Molten Salts Chemistry and Technology

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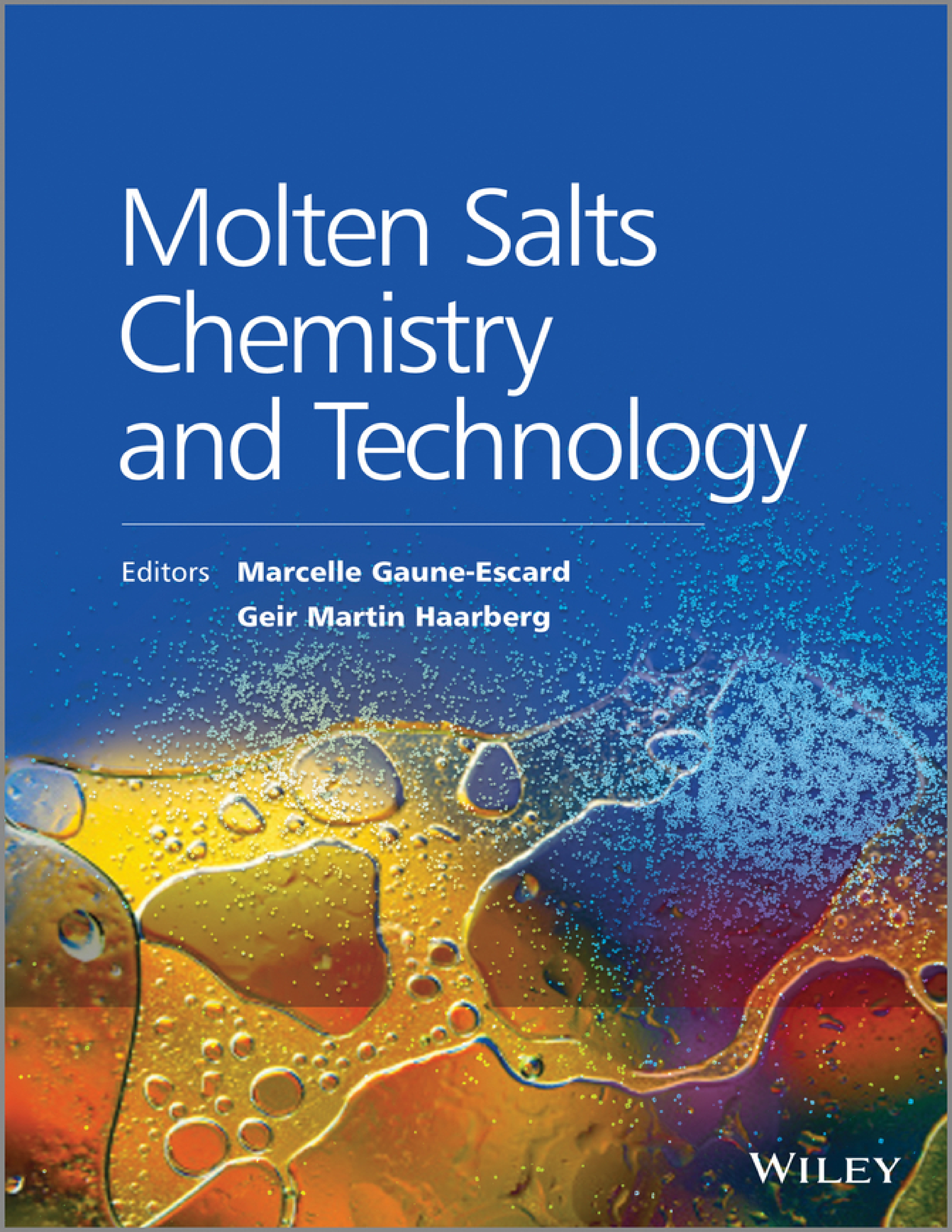

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Foreword

On the Occasion of His 80th Birthday

Douglas Inman was born on 5 September 1931 in London, UK and has had a long and outstanding career in electrochemistry mainly related to fundamental and technological experimental studies in molten salts at high temperatures. The topics were often related to the development of industrial processes for metal production.

He has made valuable fundamental contributions in the field of Electrochemistry in molten salts at large, including Electrometallurgy, Batteries, Fuel cells, Electrowinning, Electroplating, the Preparation of ceramics from molten salts, and Molten materials at high temperatures over many decades.

His contributions were very important for the development of the early theory for molten salt electrolytes. He made original approaches to develop the use of electrochemical techniques in new and important systems such as molten salts. His studies of the very fast kinetics of electrode reactions in molten salts were especially breakthrough achievements at the time.

His open and outgoing personality and excellent presentation skills have made him a very popular and inspirational person at international conferences, and he has made a lot of international contacts and collaborations. Furthermore, many undergraduates, graduates, postdoctoral students, and research associates have worked under his guidance.

Professor Inman has organised several international conferences and received many awards for scientific work: the Kroll Medal of the Institute of Materials for achievements in Chemical Metallurgy in 1994 and more recently a new award named the Inman Medal to mark the ‘outstanding scientific contribution’ he has made to electrochemical science and technology. Professor Inman, the first recipient of the award, was presented with the solid gold medal at an awards ceremony held at UCL on 16 June 2011.

He was the founding chairman of the still-existing biannual conference series ‘Molten Salt Discussion Group’, and he was twice the chairman of the ‘Euchem Conference on Molten Salts’. He has an impressive list of publications in international journals.

Professor Inman, in his 80s, is still keeping in touch with the scientific community by occasionally attending international conferences.

Outline of Career and Honours

1950	Awarded Entrance Scholarship to Imperial College, London, UK.
1950–1956	Successively undergraduate student and postgraduate student in the Department of Chemistry, Imperial College, London.
1956–1958	Scientific Officer, Metallurgy Division, A.E.R.E., Harwell, UK.
1957:	Awarded PhD at Imperial College, London
1958–1960	Postdoctoral Research Fellow, Department of Chemistry, University of Pennsylvania, Philadelphia, USA.
1960–1962	Imperial Chemical Industries Research Fellow, Department of Chemistry, University of Reading, UK.
1962–1964	Senior Lecturer, Department of Chemistry, Northampton College of Advanced Technology (which during this time became the City University), London.
1964	Promoted to Reader in the above department.
1964–1965	Founding Senior Tutor in Northampton Hall (a newly opened Hall of Residence of the City University, London.
1965	Visiting Summer Research Associate, University of Maine, USA.
1966	Nuffield Fellow, Department of Metallurgy (now the Department of Materials), Imperial College, London.
1968	Awarded DSc (Faculty of Science, University of London). Also became F.R.I.C. (now F.R.S.C.).
1972	Promoted to Reader in Chemical Metallurgy (University of London).
1976	Academic Visitor at Ecole Nationale Superieure

	d'Electrochimie et d'Electrometallurgie, Grenoble, France.
1977	Awarded Docteur Honoris Causa, Institut National Polytechnique de Grenoble.
1982	Title of Readership changed to ‘Applied Electrochemistry’.
1986	Promoted to Professor of High Temperature Electrochemistry (University of London).
1994	Awarded Kroll Medal of the Institute of Materials for achievements in Chemical Metallurgy.
1996	Became Emeritus Professor and a Senior Research Fellow of Imperial College, London.
2008	Appointed Visiting Professor in the Department of Chemical Engineering at University College, London.
2011	Awarded Inman Medal to mark his ‘outstanding scientific contribution’ to electrochemical science and technology.

Preface

Molten salts are widely used in a number of industrial applications. In connection with their exceptional properties, these fused media offer a wide panel of uses: Their thermal stability range and generally low vapor pressure are well fitted to high-temperature chemistry, enabling fast reaction rates. Their ability to dissolve many inorganic compounds such as oxides, nitrides, carbides and other salts makes them ideal solvents useful in electrometallurgy, metal coating, treatment of by-products and energy conversion. Their wide potential window between decomposition limits allows the electro-winning of highly electropositive elements or the preparation of very electronegative elements.

Molten salts play a major role in the development of energy resources. For many years, the reprocessing of nuclear wastes has been a priority for nations using nuclear energy; in that domain, different pyrochemical devices have been investigated involving molten salt solvents. Moreover, they appear as a promising route toward the emergence of safer nuclear energy (nuclear reactors, Generation IV). Quite recently, focus on thorium-based nuclear reactors aroused great expectation in terms of continuous waste molten salt processing and safety.

Now, laboratory research using fused salt is opening doors for valuable applications. Materials for energy storage devices can be successfully prepared by fused salt electrolysis: for lithium and sodium metal batteries, MFFC, lithium-hydrogen energy cycle, silicon electorefining. High-temperature molten salt batteries are also studied for high-capacity energy storage. Multicomponent alkali nitrate/nitrite melts are valuable materials for heat transport and storage in solar plants.

Historically molten salts have been and still are always widely used in industry. They remain privileged media for the surface treatment of tool steels including nitriding, nitrocarburizing, boriding and other steel surface-hardening methods. They are also well known as efficient media for heat treating not only a variety of metals from ductile iron to high-speed tool steel but also non-metals, such as glass, plastics and rubber. Indeed, this technology offers invaluable advantages that will be briefly described.

These concrete applications have induced a renewed interest for a fundamental study of the specific features of high-temperature ionic liquids and thus some chapters devoted to this description are included in the book.

The book contains 61 chapters written by authors all recognized as specialists actively working in fused salts chemistry, electrochemistry and solid state chemistry. Our purpose was to offer new aspects of Molten Salts Chemistry and Technology to readers from academia and industry. It should be useful for generating new ideas showing the interest of the molten salt route.

The present book summarizes recent advances on seven topics, namely Aluminium Electrolysis, New Processes for Electrowinning, Modeling and Thermodynamics, High-Temperature Experimental Techniques, Electrochemistry in Ionic Liquids, Nuclear Energy, Energy Technology, maintaining a link between fundamental investigations and industrial developments. It aims to present the state of the art of current research performed by the molten salt community.

Part 1

Aluminium Electrolysis

Chapter 1.1

Formation of CO2 and CO on Carbon Anodes in Molten Salts

J. Thonstad[1] and E. Sandnes[2]
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1.1.1 Introduction

There is a great body of information on the anode product on carbon anodes in cryolite-alumina melts, which is the electrolyte used in aluminium electrolysis. A typical electrolyte composition can be cryolite, that is Na_3AlF_6, with 12 wt% AlF_3 + 5 wt% CaF_2 + 2–6 wt% Al_2O_3, operating at around 960 °C. The consumable carbon anodes are baked into solid bodies from petroleum coke together with pitch, serving as binder.

For the use of carbon anodes in chloride melts containing oxides the information is much more scant. Sandnes *et al*. [1] presented polarisation curves on graphite anodes in NaCl-Na_2O and NaCl-$CaCl_2$-CaO melts. The content of CO and CO_2 in the anode gas was determined. As shown in the following, the CO_2/CO ratio varied widely. The work by Sandnes *et al*. [1] will be used to throw some light on the anode products as a function of composition and applied potential.

1.1.2 Results

1.1.2.1 Fluoride melts

The molten cryolite-based electrolyte (see above) is dissociated into Na^+ cations and AlF_6^{3-}, AlF_4^-, F^- and various oxyfluoride anions, like $Al_2O_4F_4^{6-}$. For aluminium electrolysis there are two possible cell reactions:

$$1/2\ Al_2O_3 + 3/4\ C = Al + 3/4\ CO_2 \qquad \textbf{1.1.1}$$

$$1/2\ Al_2O_3 + 3/2\ C = Al + 3/2\ CO \qquad \textbf{1.1.2}$$

The reversible E^0 of these reactions at 1000 °C are −1.187 and −1.065 V, respectively [2]. The difference in favour of Equation 1.1.2 reflects the fact that the so-called Boudouard reaction:

$$CO_2 + C = 2\ CO \qquad \textbf{1.1.3}$$

is strongly shifted to the right at this temperature.

The question whether CO_2 or CO is the primary anode product has been studied extensively [2 3] and it has been shown that, except at very low current densities, the primary product is CO_2 [2]. This conclusion has been based on carbon consumption studies (Equation 1.1.2) requires twice as much carbon per Faraday as Equation 1.1.1) and careful gas analysis, by avoiding disturbing side reactions, for example by using a diaphragm to separate the anode and cathode compartments [4]. Side reactions are reactions between CO_2 and carbon, either within pores in the interior of the anode, with carbon particles dispersed in the electrolyte, or with metal dissolved in the melt. In all cases the reaction product of these side reactions is normally CO. Dissolved aluminium can even reduce CO_2 all the way to carbon [5]. By bubbling CO_2 underneath a graphite anode it was shown [5] that, while Equation 1.1.3 did occur at zero current, the reaction ceased when the electrode was anodically polarised, even at quite low current densities (0.05–0.1 A cm^{-2}).

Most of the studies cited above were conducted in the time period between 1950 and 1980. However, as early as in 1936 Drossbach [6] demonstrated in a very elegant way how thermodynamic arguments could be applied to clarify the problem of identification of the primary anode product. If we consider the equilibrium:

$$\mathrm{CO} + 1/2\ \mathrm{O_2} = \mathrm{CO_2} \qquad \textbf{1.1.4}$$

it is seen that the CO_2/CO ratio defines a partial pressure of oxygen. In principle we can consider the primary cell reaction being:

$$1/2\ \mathrm{Al_2O_3} = \mathrm{Al} + 3/4\ \mathrm{O_2} \qquad \textbf{1.1.5}$$

The standard reversible potential of this reaction is $E^0 = -2.213$ V at 970 °C [2]. On an inert anode the anode product would be pure oxygen, so the anode potential (provided zero overvoltage) would be 2.213 V positive to an aluminium electrode. On a carbon anode the oxygen will react with carbon, and the partial pressure of oxygen will be much reduced and so would the anode potential. For the case of unit activity of alumina, the Nernst equation simply relates anode potential and oxygen partial pressure:

$$E = E^0 - \frac{RT}{3F} \ln\left(p_{O_2}^{3/4}\right) \qquad \textbf{1.1.6}$$

The so-called depolarisation, ΔE, that is the reduction in potential with respect to E^0 of Equation 1.1.5, can then be written as:

$$\Delta E = E - E^0 = -\frac{RT}{4F}\ln(p_{O_2}) \tag{1.1.7}$$

As shown by Drossbach [6], it can with good approximation be expressed as:

$$\Delta E = -\frac{0.0002T}{4}\log(p_{O_2}) \tag{1.1.8}$$

Table 1.1.1 gives some data for ΔE, log p_{O_2} and the partial pressures (%) of CO_2, CO and O_2. Drossbach's original data are used, which refer to 1161 K (= 888 °C), but the values are not far from being correct also at higher temperatures.

Table 1.1.1 Depolarisation, anode potentials and gas composition evaluated for Equation 1.1.5 at 1161 K. Reprinted from Ref. [6]. Copyright (1936) Wiley-VCH

ΔE	E	log p_{O_2}	CO_2 (%)	CO (%)	O_2 (%)
0.10	2.10	−1.73	98.1	—	1.9
0.20	2.00	−3.46	99.965	—	0.035
0.40	1.80	−6.93	100	—	—
0.60	1.60	−10.38	99.86	0.14	—
0.80	1.40	−13.84	93.4	6.6	—
1.00	1.20	−17.3	20.0	80.0	—

A typical anode potential at normal current densities (0.8–1.0 A cm^{-2}) is 1.6–1.7 V referred to aluminium. This implies that ΔE of Equation 1.1.8 is in the range 0.6–0.5 V. We see from Table 1.1.1 that the anode gas, according to equilibrium (Equation 1.1.4), then should consist of essentially pure CO_2. At very low current densities, corresponding to $\Delta E = 0.8$ ($i = 0.01$ A cm^{-2}), we can expect some CO.

It can be concluded that both experimental and thermodynamic data support the conclusion that the primary anode product is CO_2 at all normal current densities encountered in aluminium electrolysis. However, this statement anticipates that there are no secondary reactions converting primary O_2 and CO into CO_2.

1.1.2.2 Chloride melts

It is natural to compare the conditions in the cryolite system with the commonly used chloride melts. However, only limited numbers of investigations have been published on the reaction products from a carbon anode in chloride-oxide melts. A literature study by Sandnes *et al*. [1] is included here in the following. Gas chromatograph measurements are reported by Mohamedi *et al*. [7] for a $CaCl_2$ melt at 1123 K with a CaO concentration ranging from 3.3×10^{-5} mol cm^{-3} CaO (0.18 mol% CaO) to 2.7×10^{-4} mol cm^{-3} CaO (1.4 mol% CaO). At low current densities mostly CO_2 was produced with insignificant amounts of CO. At higher current densities the CO fraction increased to 10–20%. The anode outlet gas composition was measured by Cathro *et al*. [8] in a 65/10/25 mol% $MgCl_2/NdCl_3/NdOCl$ melt. At 750 °C on a high density graphite the $Cl_2/(Cl_2 + CO_2)$ mole fraction decreased from 70 to 28% by varying the current density from 0.36 to 0.089 A cm^{-2}. The effect of temperature was also studied. At constant current density 0.36 A cm^{-2}, the chlorine mole fraction decreased from 100% at 703 °C to 72% at 750 °C to 64% at 800 °C. Three types of graphite were investigated. At 750 °C little variation in the chlorine mole fraction was found between a high density graphite (1.76 g cm^{-3}), a lower density graphite (1.67 g cm^{-3}) and a carbon prepared from brown coal char. CO gas was not reported to have been analysed.