

## **METALLURGICAL ELECTROCHEMISTRY: THE INTERFACE BETWEEN MATERIALS SCIENCE AND MOLTEN SALT CHEMISTRY**

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### **ABSTRACT**

Even though molten salt electrolysis finds application in the primary extraction of metals (electrowinning), the purification and recycling of metals (electrorefining), and in the formation of metal coatings (electroplating), the technology remains in many respects underexploited. Electrolysis in molten salts as well as other nonaqueous media has enormous potential for materials processing. First, owing to the special attributes of nonaqueous electrolytes electrochemical processing in these media has an important role to play in the generation of advanced materials, *i.e.*, materials with specialized chemistries or tailored microstructures (electrosynthesis). Secondly, as environmental quality standards rise beyond the capabilities of classical metals extraction technologies to comply, molten salt electrolysis may prove to be the only acceptable route from ore to metal. Growing public awareness of pollution from the metals industry could stimulate a renaissance in molten salt electrochemistry. Challenges facing metallurgical electrochemistry as relates to the environment fall into two categories: (1) improving existing electrochemical technology, and (2) developing clean electrochemical technology to displace current nonelectrochemical technology. In both instances success hinges upon the discovery of advanced electrode materials. Thus, both for the electrochemical generation of advanced materials and the ecologically sound extraction of metals, the close coupling between materials science and molten salt chemistry is manifest.

### **INTRODUCTION**

Metallurgical electrochemistry has its beginnings in the early nineteenth century almost immediately following the announcement by Alessandro Volta of the discovery of a continuous source of electric current [1]. Sir Humphry Davy employed this new found source of electricity to decompose molten potash and isolate elemental potassium [2]. In doing so he demonstrated for the first time the feasibility of extraction of metal by electroreduction. As molten salt chemists we should take pride in the fact that Davy conducted his classical experiments in molten salts; only by doing so was he able to produce in elemental

form the alkali and alkaline earth metals.

Metallurgical electrochemistry has certainly come a long way since the middle of the nineteenth century! Molten salt electrolysis is used in the primary extraction of metals (electrowinning), the purification and recycling of metals (electrorefining), and in the formation of metal coatings (electroplating). For some metals, such as magnesium, electrochemical processes, e.g., Dow and I.G. Farben, compete with thermochemical processes, e.g., Pidgeon and Magnetherm, for the primary extraction of the metal. For other metals, such as aluminum, to this day an electrochemical process, i.e., Hall-Héroult, is the only commercially viable means for extraction of the metal.

In the light of the above, some might be tempted to consider molten salt electrolysis a "mature" field, one in which not much new can be expected to occur. This author contends that such opinion both ignores some of the important forces acting on the world metals industry and fails to recognize some of the new opportunities emerging in the broader field of materials science. The responses to these challenges will lead to the development of new molten salt technologies and stimulate a virtual renaissance of scientific research, perhaps on a par with that which accompanied the major research program sponsored by U.S. Atomic Energy Commission in the 1950's.

#### ECOLOGICALLY SOUND METALS PRODUCTION

The growing public awareness of industrial waste may prove to be a boon for metallurgical electrochemistry. Challenges as relates to the environment fall into two categories. First, there is the need to improve existing electrochemical technology in such cases where there is a pollution problem. Secondly, there is the need to develop clean electrochemical technology to displace current nonelectrochemical technology which may be incapable of meeting tighter specifications.

The extraction of aluminum in the Hall-Héroult cell is representative of the first category of challenge. It has long been recognized that the principal obstacles to improving the productivity of the Hall cell derive from limitations imposed on its design by the lack of suitable materials of construction. Historically, the driving force behind the quest for the discovery of materials for a nonconsumable anode, wettable cathode and ledge-free sidewall has been the desire to improve the energy efficiency of the Hall cell. In time, environmental concerns may well become the dominant driving force. Specifically, concerns over the consumption of carbon (0.45 kg carbon / kg aluminum) and the attendant production and emission of CO and CO<sub>2</sub> (greenhouse effect), concerns over fugitive emission of fluorine bearing compounds (pollution), and the storage and disposal of spent potliner which contains cyanide (contamination of groundwater) have all prompted renewed effort to discover alternatives to current industrial practice. Up to this point the discussion has been restricted to the effects of the use of carbon only in the electrolysis cell proper. There are concerns as well in connection with the use of carbon in other unit operations, for example, in the production of the various cell elements themselves. Anode manufacture involves a so-called prebake operation where coal tar, pitch and other ingredients are fired at elevated temperatures for extended periods of time. Among the "by products" of this process are PNA's, PCB's, SO<sub>2</sub>, and sundry volatiles.

In spite of intensive effort, no fully satisfactory material has been found for any of the key cell elements named above. It is clear that in the light of this failure a totally different approach needs to be adopted. Specifically, the problem must be posed in an entirely different way, a way that considers the peculiar conditions in an industrial cell during operation. Up to now people have examined the cell in a piecemeal fashion which has ignored important cross effects

as well as transients. Such fragmentation has its consequences: failure modes are not being anticipated and potential solutions are not being recognized. This author has coined the term, "dynamic materials system," to describe a different image of the Hall-Héroult cell [3]. The consequent analysis has led to the enunciation of a new set of criteria for the selection of anode materials. The result of this work has been the discovery not only of materials previously ignored for this application but also of new methods of operating Hall-Héroult cells.

The problem described above is not unique to the aluminum industry. Throughout the metallurgical industries concerns are mounting over the use of industrial carbon and the consequences for the workplace and the environment. This introduces the second category of challenge for metallurgical electrochemistry, namely, the development of carbon-free extraction technology to displace existing carbothermic technology. Success hinges on our ability to discover nonconsumable electrodes (carbon-free, of course) and suitable electrolyte chemistries capable of sustaining economically viable metal production rates. It may be that carbon-free metal extraction technology is the greatest challenge in all of chemical metallurgy. It is this author's opinion that as environmental quality standards rise beyond the capabilities of classical metals extraction technologies to comply, electrochemical processing may prove to be the only acceptable route from ore to metal. Put another way, the search for new materials to save an existing technology may well result in the discovery of radically new (i.e., potentially displacing) technology. Environmental conservancy and commercial profitability need not be viewed as mutually exclusive.

At the Massachusetts Institute of Technology this author has begun a major initiative to develop a suite of environmentally sound metal extraction technologies based upon direct electrolysis at very high temperatures. The concept, called pyroelectrolysis, uses molten oxides as electrolytes. Operating temperatures are high enough that the product metal is liquid, as is the case with almost all other metal-producing electrolytic extraction technologies. In deference to industrial ecology, the process is designed to be carbon-free, i.e., carbon is not used as a reagent in the preparation of cell feed or as a constituent of the electrodes in the electrolytic cell. The gas by-product is pure oxygen. With fewer unit operations, the process offers the prospect of lower capital cost than conventional extraction technologies now in place. Pyroelectrolysis appears to be broadly applicable to the extraction of a wide range of metals, including refractory metals, transition metals (Fe, Co, Ni and Mn), lanthanides (rare earth metals) and actinides (uranium, in particular). As for specific metals, work is currently under way to determine the feasibility of direct electrolytic extraction of titanium from  $TiO_2$ . Titanium was chosen for two reasons. First, this is the most abundant of the refractory metals and has the greatest near-term market potential. Secondly, all currently employed technologies for the extraction of titanium, i.e., Kroll, Hunter, and molten chloride electrolysis, are directly or indirectly electrolytic technologies: in order to be recycled the metal reductant in the Kroll and Hunter processes is recovered by molten salt electrolysis. Thus, the capital and operating costs of electric power are already built into all titanium extraction technologies. Against this backdrop the economics of pyroelectrolysis of titanium look very attractive. Direct electrolytic steelmaking is also under study, with special focus on ferroalloys such as ferrochrome and ferromanganese.

#### ELECTROSYNTHESIS OF ADVANCED MATERIALS

From the perspective of a technology capable of generating advanced materials, electrochemical processing looks extremely attractive. Advanced materials are characterized not only by their specialized chemistries, i.e., purity, doping level, etc., but also by their tailored microstructures, which

electrolysis has the potential to generate [4]. These include thin films, epitaxial layers, powders, and various nonequilibrium structures such as metastable phases, compositionally graded microstructures, and compositionally modulated microstructures. Very little has been done in the electrosynthesis of nonequilibrium microstructures.

It is evident from a consideration of the emf series in water that nonaqueous media must be used if one is to process reactive elements. The candidate electrolytes in this regard are molten salts and liquefied gases. The latter do not appear in contemporary materials processing technology, although this author has reported electroplating of metals in cryogenic media such as liquefied hydrogen chloride [5] and has claimed the cryogenic electrosynthesis of compounds [6]. What is the potential role of cryogenic electrochemistry in the synthesis of advanced materials? The answer to this question can be found by considering the unique attributes of cryogenic liquids. First, they are nonaqueous and chemically rather stable, and so, 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 molten salts 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 liquids is almost nonexistent cryoelectrodeposition has been conducted to date on an empirical basis to a large extent [5, 6]. 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.

#### SUMMARY

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. The pyroelectrolytic extraction of metal in molten oxide electrolytes and the electrosynthesis of advanced materials in cryogenic electrolytes both represent enormous commercial potential. Ultimately, for molten salts, environmental factors may prove to stimulate a much higher level of research with its attendant intellectual and commercial rewards.

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## REFERENCES

1. Volta, A.: "On the electricity excited by the mere contact of conducting substances of different kinds," *Phil. Trans.*, 1800, Vol. 90, No. 2, pp. 403-431.
2. Davy, H.: The Bakerian Lecture, "On some new Phenomena of chemical Changes produced by Electricity, particularly the Decomposition of the fixed Alkalies, and the Exhibition of the new substances which constitute their bases; and on the general Nature of alkaline Bodies," *Phil. Trans.*, 1808, Vol. 98, pp. 1-44.
3. Sadoway, D.R.: "A Materials Systems Approach to Selection and Testing of Nonconsumable Anodes for the Hall Cell," in *Light Metals 1990*, C.A. Bickert, editor, TMS, Warrendale PA, 1990, pp. 403-407.
4. Sadoway, D.R.: "Fused Salt Electroplating," in *Electrodeposition Technology. Theory and Practice*, Proceedings Volume 87-17, L.T. Romankiw and D.R. Turner, editors, The Electrochemical Society, Pennington NJ, 1987, pp. 397-413.
5. Rose, R.M. and Sadoway, D.R.: "Cryoelectrodeposition," U.S. patent no. 4,517,253, May 14, 1985; also Can. patent no. 1,246,001, December 6, 1988.
6. Sadoway, D.R. and Rose, R.M., inventors: Massachusetts Institute of Technology, assignee, "Cryoelectrosynthesis," U.S. patent, no. 4,971,663, November 20, 1990.