

A MATERIALS SYSTEMS APPROACH TO SELECTION AND TESTING OF
NONCONSUMABLE ANODES FOR THE HALL CELL

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Abstract

Based upon a global analysis of the Hall cell as a dynamic materials system a set of selection criteria has been enunciated in order to identify materials for use as nonconsumable anodes. The result has been the discovery not only of materials previously ignored for this application but also of new embodiments of anode design. Beyond the question of choice of anode material, a much broader framework for success/failure analysis has been constructed so that such factors as anode design and anode test conditions can be systematically studied.

Introduction

The principal obstacles to improving the energy efficiency and overall productivity of the Hall-Heroult cell derive from limitations imposed on its design by the lack of suitable materials of construction. Alternatively, the discovery of materials for a nonconsumable anode, wettable cathode and ledge-free sidewall would enable changes in cell design and operating practice with attendant improvements in energy and resource utilization. This paper is confined to a consideration of the issues associated with the nonconsumable anode.

In a previous publication this author in collaboration with McLeod, Lihmann and Haggerty had asserted that "the search for inert anode materials has proved to be one of the most difficult challenges for modern materials science" (1). Indeed, in spite of enormous effort no material has proven to be fully satisfactory in this application (2). Furthermore, the article cited above had expressed the opinion that a totally different approach had to be adopted (1). Specifically, it was felt that the problem had to be posed in a way that considered the conditions in an industrial cell during all phases of operation. The term, "dynamic materials system," was coined to describe this image of the Hall-Heroult cell. The consequent analysis was based upon an assessment of the thermodynamics and kinetics of the process viewed from a global perspective. On the basis of this approach a new set of criteria was enunciated for the selection of anode materials (1). 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 cells.

In an effort to validate the materials selection criteria and to demonstrate the viability of the design concepts, tests have been conducted at MIT in

cells at the 1-ampere scale and in the research and pilot facilities of an American aluminum producer at the scales of a 10-ampere cell and a 100-ampere cell. In the light of the results from these tests and in response to further analysis the criteria for materials selection have been revised. As well, a much broader framework for success/failure analysis has been constructed. The purpose of this paper is to state the revised set of materials selection criteria and to describe how it fits into this broader framework.

Literature

In a pair of articles by Billehaug and Øye the attempts to discover a nonconsumable anode prior to 1980 have been reviewed (3,4). Since then, the major efforts have been the following. Alcoa examined a variety of mixed oxides and cermet materials. The ceramic phase was nickel ferrite, while the metal phase was ferronickel or copper. A prime example was the cermet consisting of 17 weight per cent copper and 83 weight per cent mixed oxide composed of 51.7 weight per cent NiO and 48.3 weight per cent Fe₂O₃ (5). This work was terminated by Alcoa in 1985 at which time the Battelle Pacific Northwest Laboratory began to study these materials (6). Great Lakes Carbon tested cermets in which the ceramic phase was composed of hexagonal ferrite such as BaNi₂Fe_{1.5-8.4}Sb_{0.16}O₂ and the metal phase was composed of, for example, Ni_{0.7}Cu_{0.3} (7). Moltech, formerly ELTECH Electrosearch, has been investigating the behavior of a coating composed of cerium oxyfluoride (8). Lastly, at MIT there is a research program which began as a study of mixed oxide materials such as nickel, cobalt and manganese ferrites under carefully controlled synthesis and service conditions (9) and over time has come to reject these ferrite chemistries in the light of the enunciation of the aforementioned selection criteria (1). Most recently the work at MIT has concentrated on anode embodiments of the form of an oxidized reaction layer on a metal monolith.

Materials Selection

Figure 1 depicts a representation of the service conditions of a nonconsumable anode in a Hall-Heroult cell as viewed in the context of the global analysis described in the introduction of this article. Actually, Figure 1 has been drawn with specific reference to the anode embodiment currently under investigation in this laboratory, i.e., a metal monolith covered by a layer of oxide. This layer is

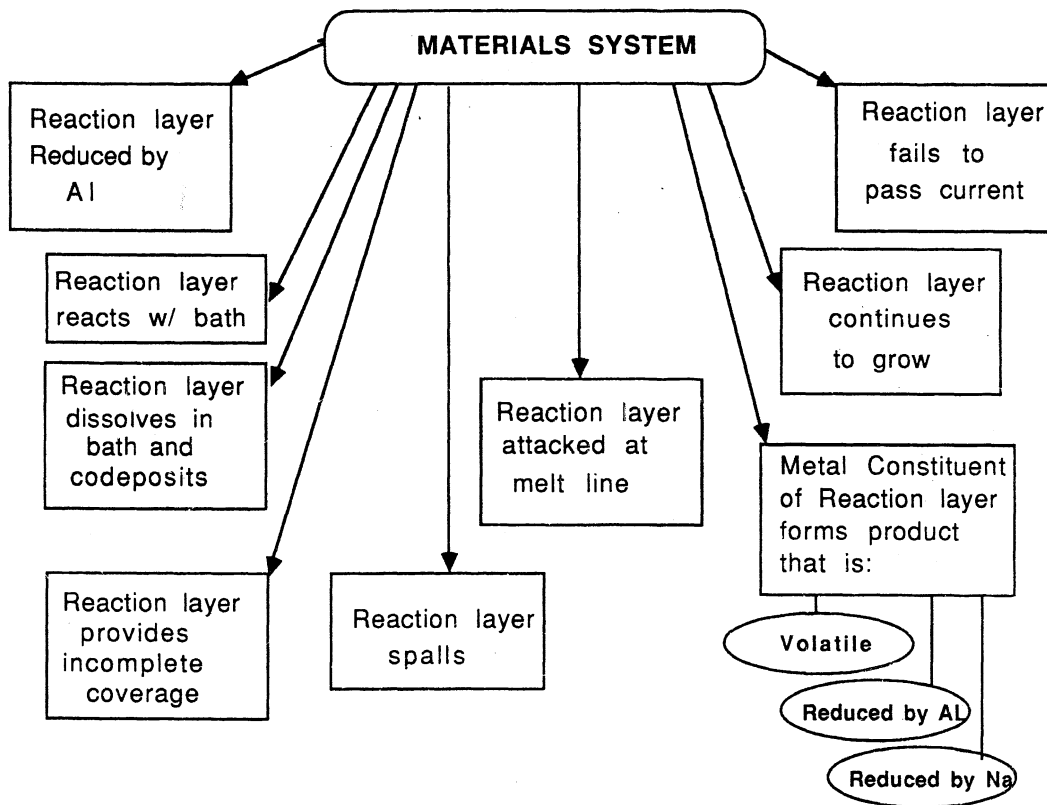


Figure 1: Stages in Materials Selection.

termed a reaction layer because it is the product of a chemical reaction between the metal and the products of electrolysis, e.g., evolving oxygen, or the electrolyte or both. To use Figure 1 more generally the reader should interpret the words, "reaction layer," to mean "candidate anode material." The criterion in each box is described below, beginning at the upper left-hand corner and moving counterclockwise to the upper right-hand corner.

Reaction layer reduced by aluminum

This is the so-called crucible criterion, i.e., is it possible to contain molten aluminum in a crucible constructed of the candidate material? Although conditions are highly oxidizing in the vicinity of the anode, the electrolyte does contain dissolved aluminum. This may not be fully consumed by the oxygen evolving on the anode. Previously, this criterion was dubbed the metal - metal oxide exchange reaction (1). Failure of a candidate anode material to satisfy this criterion results in its consumption by aluminothermic reduction.

Reaction layer reacts with bath

This criterion considers the reaction of the candidate oxide with the electrolyte. Typically, the reaction employed in this test is



as AlF_3 is the most corrosive component of the electrolyte.

Reaction layer dissolves in bath and codeposits

This criterion considers the direct dissolution of the candidate material into the electrolyte and subsequent electrochemical reduction at the cathode where codeposition with aluminum occurs. Failure to satisfy this criterion results in consumption of the anode along with contamination of the metal product. To test whether a candidate material will codeposit with aluminum requires a knowledge of the emf series in the electrolyte used in the Hall cell.

Reaction layer provides incomplete coverage

This criterion recognizes that in the case of the specific embodiment of an oxide layer on metal it is imperative that the oxide layer be crack free. Otherwise, the metal beneath is subject to direct attack by the bath. This condition is exacerbated when the electrode is anodically polarized as this can promote direct electrostripping of the metal.

Reaction layer spalls

As above, this criterion applies to the specific embodiment of an oxide layer on metal. Even if the chemistry and electrochemistry are acceptable the reaction layer may fail due to spalling. One must design the anode and generate an initial reaction layer so as to reduce the magnitude of stresses that promote spalling.

Reaction layer attacked at the melt line

Molten salts are particularly corrosive at the free surface, i.e., the gas-liquid interface. This problem can be addressed through anode design. For example, by establishing, in service, contact angles of critical value it is possible to prevent certain harmful corrosion mechanisms from operating.

Metal constituent of reaction layer forms a product that is volatile

If a metal constituent of the oxide reaction layer forms a fluoride that has a high vapor pressure, then this metal fluoride will evaporate from the melt. Indirectly, this consumes the anode.

Metal constituent of reaction layer forms a product that is reduced by aluminum

Earlier the crucible criterion tested the vulnerability of the oxide to aluminothermic reduction. However, it may be that the oxide is stable in the presence of aluminum, but that the fluoride of the same metal, for example, is less stable than aluminum fluoride. The result is aluminothermic reduction of this compound. An example of such a reaction is



where the underline on the metal product, M, denotes its dissolution in the molten aluminum cathode to form a liquid metal alloy.

Metal constituent of reaction layer forms a product that is reduced by sodium

Earlier the crucible criterion considered only metallothermic reduction of the candidate metal oxide by aluminum, and not by sodium. This was in spite of the fact that at high current density sodium is coreduced with aluminum at the cathode. However, Al_2O_3 is much stabler than Na_2O . In contrast, when it comes to fluorides, the situation is different: NaF is very stable, as is AlF_3 . As a result the metallothermic reduction of metal fluoride by sodium is an important consideration. One possible reaction is the following:



where the underline on the metal product, M, denotes its dissolution in the molten aluminum cathode to form a liquid metal alloy.

Reaction layer continues to grow

This criterion applies to the specific embodiment of an oxide layer on metal. Even if the oxide-electrolyte system is stable with respect to all other physicochemical considerations the reaction layer will fail if its thickness rises beyond a critical threshold at which mechanical stresses between the oxide and metal are great enough to cause the oxide layer to lose its integrity. One must consider mechanisms of oxide film growth in this regard.

Reaction layer fails to pass current

This criterion applies to the specific embodiment of an oxide layer on metal and in some respects is closely related to the preceding criterion. Even if the oxide-electrolyte system is stable with respect to all other physicochemical considerations the reaction

layer will fail if its electrical resistance rises beyond a critical threshold. To prevent this it is necessary to keep the ionic conductivity of the oxide at a minimum. Ideally, the oxide should be an electronic conductor.

In applying this criterion one must be careful to consider the system in its service conditions, i.e., polarized, passing direct current in a specified direction, oxygen evolving on the oxide-electrolyte interface, etc. Materials systems that in equilibrium with the Hall cell environment appear unsatisfactory may in fact be made to achieve a state of dynamic stability when placed under operating conditions, i.e., far from equilibrium.

Anode Element

In the global analysis of the Hall cell, the choice of anode material is meaningful only with reference to a specific design of anode element. In other words, the success of any choice of materials system is closely linked to the design of the anode element itself. Here, the term anode design includes not only the physical shape of the member but also the operating conditions for which it is intended. Figure 2 depicts some of the associated considerations.

Shape

Current Distribution. The shape of the anode is very important as it determines the local values of operating conditions. For example, current density cannot be presumed to be simply the value of total cell current divided by the area of the anode-electrolyte interface. With some candidate materials systems the current distribution can be expected to be highly variable.

Gas Evolution. Gas evolution is highly dependent upon the shape of the anode. The rate of gas evolution is governed primarily by current density (see below). However, the shape of the electrode determines the gas flow conditions at any given rate of evolution, e.g., extent of local variation. As the evolving oxygen can be critical in stabilizing the anode one must at the outset design an element that will emulate these beneficial conditions as they can be expected to occur on an industrial scale.

Operating Conditions

No discussion of the choice of anode material is complete without an explicit specification of the operating conditions in which the material is intended to perform.

Current Density. Current density can affect the stability of the reaction layer in several ways. As mentioned above, current density governs the rate of oxygen evolution on the anode. Among other things, high oxygen evolution rates tend to oxidize any dissolved elemental aluminum and thereby protect the anode from attack by direct aluminothermic reduction. Previously, there was reference to this effect as an example of how recognition of the kinetics of an operating Hall cell could retain materials for use as anodes that would have been rejected on the basis of thermodynamic considerations alone (1).

Bath Composition. Bath composition can greatly influence the performance of a candidate anode material. Clearly, the corrosivity of the bath is highly dependent upon such factors as bath ratio,

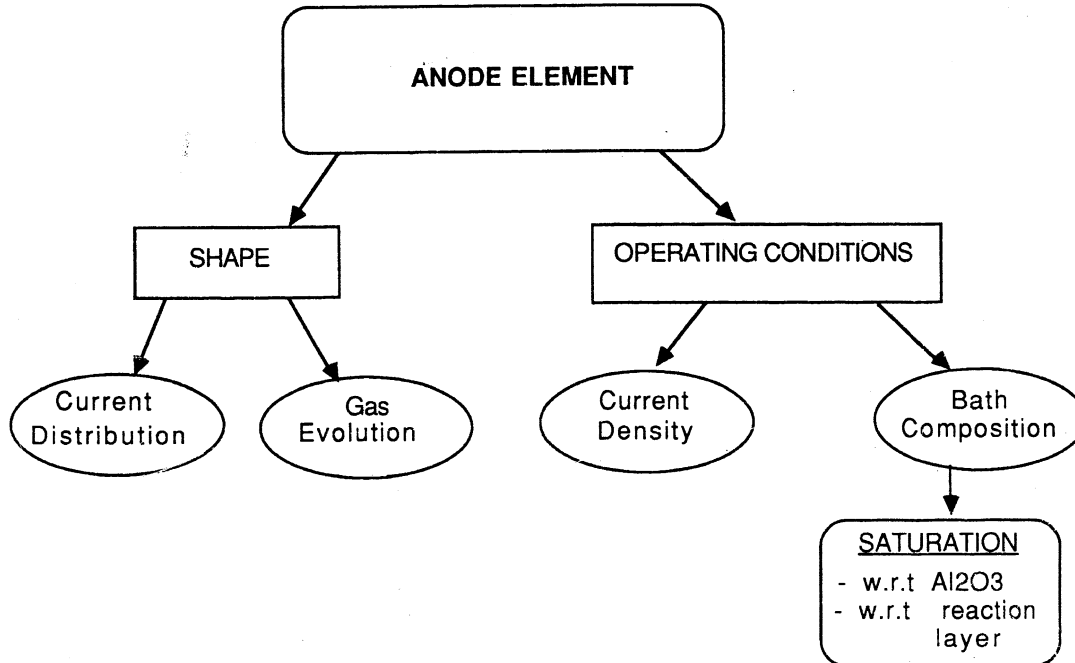


Figure 2: Stages in Anode Design.

alumina content, and the concentration of the oxide compound comprising the reaction layer.

Broader Framework for Success/Failure Analysis

Figure 3 depicts how Figures 1 and 2 fit into the broader framework for success/failure analysis. The salient feature of Figure 3 is the distinction between the anode being tested and the anode as designed, where the latter refers to both the choice of material and the intended operating conditions. In other words, laboratory tests of anode materials can be biased, favorably or unfavorably, by the choice of test element and test conditions.

With reference to the specific embodiment of the reaction layer on metal, there are two sets of issues to consider. These can be classified as problems associated with building the initial reaction layer and problems associated with maintaining the reaction layer in service, which includes steady-state operation as well as transient conditions, e.g., startup, shutdown, and power interruption. The details of these will be the subject of a future publication.

As for the test conditions, these are some the relevant questions. Should one fit the test electrode with a dielectric sleeve to limit contact between bath and electrode and thereby define the active electrode area? Should the bath be saturated with respect to alumina?

Testing of Candidate Anodes

On the basis of criteria enunciated previously (1), materials systems consisting of a reaction layer of metal oxide on a monolith of elemental metal were selected. Anode elements were designed and tested in cells at MIT at the scale of 1 A and in the research and pilot facilities of an American aluminum producer

at the scales of a 10 A and 100 A. The results were disappointing as the initial choices of materials proved to be unsatisfactory for use as anodes. However, these tests identified failure modes that had not been anticipated by the earlier analysis. This article presents the revised materials selection criteria along with a much broadened success/failure analysis. Furthermore, these tests pointed out the need to validate by experiment that candidate materials satisfy the criteria. Owing to inconsistencies and errors one cannot rely completely on the database alone.

In the light of the revisions described herein, new materials systems consisting of a reaction layer of metal oxide on a metallic monolith have been selected. In addition, the design of test elements has been revised. Further cell testing is planned at the laboratory and pilot scales.

Summary

In contrast to all other approaches which are based upon protecting the anode against its service environment, the approach described herein is based upon a radically different concept. It is precisely through chemical and electrochemical reaction with the service environment that the anode exists and its viability is maintained. The nonconsumable anode derived from the analysis presented in this article thrives in the Hall cell environment.

The implementation of this approach calls for an enumeration of failure modes. Only by formally listing all possible failure modes can one be assured of having taken steps to defend against them. Alternatively, to know how to operate a candidate anode system successfully requires that one know all the failure modes and be convinced that none of them is active.

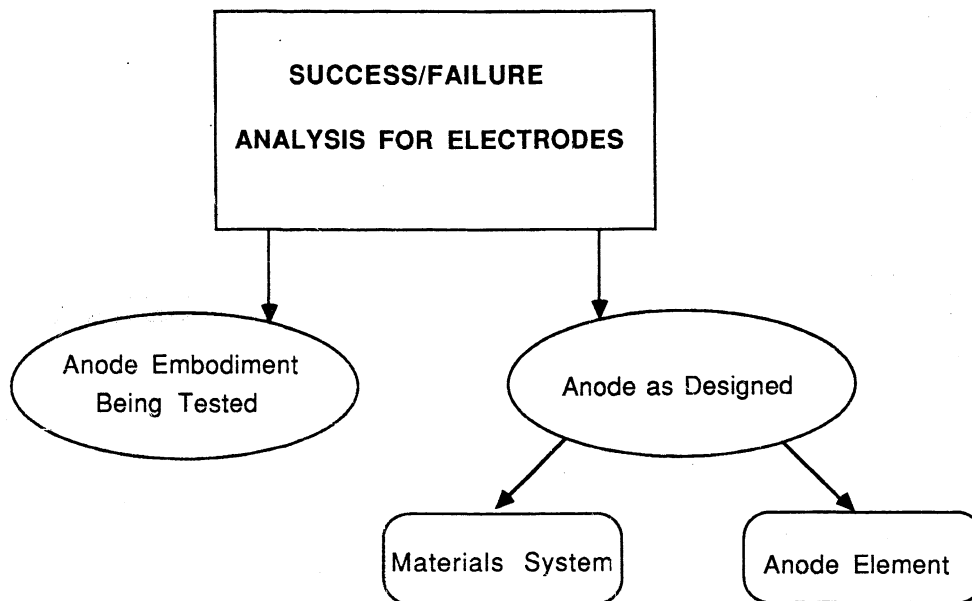


Figure 3: Broadened Framework for Success/Failure Analysis.

Finally, the results of this investigation are of value also in the design of new electrochemical processes for the extraction of other reactive metals.

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