High $T_c$ superconductors via electrodeposition process

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Abstract: The review of literature on synthesis of superconducting films via d.c. and pulse electrodeposition has been attempted. Electrodeposition and pulse electrodeposition of precursor alloys for high $T_c$ superconductors have been reported. Apart from electrodeposition from nitrate salts, recently, dissolving superconducting anode has been reported as source of deposit.

This article includes survey of electrodeposition via d.c. and pulse electrodeposition, of alloys for high-$T_c$ superconductivity. Kinetics of growth mechanism, different preparative conditions, annealing conditions, electrical and magnetic properties have been reported in detail. This survey also includes theoretical aspects and mechanism of electrodeposition process.

Keywords: Electrodeposition, superconductors, electrochemical oxidation, pulse electrodeposition

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1. Introduction

Since the discovery of high temperature superconductivity by Bednorz and Müller [1] in 1986, numerous efforts have been launched to discover new high-$T_c$ superconducting systems. Since the first report, varieties of copper oxides having high-$T_c$'s have been reported e.g. La$_2$Sr$_2$CuO$_4$ [2], Bi$_2$Sr$_2$CuO$_6$ [3], Bi$_2$Sr$_2$CaCu$_2$O$_8$ [4], Y$_1$Ba$_2$Cu$_3$O$_7$ [5], Th$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ [6], Sr-Ca-CuO [7], Hg-Ba-Ca-CuO [8,9] in the range of 77 K to 133 K. The critical temperature has been found to increase up to 164 K in Hg-Ba-Ca-CuO system if sample is cooled under very high pressure [10].

The high transition temperature with novel processing methods, being used to prepare these materials in the form of tapes and wires, offers the promise of applications in the field of sensitive electronic instruments such as (1) passive electronic system such as communication receiver/amplifiers, (2) computer hardware circuitry, (3) energy savers, (4) resonance imaging scanners and (5) superconducting quantum interface devices [11-15]. However, for this promise to become a reality, remarkable success has to be achieved in deposition of high quality thin films of this new superconductors onto different substrates. Precursor films for high-$T_c$ superconductors have been formed by sequential and simultaneous deposition of constituent metals using conventional thin film techniques [16-20] and by conventional or rapid solidification of molten mixture of constituent metals [21]. As a requirement for many electronic devices, these superconductors should be thin and have a high degree of homogeneity. The known ability to form thin films of copper oxide using electrochemical techniques suggests that electrochemistry may provide a novel synthesis route [22] for both rare-earth and rare-earth-free based superconductors.

A synthesis of superconducting films via electrochemical methods has some advantages over other techniques, such as (i) it is relatively simple, (ii) inexpensive, (iii) it has fast deposition rates, (iv) it can be used in the fabrication of large, non-planer devices, (v) it has a high efficiency in raw material utilization, (vi) it is not required to have very pure starting material and (vii) it is free from complications arising from carbon based impurities.

Electrodeposition process is successfully employed for preparation of superconductors like Sm-Ba-CuO, Y-Ba-CuO, Tl-Ba-Ca-CuO, Bi-Sr-Ca-CuO etc. [23-27]. Electrodeposition offers the following attractive features for synthesis of superconducting films:

(i) It is an isothermal process, mainly controlled by electrical parameters such as deposition potential and current density which are easily adjusted to monitor the film thickness, morphology etc.
(i) The stoichiometry, doping etc. could be controlled with a reasonable accuracy as charge for deposition and deposition time can be controlled to the accuracy of microcoulomb and msecond.

(ii) Electrodeposition usually has a low operating temperature. The obvious advantage is energy saving.

The interesting feature of electrodeposition is that the electroplating could be employed as one of the steps in the synthesis of high-$T_c$ superconductors. For example, Y-Ba-CuO superconductors have been prepared by different ways [28-31] by electrodeposition process.

(i) Direct cathodic deposition of Y-Ba-Cu alloy from aqueous or non-aqueous bath and its oxidation.

(ii) Electrodeposition of Y-Ba alloy onto Cu substrate and its oxidation.

(iii) Electrodeposition of Y-Ba-Cu coprecipitate during voltammetric cycling of copper substrate and its oxidation to obtain superconducting pellet.

(iv) Electrodeposition of Y-Ba-Cu film by using dissolving anode as source of deposit and NaOH like conduct media.

Electrodeposited films provide a highly reactive mixtures on an atomic scale, which markedly reduce the time and temperature compared to the usual oxide superconductor in calcining approach. The flexibility in electrosynthesis technique is quite attractive. A variety of deposition techniques are used for either binary, ternary or quaternary oxide depositions.

Besides the conventional d.c. electrodeposition technique, the pulse electrodeposition of alloys and their oxidation for high-$T_c$ superconductors has recently been reported by Pawar et al [32] and Bhattacharya et al [33]. Pulse electrodeposition enhances the electrical, magnetic, mechanical and structural properties. Also, there are some reports on electrodeposition of precursor films for high-$T_c$ superconductors [31] from dissolving anode.

In the last five years, since the discovery of high-$T_c$ superconductivity in copper oxides, thousands of papers on the synthesis of high-$T_c$ superconducting films have been published. In a field so new and so rapidly developing, it is impossible to make a review of all thin film superconductor synthesis routes. In this article, we will confine in reviewing the current status of electrodeposition route for deposition of high-$T_c$ superconducting films.

The scope of this review, would include a survey of formation of superconductors via electrodeposition process. Theoretical aspects of alloy deposition, via pulse and d.c. electrodeposition and their oxidation and deposition from dissolving anode as a source of deposit are discussed in detail. Different preparative parameters, effect of complexing agents, sintering conditions, structural, morphological, electrical and magnetic properties are reported. Theoretical aspects, kinetics of growth mechanism for d.c. and pulse electrodeposition have also been discussed.
2. Alloys and their oxidation for superconductivity

The definition of an alloy as given by Kremann et al [34] in the Metals Handbook is adopted here and is stated as "A substance that has metallic properties and is composed of two or more chemical elements of which at least one is metal". Alloys may be either homogeneous or heterogeneous. Homogeneous alloys consists of either a solid solution or an intermetallic compound. Heterogeneous alloys consists mixture of solid solution, intermetallic compound and virtually unalloyed elements.

2.1 Electrodeposited alloys:

Electrodeposited alloys are similar to thermally prepared alloys in structure, in that, they usually contain the same phases. Electrodeposition of alloys are concerned with practical objective of obtaining alloys in a sound, coherent, dense, massive and microscopically homogeneous state. Electrodeposited alloys may contain more than one phases present. The hardness of electrodeposited alloy is usually greater than that of corresponding thermal alloy.

Besides the protective and decorative applications of electrodeposited alloys, they have wide range of applications in solar cell, microwave, electronic devices, magnetic recorders, memory devices and recently in high-Tc superconductivity. An unusual application of alloy electroplating is the stabilization of a phase. The first process of alloy plating was reported by Elkington and Baratt [35]. Electrodeposition of alloys for their possible use in high-Tc superconductivity was reported by Lokhande et al [23].

2.2 Oxidation of alloys for superconductivity:

Precursor films for high-Tc superconductors, both rare earth based and rare earth free, have been reported [36,37]. These alloyed films are oxygen free. However, oxidation of these alloyed films is very essential, since superconducting transition temperature is oxygen dependent [38]. This oxidation is usually carried out at higher temperatures (T > 600°C). Hence, basic requirement for synthesis of high-Tc superconducting films is a good quality substrate. The substrate should not diffuse or chemically react with the deposited film and even if it diffuses to a small extent, should not alter the properties in superconducting state. MgO/Ag, SrTiO3/Ag, ZrO2/Ag, pure silver metal are generally used as substrate for high-Tc superconducting films. The films deposited under d.c. and pulse potential conditions, oxidised at suitable higher temperature show superconducting transition temperature above boiling temperature of nitrogen [39].

3. Types of electrodeposition:

As has already been mentioned the superconductors via electrodeposition process have been formed by three different methods (i) d.c. electrodeposition and (ii) pulse electrodeposition, from salt solutions and (iii) d.c. electrodeposition from dissolving anode as source of osit.
3.1. D.C. electrodeposition:

In d.c. electrodeposition the constituents of the deposition bath are adjusted empirically to obtain stoichiometric alloyed films. A conventional three electrode system is employed, with conducting cathode as substrate, reference electrode like Ag/AgNO₃, SCE (saturated calomel electrode) etc. and counter electrode such as platinum, graphite etc. Figure 1 shows schematic electrodeposition set up. Potentiostat/galvanostat allows current/voltage profiles to be run automatically, giving precise control and reproducibility of deposition parameters. In cathodic electrodeposition when the potential of the substrate (electrode) is moved from its equilibrium value towards negative potentials, the cation that will reduce first is the one with least negative (or most positive) redox potential $E^\circ$. For example [40], in a solution containing Tl⁺, Ba²⁺, Ca²⁺ and Cu²⁺, all four ions can be codeposited on the surface of the substrate when potential is negative enough. To determine the deposition potential the voltammetric cycling (or a cathodic polarisation curve) experiment is performed. The black coloured deposits are developed on the cathodic substrate. This behaviour is clearly due to the deposition of Tl-Ba-Ca-Cu precursor as described by the following reactions (the reduction potentials with respect to Ag/AgNO₃ are given in parenthesis).

$$\text{Tl}^\text{+} + 1\, \text{e}^- \rightarrow \text{Tl} (-1.36 \, \text{V})$$
$$\text{Ba}^{2\text{+}} + 2\, \text{e}^- \rightarrow \text{Ba} (-2.58 \, \text{V})$$
$$\text{Ca}^{2\text{+}} + 2\, \text{e}^- \rightarrow \text{Ca} (-2.58 \, \text{V})$$
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Cu$^{2+}$ + 2 e$^-$ → Cu (-0.74 V )
Cu$^{1+}$ + 1 e$^-$ → Cu (-0.55 V )

Figure 2 represents a cyclic voltammogram for solution containing TiNO$_3$, Ca(NO$_3$)$_2$, H$_2$O, Ba(NO$_3$)$_2$, and Cu(NO$_3$)$_2$ dissolved in dimethyl sulphoxide (DMSO) solvent. A set of anodic and cathodic waves is observed. The reduction peaks of the Tl, Ba, Ca and Cu are clearly evident of deposition of Tl-Ba-Ca-Cu alloy onto cathode substrate.

3.2. Pulse electrodeposition:

Recently, there are some reports on pulse electrodeposition of precursor films for high-$T_c$ superconductors and their oxidation [32,33,36]. The pulsed potential deposition is generally found to improve the film properties. Pulse plating has successfully been used to synthesise Bi-Sr-Ca-CuO, Y-Ba-CuO and Tl-Ba-Ca-CuO superconductors. In addition to deposition potential, current density etc. in d.c. electrodeposition there are several parameters which can be easily varied such as pulse on time and pulse off time etc.

Pulse electrodeposition has several advantages over d.c. electrodeposition. Pulse electrodeposition gives high conductivity deposits [41], enhanced plating rate [42] pore free and harder deposits [43,44] etc. Pulse electrodeposition give fine grained homogeneous deposits.

Usually, square wave pulses are used for pulse electrodeposition. However, there are variety of combinations of pulses that can be employed (Figure 3) [45]. As expected, the films deposited by pulse potential have fine grained structure in comparison to the films deposited by applying constant potential. Surface morphology of the electrodeposited alloy is very important, since, it directly influences the structure of annealed film and hence their
properties. In pulse electrodeposition, current density remains considerably higher with time than the corresponding direct current density, which leads to the higher population of adatoms on the surface of the cathodic substrate, resulting in an increased nucleation rate and therefore finer grained structure. In addition, the pulsed potential film is more uniform compared to the high porosity observed using constant potential methods [46].

3.3. Electrodeposition from superconductor anode:

This is similar to the electrodeposition of alloy from dissolving anode. In this technique, counter electrode is a superconductor pellet dissolving and getting deposited. The deposition potentials are estimated by cathodic polarisation experiment. The bath consists either conducting media like NaOH or small quantity of ions of depositing alloy to provide initial conductivity. The anode starts to dissolve in a bath and film gets deposited, which has stoichiometric composition of anode except the oxygen deficiency. Figure 4 shows the schematic diagram of electrodeposition set up using anode as source of deposit.
4. D.C. electrodeposition of alloys for high-$T_c$ superconductivity

The high-temperature superconductors are multiatomic systems with a definite percentage compositions in an appropriate ratio. The codeposition of binary, ternary or quaternary alloys for synthesis of high-$T_c$ superconductors is quite difficult because conditions favourable for deposition of the one element may differ for others. Further, the electrodeposition of precursors for high-$T_c$ superconductors becomes complicated because the deposition of definite stoichiometry is required. The governing factors in codeposition of ternary and quaternary alloys at any given temperature and current density are (1) the electrode potential of the individual ion in the electrolyte, (2) cathodic polarisation caused by the difference in deposition potentials, (3) relative ion concentration in the electrolyte, (4) the solution potential, that is dissolving tendency of electrodeposited compound and (5) the over potential of the ions on the cathode substrate. A change in these parameters is observed due to change in bath temperature, pH and current density. The direction of effect of each parameter can not be predicted, because it is impossible to estimate magnitude of such changes, especially, if more than two conditions are simultaneously varied. The role of such parameters is discussed by Brenner [47].

4.1. D.C. electrodeposition:

The condition for simultaneous d.c. electrodeposition of two or more different metals can be written as

$$E_p + n_p = E_Q + n_Q = E_R + n_R.$$  \hspace{1cm} (1)

where $E_p$, $E_Q$, $E_R$ are equilibrium potentials for $P$, $Q$, $R$ metals and $n_p$, $n_Q$, $n_R$ are overvoltages of respective metals. Activities of these metals in the compound or alloy are determined by their concentration and thermodynamic stability of the deposit. The reversible potential of a metal alloyed with one or more component should be more positive than that of pure metal.

When the standard potentials of constituents metals are far apart and metal or constituent do not interact with one another, the deposition potential may be brought together by adjusting the concentration of noble metal ions, or by changing the activity of discharging ions by a complex formation or by inhibiting the rate of reduction of the nobler metal by introducing the suitable complexing agents. The codeposition requires that the electrode potential for two ions should be sufficiently close ($< 200$ mV) to each other. Interaction between the constituents in a deposit usually shifts the deposition potentials of the deposit to the values that are positive relative to the deposition potential of the less noble constituent.

4.1.1. Mechanism of electrodeposition:

Electrodeposition of alloys via d.c. electrodeposition process for superconductivity consists steps as follows:
The complex ion is transferred or deposited as an adion to surface site include the plane surface, edges, corners or holes with the plane surface providing the primary sites.

(ii) The adion diffuses across the surface until it meets the growing edge or steps where further deposition takes place.

(iii) Continued transfer may occur until it is finally coordinated with other ions (and electrons) and becomes a part of metal and being incorporated into lattice.

(iv) Deposition of metal ions result in depletion in solution adjacent to cathode surface. These ions must be replenished if the deposition process is to continue. This replenishment or mass transport of ions can be accomplished in four ways such as (a) ionic migration, (b) convection (or continuous replacement of electrolyte) [48], (c) allowing certain time to discharge depletion layer by an application of pulse current [49] and (d) by using cylindrical deposition cell to deposit the alloy in the form of wire [50].

Electrodeposition of alloy for high- \( T \), superconducting films comprises placing of three or more ions in the solution as cations. One of them may have large deposition potential such as Ba, Sr and others have less deposition potential such as Cu, Bi etc. present in electrolyte. The formation of such compound involves following order of necessary occurrence.

(i) Transfer of solvated cations to cathode with resulting polarisation.

(ii) Neutralization of nobler ion (with small reduction potential).

(iii) Conversion of cathode surface to the layer of adsorbed anions.

(iv) Complete depolarisation of cathode with respect to less noble ion.

(v) Reduction of less noble ion at the rate of first order electron conductance.

(vi) Polarisation of the cathode, as the neutral character of surface is restored.

(vii) Building of crystal lattice and microcrystals of alloy through polarisation and depolarisation steps.

Electrodeposition of Y-Ba-Cu alloy is an example of this class. An ion on a cathode may be treated either thermodynamically or quantum mechanically and the result in either case is the same. In the first case, it has been established that the electrons can be discharged directly into solution without capacitance effect and in the second case, an anion will discharge its electron to cation if the energy level is lower in the cations. The rates of these reactions are unmeasurably faster than ordinary electrode processes and are independent of deposition potentials. A choice between these two cathodic deposition mechanism can be made after a study of the current efficiency of deposition and of the secondary products formed in the bath solution.
The factors determining the deposition process include (a) electrical double layer (one nm thick) and adsorption of ions at surface (0.2 nm to 0.3 nm away). At any given electrode, immersed in electrolyte, a double layer of charges is set up in the metal and solution ions adjacent to the surface. At solid electrode surfaces, which are usually heterogeneous, the character and constitution of double layer of charges may exhibit local variations, resulting in the changes in the kinetics of deposition and affects the over all growth process, (b) the energy and geometry of solvated ions: especially those involving complex ions. All metal ions are associated with either solvent or complexed with other solution constituents by electrostatic or co-ordinated covalent bonding. A dissolution energy is required in transferring the metal ions of solution to the growing film surface.

Factors governing the alloy deposition:

Various factors which influence the character of electrodeposits are (i) current density, (ii) agitation, (iii) bath temperature, (iv) bath composition, (v) nature of anions, (vi) hydrogen ion concentration (pH), (vii) addition of complexing agents etc. By making appropriate changes in the conditions of deposition and by adjusting the bath composition one can control the character of electrodeposits.

(i) Current density:

It is always desirable to use high current deposits and to increase the rate of deposition. Upto a certain limit, as the current density is increased, the rate of growth of nuclei and deposits obtained will be fine grained. Further increase in current density gives foggy and spongy deposits. If limiting current densities are exceeded, the concentration of metal in the cathode film decreases and the polarisation increases, while at low current densities discharge of ions occurs slowly and thus the rate of growth of nuclei exceeds the rate at which new ones form. The deposits obtained under these conditions are coarsely crystalline. Hence, the limiting current density in a given solution should be used to control the composition, thickness and fine grained deposits.

(ii) Agitation:

Agitation of the solution, in general, brings up a fresh supply of metal ions to the substrate, reduces the thickness of cathode film and hence helps in replenishment of metal ions at substrate surface. As a consequence, agitation permits higher current densities to be used for thicker deposits or agitation enhances the limiting current density. Another obvious advantage of agitation is that it sweeps away gas bubbles, which may cause pits.

(iii) Bath temperature:

The increase in temperature enhances the ionic mobilities and the rate of diffusion and hence the conductivity of the bath increases. Usually, rise in bath temperature results in increase of crystal size and decrease in polarization. At higher temperature higher current densities are possible and hence fine grained, smooth deposits are obtained. At higher temperature, cathode film is replenished rapidly and tendency towards treeing is reduced. However, many
times opposite effects are often observed, which makes it difficult to predict the best temperature of operation for any given bath and should be determined experimentally. Pendse [51] and Mujawar [52] reported the effect of temperature on Dy–Ba–CuO and Bi–Sr–Ca–CuO alloyed films from complexed bath. Figure 5 shows the variation of film thickness of Dy–Ba–Cu alloy with temperature. From the figure, it is seen that 40°C temperature gives the optimum thickness of film. The authors have also reported microstructural changes with temperature. It was found that the films obtained at 40°C are fine grained, uniform and adhesive to the substrate.

(iv) Bath composition:

The alloy deposition from aqueous and non-aqueous solutions is possible. Higher possible concentrations of metal constituents in bath are always preferred because they give (a) higher conductivity, (b) higher limiting current density and (c) higher cathode efficiency. Its disadvantages are (1) increase in production cost, (2) the tendency to crystallize out if evaporation occurs or temperature is lowered and (3) probable decrease in anode efficiency. Increase in metal concentration under a given condition decreases cathode polarisation, increasing crystal size. Though concentration polarisation is small its effect on deposit composition is considerable. However, to obtain an alloy deposit of the required stoichiometry, bath composition of metal ions should be adjusted properly for any given condition; because for any given condition, deposit composition strongly depends on the concentration of metal in the bath. For example, to obtain Bi–Sr–Ca–Cu deposit at ambient temperature in the required stoichiometry $2 : 2 : 1 : 2$ bath composition should be $\text{Bi}^{3+}$ ($20 \text{ mM}$), $\text{Sr}^{2+}$ ($68 \text{ mM}$), $\text{Ca}^{2+}$ ($48 \text{ mM}$) and
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$\text{Cu}^{2+} (5 \text{ mM})$ at $-4 \text{ V vs Ag/AgNO}_3$ deposition potential at ambient temperature. For clarity, the relation between deposit composition with bath composition is depicted in Figure 6.

![Figure 6. Relationship between electrolyte composition and electrodeposited film composition for films deposited at $-4 \text{ V vs Ag/AgNO}_3$ at room temperature in DMSO, non flowing electrolyte.](image)

Maxfield et al [53] reported this relation for deposition of Bi-Sr-Ca-Cu alloy at $-4 \text{ V vs Ag/AgNO}_3$ from non flowing electrolyte formed in DMSO solvent.

(v) Nature of anions and cations:
The cathodic deposition of metals from solutions of their salts is affected by the nature of the salt anions. The effect of the anions on the over potential and on the nature of deposit is reported for many alloys and metals. Usually the over potential decreases from anion to anion as follows:

$$\text{PO}_4^{3-} > \text{NO}_3^- > \text{SO}_4^{2-} > \text{ClO}_4^- > \text{NH}_4^+ > \text{SO}_4^2^- > \text{Cl}^- > \text{Br}^- > \Gamma^-.$$  

The tendency to form coarse grained deposits increases in the order indicated. Presence of different cations apart from the metallic ions increases the over potential. These cations are usually $\text{NH}_4^+$, $\text{Na}^+$, $\text{K}^+$, $\text{H}^+$ etc. Out of these cations effect of $\text{H}^+$ ions, pH, is discussed in detail separately.

(vi) Hydrogen ion concentration pH:
All aqueous solutions contain $\text{H}^+$ ions. On electrolysis these $\text{H}^+$ ions migrate towards the cathode substrate and may get discharged to form hydrogen gas. The cathode efficiency, therefore mainly depends upon what proportions of the current are used for deposition of metal and hydrogen gas. As this efficiency and hydrogen discharge potential partly depends upon concentration of hydrogen ions (pH), it is important to know and to control these concentrations. A hundred percent cathode efficiency means that no hydrogen is discharged while a zero efficiency means only hydrogen is discharged. A low pH in bath permits the use of high current density to produce sound deposit at a relatively high efficiency [54]. In one of
the few papers on the pH effect on cyanide bath it was shown that, the effects of pH on anode
and cathode efficiencies are highly specific [55].

(vii) Addition agents:

It is well known that, in electrodeposition of metals, addition of small quantities of such
substances as gelatin, glue, albumen sugar, agar, aldehyde etc. results in production of
smooth fine-grained and microcrystalline deposits. Such substances are known as addition
agents and depending on their specific effects that they produce, they are called as levelers,
brighteners, stress reducers, etc. These addition agents are generally organic compounds.
Addition agents favours the formation of fresh nuclei and fine grained deposits are obtained.
They are generally consumed in deposition process. They may be decomposed [56] and the
product in part incorporated into deposit [57,58] or released back into the electrolyte.

4.2. Alloy deposition from uncomplexed bath:

A complexing agent is a substance which when present in a plating bath in small
concentration relative to that of metal, produces desirable effects on the surface morphology,
in general appearance of the deposit. However, there are several reports on synthesis of high
$T_c$ superconductors from a bath not containing complexing agents. In principle,
electrodeposition from both aqueous and non-aqueous solutions is possible, with preference
towards non-aqueous methods because in aqueous solutions the reduction of water ($-1.23 \, \text{V vs NHE}$) is kinetically more favourable than the alkaline metals ($<-2.0 \, \text{V vs NHE}$). Almost
all the families of high-$T_c$ superconductors have been reported via an electrodeposition
process, without using any complexing agents.

4.2.1. 1–2–3 system

Electrodeposition of precursors for high-$T_c$ superconducting films have been reported from
both aqueous and non aqueous uncomplexed bath.

(i) Aqueous bath:

The deposition potentials of samarium and barium are greater than $-2\, \text{V vs NHE}$ and their
deposition on noble metal (non-reactive) is not possible. However, codeposition of ternary or
quanternary alloy consisting such elements is possible if one of the constituent has very small
reduction potential [47]. In superconductor materials copper is metal having small reduction
potential ($-0.74 \, \text{V vs Ag/AgNO}_3$). Pendse and Pawar [59] first time reported the synthesis of
Dy–Ba–CuO superconductors from aqueous bath. Dense, uniform and adhesive Dy–Ba–Cu
alloy was deposited onto economic and easily prepared MgO pellets with fluorine doped tin
oxide (FTO) conducting layer sprayed. This technique to prepare polycrystalline MgO pellet
substrates is discussed by Pawar et al [60]. Electrodeposition of Dy–Ba–Cu alloy onto
MgO/FTO pellets and stainless steel substrates was carried out from aqueous uncomplexed
bath. Electrolytic baths were prepared by dissolving dysprosium nitrate (100 mM) barium
nitrate (100 mM) and copper nitrate (60 mM) in double distilled water. To estimate deposition
potentials cathodic polarisation experiment was performed. It was found that the deposition
potential for Cu is smaller than Dy and Ba. For the Dy–Ba–Cu alloy deposition, \(-0.97\) V vs SCE potential was applied. Black coloured deposits of 3 to 4 micron thickness were obtained for deposition period of 20 minutes. Current density was in the range of 6 to 8 mA/cm\(^2\). It was found that Dy–Ba–Cu alloy deposited under these conditions was in the stoichiometric ratio 1 : 2 : 3 with \(\pm 10\%\) variation.

Zurowski \textit{et al} [22] first reported the possibility that electrochemical technique may provide a novel synthesis route for superconducting Y–Ba–CuO films. Slezak and Wieckowski [61] reported the successful synthesis of high-T\(_c\), Y–Ba–CuO superconductor from aqueous bath. Deposition potential was \(-2.5\) to \(-4\) V vs NHE. Authors reported, successful synthesis of coprecipitate with 1 : 2 : 3 stoichiometry with copper foil substrate immersed in electrolyte containing yttrium, barium and copper hydroxides. pH of the bath was 6.5. Co-precipitate obtained was used in the form of pellets for their application in high temperature superconductivity.

Pawar \textit{et al} [62] reported the synthesis of Y–Ba–CuO superconductors from aqueous bath onto silver substrate. Deposition bath was prepared by dissolving nitrate salts in double distilled water. Bath composition was Y(NO\(_3\))\(_3\) (60 mM), Ba(NO\(_3\))\(_2\) (88 mM) and Cu(NO\(_3\))\(_2\) (20 mM). Deposition potential was in the range of \(-1.0\) to \(-1.2\) V vs SCE. Black coloured deposits of 2 to 3 micron thickness were obtained in the 1 : 2 : 3 stoichiometric ratio.

(ii) Non-aqueous bath:
In electrodeposition of alloy for high-T\(_c\) superconductivity, generally non-aqueous baths are preferred. Dy–Ba–Cu alloy of 2 to 3 micron thickness were successfully synthesised. Pawar \textit{et al} [63] had deposited Dy–Ba–Cu films onto MgO pellets from acetone bath. Current densities were found to lie in the range of 14–15 mA/cm\(^2\).

Bhattacharya \textit{et al} [64] reported synthesis of Y–Ba–CuO superconductors from dimethyl sulphoxide (DMSO) bath onto various substrates such as MgO, ZrO\(_2\) and Ni-strip coated with 100 to 500 Å thick silver layer. The deposition bath consisted nitrate salt solution of yttrium, barium and copper. The constituents of the electrodeposition bath were adjusted empirically for the optimal deposition potential was in the range of \(-2.5\) V to \(-4\) V vs Ag/AgNO\(_3\). The composition of the alloyed films was found 1 : 2 : 3 with \(\pm 10\%\) variation.

Weston \textit{et al} [30] reported the synthesis of Y–Ba–Cu alloyed films from non-aqueous bath formed with DMSO and dimethyl formamide (DMF). Bath composition of yttrium nitrate, barium nitrate and copper nitrate were changed and deposit composition was studied for a constant deposition potential. It was found that 15 mM, 20 mM and 16 mM concentrations of Y\(^{3+}\), Ba\(^{2+}\) and Cu\(^{2+}\) ions gives 1 : 2 : 3 stoichiometric depositon. It was reported that, deposition potential for DMF bath is higher than DMSO bath. Deposits of 1 to 2 micron thickness was obtained for deposition period of 1 hour.

Pawar \textit{et al} [28,65] reported the electrodeposition of Y–Ba–Cu alloyed films from DMF and DMSO bath. It was found that deposition potential was in the range of \(-1.5\) to \(-3.5\) V vs SCE for different substrates such as stainless steel, copper, brass and FTO coated glass.
substrates. Films of 3 to 4 micron thickness were obtained for deposition period of 25 minutes. Current density was in the range of 6 to 12 mA/cm$^2$. Figure 7 shown the cathodic polarisation curves for yttrium, barium, copper and Y-Ba-Cu alloy from DMSO bath onto silver substrate.

4.2.2. Tl-Ba-Ca-Cu alloy deposition:

Bhattacharya and Blaugher [40] have reviewed the electrodeposition of Tl-Ba-Ca-CuO superconductors in detail. Generally, nitrate salts were dissolved in non-aqueous solvents. From a solution, containing Tl$^{+}$, Ba$^{2+}$, Cu$^{2+}$ and Ca$^{2+}$, all four ions can be codeposited on the surface of the cathodic substrate when the potential is negative enough. The deposition bath consisted of 33 mM Tl(NO$_3$)$_3$, 40 mM Ca(NO$_3$)$_2$·4H$_2$O, 60 mM Ba(NO$_3$)$_2$ and 66 mM Cu(NO$_3$)$_2$·6H$_2$O. Potential was −4 V vs Ag/AgNO$_3$, and the rate of deposition was 1 micron/minute. The films were found to show typical composition of annealed film as measured by electron probe micro analysis (EPMA) as Tl/Ba/Ca/Cu (2/1.87/2.69/3.89).

4.2.3. Bi(Ph)–Sr–Ca–Cu and Bi–Sr–Ca–Cu alloy deposition:

Pawar et al [66] reported the electrodeposition of Bi–Sr–Ca–Cu alloyed films from aqueous bath onto stainless steel, copper, brass etc. substrates. Bath was prepared by dissolving 15 mM Bi(NO$_3$)$_3$, 200 mM Sr(NO$_3$)$_2$, 200 mM Ca(NO$_3$)$_2$ and 100 mM Cu(NO$_3$)$_2$·6H$_2$O. Deposit obtained was in the stoichiometric ratio 2 : 2 : 1 : 2 with ± 10% variation. It was reported that all four ions can be codeposited onto various substrates by applying constant potential in the range of −1.75 to −2.25 V vs SCE. Current density was in the range of 35 to 40 mA/cm$^2$ and thickness was 1.5 micron for deposition period of 30 minutes. Black
High Tc superconductors via electrodeposition process

Coloured deposits obtained were smooth, uniform and adhesive to the substrates. However, substrates used in this study could not stand the high temperatures at which such films have to be oxidised to produce the superconducting phase.

First successful synthesis of this family from non-aqueous bath was reported by Maxfield et al [53]. On the MgO/Cu or Ag single crystal substrates, superconductor precursor films of 2 microns thickness were obtained. The grains were nodular dendrites. It was found that, metal composition in deposit is dependent on bath composition. The electrochemical formation of Bi–Sr–Ca–Cu and Bi(Pb)–Sr–Ca–Cu precursors is distinct from conventional alloy electroplating in that:

(i) extremely non-noble metals (Sr, Ca) are deposited along with metals having much more positive reduction potentials.
(ii) an aprotic solvent is the preferred electrolyte medium, and
(iii) the concentrations of four or five metal cation species, rather than two, are controlled to obtain desired deposit compositions.

For each set of electrolyte the relationship between electrolyte composition and deposit composition was found and is depicted in Figure 6.

Electrodeposition of Bi–Sr–Ca–Cu alloy from non-aqueous acetone bath had been reported by Pawar and Mujawar [67]. In their study, the detailed mechanism of electrodeposition of Bi-based precursors is discussed. It was found that, current density was drastically decreased within first few seconds and then shows sinusoidal nature. Authors attributed this behaviour of current density is due to charging and discharging of electrical bilayer formed at cathode surface. The weight of deposits, obtained for the different deposition potentials, were estimated. It was found to show a linear relation initially and then to increase more rapidly. This variation of weight of deposit with deposition potential is shown in Figure 8. This type of behaviour was confirmed by variation in current density with deposition potential (Figure 9).

![Figure 8](image-url) Weight deposited per square cm with variation of deposition potential for 10 minutes deposition period of Bi–Sr–Ca–Cu alloy from acetone bath.

![Figure 9](image-url) Variation of current density with potential for different deposits of 15 second time.
4.3. Electrodeposition from complexed bath:

Electrodeposition of rare earths and alkaline earth metals from an aqueous solution bath is difficult, as these are metals which have electrode potentials that are significantly higher than hydrogen reduction potential and during deposition, aqueous solvent is decomposed instead and hydrogen is evolved \[68\]. The deposition of such metals is possible if one is able to shift the reduction potential of such metals to a value lower than the reduction potential of hydrogen. Generally, such favourable shifts has been obtained by forming complex or by using different substrates \[69-71\]. These complexing agents can be used in both aqueous and non-aqueous bath, since they help in both reduction of deposition potential as well as the formation of pairing of two or more different metals and stoichiometry of the deposit can be maintained \[72,73\].

4.3.1. 1-2-3 system:

The alloyed films of Sm-Ba-Cu and La-Ba-Cu were deposited by applying constant d.c. potential from complex bath onto different substrates such as stainless steel, copper, brass, titanium and FTO coated conducting glass. Madhale et al \[74\], in their study used the complexes formed by adding oxalic acid, EDTA, NTA, sodium citrate, sodium acetate etc. Authors reported that oxalic acid is suitable complexing agent for Sm-Ba-Cu and La-Ba-Cu deposition. Uniform, black coloured deposits were obtained. However, substrates used in this study were not suitable for high temperature oxidation.

Electrodeposition of Dy-Ba-Cu precursor for superconducting films have been reported from aqueous and non-aqueous complexed bath \[64,75,76\]. It was found that from non-aqueous complexed bath, good quality deposits are obtained. The complexes were formed with EDTA, sodium citrate, sodium nitrate and oxalic acid. Non aqueous solvent was
High Tc superconductors via electrodeposition process

Variation of thickness of Dy-Ba-Cu alloyed films from complexed and uncomplexed bath is depicted in Figure 10. Current density behaviour with time was different for different complexing agents. Black deposits of 2 to 4 micron thickness were obtained for deposition period of 30 minutes. Deposition potentials were in the range of −1.5 to −2.1 V vs SCE. It was reported that, EDTA is a suitable complexing agent for Dy–Ba–Cu alloy deposition.

4.3.2. Bi–Sr–Ca–Cu alloy deposition:

Pawar and coworkers [67, 77–81] had reported the electrodeposition of Bi–Sr–Ca–Cu alloy from complexed bath. The non-aqueous organic solvent was acetone. Black coloured deposits of 4-6 microns thickness were obtained for deposition period of 30 minutes. It was found that current density behaves sinusoidally for longer deposition period. In their study [67], authors reported the detailed mechanism of electrodeposition of Bi-Sr-Ca-Cu alloyed films. Figure 11 shows the variation of current density with deposition period for complexed bath.

Before applying potentials all the ions along with water molecules present in bulk are in rest position. After application of potential most of ions migrate towards the cathode surface, where few of them get deposited on the cathode substrate, and remaining ions form a charged bilayer near substrate surface. The rate of ionic reduction during simultaneous discharge may change as a consequence of the change in double layer structure. The concentration in the double layer is related [81] to the concentration in the bulk of the solution and is given by the relation

\[ \alpha_{\text{sur}} = \alpha_{\text{sol}} \exp\left[-\frac{ZF\psi}{RT}\right]. \]
where \((a)_{\text{surf}}\) is ionic activity in surface layer; \((a)_{\text{sol}}\) is ionic activity in the bulk solution; \(F\) is Faraday constant; \(Z\) is ionic charge, \(\psi\) is mean potential value, \(R\) is gas constant, \(T\) is absolute temperature.

Due to the formation of space charged layer, the total resistance of cell increases, causing a decrease in current. After some time unstable charged layer was found to get deposited on the cathode surface, decreasing cell resistance and causing rise in current. As this behaviour is periodic, current density shows sinusoidal behaviour.

5. **Pulse electrodeposition of alloys for high-\(T_c\) superconductivity**

Pulse electrodeposition technique can be advantageously used for synthesis of superconducting films. Pulsed potentials are successfully used for deposition of Bi-Sr-Ca-Cu, Y-Ba-Cu and Tl-Ba-Ca-Cu alloyed films from aqueous and non-aqueous baths [36,40,82].

5.1. **Conditions for pulse electrodeposition**

In pulse plating, the important relationships used are:

\[
\text{duty cycle (\%) } = \frac{\text{on time}}{\text{off time} + \text{on time}} \times 100
\]

and average current density

\[
I_a = I_p \times \text{duty cycle.}
\]

The average current density is similar to that used in d.c. electrodeposition. Duty cycle can be changed from 1% to 100% and pulse on time and pulse off time can be adjusted from microsecond to seconds. Though, different combinations of pulses can be used, generally square wave pulses of 50% duty cycle are applied for deposition of precursors for superconducting films. Shazley [83], in his review reported the high speed metal deposition with long off time. Puippee and Ibl [84] presented a simple mathematical equation, in order to check, whether the selected on-off times of pulses are reasonable and within limitations caused by charging and discharging of double layer. According to authors, the charging time of double layer \((t_c)\) and time of discharging of double layer \((t_d)\) may be calculated as:

\[
t_c = \frac{17}{T_p}
\]

\[
t_d = \frac{120}{T_p}
\]

where time is in seconds and \(I_p\) is pulsating peak current density irrespective of the system. If pulse on time is more than charging time and off time is much less than discharging time of double layer, pulse current will behave like a rippled d.c. However, if pulse on time is much smaller than charging time of charged bilayer then fine grained, smooth deposits are obtained, but large deposition period is required. Hence, optimum condition for good quality deposit may be written as [85]:

\[
\text{duty cycle (\%) } = \frac{1}{2} \times \left( \frac{1}{2} \right)
\]
The kinetics of pulse electrodeposition of Y–Ba–Cu alloyed films is discussed by Pawar et al. [86] using cathodic polarisation studies, charge passed through bath and duty cycle. In their report, it was found that cathodic polarisation curves are similar to junction diode characteristics and obey the equation

\[ I = I_0 \left[ \exp\left(\frac{eV}{nKT}\right) - 1 \right] \]

where \( I \) is average current passing through bath; \( I_0 \) is current constant; \( V \) is applied peak to peak potential of pulse; \( K \) is Boltzmann constant; \( n \) is junction ideality factor. Validity of this equation was studied by plotting \( \ln(I) vs V \) and it was found that, it shows linear variation. Figure 12a shows cathodic polarisation curves for yttrium, barium and copper deposition from aqueous acidic bath. Figure 12b shows cathodic polarisation curve for Y–Ba–Cu alloy at 50 Hz frequency and 50% duty cycle. It was found that plot of \( \ln(I) vs V \) shows linear behaviour.

Pawar and Shinde [87] studied the mechanism of pulse electrodeposition of Bi–Sr–Ca–Cu alloyed films and reported that pulse on time must be less than 10 m second, for smooth, uniform and fine grained deposits. It is reported that, value of the electrolytic deposition cell current for individual elemental deposition are larger than for alloy deposition current. This may be attributed to the fact that the simultaneous transport of ions towards cathode in alloy deposition are complex processes interlinked to each other giving rise to locking their free ionic motions. Alternatively, it may be possible that all positive ions may
form big complex molecule reducing their transport velocity and hence current in pulse electrodeposition was defined as:

\[ I = N \cdot Z \frac{u V_1}{V_2} + \text{Electronic current}, \]  

where \( N \) is number of positive ions moving towards the cathode substrate and getting deposited on cathode, \( Z \) is valency of positive ion, \( u \) is velocity of ion and \( V_1 \) and \( V_2 \) are potential applied to the deposition cell and theoretical reduction potential respectively. In the electrolytic deposition cell, the contribution due to the electronic current is smaller than ionic transport current. At any given fixed potential, \( V \), and at constant temperature, \( T \), the velocity, \( u \), of the transport ion may not differ much for different ions. Thus \( I \) is mainly governed by the positive valency of ions.

Pulse electrodeposition gives fine grained smooth deposits, since, replenishment of electrical bilayer adjacent to the cathode surface takes place. Hence though very small, current density is affected by frequency at constant duty cycle. Pawar and Shinde [88] reported that there is a big plateau in the variation of current density with frequency and fine grained deposits are obtained at the beginning of the plateau.

5.2. Pulse electrodeposition of alloys:

Pulse electrodeposition of various superconductor films have been reported from aqueous and nonaqueous bath at 50% duty cycle. Perfect square wave pulses and super imposed square waves were employed for deposition of precursors for high-\( T_c \) superconducting films.

5.2.1. 1–2–3 system:

Bhattacharya et al [89] reported first time pulse electrodeposition of Y–Ba–Cu alloy onto SrTiO\(_3\)/Ag substrate. Superimposed pulse of one second on and off times each of ~4 V peak potential in ~1 V vs Ag/AgNO\(_3\) d.c. potential was employed. Duty cycle was 50%. The bath composition for deposition of YBCO thin films was 40 mM Y(NO\(_3\))\(_3\)\(_2\)\(\cdot\)6H\(_2\)O, 65 mM Ba(NO\(_3\))\(_2\) and 94 mM Cu(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O dissolved in DMSO. Deposition rate was 0.5 micron/minute onto a MgO single crystal substrates with silver coating and [100] orientation.

Pawar and coworkers [65,90] reported the pulse electrodeposition from aqueous and non-aqueous bath. In their study, pulse frequencies were in the range of 10–125 Hz and duty cycle was 50%. Depositions of 2 to 3 micron thickness were obtained. It was found that frequency plays an important role in alloy deposition. Typical plot of variation of film thickness with pulse frequency is depicted in Figure 13. It was found that, thickness is maximum at 50 Hz pulse frequency. Peak potential for deposition was ~1.2 V vs SCE. Deposition period for his study was 10 minutes. Peak current density was in the range of 20–25 mA/cm\(^2\). Black coloured, uniform, smooth, adherent deposits were obtained at 50 Hz pulse frequency.

Non-aqueous organic solvents used were DMSO and DMF. It was found that deposition potentials for deposition of Y–Ba–Cu alloy from non-aqueous bath are higher than
aqueous bath. Bath compositions were similar for both aqueous and non-aqueous baths. Thickness of deposit was 3 to 4 microns for deposition period of 30 minutes current densities were in the range of 10 to 15 mA/cm². Deposits obtained from non-aqueous bath were more uniform than aqueous bath.

5.2.2. Tl–Ba–Ca–Cu alloy deposition:

Bhattacharya et al. [89] reported pulse electrodeposition of Tl–Ba–Ca–Cu alloyed films from non-aqueous DMSO bath system. The superimposed pulse of -4 V vs Ag/AgNO₃ on -1 V vs Ag/AgNO₃ of 50% duty cycle was used for deposition. On and off time of pulse was 10 second each. Bath constituents were 20 mM TiNO₃, 38 mM Ba(NO₃)₂, 102 mM Ca(NO₃)₂·4H₂O and 38 mM Cu(NO₃)₂·6H₂O dissolved in DMSO. Rate of deposition for pulse-deposition was 0.15 micron/minute and was lower than d.c. deposition (0.5 micron/minute). The pulse electrodeposition was carried out onto single crystal SrTiO₃/Ag substrates. The thickness of the films was 1 micron.

5.2.3. Bi–Sr–Ca–Cu and Bi(Pb)–Sr–Ca–Cu alloy deposition:

Precursors for high-\( T_c \) superconductors via pulse electrodeposition route of Bi-families was first reported by Pawar and Shinde [82,87,90]; Bi–Sr–Ca–Cu alloyed films of 2 to 3 micron thickness were deposited at -1.52 V vs SCE peak potential at 25 Hz frequency of square wave pulse. It was found that 20 m second or less on time gives good quality films of Bi–Sr–Ca–Cu alloy. The substrates were silver foil and stainless steel. Current density was in the range of 30–35 mA/cm² for aqueous bath.
DMSO and DMF were used as organic solvent and study was extended to non-aqueous bath. Authors reported the role of frequency in electrodeposition of Bi-Sr-Ca-Cu

![Graph](image)

**Figure 14.** Variation of cathodic current density with pulse frequency for Bi-Sr-Ca-Cu alloy deposition from DMSO bath

![Graph](image)

**Figure 15.** Variation of cathodic current density with deposition time for electrodeposition of Bi-Sr-Ca-Cu alloy from DMSO bath as a function of duty cycle.
High $T_c$ superconductors via electrodeposition process

alloy [91,92]. Figure 14 shows the variation of current density with applied square wave pulse frequency. It was found that current density is function of frequency of square wave pulses. It also depends on on-off time and charging time of bilayer formed near cathode surface. In case of Bi–Sr–Ca–Cu alloy deposition with an application of square wave pulse current density does not show sinusoidal behaviour after initial rapid fall. This might be due to the replenishment of bilayer near cathode surface with the application of off time. Typical plot of variation of cathodic current density with deposition time for Bi–Sr–Ca–Cu alloy is depicted in Figure 15 as function of duty cycle.

Shinde and Pawar [93] had reported the role of duty cycle in the growth of Bi–Sr–Ca–Cu alloyed films and found that at higher duty cycle, the films are thick and non-uniform but at lower duty cycle the films are uniform but thin. This study was carried out for nitrate salt solution in dimethyl sulphoxide solvent.

Bhattacharya et al [33] had reported electrodeposition of thin films PSBCO from a single electrolyte solution of nitrates of Pb(II), Bi(III), Sr(II), Ca(II) and Cu(II) dissolved in DMSO at $-4 \, V$ vs Ag/AgNO₃ peak potential. It was found that it is essential to dry the films quickly.

6. Electrodeposition of precursor superconductors onto non-planer geometries

The development of useful high temperature superconductor (HTSC) wires has shown outstanding progress over the past few years. Most of the attempts to synthesize HTSC superconducting wires were by Powder-in-tube technique [94]. However, this technique is not applicable to large scale process. Electrodeposition is the technique which can be advantageously used for synthesis superconducting layers onto conducting wire substrates. Also, it can be used for deposition of precursor superconductors. Pawar et al [95] for the first time reported the deposition of precursors onto pancake type structures via an electrodeposition process.

6.1. Mechanism of deposition:

The electrodeposition of Bi–Sr–Ca–Cu and Y–Ba–Cu alloyed layers onto silver wires have been reported first time by Pawar et al [95,96]. Authors had fabricated new type of cell (schematic sketch is shown in Figure 16) and found that using such type of cell electrical bilayer has been replenished. For both YBCO and BSCCO systems variation of cathodic current density with deposition time was typical. Figure 17 shows the variation in cathodic current density with deposition time for deposition of Y–Ba–Cu alloy deposition. The current density was found to decrease within first few minutes and then increases to attain some saturation value. This variation is reported due to following cause:

The drastic fall in current is due to the formation of bilayer. However, charges are crowded. The charged bilayer formed near the cathode substrate is cylindrical in shape and
Figure 16. Schematic sketch for electrodeposition onto wire substrates.

Figure 17. Variation in cathodic current density for deposition of Y-Ba-Cu alloy onto silver substrate from DMSO bath.
High $T_c$ superconductors via electrodeposition process

Positive charges are crowded as shown in Figure 18. Due to Coulombic repulsion ions repel each other and hence bilayer gets disturbed. Hence cathodic current density increases. After replenishment of bilayer, the ions are getting deposited with some constant rate keeping current density constant.

6.2. Electrodeposition onto wire substrates:

Pawar et al [97] reported the Y-Ba-Cu alloy deposition onto silver wire from dimethyl sulphoxide bath. Deposition potential was $-1.6$ to $-1.8$ V vs SCE. The current density was 2-4 mA/cm$^2$ and thickness lies in the range of 4 to 6 microns for deposition period of 15 minutes.

The Y-Ba-Cu alloy deposition onto silver coils has been reported [98]. Deposition potential was $-0.7$ to $-1.0$ V vs SCE layers of 6 to 7 microns were coated within 30 minutes. These coils were oxidised at $750^\circ$C for 15 minutes and tested for superconductivity.

Shinde and Pawar [99] recently reported the pulse electrodeposition of Bi-Sr-Ca-Cu alloyed films onto the silver wire substrates. Single salt solution of the nitrates of Bi, Sr, Ca and Cu in dimethyl sulphoxide was used in their study. Graphite cylinder itself working as cell was used for the deposition. Depositions were carried out in the potential range of $-0.7$ to $-1.0$ V vs SCE. Thickness of the alloyed layer was 2 to 3 microns.

6.3. Electrodeposition onto the coil substrates:

Recently, Chatterjee et al [100] and Bhattacharya [101] reported the electrodeposition of Bi-Sr-Ca-Cu alloyed layers onto silver coil substrates from the solution of the oxides mixed in nitric acid.

Pawar et al [95] reported the electrodeposition of Y-Ba-Cu alloyed layers onto silver coils. It was found that deposition potential is in the range of $-1.0$ to $-1.2$ V vs SCE alloyed layers of thickness 2 to 4 microns were deposited during 30 minutes deposition period. These alloyed layers, after oxidation were found to show superconductivity above 77 K.
7. Electrosynthesis from superconductors

Electrodeposition from the non-soluble materials is not new and that from soluble anodes or dissolving anodes, is well-known. Recently, Pawar et al. [3] reported the synthesis of Y-Ba-CuO films by using a dissolving anode as the source of deposit.

7.1. Electrosynthesis from dissolving anode:

Of the methods of replenishing an alloy plating bath, the simplest and most desirable is the use of single phase alloy anode having the same composition as desired in the deposit. The anode should dissolve cleanly. A single phase alloy, generally, dissolves anodically as if it consisted of single metal; that is, the two or more metals dissolve in the same ratio as that they are present in alloy. The utilization of soluble anodes in plating baths is limited because most soluble alloys after application of potential are heterogeneous; consisting two or more phases which differ in their potential against the solution and hence, in their relative rates of anodic attack. Such heterogeneous alloys may not dissolve uniformly. The more active phase dissolves preferentially and the less active phase then falls to the bottom of vessel.

![Graph](image)

**Figure 19.** Anodic polarization curves for YBCO anode onto silver substrate from DMSO bath.

The actual anode corrosion of heterogeneous alloy is more complicated that one would expect on the basis of static potentials of phases because unpredictable factors enter in. During passage of the current, the polarization at the anode may be sufficient to cause the more noble phase to dissolve at least partially, when normally this would not be expected. On the other hand, the exposed more noble phase may exert a screening or protective effect on the more reactive phase and hinder its solution which is generally unexpected [102]. Hence, anode used should be homogeneous or separate anodes of required metals should be used.
7.2. Y-123 deposition:

Recently, we have studied the deposition of Y-Ba-CuO superconductor from soluble Y-Ba-CuO pellet as anode. These pellets were prepared by solid state reaction method described by Zandbergen et al [103]. Figure 19 shows the polarization curve for Y-Ba-CuO pellet in DMSO bath. It was observed that deposition starts after -1 V vs SCE cathode potential. Current density was in the range of 3 to 4 mA/cm² after 5 minutes deposition. Typical plot of variation of cathodic current density with deposition period is shown in Figure 20.

![Figure 20. Variation of current density with deposition time for dissolving YBCO anode](image)

The deposit thickness was to 2 to 3 microns after deposition period of 30 minutes. Initial conductivity was provided by adding small quantity of nitric acid, NaOH or 1 : 2 : 3 composition of nitrate salts of yttrium, barium and copper.

8. Post deposition treatments and superconducting properties

After electrodeposition of precursors for high-$T_c$ superconductors, it is essential to give thermal heat treatment to obtain cuprate superconductors. It is well known the CuO planes are essential for superconductivity and oxygen content plays an important role in superconductivity. For example, in $Y_1Ba_2Cu_{3-\delta}O_y$ system, if $\delta > 0.5$ then the sample shows insulating behaviour [104]. In the materials having $\delta = 0.5$ to zero the structure is perovskite based and sample shows superconductivity. Also the oxygen content affects electrical and magnetic properties. To obtain an optimum oxygen content in the alloyed film it is necessary
to give a proper post deposition treatment. Table 1 gives the comprehensive information of superconducting properties and post deposition treatments reported for various electrodeposited superconducting systems.

Table 1. Different superconducting films reported via electrodeposition method postdeposition treatments and superconducting properties.

<table>
<thead>
<tr>
<th>System</th>
<th>Furnace Cond. Temp/Hr.</th>
<th>Substrate</th>
<th>( T_c ) R=0</th>
<th>Critical current density at 4 K</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-Ba-CuO</td>
<td>Preheated furnace</td>
<td>Ni-strip</td>
<td>74 K</td>
<td>500 A/cm²</td>
<td>Bhattacharya et al [107]</td>
</tr>
<tr>
<td>(DMSO bath)</td>
<td>1050°C 1 min</td>
<td>MgO</td>
<td>78 K</td>
<td>3960 A/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrO₂</td>
<td>91 K</td>
<td>4000 A/cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag wire</td>
<td>74 K</td>
<td>500 A/cm²</td>
<td></td>
</tr>
<tr>
<td>*(DMSO bath)</td>
<td>Heated in furnace</td>
<td>Ag-strip</td>
<td>93 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(DMSO bath)</td>
<td>800°C 10 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*(DMF bath)</td>
<td>Heated in furnace</td>
<td>Ag-strip</td>
<td>89 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(DMF bath)</td>
<td>850°C 10 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*(Aqueous bath)</td>
<td>Heated in furnace</td>
<td>Ag-strip</td>
<td>78 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Aqueous bath)</td>
<td>850°C 5 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy-Ba-CuO</td>
<td>680°C for 20 min</td>
<td>*(MgO/FTO</td>
<td>67 K</td>
<td></td>
<td>Pawar and Pendse [59]</td>
</tr>
<tr>
<td>(Aqueous bath)</td>
<td>650°C 2 hrs.</td>
<td>*MgO/FTO</td>
<td>72 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone bath</td>
<td>850°C 10 min</td>
<td>SrTiO₃/Ag</td>
<td>112 K</td>
<td>56000 A/cm²</td>
<td>Bhattacharya et al [40]</td>
</tr>
<tr>
<td>*(Ti-Ba-Ca-CuO</td>
<td>750°C 15 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi-Sr-Ca-CuO</td>
<td>750°C 1 hr.</td>
<td>*(MgO/FTO</td>
<td>76 K</td>
<td></td>
<td>Pawar and Mujawar [77]</td>
</tr>
<tr>
<td>(Aqueous complexed bath)</td>
<td>900°C 3 min.</td>
<td>*(MgO/FTO</td>
<td>90 K</td>
<td></td>
<td>Pawar and Mujawar [81]</td>
</tr>
<tr>
<td>(Acetone complexed bath)</td>
<td>850°C 10 min</td>
<td>*MgO/FTO</td>
<td>72 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*(Aqueous bath)</td>
<td>850°C 10 min</td>
<td>Ag-strip</td>
<td>78 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*(DMF bath)</td>
<td>850°C 15 min</td>
<td>Ag-strip</td>
<td>83 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi(Pb)-Sr-Ca-Cu</td>
<td>880°C 3 mm.</td>
<td>Al₂O₃/Ag</td>
<td>42 K</td>
<td></td>
<td>Bhattacharya et al [111]</td>
</tr>
<tr>
<td></td>
<td>850°C 2.5 mm</td>
<td>MgO/Ag</td>
<td>62 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>850°C 2.5</td>
<td>70 K</td>
<td>400 A/cm²</td>
<td>Maxfield et al [53]</td>
</tr>
</tbody>
</table>

* Polycrystalline substrates
+ Pulse electrodeposited films

8.1. Oxidation of alloys:

8.1.1. Direct oxidation:

Electrodeposited films consist of the precursors of the components of a high-\( T_c \) superconductor in the required stoichiometry. These films must be subjected to different heat treatments to obtain superconducting phase. Direct oxidation of alloys is used in the field of electrodeposition of high-\( T_c \) superconductivity.
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The direct oxidation method used consists of heating the alloy to an appropriate temperature in a controlled atmosphere. As is evident from Table 1, this method needs that alloys should be heated to high temperatures. This method may be considered as Tarnish reaction. These reactions are of solid with a gas or liquid. In the process of oxidation of alloys for high-$T_c$ superconductors, the reaction is in between solid and gas. In the case of thick films ($W > 1000^\circ$ A), two types of laws are observed relating thickness and time of oxidation:

(i) $W = A \cdot t$ (linear dependence) \hspace{1cm} (10)
(ii) $W^2 = B + Ct$ (parabolic dependence) \hspace{1cm} (11)

where $A$, $B$, $C$ are constants.

In the linear relation the gas reaches the metal surface, whereas the parabolic law applies to the growth which is limited by diffusion through a coherent solid film. The parabolic law depends on the properties of the bulk solid material.

In the reaction of metal $M$ with a gas $x$ to give $Mx$ following transport phenomena are assumed: Figure 21 represents the interstitial cation vacancies from I to II or of cation vacancies and interstitial anions from II to I. Electronic transport may take place as depicted in

Figure 21. Schematic representation of transport phenomena in the oxide layer growth.

Figure 21. The hole current balances the current due to charged vacancy. The hole vacancy concentrations are generally different, also their gradients are different. Due to different diffusivities, a separation in charges is produced. The potential difference produced due to separation in charges reaches to steady value when there is no net current. Hence, oxidation of alloyed film having thickness $W > 1000^\circ$ AU obeys eq. (11).

8.1.2. Electrochemical oxidation:

This process is also called as the electrochemical oxygen intercalation into oxide networks. Grenier et al [105] reviewed the electrochemical oxidation of the La–M–O where $M = \text{Ni, Cu}$. It is reported that the diffusion phenomena strongly depends on electrode features such as
structure, texture and physical properties. The electrochemical oxidation of both the thin films and the bulk precursor superconductors is possible. The oxidation of the material is done at room temperature. This process has the advantage of the energy saving.

The cyclic voltammogram is recorded by using convention at three electrode system with KOH like electrolyte and graphite or platinum like counter electrode. The electrochemical oxidation of La–CuO starts above 700 mV as oxygen evolution starts at 700 mV in KOH solution [106]. Reaction of the oxygen evolution can be written as

\[
4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4e^-
\]

The applied potential for the electrochemical oxidation is usually selected at the beginning of the plateau in voltammogram.

In case of the La$_2$CuO$_{4+\delta}$, it is reported that starting material behaves as antiferromagnetic, $P$-type semiconductor. But after electrochemical oxidation, its electrical resistivity and thermoelectric power at 300 K strongly decrease by a factor of 50 and 10 respectively. Hence it is clear that, electrochemical oxidation is possible. Further, the thermal evolution of resistivity of the electrochemically oxidised La–CuO material shows typical metallic behaviour and exhibits a superconducting transition around 50 K (Figure 22) [106].

8.2. 1–2–3 system:

Various precursors of Y–Ba–Cu, Dy–Ba–Cu, Sm–Ba–Cu etc. for 1–2–3 superconductors have been reported via d.c. and pulse electrodeposition route.

8.2.1. D.C. electrodeposition:

Madhale et al [74] reported the electrodeposition of Sm–Ba–Cu and La–Ba–Cu onto stainless steel copper brass etc. substrates. However, these substrates cannot stand at high temperature required during oxidation. Pendse and Pawar [59] reported successful synthesis of high-$T_c$
**High Tc superconductors via electrodeposition process**

superconducting films of Dy–Ba–Cu alloy onto polycrystalline MgO substrate. Films oxidised at 680°C for 20 minutes and then furnace cooled to room temperature were found to show superconductivity, with \( T_c \) onset and \( T_c (R = 0) \) at 100 K and 67 K respectively. Authors also reported the superconductivity in Dy–Ba–CuO system electrodeposited from non-aqueous complexed bath (with organic solvent acetone). Films were annealed at 830°C for 1 hour were found to show superconductivity with \( T_c \) onset and \( T_c (R = 0) \) with 100 K and 72 K. Pawar *et al* [75] also discussed the role of annealing temperature on superconducting properties of electrodeposited films. Figure 23 shows the resistivity dependence on annealing temperature for Dy–Ba–CuO films deposited at constant preparative parameters and annealed at various temperatures.

![Graph showing resistivity vs temperature](image)

**Figure 23.** Resistivity vs temperature as function of annealing temperature of Dy–Ba–CuO films, onto polycrystalline MgO substrates

Bhattacharya *et al* [89] synthesised Y–Ba–CuO films and studied various electrical and magnetic properties. The role of the substrates on superconducting properties of electrodeposited Y–Ba–Cu alloyed films annealed in preheated furnace at 1050°C for 1 minute and then furnace cooled to room temperature is reported by authors [107]. Typical plot of resistivity variation with temperature for Y–Ba–CuO films onto different substrates annealed at similar conditions is depicted in Figure 24.

Mutual inductance measurements were performed to confirm the resistance vs temperature measurement data and also to estimate the volume uniformity of the superconducting phase in the Y–Ba–CuO film onto the MgO substrate. The test samples were placed between two uniaxial coils (a drive coil and pick up coil) separated by 3/8 inch. A choice of constant gap provided a means of eliminating the background eddy current signals from the sample holder. An oscillating electrical current was passed through drive coil which generates magnetic field resulting in induction of signal in pick up coil. At temperature higher than \( T_c \), magnetic field passed through sample unhindered and induced a signal in pick up
coil. At colder temperature than $T_c$, material become superconducting and blocks magnetic field. The signal in pick up coil is then reduced. The inductance of a sample grown on MgO single crystal is shown in Figure 25. The peak of the latter coincides with $T_c$. The magnitude of real part in inductance corresponds to volume uniformity of superconducting phase and in the said sample it was 70%. Rest of the phases were impurity phases and were recognized by XRD analysis as BaCuO$_2$, Y$_2$Cu$_2$O$_5$ etc. The critical current densities were 4000 A/cm$^2$ in zero field at 4 K and 360 A/cm$^2$ at 77 K, zero field for a 5 micron thick film.

Pawer et al [108,109] reported that Y–Ba–CuO films onto silver substrate annealed at 800°C for 10 minutes show superconductivity with $T_c$ onset and zero resistivity at 80 K and 78 K samples deposited from aqueous bath were fine grained and grain size was improved after oxidation.
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Plate 1

Figure 26. Microphotographs of Y-Ba-Cu alloyed films at pulse frequency of (a) 25 Hz, (b) 50 Hz
Figure 26. Microphotographs of Y–Ba–Cu alloyed films at pulse frequency of (c) 100 Hz and (d) 50 Hz oxidised at 850°C.
8.2.2. **Pulse electrodeposition:**

Bhattacharya *et al.* [107] reported the superconductivity in the pulse electrodeposited films. The pulse electrodeposition YBCO film annealed at 1050°C for 1 minute on MgO/Ag substrate shows zero resistivity at 78 K and yields a $J_c$ (1 $\mu$V/cm $J_c$, criterion) of 5160 A/cm$^2$ at 4 K and zero magnetic field, while $J_c$ is 142 A/cm$^2$ at 4 K and magnetic field ($H = 500$ Oe) perpendicular to film surface. Pawar *et al.* [86,109] reported that Y–Ba–Cu alloyed films annealed at 850°C for 10 minute from DMF bath and 800°C for 10 minute from DMSO bath shows $T_c$ ($R = 0$) at 89 K and 93 K respectively. We see that critical current density of pulse electrodeposition film is higher than d.c. electrodeposited films. Microstructural study has been conducted by Pawar *et al.* [109] and they reported that at optimum frequency of 50 Hz, good quality, uniform, homogeneous and adhesive films were obtained. Figure 26 shows the microphotographs of Y–Ba–Cu alloyed films deposited at different frequencies from aqueous bath.

8.3. **Tl–Ba–Ca–CuO superconductors:**

8.3.1. **D.C. electrodeposition:**

Maxfield *et al.* [26] reported the synthesis of superconducting Tl–Ba–Ca–CuO films from DMSO bath onto MgO/Ag substrates via d.c. electrodeposition process. Bhattacharya and Blaugher [40] reviewed the electrodeposition of Tl–Ba–Ca–CuO superconductors. The electrodeposition was carried out onto SrTiO$_3$/Ag substrates. The films annealed at 1050°C for 10 minutes were found to show superconducting transition temperature $T_c$ ($R = 0$) at 112 K. The electrodeposited Tl-based superconductors onto silver foil annealed at 850°C for 10 minutes were found to show superconductivity with $T_c$ onset and zero resistivity at 115 and 112 K respectively. Authors [110] also reported the growth mechanism and kinetics of phase transition in Tl-based superconductors on Ag substrates. Their experiments and analysis on the role of Ag on the phase development suggests the following behaviour:

1. Ag in general will reduce the temperature at which liquid phase appears.
2. At high concentrations of Ag either at an interface (thin layer of Ag) or uniformly distributed excessive liquid results producing an incongruent decomposition.
3. If the Ag concentration is dilute, the melting will result in a quasi congruent condition with no change in composition; that is melting of nominal 2223 composition will result in the development of 2223 phase.
4. Ag in dilute amounts may influence the nucleation and growth, as opposed to a simple catalytic mechanism. A catalyst would increase the kinetics proportional to the Ag concentration with no change in the equilibrium conditions, which does not agree with the observed results.

Figure 27 shows schematic phase diagram for Tl–Ba–Ca–CuO superconductors. The dependence of critical current density with magnetic field was studied by authors and reported
that films shows 20,000 A/cm² critical current density at 4 K with zero field onto silver substrate. Figure 28 shows dependence of critical current density with magnetic field. The films deposited onto SrTiO₃/Ag were highly polycrystalline and shows higher critical current density 56,000 A/cm² at 77 K with zero field.
8.3.2. Pulse electrodeposition:

Pulse electrodeposition has been reported by Bhattacharya et al [111] to obtain more uniform, smooth and fine grained polycrystalline TI–Ba–Ca–CuO superconductors onto SrTiO₃/Ag substrate. Annealing conditions were similar for d.c. and pulse electrodeposition critical current density for pulse current was studied and is depicted in Figure 29. Critical current density for pulsed current was 2700 A/cm². It was found that a significant improvement in critical current density of electrodeposited TBCCO films could be obtained when films are deposited under pulsed potential conditions [101]. Using electron probe for microanalysis EPMA, a typical composition of the oxygen annealed film was (Ti/Ba/Ca/Cu/O) 2/2.67/2.69/3.89/12.15.

8.4. Bi(Ph)–Sr–Ca–CuO and Bi–Sr–Ca–Cu system:

8.4.1. D.C. electrodeposition:

Maxfield et al [53] reported that Bi–Sr–Ca–Cu alloyed films onto MgO/Ag single crystal substrates deposited at –4 V vs Ag/AgNO₃ and annealed at 850°C to 875°C for 2 to 5 minutes shows superconductivity with Tc onset and zero resistivity at 80 K and 67 K respectively. Pawar and Mujawar [77,81,112] reported that BSCC alloyed films onto MgO/FTO polycrystalline pellet substrates annealed at 840°C show Tc onset and zero resistivity at 95 K and 76 K respectively for the aqueous bath deposition. However, films deposited from acetone bath with EDTA as complexing agent annealed at 900°C for 3 minute show onset at 100 K and zero resistivity at 90 K.

Bhattacharya et al [111] reported that PBSSCO films annealed at 880°C for 30 minutes and cooled slowly to 200°C in 13 hrs. and 30 minutes and quenched down to room temperature shows superconductivity at 62 K substrates were MgO and Al₂O₃ single crystals. Current density was 500 A/cm² for films onto MgO substrate at 4 K temperature with

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Figure 29. The I–V characteristics for pulsed current for TBCCO thin film
zero field. Sample shows predominantly 2212 phase. Figure 30 shows XRD pattern of (Pb Bi)$_2$Sr$_2$Ca$_2$O$_9$ sample onto Al$_2$O$_3$ substrate.

8.4.2. Pulse electrodeposition:
Pawar and Shinde [91,92,113] reported that pulse electrodcposited BSCC alloyed films onto silver foil substrates, annealed at 850°C from aqueous bath show $T_c(R = 0)$ at 72 K. For DMF and DMSO bath, $T_c(R = 0)$ were 83 K and 78 K respectively. The enhancement in $T_c$ of samples from non-aqueous bath might be due to formation of non-superconducting phases in the film during electrodeposition from aqueous bath. Authors also reported that, pulse electrodeposited films are more uniform, homogeneous and adhesive than d.c. electrodeposited films. Figure 31 shows the microphotographs of d.c. and pulse electrodeposited Bi–Sr–Ca–CuO samples with a magnification of 500 X. It was found that samples turn dark black in appearance after oxidation.

8.5. Superconducting non-planar geometries:
Electrodeposition technique can be advantageously used for the synthesis of superconducting layers onto non-planar geometries such as wires and coils. Till date superconducting wires and coils of Bi–Sr–Ca–CuO, Y–Ba–CuO and TBCCO are reported in the literature.

8.5.1. Superconducting wires:
Shinde [114] reported the synthesis of pulse electrodeposited wires of the BSCCO system. Precursor alloys of the BSCCO system after the oxidation at 750°C in oxygen atmosphere for 15 minutes were found to be superconducting at 70 K. Pawar et al [96] had also reported the synthesis of the superconducting wires of the YBCO and BSCCO system via d.c. electrodeposition process. For the superconducting layers deposited onto silver wires the maximum $T_c$ was 79 K for the YBCO system.

8.5.2. Superconducting coils:
The synthesis of superconducting coils with these brittle ceramics is very difficult, but electrodeposition technique has been advantageously used for the synthesis of
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(a) D.C. electrodeposition as deposited.

(b) D.C. electrodeposition oxidised at 850°C for 30 min.

Figure 31. Microphotographs of Bi–Sr–Ca–Cu alloyed films and oxidised Bi–Sr–Ca–CuO films with a magnification of 500 X
Figure 31. Microphotographs of Bi–Sr–Ca–Cu alloyed films and oxidised Bi–Sr–Ca–CuO films with a magnification of 500 X.
superconducting coils. Chatterjee et al. [100] reported the synthesis of Bi–Sr–Ca–Cu alloyed layers onto silver coil and their successful conversion into superconducting coil at 76 K after oxidation. Tonape [115] reported the synthesis of the superconducting coil of YBCO. These coils were studied for the inductance measurement. It was found the inductance of the coil drops suddenly at liquid nitrogen temperature. These coils were found to exhibit superconducting transition at 80 K. Figure 32 shows the resistivity dependence of the superconducting layer onto silver coil and Figure 33 shows the photograph of superconducting coils and a tape grown on silver substrate.

Figure 32. Temperature dependence of resistivity of the BSCCO coil

Figure 33. Photographs of the electrodeposited superconducting layers onto silver tape and coil substrate.
9. Conclusion

The synthesis of superconducting films via the electrochemical route possesses many advantages. It is an easy and economic technique; there is no need of highly purified starting materials, etc. Electrodeposition offers flexibility in choosing different steps in forming the compound precursor for high-$T_c$ superconductivity. The electrical and magnetic properties of these superconducting films via electrodeposition process are comparable to the properties of films prepared by using other deposition techniques. Pulse electrodeposition gives more uniform, smooth, fine grained films. The enhancement in $T_c$ and critical current density are other advantages of pulse electrodeposition in high-$T_c$ superconductivity. Different superconductor systems can be synthesised via electrodeposition route onto non planer and large area substrates.

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