

Contribution of Electricity to Materials Processing: Historical and Current Perspectives

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Editor's Note: Antoine Allanore presented the material in this paper at the TMS 2012 Annual Meeting & Exhibition as the co-recipient of the Vittorio de Nora Prize for Environmental Improvements in Metallurgical Industries. Also receiving the award was Jim Yurko. Allanore and Yurko's mentor for this research, Donald Sadoway, the John F. Elliott Professor of Materials Chemistry, Massachusetts Institute of Technology, is the Extraction & Processing Division Distinguished Lecturer at TMS2013 and is highlighted in the "Meet a Member" article in this issue of *JOM*. The de Nora Prize recognizes outstanding materials science research and development leading to the reduction of environmental impacts, particularly greenhouse gas emissions.

INTRODUCTION

Most major materials extraction processes are more than 100 years old, developed at a time of limited awareness of their environmental impact and the issue of resources limitations. In this context, it is proposed to look back at materials processes progress in parallel with the history of electric power generation. This overview reveals that

electricity became a key energy vector for chemical and materials processing in less than a century. The role of electricity in the production of the highest tonnage metals (i.e., aluminum and steel) proved to be crucial, leading to higher productivity and lower energy consumption for both metals. Finally, a review of the recent developments in electrolytic steel shows that new electricity-based processes are possible, offering the opportunity for a symbiosis between future carbon-free power generation and materials processing.

THE AVAILABILITY OF ELECTRICITY: A TIMELINE

The impact of electricity on worldwide technological development is hard to summarize. The upper part of Figure 1 presents the timeline in the mastering of electricity and reveals that electric power became available quantitatively

and reliably only at the beginning of the 19th century, thanks to a first key invention: the battery, by A. Volta in 1799. Several decades elapsed before the second key discovery: a device that was able to reliably convert mechanical power to electricity, invented by M. Faraday in the form of a disk generator in 1831. The battery and the disk were both immediately adopted by scientists in their laboratories as a source of electricity. The successful demonstration of the electromagnetic conversion method led to numerous developments, and in particular to the invention of the dynamo for high power application by C. Wheatstone and W. Siemens simultaneously in 1867. The next key steps in this timeline are the invention and construction of the first dam for electric power generation, which occurred presumably close to Niagara Falls, New York (Schoelkopf Power Station No.

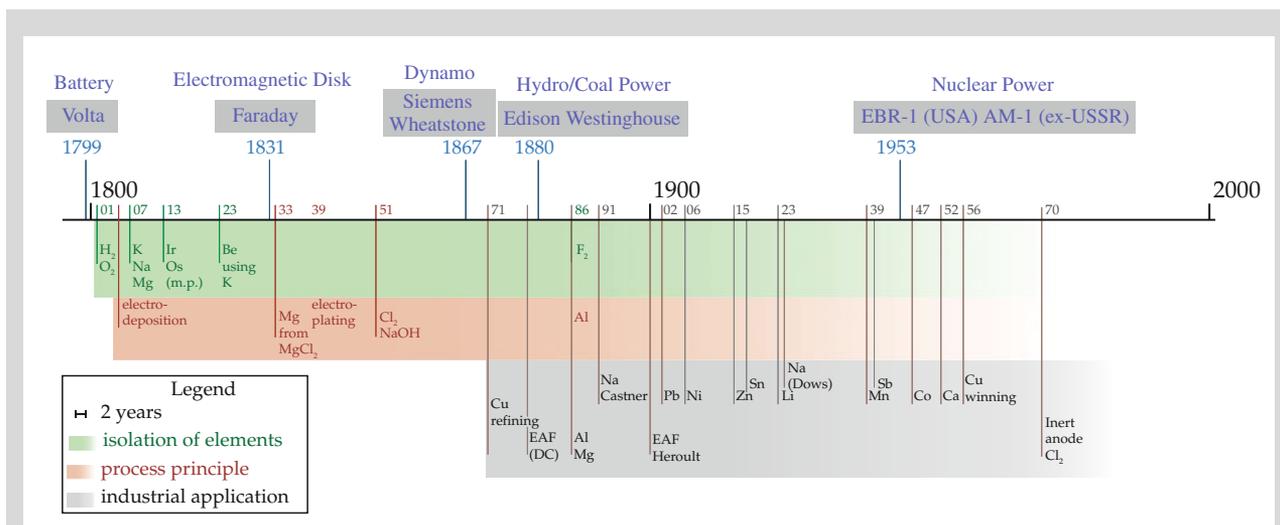


Figure 1. Selective timeline of development in electricity generation (top), application of electricity for isolation of elements, demonstration of process principles and industrial applications.

1, 1881). One year after, the first coal-fired power station was built and operated in New York City (Edison's Pearl Street Station, 1882).

A century of inventions and developments passed before the reliable generation of large quantities of electricity was possible. This achievement is considered as one of the pillars of the 2nd industrial revolution.

ADOPTION OF ELECTRICITY: THE ROLE OF CHEMISTS

As illustrated in the center of part of the timeline in Figure 1, 'philosophers' of the early 19th century were well ahead of their time and immediately embraced this new form of energy as a method to isolate elements and investigate their physical properties.

As early as 1807, the potential difference at the terminal of a battery was identified by chemists as a powerful tool for the investigation of the 'true elements of bodies.' It indeed allowed the experimentalists to expose any chemical media to a finite and controllable difference of chemical potential. Helped by the availability at the Royal Society of the world's largest battery, H. Davy became a chemist of standing and isolated alkaline and alkaline earth elements thanks to electrolysis.¹ The isolation of these reactive elements was a first in chemistry and helped in less than two decades to separate other elements thanks to metallothermic reaction (e.g., beryllium [glucinium] by reduction of its chloride salts with electrolytic potassium).^{2,3} Less than two decades after Volta's invention, electricity was also identified as a means to provide heat and obtain temperatures hardly achievable with previous laboratory techniques: J.G. Children melted metallic iridium and osmium in 1813 using a battery as electricity source.⁴ It is also thanks to electricity that H. Moissan—who isolated fluorine thanks to electrolysis in 1886⁵—was able to reach temperatures in excess of 3,000°C in his electric furnace that relied solely on arc-generated radiative heat.⁶ It is with this tool that he investigated diamond synthesis and the melting point of refractory oxides.

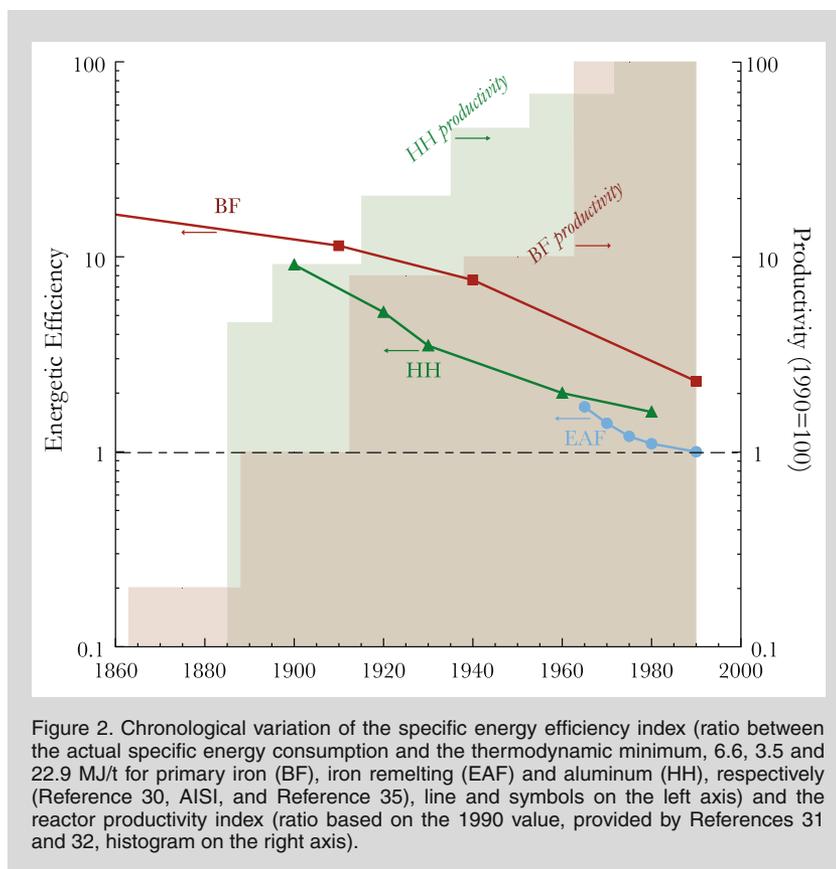


Figure 2. Chronological variation of the specific energy efficiency index (ratio between the actual specific energy consumption and the thermodynamic minimum, 6.6, 3.5 and 22.9 MJ/t for primary iron (BF), iron remelting (EAF) and aluminum (HH), respectively (Reference 30, AISI, and Reference 35), line and symbols on the left axis) and the reactor productivity index (ratio based on the 1990 value, provided by References 31 and 32, histogram on the right axis).

The use of a continuous source of electricity and the principle of electrolysis were also adopted by chemists to produce essential gases in significant quantities and in pure form: hydrogen,⁷ oxygen,⁷ or ozone. This last gas was initially identified as the "odor of electricity" because of its production during thunderstorm and its first isolation by electrolysis is due to C.F. Schönbein.⁸ The remarkable efficiency of electrolysis for separation has continued to be appraised by chemists in the 20th century, for example, after the discovery of deuterium for the forthcoming production of heavy-water.⁹ The production of chlorinated compounds by electrolysis—though chlorine as an element was isolated and identified by L.J. Gay-Lussac in 1809 without assistance of electricity—was also an early discovery and scaled up at the pace of industrial electricity deployment.^{10,11} The chlor-alkali production ultimately became one of the most important processes in the chemicals industry,¹² consuming around 3% of the electricity in the United States. Interestingly, C.A. Hampel,

the chemical engineer, mentions in his encyclopedia "The chlorine industry . . . produces the two greatest tonnage products of the electrochemical industry. . . . This statement neglects the production of steel made in electrical furnaces."¹³ It is in the chemical industry that electrochemical experts see the last technical breakthrough in industrial electrochemistry for energy and the environment: the dimensionally stable anode (DSA®) for chlorine evolution invented by H. DeBeer and industrialized by the V. & O. DeNora in the 1970s.¹⁴

CONTRIBUTION OF ELECTRICITY TO METAL PROCESSING

The timeline in Figure 1 also shows that many philosophers at the time of Alessandro Volta were not only chemists, but also metallurgists. In 1805, three decades before Faraday's laws on electrolysis, L. Brugnatelli demonstrated the principle of electrodeposition of gold using Volta's battery.¹⁵ In 1808, H. Davy demonstrated the use of an arc to melt and join metal, thus

giving birth to fusion welding techniques. These early successes initiated an intimate relationship between electricity and metallurgy at both low and high temperatures.

In less than 70 years, the field of application of electrolytic methods in aqueous-based electrolyte was broadened and investigated for the extraction or manufacturing of most common metallic elements (33 out of 70) (e.g., for plating, refining or forming).¹⁶ Industrial electrolysis at low temperature is nowadays a key process for primary metal extraction and refining, and enables the large-scale availability of some of the most important metals.

Electrolytic techniques for metal separation at high temperatures in molten salts were also applied early as pioneered by H. Davy in 1807.¹ The corresponding industrial processes were designed and operated less than a century later, for sodium (from sodium hydroxide by Castner in 1891¹⁷ and later sodium chloride electrolysis by Downs¹⁸), magnesium (chloride electrolysis principle by Faraday in 1833¹⁹), lithium (commercial production started in 1923 from chlorides) or rare-earth elements (in chlorides or fluorides^{20,21}). One metal, isolated before the advent of electrolysis, has led to one of the

most fascinating business and technological adventures of the 20th century: aluminum. Considered as a precious metal before the invention of molten cryolite electrolysis simultaneously by C.M. Hall²² and P. Héroult²³ in 1886, aluminum has become a commodity in less than 25 years.

The use of electricity for high-temperature metal extraction or refining in electric furnaces was also promptly adopted, with a very sound physical understanding of the thermodynamics attributes of electricity.²⁴ The invention of the direct arc-heating furnace is credited to W. Siemens^{25,26} as early as 1878. At that time, an arc was created between an electrode and the material to be processed. The combination of direct arc and resistance heating was patented in 1887 and operated in France (La Praz) to melt steel for the first time by the very same P. Héroult in 1900.^{27,28} In this specific case the arc was generated between two electrodes through a resistive medium—a slag—in contact with the material of interest. After several decades of domination by the Héroult type of furnace, and after its important transition from alternating current to direct current operation, direct arc heating furnaces for smelting operation became commercially avail-

able to process oxide materials and are used today for the extraction of a wide range of products, from ferro-alloys to platinum group elements.²⁹

BENEFITS OF MATERIALS PROCESSING WITH ELECTRICITY

The use of electricity in metal production provides unique process attributes, including low capital cost, high purity of the metal product, easy process control, and flexible production capacity. These key features shall not mask another asset of the industrial application of electricity: using electricity helps to reduce energy consumption and improve productivity.

In the context of the promotion of sustainable materials processing techniques, it is of interest to recall the trend in the energy intensity for aluminum production (Hall-Héroult electrolytic process [HH]) along with the increase in the corresponding reactor productivity (Figure 2). The energy index is defined here as the ratio of the actual specific energy consumption (best available technique) to the thermodynamic minimum for the oxide separation into its constitutive elements (metal and oxygen) in the case of primary extraction, and minimum heat needed to melt the metal in the case of the EAF. This is a fair comparison for production of primary aluminum and steel since both processes rely on the use of carbon as reactant and ultimately produce CO₂. These data are praised by the aluminum sector and are worth sharing with the whole materials community: the use of electricity led simultaneously to a rapid and drastic reduction of the specific energy consumption and a considerable increase in the cell capacity (productivity per square meter of cathode). For comparison, the time variation of the energy consumption for primary steel production (ironmaking, blast-furnace based [BF]) and steel electric remelting (electric arc furnace [EAF] based) is presented in Figure 2 revealing a similar rate of improvement during the same period, though limited to an energetic efficiency factor slightly higher than 2 for BF, while aluminum is close to 1.5.

The less favorable efficiency for ironmaking may be due to the reliance

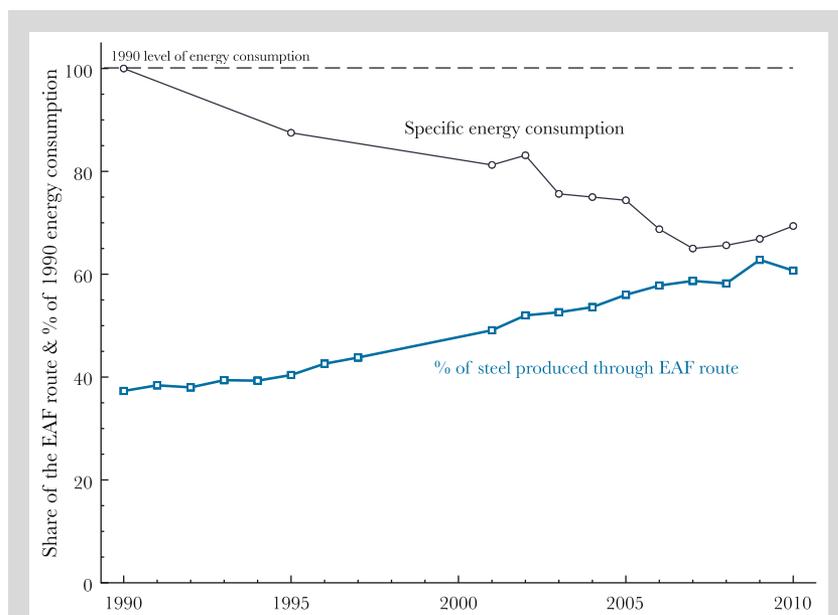


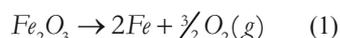
Figure 3. Chronological variation of the share of the electric arc furnace route (square) and the specific energy consumption for steel production (ratio between the actual specific energy consumption and the value in 1990, circles) in the United States [AISI and Iron and Steel Technology].

on a gas-solid reduction reaction which requires numerous pre- and post- operations, ultimately leading to temperature discontinuities and energy losses along the various steps.³² As a matter of fact, some ironmaking integrated plants are operating today close to what is considered an optimal level of energy consumption. Interestingly, in the United States and some other countries, a significant reduction in energy consumption and CO₂ emissions for steelmaking occurred at the end of the 20th century (Figure 3), coinciding with a more intensive use of the electric arc furnace. This demonstrates that using electricity for steelmaking is a modern reality and actually provides benefits.

THE IRONMAKING DILEMMA

The ironmaking issue is a key challenge both from societal and engineering standpoints. The immediate availability of carbon sources, initially as charcoal, tied the iron smelting operation to carbon around 4,000 years ago.³³ This successful relationship is a gift to humanity: both carbon and iron oxide are abundant, the Gibbs energy of formation of iron oxide is low—it is relatively easy to reduce iron oxide to metal—carbon provides unique mechanical properties to iron and, finally, the amount of heat generated during the combustion of carbon allows the production of molten metal. Without any attempts to criticize the technological and scientific developments that shaped the existing steel industry processing it is of interest to review the fundamental nature of iron extraction.

Adopting a holistic approach—backed up by thermodynamics—one can depict the extraction of iron from the oxide as a separation process, an operation which, in principle, does not require the use of another chemical. To be efficient, this step requires careful monitoring of the amount of chemical energy equivalent to work in thermodynamic terms.³⁴ This is needed to separate the oxygen anions from the metal (reaction 1):



Simultaneously, a definite amount of heat is needed to sustain the reaction and obtain the metal in the liquid form.

A carbonated chemical (carbon, or, more accurately, CO) was used originally to provide the work needed to conduct the separation, but its reaction with the iron oxide is difficult to master on a large scale. An advanced reactor to operate this reaction has therefore been developed: the blast furnace.

As noticed in the ironmaking flow sheet (Figure 4), a number of reactors have been added to the BF to produce virgin steel at high tonnage today. Indeed, to cope with the gas/solid reaction principle and provide high enough productivity, ancillary steps have ingeniously been designed to prepare the compounds needed for the reduction (lime, sintering/pelletizing, and coke plant). Because the reduction temperature is achieved by combustion, oxygen is used in the blast, requiring nitrogen separation for higher efficiency. At that stage, the reactants, fluxes, and fuels are ready to be introduced in the BF. These preparations are required to achieve

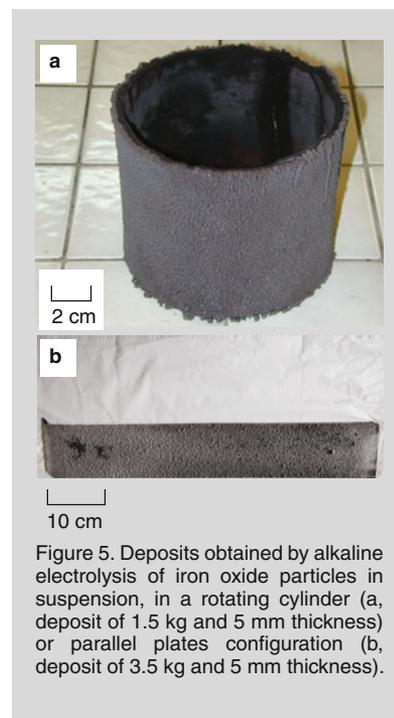


Figure 5. Deposits obtained by alkaline electrolysis of iron oxide particles in suspension, in a rotating cylinder (a, deposit of 1.5 kg and 5 mm thickness) or parallel plates configuration (b, deposit of 3.5 kg and 5 mm thickness).

the simultaneous control of the three most important chemical engineering phenomena in the reduction step: the gases, solids, and liquids pattern; the advancement of the reaction; and the heat balance. Despite these astonishing engineering developments, and because of the large affinity of carbon for iron, the level of the former element in the product out of the BF (“pig iron”) is too high for most applications. A decarbonization step (basic oxygen furnace or converter) is therefore added in which oxygen is used to eliminate the excess of carbon reductant initially introduced. It is only after these processing steps that steel of acceptable carbon content is obtained, and physical metallurgists can operate.

We therefore see that the chemical approach for steel production in a single high-capacity reactor requires large capital investments in both the BF and its ancillary reactors and is likely to pose some challenges in reducing further the energy consumption.³² Furthermore, one of the key consequences of the dependency on carbonated compounds is the nature of the gases ultimately emitted, CO and CO₂. In the early 21st century, it was established that the most advanced integrated steel mills have a greenhouse gases intensity of around $1.8 \text{ tCO}_2 \cdot \text{t}_{\text{HotRolledCoil}}^{-1}$.³⁵

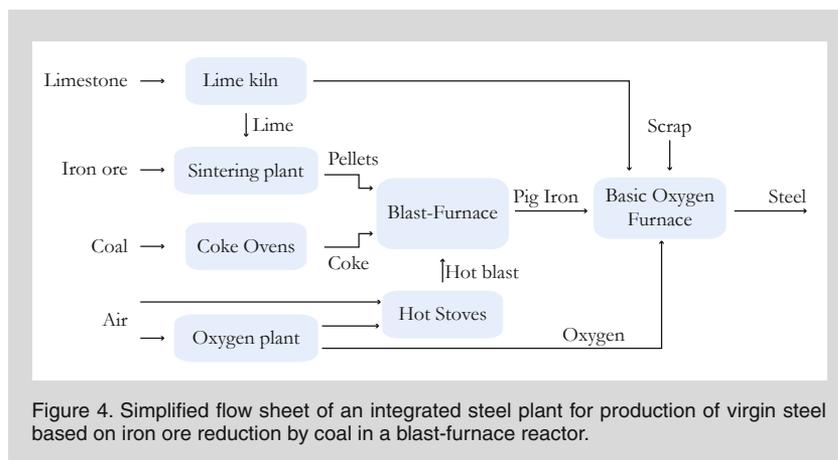
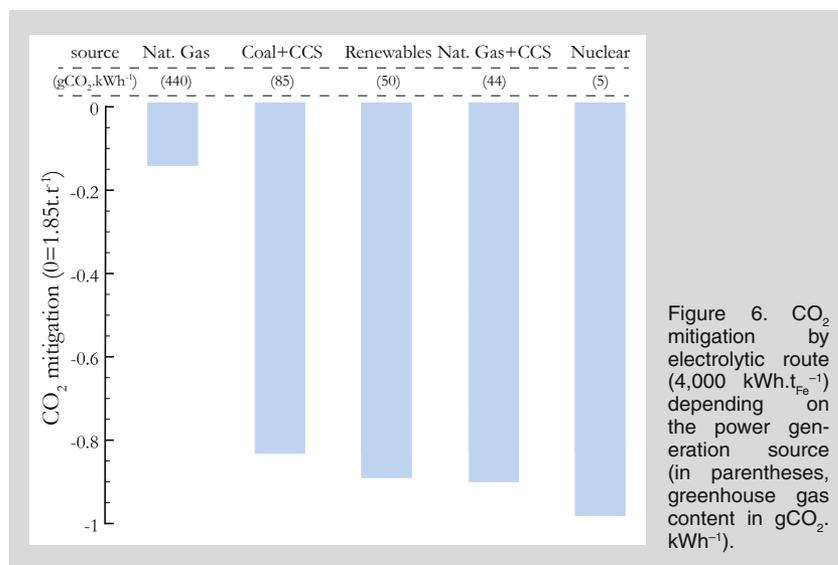


Figure 4. Simplified flow sheet of an integrated steel plant for production of virgin steel based on iron ore reduction by coal in a blast-furnace reactor.



From the society perspective, the low price-point of steel (less than 0.6 \$.kg⁻¹) and its world annual consumption (1.5 billion tonnes), make its sustainability issue of key importance: steel currently ranks number 1 among all materials in terms of greenhouse gas impact in most developed countries. This reality was acknowledged as early as the 1990s by steelmakers and metallurgists,^{36,37} and ultimately lead to the bold decision of the steel industry to investigate new methods for steel production all around the globe, with various approaches and targets (for example, Ulcos in Europe in 2004, AISI CO₂ Breakthrough in North America in 2005, and Course 50 in Japan in 2008). Some of these approaches, interestingly, consider taking further advantage of electricity for steelmaking, thus bridging the existing technological gap between iron and the other metals.

CHALLENGES IN ELECTROCHEMICAL EXTRACTIVE TECHNIQUES

The description provided previously does not imply the absence of technical challenges in electrochemical technologies.

Metal extraction by aqueous electrochemistry suffers many limitations for high throughput and low specific energy consumption. The low current density—typically less than 0.05 A.cm⁻²—the limited cell height, the large inter-electrode distances, the presence of a physical separator

between the electrodes, or the limited deposit thickness due to dendritic growth are individually or collectively responsible for these limitations.

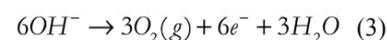
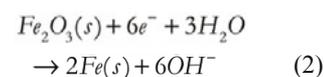
High current densities are obtained in molten salts but in processes that produce solid metal lead to dendritic or powder deposits. This product form requires significant additional energy downstream for rinsing and salts recovery, as well as numerous pre- or post- processing steps (powder handling, compaction, remelting). One of the key issues for the sustainability of molten-salts electroextraction processes is the absence of satisfactory inert anode materials (which could replace consumable carbon electrodes and sustains oxygen evolution). This “ultimate materials” challenge,³⁸ despite some pioneering efforts, remains current, in particular for fluoride-based electrolyte.

DIRECT OXIDE PROCESSING AT LOW AND HIGH TEMPERATURE BY ELECTROLYSIS

Innovative approaches therefore are needed to adapt electrolytic techniques for tonnage production of metals. Two paths have recently been proposed and demonstrated for iron, at low and high temperature. These techniques are not limited to this element by any means, but they do point the way with respect to such high tonnage–low cost metal.

At low temperature (100°C), the

electrolysis of iron oxides particles in suspension was patented in 1918.³⁹ It consists of the electrolysis of iron oxide particles (hematite, typically) in a concentrated aqueous alkaline electrolyte (pH=15, 100°C). The particles are suspended at relatively high concentration and are subjected to electrolysis following reaction (2) on the cathode and (3) on the anode:



It is only recently that an insight into the cathode reaction mechanism has been provided, revealing a topochemical electroreduction mechanism of an oxide slab⁴⁰ operative in absence of bulk solid-state diffusion. This mechanism, involving reaction of particles directly in contact with the cathode without dissolution of iron ions in the bulk electrolyte,⁴¹ prevents loss of efficiency through ion valence shifting between the cathode and the anode.

The mechanism justifies the high selectivity of the process (selectivity higher than 90%), the high current densities (up to 1.5 A.cm⁻²),⁴² and the advanced energetic efficiency (higher than 80%). This last feature is partly inherited from the high conductivity of the sodium hydroxide electrolyte, the absence of a separator, and the availability of high efficiency oxygen evolving anodes for such electrolyte. This unusual electrolysis configuration, which involves suspension handling and particle-metal surface interactions,⁴³ has been operated in various cell designs (plates, cylinders)⁴⁴ and lead to the development of large-scale innovative reactor design for iron production, which produces plates up to 3.5 kg and 5 mm thickness (Figure 5).

The commercial version of the process is envisioned with a vertical stacking of the cells to reduce the footprint of the extraction process. Meanwhile, the energy consumption has reached values (2,600 kWh.t_{Fe}⁻¹) close to the thermodynamic minimum as an illustration of the ability of electrical technique to lead to the rapid development of processes with high energetic

efficiency.

At high temperatures, the concept of molten oxide electrolysis (MOE) championed by D. Sadoway⁴⁵ has been developed for a suite of metals, including iron. The key idea is to operate in a molten oxide electrolyte—a slag, in pyrometallurgist language—in a configuration very similar to the HH cell. The operating temperature of 1,600°C allows the direct production of liquid metal in a semi-continuous manner and the presence of an oxide melt enables the building of a frozen side-wall. The demonstration of simultaneous iron production and oxygen generation at the bench scale has been published recently.^{34,46} Efforts have been conducted to find an anode material that sustains the corrosive oxide environment⁴⁷ and the oxygen evolution at such temperature. The foreseen current density (above 2 A.cm⁻²), the absence of carbon in the reactor, and the low capital costs are among the key assets of this technology and explain the continued interest and support of this technique by steel producers worldwide. The process operates in an optimized energetic set-up being the synthesis of an electrolytic cell and an electric arc furnace. The corresponding minimum energy consumption for MOE-steel is then 2,600 kWh.t_{liquid Fe}⁻¹ which, taking into account typical heat losses in advanced high-temperature electrolysis cells (40%), translates to around 3,600 kWh.t_{liquid Fe}⁻¹. In such conditions, as presented in Figure 6, CO₂ mitigation for steelmaking could be achieved as early as 2013, for example, using a natural gas combined cycle power plant. Thus carbon-free sources of electricity can ultimately provide greenhouse-gas-free steelmaking thanks to electrolysis.

Both approaches have key common features: 1) iron ore particles are directly reduced with the corresponding ability to process fines or ultrafines ore; 2) perfectly controlled energetic conditions are determined solely by the electrolyte composition and the cell design; and 3) metal of unique metallurgical composition is produced. It is important to realize that MOE provides the advantage of directly producing molten iron at high throughput in a continuous

manner, making it ideally designed for tonnage metal production such as steelmaking.

CONCLUSION

Electricity in materials processing has a key role. For the extraction of metals in particular, it is noticeable that the process efficiency and productivity have been significantly improved at a high pace, leading to a reduction of the corresponding energy consumption as illustrated for aluminum. Electricity has also become a key energy vector in steelmaking and thanks to new concepts in electrochemistry, one may foresee its usage for primary iron production as well. Recent results indeed suggest that significant mitigation of the greenhouse gas impact of ironmaking is possible with electrolytic steel, in particular in the context of a decarbonization of power generation or the creation of a CO₂ emissions trading system.

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