ECS Classics

Hall and Héroult and the Discovery of Aluminum Electrolysis

by Theodore R. Beck

A simultaneous invention of an important industrial electrochemical process by two men on two different continents appears improbable. Yet that is what happened. One was in the United States and the other in France. Each inventor was born in the same year, 1863, and at age 22 each independently developed the same technology to produce aluminum by electrolysis. They were rather different personalities.

Charles Martin Hall[1-4] was born into an educated family and attended Oberlin College. He was a studious scientist who deliberately, step by step, arrived at his process. The father of Paul Louis Toussaint Héroult[6-8] was a tanner and Paul Héroult was expected to continue in that business. Instead, he attended a school of mines where he was dismissed after the first year because he spent his time thinking about how to produce aluminum rather than his studies. He was more of an intuitive thinker, and on inspiration, first electrolyzed alumina in molten cryolite in his father's tannery.

The technology of these two inventors is now known as the Hall-Héroult Process. Hall and Héroult were among the earliest members of ECS, then named "The American Electrochemical Society."

Charles Martin Hall

Charles Martin Hall

Charles Martin Hall[3] was born on December 6, 1863 in Thompson, Ohio. His parents were Herman Bassett Hall and Sophronia H. Brooks. His father graduated from Oberlin College in 1847 and studied for three years at the Oberlin Theological Seminary. After ten years doing missionary work the family returned to Ohio in 1860 and to Oberlin in 1873.

Hall was taught to read by his mother and by the age of six he was reading his father's 1840s college chemistry book. He spent three years at Oberlin High School and a year at Oberlin Academy. During this period he carried out chemistry experiments in the kitchen and in the woodshed attached to the house. In 1880 at the age of 16 he enrolled in Oberlin College. There he came under the influence of Professor Frank Fanning Jewett, who had undergraduate and graduate training at Yale University. Jewett told Hall that fortune awaited the person who developed an economical method for producing aluminum from its oxide. Hall told a fellow student that he intended to be that person. His first experiments were in his senior year in Jewett's laboratory.

After graduation Hall continued tests in the woodshed and his sister, Julia B. Hall, helped him in his work. She had also studied chemistry and followed his experiments closely. The sources of electric current for his tests were Bunsen-Grove cells consisting of a zinc metal electrode in sulfuric acid solution surrounding a porous ceramic cup containing a carbon rod immersed in concentrated nitric acid. Earlier experiments in Jewett's laboratory in aqueous solution were unsuccessful and Hall turned to molten fluoride salts. He used a gasoline fired stove to heat a clay-lined iron tube in which he eventually melted cryolite, Na_3AlF_6, as a solvent for aluminum oxide, Al_2O_3. He obtained a grayish deposit on the cathode, probably silicon, but no aluminum on repeated tests. He subsequently used graphite lining in the tube with aluminum fluoride, AlF_3, added to the cryolite to lower the melting point. After several hours and subsequent cooling, several small silvery globules were found, which Jewett confirmed were aluminum. The anode was carbon which was consumable in the overall reaction

$$Al_2O_3 + 3/2\ C \rightarrow 2\ Al + 3/2\ CO_2$$

On July 9, 1886 Hall applied for a U.S. patent. He found that Paul Héroult had previously been granted a French patent on April 23, 1886 for a comparable process based on alumina in cryolite. Evidence from Hall's family and Jewett, including two postmarked letters to his brother George, helped to establish the priority of Hall's discovery in the United States. He obtained his U.S. patent number 400,655 in 1889. At first his relationship to Héroult was cool but they later became good friends.

Hall's first attempt at commercialization was with the Cowles Company in Cleveland. He worked by himself there where he produced over a pound of aluminum with a rather crude cell, but negotiations broke down with Cowles. He then approached the Pittsburgh Testing Laboratory of Alfred E. Hunt and obtained an agreement for commercial development. Hunt raised $20,000 cash from a few friends and the Pittsburgh Reduction Company was started on September 18, 1888 in a building in Pittsburgh. Hall and the first employee, Arthur Vining Davis, built the first commercial pilot plant. The steel cells had a baked carbon lining containing the electrolyte and 3-inch diameter cylindrical carbon anodes as shown in Fig. 1. The cells were called pots and the electrolyte called bath, a terminology that survives to the present. The basic design remains essentially the same today for prebake carbon anode cells except for increase in scale, hooding, and fume recovery.

In 1890 the company received funding from the Mellon banking family in Pittsburgh, which, four years later, funded expansion to a new plant at Niagara Falls. The company headquarters remained in Pittsburgh, the home of the Mellon financial empire. The company changed its name to the Aluminum Company of America or Alcoa.

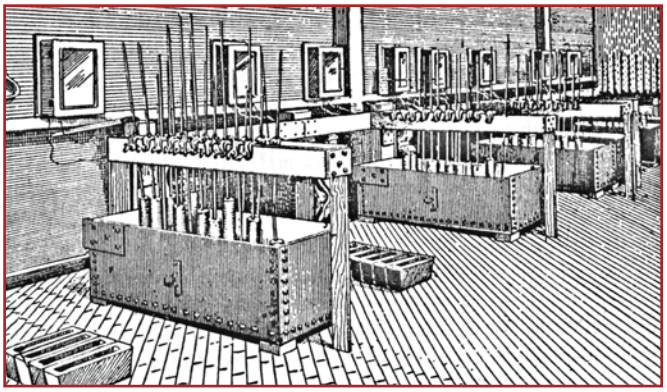

Fig. 1. *Sketch of original cell room.[5] (Alcoa image – used with permission.)*

[As a side note, Hall used the aluminum spelling in an advertising handbill for his new electrolytic method of producing the metal, despite his constant use of the aluminium spelling in all the patents he filed between 1886 and 1903. Hall's domination of production of the metal ensured that the spelling aluminum became the standard in North America. In 1926, the American Chemical Society officially decided to use aluminum in its publications. American dictionaries typically label the spelling of aluminium as a British variant.]

Hall continued his research and development for the rest of his life and was granted 22 U.S. patents. He served on the Oberlin College Board of Trustees. He was Vice President of Alcoa until his death in 1914 in Daytona, Florida. He received the Perkin Medal by the Society of Chemical Industry in 1911. Paul Héroult attended. Hall died unmarried and childless and was buried in Westwood Cemetery in Oberlin. He left the vast majority of his $45 million estate to charity. Five million went to Oberlin College.

Paul Héroult

Paul Louis T. Héroult[10]

Paul Héroult[6] was born on April 10, 1863. His father managed a small tannery on the banks of the Orne River in Saint-Benin in France. His father had a friend, Mr. Belliot, a lawyer with a magnificent personal library where Héroult spent hours reading science, research, and discovery. Of particular interest was a work by Sainte-Claire Deville on aluminum, its properties, production, and applications, which he read when he was 15 years old. Deville had produced some aluminum by sodium reduction of aluminum chloride. At that time aluminum was as expensive as silver and used only for luxury items and jewelry. Héroult wanted to make it cheaper.

Héroult entered the École des Mines at the age of 19. He developed a friendship with his chemistry professor who was also fascinated by aluminum. While a student he spent his time thinking about electrolysis of aluminum compounds rather than studying his required subjects. He failed his first year and was dismissed from the school. He had none of the attributes of the traditional scholar.

Héroult returned to the tannery. His father had died unexpectedly in 1883 leaving him the tannery buildings. He used the buildings for his experiments on electrolysis with a few fellow students from École des Mines. His mother gave him her last 50,000 francs to purchase a 400 ampere, 30 volt dynamo. In April 1886 he succeeded in making small amounts of aluminum with alumina dissolved in cryolite electrolyte. His inventions appeared suddenly out of the blue. He applied for a patent on April 23, 1886. He collaborated with Austrian Karl Josef Bayer, who developed the process for winning pure alumina from bauxite in 1887.

Héroult died aboard his yacht in the Mediterranean, close to Antibes, in May 9, 1914.

Production of aluminum in 1900, metric tons[9]	
USA	1,650
Switzerland	1,232
France	800
England	500
Germany	500
Total*	4,682

**In 2013 the production was 49,700,000 metric tons.*

About the Author

Theodore R. Beck received a PhD in chemical engineering at the University of Washington in 1952. His whole career has been in the field of electrochemical engineering. For five years he managed the 10,000 ampere aluminum cell research at Kaiser Aluminum. He then carried out research and development in chlorate, perchlorate and manganese metal production at American Potash & Chemical. At Boeing Aerospace in Seattle he did development work on batteries and fuel cells for the space program and in the Boeing Scientific Research Laboratories he did research on stress corrosion of titanium for the supersonic transport program. From 1972 to 1995 he had his own contract research company, Electrochemical Technology Corp., doing research for government and industry. Most recently he has focused on new technology to produce aluminum with lower temperature eutectic electrolyte, CuNiFe anodes, and titanium diboride cathodes. He has several papers and patents on this technology. He is a past President of The Electrochemical Society and has been awarded The Acheson Medal, Honorary Member, Fellow and the Corrosion Division Award.

References

1. https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/aluminumprocess.html. Accessed 25 January, 2014.
2. https://www.acs.org/content/dam/acsorg/education/whatischemistry/landmarks/aluminumprocess/hall-process-aluminum-by-electrochemistry-commemorative-booklet.pdf. Accessed January 25, 2014.
3. http://en.wikipedia.org/wiki/Charles_Martin_Hall. Accessed January 25, 2014.
4. http://explorepahistory.com/hmarker.php?markerId=1-A-31F. Accessed January 25, 2014.
5. J. D. Edwards, F. C. Frary, and Z. Jeffries, *Aluminum and Its Production*, p. 23, McGraw-Hill Book Company, Inc., New York, NY (1930).
6. http://en.wikipedia.org/wiki/Paul_Héroult. Accessed January 25, 2014.
7. http://nautilus.fis.uc.pt/st2.5/scenes-e/biog/b0047.html. Accessed January 25, 2014.
8. http://corrosion-doctors.org/Biographies/HéroultBio.html. Accessed January 25, 2014.
9. A. Minet, *Production of Aluminum and Its Industrial Use*, p. 138, John Wiley & Sons, Inc., New York, NY (1905).
10. Aluminium Industrie Aktien Gesellschaft. Archiv des Alusuisse Forschungsinstituts Neuhausen, Schweiz. http://upload.wikimedia.org/wikipedia/commons/6/6b/Paul_T._Héroult.jpg. Accessed January 28, 2014.