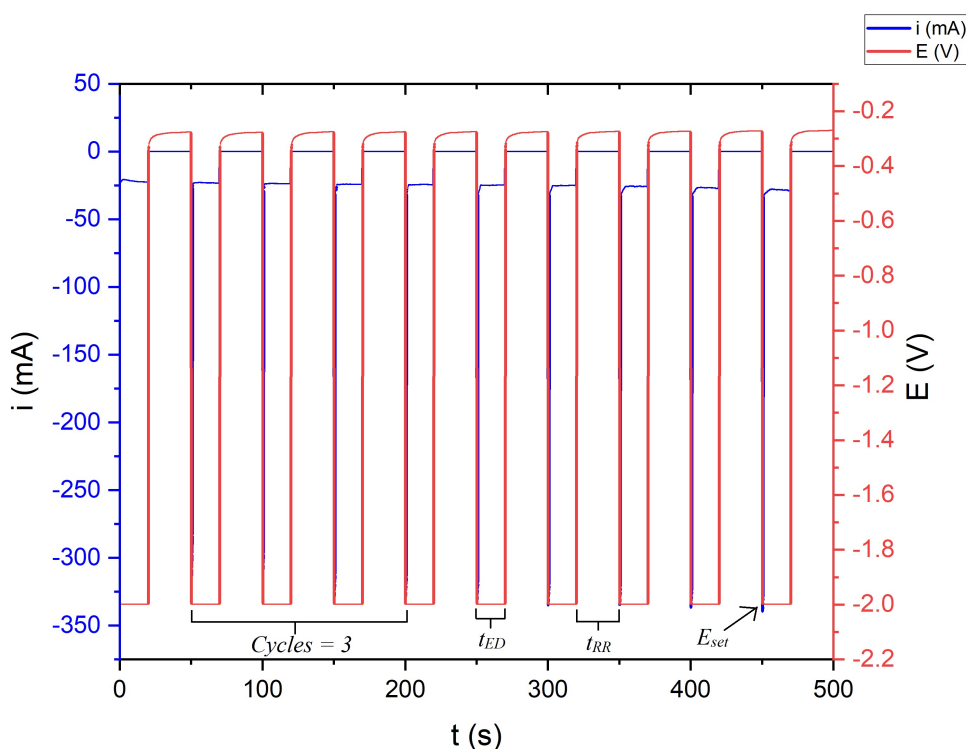
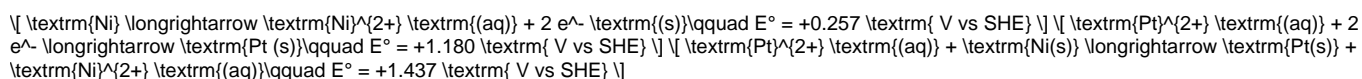


Figure 2. Typical i - V curve recorded in EDRR process: Cell potential E_{set} is -2.0 V vs Ag/AgCl, deposition time t_{ED} 20s, open circuit voltage time t_{RR} 30 s and 10 cycles. Figure: Sami Jääskelä.

Electrochemical-redox replacement is relative method for a surface-limited redox replacement (SLRR) but it is used to obtain rough surfaces by overpotential.^[3] Electrochemical-redox replacement is conducted within two steps and it can be achieved in an electrolyte which contains two different metal ions and other one is more noble metal.^[3] First, the deposition of sacrificial metal is obtained by means of electricity (ED-step) following by spontaneous replacement of more noble metal when applied potential is cut off (RR-step). Ni/Pt nanoparticle formation can be achieved with EDRR process where electrolyte contains high amount of nickel and dilute amount of platinum.^[3] In the ED-step, Ni^{2+} is first deposited onto the surface of electrode following by spontaneous redox replacement of Ni (s) and Pt^{2+} . Half reactions and cell reaction for the process are following:



Above described EDRR process allow to control nanoparticle size, density and Ni/Pt content of deposited nanoparticles when process parameters are adjusted to appropriate values. Obtained nanoparticles has been shown to become activated for photocatalytic hydrogen evolution due to deposited Ni/Pt nanoparticles.^[3]

Kinetics

Growth rate of the electrochemical deposition is related to Faraday's law:^[5]

$$\text{Rate}(\mu\text{m h}^{-1}) = 3.6 \times 10^4 \times \frac{Z \times CE \times J}{M}$$

Where CE is the current efficiency, J is current density (mA cm^{-2}) and M is density of metal (g cm^{-3}). Z is determined as follows:

$$Z = \frac{M}{nF}$$

Where M is molecular weight, n is number of electrons involved to the reaction and F is Faraday constant 96485 C mol^{-1} .

The mass transport of metal ions will be the upper limit for deposition rate in the surface of working electrode.^[5] Without convection or mixing the current decreases with respect to time when metal ions are consumed nearby working electrode. Cottrell equation describes the phenomena by following equation:

$$j(t) = \frac{n F \sqrt{D} C}{\sqrt{\pi t}}$$

Where n is number of electrons, F is Faraday constant, D is diffusion coefficient, t is time and C is concentration of metal in the solution.

Materials in electrochemical cell

As an electrochemical cell goes through electron transfer between electrode in certain potential range, electrode materials affect on the phenomena. An important feature of electrodes is that the electrode material does not reduce or oxidize. Potential window of a material describes on which potential range the electrode can used. Typical materials used as electrodes are metals (Pt and Au), liquid metals (Hg, amalgams), graphite and semiconductors (Si and ITO).^[6] Electrolyte solution must also be conductive and charge is carried with ions. The most common electrolytes are ionic solutions of H^+ , Na^+ or Cl^- in water or non-aqueous solvent.

Electrode properties can be tuned for desired electrochemical deposition process. For instance, silicon wafer can be coated with pyrolysed carbon that provides wider potential window and different morphology for working electrode.^[7]

Figure 3 shows the morphology of pyrolysed carbon coated silicon wafer which contains microscale pillars.



Figure 3. Pyrolysed carbon coated electrode used on deposition of nickel in EDRR process. Figure: The SEM image was obtained with a table top SEM Hitachi TM4000plus by Sami Jääskelä and coworkers.

Tabulated standard potentials (denoted as E^\ominus) are measured with standard hydrogen electrode (SHE). Convention in SHE is that the reduction of hydrogen gas is zero and the measurements are conducted in condition where the activity of species are unity. It is common that different reference electrodes are used in research such as saturated calomel electrode (SCE) which potential is 0.242 V vs SHE and silver-silver chloride electrode (Ag/AgCl) which is 0.197 V vs SHE.^[6]

Cyclic voltammetry

Cyclic voltammetry studies can be used to determine at which potential range different redox reactions occurs.^[6] In this study, WE potential is ramped linearly for a certain period a time followed by potential switching on the opposite direction. Potential changes are monitored during the study and different reactions can be identified as peaks. The study can be also carried out with ramped current which gives potential peaks. Figure 4 shows typical cyclic voltammetry curve for reversible reaction:

$[M^{n+} + e^- \rightleftharpoons M]$

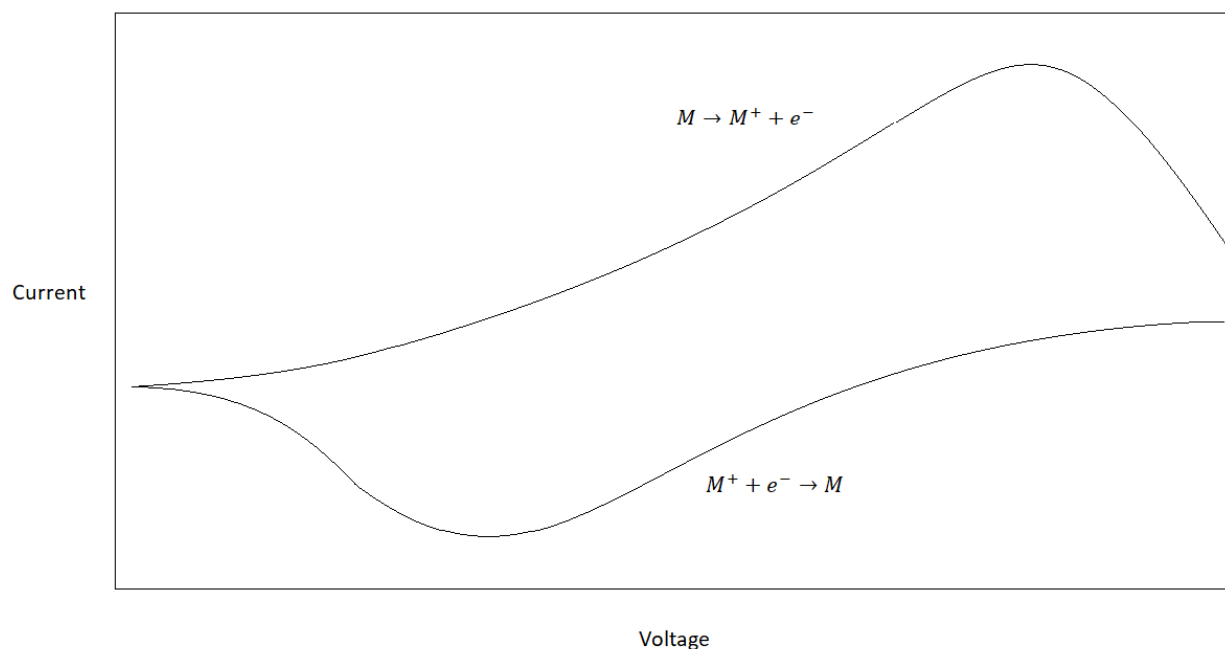


Figure 4: Typical i-V curve obtained from cyclic voltammetry studies. Figure: Sami Jääskelä.

In the cyclic voltammetry study shown in the Figure 4, deposition rate of metal M^+ increases gradually with respect to increasing potential. As the potential reaches appropriate value, a current peak appears in the curve which is the highest deposition rate for reduction reaction. It is good to notice that competing reactions can occur in the same potential range as the reduction of the metal. For instance, hydrogen evolution typically can be identified at the beginning of reduction of a metal.^{[7] [8]} Note that the cyclic voltammetry described here is expressed by International Union of Pure and Applied Chemistry (IUPAC) conventions. US convention express the reduction as an opposite sign.

References

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