

## The continued development of multilayered and compositionally modulated electrodeposits

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### Abstract

Traditionally, electroplating has involved the continuous deposition of a single layer of metal at constant current. However, electrodeposition of alternate layers can offer benefits such as reduced wear, improved corrosion resistance and higher tensile strength. The alternate layers can involve different morphology or thickness of metal, different metals or the alloy composition of layers with and without included particles. In the case of a single bath, electrocrystallisation is continuous but layers can be tailored to have different chemical composition, phase composition, morphology and microstructure. The composition of layers can also be systematically modified in a gradient fashion. The thickness of each metal layer can vary from  $>20\ \mu\text{m}$  down to  $\approx 1\ \text{nm}$ ; in the case of nanometre thick layers, up to 500 layers of 1 nm thick individual layers might be involved. Compact multilayer deposition from a single bath is often achieved by applying a potential waveform in the laboratory or pulsed current in industry. While multilayer electrodeposition is going through a phase of rediscovery, growth and diversification, the field can be traced back to a patent involving Cu-Ni multilayers, in 1905. Progress in multi-layered electrodeposition has made use of contemporary trends in electroplating research, including self-assembled layers, nanowire arrays and the use of deep eutectic solvents for electrolytes. The developing uses of multilayer deposits are seen to span industries as diverse as wear and corrosion resistant coatings, toolbits and heavy engineering. Speciality uses include electronic, optical and magnetic materials as well as catalytic electrode surfaces for electrochemical technology. Recommendations are made on aspects which deserve further R & D.

**Keywords:** deposit composition; electroplating techniques; gradient deposit; pulsed current.

## List of Symbols

Symbol	Meaning	Units
$E$	Electrode potential	V
$E_{cell}$	Cell voltage	V
$F$	Faraday constant (96 485)	C mol <sup>-1</sup>
$I$	Current	A
$I_M$	Current used to deposit metal	A
$j$	Current density	A cm <sup>-2</sup>
$M$	Molar mass of metal	g mol <sup>-1</sup>
$N$	Number of electrodeposited layer pairs	Dimensionless
$q$	Electrical charge	C = A s
$x$	Thickness of deposit	cm
$x_A$	Thickness of deposit A	cm
$x_B$	Thickness of deposit B	cm
$t$	Time	s
$z$	Electron stoichiometry	Dimensionless
Greek		
$\psi$	Current efficiency for metal deposition	Dimensionless
$\rho$	Density of metal	g cm <sup>-3</sup>

## Abbreviations

CE	Counter electrode
CMA	Cyclic modulated alloy
CMAM	Compositionally modulated alloy multilayer
CMM	Compositionally modulated multilayer

CVD	Chemical vapour deposition
DVM	Digital voltmeter
GMR	Giant magnetoresistance
ITO	Indium tin oxide
MDM	Metal dielectric metal
MEMS	Miniature microelectromechanical systems
MIM	Metal insulator metal
NMM	Nanoscale metallic multilayers
PECVD	Plasma enhanced chemical vapour phase deposition
PVD	Physical vapour deposition
RCE	Rotating cylinder electrode
RDE	Rotating disc electrode
RE	Reference electrode
RSM	Response surface methodology
SEM	Scanning electron microscope
TEM	Transmission electron microscope
WE	Working electrode

## **1. Introduction**

Natural, layered materials include nacre [1] or tortoise shell (which shows remarkable hardness and rigidity) and graphite (known for its high electrical conductivity and lubricity). Over the last decade, synthetic layered 2-dimensional structures have come into sharp focus and surface finishing techniques offer an established, versatile route to their synthesis or application as nanostructured coatings [2], especially graphene derivatives [3] and composite coatings.

The literature on multilayer coatings has traditionally been dominated by very thin (nanometre thick) films produced by dry, vacuum deposition techniques (PVD and CVD including PECVD) together with the physical and materials physics properties of the films. Electroplating has a long, distinguished history as a technology for the controlled deposition of single metal and alloy coatings [4, 5]. Following suitable pretreatment of the metal substrate to facilitate good nucleation, a constant current,  $I$  is normally applied to a known area of cathode,  $A$  using a smooth, direct current power supply. If the current density,  $j$  over the cathode is uniform and the current efficiency,  $\psi$  is constant, metal deposition takes place at a predictable rate. If deposition is uniform, the average coating thickness,  $x$  may be controlled by adjusting the deposition time,  $t$  according to Faraday's laws of electrolysis [6]:

$$x = \frac{M}{\rho z F} \psi j t \quad (1)$$

where  $M$  is the molar mass of the depositing metal,  $\rho$  is its density,  $z$  is the electron stoichiometry and  $F$  is the Faraday constant. The current efficiency,  $\psi$  is the ratio of the current used to deposit metal,  $I_M$  to the total current,  $I$ :

$$\psi = \frac{I_M}{I} \quad (2)$$

The thickness of metal deposited can be altered by:

- a) adjusting the current,  $I$ , hence the current density,  $j = I / A$ , which is a common means of control,
- b) controlling the cathode potential,  $E$  vs. a reference electrode, the potentiostatic technique often being preferred in the research laboratory, where a reference electrode can be included in the cell and a potentiostat is available as a specialised, feedback-controlled power supply.

- c) choosing a different deposition time,  $t$ , hence the electrical charge passed,  $q$ , which is another common strategy,
- d) selecting a metal of different density,  $\rho$  and molar mass,  $M$ ,
- e) choosing a metal deposition reaction which involves a different number of electrons,  $z$ , or
- f) improving the current efficiency,  $\psi$  by changing the electrode potential,  $E$ , perhaps by choosing a different bath composition or using additives,
- g) using different electrode and cell geometries or
- h) changing the relative electrode/bath movement by cathode movement or bath agitation.

Equation (1) allows the versatility and control of electroplating to be appreciated as a coating technique. Typically, layer thickness,  $x$  can vary from less than a nanometre to tens of micrometres, by suitable choice of electrical current and deposition time.

The electrode potential,  $E$  is related to the current density,  $j$  at the cathode via polarisation. It is unfortunate that more surface finishing pilot-scale and industrial practice does not routinely monitor the electrode potential as the potential difference between the cathode and a reference electrode close to it [7]. The electrode potential affects important aspects of deposition [8], including:

- a) the morphology and grain structure of deposits,
- b) the surface roughness,
- c) the elemental and phase composition of alloy coatings,
- d) the current efficiency for metal deposition and

e) the phase composition of alloy deposits.

Pulse plating in the laboratory is often carried out by potentiostatic control but normally current is pulsed in industry (section 3.1), offering several improved grain structure and morphology together with enhanced physical properties in deposits [9-11], a 385 page monograph having appeared in 2012 [9]. Improvements in our understanding of pulse plating and operational factors affecting its efficiency have significantly contributed to the development of electrodeposited metal multilayers. For example, Ibl and colleagues provided a clear appreciation of mass transfer of electroactive species towards the cathode and capacitance at the cathode/electrolyte interface [12]. Landolt contributed to a wider appreciation of pulse plating parameters in alloy electroplating [13]. Puipe provided a monograph on pulse plating of metals in 1987 [14]. As illustrated in a recent review by Liu et al [15], pulse electrolysis continues to make a diverse contribution to energy conversion and chemical synthesis as well as surface finishing.

## **2. Multilayered Coatings**

Rather than deposit a single, continuous coating on the workpiece, electrodeposited underlayers were considered throughout the 1960s and 1970s [16], examples being the use of copper and nickel to reduce through porosity and corrosion in nickel/chromium deposits and copper to provide a controlled nucleation and growth of subsequent, thin gold deposits, to minimise porosity, maintain good electrical conductivity and achieve effective electrocrystallisation in electronic contacts.

Developments in pulsed electroplating and improved processing have facilitated electroplating of a number of discrete layers in a controlled sequence in multilayer deposition. A common strategy (Figure 1) is to deposit alternate layers of A and B, where A and B may be different

thicknesses of the same metal or alloy, different metals, different alloy compositions or a single metal and the same metal containing one or more included particles in a composite coating.

The literature also refers to compositionally modulated metal multilayer (CMMM) or compositionally modulated alloy multilayer (CMAM) coatings, by repetition of very thin layers of two different materials (in the form of pure metals, alloys or composites).

Developments in electrodeposition of multi-layered coatings are highlighted in the timeline of Figure 2, including:

- a) an Edison patent involving Cu-Ni multilayers in 1905 [18],
- b) a paper by Blum on electrodeposited Cu-Ni multilayers in 1921 [19],
- c) an extensive review by Brenner in 1963 [20],
- d) In 1970, Koehler considered multilayers as a possible approach to build a strong solid [21],
- e) Fundamental studies of pulsed electrolysis by, e.g., ETH, Zurich workers [12-14],
- f) Cohen et al [22] electrodeposited Ag-Pd layered structures as a possible substitute for hard gold in electrical contacts in 1981, viewing CMAM coatings of relatively thick layers (e.g., < 100 nm) of an alloy rich in Ag, alternating with thin layers (e.g., 1-10 nm) rich in Pd as a logical progression.
- g) In 1984, Tench and White potentiostatically deposited Ni/Cu multilayers by double-pulse plating in a nickel sulphamate bath having copper added, achieving pure Cu layers at  $-0.2$  V vs. SCE and Ni rich layers at  $-1.75$  V vs. SCE [23]. Layer thicknesses as low as 100 nm were achieved, which were interesting for their enhanced tensile strength, compared to pure nickel.
- h) In 1986, Puipe authored a monograph on the theory and principles of pulse plating [14].

- i) In 1987, Yahalom and Zadok, laid down some of the major requirements for an electroplating bath and the pulse-plating conditions needed to electrodeposit an alternating Cu-Ni multilayer of nanometre thick individual layers, including a sufficient separation in the deposition potentials of the noble (Cu) and less noble (Ni) metals [24].
- j) An early review of electrodeposited multilayers in 1994 [25].
- k) Studies on pulse plating of zinc-alloy multilayers as sacrificial coatings for corrosion protection of steel, in 1998 [46].
- l) An extensive review of electrodeposited multilayers for giant magneto resistance, GMR in 2010 [55].
- m) An historical review of pulse plating in the surface finishing of metals, including multilayers, in 2018 [10].
- n) An illustrated review of modern developments in nanostructured electrodeposits and anodised layers in surface finishing, in 2019 [7].

Driving forces for electrodeposition of multilayers include improvements in:

- a) the size or distribution of mechanical stress, leading to stronger and more ductile coatings [26].
- b) corrosion protection via reduced through porosity in the coating [27].
- c) magnetic properties of the electroplated layers [28].
- d) the optical characteristics of the coating [29, 30].
- e) electronic properties of the multilayer coating [31]

The benefits of multilayered coatings can be classified, e.g, [32] into:



- a) A *thin film effect* down to an atomic or molecular scale has allowed new structures to be realised for semiconductors.
- b) An *interfacial effect* between sharp layer interfaces can be used to realise a coherent superlattice (containing an ideal, 3 dimensional arrangement of atoms) which gives rise to a new structure.
- c) A *coupling effect* due to inherent property differences between adjacent layers. Examples include magnetic susceptibility or optical coupling.
- d) A *periodic effect* of increased intensity of diffracted light reflectivity has been demonstrated in soft x-ray mirrors consisting of a precisely regular, alternation of heavy metals (e.g., Mo, Ni) and light materials (such as C or Si).

While the historical development of multi-layered electrodeposition has been focused on cathodically deposited metals and alloys, it is important to be aware that anodic deposition of metal oxides and many other compounds is possible. Combinations of such materials, coupled with a degree of control over their nanostructure and porosity, even from a single bath, opens the door to many coating materials, architectures and even device fabrication. The possibility of using open-circuit, including electroless deposition and other application techniques, such as sol-gel and electrophoresis, markedly increases coating diversity and applications.

### **3. Techniques for Electrodeposition of Multilayers**

The major factors influencing the deposit composition/quality and rate of plating may be classified broadly into process strategy, type of electrical control, bath parameters and electrode/cell conditions, as shown in Figure 3.

### 3.1 Choice of Electroplating Bath

The change in elemental composition, morphology or phase composition of adjacent layers can be carried out in a) abruptly, in a step change or b) gradually, in a progressive change over time. In the latter case, compositionally modulated or gradient coatings can be achieved. These changes may be controlled by altering one or more of the following:

- a) cathode potential,  $E_c$ ,
- b) cathode current density,  $j$ ,
- c) concentration,  $c$  of the electroactive species, or
- d) a characteristic electrode/electrolyte velocity,  $v$ .

Multilayered deposits can be achieved using a single or dual bath technique. In the former, one bath is used to deposit alternate layers of A and B. The dual bath technique can be used to deposit a wide range of multilayer types, including a) layers where one component is present as islands, b) layers where both components are present as islands and c) both components form continuous layers Haseeb et al have provided examples of bimetallic Cu/Ni and hard/soft NiP/Sn multilayers [17]. Due to its convenience, flexibility and ease of scale-up, the use of pulsed current electrodeposition in a single bath has become a favoured approach.

### 3.2 Electrical Control

In principle, the electrode potential vs. a reference electrode,  $E$ , the cell current,  $I$ , or the electrolysis time,  $t$ , hence the electrical charge,  $q$  could be controlled. In practice, control of the cathode potential is common in laboratory studies, using a computer controlled potentiostat to adjust the potential to the required value with time, using a feedback controlled, direct current power supply, while monitoring the current. In industry or on scale-up, high current

potentiostats prove expensive and many operators have little process experience. Practitioners can be reluctant to incorporate a reference electrode, due to the fragility of some laboratory versions, but this results in no measurement of cathode potential. Traditionally, electroplating processes use constant current, although the opportunity to monitor electrical charge, cathode potential and cell voltage should never be neglected as these can prove to be valuable in process monitoring and fault diagnosis (Figure 4).

The development of pulse current electroplating transformed the ability to deposit alternate nanolayers of two different metals, A and B. A purpose built d.c. power supply (normally under computer control) is used to pulse the current between two predetermined values (Figure 5). Variables include the pulse shape (a square wave being common), on-time, off-time and frequency. If metal A is nobler than B, a single bath can be used having a high concentration of B and a much lower concentration of metal A. The deposition potential of A is chosen to correspond to the limiting current density, while achieving an acceptable morphology and minimising side reactions. The layer thickness can be controlled by adjusting the pulse on time (hence electrical charge) corresponding to a maximum deposition rate of A. Metal B is deposited at the most negative potential to minimise deposition of A while avoiding a loss of current efficiency due to hydrogen evolution.

The increasing availability of software for computer controlled pulse power supplies has encouraged the diversity of electrical control and monitoring strategies. For example, it is possible to potentiostatically control the deposition of one layer then galvanostatically deposit an alternate layer (as seen in section 4.5).

### **3.3 Electrode/Electrolyte Movement**

Relative movement between the cathode and the electrolyte is important in providing adequate mixing and a reasonable rate of mass transport of metal ions to the cathode surface. Electrolyte agitation can be achieved by several approaches, including:

- a) stirring, using an overhead, rotating paddle or a magnetic stirrer follower,
- b) pumped flow, possibly via flow eductors in the bath,
- c) ultrasonication,
- d) cathode reciprocation, or rotation in the case of RDE and RCE cathodes.

Increasing attention to controlled flow past planar cathodes in a rectangular channel or wall jet impingement of electrolyte on a flat disc is needed.

#### **4. Examples of Multilayered Electrodeposits**

Several examples serve to illustrate history, scope, properties, diversity and continued progress in the development of electrodeposited multilayers.

##### **4.1 Cr-Ni for Improved Tensile Strength and Fatigue Resistance**

Torres-Gonzalez et al. studied residual stress and microhardness in chromium multilayers deposited by pulsed current from three baths, a standard chromic acid electrolyte, a commercial bath and one containing a silicon hexafluoride catalyst at 35-55 °C [33]. In an earlier study [34], the authors showed that deposits from standard and catalyzed baths at a temperature between 20 and 70 °C had an equiaxial or columnar microstructure. Each one of these microstructures has different mechanical and corrosion characteristics and is suitable as a starting point to obtain crack free chromium deposits.

Benaben et al. have considered multilayer electrodeposits to enhance the corrosion resistance enhancement of chromium electrodeposits [35]. Fine grained and microcracked chromium multilayer deposits were obtained from three different baths using a square wave pulsed current. Deposition conditions included 35°C or 55 °C at a current density of 10 or 70 A dm<sup>-2</sup>. Combinations of columnar and equiaxial microstructured layers provided particularly effective corrosion protection to a steel substrate.

Rousseau and Benaben studied the electroplating of nickel and chromium compositionally modulated multilayers on steel from a single bath under square wave, pulsed current control in a hydrochloric acid containing, reduced Cr(VI) bath containing Ni<sup>2+</sup> and Cr<sup>3+</sup> [36]. At a low cathodic potential, the reduction rate of nickel is slow and controlled by diffusion, while chromium is deposited rapidly. At a more negative potential, only nickel is reduced. A cylindrical steel cathode, 1 cm diameter and 4 cm long was surrounded by a mild steel anode in an acidic (pH ≈ 0) bath. The trivalent chromium bath used had low throwing power and the chromium deposits were very sensitive to structural defects on the substrate. An example of alternating nickel (light) and chromium (darker) layers, each 0.5 μm thick, is shown in Figure 6. The authors adopted the following strategy, maintaining an equal thickness of rich-chromium and nickel layers Individual layer plating times,  $t_{Ni}$  and  $t_{Cr}$  were varied from 200 and 20 s; 100 and 10 s; 50 and 5 s; 30 and 3 s. These times were chosen to realise sublayer thicknesses of 2, 1, 0.5 and 0.3 μm. Four different cycles ( $t_{Ni} + t_{Cr}$ ) were repeated until the total coating thickness was 50 μm. Insertion of nickel layers decreased the incidence of microcracking through the chromium layers, although some long individual cracks were seen through the multilayers.

## 4.2 Cu-Sn for Corrosion Resistance and Battery Electrodes

Figure 7 shows a cross-sectional view of alternating multi-layers of tin (lighter area, 1  $\mu\text{m}$  thickness) and copper (darker area, 10  $\mu\text{m}$  thickness) deposited from alternate tin and copper methanesulfonic acid baths containing a perfluorinated cationic surfactant to help control electrocrystallisation. The Sn layer was deposited at  $-0.5\text{ V}$  vs. Ag|AgCl for 5 minutes from a bath containing  $0.05\text{ mol dm}^{-3}\text{ SnSO}_4 + 2.3\text{ mol dm}^{-3}\text{ MSA} + 0.01\text{ mol dm}^{-3}\text{ hydroquinone} + 0.01\% \text{ vol. DuPont ForaFac 1098 cationic perfluorocarbon surfactant}$ , while the copper layer was deposited at  $-0.4\text{ V}$  vs. Ag|AgCl for 10 minutes from a  $0.1\text{ mol dm}^{-3}\text{ CuSO}_4$  bath. Deposition was carried out at  $25\text{ }^\circ\text{C}$  on a 316L stainless steel cylindrical electrode rotated at 1000 rpm [37]. Nodular outgrowths of tin are evident, due to partial mass transfer controlled deposition, while the copper layers remain compact under these conditions.

#### **4.3 Ni-ceramic Compositionally Modulated Layers for Wear Resistance in Tribology**

The use of electroplated multifunctional and nanostructured coatings has been concisely reviewed, including compositionally modulated Ni-P layers [38]. An example of Ni-SiC multilayer deposition was provided by Garcia-Lecina et al. [39]. Functionally graded coatings were deposited by including SiC particles (of mean diameter 2  $\mu\text{m}$ ) from an additive-free Watts nickel bath at  $55\text{ }^\circ\text{C}$  containing different concentrations of SiC. A current density of 1.5 to 5.0  $\text{A dm}^{-2}$  was used. In a SiC concentration range of 20-50  $\text{g dm}^{-3}$  in the bath, the deposit SiC concentration was approx. constant at 4%wt. The zeta potential and particle size of the SiC particles dispersed in the bath were measured. The hardness of the gradient deposit varied continuously through the depth of the deposit, being as high as 800  $\text{kg mm}^{-2}$  at a deposit thickness of 10  $\mu\text{m}$ , falling to 560  $\text{kg mm}^{-2}$  at a depth of 50  $\mu\text{m}$ . Unfortunately, the authors did not control bath agitation to control the inclusion level of particles in the deposit, despite this approach being well established, e.g. [40-42].

Noroozi et al considered a gradient Ni-Al<sub>2</sub>O<sub>3</sub> coating deposited from an acid sulphate, Watts bath at controlled stirring rates [43]. The wear and corrosion resistance of the functionally graded Ni-Al<sub>2</sub>O<sub>3</sub> coating were higher than a single layer Ni-Al<sub>2</sub>O<sub>3</sub> composite coating. The authors attributed this to a smaller mechanical mismatch between the coating and substrate in the functionally graded composite coating. Bostani et al studied a functionally gradient nickel coated ZrO<sub>2</sub> composite coating from an electroless nickel bath at different bath stirring rates. [44]. More.

In these studies, the authors rationalise their results by considering a classical model due to Guglielmi which considers two successive adsorption steps; the first step, the particles are loosely adsorbed while the particles are irreversibly adsorbed in the second step [45]. Unfortunately, no information was given about the flow regime (laminar, transitional or turbulent), presence of secondary flows, stirrer type, location, material and shape, just its rotation speed, which was varied from 150 rev min<sup>-1</sup> to 250 rev min<sup>-1</sup>, to increase the hardness of the deposit. In a static bath, no alumina particles were codeposited with nickel. The alumina content of the deposit did not increase in a monotonic fashion as the stirring speed was increased. The Gulglielmi model also underestimates the importance of the potential dependence of adsorption on particle surfaces and the role of electrokinetics, particularly electrophoresis, in composite electrodeposition.

Majidi et al deposited up to six layers of Ni-Al<sub>2</sub>O<sub>3</sub> composite from an ultrasonicated Watts nickel bath containing 50 g dm<sup>-3</sup> Al<sub>2</sub>O<sub>3</sub> nanoparticles at 5 A dm<sup>-2</sup> [46]. A duty cycle of 20–80% and fixed frequency of 100, 550 and 1000 Hz were used in galvanostatic pulse deposition. The importance of duty cycle (20, 50 or 80%) was examined at a frequency of 100–1000 Hz. The deposits contained 2.4-6.4% vol Al<sub>2</sub>O<sub>3</sub>. Using pin on disc testing with a 7 mm alumina ball pin on a flat steel sample of the deposit, the authors reported that the wear resistance of the coatings

increased at higher frequency and larger duty cycles, the latter being more important. The multilayers were also claimed to provide improved corrosion resistance, compared to single layers or pure nickel coatings, in  $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  at  $25 \text{ }^\circ\text{C}$ . Unfortunately, this study contains a limited spread of variables and lacks sufficient data points. Missing details include a) the size and shape of the alumina nanopowder, the geometry of the electrodes, cell and ultrasonic horn, the corrosion half-cell reactions. It is also unclear which single control variable was altered to achieve the deposit micrographs shown. The layer sizes are not given directly but can be estimated as  $15\text{-}18 \text{ }\mu\text{m}$  from cross-sectional SEM micrographs. The authors consider that their results can be rationalised using the established Celis et al model [47] but no quantitative details or attempts at curve fitting are attempted.

#### **4.4 Zn-M multilayers for Corrosion Protection of Steel**

Improved corrosion protection of steel is one of the traditional and most common areas for multilayer research. In the 1980s and 90s, sacrificial, zinc alloy multilayer coatings were revisited as better, more cost effective coatings for automotive steel were sought, Zn-Fe, Zn-Ni and Zn-Co being the most common [48]. Research at Loughborough University has considered a range of compositionally modulated and multilayer deposits, including ones from single and dual baths using controlled agitation and pulsed electrodeposition [49-52]. Using a membrane divided laboratory electroplating cell, the best corrosion protection was seen in a two layered Co/Zn CMAM coating deposited at  $25\text{-}30 \text{ }^\circ\text{C}$  from a highly agitated sulphate bath at pH 2 [51]. To prevent undue internal stress in the multilayers, Bahrololoom et al investigated these types of waveform in Co/Zn multilayer deposits on steel and found operating conditions which showed no crack formation, even in thick deposits after bending [52], as shown in Figure 8.



As noted by Bakonyi and Hansal in a recent review of pulse plating [10], Zn–Fe CMA electrodeposits from the Loughborough group typically had a total thickness of about 10–20  $\mu\text{m}$  with an individual layer thickness of approx. 1  $\mu\text{m}$ . In 2008, Thangaraj et al. reported the preparation of similar coatings with a comparable total thickness in 2008 in which the coatings were made up from <600 layers, using a layer thicknesses as low as 10 nm. These nanoscale zinc rich (Zn–Fe)/iron rich (Zn–Fe) multilayers were reported to have mean corrosion rates as low as 0.025  $\text{mm y}^{-1}$ ) in 5% NaCl at 25 °C [53].

Bahadormanasha et al. studied the electrodeposition of nanocrystalline Zn/Ni multilayer coatings from a single bath together with the importance of current density and number of layers on the deposit characteristics [54]. A response surface model demonstrated that the corrosion resistance was more effective in deposits containing a higher number of layers.

The literature can be unclear about the number of layers required to optimise corrosion protection of a substrate. In a study of Ni–W multilayer coatings [55], the corrosion behaviour progressively improved until 300 layers. A further increase in the number of layers led to worsening corrosion resistance. This was attributed to interlayer diffusion. More layers can increase the time needed for diffusion of the corrosive agent but excessive multilayers can restrict diffusion and result in lateral spreading of corrosion along a layer, as shown schematically in Figure 9 [55].

#### **4.5 Co–Cu/Cu Multilayers for Giant Magnetoresistance, GMR**

The GMR effect was discovered in 1988 in nanoscale metallic ferromagnetic/non-magnetic (FM/NM) multilayers. GMR refers to a quantum mechanical magnetoresistance effect seen in thin film structures of alternating ferromagnetic and nonmagnetic layers. The effect manifests

itself as a significant decrease (typically 10– 80%) in electrical resistance in the presence of a magnetic field. Early processing used physical vapour deposition but electrodeposition techniques emerged in 1990. Mosca et al. described oscillatory interlayer coupling and giant magnetoresistance in Co/Cu multilayers in 1991 [56]. A Nobel Prize award to Albert Fert and Peter Grünberg for the discovery of giant magnetoresistance in 2007 has encouraged the rapid expansion of interest in production techniques, although traditional approaches have focussed on vacuum deposition. In 2010, Bakonyi and Peter have extensively reviewed electrodeposited multilayers which show GMR [57]. The review noted the prominence of Co-Cu layers and provided an important critique of the literature on electrodeposition of multilayers showing GMR. To echo and augment their comments, shortcomings in the literature include:

- a) an unsuitable electrode geometry,
- b) lack of attention to cell geometry,
- c) failure to adequately monitor or control cathode potential, and
- d) impurities in the electrolyte.

Particularly in the case of multiple layers requiring a crisp profile, it is clear that the need for uniform thickness, composition and morphology of deposits, demands adequate control of electrocrystallisation during nucleation and growth, including pretreatment, together with an appropriate local reaction environment at the cathode. Such control over reaction environment includes appropriate attention to aspects of electrochemical engineering to:

- e) minimise side reactions,
- f) achieve uniform electrode potential, current density and concentration profiles over the cathode surface,
- g) ensure well-defined electrolyte flow to and from the cathode.

Such considerations mean that further attention to classical electrode and cell designs is justified, particularly the rotating cylinder electrode [58,59] and controlled flow rectangular channel cells [60,61].

Correlation of microstructure and giant magnetoresistance in electrodeposited Ni–Cu/Cu multilayers was considered by Cziraki in 1997 [62]. A later paper by the same group studied Co–Cu/Cu GMR multilayers [63].

Both multi-layered films and multilayers of nanowire arrays have been used to display GMR properties. Alternate multilayers of Co-Cu and Cu were potentiostatically deposited on an ITO glass substrate from an acid sulphate bath at pH 2 [64].

Co-Fe/Cu multilayers were electrodeposited from sulfamate, sulfate, ammonium chloride and sodium citrate baths using galvanostatic pulse plating of the magnetic layer and potentiostatic pulsed deposition of the copper layer to deposit Co-Fe(5 nm)/Cu(5 nm) multilayers [65]. The deposition potential during copper deposition, which was dependent on the bath composition and the  $Fe^{2+}/Co^{2+}$  concentration ratio, was optimized for each bath by monitoring the current transients. The copper deposition was carried out potentiostatically, as the authors considered that avoiding dissolution of the previously deposited magnetic material and codeposition of magnetic atoms with the Cu atoms were critical. All of the deposited multilayers showed GMR behaviour (a maximum GMR of approx. 4% being achieved).

#### **4.6 Cu-In-Bi-Sn as Solder Bump Interconnects for Electronic Circuits**

Kaltwasser et al have described the formation of solder bumps via sequential, multilayer electroplating of base metals a, b, and c [66]. As indicated in Figure 10, the two outer metal layers, a and b (e.g., bismuth and indium) form the low melting point solder shell. The lowermost metal layer c is the high melting point (72 °C) solder alloy (ab), i.e., the core and is used in a final reflow step to increase the melting point of the interconnect. (A). The

electroplated core (c) is a higher melting point solder ( $>156\text{ }^{\circ}\text{C}$ ) which remains solid during the assembly process and helps anchor the solder to the substrate. (B) During self-assembly, the low melting point shell is molten and is used to capture and align the distributed parts in heated water ( $<100\text{ }^{\circ}\text{C}$ ) by wetting the metal contacts. The approach makes use of the versatility of methanesulphonic acid electrolytes, which are able to support high concentrations of several metals and delivering compact deposits at a moderate current density [67].

## **5. Recent developments and critical topics**

Tribological coatings remains a major direction for R & D in multilayer deposits and Khadem et al have provided a timely review of friction and wear reduction capable by the use of such coatings [68] The authors stress the ability to tailor the mechanical and physical properties of coating materials by appropriate choice of metallic, covalent or ionic chemical bonding between elements in the deposited film.

Nanowires provide a specialised subject area in multilayer deposition but their study is important in providing high surface area, directional structures with tailored physical properties. Kamimura, Hayashida and Ohgai, have recently considered the performance of electrochemically synthesized Co/Cu multilayered nanowire arrays of very large aspect ratio [69]. Research is blossoming in this area and continues to accelerate as experimental techniques are refined, production techniques continue to be explored [68] and the strategic properties of such arrays, conveniently produced by electrochemical deposition [71], sometimes via anodised templates [70]. Despite much progress in the electrodeposition of multilayers, few studies offer a quantitative rationalisation of the importance of operational parameters on deposit properties, despite an early offering by Gabe and Green on the mathematical modelling

of CMA multilayered coatings [72]. A 2017 paper has adopted a response surface methodology (RSM) approach in an attempt to rationalise the effect of operational variables on electrodeposition properties in Zn/Ni multilayer coatings from a single, acid sulphate bath [73].

Compositionally modulated and gradient coatings continue to evolve and diversify. A recent review in a journal issue dedicated to electrodeposition of 2-D layered materials has considered graphene reinforced metal matrix composites for enhanced mechanical and physical properties [74].

S'aenz-Trevizo and Hodge have recently provided a general review of nanoscale metallic multilayers, with a view to the improved design of engineering materials [75]. Mechanical, optical, magnetic and radiation tolerance properties are considered and a useful compendium of materials properties is offered. The authors focus on vapour deposition, evaporation and magnetron sputtering techniques, neglecting the fast evolving, complementary techniques of sol-gel coating and electrodeposition of multilayers.

A recent contribution has described the use of cathodically deposited multilayers to form active materials for lithium ion batteries [76]. Up to 70 electrode pairs were formed. Copper, nickel, and NiSn (a lithium ion battery active negative electrode material) were galvanostatically deposited at 10, 5 and 5 mA cm<sup>-2</sup>, respectively, using a tin anode for the NiSn alloy deposition:



The LMO was produced first by electrodepositing manganese hydroxide potentiostatically at 1.8 V using a platinum anode electrode. The hydrogen evolution resulted in local generation of hydroxyl ions which chemically reacted with  $\text{Mn}^{2+}$  in solution to deposit a porous film of  $\text{Mn(OH)}_2$ :



The nanoporous manganese hydroxide films were converted into active LMO battery positive electrode material, containing lithiated  $\text{MnO}_2$ , following immersion in a molten lithium salt.

Adhesive bonding and electrical isolation of the individual anode and cathode pairs is achieved by a polyethylene separator. Hot pressing at 160 °C and 2 MPa sealed the layers together at the intersection of the spacing posts of one layer to the bottom of the next layer, in the interdigitated geometry, as shown in Figure 11a). The assembled battery is shown in Figure 11b). The Ni-Sn and LMO layers had a thickness of 0.1 or 0.2  $\mu\text{m}$  and 0.4 or 0,8  $\mu\text{m}$ , respectively with an interlayer spacing of 10  $\mu\text{m}$ . The battery had a claimed volumetric energy density <193 W h  $\text{dm}^{-3}$ , a volumetric power <1233 W  $\text{dm}^{-3}$  with an energy output <20 mW h and could deliver <178 mW power.

Examples of established and developing applications for electrodeposited multilayers are classified into the categories of (i) tribology, (ii) cutting and shaping, (iii) electrode coatings, (iv) corrosion protection, (v) magnetic materials and (vi) other speciality materials, in Figure 12.

General trends in electrodeposition research have been reflected in recent literature on multilayer and compositionally modulated electrodeposition. Examples include a) the use of ionic liquid electrolytes, such as 1-ethyl-3-methylimidazolium chloride, to deposit Fe<sub>50</sub>Pt<sub>50</sub>/Fe<sub>2</sub>Pt<sub>98</sub> magnetic multilayers [77], b) achieving self-organised layers of Co-Sn from a choline chloride/ethylene glycol deep eutectic electrolyte containing CoCl<sub>2</sub>·6H<sub>2</sub>O and SnCl<sub>2</sub>·2H<sub>2</sub>O without additives [78] and c) tailoring of Ni/Co alloy layers by controlling the pulse on time and feeding jets of Ni or Co acid sulphate-chloride electrolytes, from different reservoirs, towards the cathode [79].

## 5. Summary

1. Multilayer electrodeposition is going through a phase of rediscovery, growth and diversification; the field can be traced back to a patent involving Cu-Ni multilayers in 1905.
2. Early studies of multilayer deposits were often motivated by the possibility of producing higher tensile strength and ductility; modern endeavours tend to focus on the promise of better corrosion protection or particular electronic, magnetic or optical properties.
3. Earlier studies also tended to consider different metals or compositionally modulated alloy compositions; coatings have now diversified to include particle-metal matrix composites.
4. The choice of a single or dual electroplating bath is long established. A single bath enjoys the benefits of simplicity and ease of processing/scale-up. Differences between adjacent layers may be induced by step changes in electrode potential, current density, pulsed current parameters or operational variables including agitation or electrode movement.
5. While multi-layered electrodeposits remain specialised, their use has diversified to industries including speciality electronic materials and aerospace.

6. Progress in multi-layered electrodeposition has made use of contemporary trends in electroplating research, including self-assembled layers, nanowire arrays and the use of deep eutectic solvents for electrolytes.

7. Unfortunately, some of the literature on electrodeposited multilayers is poorly documented. Specifications should always include the substrate material and geometry, the composition of layers, their thickness, the number of layers, the thickness of any separating layer, the microstructure and phase composition of layers as well as the total deposit thickness.

## **6. Further Research and Development**

Several aspects require particular attention in further laboratory research studies and industrial development.

1. A systematic study of multilayer coatings from liquid electrolytes and a comparison of deposit properties with vapour deposition techniques is long overdue and needed to stimulate progress in electrodeposited multilayer processing.

2. Electrochemical data, including polarisation and current vs. time behaviour, which are essential to an improved understanding of multilayer deposition, are missing from many studies.

3. Pretreatment has become increasingly important in early nucleation and growth to achieve ever thinner coatings, faster layer deposition and multiple, but well-defined, successive layers.

4. The effect of bath additives on the morphology, phase composition and continued nucleation/growth of successive layers.



5. Despite through-porosity being a particular problem in thin coatings and those used in corrosion protection but a systematic, quantitative treatment of porosity measurements in multilayer deposits does not exist.
6. Continued diversity of coating materials, e.g., doped ceramic, conductive polymer and polymer-metal or ceramic-metal composite multilayers by appropriate anodic and/or cathodic electrodeposition.
7. Combinations of materials alternately deposited cathodically or anodically, coupled with a degree of control over their nanostructure and porosity, even from a single bath, opens the door to many coating materials and architectures. The possibility of using open-circuit, including electroless deposition and other application techniques, such as sol-gel and electrophoresis, markedly increases coating diversity and applications.
8. Electrodeposition is increasingly competing with vacuum deposition methods for deposition of multilayered biomaterials, including hydroxyapatite [80]
9. Improved diversity of fabrication together with fine control over operating conditions can be used to realise more complex surfaces and even complete devices (possibly for MEMS applications) via electrodeposition of multilayers, possibly in combination with electrochemical surface finishing-assisted 3D printing [81].
10. Quantitative studies of internal stress development during electrodeposition of multilayers are needed to track the dynamic development of coating stress over time and the effect of bath additives to moderate electrocrystallisation.
11. Many modern materials demand high purity or fine control of dopant levels together with tailored morphology, elemental/phase composition and nanostructure. Examples include semiconductors, speciality electrocatalysts, magnetic and optical materials. To electrodeposit engineered multilayers of such materials, it seems likely that bath additives will be limited and

electrolyte flow/agitation conditions, as well as pulsed waveform parameters, will need careful tuning. Such stringent control of operating conditions is poorly met by traditional processing in open-topped, rectangular cross-section vats. Instead, tailored ultrasonic transducers, elaborate electrolyte eductor networks or controlled flow past planar cathodes in rectangular channel cells may be needed.

12. In view of the increasing demands on reaction environment and control of operational parameters, computational modelling of multilayer electrodeposition will be an important activity to achieve a suitable reaction environment at the cathode surface.

13. Due to increasing interest in controlled porosity, porous, 3-dimensional films, in applied electrochemistry, it will be important to implement such layers (possibly under dynamic potential control) into multilayer electrodeposits to realise improved technology, such as wearable, flexible electronics sensing and energy conversion devices.

14. More detailed aspects of deposit microstructure in multilayer electrodeposits, the complex interactions between microstructure and operational parameters together with expanding application sectors are considered in a recent review [82].

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## Figure Captions

- Fig. 1** A definition sketch showing alternating multilayers of electrodeposits A and B, having a thickness  $x_A$  and  $x_B$ , respectively. There may be  $N < 600$  layer pairs of A and B; the thickness of individual sublayers can be in the range 1-1000 nm, providing an overall coating thickness  $< 25 \mu\text{m}$ .
- Fig. 2** A timeline showing highlights during the development of electrodeposited multilayers.
- a) Edison patent involving Cu-Ni multilayers, in 1905 [18].
  - b) Blum paper on electrodeposited Cu-Ni multilayers, in 1921 [19].
  - c) A two-volume treatise on electrodeposition of alloys by Brenner in 1963 [20].
  - d) Koehler considered multilayers as an attempt to build a strong solid in 1970 [21].
  - e) Fundamental studies of pulsed electrolysis by, e.g., work at ETH, Zurich [12-14].
  - f) Cohen et al. paper on cyclic multi-layered alloys in 198 [22].
  - g) Tench and White paper on tensile properties of nanostructured Ni-Cu multilayers in 1984 [23].
  - h) Puipe monograph on the theory and principles of pulse plating, in 1986 [14].
  - i) Yahalom and Zadok paper on electrodeposited, composition-modulated alloys in 1987 [24].
  - j) An early review of electrodeposited multilayers, in 1994 [25].
  - k) Studies on pulse plating of zinc-alloy multilayers as sacrificial coatings for corrosion protection of steel, in 1998 [40].
  - l) An extensive review of electrodeposited multilayers for GMR in 2010 [57].
  - m) An historical review of pulse plating in the surface finishing of metals, including multilayers, in 2018 [10].

n) An illustrated review of modern developments in nanostructured electrodeposits and anodised layers in surface finishing, in 2019 [7].

- Fig. 3** Important conditions and operational parameters which affect multilayer deposit quality, divided into process strategy, type of electrical control, bath parameters and electrode/cell conditions.
- Fig. 4** Electrical connections and measurements in electroplating. After [77] with modifications. a) potentiostatic control, where the cathode is connected as the working electrode of a potentiostat, which controls the working electrode potential with respect to a reference electrode and monitors this potential,  $E$  and the current,  $I$  flowing through the WE. It is useful to monitor the cell voltage,  $E_{cell}$  using a digital voltmeter, DVM. b) galvanostatic control of the current,  $I$ , where the cathode and anode are directly connected to the negative and positive terminals, respectively, of a DC power supply. It is useful to incorporate a reference electrode in the cell to facilitate measurement of the potential,  $E$  between the WE and RE, using a high impedance DVM.
- Fig. 5** Idealised representation of pulsed current electrodeposition of alternate layers of metals A and B, where the former is the more noble metal. After Yahalom and Zadok [24]; modified by Bakonyi and Hansal [10]. The limiting current density for metal A is  $j_{LA}$ , while  $j_B$  is the current density for metal B.
- Fig. 6** Alternating layers of nickel and chromium from a pH  $\approx 0$  trivalent Cr bath on a steel substrate. Alternating nickel (light) and chromium (darker) layers are each 0.5  $\mu\text{m}$  thick. After Rousseau and Benaben [36].
- Fig. 7** Sn-Cu multilayers for corrosion resistance and battery electrodes. A cross-sectional SEM of alternating 1  $\mu\text{m}$  thickness of tin (lighter area) and 10  $\mu\text{m}$  thick copper layers deposited from methanesulfonic acid electrolytes containing a perfluorinated cationic surfactant. The Sn layer was deposited at  $-0.5\text{ V vs. Ag|AgCl}$  for 5 minutes, while the Cu layer was deposited at  $-0.4\text{ V vs. Ag|AgCl}$  for 10 minutes on a 316L stainless steel rotating cylinder cathode rotated at 1000 rpm. After Low and Walsh [37].
- Fig. 8** SEM cross-section of an electrodeposited 20 Zn-Co multilayers (with a total thickness 20  $\mu\text{m}$ ) for corrosion protection of steel. The multilayered Zn-Co CMAM coating shows no cracks and there was good adhesion to the substrate after a bend test. After Bahroloom et al [50].

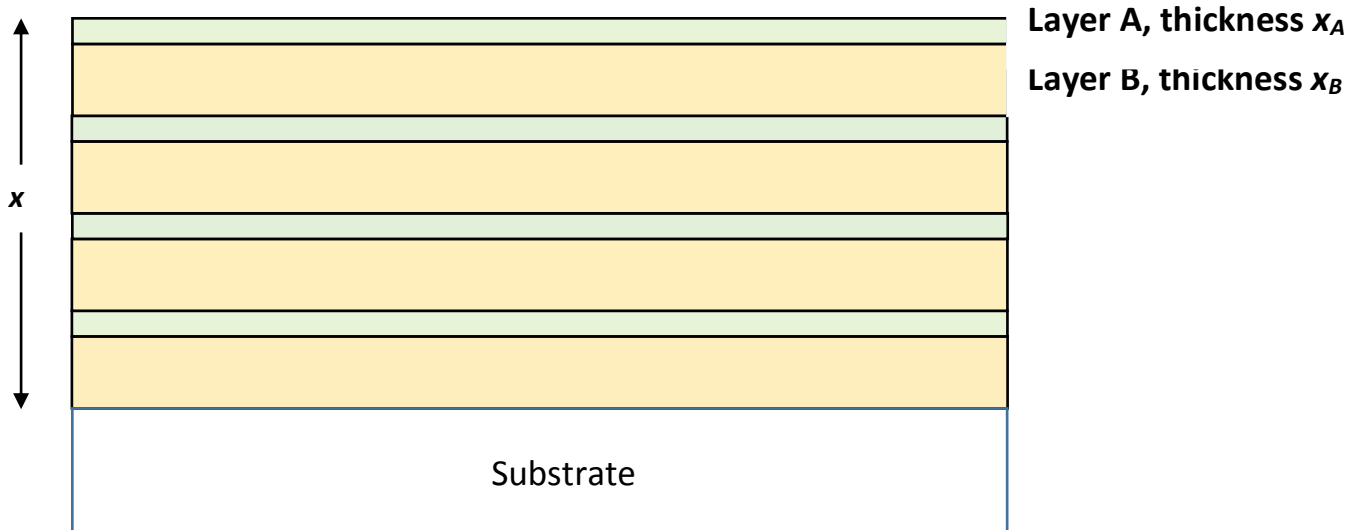
**Fig. 9** Schematic representation of corrosion taking place in a) a single layer coating and b) an excessive number of multilayer coating of Ni-W on steel. After Elias and Hegde [55].

**Fig. 10** Electrodeposition of multilayer solder bumps with tailored transformation imprinted melting points used to assemble dies at 75 °C which create high melting point interconnects. A) Electrodeposition bath containing an array of copper-pads (receptor sites) on flexible polyimide. The metal layers a, b, and c are deposited in separate electroplating baths. B) The solder bumps are a high melting point solder (core), metal layer, c and a low melting point solder (shell alloy, ab with a melting point of 72 °C). The low melting point shell facilitates assembly at low temperatures while self-assembly is carried out in a water at a temperature above the melting point of the shell. The solder wets the Au coated contact (binding side) on the die; reduction of the interfacial free energy of the molten solder alloy, ab drives capture and alignment. C) A short high temperature reflow step transforms the entire electrodeposit into a high melting point interconnect alloy, abc. After Kaltwasser et al. [64].

**Fig 11** A stackable lithium ion battery architecture produced via electrodeposited multilayers of active electrode materials (lithium manganese oxide, LMO as cathode and a Ni-Sn alloy cathode) hot pressed to form a vertically interdigitated assembly, showing a) The fabrication of components/multilayers in the battery and b) The assembled battery. After Synodis et al. [76].

**Fig. 12** Application areas for electrodeposited multilayers, showing examples of deposits, numbers of layers and industrial sectors. Coating application sectors are classified into six areas, namely (i) tribology, (ii) cutting and shaping, (iii) electrode coatings, (iv) corrosion protection, (v) magnetic materials and (vi) other speciality materials.

Fig. 1



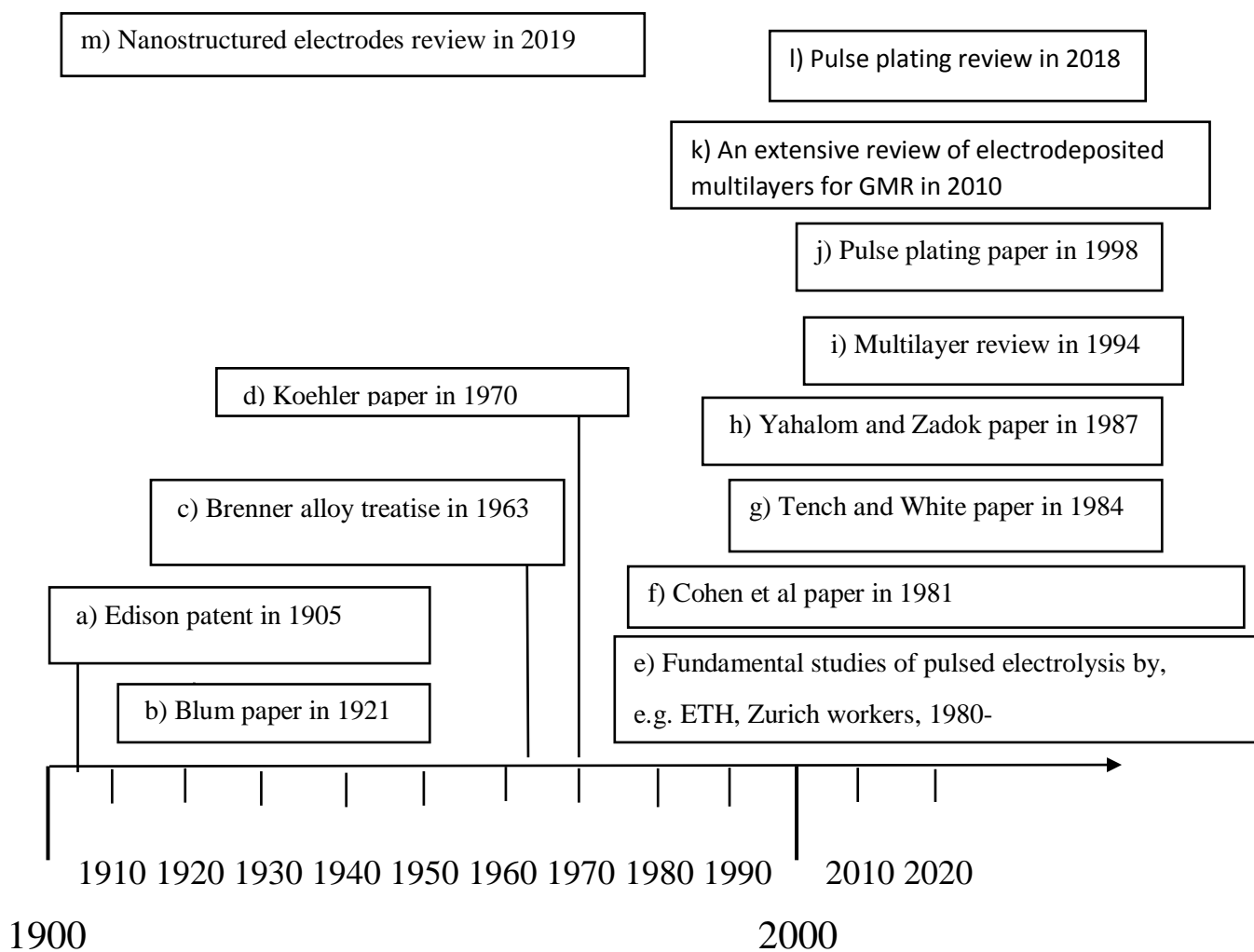


Fig. 2

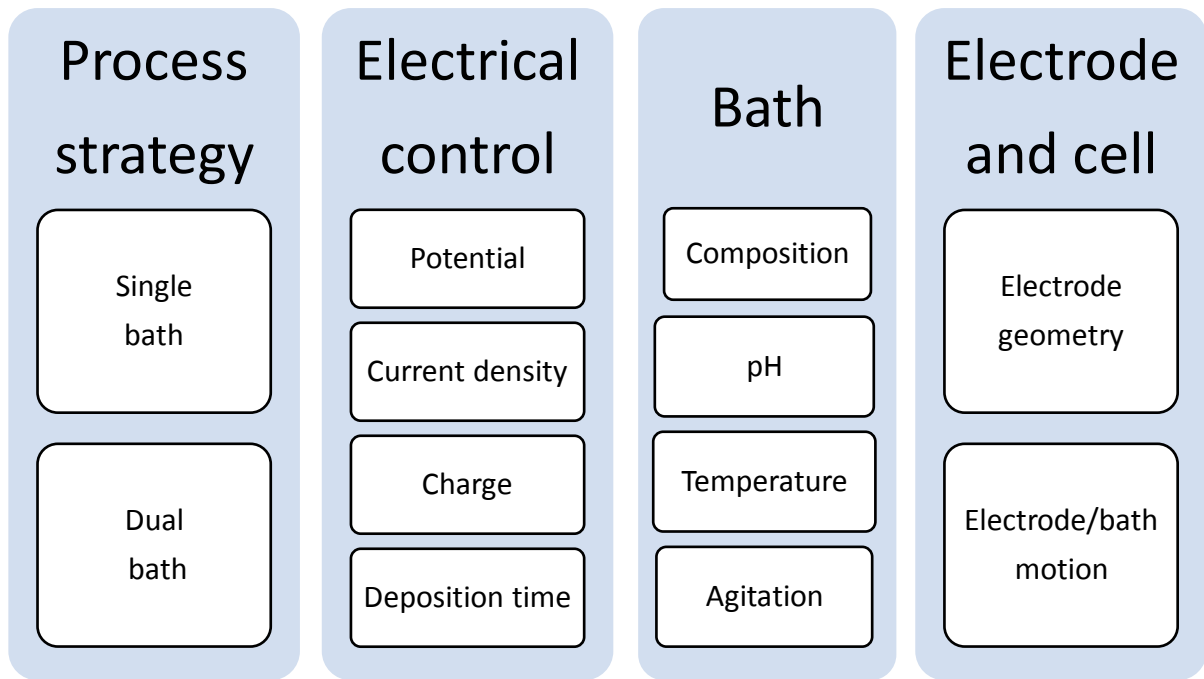


Fig. 3

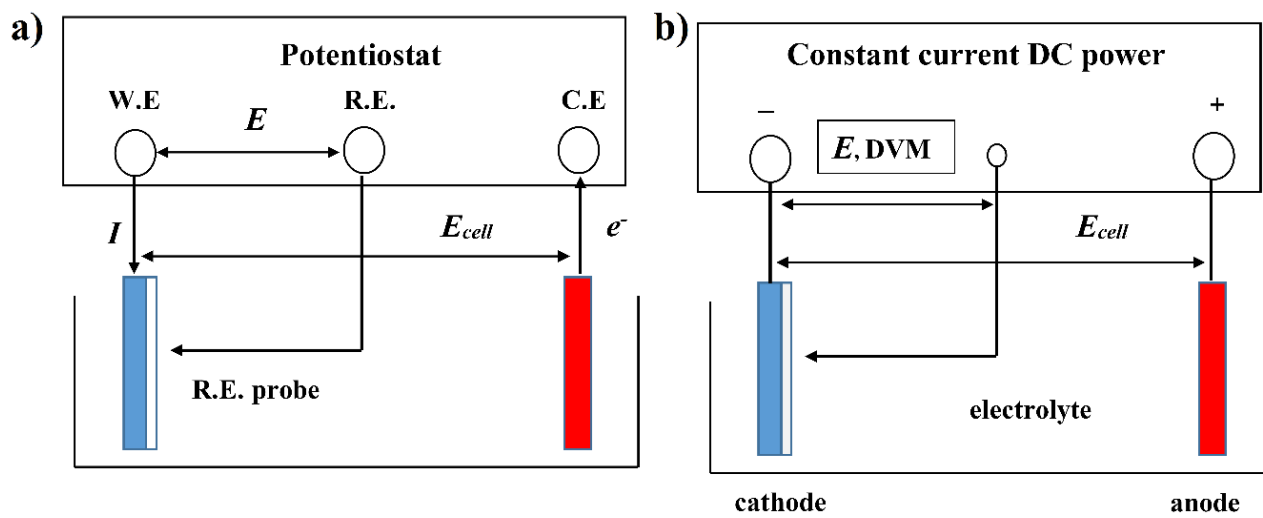


Fig. 4



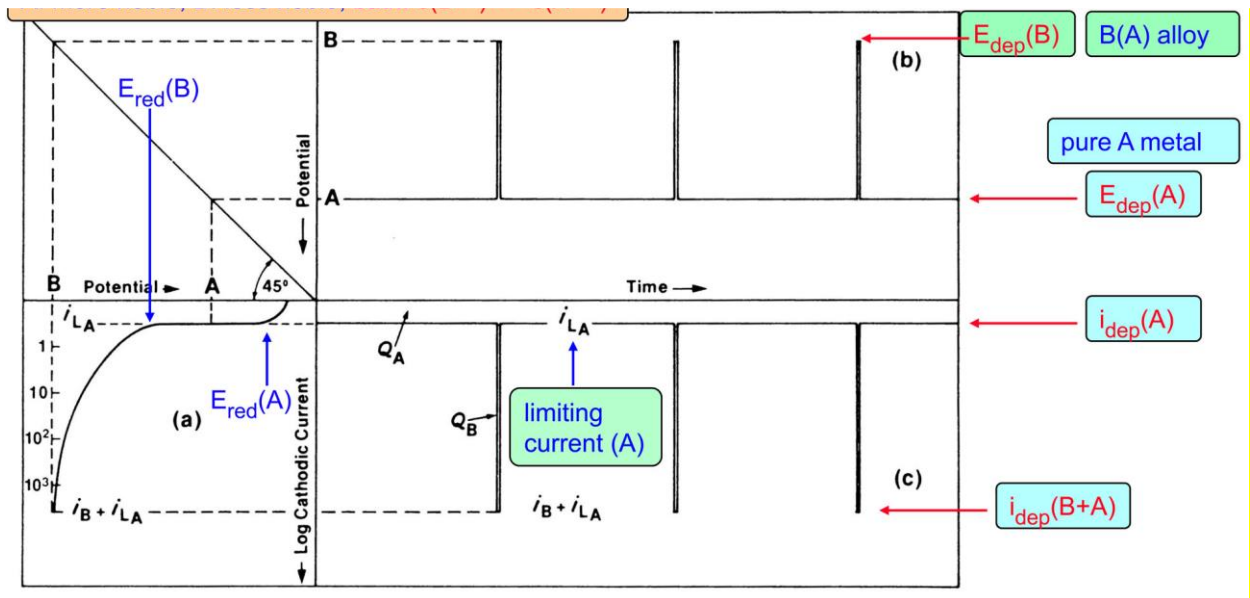


Fig. 5

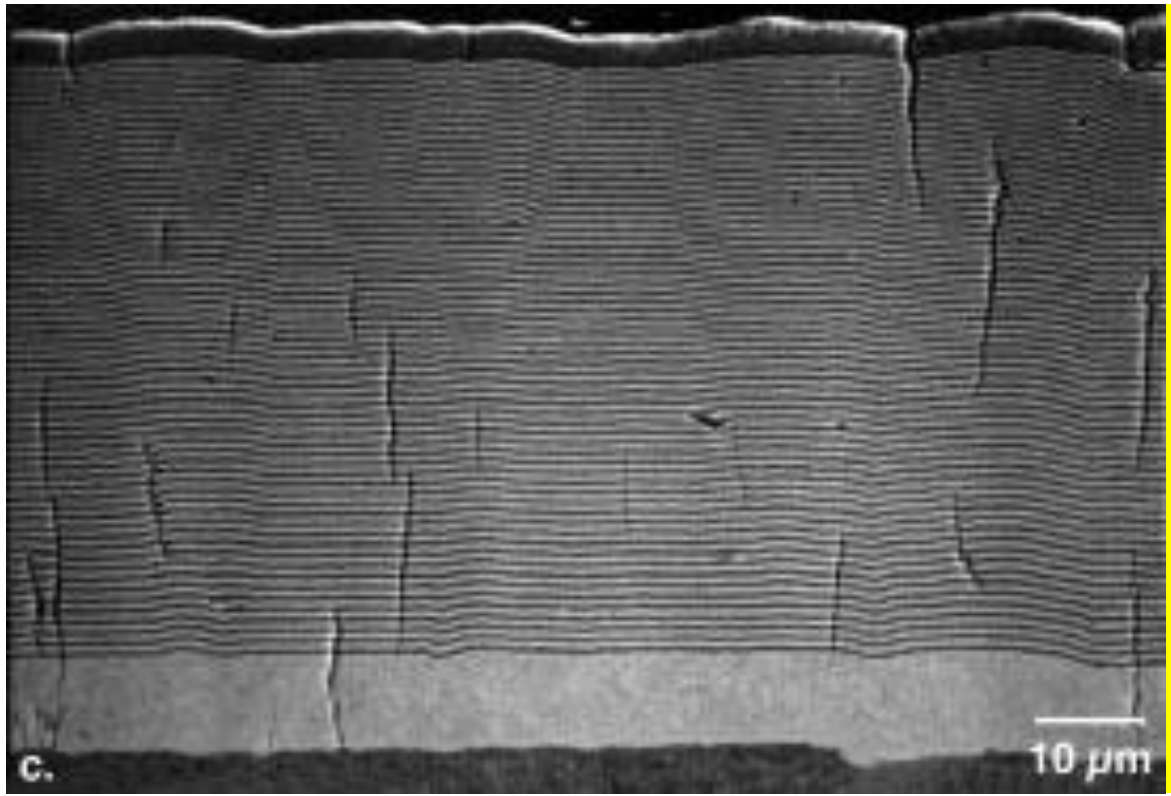
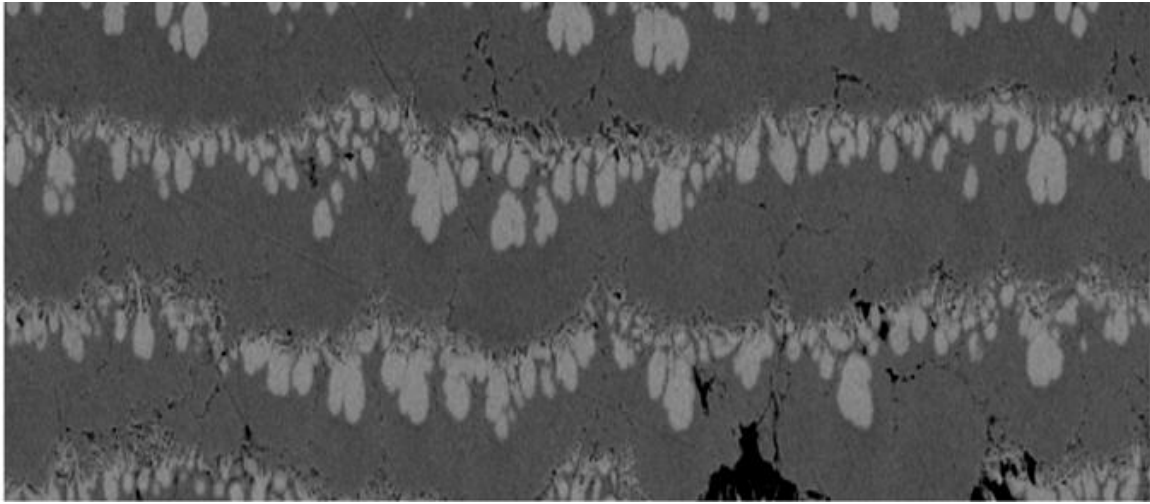
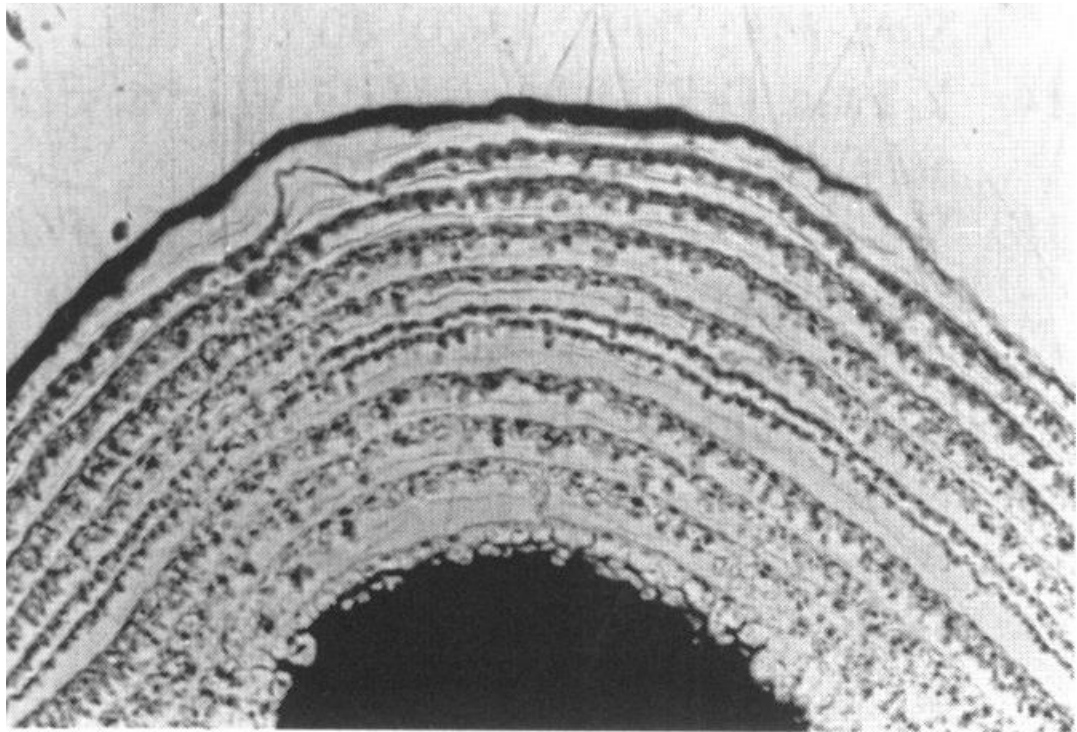


Fig. 6



—  
10  $\mu\text{m}$

Fig. 7



10 μm

Fig. 8

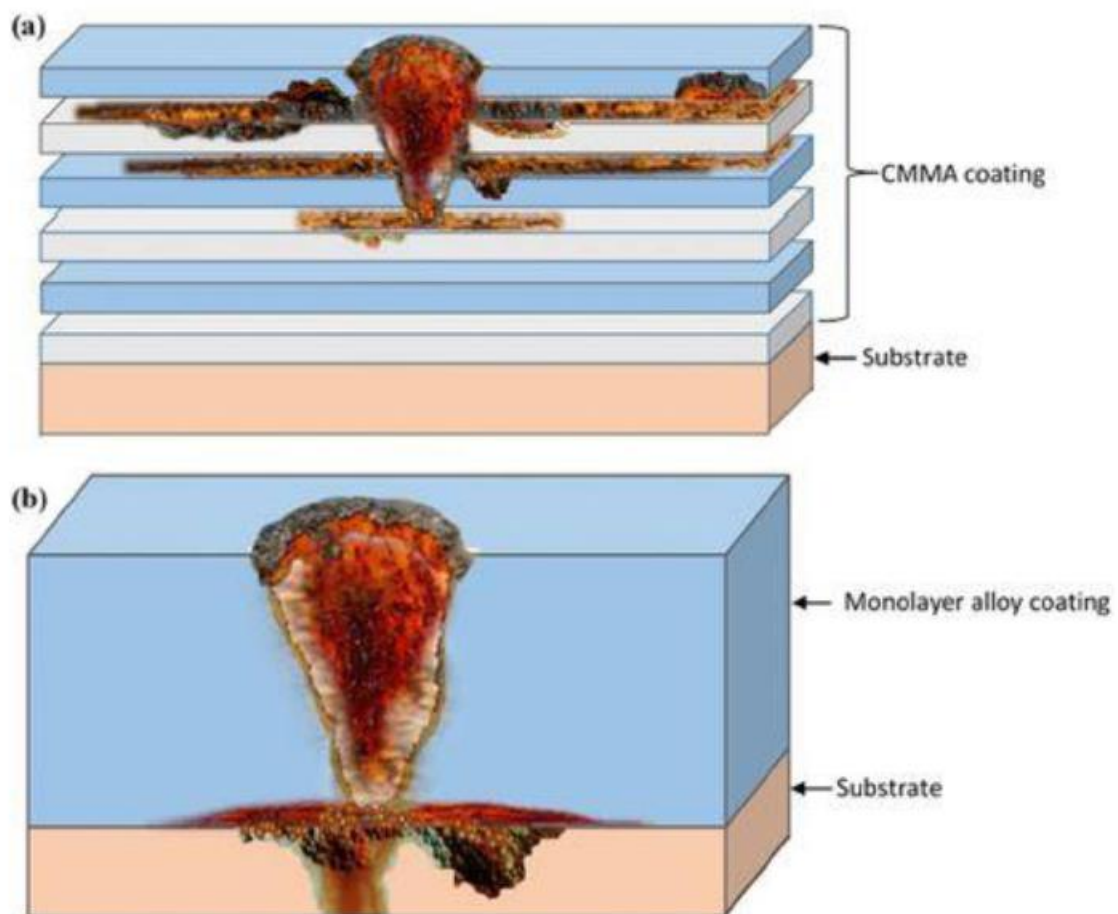


Fig. 9

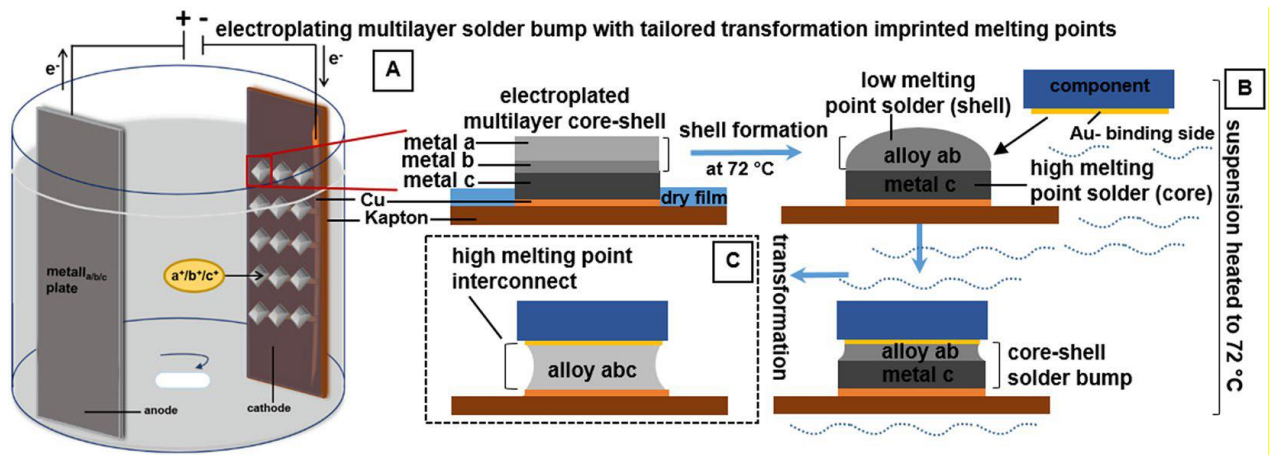


Fig. 10

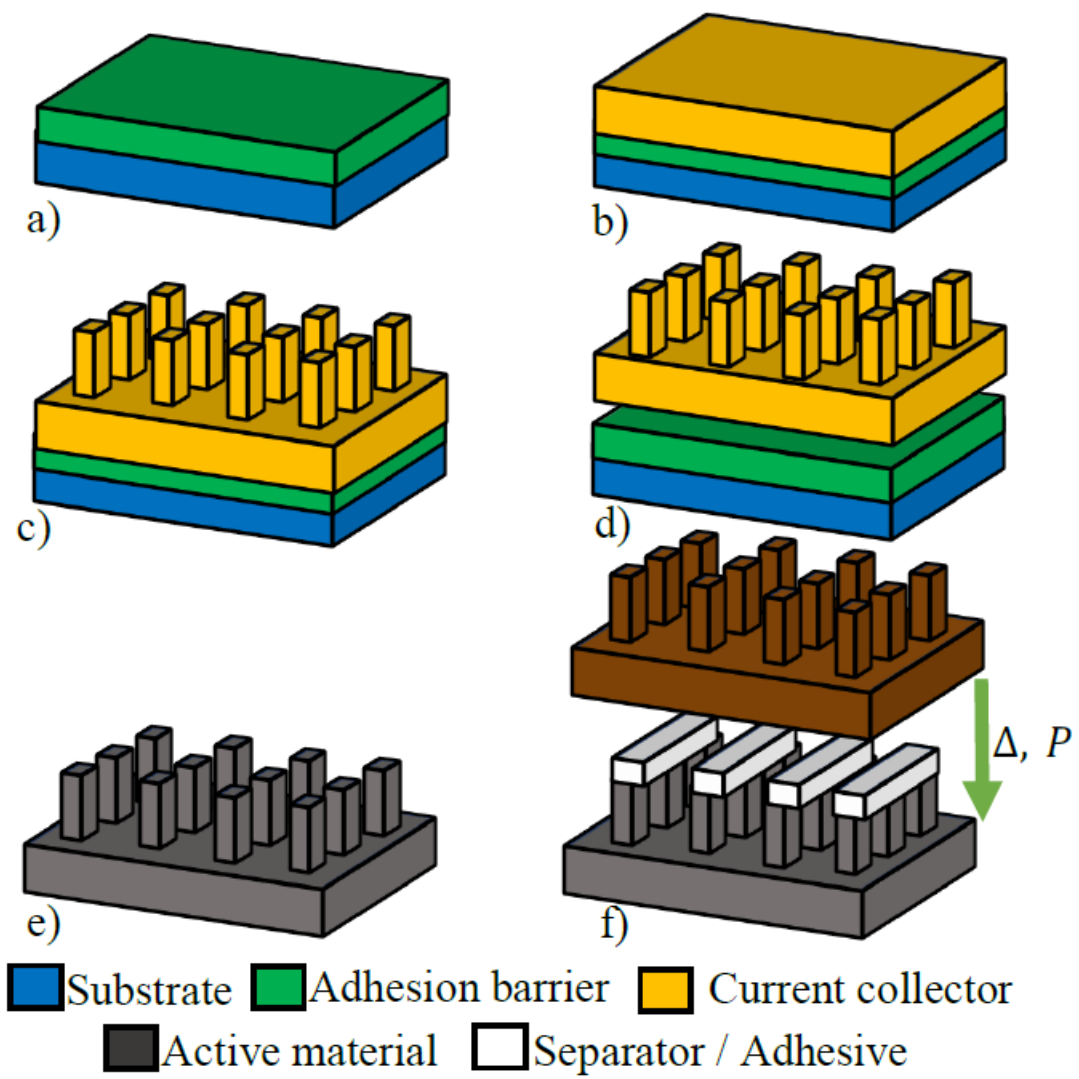
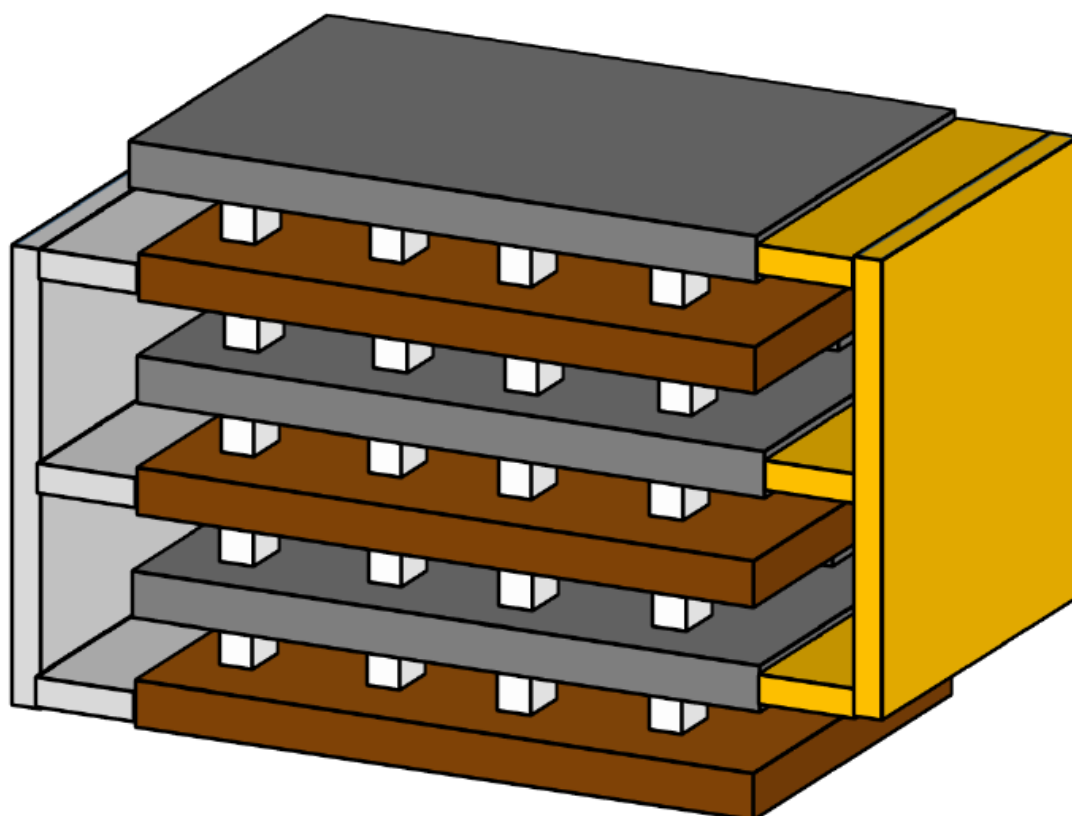


Fig. 11a)




- |   |   |   |
|---|---|---|
|  Ni Cathode CC |  LMO Cathode |  Spacing Pillars |
|  Cu Anode CC   |  NiSn Anode  |   |

Fig. 11b)



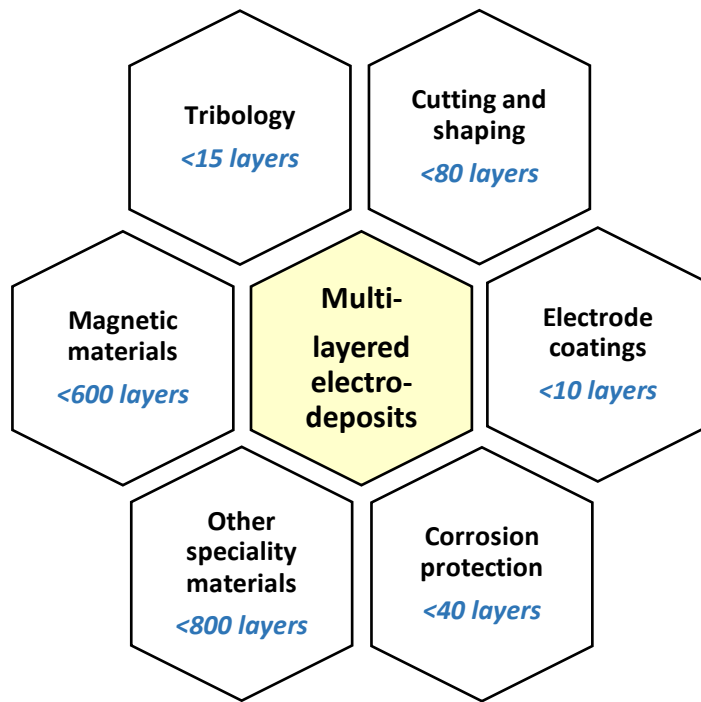


Fig. 12