ELECTRODEPOSITION FROM MOLTEN SALTS

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ABSTRACT. The principles of electrodeposition are highlighted and
attention focused on the electrodeposition of the refractory (transition) metals. The advantages and disadvantages of molten salts for
electrodeposition and such complications as volatilization, disproportionation, polymerization and precipitation, which are particularly
important in the case of the refractory metals, are discussed, along
with the kinetics and the forms of the electrodeposits.

1. INTRODUCTION

The electrodeposition of metals (and non-metals and compounds, a topic
of growing relevance) from molten salts is very important technologi-
cally. Although at the moment we are seeing a contraction of smelt-
ing capacity in the Western world in, for example, the case of alumi-
num, the use of molten salt electrolysis for specialized high-technology
applications is likely to grow.

It is impossible to cover comprehensively the wide range of elec-
trodeposition processes employing molten salts which exist for most,
if not all, of the metals of the periodic table. In this chapter
therefore, I will highlight the principles and focus attention on
the electrodeposition of the refractory (transition) metals. The im-
portance of these nine elements of groups IV, V and VI of the periodic
table in various existing or potential high-technology applications has
motivated much research on electrolytic routes involving molten salts
in recent years.

Electrodeposition or electrolysis may be subdivided into electro-
winning, electrorefining, electroplating and electroforming. In elec-
trowinning the object is to obtain the metal in a pure or semi-pure
form by electrolytic extraction from a compound of the metal dissolved
in the molten salt. In electrorefining the metal is transferred by
electrolysis from an impure anode to a pure cathode and the impurities
left in the anode residue as metals are the molten salt solution as
ions. In electroplating the aim is to electrodeposit a thin, coherent,
adherent, impervious coat of metal on a substrate to protect it from
corrosion/erosion. In electroforming, which is an extension of elec-

troplating, a thick plate is electrodeposited on a disposable substrate, to produce an article with independent integrity.

The first of these differs fundamentally from the others in that gas is usually produced at the anode. Although the formation of coherent metal is less important in this case, it is nevertheless a desirable objective of research to improve the forms of electrowon deposits in order to avoid deleterious post-electrolysis separations.

2. ADVANTAGES AND DISADVANTAGES OF MOLTEN SALTS FOR ELECTRO-DEPOSITION

Molten salts possess a number of unique properties which facilitate efficient electrodeposition.

The most common solvent components are the alkali and alkaline-earth halides and these all possess very negative Gibbs free energies of formation. In electrochemical terms this implies a high decomposition voltage. In practice some lowering of this decomposition voltage may take place when the activity of the deposited solvent metal is lowered either through interaction with the solvent cations or through its interactions with the electrode substrate, or both.

Overpotentials due to cathodic polarization are often small. This is desirable from the point of view of energy efficiency but mass transfer-controlled processes generally lead to dendritic deposits which are difficult to separate from occluded frozen melt after electrolysis.

The good ionic conductivities ($2-9 \, \text{Ωcm}^{-1}$) of molten alkali and alkaline earth metal salts and their mixtures are another desirable feature, both from the point of view of power losses and of temperature control by Joule heating.

Molten salts are powerful solvents for inorganic materials. This can be a disadvantage however, for instance in limiting the choice with regard to the materials chosen as cell containers.

The use of high temperatures per se must be considered a disadvantage. Apart from the problems mentioned above, an extra energy expenditure must be incurred to keep the systems in a liquid state. The hydrolysis of many of the hygroscopic salts employed as solutes and solvents can cause difficulties when their use is required on a large scale. Purification is often a prolonged process which necessitates considerable peripheral handling facilities. Other disadvantages arise from the high volatility of (e.g.) many of the high oxidation state refractory metal halides (particularly chlorides). Specific disadvantages arise from anodic reactions where energy considerations are often in conflict with efforts to maintain cathode product purity. For example, the substitution of oxygen evolution at an inert anode by $\text{CO}_2$-$\text{CO}$ evolution at a carbon anode saves electrical energy but $\text{CO}_2$/$\text{CO}$ may back-react with the refractory metal deposited on the cathode to produce carbides. Finally, if it is necessary to divide the electrolysis cells into anode and cathode compartments by means of porous ceramic diaphragms, corrosion of the metals by the melts is facilitated by the large surface areas involved.