

Electrochemical Salt Splitting

by David Genders

Salt splitting is a relatively new technology dependent on the availability of modern membranes. Its development has usually been driven by one of two major factors, both environmentally based. The first is the desire to produce caustic soda without the co-production of chlorine, and the second is the increased cost of disposing of heavily laden salt solutions.

Caustic is in Demand

Caustic soda is produced in the USA at a rate of 14 million tons per year, almost entirely by the electrolysis of brine. In this process chlorine is produced at the anode and caustic soda at the cathode in stoichiometric quantities. There is a growing awareness of the need for new processes for the manufacture of high purity sodium hydroxide that do not lead to co-production of chlorine. This requirement exists because the chlorine and sodium hydroxide markets are rarely in balance. Despite the high demand for chlorine in the last two years, it is still expected that environmental pressures on chlorine will lead to an increased demand for caustic over the coming decade. Predictions are for a long-term trend in which the demand for sodium hydroxide will outstrip that for chlorine. Several present markets for chlorine are expected to experience significant downturns due to environmental pressures or concerns about health hazards; these include pulp and paper bleaching, fluorocarbons, water treatment and chlorinated hydrocarbons. At the same time, the demand for sodium hydroxide is predicted to continue to grow. Another trend is towards modular plants that allow the manufacture of chemicals on various scales including generation on a relatively small scale at the site of use.

Recycling Process Streams

Increasingly, environmental regulations are putting more stringent limitations on the amount of solid and liquid waste that may be discharged. Recycling salt solutions as acids and bases not only avoids a waste disposal problem, but also provides credit in lieu of the raw material that would otherwise need to be purchased.

Splitting Sodium Sulfate to Caustic and Sulfuric Acid

Sodium sulfate can be effectively split electrochemically into sulfuric acid and sodium hydroxide in a three compartment cell (1) such as shown schematically in Figure 1.

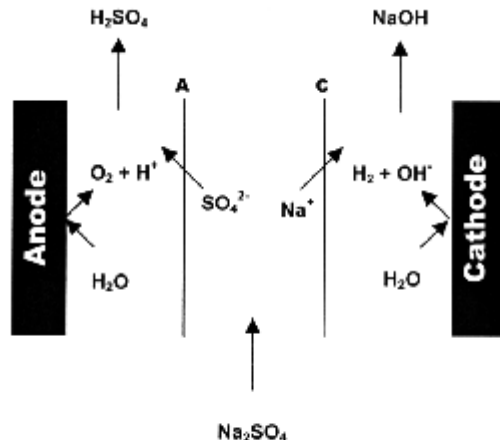


Figure 1: Sodium Sulfate Salt Splitting

Sodium sulfate is passed through the central compartment; under the influence of the potential field, the sulfate is transported through the anion permeable membrane into the anolyte and sodium ions pass through the cation permeable membrane into the catholyte. The anode and cathode reactions generate proton and hydroxide respectively and hence the sulfuric acid and caustic soda accumulate in the anolyte and catholyte. One of the limitations of this approach is the concentrations of acid and base that can be efficiently formed in the cell. As the acid concentration builds in the anolyte compartment, the current efficiency for the process drops markedly. This loss in current efficiency is primarily due to the back migration of protons from the anolyte compartment across the anion exchange membrane into the central compartment. This makes the pH in the central compartment acidic, thereby also reducing the current efficiency for production of sodium hydroxide. The back migration of protons across anion exchange membranes is well known and several manufacturers have developed membranes specifically designed to minimize this leakage. One such membrane is Tokuyama Neosepta ACM. However, even with these specialty membranes the pH in the central compartment still drops.

One of the consequences of having a low pH in the central compartment is a limitation on the type of cation exchange membrane that can be used. High performance, bilayer cation exchange membranes (for example DuPont Nafion® 902) contain perfluorinated polymers with sulfonic acid exchange groups on one side and carboxylic acid exchange groups on the other side. The weak acid exchange material limits the back migration of hydroxide ions during the production of caustic allowing higher caustic concentrations (32% by weight) to be reached at good current efficiencies. However, to maintain conductivity in the membrane, the carboxylic acid functionality must not become protonated. Since these weak acid exchange groups have a pKa of 2 - 3, the pH in the central compartment cannot be

such that a significant portion of the charge is carried by protons. If the central compartment does become acidic, then membranes with strong acid exchange groups must be used (for example DuPont Nafion® 324 or 350). This limits the caustic concentration that can be achieved at good current efficiency to 15 - 20% by weight.

Salt Splitting To Caustic and Ammonium Sulfate

Several strategies have been used to mediate the effects of proton back migration. A good example of this is found in technology developed at The Electrosynthesis Company (ESC) in conjunction with Ormiston Mining (2). Figure 2 shows a schematic of a process in which the products are caustic soda and ammonium sulfate. Clearly, one advantage of such a process is that protons generated at the anode are neutralized by the addition of ammonia gas. This prevents the central compartment from becoming acidic and, therefore, improves the current efficiency for caustic production. In addition, the possibility exists for using high performance bilayer membranes to make higher product concentrations directly in the electrochemical cell. The anode product in this process, ammonium sulfate, is used extensively as a fertilizer.

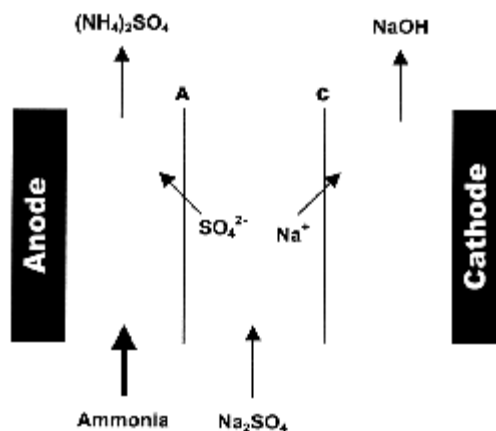


Figure 2: Production of Caustic and Fertilizer

The process operates efficiently producing high concentrations of caustic soda and ammonium sulfate. The cell is operated in a three compartment mode separated by a Neosepta® AMH anion exchange membrane from Tokuyama and a Nafion 902 bilayer cation exchange membrane from DuPont. The pH of the anolyte is maintained between 1 and 2. The cell operates at current densities of up to 2.5 kA m⁻² producing 32% caustic at current efficiencies in excess of 95%.

Bipolar Membranes

An alternative method for salt splitting utilizes bipolar membranes (3). These membranes allow for the formation of hydroxide and protons from the splitting of water without the coproduction of hydrogen and oxygen. Figure 3 shows a diagram of part of a cell stack using this technology. A typical stack may have >100 bipolar membranes with assorted anion and cation membranes between a pair of electrodes. This technology has the advantage of reduced power requirements and potentially cheaper cell stacks. However, to date these membranes still suffer stability problems as well as unwanted transport across the membrane interface. In the above example, the latter would lead to sulfate contamination in the caustic stream, or sodium contamination in the sulfuric acid stream.

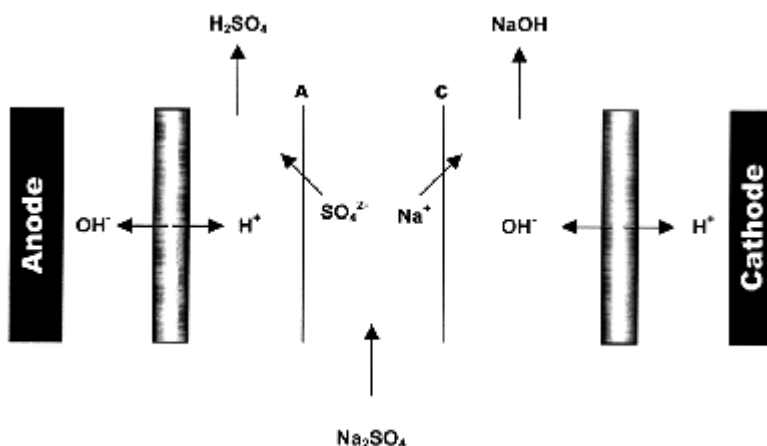


Figure 3: Salt Splitting of Sodium Sulfate with Bipolar Membranes

Gas Diffusion Electrodes

Power cost is almost always an important consideration in electrochemical salt splitting operations. One approach to reducing this, through lower cell voltages, is to use a hydrogen depolarized anode. In these cells the hydrogen gas produced at the cathode is returned to the anode and oxidized to protons at a gas diffusion electrode. This technique can lower the cell voltage by over a volt. The Hydrina™ process piloted by DeNora (4) is a good example of this. Here a cation exchange membrane is also placed immediately adjacent to the anode to prevent the anode from flooding under the hydraulic head of the electrolyte solutions.

Caustic Without Chlorine

Processes that produce caustic soda without the coproduction of chlorine afford the opportunity to redress the balance in caustic chlorine production. We have already discussed the importance of power costs in the economics of such processes and it therefore follows that any process that produces caustic as a commodity chemical must operate at a very low overall cell voltage. This point is particularly important when an economic credit for waste disposal of a salt cannot be taken.

The Electrosynthesis Company has been developing a process for the production of caustic from sodium carbonate that is expected to meet these requirements (5). The basis of the technology is shown in Figure 4. The process takes advantage of gas diffusion electrode technology to accomplish low cell voltages; moreover, the high anolyte pH allows additional power savings. Figure 5 shows current potential curves for the oxidation of hydrogen at a platinum catalyzed gas diffusion electrode. As would be expected, there is a considerable voltage advantage realized by running the electrode in a basic environment compared to the acidic electrolyte. The potential of the electrode in the carbonate solution is controlled by the pH of the electrolyte at the catalyst site. Hence at higher current densities, the protons are formed more rapidly, sending the pH within the electrode structure more acidic. Clearly, in designing electrodes for this process one would fabricate the structure such that the highest pH is maintained at the catalyst surface.

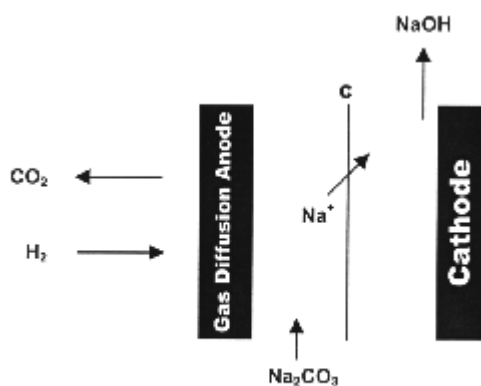


Figure 4: Caustic from Sodium Carbonate without the Co-Production of Chlorine

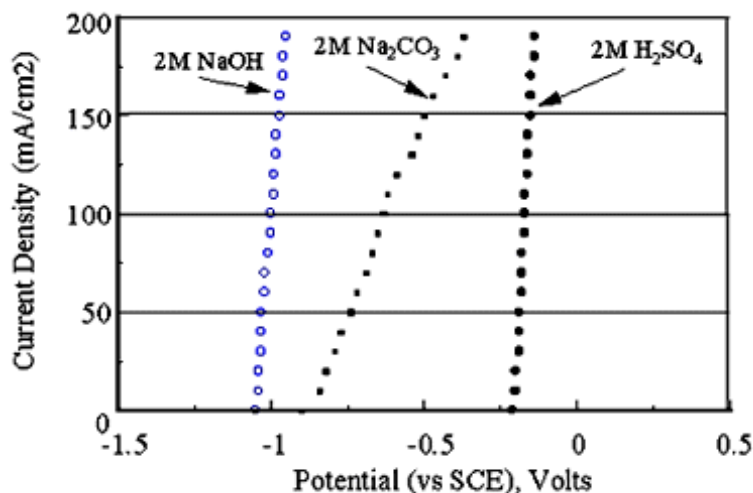


Figure 5 - Oxidation of Hydrogen as a Function of pH

The process is able to produce high purity caustic at concentrations up to 32% at current densities of 2.5 kA m^{-2} with a cell voltage of less than 1.6 volts. This corresponds to a total energy consumption of less than 1200 kWhr/ton of caustic. Table 1 shows a comparison of the power consumptions required for several caustic producing technologies.

Table 1: Energy Consumption for the Production of 1Ton of Caustic

Process	Energy (kWhr/T)
Chloralkali	<2300
ESC/Ormiston Three Compartment Cell	3600-4000
Hydrina™	1700-2000
ESC Caustic without Chlorine Process	1200

Salt Splitting of other Inorganic and Organic Salts

Obviously, electrochemical salt splitting has much wider applications and may be appropriate to virtually any salt providing the economics are favorable. Salts, MX, could include those for example where M is Li⁺, Na⁺, K⁺, ammonium, quaternary ammonium; and where X is halide, nitrate, phosphate, borate, formate, acetate, etc.

Using membranes to affect this type of conversion avoids the generation of a salt thereby eliminating a waste disposal problem. The use of conventional electrodes in this type of salt splitting will require being sure that the inorganic salt or organic acids are not oxidized at the electrode. In many cases additional membranes or bipolar membranes are used to avoid this unwanted oxidation.

An example of this type of salt splitting is the recovery of lactic acid from sodium lactate (6). The latter is produced from starch in a fermentation process and the lactic acid is traditionally isolated through several liquid extraction steps, an esterification process and an ion exchange process. All of these steps are replaced in the electrochemical process by use of a salt splitting cell incorporating bipolar membranes. This process is currently being operated in Japan.

Conclusions

Salt splitting processes have been around for several decades. During that time considerable advances have been made in bringing the power requirements down to a viable level. However, a successful technology for treatment of sodium sulfate wastes will likely require additional economic incentives such as the coproduction of a saleable product (for example ammonium sulfate), or credits for the elimination of a waste stream. Technologies for the production of commodity quantities of caustic will need to rely on very low power costs and an increasing imbalance in caustic chlorine production. Recent increases in the price of caustic should maintain a high level of interest in these technologies. Moreover, the trend toward modular on-site production of chemicals will facilitate the implementation of electrochemical technologies.

References

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Dr. David Genders is President at The Electrosynthesis Company, Inc. Current research activities range from electrosynthesis to salt splitting and from sensors to batteries. Dr. Genders has co-authored ten patents while at The Electrosynthesis Company and has recently edited two popular books on electrochemistry: *Electrosynthesis - From Laboratory to Pilot to Production* and *Electrochemistry For A Cleaner Environment*. Both books are available from The Electrosynthesis Company.

Salt splitting applications are not limited to those discussed in this article. If you have an application that you consider may benefit from electrochemical salt splitting, please send e-mail to info@electrosynthesis.com.