

Synthesis of Advanced Materials by Electrochemical Processing in Nonaqueous Media

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4.1 Introduction

Advanced materials are characterized not only by their specialized chemistries, *i.e.*, purity, doping level, etc., but also by their tailored microstructures. Through processing one attains compositional and microstructural goals and produces materials to specification. This chapter discusses electrolysis from the perspective of materials processing, in particular, the potential of electrochemical processing to generate advanced materials. These include thin films, epitaxial layers, powders, and various nonequilibrium structures such as metastable phases, compositionally graded microstructures, and compositionally modulated microstructures.

Electrolysis is based upon electron-transfer with ionic species. Why, then, electrolysis in nonaqueous media? Unfortunately, aqueous solutions are unsuitable as media for processing reactive elements. At decomposition potentials negative enough to deposit these elements hydrogen evolution occurs. Furthermore, in certain cases the elements so deposited immediately react with water in a metallothermic reduction. To a first approximation aqueous electrochemistry is restricted to the energy window bounded by the hydrogen and oxygen evolution reactions. Kinetic factors extend these limitations somewhat, but not far enough to allow electrolysis of highly reactive metals and their compounds. Hence, there is a need to exploit nonaqueous electrolytes, of which there are three categories, characterized primarily by their temperature regimes of stability: at ambient temperature, organic electrolytes; at elevated temperatures, molten salts; at subambient and cryogenic temperatures, liquefied gases. This article is confined to a discussion of the latter two. In metallurgical applications organic electrolytes play a very small role. This is in part due to their poor ionicity, which results in low electrical conductivity and inability to dissolve reactants. As well, organic electrolytes can have some or all of the following characteristics: low flash point, carcinogenic, react violently with water.

To repeat, then, electrodeposition in nonaqueous media may be the only way to deposit certain elements. However, for other elements that can be deposited from aqueous solutions, electrolysis in nonaqueous media may offer advantages in terms of the specific resulting composition and microstructure of the deposit. For example, chromium deposits produced by fused salt electrolysis in halide melts are very low in hydrogen, a condition difficult to achieve in deposits generated in aqueous media. Furthermore, fused

salt electrolysis offers opportunities to make coatings on easily oxidizable metals which are difficult to plate in aqueous media. For example, niobium and tantalum can be electroplated with platinum group metals only by fused salt electrolysis despite the fact that the latter are easily electrodeposited from aqueous media.

By way of introduction to the field of molten salts the reader is directed to the collections by Blander,¹⁾ Sundheim,²⁾ Mamantov,³⁾ and Mamantov and Marassi,⁴⁾ as well as the monographs by Lumsden⁵⁾ and Bloom⁶⁾. A brief overview can be found in the two-volume set by Richardson⁷⁾. Electrochemistry of molten salts is treated in the monograph by Delimarskii and Markov.⁸⁾ Basic property data have been compiled by Janz in a handbook⁹⁾ with supplements published in the *Journal of Physical and Chemical Reference Data* (Refs. 10 and 11, for example). The properties of the most common solvent systems have been collected by Plambeck¹²⁾. The industrial applications of molten salts are treated in books edited by Lovering¹³⁾ and Kuhn.¹⁴⁾ Current research and reviews are reported in several series: *Advances in Molten Salt Chemistry*,¹⁵⁾ *Molten Salt Techniques*,¹⁶⁾ as well as in proceedings volumes from international symposia held under the umbrella of the Electrochemical Society.¹⁷⁾ As for archival publications, the journals where molten salt research is apt to be reported include the *Journal of the Electrochemical Society*, *Electrochimica Acta* and the *Journal of Applied Electrochemistry*. There is a substantial amount of activity in the former Soviet Union, especially in Russia and Ukraine, with the result that much of the molten salt literature is not published in English, e.g., *Rasplavy*, or *Melts*, published in Sverdlovsk, and *Ukrainskii Khimicheskii Zhurnal*, or the Ukrainian Journal of Chemistry, published in Kiev.

4.2 Characteristics of Electrochemical Processing

Electrolysis is an electrochemical process, *i.e.*, a process in which chemical reaction is accompanied by electron transfer. Electrolysis is performed in a reactor called an electrochemical cell, which is a device that enables electrical energy to do chemical work, which in the context of this article is the generation of an element or a compound. This, in turn, must first be dissolved in an ionic solution from which elements are deposited by the passage of electrical current with its attendant electron-transfer reactions at each electrode. Fig. 4.1 shows a prototypical electrolysis cell in which the electrolyte is a molten salt. Its principal components are the electrolyte, the electrodes, and the container (sidewalls and floor). The electrolytes are multicomponent melts of either chlorides or fluorides.

Chlorides offer the advantages of a lower operating temperature and of a greater choice of electrode and container materials. As for disadvantages, chlorides react with moisture: some are hygroscopic, even deliquescent, while others decompose by hydrolysis. Hydrolysis prevents dehydration, *i.e.*, simple heating will not result in the removal of the water of hydration from niobium pentachloride:



Instead, hydrolysis occurs to convert the pentachloride to oxychloride with attendant emission of hydrogen chloride gas:



Niobium oxychloride, NbOCl_3 , is much stabler than NbCl_5 and thus much more difficult to

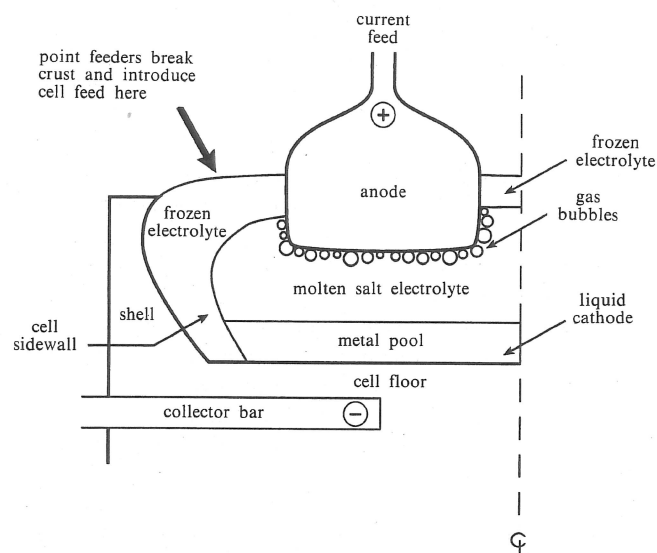


Fig. 4.1 Prototypical Electrolysis Cell.

electrolyze. Furthermore, the oxychloride contains oxygen which at the carbon anode reacts in preference to chlorine and forms carbon monoxide and carbon dioxide; the result is an increase in anode consumption rate. To assure metal purity it is imperative that the electrolyte be free of the impurities formed by reaction with moisture. This adds to the number of unit operations in cell feed preparation from source materials and furthermore puts strict requirements on the operating conditions of the electrolysis cell.

Fluorides, on the other hand, have the advantage of being less reactive with moisture. Additionally, fluorides can dissolve oxides directly. This avoids fluorination which requires reaction with ammonium bifluoride, for example. The use of an oxide-based cell feed in principle simplifies the process flowsheet and reduces capital and operating costs. Unfortunately, the higher melting points and greater corrosivity of the fluorides severely limit the choice of materials of construction in the physical plant. In the case of materials processing, this means greater risk of inflicting thermal damage on the substrate. Another disadvantage is the relatively low solubility of refractory-metal oxides in molten fluorides. Since the limiting current density scales directly with concentration the low solubility of oxide feed in fluoride melts limits cell productivity by setting a rather low ceiling on the maximum practical operating current density.

During electrolysis electric current is passed from the anode through the electrolyte to the cathode. The electrolyte must be strictly an ionic conductor, while the electrodes must be electronic conductors. The anode can be either consumable or nonconsumable. Consumable anodes are found in various electrolytic processes. In electrorefining, the anode consists of an impure form of the metal to be purified. In electroplating, the consumable anode may act as the feedstock for the deposited metal. In electrowinning, the consumable anode consists of a material that reacts with the products of the anodic reaction, e.g., a

carbon anode in the presence of evolving anodic oxygen. Used primarily in electrowinning, nonconsumable anodes consist of materials inert to chemical and electrochemical attack. In chloride electrolytes carbon commonly serves as a nonconsumable anode. There is no fully satisfactory nonconsumable anode for use with fluoride-based electrolytes. With reference to the Hall cell for the electrolytic extraction of aluminum this author has defined a new approach for discovering nonconsumable anodes for use in fused salt electrolysis operations and has described the relevant set of selection criteria.¹⁸⁾

As for cathode materials, carbon, refractory metals such as tungsten, molybdenum, and tantalum, as well as low carbon steel have all been employed. In practice, the cathode functions only as the current lead. During electrolysis the cathode material is separated from the electrolyte by the product metal or compound which is produced in solid form unless a host low melting metal is employed as a liquid cathode. Production of solid metal and liquid alloy each has its advantages and disadvantages. When the cell product is solid metal it is not necessary to purify it of large amounts of host cathode metal. The disadvantage is that solid metal deposited from molten salts is invariably dendritic. This results in salt entrainment with the need for some form of subsequent treatment for salt removal. The production of liquid metal solves the morphological problem and facilitates easy removal of product from the cell by siphoning; however, this approach has its faults, the principal one being the need to refine the refractory metal out of the product cathode metal alloy.

The electrolyte is contained in a steel shell lined with carbon block. With chlorides a lining of ceramic or low carbon steel is acceptable. It is also possible to operate with a sidewall of frozen electrolyte. Current densities are in the neighborhood of 1 A cm⁻² for electrowinning molten metal; for reasons related to assuring morphological stability current densities in electroplating cells are about an order of magnitude lower and range from 10 to 100 mA cm⁻². Cell operating temperatures span 400° to 1000°. Cell voltages depend upon the particular melt chemistry and cell design which determines the contribution of the ohmic resistance of the bath. During electrolysis the voltage required to drive the process is substantially higher than the reversible potential as calculated by the Nernst equation, which for metal halide, MX_n, in a multicomponent molten salt solution and in equilibrium with pure metal, M, and pure gas X₂ at atmospheric pressure, can be expressed as

$$\mathcal{E}_{MX_n} = -\Delta_f G^\circ_{MX_n} / (n\mathcal{F}) - (RT/n\mathcal{F}) \ln a_{MX_n}, \quad (4.3)$$

Where $\Delta_f G^\circ_{MX_n}$ is the standard Gibbs free energy of formation of MX_n, \mathcal{F} is the Faraday constant, 96487 C mol⁻¹, R is the gas constant, 8.314 J mol⁻¹ K⁻¹, T is the temperature in Kelvins, and a_{MX_n} is the activity of MX_n in the electrolyte solution. \mathcal{E}_{MX_n} is a function of electrolyte composition and temperature. The difference between the equilibrium potential and the applied voltage is due to kinetic factors which increase the energy consumption of the cell. The cell voltage for the electrolytic decomposition of MX_n is given by¹⁹⁾

$$V_{\text{cell}} = \mathcal{E}_{MX_n} + (\eta_a + \eta_c)_{\text{cathode}} + (\eta_a + \eta_c)_{\text{anode}} + \eta_{\text{electrodes}} + \eta_{\text{ohmic}}, \quad (4.4)$$

where \mathcal{E}_{MX_n} is the reversible potential or equilibrium decomposition potential given by the Nernst equation; η_a is the activation overpotential at the electrode and is a function of electrolyte composition, current density and temperature; η_c is the concentration

overpotential at the electrode and is a function of electrolyte composition, current density and temperature; $\eta_{\text{electrodes}}$ includes the voltage drops associated with the electrodes themselves, with the bus bars, and with the electrical contacts between them; and η_{ohmic} , the ohmic overpotential or IR drop, is due to the electrical resistance of the electrolyte itself and is proportional to current density and interelectrode distance and inversely proportional to the electrical conductivity of the electrolyte and to the electrode area. Existing industrial molten salt electrolysis cells operate at voltages three to five times the value of the Nernst potential.

Cell productivity is expressed in terms of several figures of merit. Current efficiency can be loosely defined as the ratio of the number of equivalents of metal product to the number of moles of electrical charge delivered to the cell by the power supply. As such, current efficiency is effectively a measure of compliance with Faraday's laws of electrolysis. In electrowinning cells cathodic current efficiencies of 60 to 80 per cent are not uncommon. These figures are well below those reported for the electrolytic production of aluminum which typically attains current efficiencies exceeding 90 per cent. Voltage efficiency is the ratio of the equilibrium decomposition potential to the applied cell voltage. Quite simply, voltage efficiency expresses the deviation from the Nernst equation and is a measure of inefficiency due to kinetic factors cited above. In the electrolysis of fluorides voltage efficiencies are typically below 50 per cent, while in the electrolysis of chlorides values below 25 per cent have been reported.

4.3 Electroplating

Fused salt electrolysis can also generate coatings. Representative of the types of coatings so formed are those comprising the refractory metals. By way of illustration the following treatment draws upon results for refractory metals. The range of compositions includes elements, alloys, and compounds. Indeed, electroplating of refractory metals has received somewhat more attention than electrolytic extraction of these metals. At least on the basis of reports in the open literature, the most thoroughly studied metals from the perspective of electroplating are molybdenum²⁰⁻²³⁾ and titanium.^{24,25)} Other metals, however, continue to receive attention: niobium,^{26,27)} tantalum,^{26,28,29)} chromium,³⁰⁻³³⁾ and tungsten.³⁴⁾ Electrodeposited coatings can be pure metal, metal alloy, or compounds. Reports of research on the electrodeposition of alloys include Mo-Nb,³⁵⁾ Ni-Ta,³⁶⁾ and Ni-Nb.³⁶⁾

As for electrodeposition of compounds containing refractory metals, the earliest work was concentrated on the production of carbides, largely for the purposes of generating abrasion-resistant coatings.^{34,37)} Coatings of titanium diboride have been deposited both to impart corrosion resistance against attack by liquid metal^{38,39)} and to offer abrasion resistance.⁴⁰⁻⁴²⁾ More recently, investigators have begun studying the associated electrode processes.⁴³⁾ Generation of tungsten carbide coatings has been driven by the desire to form material for use in abrasion-resistant coatings.^{34,44,45)} Studies of electrochemical fundamentals have begun.⁴⁶⁻⁵⁰⁾ Other refractory metal compounds whose electrosynthesis has been reported include zirconium diboride,^{48,50)} chromium boride,⁵¹⁾ molybdenum disilicide,⁵²⁾ tantalum carbide⁵³⁾ and molybdenum carbide.⁵⁴⁾ More recently, attention has turned to a broader array of materials syntheses, including metal matrix composites⁵⁵⁾ and refractory-metal oxides containing controlled subvalent forms of the refractory-metal

ion.⁵⁶⁾ In the case of the latter, electrosynthesis from fused salts has facilitated the generation of compounds otherwise produced thermochemically at high temperatures and high pressures.

An alternative to electrosynthesis of refractory-metal oxide compounds is anodization. The distinction between the two processes is that anodization is a process for the faradaic oxidation of elemental metal present as the anode substrate. In contrast, electrosynthesis is a process for the faradaic discharge of both metal and oxygen (both present in the electrolyte) to form a compound on an electrode substrate. While refractory metals can be anodized in aqueous media, fused salt anodization offers certain advantages in product quality, both in terms of chemical composition and microstructure.⁵⁷⁾

4.4 Cryogenic Electrolytes

Cryogenic electrolytes do not appear in contemporary metallurgical technology. Electroplating of elemental refractory metal from subambient and cryogenic liquids has been reported, but not at the commercial scale.⁵⁸⁾ At the time of this writing the viability of electrosynthesis of compounds in cryogenic media is under investigation in the author's laboratory at the Massachusetts Institute of Technology.⁵⁹⁾ Reference is made below to future prospects for electrochemical processing in these media.

4.5 Future Directions

When viewed in the context of materials processing, fused salt electrolysis has many fine attributes. However, unresolved technical issues continue to impede its further commercialization. These include low cathode current efficiency, anode effect (restricted to fluoride-based electrolytes processing oxide feed), purity of metal product, corrosion of cell components, and heat balance of the cell. Losses of power efficiency can be traced to the fact that the refractory metals exhibit multiple valency in these melts. This can lead to redox looping or parasitic reaction of subvalent ions with metal product. Furthermore, as mentioned above, most cells produce solid metal. Solid electrodeposits obtained in molten salts are typically dendritic or powdery, but rarely smooth, especially when the metal is of high purity. To deal with multiple valency one can optimize bath chemistry,^{60,61)} use a diaphragm to separate specified ions from one another while allowing selected mass transfer between regions of the cell, an approach very popular with designers of titanium electrowinning cells,⁶²⁻⁶⁴⁾ or invent divided cells featuring staged reactions.⁶⁵⁾ The morphological problem has been attacked in some cases by employing molten metal cathodes (Refs. 66 and 67, for example). The use of leveling agents, while potentially beneficial, has been examined for electroplating,²⁰⁾ but evidently not for electrowinning where the goal is to produce metal of the highest purity.

Besides the strictly technical issues there are other concerns. For example, in designing new electrolytic processes one must look carefully at capital costs as well as operating costs. If fused salt electrolysis is to compete effectively with nonelectrochemical materials processing, steps must be taken to design flowsheets with a minimum number of unit operations. More attention must be paid to environmental, health and safety issues. Clearly, the ecological soundness of new processes must be considered from the time of their invention. It is the opinion of this author that electrolysis is uniquely positioned

to tackle these problems which, if left unsolved, threaten to cripple the metals industry.

From the perspective of a technology capable of generating advanced materials, fused salt electrolysis looks attractive.⁶⁸⁾ Advanced materials are characterized not only by their specialized chemistries, *i.e.*, purity, doping level, etc., but also by their tailored microstructures, which fused salt electrolysis has the potential to generate. These include thin films, epitaxial layers, powders, and various nonequilibrium structures. Powders of a number of refractory metals and their compounds have been produced by fused salt electrolysis: titanium,⁶⁹⁻⁷¹⁾ niobium,⁷²⁾ tantalum,⁷²⁾ chromium,⁷⁰⁾ tungsten,^{70,73)} tungsten carbide⁴⁵⁾ and in general.⁷⁴⁾ As for nonequilibrium structures, fused salt electrolysis has the capacity to produce metastable phases, compositionally graded microstructures, and compositionally modulated microstructures. To date there has been very little use of fused salt electrolysis to generate nonequilibrium structures of refractory metals. There are isolated reports in the literature of metastable phase formation⁷⁵⁾ and deposition of single crystals with preferred orientation.⁷⁶⁾ These results were restricted to refractory *metals* and not their *compounds*. Among the layered structures reported in the literature is molybdenum carbide on diamond.⁷⁷⁾ Overall, this field is severely underexploited.

Earlier in this article liquefied gases were named as a class of inorganic electrolytes. What is their potential role in the electrosynthesis of advanced materials? What is to be gained by processing in such media? First of all, these electrolytes are anhydrous and chemically stable. Thus, in principle, one should be able to electrodeposit elements that cannot be plated from aqueous solutions. Secondly, the processing temperatures are very low with the result that thermal damage to the substrate is minimized. Thirdly, at these low processing temperatures the kinetics of deposition are expected to be controlled by charge transfer rather than by mass transfer. This tends to favor surface smoothing and the production of coatings of uniform thickness; alternatively, the process can be said to have good throwing power. There are other microstructural consequences. Low temperature processing enhances nucleation and restrains growth. Deposits are expected to be microcrystalline, or perhaps even amorphous. If sharp interfaces are sought, electrodeposition at cryogenic temperatures is unique in that it is a process operative at low temperatures and driven by low energy. Diffusion distances are extremely short; diffusion times are extremely long. These are precisely the process characteristics necessary for materials processing at nanoscale dimensions. Fourthly, the preparation of the electrolyte involves the condensation of a gas with the result that the solutions have the potential to be uncommonly free of contaminants. This puts cryogenic electrolytes at an advantage over high temperature electrolytes which tend to dissolve, albeit sparingly, even the most refractory crucibles. When high purity is a concern, cryogenic electrolytes are excellent processing media.

As a consequence of the fact that the data base for these media is almost nonexistent cryoelectrodeposition has been conducted to date on an empirical basis to a large extent. Vital information such as compound solubilities and decomposition potentials, which are essential in describing the chemistry and electrochemistry of the process, is unreported. Even the state of the metallic ion in solution is unknown. There is much to be done in researching the physical chemistry of these liquids before commercial viability can be properly assessed.

4.6 Conclusion

While molten salt electrolysis has proven its viability in metallurgical processing, in the opinion of this author the technological applications of electrochemical processing in nonaqueous media have not been exhausted. As an example, the electrosynthesis of refractory metal compounds in cryogenic electrolytes represents enormous commercial potential. Finally, as environmental quality standards rise beyond the capabilities of classical metals processing technologies to comply, electrolysis may prove to be the only acceptable route from ore to metal.

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