东北大学八十周年校庆学术著作

李庆峰　邱竹贤　编著

铝的电化学
——从生产到应用

Applied Electrochemistry
of Aluminum
—Production and Applications

Li Qingfeng · Qiu Zhuxian

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中文序

铝的电化学在基础理论和应用技术方面都具有重要的意义。作为元素电化学的一个独特的分支，其所涉及的电解质体系范围非常广泛，有熔点在1000℃以上的金属氟化物，有熔点介于几十度到几百度的金属氯化物和溴化物，有室温下的有机熔融盐，有酸碱盐的水溶液体系，有各种有机溶液介质，还包括固态电解质。从应用的角度说来，铝的电化学涉及到应用电化学的许多技术领域，包括金属的电解生产，精炼，电镀，阳极氧化和其他表面处理，一次电池和二次电池，电解电容器，腐蚀以及阴极保护等。

铝的电化学的雏形，最早出现于 1976 年，当时J. A. Plambeck 为 A. J. Bard 主编的《元素电化学百科全书》第六卷撰写了“铝的电化学”一章。此后的三十年来，铝的电化学的基础理论研究和相关技术开发取得了长足的进展，现已发展成为一个较为完整的元素电化学的新分支。半个多世纪以来，东北大学轻冶教研室在邱竹贤院士的指导下，在这一领域的诸多方面，尤其是铝电解及精炼的理论和技术方面，进行了许多开创性的研究，为铝的电化学的形成和发展做出了卓越的贡献。

本书试图全面系统地阐述铝的电化学理论和应用体系，尤其侧重技术方面的开发现状和最新进展。关于本书的构思，始于 1991 年，当时两位作

者还都在原东北工学院的有色金属冶金系任教。后来作者之一的李庆峰到了丹麦技术大学化学系工作。1994年底，邱竹贤教授和已故的缪秀茳女士在访问挪威的途中，顺访了哥本哈根。本书的大纲是在那次的访问中拟定的。由于种种原因，全书直到2001年底才完稿。其中的几章（第四章，第六章，第七章）是在最初的几年里完成的，这次最后定稿时，又做了补充和修改。书中的第二章和第三章，由邱竹贤教授撰写，其余章节由李庆峰完成，并最后定稿。

本书作者感谢东北大学的老师和同学在多年的科研探索和本书的撰写过程中给予的热情帮助，感谢东北大学八十周年校庆学术著作出版基金的资助，感谢东北大学出版社的孟颖女士在编辑书稿过程中的巨大帮助。李庆峰还要感谢丹麦技术大学化学系的 Niels J. Bjerrum 教授和各位同事在本书撰写过程中所给予的支持和帮助。

作　者
2002年7月于沈阳

Preface

Electrochemistry of aluminum is of special importance from both theoretical and technological point of view. It covers a wide range of electrolyte systems from molten fluorides at around 1000℃ to room temperature molten salts, from aqueous to various organic media and from liquid to solid electrolytes. Technologically it involves many important aspects of applied electrochemistry: electrolytic production and refining of metals, electroplating, anodizing and other electrochemical surface treatments, primary and secondary batteries, electrolytic capacitors; corrosion and protection and so on.

The research activity in this connection has been so active and extensive that a rather well-defined field of electrochemistry of aluminum was already recognized in 1970s by Plambeck in *the Encyclopedia of Electrochemistry of the Elements* (Vol. 6, edited by A. J. Bard, Marcel Dekker, 1976). In recent years many advances in understanding the basic electrochemistry of aluminum and exploration of the related technologies have been achieved. This book is attempted to present a comprehensive review of the advances in the fundamental research with emphasis on the applied aspects. The idea of the book was conceived in the early 1990s, while both authors worked at Northeastern University, China. One of the authors, Li Qingfeng, moved to Technical University of Denmark in 1992. The scope of the book was first defined in 1994, when Professor Qiu Zhuxian and Ms Miao Xiujiang, on their way to Trondheim, Norway, visited us in Copenhagen. The book, however, was not complete until later 2001. Some chapters were written early (Chapters 4, 6 and 7) and major revisions were made by the time when the manuscript was finalized. Chapters 2 and 3 of the book were written by Qiu Zhuxian, the rest and the finial version by Li Qingfeng.

Li Qingfeng gratefully acknowledge the help and encouragement from Professor Niels J. Bjerrum and the Materials Science Group, Department of Chemistry, Technical University of Denmark, where the main work on this book was done. Professor Qiu would thank his colleagues and students at Northeastern University, China, for helps in preparation of the manuscript. Financial support from Northeastern University is sincerely acknowledged since otherwise the printing of this book would be impossible. The authors are grateful for the invaluable assistance of Ms Meng Ying in preparation of the manuscript.

Qiu Zhuxian and Li Qingfeng

July 2002, Shenyang

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Chapter 1

Introduction

Aluminum is the most abundant metallic element, making up more than 8% of the earth's crust. As a metallic chemical element in Group III of the periodic table, aluminum has an atomic number 13, atomic weight 26.98154. Pure aluminum is soft and lacks strength, but it can be alloyed with other elements to increase strength and impart a number of useful properties. Alloys of aluminum are light, strong and readily formatable by many metal working processes. They can be easily joined, cast, or machined and accept a wide variety of finishes. With a density about one third that of ferrous alloys, aluminum is used in building and construction, transportation (land, air and sea), beverage cans, other packing applications, consumer durable, equipment and machinery. The usefulness of aluminum is enhanced by its tendency to form an adherent oxide surface that resists corrosion.

The largest market for aluminum comprises containers and packaging. Beer and beverage cans have been the largest segment since the light weight and high recycle rate make aluminum cans very energy efficient and environmentally attractive. The second largest market is building and construction. Transportation field is another large market for aluminum, for example, in commercial and military aircraft and automobiles. Having a volume electric conductivity—only 62% of that of copper, aluminum is almost exclusively used for high voltage electrical transmission lines and other electrical conductors.

1.1 Physical properties

Aluminum is a silvery metal having a density of ca. 2.7 g/cm^3 at 20℃. Aluminum crystallyzes in the face-centered cubic structure with edge of the unit lattice cube being 0.40495 nanometer. Aluminum is known for its high electrical and thermal conductivities and high reflectivity. The electrical conductivity of very pure aluminum at room temperature is over 64% (by volume) of the International Annealed Copper Standard. At temperatures below 50 K, the electrical resistivity of pure aluminum is less than that of copper and silver of very high purity. Aluminum becomes superconductive below 1.2 K. A summary of physical properties of aluminum is listed in Table 1.1.

Table 1.1 Physical properties of aluminum.

Properties	Values or expressions as function of temperature
Atomic number	13
Atomic weight	26.981 54
Crystal structure, 4~933 K	Face-centered cubic
Lattice constant, 298 K	0.409 6nm
Melting point	933.52K (660.32℃)
Boiling point	2 767K
Massic heat capacity (solid), 298K	0.897 2 kJ/(kg·K)
0~200 K	$-5.342\times10^{-4}+5.133\,9T+1.063\,2\times10^{-3}T^2-4.981\times10^{-5}T^3+7.50\times10^{-8}T^4$, kJ/(kg·K)
300~933.5 K	$418.61+2.933\,8T-6.083\,9\times10^{-3}T^2-6.098\times10^{-6}T^3-2.10\times10^{-9}T^4$, kJ/(kg·K)
Massic heat capacity (liquid)	1.273 5 kJ/(kg·K)
Heat of fusion	3.97×10^5 J/kg
Heat of vaporization	10.777×10^6 J/kg
Tensile strength	50 MPa
Young's modulus	65 000 MPa
Density (solid), 298 K	2 698 kg·cm^3
298~933.5 K	$2\,852-0.888T+1.52\times10^{-3}T^2-9.85\times10^{-7}T^3$, kg/m^3
Density (liquid), 933.5~1173 K	$2\,546-0.165\,9T-2.91\times10^{-8}T^3$, kg/m^3
Electrical resistivity, 298 K	26.55 nΩ·m
273~933.5 K	$3.992+0.49\times10^{-2}T+20.39\times10^{-9}T^3$, nΩ·m
933.5~1 473 K	$10.398+1.475\times10^{-2}T$, nΩ·m

Table 1.1(continued)

Properties	Values or expressions as function of temperature
Thermal conductivity, 298 K	237 W/(m·K)
200～933.5 K	$222.2+701.8\times10^{-4}T^2-253.9\times10^{-9}T^3+166.2\times10^{-12}T^4$, W/(m·K)
933.5～2200 K	$0.681+4.589\times10^{-7}T^2-2.466\times10^{-10}T^3+3.722\times10^{-14}T^4$, W/(m·K)
Surface tension, 933.5～1273 K	$1.01-0.152\times10^{-3}T$, N/m
Viscosity, 933.5～1373 K	$0.1492\exp(1985/T)$, mPa·s
Linear expansion, 213～373 K	$L_{273K}[1+(22.17t+0.012t^2)\times10^{-6}]$
Vapor pressure, 1 000～2 600 K	$\mathrm{Exp}[17.336-(34\,599/T)-(1.4421\times106/T^2)]$, kPa
Magnetic susceptibility, 298 K	0.016 $m^{-3}\cdot g\cdot atom^{-1}$
Reflectivity at 0.9～12 μm	>0.9

1.2 Chemical properties

The electronic configuration of an aluminum atom is $1s^22s^22p^63s^23p^1$. There are 3 electrons in its outer orbits, 2 in the 3s orbit and 1 in the 3p orbit. The ionization energy of the 3p electron is 574.5 kJ/mol and the ionization energies of the 3s electrons are 1800 and 2730 kJ/mol, respectively. In general aluminum is trivalent, and at high temperatures there may be stable monovalent compounds.

Aluminum is stable in air and resistant to corrosion by seawater and many aqueous solutions and other chemical agents. This is due to protection of the metal by a tough, impervious film of oxide formed on the surface. Without this protective film, aluminum is a reactive metal with poor corrosion resistance. Whenever a freshly created aluminum surface is exposed to air or water at room temperature, an oxide film forms immediately and grows to a thickness of about 5 nm (50 Å) in air and to a somewhat greater thickness in water. Molten aluminum is protected by a much thicker oxide skin so that oxidation of the liquid also proceeds very slowly with no agitation. In finely divided form, aluminum reacts with water to form hydrogen and aluminum hydroxide.

At a purity greater than 99.5%, aluminum resists attack by most acids but dissolves in aqua regia. It is used in the storage of nitric acid, concentrated sulfuric and organic acids and many other chemical reagents. Its oxide film dissolves in alkaline solutions and corrosion is rapid to give soluble alkali metal aluminate and hydrogen:

$$2Al + 2OH^- + 6H_2O = 2Al(OH)_4^- + 3H_2 \quad (1.1)$$

Aluminum is amphoteric and can react with mineral acids to form soluble salts and evolve hydrogen:

$$2Al + 6H_3O^+ + 6H_2O = 2Al(H_2O)_6{}^{3+} + 3H_2 \quad (1.2)$$

At high temperatures aluminum reduces many compounds containing oxygen, particularly metal oxides. These reactions are used in the manufacture of certain metals and alloys of the type:

$$3MO + 2Al = Al_2O_3 + 3M \quad (1.3)$$

Aluminum reduces silicates, especially glass. Aluminum reacts with halogens to form the trihalides ($AlCl_3$, $AlBr_3$, AlF_3). By passing these gases over aluminum at elevated temperatures, the gaseous monohalides can be formed:

$$AlCl_3 + 2Al = 3AlCl \quad (1.4)$$

At high temperatures aluminum combines with carbon, nitrogen, sulfur, and phosphorus to form Al_3C_4, AlN, Al_2S_3 and AlP_9 respectively. Aluminum is attacked by salts of more noble metals, for example, compounds of mercury.

Aluminum is a negative ion usually given the formula $AlO_2{}^-$ and derived from aluminum hydroxide. Aluminum hydroxide is an amphoteric substance and thus can react with a strong base such as sodium hydroxide, to form sodium aluminate:

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O \quad (1.5)$$

It also reacts in a more usual manner with acids to form aluminum salts. Solutions of aluminates are strongly basic and the reaction is easily reversed even by weak acids to form the insoluble aluminum hydroxide. This is the basis for the commercial use of sodium aluminate in the clarification of water.