# Gas Transport Mechanism for Bubble Nucleation in Aluminium Electrolysis

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A Thesis Presented for the Degree of Doctor of Philosophy

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Melbourne, Australia

2019

#### Declaration

I, Epma Putri, declare that this thesis titled "Gas Transport Mechanism for Bubble Nucleation in Aluminium Electrolysis" is my work and has not been submitted previously, in whole or in part, in respect of any academic award. No material, to my best of knowledge, has been published in any form by any other person except where due reference is made.

Epma Putri July 2019

### Certification

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

**Professor Geoffrey Brooks** 

Dr. Graeme Snook

Dr. Ingo Eick

#### Abstract

Over the past century, research on different aspects of Hall-Héroult cell were conducted to increase energy efficiency, improve productivity, and reduce emissions in primary aluminium production. The existence of  $CO_2$  bubbles underside of the anode causes instability due to bubble turbulence and increases the ohmic voltage drop resulting in higher energy consumption. Despite the important role of the bubble layer, the details of bubble nucleation behaviour and the gas transport mechanism for the underside of the anode are not completely understood. The aim of this study is to improve understanding of the  $CO_2$  gas transport mechanism in correlation with the material properties such as porosity and permeability of anode material.

The CO<sub>2</sub> gas diffusion characteristics were first investigated via measuring anode porosity with three different techniques. Mercury intrusion porosimetry (MIP) measures pore sizes in the range of 6 nm to  $10\mu m$ , optical microscopy can measure the pore sizes in the range of 10 to  $100\mu m$  and X-ray Tomography (CT) technique can be used to measure porosity for pores between 50  $\mu$ m to 100  $\mu$ m. In this study, the MIP technique was used to measure average pore size for the theoretical prediction of CO<sub>2</sub> gas diffusion. This technique was selected because it measures the minimum diameter associated with pore entrance that cannot be detected by optical microscopy and CT. MIP was also used to measure the permeability and tortuosity of the anode samples.

The diffusion experiments were conducted by flowing  $CO_2$  gas into the anode sample at elevated temperatures to 960°C. The concentration change detected by a mass spectrometer was used to calculate the diffusion coefficient using curve fitting from diffusion theories. The value obtained varied from 1.38 x10<sup>-6</sup> m<sup>2</sup>/s to 7.89 x10<sup>-6</sup> m<sup>2</sup>/s for temperatures from 20 °C to 960 °C compared to Golovina's experiments that ranged from 2.25 x10<sup>-7</sup> m<sup>2</sup>/s to 9.47 x10<sup>-7</sup> m<sup>2</sup>/s over the range 25 °C to 600°C.[1] The impact of temperature, average pore size, and permeability on the diffusion coefficient were investigated. A high diffusion coefficient was measured in carbon samples with larger average pore size and higher permeability. An increasing trend of measured diffusion coefficient with an increase in pore size and permeability was observed. It was found that measured diffusion coefficients were not significantly affected by temperature over the range of 600°C to 960°C. This low dependence on the temperature was caused by convective flow effects, changes in diffusion mechanism and the onset of the Boudouard reaction for these carbon anode samples.

A finite element method was used to determine solutions for gas transport mechanism in porous media and simulate results of experimental work. The simulation work predicted that

the gas diffusion coefficient measurements would be affected by convective flow. The modelling predicted that the anode samples with lower permeability would have gas transport dominated by diffusion.

Diffusivity of  $CO_2$  in molten salt was determined theoretically and attempted experimentally. The Einstein-Stokes equation and its modification using Sutherland and Glasstone approach were used to calculate the  $CO_2$  diffusion coefficient in cryolite and compared to experimental results from previous authors for different fluids. Sutherland's equation was chosen based on the similarity of the experimental result with prediction for  $CO_2$  in water and NaNO<sub>3</sub>. The predicted  $CO_2$  diffusion coefficient in cryolite at 960°C using Sutherland's equation is 2.74x10<sup>-9</sup> m<sup>2</sup>/s. The previous experimental results from Rolin [2] gave a broad range of results from  $10^{-9}$  to  $10^{-12}$  m<sup>2</sup>/s while Vetyukov and Acquah [3] provided values between  $10^{-11}$  to  $10^{-12}$  m<sup>2</sup>/s. Two different techniques, the gravimetric method and absorption-desorption method were attempted to verify this number, but no reliable results were obtained. The main reason for this difficulty is due to the very low solubility of  $CO_2$  in the molten bath. The changes caused by the dissolving of  $CO_2$  in the molten bath are too low to be detected by the apparatus (micro balance and mass spectrometer) and the signals obtained were dominated by random errors and instrument noise. Furthermore, the corrosive nature of cryolite at high operating temperature limits the material and technique selection for diffusion measurements.

The present study compared different anode porosity measurement techniques and found MIP is the most suitable for predicting a diffusion coefficient for CO<sub>2</sub> and quantitatively measured the diffusion coefficient for three anode materials. However, the measurement of pure diffusion is difficult to obtain because the convective flow effect cannot be avoided in the experimental work and needs to be taken into consideration. This result showed the gas transport mechanism for bubble nucleation in Hall-Héroult cell is likely to be dominated by diffusion in porous solid because the diffusion coefficient in molten salt is three orders of magnitude lower than the diffusion coefficient for the anode material.

#### Acknowledgements

The research was carried out at the Swinburne University of Technology at department of mechanical engineering. The financial support of this project has been provided by Hydro Aluminium and the Research Council of Norway and is gratefully acknowledged.

I would like to express my deepest gratitude to Professor Geoffrey Brooks. His encouragement to do my Ph.D from overseas, guidance and support through the journey was very important for me. I always enjoyed our discussions and his enthusiasm regarding the research topic. His advice to solve problem and persistent to accomplish any goal motivated me to grow as researcher.

I would like to express my warmest gratitude for Dr Graeme Snook for the encouragements and inspiring advice through the journey. I will not forget the valuable discussions and suggestions that helpful in improving my skills and my confidence. His commitment towards the project was significant.

To my external supervisor, Dr. Ingo Eick, I would like to thank for his valuable discussions and introducing me to the aluminium industry. The industrial visit to Norway and Germany was an unforgettable part of my Ph.D journey. I am thankful for Dr Nancy Holt who allowed me to visit Hydro and gave warm welcome and support, Dr Lorentz P Lossius who provide the samples and gave valuable discussion about anode production. Dr Stein Rørvik who conducts the CT and image analysis in SINTEF, and valuable discussion when it comes to help with the imaging technique.

I owe sincere thankfulness to Katie McGregor and Theo Rodopoulus whom authorised financial support from CSIRO even after it took longer than planned to complete. Special thanks to Mark Cooksey, Malisja De Vries who assisted me in TGA experiment, Chris Sheedy who conducted ICP for the anode carbon samples, David Moleenar, Mike Horne, Mikko Vespelain, Bita Bayatsarmardi, Rebecca Dawkins, David Macedo who always help me in CSIRO.

I would like to thanks Dr Akbar Rhamdani as my chair committee, Kevin Nievart who helped me in MIP installations, Andrew Moore and Krzysztof Stachowicz helped me in diffusion rig installations, Sylvia Mackie who helped me in English writing and communication skill and special thanks for HTP group members for valuable discussion, Mehedi, Suneeti, Hasnat, Reiza, Firdaus, Bapin, Jaefer and Robin.

I also want to mention all help from my friend Teh Gina, Nyoman and Nelayan Squad who made me feel like I had family in Australia. Special thanks to Jason Zeinstra who supported me endlessly. Finally, I would like to acknowledge the support provided by my family during the preparation. Thanks to my siblings – Bang Yos, Aldo and my extended families for their loving support and prayers. This thesis is dedicated to my beloved parents, Iskandar Muda and Yanti Yulianti. They have always support me in any conditional way to help me achieve my dreams since my childhood until now.

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## Nomenclature

Symbol	Description
I	Electric Current
t	Time
F	Faraday constant
М	Molecular mass
Р	Energy produced at the electrode
Т	Temperature
Z	Number of electron involved in the electrode reaction
Erev	Reversible or Nernst potential
η <sub>sa</sub>	Surface overvoltage
$\eta_{ca}$	Anode overvoltage at
$\eta_{cc}$	Cathode overvoltage at
R <sub>el</sub>	Electrolyte resistance
$R_{bub}$	Bubbles resistance
$R_{an}$	Anode resistance
R <sub>ca</sub>	Cathode resistance
R <sub>ex</sub>	External resistance
$E_{cell}$	Total voltage of cell (V)
Pg	Pressure of dissolved gas
Pı	Pressure in the liquid
$\sigma_{\text{eg}}$	Liquid/gas interfacial tension
R <sub>crit</sub>	Critical radius of bubble
$D_{bub}$	Bubble diameter
m₁	Dry mass

m <sub>2</sub>	Mass of the immersed test piece
m <sub>3</sub>	Mass of the immersed test piece
$ ho_b$	Bulk density
r	Pore radius
$\gamma_{Hg}$	Mercury surface tension
θ	Contact angle between mercury and carbon
$V_{P}$	The volume of the porosityfrom the measurement of and ()
$V_{B}$	Bulk volume ()
$V_{Sk}$	Skeletal volume
φ	% Porosity
S	Pore surface Area
$d_{mean}$	Mean pore diameter
Ν(δ)	Number of elements of dimension $\delta$
δ	Smallest dimension after n divisions
D <sub>f</sub>	Fractal dimension
Pt	Threshold pressure
$L_{max}$	Hydraulic conductance is maximum
S(L <sub>max</sub> )	The fraction of total porosity filled at $L_{max}$
τ	Tortuosity
k	Permeability
CT	CT number of the volume
$CT_{max}$	Maximum CT number allowed in the sample.
Q	Fluid flow rate
Ug	superficial velocity
Re	Reynolds number

- $\bar{\mu}$  Effective viscosity at the wall
- k<sub>b</sub> Boltzmann constant
- K<sub>n</sub> Knudsen number
- C(x,t) Concentration fuction in certain thickness and time and
- *erfc* is the complementary error function
- D<sub>K</sub> Knudsen diffusion
- D<sub>m</sub> Molecular diffusion
- D<sub>eff</sub> Effective diffusion
- X<sub>i</sub> Gas mole fraction
- $J_i^T$  Total diffusive and advective molar flux,
- N Molar diffusion flux
- $\omega$  Angular velocity of the electrode
- K<sub>L</sub>a' Volumetric coefficient of liquid-phase mass transfer
- $N_{\varepsilon \ddot{o}}$  Eotvös number
- *Ri* Reaction rate

# **Chapter 1**

#### 1. Introduction

#### 1.1. Research Motivation

In the Hall-Héroult cell, aluminium is produced by electrochemical reduction of alumina ( $Al_2O_3$ ) in molten cryolite (NaAIF<sub>6</sub>) enriched with fluorides as its electrolyte. Although this method has been used in the industrial scale for the last century, many aspects of it can be improved to reduce energy consumption for economic and environmental sustainability. Aluminium electrolysis is a highly energy-intensive industry with more than 3% of the world's entire electrical supply used in the extraction of aluminium [4]. While the past technology achievements have increased the current efficiency of aluminium cells up to 96 % and lowered the specific energy consumption to 12.5 DC kWh/kg Al, the industry continues to pursue research to increase energy efficiency, improve productivity, and reduce emissions from primary aluminium production, [5].

Over the past decade, the relationship between the gas bubbles generation of carbon anodes related to ohmic voltage drop has attracted attention, due to energy saving possibilities for the smelting process. Understanding bubble nucleation behaviour is essential to reducing bubble-induced voltage. The complexity of the anode bubble process lies in the fact that the carbon dioxide gas produced by the multi-step electrochemical reaction can diffuse through the porous anode and the electrolyte bath; consequently the bubble generation is affected by its properties such as composition, porosity, and permeability of the anode material. In particular, the correlation between gas diffusion, anode and bath properties remains unclear.

This study attempts to provide more detailed investigations regarding gas transport mechanism for bubble nucleation in aluminium electrolysis and provide data for the simulation of bubble formation and transport. Therefore, experimental study will be conducted to predict and measure the diffusion coefficient of CO<sub>2</sub> in both mediums to support this objective. This study is primarily focused on developing a fundamental understanding for the transport phenomena related to bubble nucleation; in conjunction with anode and bath properties in aluminium smelting process. Thus, the aim of this work will be to address the following fundamental questions regarding the diffusion process and its properties in Hall-Héroult process:

- Is it possible to characterize anode porosity as basis measurement for diffusion experiment?
- Does the anode properties affect the diffusion process?

- Is it possible to measure diffusion coefficient without affected by convective flow?
- What are the factors responsible for the gas diffusion process?
- What is the relative importance of CO<sub>2</sub>/CO diffusion process on bubble nucleation?

#### 1.2. Thesis Overview

This thesis is organized into ten different chapters. In Chapter 2, the literature on the fundamental aluminium electrolysis process, anode production, energy consumption and bubble generation is described. Chapter 3 provides an overview on different anode characterization techniques (Hydrostatic method, Mercury Intrusion Porosimetry, Image analysis using optical microscopy and CT) for measuring porosity. In Chapter 4, theories on measurement and modelling of diffusion coefficients for both porous solid and molten salt are examined.

Chapter 5 describes the conclusion drawn from literature review and identified the research issues from this study. Chapter 6 discusses the relationship between porosity and anode physical properties such as density, permeability and anode reactivity. Chapter 7 describes experimental studies to investigate the diffusion coefficient with different anode sample and theoretical predictions for diffusion in a porous solid. Chapter 8 provides the analysis of convective flow and its relation to temperature using a finite element method. In Chapter 9, prediction of diffusion coefficient of CO<sub>2</sub> in cryolite and experimental work for measuring diffusion in molten salt are described. In Chapter 10, the major conclusions from the study are presented. The recommendations for future study are also included in this chapter

#### 1.3. Publications from This Research

- Epma Putri, Geoffrey Brooks, Graeme A. Snook, Ingo Eick. "Anode characterisation and gas diffusion behaviour in aluminium smelting." In *AIP Conference Proceedings*, vol. 1805, no. 1, p. 040001. AIP Publishing, 2017.
- Epma Putri, Geoffrey G. A. Brooks, Graeme Snook, Stein Rørvik, Lorentz P Lossius, and Ingo Eick," Understanding the Anode Porosity as a Means for Improved Aluminium Smelting." In *TMS Annual Meeting & Exhibition*, pp. 1235-1242. Springer, Cham, 2018.
- Epma Putri, Geoffrey G. A. Brooks, Graeme Snook, Lorentz P Lossius, and Ingo Eick," Diffusion and Flow of CO<sub>2</sub> in Carbon Anode for Aluminium Smelting accepted in Metallurgical transaction B, December 2018

# Chapter 2

### 2. Background and Theory

#### 2.1. The Hall-Héroult Process

Aluminium is the third most abundant element in the earth's crust with approximately 8.1% weight of the earth solid surface. It is found rarely in its pure elemental state due to its strong affinity with oxygen in the form of hydroxides such as bauxite and various oxides. The Hall-Héroult process is the only industrial-scale smelting process for extracting aluminium from alumina.[6] The process invented independently by Charles Hall from USA and Paul Héroult from France in 1886. Aqueous electrolytes cannot be used because hydrogen is evolved in an aqueous electrolyte before aluminium can be produced by reduction. Instead, the Hall-Héroult cell uses molten salt as its electrolyte. The molten salt used for electrolysis is referred to as cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and allows electrolysis of the dissolved alumina as it is one of the few solvents that will appreciably dissolve alumina. Apart from the development of the carbon anodes formed, the electrolytic process principally remains the same. For the past century, technology improvement in materials selection, magnetic compensation, process control and the application of advanced mathematical modelling through larger cell operation and cell productivity enhancement have led to increased performance and lower environmental impact.[7]

Aluminium is produced by alumina reduction in a molten salt bath containing mainly cryolite and aluminium fluoride at the temperature ~960° C. Figure 2.1 schematically shows a cross section of the cell with key materials used in the electrolytic reduction cell. The cell consists of carbon cathode blocks, carbon anode blocks and the ramming paste inside the steel shell that protects the pot from thermal and chemical expansion. The anode and cathodic metal are arranged horizontally as the distance between them is about 3 to 6 cm to ensure sufficient heat is generated. The pot is also equipped with a crust breaker and an alumina feeder under automatic control to maintain uniform distribution of dissolved alumina into the anode-cathode gap throughout the bath volume for optimum cell performance.[8]

During the electrolytic process, molten aluminium is obtained underneath the electrolyte when the direct current is passed between the anodes and the carbon cathode. Oxygen containing ions from the alumina are released into the electrolyte, diffuse to the anode and react with carbon resulting in the oxidation to form  $CO_2$  and CO. Even though CO gas is thermodynamically favoured at high temperature, formation of  $CO_2$  gas dominates the process at high current density as the result of non-equilibrium conditions in the Hall-Héroult cell [9]. CO gas is produced as a secondary product and is associated with re-oxidation of dissolved metals [10].

The CO<sub>2</sub> gas is generated in anode as the result of multi-step chemical reactions; with overall reaction is:

$$2Al_2O_3 + 3C = 4Al + 3CO_2$$
 Equation 2-1

Based on stoichiometric calculation, 1 tonne of pure primary aluminium output, requires 1889 kg of alumina and 333 kg carbon from anodes. This amount of alumina is produced from 5571 kg of bauxite through the Bayer process on average [4]. In a modern aluminium smelter, one or more potlines consist of 300 to 350 Hall–Héroult cells arranged in series with an operating current up to 500 kA for the latest generation. A typical smelter will produce 300,000 metric tons per year and the largest smelters can produce up to 1 million metric aluminium tons per year [11].



Figure 2-1 Diagrammatic Hall-Héroult cell with prebaked anode [12]

As a result of reaction with the electrolyte, the anode is gradually consumed and has to be replaced after 22 to 26 days [13]. The cell is operated so that sidewalls are protected with frozen cryolite and the upper bath is covered with alumina crust. However, the carbon sidewalls are still degraded due to electrolyte and aluminium attack. Therefore, over the past thirty years, SiC and  $Si_3N_4$  bonded SiC materials have been increasingly used as replacement of carbon sidewalls due to lower electrical conductivity and higher resistance in electrochemical wear. [7]

The molten electrolyte bath consists principally of cryolite (Na<sub>3</sub>AlF<sub>6</sub>) with excess AlF<sub>3</sub> (6 to 13%) and CaF<sub>2</sub> (4 to 6%) along with a regular feeding of Al<sub>2</sub>O<sub>3</sub> (2 to 4%). [10] Solubility of alumina decreases with decreasing NaF/AlF<sub>3</sub> ratio and increasing alumina content. Proportion of LiF and MgF<sub>2</sub> are sometimes added to lower freezing point of the bath, however this can increase the quantity of Li and Mg in the product. Generally, the main concern of additive usage for lowering freezing point is the resultant decreasing ability to dissolve alumina [10,14].

Faraday's law is applied to calculate the amount of product deposited in the cathode. From this theoritical calculation 1 Ampere-hour forms 0.335 gram aluminium, as shown in Equation 2.2.

$$P = \frac{M}{zF}$$
. I. t Equation 2-2

Where P is the amount of energy produced at the electrode, M is molecular mass (gram per mole), Z is the number of electron involved in the electrode reaction (here Z = 3), F is Faraday constant, I is current (Ampere) and t is the time (seconds) [13].

#### 2.2. Anode Production

Two different types of anode carbon are utilized in the cell, Søderberg anodes and prebaked anodes. The comparison between these anodes is illustrated in Figure. 2.2. The major advantage of Søderberg anodes is the continuous self-baking process using only a briquetting stage so that the process involves less disturbance. Comparatively more manufacturing steps are required to produce the prebaked anodes. Initially, the carbon paste is shaped and baked in the optimum temperature at 1250°C [15].



Figure 2-2 Stage process comparison between baked anode and Søderberg anode [16]

The prebaked anode is roded for installation and has to be replaced after 22 to 26 days usage. The prebaked anode presents better quality and consistent results in addition to lower anode consumption, lower emission and greater efficiency than the Søderberg anode. In 2010, world primary aluminium production was dominated by prebaked anode usage at around 86% [4]. Only prebaked anode cells are addressed in this review, although the results could possibly apply to Søderbergcells. [4,13].

#### 2.3. Anode Carbon Properties

Anode properties and performance are related to three fundamental components: carbon microstructure, impurities, and porosity accompanied by their interactions [17]. Baked anodes are made from a mixture of coke and butt grain which is joined by binder matrix consisting of coked pitch and coke, as shown schematically in Figure 2.3 The microstructure of anode is associated with carbon consumption during reduction process. There are two possible reasons of excess anode carbon consumption namely back reaction with carbon dioxide as electrolysis product ( $CO_2$  burn) and the reaction with oxygen at the exposed top surface of the anode (air burn). These reactions predominantly attack the binder matrix by selective burning. The systematic arrangement of crystallite contributes to the increase of real density. Uniform coke distribution as a filler achieved by anode compaction also lowered anode reactivity [18].

There have been a number of studies in anode composition to evaluate its influence on anode consumption. In one study, Fischer and Perruchoud [18] utilized x-ray fluorescence apparatus to examine the impurities and its impact from used anode. This experiment showed that sulphur is the main elemental impurity component, followed by sodium and iron increasing the anode reactivity. In later studies, by Suriyapraphadilok et al. [19] the measurement of the amount of inorganic material was carried out by inductively coupled plasma (ICP). The chemical analysis identifies very high iron content in this sample and other major inorganic contents are sulphur, sodium, aluminium, and calcium.

Furthermore, Houston and Øye [20] indicated the level of reactivity of chars (or cokes) made from lignite in  $CO_2$  and air followed the order of Na > K > Ca > Fe. These inorganic matters are well known as catalysts for air oxidation. These results are consistent with the findings of Walker and Raats [21] who found that sodium had the strongest catalytic effect for the carboxy reaction despite the presence of other catalytic metals. It can be concluded that the catalysts enhanced the reactivity of chars under oxidation with variations of anode consumption rates. However, not all cokes are significantly sensitive to the sodium catalytic effect [21].

The third aspect that influences the anode carbon properties is the porosity. Far-wharton et al.[22] identified three electrochemical reactions that occur during the electrowinning of

aluminium. These reactions are: carbon dioxide evolution, carbon monoxide evolution, and chemical reaction between carbon dioxide and carbon, which take place in the sub-surface pore structure. The latter two reactions rely on the carbon structure or real surface area and porosity of the constituent carbons. This will be explained in the next section



Figure 2-3 Composition of a baked anode (a) grains > 0.1 mm. (b) binder-matrix (mixture of dust and pitch (c) macro porosity > 5  $\mu$ m (open and close)[18].

### 2.4. Molten salt electrochemistry

Molten salts have drawn attention over the past century in various fields including: theoretical and applied electrochemistry, analytical principles of chromatography, non-aqueous solvents, thermochemistry, fuel cells and batteries, corrosion science, and nuclear technology [23]. One of the most important molten salt utilisations is for aluminium production in the Hall-Héroult cell.

The molten electrolyte bath consists principally of cryolite (Na<sub>3</sub>AlF<sub>6</sub>). Cryolite is the only suitable material for the aluminium reduction purposes because its properties allow it to dissolve aluminum oxide, to conduct the electric current without self-decomposition and form a cell lining protective frozen ledge [7]. Furthermore, it is important to operate in the highest current efficiency at minimum energy consumption in electrolytic process. The operating cryolite molar ratio of NAF: AlF<sub>3</sub> is 2.0-2.5 in modern alumina reduction cells, while the mass ratio of NaF/AlF<sub>3</sub> is called the bath ratio (numerically half of cryolite ratio). The electrolytic bath typically contains excess AlF<sub>3</sub> (6 to 13%) and CaF<sub>2</sub> (4 to 6%) along with a regular feeding of Al<sub>2</sub>O<sub>3</sub> (2 to 4%).[14] Solubility of alumina decreases with decreasing NaF/AlF<sub>3</sub> ratio and increasing AlF<sub>3</sub> content [14,24].

There have been several studies in the literature investigating additives used to improve chemistry and physical properties of cryolite. One of the most important requirements for ideal additives is the ability to lower the liquidus temperature, the lowest operating temperature where the precipitations of aluminium formed. Tarcy et al [5] reported that lowering the operating temperature enhanced the current efficiency by about 0.18%. However, to achieve longer lifetime usage of cell lining by a frozen electrolyte layer forming, the cell must be operated 10 to 15°C above the eutectic temperature and alumina content less than eutectic composition. High operating point will results in melting frozen ledge resulting shorter cell life and various anode problem that reduce the cell productivity [14,24].

The physicochemical properties of cryolite-alumina melts with additions of AIF<sub>3</sub>, CaF<sub>2</sub>, LiF, and MgF<sub>2</sub> have been studied extensively. Haupin [25] summarizes the influence of additives in the Hall-Héroult cell. It can be seen in the NaF-AIF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> phase diagram shown in Figure 2.4. that the liquidus temperature of cryolite varies by the addition of alumina and alumina fluoride. Due to small amount of calcium oxide impurity in the alumina concentration, calcium fluoride lowered the liquidus temperature about 2.9° C per weight percent. The other additives are LiF and MgF<sub>2</sub>, lithium fluoride is superior to all other additives with respect to the physicochemical properties of the electrolyte. The additives consumption varies 2 to 3 Kgs of LiCO<sub>3</sub> per ton of aluminium to maintain a concentration of 1.5 to 3 mass% of LiF.



Figure 2-4 The NaF-AIF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> system [25]

Even though the additives give great advantages by lowering freezing point of the cryolite from 1011 ° C to 970°C resulting in decreased energy consumption, it is always accompanied by

reduced ability to dissolve alumina (from 15 wt% to about 6 wt %). The alumina is fed periodically to avoid the "anode effect". This phenomenon occurs if the alumina content falls below 2%. A gas film covers the anode preventing the ability to wet the anode surface. This results in a higher electrical resistance 10 to 15 times the normal level. [26]

Physical data for electrode and electrolyte reaction in the aluminium electrolysis cell is difficult to obtain due to the extreme temperature and corrosive environment in the bath. Chemical calculations and simulations of the Hall-Héroult two-phase electrolysis properties were performed by Mandin[27]. The bath reaction can be classified as dissolution reactions, equilibrium reactions and electrochemical reactions by considering the motion of seven species  $AIF_4^-$ ,  $AIF_5^{2^-}$ ,  $AIF_6^{3^-}$ ,  $AI_2OF_6^{2^-}$ ,  $AI_2O_2F_4^{2^-}$ , F- and Al. The consumed anode electrochemical caused by cathode reactions in the aluminium production and current supply at the reactor bottom explained with the following equations:

$$AIF_{4^{-}} + 3e^{-} = AI_{(1)} + 4F_{-}$$
 Equation 2-3

$$AIF_5^{2-} + 3e^- = AI_{(1)} + 5F_-$$
 Equation 2-4

$$AIF_6^3$$
- +  $3e^-$  =  $AI_{(1)}$  +  $6F_-$  Equation 2-5

The following electrochemical reactions occur at the anodes:

$$AI_2O_2F_4^{2-} + 4F^- + C = 4e^- + CO_2 + 2 AIF_4^-$$
 Equation 2-6

$$AI_2OF_6^{2-} + 4F^- + C = 4e_- + CO_2 + 4AIF_4^-$$
 Equation 2-7

The solubility and diffusivity of CO<sub>2</sub> in cryolite will provide important information to simulate the actual bath reaction in Hall-Héroult Cell. Rolin [2] reported that the saturation concentration and the diffusivity of CO<sub>2</sub> in molten cryolite at 960°C are very low, only 3 to 5 x 10<sup>-6</sup> mol/cm<sup>3</sup> and  $10^{-5}$  -  $10^{-8}$  cm<sup>2</sup>/s respectively [15]. Alternatively, Vetyukov and Acquah [3] proposed the solubility value is ~5 x 10<sup>-6</sup> mol/cm<sup>3</sup> and the diffusivity coefficient is  $10^{-7}$  -  $10^{-8}$  cm<sup>2</sup>/s. However, this data has not been thoroughly investigated and may need to be updated. Therefore, CO<sub>2</sub> solubility and diffusivity measurement will be discussed in Chapter 4.

#### 2.5. Energy Consumption in Hall-Héroult Cell

One of the major drawbacks in the Hall-Héroult process is the high energy consumption leading to high operating costs. The theoretical amount of energy required is 6.4 kWh at 960° C includes the thermodynamic energy needed by the reaction to produce aluminium and the additional energy required to heat the reactant from room temperature to the controlled operational temperature.[28] However, the energy consumed by the process to produce 1 kg aluminium in practice is about 13 kWh [6]. Furthermore, Haupin et al [10] reported a thermodynamic theoretical calculation in a large modern cell (>300 kA) operating at 960° C, 4.19 volts, 96% current efficiency, 25°C ambient temperature with 10% alpha alumina

saturation lead into  $\sim$ 50% energy efficiency with carbon anodes. Therefore energy efficiency has an important role in lowering production cost.

Figure 2.5 illustrates the schematic representation of cell voltage and energy distribution. The energy plot shows that only 6.324 kWh/kg energy contributes to the production of aluminium. In practice, the cell design, amperage, anode size and thermal insulation are already determined, therefore cell voltage which is related to anode-cathode distance (ACD) is the main factor which determines the heat loss in the operating cell. In the current technology, The ACD cannot be reduced any further due to the increased back reaction between alumina and carbon and the strong movement of the magnetic field in the cell. The ACD allowed heat flow to maintain the correct bath temperature through the sidewall to form a protective frozen layer to enhance the sidewall lifetime [13].

The total cell voltage calculation is shown in equation 2.8 where I is cell current or line current (kA). Table 2.1 summarize the component detail and explanation of voltage distribution estimation in the aluminium reduction process.

$$\text{Ecell} = \text{E}_{\text{rev}} + \eta_{\text{sa}} + \eta_{\text{ca}} + \eta_{\text{cc}} + \text{IR}_{\text{el}} + \text{IR}_{\text{bub}} + \text{IR}_{\text{an}} + \text{IR}_{\text{ca}} + \text{IR}_{\text{ex}} \qquad \qquad \text{Equation 2-8}$$

Understanding the voltage characteristic of each component means that the specific target of energy efficiency improvement can be achieved. However, there is still no agreement among researchers about the relationship between the anode geometry and the over potential which varies with the alumina content of the electrolyte. This is because of the variable substance characteristics of the carbon and geometry is hard to study at scale [29].

Data in Table 2.1 presents the most significant overvoltage resulting from electrolyte resistance. This is influenced by electrolyte material resistance as a function of the anode cathode gap and the cross sectional area of current flow. In industrial practice, the electrically non-conducting bubble layer formed as the result of  $CO_2$  gas generation will add to the resistance experienced by the cell. The bubbles constrain the current passage that passes through the electrolysis cell and increases the electrolyte resistance. Here the voltage drop caused by bubbles formation itself contributes ~0.25 V of the total cell voltage as shown schematically in Figure 2.5. The representation of bubble behaviour is shown schematically in Figure 2.6

Although a few studies on bubble resistance have been performed using physical modelling, there is still limited information available on gas film characteristics due to the high temperature molten salt experimentation limitation. The verification of the laboratory or physical modelling results is difficult to implement in industrial cell. Snook et al [30] measured dynamic bubble resistance for non-steady state using the Fast Fourier Transform Current Pulse (FFTCP). A

Randles equivalent circuit was used to validate this technique and applied to aqueous solution of 1 M KOH with bubbles generated from two opposing vertical platinum electrodes. This instrument has enabled in-situ measurement for capacitance values, anode bubble coverage, the available electrode surface area assessment during electrolysis and accurately compensate for the IR-drop in laboratory-scale cells for currents of up to 10 A .[31]

	Component	Explanation	Contribution
			voltage values
			(V)
	Reversible or		
E <sub>rev</sub>	Nernst	Voltage required to hold the cell in equilibrium.	1.222
	potential		
η <sub>sa</sub>	Surface		0.466
	overvoltage		0.400
η <sub>ca</sub>	Anode	Over voltages result from concentration gradients and the kinetics of surface reactions at the electrodes.	0.036
	overvoltage		
	at		
η <sub>cc</sub>	Cathode		0.032
	overvoltage		
	at		
R <sub>el</sub>	Electrolyte	The voltage drop across the region where	1 33/
	resistance	electrolysis is occurring	1.554
R <sub>bub</sub>	Bubbles	The voltage drop resulting from bubble formation	0.25
	resistance		
R <sub>an</sub>	Anode	The voltage drop in anode	0.35
	resistance		
R <sub>ca</sub>	Cathode	The voltage drop in cathode	0.35
	resistance		
R <sub>ex</sub>	External	The voltage drop across the other elements in the	0.15
	resistance	process, i.e. anodes, cathode, busbar etc	
Ecell	Total voltage of cell (V)		4.19

Table 2-1 Typical voltage distribution in Hall-Héroult Cell [10]



Figure 2-5 Cell voltage and energy distribution in an aluminium reduction cell [10]



Figure 2-6 Representation of electrolysis reaction zone in the Hall-Héroult cell [32]

The bubble induced flow causes instability due to bubble turbulence, and the flow increases the ohmic voltage drop in the region containing a mixture of bubbles and electrolyte underneath the anode surface, thus, in turn resulting in higher energy consumption for the smelting process [33]. In contrast, the bubble formation has positive role in dissolution of alumina powder along with natural convection and the magnetic field. It also improves the mixing in the cell, increasing the dissolution rate of alumina and protecting the frozen sidewall as the result of a uniform temperature field [34]. The behaviour and the importance of bubble layer formation will be discussed further in the next section.

#### 2.5.1. Bubble Generation

In recent years, there has been an increasing amount of literature on using anode bubble behaviour to reduce the negative effect from the bubble formation. The bubble nucleation and movement in the Hall-Héroult process is complex due to surface tension, bubble shape, and anode characterization [35]. The growth cycle starts with a slow, latent period in the early period of the nucleation of a bubble. The smaller the bubble, the higher surface tension required to overcome the restrictive force of the surface tension. [36] The bubble formation is distinguished in five important stages namely bubble nucleation, growth, detachment, coalescence and bubble release. In subsequent sections, this review will focus on bubble nucleation with the correlation between gas diffusion, anode and bath properties.

#### 2.5.2. Bubble Nucleation

The bubbles are formed as the result of continuous  $CO_2$  and CO gas evolution under carbon anode during electrolysis. The gas release rate can reach as high as0.2 cm<sup>3</sup>/s per square cm of anode surface in commonly used cells. Thonstad [9] conducted a small scale experimental procedure using an anode dipped in a graphite container filled with electrolyte. He observed that  $CO_2$  was mainly produced as the result of non-equilibrium conditions in the Hall-Héroult cell. Additionally, the reaction of  $CO_2$  gas with carbon anode forms CO gas which doubles the anode gas volume and becomes supersaturated within electrolyte forming gaseous phase. These gases are stored in the pores and coalesced into bubbles periodically in preference to nucleation sites on the bottom surface of the anode [37]. The bubble nucleation reaction takes place at the interface between active electrolysis sites and the porous anode with approximately 15 to 25 % interconnected pores [38].

Classical nucleation applied in fundamentals of electrolytic gas evolution is described by Vogt [37]. He demonstrated a correlation between the sum of vapour pressure of pure solvent and partial pressure of dissolved gas ( $P_{g}$ ), Pressure in the liquid ( $P_{I}$ ), and the liquid/gas interfacial tension ( $\sigma_{eg}$ ) to form critical radius of bubble ( $R_{crit}$ ).

$$R_{crit} = \frac{2\sigma_{eg}}{P_g - P_l}$$
 Equation 2-9

Equation 2.9 shows that the bubble must reach a critical size to have a tendency to grow larger. Additionally, this condition can also be applied into bubble nucleation through imperfection, or pore size in anode surface needing to be larger that critical size. The bubble grows via the supply of dissolved gas from the electrolyte.

A non-classical nucleation theory explained by Jones et al. [39] can be used to predict the bubble formation in the supersaturated solution which depends on steady production of gas. The mechanism where there is no nucleation energy barrier to overcome is illustrated in Figure. 2.7. This nucleation starts in the pre-existed cavities with much greater radius than critical bubble radius, as the supersaturation decreases the critical radius grows to equal value of the cavity meniscus and bubble production ceases.



After Supersaturation



Figure 2-7 Non classical bubble nucleation [39]

This theory supported by Xue and Oye [40] who identified the linear relation between voltage and time during the initial growth of bubble, the bubble diameter  $D_{bub}$  should obey:

#### $D_{bub} \propto \sqrt{t}$

They suggested that bubble nucleation begin with low to moderate levels of super saturation due to short time between bubble generation and release with steady gas production of gas rather than abrupt gas production of bubble in classic nucleation [41]

#### 2.5.3. Anodic Bubble Behaviour

Laboratory scale electrolysis experiments, physical models and mathematical models have been used to study the bubble behaviour due to the difficulties of industrial measurement. Fullscale water models with dimensional similarity were used by Fortin et al [42] to observe the shape of the bubble and in particular its volume. The small bubble shape is spherical, then increases its size by collision forming bigger bubbles (coalescence), whereas the large bubbles are highly deformed under the force of buoyancy a shown in Figure 2.8. In the later study, Chen [43] improved the water model with dynamic similarity to the real cell. He reported that the shape of the bubble transformed from ellipsoid to crescent as the gas flow rates increased. Furthermore, the detachment of the bubble occurs when the movement forces of the bubble overcome the forces that keep bubble stationary at the nucleation site.



Figure 2-8 Fortin bubble with the "head" and "tail" shape [42]

With same objective as the previous research, Perron et al. [44] conducted an experiment using a low temperature water model and identified there are two different bubble shape regimes as "creeping bubble" and "bubble in wetting film". These mechanisms are illustrated in Figure 2.9. Bubble shape (a) and (b) belonged to creeping zone where the bubbles travel along with the line and contact area between bubble and anode during the creeping motion, there is a "dry spot". In this zone, the surface and gravity forces are always in a delicate equilibrium. In this regime the contact line of the bubbles is elliptic and the longer axis lies in the direction of the displacement. Then, the bubble starts to form a liquid layer and an elongated shape due to the movement and acceleration. Finally, the wetting film zone is shown in part d where the liquid separates in the higher portion of the contact surface, and the bubble
regains a near circular form. Flat shaped bubbles are caused by buoyancy forces while semi spherical shaped bubbles shape are mainly affected by the contact angle between gas, carbon and electrolyte [26].



Figure 2-9 Regimes of movement of bubble [44]

Furthermore, anode coverage, bubble velocity and gas release frequency, which are related to current density, anode cathode distance (ACD), and anode inclination angle have been investigated. Solheim et al. measured liquid velocity through a mathematical model and they reported when the ACD is less than 3 cm that the resulting bubble velocity was slower. This result is in contrast with the results of Fortin et al. [42] where it was reported that ACD has no effect on bubble velocity.

Peng et al. [45] reported that increasing anode inclination angle resulted in smaller bubble detachment volume and faster bubble sliding velocity. These findings are in agreement with Das et al. [46] experiments using low temperature glycerol and water bath modelling with dynamic similarities taken into consideration. They measured the smaller bubble size at higher anode inclination and observed that increasing liquid surface tension produced bigger bubbles. Moreover, it is reported that smaller bubbles resulted from higher accumulated gas volume as well as higher resistivity in the bubble layer with the addition of i-propanol [47].

It should be noted that several previous studies have focused on bubble removal through understanding bubble behaviour in the function of electrolytic process components such as the effect of current density, anode cathode distance, anode inclination angle, and bubble velocity. However, there are only limited studies available on the mechanism of the anode gas transfer between electrolyte site and the porous anode. It is important to understand the influence of the gas transfer mechanism in bubble formation in order to improve the design and operation of the Hall-Héroult process [44,46].

Einarsrud et al. developed an anode bubble volume of fluid (VOF) model simulation to examine the global behaviour and gas transfer mechanisms with the assumption that molecular gas supersaturated the electrolyte. They proposed two possibilities of the gas path, namely transport through pores in the anode or through the bath as depicted in Figure 2.10. The simulation was done using the FLUENT program and the results were validated against result of a laboratory scale electrolysis cell. According to this modelling approach, transport through bath result is well reproduced compared with transport through pores in electrolysis cell verification. However, detailed experiment and thorough investigation is required to verify the physical significance compare to the industrial cell. Furthermore, they outlined that gas diffusivity and active anode pores are dynamically related with temperature and bath composition.



Figure 2-10 Sketch of two possibilities for transport of molecular CO<sub>2</sub>[41]

In another study, Poncsák, and Kiss [48] suggested three hypotheses are theoretically possible :

- Gas is dissolved and diffused through molten cryolite;
- Gas is stored inside the highly porous anode and transferred through a thin superficial layer;
- Gas is captured on the anode surface by adsorption mechanism and migrates to the bubble by desorption along solid gas interface.

In the simulation, these three models are tested to produce bubbles with a typical bubble detachment size (3 to 6 mm) and times to reach this size (0.5 to 0.6 s) based on Utigard et al.[26] experimental observation. They reported that majority of anode gas can be stored in adsorbed form and transferred through a thin superficial layer of the porous anode. This gas transfer model produces typical detachment size after 0.2 to 0.3 second with few assumptions about constant current mass exchange, and bubble coverage. Figure 2.11 shows the computational area in gas diffusion through porous anode located at the centre of anode bottom.

Comparatively, transfer through electrolyte model shows a very slow growth of bubble radius due to low  $CO_2$  diffusion coefficient in the molten cryolite. For the adsorption model, the lack of precise adsorption coefficient data underestimates considerably the real volume necessary to store gas in the pores.



Figure 2-11 Computational domain for the gas transport through the anode pores [48]

Further study is required to estimate gas adsorption distribution because of lack of precise data. Therefore, it is necessary to study anode characteristics to understand the fundamental of CO/  $CO_2$  gas transport mechanism.

# 2.7.Summary

Aluminium is produced in the Hall-Héroult cell by electrochemical reduction of aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) in an electrolyte mainly consisting of molten cryolite (Na<sub>3</sub>AlF<sub>6</sub>). Cryolite was chosen for the electrolyte due to its ability to dissolve Al<sub>2</sub>O<sub>3</sub>, to make cell lining protective frozen ledge and also conduct the electric current without self-decomposition. One of the main concerns in the Hall-Héroult process is high energy consumption leading to high operational cost. The electrolytic process principally remains the same, however, there have been significant advances in technology leading to improvements in energy efficiency and productivity, reducing greenhouse gas emissions over the last few decades.

More recent attention on energy consumption has focused on understanding bubble removal to specifically target the improvement of the cell voltage and energy distribution. The bubbles constrain the current passage that passes through the electrolysis cell and increases the electrolyte resistance thus, in turn results in higher energy consumption for the smelting process with estimation to contribute 0.25 V to the overall voltage, in addition to the 1.33 V specifically due to the electrolyte.

Several previous studies have focused on bubble removal through understanding bubble behaviour in the function of electrolytic process components such as the effect of current density, anode cathode distance, anode inclination angle, and bubble velocity. However, there are only limited studies available on the mechanism of bubble nucleation and the anode gas transfer between electrolyte site and the porous anode. It is important to understand the influence of the gas transfer mechanism in bubble formation in order to improve the design and operation of the Hall-Héroult process.

# **Chapter 3**

# 3. Anode Characterization Techniques

## 3.1. Introduction

The focus of this chapter is to describe the theoretical background for the characterization techniques utilised to study the porosity of the anode carbons and the influence of this porosity on properties, such as permeability and reactivity in the carbon anode for aluminium production. Characterization techniques used in this thesis include: Water Intrusion Porosimetry (WIP), Mercury Intrusion Porosimetry (MIP), X-Ray computerized tomography (CT), and Microscopy and Image analysis are described in the following sections.

## 3.2. Water Intrusion Porosimetry (WIP)

The principles of this technique is by sample saturation using liquid with known density. Porosity determination is based on Archimedes's principle to calculate the total volume in the sample. Pore volume was calculated by the weight difference between the fully saturated and dehydrated states. WIP is a non-destructive test because the same experimental sample can be reused to measure bulk density, grain density, and porosity.[49]

The liquid saturation and immersion techniques have been used in many disciplines such as the material sciences, ceramic industry, archaeology, mining and petroleum industry. Previous studies have reported that with specific customisation for the particular material, this technique can measure porosity effectively in a wide variety of materials. The efficiency of the fluid to saturate and immerse entire pore network in the sample affected the accuracy of porosity measurements.[50] The requirement for the saturating liquid are:

- 1. low surface tension and a high wettability,
- 2. low viscosity,
- 3. high vapor pressure and slow evaporation rate,
- 4. low reactivity with the porous material,
- 5. stable composition and density,
- 6. non-hazardous and have safe handling properties

The water immersion porosimetry (WIP) technique use water as both the saturating and immersing fluid. The sample needs to be heated before the experiment to ensure the accessibility of the pore network. The pre-treatment temperature must be high enough to remove volatile hydrocarbons and impurities without altering the solid organic and inorganic framework. [49][50]

The sample is placed inside the bulk density and apparent porosity testing machine under vacuum to ensure that all the air has been removed from the open pores. The immersion liquid (water) is progressively introduced with maintained pressure. The mass of the immersed test

piece  $(m_2)$  is determined by weighing a suspended test piece completely immersed in a quantity of the liquid, the sample is removed from liquid and excess liquid is immediately weigh  $(m_3)$ . The samples are immediately weighed in air to ensure that evaporation of the water does not lead to any appreciable loss in mass during the weighing operation. After all the mass data collection is completed, the bulk density (d) and open porosity were given by the equation:

$$\rho_{b} = \frac{m1}{m3 - m2} x \rho_{w}$$
 Equation 3. 11

Apparent porosity 
$$=\frac{m_3-m_1}{m_3-m_2}x_{100}$$
 Equation 3.12

#### 3.3. Mercury Intrusion Porosimetry (MIP)

Mercury porosimetry is an established technique using liquid mercury penetration into the sample with applied pressure for measuring porosity characteristics of solids. [51] Mercury is utilized as the liquid of choice for intrusion porosimetry because of its non-wetting properties to most solid materials. The comparison between water and mercury wetting properties is illustrated by Figure 3.1.The relation between pressure with surface tension and the angle of contact with the solid surface is directly proportional while it is inversely proportional with diameter of capillary as required force for non-wetting liquid to enter the circular cross section of the capillary as described in Washburn equation based on the assumption of cylindrical pores as follows:[52]

$$P = \frac{2\gamma \cos\theta}{r}$$
 Equation 3.13

Where **r** is the pore radius (Å),  $\gamma_{Hg}$  is the mercury surface tension (0.48 N/m),  $\theta$  is the contact angle between mercury and carbon (140°) and P the applied mercury pressure (Pa).

The mercury porosimeter consists of a pressure vessel, pressure transducer, vacuum and high-pressure pumps and a pressure intensifier. The other essential part of the setup is a penetrometer which is a sample-holder accommodating the specimen which is intruded by the mercury. This penetrometer consists of two factory-joined parts: a glass bulb for the sample placement and a plastic stem coated by a thin metal layer. A schematic drawing of a penetrometer containing a porous sample can be seen in Figure 3.2. The analysis is conducted in two separate procedures; namely low pressure and high pressure analysis. At low pressure analysis, the mercury enters and fills the penetrometer and in high pressure analysis, the volume of mercury in the penetrometer stem changes due to progressively pressurized oil entering the stem and expulsing the mercury into the penetrometer bulb. Due to the difference in electrical conductivity between mercury (an electrical conductor) and the oil and the plastic wall of the stem (which is dielectric), the replacement of the mercury by the

oil induces a change of capacitance in the stem. The volume change in the penetrometer stem is calculated by the electric capacitance difference and measured by the apparatus during analysis. The volume of mercury present within the porous sample is estimated as a function of mercury pressure after corrections for volumetric changes related to compressibility of the penetrometer and mercury.[53]



Figure 3-1 Liquid-solid contact angle for Hg and water. [53]

The MIP method has many advantages, which include: 1) Fast determination speed, usually required 1 to 2 hours for a single sample ; 2) High pressure measurement that is suitable for cores with different permeability ; 3) Ability to test irregular shaped samples ; 4) Wide measurement range for pore diameters from 3 nm to 100  $\mu$ m.[52]

This method also has several disadvantages. It does not measure the actual pore size, instead determines the largest entrance to the pore. The exertion from high pressures can also be subject to errors in the porosity interpretation due to further compaction or collapse of loosely packed material. Moreover, this technique has size range limitations. The smallest pore size depends on the maximum pressure while the largest measurable pore size is dependent on the height of the sample which determines the minimum head pressure. For example, in the instrument with 400 MPa maximum pressures, the smallest pore size that can be detected is 3.5 nm and the maximum pore size is 1 mm diameter in a 1 cm high sample [51]. Scanning Electron Microscopy (SEM) or optical micrographs results will always show larger pore sizes when compared with mercury porosimetry. The information from the data that can be obtained from MIP will be explained in the next sub-section.



Figure 3-2 Mercury porosimetry technique basics.

(a) - schematic description of a penetrometer showing the partial volumes used for calculation of sample density, (b) charts of cumulative porosimetric curves showing the three basic phases of analysis and (c) the linked terms of total and free porosity and (d) chart of incremental porosimetric curve calculated from the cumulative one [54].

## 3.3.1. Density and Porosity

The density and porosity are important properties of the carbon anode. Higher density means a reduced porosity and a reduced permeability that should extend the operational life of the anode. However, excessive density will lead to poor thermal shock resistance and fracturing of the anode upon first use in an electrolysis cell.[18]There are different definitions of density, with the simple definition of density being the mass of an object divided by its volume. The mass measurement itself is straightforward, but it is the determination of the material volume that makes the density value different, as depicted in Figure 3.3. Bulk volume is measured as the volume within the whole particle, while apparent or skeletal volume is the bulk volume from the bulk volumes. In the MIP measurement, the lowest pressure recorded at the beginning of the analysis before filling the mercury was used to calculate the bulk density. At highest pressure point which all pores are filled with mercury, skeletal density is calculated from sample volume subtracted by mercury volume. [51]



Figure 3-3 Comparison of different volume determinations.[55]

The volume of the porosity  $(V_P)$  from the measurement of bulk volume  $(V_B)$  and skeletal volume  $(V_{Sk})$  can be determined from the equation

$$V_{P} = V_{B} - V_{Sk}$$
 Equation 3.14

Porosity of the sample was obtained as follow:

% Porosity = 
$$\varphi$$
 = (V<sub>P</sub>/V<sub>B</sub>) x 100%. Equation 3.15

## 3.3.2. Pore Characteristic and Size Distribution

Total pore volume ( $V_{tot}$ ) can be directly determined by measuring the total volume of mercury required to fill all accessible pore. Specific pore volume in units of volume per unit mass was obtained by dividing  $V_{tot}$  by the mass of the sample.[53] Following the calculation of total volume of intrusion, the total area of pores can be calculated using the cylinder pore model. [56]

$$S = \frac{1}{\gamma_{Hg}|cos\theta|} \int_0^{Vtot} P dV$$
 Equation 3.16

The mean pore diameter ( $d_{mean}$ ) is calculated by Equation 3-17. This equation is based on an assumption of the cylindrical shape of pores which are open at the ends. This information can be used for the diffusion model calculation later in chapter 7 for diffusion in porous media.

$$d_{mean} = 4 \frac{Vtot}{s}$$
 Equation 3.17

Pore size is obtained by applying the Washburn equation to the measured pressure associated with the pores as illustrated in Figure 3.4. Its distribution can be represented both in cumulative and incremental ways. The subtraction between original and remaining volume in the penetrometer stem in different pressure is the cumulative volume (V<sub>c</sub>). The plot of the volume of mercury intruded into the sample as a function of the diameter provides a quick indication of how the sample takes up the mercury during the intrusion and how much of it is trapped after extrusion. The sharp rise in the curves indicates a large volume of openings in that size range. The Incremental volume is calculated by the difference between the

cumulative volume ( $V_c$ ) measured at a pressure (P) from the cumulative volume measured at a higher pressure. The plot of incremental intrusion volume versus pore entrance diameter provides the indication of the size distribution.



## 3.3.3. Fractal Dimension

Recently, considerable literature has grown up around study of porous structures and surfaces using fractal analysis. [57] The fractal approach can be implemented as alternative way to characterize complex geometries such as the surface area or pore structure of materials that relies on the concept of self-similarity. Comparison of fractal dimensions can be used to determine the correlation of porosity and fluid transport characteristics. The fractal dimensions become one of important physical parameters when studying fluid flow through materials. The fractal geometry in porosity indicated the physical processes that formed the material. The data of fractal analysis collected from mercury porosimetry may be added with extra textural information to the results of traditional determinations. [57]

The fractal dimension is used for the description of the fractal geometry which is described as a non-integer dimension. Classical geometry describes points as having zero dimension, lines and curves having one dimension, squares and circles having two dimensions and cubes and spheres having three dimensions [58]. The methodology to understanding fractal dimension in porosity using MIP described by Alvarado and Gonzalez [59]. The comparison between fractal geometry and classical geometry is depicted in Figure 3.5. In general, a fractal whose pieces are scaled by different amounts in the x- and y-directions is described as self-affinity and shown in equation 3.18.

$$N(\delta) = \delta^{-Df}$$
 Equation 3.18

where  $N(\delta)$  is the number of elements of dimension  $\delta$ ,  $\delta$  is the smallest dimension after n divisions, and  $D_f$  is the fractal dimension Total area of the object is equal to the number of elements of dimensions times the area of each, or

A = N(
$$\delta$$
)  $\delta^2$  Equation 3. 19

After insertion of equation 3.18 into equation 3.19, the following formula was obtained:

$$A = \delta^{(2-D_f)}$$
 Equation 3.20

From derivation of above equation, the volumetric fractal dimension yielding

$$V = \delta^{(3-Df)}$$
 Equation 3.21

Equation 3-22 showed the volumetric fractal dimension using pressure scale instead length scale in previous equation. Where Pt is threshold pressure, the pressure at which fluid first percolates through a porous medium.[53]

$$V = (P-P_t)^{(3-D_f)}$$
 Equation 3.22

By applying logarithm, this equation gives

$$Log (V) = (3-D_f) log (P-P_t)$$
 Equation 3.23

Plotting this equation as log (V) vs the log (P-Pt) plot gives  $(3-D_f)$  as slope to obtain the fractal dimension of the pore. The method is applicable when there is one or more linear regions on log plot intrusion volume versus pressure.





#### 3.3.4. Permeability

Permeability is a property of the material that depends on the characteristics of the fluid flow, such as flow rate, viscosity of the fluid in relation with applied pressure or potential gradient. Katz and Thompson [12] developed mass transport studies in facilitating the prediction of fluid permeability of material using MIP. There are two parameter that will be used to measure the permeability from a single mercury injection capillary pressure curve data. The first equation shown in Equation 3-24 was derived from percolation theory mentioned in the previous sections by measuring conductivity formation factor (consductance ratio)  $\sigma/\sigma_0$  and characteristic length L<sub>c</sub>.

$$k = \frac{1}{226} (Lc)^2 \frac{\sigma}{\sigma o}$$
 Equation 3.24

Estimation of the conductance ratio from the mercury intrusion data can be calculated using equation 3-25. The other parameters required is the pore size when the hydraulic conductance is maximum ( $L_{max}$ ), and the fraction of total porosity  $\phi$  filled at  $L_{max}$  (S( $L_{max}$ )). Permeability determination will be further explained in Appendix B.

$$\mathbf{k} = \frac{1}{89} (\mathbf{L}_{\text{max}})^2 \frac{\mathbf{L}_{\text{max}}}{\mathbf{Lc}} \Phi \mathbf{S}(\mathbf{L}_{\text{max}})$$
Equation 3.25

#### 3.3.5. Tortuosity and Tortuosity Factor

Tortuosity defined as ratio of actual distance between two points ( $I_e$ ) to the minimum distance the same two points (I) as depicted in Figure 3.6. It is an intrinsic characteristic expressing the geometrical property of pore structure, may indicate pore connectivity and can be assumed to be independent of the characteristics of penetrating fluid.



Figure 3-6 Definition of tortuosity

Tortuosity data can be obtained from mercury intrusion porosimetry using Hager and Katz-Thompson given below (equation 3-26).[53]

$$\xi = \sqrt{\frac{\rho}{24 \, k \, (1 + \rho V_{tot})}} \int_{\eta = r_c, min}^{\eta = r_c, max} \eta^2 f_v(\eta) d\eta \qquad \text{Equation 3.26}$$

Where  $\tau$  is tortuosity,  $\rho$  is fluid density (mass/volume); *k* is permeability (area); *V*<sub>tot</sub> is total pore volume (volume/mass);  $\int_{\eta=r_c,min}^{\eta=r_c,max} \eta^2 f_{\nu}(\eta) d\eta$  is the integral of the pore-throat volume distribution over the pore-throat size derived from MIP data. The tortuosity value during the analysis will be affected by changes in material permeability.

The interconnected pore path in porous material act as channel for fluid flows through. The effect of pore orientation, connectivity, size variation in the interconnected pore path is called tortuosity factor. This number is an indicator of the fluid diffusion in porous solid efficiency mainly used in the area of heterogeneous catalysis. [53] The terms tortuosity and tortuosity factor express two different characteristics of a material. Tortuosity factor ( $\tau$ ) is the ratio of tortuosity to constriction ( $\sigma$ ) as shown in equation below

$$au = rac{\xi}{\sigma}$$
 Equation 3.27

The constriction factor is a function of area ratio  $(A_2/A_1)$  as shown in Figure 3.7. The tortuosity factor of porous media was derived from Fick's first law of diffusion by Carniglia.[61] For nonintersecting cylindrical pores, a simple relationship requiring data of total pore volume  $(V_{tot})$  and bulk density  $(\rho_b)$  can be used to calculate  $\tau$ , as shown in Equation 3.28.

$$\tau = 2.23 - 1.13 V_{tot} \rho_b \qquad \qquad \text{Equation 3.28}$$

This relationship is limited to values of  $\tau$  ranging from 1 to 2.2, Where  $0.05 \le V_{tot}\rho_b \le 0.95$ .



Figure 3-7 Area ratio for constriction factor

### 3.3.6. Anode Characterization using MIP

Significant progress in studies of anode porosimetry have been achieved through the investigations by Sadler and Algie [62]. They performed mercury porosimetry to investigate internal oxidation within the anode butt. In their studies, the pore entrance radius (PER)

measurement reported values in the range of 0.002 to 100  $\mu$ m with most of the measured porosity located in the range of pore radius around 1 to 5  $\mu$ m (Figure 3.8). Engvoll [63] observed similar porosity identification in the range 0.0037 to 80  $\mu$ m. Alternatively, Suriyapraphadilok [19] performed similar measurements with helium pycnometer which gave higher factors of pore volume than the results reported from previous research due to the higher accuracy when compared with mercury porosimetry. The repeatability of mercury porosimetry experiment is better than 1% standard deviation despite the various assumptions and experimental factors affecting the absolute accuracy of the data. In general, results from the experiments are useful in comparative studies of similar materials.

Experiments by Sadler and Algie [62] indicate that the anode porosity profile influences the sub-surface reaction between carbon dioxide and carbon anode via pore growth and enlargement of fine porosity (< $0.01\mu$ m). Changing of the porosity size in each of these PER ranges is illustrated in Figure 3.9. Furthermore, motivated by this study, mathematical modelling is attempted by Ziegler [64]. These models are proposed to gain understanding of carbon dust formation and sub-surface carboxy reaction in anodes. Comparatively, the model results accurately describe the reaction localization on the submerged sides of the anode. However, in this model, the anode microstructure is treated as homogenous, in contrast with the real industrial cell. In addition, to achieve more accurate modelling, improvement of cell modelling should consider effects of multiple microstructural length scales.



Figure 3-8 Pore volume distribution of anode butt [62]



Figure 3-9 Porosity development profiles with PER range [62]

## 3.4. Microscopy and Image Analysis

Microscopy and image analysis are the technologies used to characterize the pores that are too large for the mercury porosimetry measurement. These methods can give an overview of the size relatively independent of the way that they are connected. In addition, information on how the pores are arranged can be obtained. However, the disadvantage of the image analysis technique is the smallest measurable pore size depends on the chosen magnification and the resolution of the image digitizing system [65]. The other challenges are to differentiate coke, pitch, and pores in anodes. Even with Scanning Electron Microscopy (SEM), these components all appear black in the image and are hard to be analysed [66].

Numerous methods of image analysis have been proposed for coke (matrix and pore) and anode (coke matrix, pitch, and pore) using fluorescent materials or polarized light. With an area coverage of approximately 1 cm<sup>2</sup>, optical microscopy is proven to be an efficient technique to analyse larger surfaces compared to those used for SEM. Rorvik and Øye [65] have conducted anode porosity investigations using microscopy and image analysis. They used two pilot anodes which have identical raw materials but were made using different mixing methods; namely an intensive mixer and a batch mixer. These samples were impregnated with fluorescent epoxy which will light up the pore under the ultraviolet light of the microscope. Then, the sample is analysed using a high-end microscope and a computer equipped with a motorized stage controller.

Furthermore, work by Rorvik et al [67] utilized a software package, ImageJ developed by National Institute of Health as shown in Figure 3.10. The picture of the sample is taken using polarized light and and using two filters. The image analysis software converts the picture into a binary image and processes this image to analyse the coke, pitch and pore distribution of the green anode. This method successfully differentiated the components inside the anode. However, a lot of information is lost when a picture converted to the binary image. Qiao and Eser [68] used Robert's edge detection algorithm to determine pores in their coke sample. They used the algorithm to identify the grain boundaries and contrast stretching to differentiate the colour between pore and coke particles and used thresholding to binarize the image. Nevertheless, this technique is not suitable for pore identification due to the presence of pitch that also creates edges with a similar colour when compared with pores.

In his more recent research, Rorvik et al. [69] determined the classification of the pores in industrial anode using microscopy and image analysis. He divided the pores into 4 different classes associated with certain production steps to be:

- 1. Pores too small to be classified (light blue)
- 2. Coke calcination pores producing elongated pores (orange)
- 3. Coke gas bubble pores producing round pores (purple)
- 4. Binder pores due to imperfect mixing producing irregular pores (green)

The image analysis program used by Rorvik et al. colour the pores according to their class based on aspect ratio, surface roughness and degree of circularity. Another description in pore structure parameter for image analysis of the carbon anodes is shown in Table 3-1. Furthermore, it can be seen in in Figure 3.10 that the pores generated by imperfect mixing and baking pores (the latter classification) are by far the dominant class.



Figure 3-10 Anode pore classification by image analysis [69]



## Table 3-1 Pore structure parameter [70]

## 3.5. X-Ray computerized tomography (CT)

X-Ray computerized tomography (CT) is a nondestructive technique for visualizing features in the interior of opaque solid objects. Digital information on their 3-D geometries is generated by two-dimensional X-ray images taken around a single axis of rotation. As the X-rays pass through the object being scanned, the signal is attenuated by scattering and absorption. The number for attenuation of a mono-energetic beam through a homogeneous material is called the CT number and is expressed in Hounsfield Units (HU) [71]. The X-Ray attenuation coefficient and ranges from -1000 for air to +3000 for very dense materials such as metals [72].

Full-scale anode characterization can be obtained using X-Ray computerized tomography (CT). The porosity of a homogeneous material can be calculated by the following relation:

$$p = \left(1 - \frac{\overline{CT} + 1024}{CT_{max} + 1024}\right) x \ 100$$
 Equation 3.29

Where p is the total porosity volume fraction in %,  $\overline{CT}$  is average CT number of the volume considered,  $CT_{max}$  is the maximum CT number allowed in the sample.  $CT_{max}$  is limited to 980

HU, i.e. a value close to that of graphite (960 HU) to overcome the overestimation [73] while 1024 is the CT number of water as the calibration sample. Nevertheless, it is difficult to determine the  $CT_{max}$  due to the non-homogenous composition of the prebaked anode. Besides carbon, other impurities with very high voxel intensity are present. Voxel is a volume element like a tissue slice that corresponds to a picture element (pixel) in an image. Moreover, even only one voxel related to the impurities would be sufficient to result in an overestimated porosity percentage of the sample.

Sommerseth [74] evaluated anode surfaces with respect to anode consumption, density, pore size distribution and real active area before and after electrolysis. Through CT scanning, anode surface and pores in the anode structure can be investigated. As illustrated in Figure 3.11, the particles high in porosity (so called "bubble coke") has lower consumption rate and poorer wetting characterization towards the electrolyte than the bulk material. Therefore, the author concluded a possible reason for coke bubble consumption is because of high porosity grains with high electronic resistivity rather than CO<sub>2</sub> gas being blocked by electrolyte penetration.

In more recent research, Rørvik and Lossius [75] evaluated pore size distributions of large pores (voids) in a baked anode 50 mm core from the different mixing configurations which corresponds to pores size range 50 to 1000  $\mu$ m. It was also possible to extract and visualize features (such as pores) as a 3D view, as shown in Figure 3.12, even though this approach are more useful to visualize metal impurities or electrolyte penetration rather than porosity.



Figure 3-11 CT Imaging of anode a) before electrolysis b) after electrolysis [74]



Figure 3-12 Pores in a coke grain shown as a rendered surface; carbon is transparent [75]

# Chapter 4

## 4. Measurement and Modelling of Diffusion Coefficients

### 4.1. Gas Transport Mechanism in Porous Solid

Gas transport in porous structures becomes important in the analysis of bubble nucleation and it will be discussed in this section. Gas phase momentum consists of advective and diffusive components induced by pressure and concentration gradients.[76] Firstly, advective and diffusion will be discussed separately, followed by a description of the coupled mechanism.

## 4.1.1. Gas Phase Advective

Advective transport mechanism is described as the movement of some quantity via the bulk flow of a fluid. Figure 4.1 shows the fluid flow rate  $\mathbf{Q}$  (m<sup>3</sup>s<sup>-1</sup>) through a cross sectional area of porous medium  $\mathbf{A}$  (m<sup>2</sup>). Thus, the superficial velocity  $\mathbf{U}_{g}$  is the total flow rate divided by the cross-sectional area. The velocity within the bed ( $\mathbf{U}$  – interstitial velocity) will be greater than the superficial because of the area available for fluid flow will be limited by the existence of the particles. Fluid continuity was preserved by squeeze the flow of the fluid will have to through a smaller area. [76]The relation between  $\mathbf{U}$ ,  $\mathbf{U}_{0}$  and porosity  $\varepsilon$  shown in equation 4.2.



Porous medium

Figure 4-1 Illustration of fluid flow through a porous medium

$$U = \frac{U_g}{\epsilon}$$
 Equation 4-1

#### 4.1.2. Flow Regime

Reynolds number (Re) is a dimensionless quantity in fluid mechanics to define the ratio of momentum forces to viscous forces as shown as:

$$Re = \frac{\rho_g VL}{\mu_g}$$
 Equation 4-2

Where  $\rho$  is the density of the gas,V is the velocity of the fluid,  $\rho$  is the density of fluid,  $\mu$  is the viscosity of fluid, L is Length scale, channel length. The Reynold number can be used distinguish and predict similar flow patterns for two types of different flow

regimes,namely laminar or turbulent flow. In fluid flow of a porous medium, the fluid velocity and the characteristic linear dimension in Reynolds number is modified to compensate some energy loss due to viscous and form drags. Kozeny [77] deduced the characteristic linear dimension (d) as the volume open to the fluid flow divided by the surface area over which it must flow by equation 4.3.

$$d = \frac{AL\varepsilon}{AL(1-\varepsilon)S_{\nu}}$$
 Equation 4-3

Thus, by incorporating equations (4.1) and (4.3), the modified Reynolds number shown in equation 4.4

$$Re_{1} = \frac{\varepsilon}{(1-\varepsilon)S_{v}} \frac{\mathsf{U}_{0}}{\varepsilon} \frac{\rho_{g}}{\mu_{g}} = \frac{\mathsf{U}_{0}\rho_{g}}{(1-\varepsilon)\mu_{g}S_{v}}$$
Equation 4-4

The Reynold number assesses the ratio of inertial to viscous forces in the fluid. This dimensionless number provides information when the inertial effects become significant. The conventionally applied threshold to indicate significant turbulence in porous solid is 2.[78]

#### 4.1.3. Darcy's Law

In the case in porous media which is generally low velocity, Darcy's law is used to analyse gas phase advection and is applicable for laminar flow (Re<sub>1</sub>< 2) without boundary shear flow [79]. Darcy [80] states that the average of the fluid velocity (U<sub>o</sub>) based on the entire cross section of the flow and related to the porosity is directly proportional to the gas-phase permeability (k<sub>g</sub>) and, the gas-phase pressure gradient ( $\nabla P_g$ ) as written in the Equation 4.5. Furthermore, by neglecting body forces such as gravity (g) Equation 4.6 was obtained.[81]

$$\mathbf{U}_{\mathbf{g}} = -\frac{\mathbf{k}_g}{\mathbf{\mu}_g} \quad (\nabla \mathbf{P}_g - \mathbf{\rho}_g g)$$
 Equation 4-5

$$\nabla \mathsf{P}_g = -\frac{\mathsf{\mu}_g}{\mathsf{k}_g} \mathsf{U}_g \qquad \qquad \mathsf{Equation 4-6}$$

Although the Darcy law is commonly used to govern porous media flow, it does not cover all the practical ranges of flow in porous media. To account for this non-linearity, a number of formulations have been suggested. Forchheimer equation is more appropriate to use when the pore velocities increase, the flow becomes turbulent, and flow becomes non-linear. The Forchheimer equation is shown in Equation 4.7 where  $C_f$  is a constant with value approximately 0.55. [82]

$$\nabla \mathsf{P}_g = -\frac{\mu_g}{\kappa_g} \mathbf{U}_g - \mathbf{C}_f k_g^{-1/2} \,\rho_g \big| \mathbf{U}_g \big| \mathbf{U}_g \qquad \qquad \text{Equation 4-7}$$

Brinkman extension is used in Darcy's law when wall shear is important and includes the effect of wall or boundary shear on the flow velocity. The coefficient  $\bar{\mu}$  is an effective viscosity at the

wall, which in general is not equal to the gas viscosity,  $\mu$ g, as discussed by Nield and Bejan [83] as shown in equation 4.8.

$$\nabla \mathsf{P}_g = -\frac{\mathsf{\mu}_g}{\mathsf{k}_g} \mathbf{U}_g + \quad \overline{\mu} \, \nabla^2 \, \mathbf{U}_g \qquad \qquad \text{Equation 4-8}$$

## 4.1.4. Gas Phase Diffusion

Diffusion can be defined as the net transport of matter in a system by random molecule motion. The movement acts to remove chemical potential differences and will eventually produce an equilibrium state of concentration [84]. In porous media, diffusion can be categorised by different mechanisms; namely pure molecular diffusion, pure Knudsen diffusion, mixed diffusion and random porous material diffusion as shown schematically in Figure 4.2. The dominant mechanism can be predicted by the ratio between the mean free path and pore size of the porous media. This ratio is known as the Knudsen number ( $K_n$ ) and is calculated

$$K_{n} = \frac{\lambda}{d_{p}}$$
Equation 4-9  
$$\lambda = \frac{K_{b}T}{P\sqrt{2}\pi d_{\pi}^{2}}$$
Equation 4-10



Figure 4-2 Distinct mechanism by which molecular species get transported (a) pure molecular diffusion; (b) pure Knudsen diffusion; (c) mixed diffusion; d) random porous material

Where  $k_b$  is the Boltzmann constant (1.3807 x 10<sup>-23</sup> J/K), T is the temperature of gas (K), P is the gas pressure, and  $d_g$  is the effective diameter of gas molecule that can be estimated using appropriate covalent and Van der Waals radii.[85]

Molecular diffusion is observed in solid with large pores with high system pressure and dominates if the Knudsen number ( $K_n$ ) is smaller than 0.1. Because the pore size is greater than the free path of the diffusing gas, the molecule-molecule collision is more significant when compared to the molecule-wall collision. Furthermore, consideration of the Knudsen diffusion becomes more necessary for Knudsen numbers greater than 10. When the free path of the diffusing gas is much larger than the pore size; the molecules collide with the wall more often than between themselves [85]. Hence, molecule-wall collisions become more significant. Alternatively, the surface diffusion mechanism is not dependent on the Knudsen number and occurs along the pore wall surface in parallel to the other diffusion mechanisms. This mechanism becomes dominant for micro pores and strongly absorbed species.

## 4.2. Modelling of Gas Transport in Porous Solids

Information about the properties of the components, physical laws and characteristics of the porous media are required to quantify the gas transport in porous media by theoretical models. Most of the simulations have been used as mass balance calculation that relate to mass flux intensity and driving forces. A number of theoretical models with different diffusing gases in the porous solids will be discussed in the forthcoming sections.

## 4.2.1. Molecular Diffusion

Fick's law is proposed to describe the molecular diffusion in clear fluids (non-porous media). The Fick's law consists of two laws; this approach is extensively employed for porous media by modifying the formula and introducing a porous media factor. The Fick's first law explaining the gas diffusion in steady state condition is shown in Equation 4.11.

$$J_A^{\rm M} = -c \, D_{\rm AB, CF} \, \nabla_{\rm XA}$$
 Equation 4-11

Where  $J_A^M$  is mole flux of component A, in one dimension in a clear fluid (no porous medium), c is the concentration of the gas, DAB,CF is the diffusion coefficient in a clear fluid, and xA is the mole fraction of component A.[86]

Fick's second law (shown in Equation 4.12) can represent the diffusion through the thin layer of anode gas in Hall-Héroult cell [48]. This law used to describe diffusion mechanism in which the concentration change is a function of time (non-steady state), as the result of the anode's ability to preserve and transport the gas towards the growing bubbles. Moreover, the transport mechanism is promoted by the high gas pressure present due to the high generation rate of gas and the low solubility of the  $CO_2$  in the molten cryolite [87]. The Fick's second law is a partial differential equation in one dimension as follows:

$$\frac{\partial C}{\partial_t} = D_{CO_{2,c}} \frac{\partial^2 C}{\partial x^2}$$
 Equation 4-12

Where C is the concentration in dimensions of amount of substance (mol/m<sup>3</sup>),  $D_{CO_{2,c}}$  is the diffusivity coefficient of the CO<sub>2</sub> (m<sup>2</sup>/s) in the anode, t is time (second), and x is the over which the diffusion occurs in this case the thickness of the sample. The solution for equation 4.13 in a simple case of one dimension (taken as the *x*-axis) diffusion with time *t* from a boundary location at position x=0 is shown in Equation 4.12 where the initial concentration value maintained at a value C<sub>0</sub>. C(x,t) is the concentration fuction in certain thickness and time and, *erfc* is the complementary error function.

$$C(x,t) = C_o \operatorname{erfc}\left(\frac{x}{\sqrt{D_{CO_{2,c}}t}}\right)$$
 Equation 4-13

With the assumption that the concentration of gases in the environment is constant and the diffusion space is semi-infinite. The boundary condition is set as C (x, 0) = 0, x>0 and C (x, 0) = C<sub>0</sub>,  $x \le 0$ . Then the solution is amended only with coefficient  $\frac{1}{2}$  in front of  $C_0$  Because the diffusion now occurs in both directions, then it is simplified as shown in Equation 4.14.

$$x = 2\sqrt{D_{CO_{2,c}}t}$$
 Equation 4-14

Where C is the concentration in mol/m<sup>3</sup>,  $D_{CO_{2,c}}$  are the diffusivity of the CO<sub>2</sub> in the anode respectively [88]. Diffusion following the Fick's first and second laws is termed Fickian diffusion. The diffusion coefficient is temperature dependent and for ideal systems follows an Arrhenius relationship [89]. Therefore, can be estimated as

$$D = Do \exp\left(\frac{-Qd}{K_B bT}\right)$$
 Equation 4-15

Where Do is temperature-independent pre-exponential (m<sup>2</sup>/s), Qd is the activation energy for diffusion (J/mole or eV/atom), and  $k_b$  is the Boltzmann constant (1.3807 x 10<sup>-23</sup> J/K). Stefan-Maxwell equation is used for multi-component gases because the Fick's law is restricted to the binary gas application. The concentration gradient for each component can be determined by Stefan-Maxwell equation as follow:

$$\nabla xi = \sum_{j=1}^{n} \frac{1}{cDij} (x_i N_j - x_j N_i)$$
 Equation 4-16

#### 4.2.2. Knudsen Diffusion

As was mentioned in the previous section, Knudsen diffusion becomes important when Knudsen numbers are greater than 10. Molecule-wall collisions become more significant at low pressure and small pore diameters. The collision between molecules and the wall is more often than between molecules because the free path of gas is restricted by the geometry of the pore channel and the flux depend on the density gradient of the gas species [90]. The molecular flux of gas i ( $J_{iK}$ ) due to Knudsen diffusion is estimated using the general diffusion equation given.

$$J_{iK} = -D_{iK} \frac{\partial ci}{\partial x}$$
 Equation 4-17

Where  $D_{iK}$  is the Knudsen diffusivity and  $\frac{\partial ci}{\partial x}$  is concentrantion change along with diffusion length. The Knudsen diffusivity of gas species i is given by equation 4.18.

$$D_{iK} = \frac{dp}{3} \sqrt{\frac{8RT}{\pi Mi}}$$
 Equation 4-18

Mi represents the molecular weights of gas species i, and dp is the mean pore size of the porous media.

### 4.2.3. Combined Mechanism

Khrisna and Wesselingh [91] proposed that bulk and Knudsen diffusion mechanisms occur together, and it is better to take both mechanisms into account rather than assume which mechanism is controlling. The contribution of each mechanism (molecular and Knudsen diffusion) can be estimated by examining the manner in which (Dt<sub>eff</sub>) varies with either pressure or temperature as given in Equation 4.19.

$$\frac{1}{D_{teff}} = \frac{1}{D_m} + \frac{1}{D_k}$$
 Equation 4-19

Where  $D_{eff}$  is the total diffusivity measured in experiment,  $D_m$  is the apparent molecular coefficient, which depends on intermolecular collisions, and  $D_k$  is the Knudsen coefficient, which depends on collisions with the pore walls.

A plot of reciprocal coefficients obtained at a single pressures and various temperatures should be a horizontal line with respect to pressure if the mechanism is pure Knudsen flow, a straight line with a positive slope going through the origin results if the mechanism is normal diffusion, and finally a straight line with an appreciable intercept if a combined mechanism exists [92].

The basis on theoretical calculation of effective diffusion coefficient is with assumption of straight and cylindrical pores aligned in a parallel array. However, in most of porous materials there is a variety of pore orientation, connectivity, size, twisted and interconnected with one

another. Therefore, reasonable approximation of average pore size will be required to calculate effective diffusion coefficients as shown in equation 4.20, where  $\phi$  and  $\tau$  are the porosity and tortuosity of the porous media.[85][93]

$$D_{eff} = \frac{\varphi}{\tau} D$$
 Equation 4-20

One of drawback from Fick's law is the assumption that gas flux is always proportional to pressure gradient. However, the interaction between advection and diffusion of a fluid through a porous medium cannot be ignored. Therefore, different models have to be developed to overcome the disadvantages, an advective–diffusive model (ADM) is proposed. This model combines the Fick's law to calculate molecular diffusion and Darcy's law to predict the viscous flow. Software TOUGH2 commonly used for gas flow and transport simulation in fractured and porous media in nuclear waste, environmental, and geothermal applications. [94] The advective–diffusive model is shown in Equation 4.21 where  $k_i$  is effective permeability,  $\mu_g$  is gas viscosity,  $\rho_g$  is gas density,  $D_{ij}$  is binary gas diffusivity,  $\omega_i$  is mass fraction of gas species i, and Pt is total gas pressure [95]. An explicit analytical expression representing the flux from this model can be used directly in the mass conservation to calculate the concentration distribution of the species [96,96].

$$J_{i} = -\frac{ki}{\mu g} \rho_{g} \omega i \nabla pt - D_{ij} \rho_{g} \nabla \omega_{i}$$
 Equation 4-21

Alternatively, another model is developed to describe gas transport through porous media from Stefan–Maxwell formulation where Knudsen diffusion is taken into account [91]. This model is referred as the Dusty-Gas Model (DGM). The porous medium is treated as one component of the gas mixture, consisting of giant molecules ('dust') act as dummy, or pseudo, species in the mixture as held fixed uniformly in space. The key aspects of the DGM is the combination of diffusion and advection, also depends on the square-root of the molecular weight of the gas.[85] The formula is given in Equation 4.22 and 4.23.

$$\sum_{j=1}^{n} \sum_{j\neq 1}^{X_i J_j^D - X_j J_i^D} - \frac{J_i^D}{D_{ik}} = \frac{p_t \nabla X_i}{RT} + \frac{X_i \nabla p_t}{RT}$$
Equation 4-22

$$\sum_{j=1}^{n} \sum_{j\neq 1}^{X_i J_j^T - X_j J_i^T} - \frac{J_i^T}{D_{iK}} = \frac{p_{t \nabla X_i}}{RT} + \left(1 + \frac{k_0 p_t}{D_{iK} \mu_g}\right) \frac{X_i \nabla p_t}{RT}$$
Equation 4-23

Where X<sub>i</sub> is gas mole fraction,  $J_j^D$  is diffusive molar flux of gas species j,  $J_j^T$  is total diffusive and advective molar flux, Pt is total gas pressure, R is gas constant, T is temperature,  $D_{ij}$  is binary diffusivity in free space,  $D_{iK}$  is Knudsen diffusivity of gas species I, and k<sub>0</sub> is the gas permeability. The DGM has higher accuracy compare to Fick's law by including all possible interactions and collisions of gas species. However, its complexity is often a challenge for commercial software to model the multicomponent gases [94].

## 4.3. Diffusion Coefficient Measurement Techniques in porous solid

Gas diffusion coefficient determination is critical to understand its physical properties and gas movement analysis in porous solid. The diffusion coefficient measurement is divided into steady state and dynamic conditions. In steady state conditions, the principle of stationary counter current described by Wicke and Kallenbach [97] is often used and modified. The cell consists of upper and lower compartment separated by the cylindrical porous material. Different gas A and B from each of the compartments can pass through the porous separator. Transport characteristic can be estimated by concentration obtained from a gas detector placed in the outlet streams and outlet gas flow rate as depicted in Figure 4.3. However, this method has disadvantages due to the requirement for the analytical instrument and equal pressure in both compartments [98].



Figure 4-3 Porous sample placed in cylindrical holes of the impermeable cell partition of Wicke-Kallenbach diffusion cell

To overcome the Wicke-Kallenbach cell limitation, a diffusion cell based on Graham's law [99] Equation 4.25 is proposed. The Graham's law describe the molar diffusion flux ( $N_A$ ,  $N_B$ ) is inversely proportional to the square root molecular weight ( $M_A$ ,  $M_B$ ).

$$\frac{N_A}{N_B} = -\sqrt{\frac{M_B}{M_A}}$$
 Equation 4-24

The Graham's cell offers simpler determination of flux density of individual gas and eliminates the necessities of maintaining pressure at the outlet cell compartment. Nonetheless, gas pair choices is restricted to non-absorbable inert gas (e.g., H<sub>2</sub>, He, N<sub>2</sub>, Ar) to avoid the surface diffusion and to achieve accurate measurement [100].

The chromatographic method is well-established technique for dynamic conditions due to simplicity and the speed of data acquisition [101]. The method involves gas component A (the solute) to be injected into continuously flow component B act as a carrier gas into columns packed consist of porous particles. The effective diffusivity is determined from response analysis of zone broadening on tracer concentration by a suitable detector. Nonetheless, there are four unknown parameters that have to be determined independently such as theoretical impulse response for porous particles, h (t); the pellet diffusion time,  $t_{dif}$  which contains the effective diffusion coefficient; tc, the mean residence time of the carrier gas in the inter-particle space in the theoretical analysis [86].

Alternatively, inverse gas chromatography (IGC) is developed for wider application in powder, fibre, and film characterization in its native state and less approximation of equation to describe the experimental data. The basic principle of this technique is analysing the retention process by eluting known mobile phase through the sample in column pack as the stationary phase[102].

The IGC method has advantages compared to other analysis technique for relatively minimum sample preparation. [103] It should be noted that a wide range of adsorption energy information can be gathered by a combination of traditional IGC with the thermal ramped desorption approach. It is a technique where volatile matter in the sorbent flow gas is heated and concentrated prior to injection for detection by gas chromatography [104].

The experimental arrangement of the RF-GC technique is shown in Figure 4.4. The samples was heated at 573.6 K for 20 h under a continuous carrier gas flow and cooled to the working temperature. Then, 1 cm<sup>3</sup> (under the atmospheric pressure) gas is injected into the system. Nitrogen as carrier gas flow used to reverse the procedure started after the appearance of the continuously rising concentration-time curve. The electronic valve controlled automatically with each reversal always lasting 6 s. The diffusion coefficients were obtained from sample peaks data and complex calculation [105].

Kapolos et al. [105] confirmed that values of the diffusion coefficient from of hydrocarbons diffusing into alumina experimentally results in the same magnitude as those calculated by well-known formula of Knudsen diffusion coefficient Equation 4.26.

$$D_K = 48.5 \ d_o \left( \sqrt{\frac{T}{M_A}} \right)$$
 Equation 4-25

Where  $d_o$  is the diameter of the pore tube, T is temperature,  $M_A$  is the molecular weight. This formula predicts the diffusion coefficient of Knudsen diffusion will be inversely proportional to the square root of molecular weight; this is same as predicted by Graham's law [106].



Figure 4-4 Experimental arrangement of the RF-GC technique for measuring diffusion coefficients in porous solids [105]

The other diffusion experiment technique is GD-NMR (gas diffusion nuclear magnetic resonance). It is a non-invasive method that have been studied extensively for a wide variety of porous materials for the past 50 years [107]. The technique can be applied under steady or dynamic condition without interfering the internal process. It can measure diffusion path range between 100 nm to  $100\mu m$ . The principle is based on relaxation time response as a result of reaction of nuclei magnetism spin with surrounding [108]. In addition, porous media characteristic such as surface-area-to volume ratio, average pore size and visualizations of fluid transport under flow can be obtained by NMR. However, this method is limited into porous media that having very small concentration of paramagnetic ions and unable to examine multi pore length scale due to slow spin depolarization at pore surface [109].

## 4.3.1. Carbon Dioxide Diffusion Coefficient Measurement in Porous Carbon

Variation of the CO<sub>2</sub> diffusion coefficient in porous coal at elevated temperature was investigated by Golovina [1]. The experiment apparatus consist of upper and lower chamber separated by coal plates with thickness 1.5mm mounted in complete seal as shown in Figure 4.5. After the furnace is heated to the intended temperature, nitrogen gas was used to flush the chamber. Then, the carbon dioxide was circulated from the upper chamber while simultaneously turning on the burette tap and measuring the time using a stopwatch. Furthermore, the experiments were conducted in the temperature range between 200 to 600°C, while pressure in both chambers was kept constant. The percentage and concentration of carbon dioxide in the volume of nitrogen was measured by the burette, so the volume of carbon dioxide diffused into carbon sample can be calculated. The diffusion coefficient of

carbon dioxide can be approximated by equation 4.27 where s is surface area and I is the thickness of anode as follow.

$$D_{eff, CO2} = \frac{Vco_2 \cdot l}{St}$$
 Equation 4-26

The major difficulty during experiment was to keep the pressure equal in both compartments. This, for the most part, explains a rather big spread of experimental points. The relation between the diffusion coefficient and temperature can be determined using modified Arrhenius calculation in equation 4-28. Plotting log  $D_{eff}$  versus  $\log \frac{T}{T_0}$  as shown in Figure 4.6, value of Do and n constant can be obtained. Diffusion coefficient results are plotted into graph and the following expression obtained

$$D = Do \exp\left(\frac{T}{T_0}\right)^n$$
 Equation 4-27

$$D_{CO2,c} = 2.2 \cdot 10^{-3} \left(\frac{T}{293.15}\right)^{1.34}$$
 Equation 4-28

The study from Golovina [1] has only been carried out up to 600° C before Boudouard reaction took place and influenced the overall reaction, so it is not clear whether the results are applicable to anode carbon. Moreover, the contribution of pore structure related to Knudsen diffusion mechanism was also neglected.



Figure 4-5 Scheme of the apparatus used in Golovina's experiment. [1]



Figure 4-6 Log  $D_{eff}$  versus log T/T<sub>o</sub> · [1]

In another study, Hugo [110] investigated the influence of pore structure on the effective diffusion coefficient of  $H_2$  into graphite. The stationary counter-courent experiment is conducted by chemical conversion of para- $H_2$  to ortho- $H_2$  on high active catalyst (Pt Alumina) which is passed by a stationary hydrogen flow enriched with para- $H_2$ . Consequently, the molecular and Knudsen diffusion coefficient were obtained by measurement of differential pressure in different temperature. The porous media characteristics such as porous media factor ( $\Psi$ ); the ratio of porosity ( $\phi$ ) to tortuosity ( $\tau$ ) were determined in separate experiment.

In addition, Evan et al. [92] conducted the experiment to compare mixture of helium and argon gas diffusion coefficient into graphite in steady state counter flow with uniform and non-uniform pressure for both inlet and outlet sides. The diffusion coefficient collected in non-uniform pressure was similar with those obtained under uniform condition. Therefore, provided that small pressure drop present and constant with time, Evan et al. [92] claimed that it is not necessary to maintain uniform total pressure to determine the correct coefficient.

## 4.4. Gas Transport Mechanism in Molten Salt

The other possibility of gas storage and transfer regarding bubble nucleation is through molten bath. According to Einarsrud's [41] modelling approach, the gas transport mechanism through cryolite bath appears to well reproduced compare with transport through pores in electrolysis cell verification. They outlined that gas diffusivity and active anode pores in the case of saturation concentration in the industrial process are dynamic related with temperature and bath composition. However, detailed experiment and thorough investigation required. Consequently, it is necessary to study gas solubility and diffusion in molten salt to understand the fundamentals of CO/  $CO_2$  gas transport mechanism.

#### 4.4.1. CO<sub>2</sub> Solubility in molten salt.

Molten salts is acknowledged as reaction media due to excellent characteristic in high temperature stability, catalytic effect, low vapour pressure and heat transfer. Furthermore, in the electrochemical system, rate of reaction in molten salt depends on solubility and diffusivity [111]. These two physicochemical properties are directly proportional to temperature, pressure and varied with electrolyte composition. Solubility is defined as the quantity of substance that will dissolved into solution to form a saturated solution and expressed in terms of maximum volume or mass of the solute that dissolve in a given volume or mass of a solvent [112]. In theoretical and practical application, the solubility of non-inert gas in molten salts, for example chlorine in cryolite or carbon dioxide and gases in molten carbonates, provide important information in extractive metallurgy field. Moreover, structural properties of molten salt can be investigated using the solubilities of inert gas information [113].

The material selection for the experiment assemblies is the critical requirement of the method due to the corrosive nature of molten salts. The various experimental technique for measuring  $CO_2$  gas in molten salts are summarised in Table 3.1. There are two types of solubility aspect used in the technique, firstly is the physical solubilities where melts were considered to absorb  $CO_2$  gas in a molecular form (methods 1 to 4). However, these methods have limitation to temperatures above 1273 K. Alternatively, chemical solubility as in methods 5 and 6 to the melts which were considered to absorb  $CO_2$  gas chemically according to the following equation [114].

$$CO_{2(g)}+O_{2(melt)}=CO_2^{-3}_{(melt)}$$
 Equation 4-29

Wagner [115] has proposed a measurement for the basicity of slags called the carbonate capacity. This method quantify physically absorbed  $CO_2$  evolved from the melt on freezing accurately in strong basicity melts by considering physical solubility of  $CO_2$  gas is negligibly small compared with the chemical solubility of  $CO_2$  gas. This method proven to be accurate for the melts with strong basicity.[115] The thermographic method is limited on melts with large solubilities of  $CO_2$  and have negligibly rate of evaporation in comparison with the absorption amounts of  $CO_2$ . Although measuring solubility in the quenching method is difficult for undissolved gas in aqueous acid solution, this method is widely used due to the simplicity of the apparatus.

## 4.4.2. Solubility of CO<sub>2</sub> in Cryolite

Study in the solubility of  $CO_2$  and in cryolite saturated with alumina have important role for understanding possible reactions between the entities would reduce Faradaic efficiency in the Hall-Héroult cell. Förland et al. [116] estimate the solubility of  $CO_2$  in alumina saturated

cryolite based on the specific gravity determination. Haupin [14] measurement of the  $CO_2$  solubility in cryolite is 0.10 x 10<sup>-3</sup> moles liter<sup>-1</sup> atm<sup>-1</sup>. This value was obtained at 1303 K with quenching method. Firstly, the sample was withdrawn from the melt using nickel crucible after  $CO_2$  has absorbed in cryolite. After rapid cooling, the sample was heated to 773 K for releasing the amount of  $CO_2$  evolved using a mass spectrometer. However, the limitation of this technique is not all the  $CO_2$  is desorbed on heating to 773 K.

No	Method	Molten salts	References
1	Volumetry	NaCl, KCl, Kl	Bratland et al. [117]
	Measure the volume change of	KCI	Novozhilov et al. [118]
	CO <sub>2</sub> gas during CO <sub>2</sub> absorption	ZnCl <sub>2</sub>	Borodzinski et al. [119]
		ZnCl <sub>2</sub> - KCl, ZnCl <sub>2</sub> - NaCl	Sokolowski and
			Borodzinski [120]
		$Na_3AIF_6-AI_2O_{3,}$	Bratland et al. [121]
2	Manometry	Na <sub>2</sub> CO <sub>3</sub>	Andresen [122]
	Measure pressure change during		
	CO <sub>2</sub> absorption		
3	Stripping Method	NaCl, KCl	Grjotheheim et al. [123]
	Measure the amount of the $CO_2$	NaNO <sub>3</sub>	Field and Green [124]
	by gas chromatography ,	$ZnCl_2,  ZnBr_2,  SnCl_2,$	Sada et al. [125]
	chemical analysis or infrared	NaNO <sub>3</sub>	
	absorption analysis. The $CO_2$ gas	Alkali halide and alkali	Sada et al. [126]
	was expelled from melt by	nitrate	
	introducing inert gas.		
4	Chilling method	NaCl, KCl, KBr, Kl	Bratland et al. [117]
	Measure absorbed CO <sub>2</sub> evolved	$Na_3AIF_6-AI_2O_3$	Förland et al. [116]
	on quenching on Ascarite	NaCl, KCl, KBr, Kl,	Bratland et al. [117]
		KF, NaF, NaNO₃	Bratland and Krohn
			[127]
5	Thermogravymetry	Na <sub>2</sub> O- SiO <sub>2</sub>	Berjoan and Coutures
	Measure weight change during		[128]
	CO <sub>2</sub> absorption	$Na_2O-P_2O_3-SiO_2$	Yamato and Goto [129]

Table 4-1 Methods for determining CO<sub>2</sub> solubility.

6 Quenching Method

Measure the amount of extracted

6.1	CO <sub>2</sub> gas aduring vacuum fusion	Na <sub>2</sub> O- SiO <sub>2</sub>	Pearce [130]
	by gas buret	Na <sub>2</sub> O- B <sub>2</sub> O <sub>3</sub>	Pearce, ML [131]
6.2	$\begin{array}{llllllllllllllllllllllllllllllllllll$	Na <sub>3</sub> AIF <sub>6</sub> -AI <sub>2</sub> O <sub>3</sub>	Haupin [14]
6.3	Samplewasdissolvedinaqueousacid solution;CO2wasabsorbed in Ascarite	CaO-Al <sub>2</sub> O <sub>3</sub> , CaO-CaF <sub>2</sub> , BaO-BaF <sub>2</sub> , Na <sub>2</sub> O- SiO <sub>2</sub> , K <sub>2</sub> O- SiO <sub>2</sub> , Li <sub>2</sub> O- SiO <sub>2</sub>	Kawahara et al. [132]
		Na <sub>2</sub> O- SiO <sub>2</sub>	Maeda et al.[133]
6.4	Measure ammount of absorbe CO <sub>2</sub> by infra red absorption analysis	Na <sub>2</sub> O- Fe <sub>2</sub> O <sub>3</sub> , CaO- Fe <sub>2</sub> O <sub>3</sub>	Sumita et al. [134]
6.5	Measure ammount of absorbed CO <sub>2</sub> by CO <sub>2</sub> tracer technique	Na <sub>2</sub> O- CaO- Fe <sub>2</sub> O <sub>3'</sub>	Mahieux and Ribaud [135]
		$Na_3AIF_6-AI_2O_3$	Numata and Bockris [136]
		Silicate	Mysen et al. [137]
6.6	Measure evolve CO2 as resultan of fusion reaction with $B_2O_3$ or KBF <sub>4</sub> using carbon analyzer. by the weight loss method.	Na <sub>2</sub> O-SiO <sub>2</sub> , NaCl-Na <sub>2</sub> O	Koyama and Hashimoto[114]

Bratland et al. [121] measurement value of  $CO_2$  solubility in cryolite is  $1.17 \times 10^{-3}$  moles liter <sup>1</sup>atm<sup>-1</sup>. The value of solubility is obtained by using volumetry method based gas volume differences measurement of as resultant of  $CO_2$  absorption in the melt. However, a small change in gas volume associated with the evaporation of the melt will affect the solubility value significantly. The apparent difference of solubility value between these two techniques made it difficult to compare. A radiotracer method was developed by Numata and Bockris [136] to verified the results from previous experimental method. The comparison between the results from Bratland et al. in cryolite saturated with 12.1 weight percent of alumina with Numata's data in cryolite saturated with 5.33 weight percent of alumina Al<sub>2</sub>O<sub>3</sub>, they show a good agreement are presented in Figure 4.7.


Figure 4-7 CO<sub>2</sub> solubility comparison.[136]

## 4.5. Diffusion Coefficient Technique in Molten Salts.

Jans and Bansal [23] have presented a comprehensive summary of diffusion coefficient in single and multi-component salt system as basic properties of fluid system. The purpose of this chapter is to review the literature related to diffusion coefficient measurement technique in molten salt. The different methods may be collected under two broad divisions, namely electrochemical and non- electrochemical techniques as follows.

## 4.5.1. Electrochemical Method

**Chronoamperometric** is one of the electrochemical techniques widely applied to measure the gas solubility and diffusivity in molten salts. This technique compromises the potential of a working electrode is stepped from equilibrium value at  $E_1$  to potential  $E_2$  is shown in Figure 4.8a. Measurement of current with time shown in Figure 4.8b. The current decreases because oxidation used up at electrode surface and diffusion coefficient can be calculated using :

$$D = \left[\frac{4\tau I^2}{\pi n^2 F^2 A^2 C O_2^2}\right]$$
 Equation 4-30

Where D is the diffusion coefficient for species j in cm<sup>2</sup>/s,  $\tau$  is the transition time, I is the constant electrolysis current, n is number of electrons involved in the electron transfer step, F is Faraday constant (96.485 C/mol) A is area of the (planar) electrode in cm<sup>2</sup> and Co is initial concentration of the reducible analyte j in mol/cm.



Figure 4-8 a) Schematic illustration of the potential stepping in chronoamperometry, (b) the resulting current variation with time

Djokic et al [138] conducted chronoamperometry experiments to determine sensor anode performance from different carbon materials with graphites and glassy carbon in aluminacryolite melts at 1010 °C. The experiment's results showed that the nature of the carbon anode material effecting the current response behaviour. The glassy carbon are diffusion controlled and have the best performance inside the cryolitic melt. Alternatively, the graphite was not fully controlled by diffusion nor have reproducible results. This phenomenon cause by kinetic reactivity of glassy carbon for anodic oxidation significantly faster and irreversible changes of the graphite surfaces.

**Chronopotentiometry** is a technique of monitoring potential change of working electrode as function with time using a constant current, or a current step. The time measured when from the start to the rapid change in potential was called the transition time. This quantity was affected by the areas of the electrode, the bulk concentration and the number of electrons involved in the reaction as shown in Sand equation below.

$$i \tau^{\frac{1}{2}} = -\frac{nFC^{\infty}\pi^{\frac{1}{2}}D^{\frac{1}{2}}}{2}$$
 Equation 4-31

The electrochemical behaviour of anodic reaction in molten cryolite and alumina is studied using a chronopotentiometric techniques by Thonstad [139]. The diffusion coefficient of dissolved alumina is found to  $1.5 \times 10^{-5}$ cm<sup>2</sup>/s in molten cryolite at  $1020^{\circ}$ C. This result is in disagreement with data from Shurigin et al [140] regarding the kinetics of the dissolution of alumina and cryolite melts. The diffusion coefficient was obtained to be  $0.72 \times 10^{-5}$  cm/s at  $1080^{\circ}$ C and the diffusion coefficient value decreased with decreasing alumina content.

**Rotating disk electrode** (RDE) is a technique that measuring the variation of surface concentration and product by changing the rotation rate to achieve condition of under forced convective mass transport. The advantages from this technique is the reaction orders can be set up by the rotation rate without the having more concentrations. [141] Solution was put into

rotating electrode disc and will form a thin layer with no convection in the surface. This layer is controlled by diffusion only with homogenous thickness across the disc [142]. In the rotating disc electrode, the mass transport problem by convective diffusion has been solved by Levich as shown in the Equation 4.32.

$$i = 0.620 n F A D^{2/3} \omega^{1/2} V^{-1/6} C$$
 Equation 4-32

Where i is the current, n is the number of electrons transferred, F is the Faraday constant, A is the electrode area, D is the diffusion coefficient,  $\omega$  is the angular velocity of the electrode, v is the kinematic viscosity, and C is the analyte concentration [23]. The inadvertent influx of air (CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O) is become one of critical requirement of measuring the diffusion coefficient accurately due to difficulty of maintaining perfectly controlled atmosphere over the melt while rotating. [143]. Frazer and Thonstad [142] used this experimental technique for determining solubility and diffusion coefficient for the dissolved alumina. The results was in the range of 1.8 to 2.29 10<sup>-6</sup> cm<sup>2</sup>s<sup>-1</sup> at 1023 K. and estimated to be five times lower than values encountered at traditional aluminum smelting temperatures (~1233 K).

**Rotating ring disk electrode (RRDE)** has important addition of second working electrode in the form of a ring around the central disk of the first working electrode from RDE. A non-conductive barrier was separated the two electrodes and controlled by potentiostat in the system. [141] The main advantage for using this technique is the observed currents are free of interferences from double-layer charging when the ring is held at constant potential. [144].

RRDE was used by Stojanovic et al. [144] to obtain electrochemical data in cryolite-based electrolytes. This technique has shown it is possible to detect a sub-valent intermediate species such as AI (I) that presumably exist as complex oxyfluoride ion. The results confirm present hypotheses that both soluble and insoluble aluminium ion reaction product are formed in electrodeposition. Furthermore, the chemical dissolution of insoluble aluminium into the bulk electrolyte is primarily responsible for the loss in current efficiency in aluminium smelting cells.

In particular, the electrochemical method is quite rapid compared to other techniques. The diffusion coefficient determination is optimum where the values of diffusion coefficient are small ( $\sim 10^{-6}$  to  $10^{-8}$  cm<sup>2</sup>s<sup>-1</sup>). These techniques are also suitable for highly viscous melt (BeF<sub>2'</sub> ZnCl<sub>2</sub> containing melts) measurement. However, the limitations are the diffusion experimental data is frequently affected by electrode reaction, the effective area of working electrode and electro activity diffusion species to be sensed by electrochemical approach.

## 4.5.2. Non-Electrochemical Method

Different approach is used to determine the diffusion coefficient in molten salt, some of the principle methods in the non-electrochemical method are briefly examined. The advantages and limitation of each method is discussed.

## 4.5.4.1. Lag-time technique

The non-electrochemical techniques use gas absorption rate in the liquid as the basis of the measurement. One of technique that can be used for measuring diffusion coefficient in liquid is lag-time technique. A major advantage of this technique is gas diffusivity and solubility can be determined in a single experiment in both transient and steady state conditions.[145] The pressure transducer is installed to monitor the pressure responses between the upstream and downstream, separated by the membrane in the permeation chamber as shown in Figure 4.9.



Figure 4-9 Schematic of diffusion cell experimental setup [146].

Morgan [146] et al measured the diffusion in ionic liquid as potential of CO<sub>2</sub> capture for environmental aspects. The ionic liquid is a molten salt which melts at a lower temperature. This approach is applied for determining the diffusion coefficients in ionic liquids because of their non-volatility so that the liquid vaporization will be negligible and material loss of the experiment. The experiment was conducted in the temperature range from 30 °C to 70 °C for  $CO_2$  absorption in ethylene, propylene, 1-butene, and 1,3-butadiene in five imidazolium-based ionic liquids and one phosphonium-based ionic liquid. The diffusion coefficient obtained in the experiment are in the range of  $10^{-6}$ cm<sup>2</sup>/sec. This value showed that  $CO_2$  diffusion in ionic liquid is smaller compared to traditional hydrocarbon solvents and water, but the dependence on viscosity is lower while diffusivity on temperature and the size of the solute gas is higher than that for nonpolar solvents.

The binder-free glass was selected to form RTIL membrane due to their hydrophilic nature and thickness to ensure the wettability of the ionic liquids and measurable lag times [147]. The drawback of this technique is when the gas solubility in the membrane medium is low <0.01 mol/(L atm) due to the impracticable to differentiate accurately solubility and diffusion coefficient in the experiment.

## 4.5.4.2. Transient Thin-Liquid-Film Method

In the experiment conducted by Hou and Baltus [148], measurements were performed at low  $CO_2$  pressures to provide the diffusivity under infinite dilution conditions at temperatures in the range of 283-323 K. The experimental technique is monitoring the pressure in the sample chamber when the gas is introduced to the sample in desired temperature and pressure (1-2 bar) as shown in Figure 4.10. The pressure transducer measured every second of pressure decrease when  $CO_2$  absorbed in the sample. The experiment length was 12 to 14 hour depending on the operating temperature of the ionic liquid. The pressure was curved fitted to the diffusion model for solute uptake shown in Equation 4.34 to determine the solubility and diffusivity of gas in the liquid.





$$\ln \frac{P}{P_o} = \left(\frac{k}{H_{CO_2}}\right) \sum_{n=o}^{\infty} \frac{1}{(2n+1)^2} \{ exp\left[\frac{(2n+1)^2(\pi)^2 D_{CO_2} t}{4L^2}\right] - 1 \}$$
 Equation 4-33  
$$k = \frac{8RT V_{IL} \rho_{IL}}{(\pi)^2 V_{CO_2} M W_{IL}}$$
 Equation 4-34

Where  $H_{CO2}$  is Henry's law constant of  $CO_2$  in an ionic liquid (bar), L is depth of ionic liquid (cm), MW<sub>IL</sub> is molecular weight of ionic liquid (g/mol), n is number of moles of CO<sub>2</sub> (mol), P is total pressure in the vapour phase (bar), P<sub>0</sub> is initial pressure of CO<sub>2</sub> in the vapour phase (bar), V<sub>IL</sub> is volume of ionic liquid (cm<sup>3</sup>) and  $\rho_{IL}$  is density of ionic liquid (g/cm<sup>3</sup>).

Nonlinear least-square method is used to determine the two variables  $H_{CO2}$  and  $D_{CO2}$  to be fitted to the experimental pressure decay data with few assumptions made. The calculated value of Henry's law constants were in the same agreement with previous measurements reported for these ionic liquids in the range of 25.5-84 bar [149,150]. The diffusion coefficient of room temperature ionic liquid (RTIL) were measured in the magnitude of  $10^{-6}$  cm<sup>2</sup>/s This result is in agreement with another study about diffusivity in RTIL and were generally one magnitude smaller than the conventional solvent.[146,151]

The study showed that the ionic liquid anion affected the  $CO_2$  solubility more strongly compared to the cation of the ionic liquid.[148] In contrast, the measured diffusion coefficients were affected by the cation as well as the anion. The  $CO_2$  diffusion coefficient were observed to be more dependent to temperature than observed for  $CO_2$  solubility in the RTIL. The correlation between the diffusivity with the operating temperature, viscosity, density and molecular weight were shown in excellent agreement as reported previously by others. [148]

## 4.5.4.3. Gravimetric Method

Intelligent Gravimetric Analyzer (IGA) was utilized by Shiflett and Yokozeki [152] to measure the solubility and diffusivity of CO<sub>2</sub> in 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF4]). The apparatus was integrated with computer control that automatically monitored the weight change, pressure difference and operating temperature to ensure reproducible results. However, the change of gravitational balance namely buoyant force, aerodynamic drag forces, volumetric changes due to variation of pressure and temperature must be implemented for accurate results. [152]

The experiment was conducted at four isotherms (at 283.15, 298.15, 323.15, and 348.15 K), once the desired temperature attained and stable the pressure will be adjusted to the isobar set-point up to 2.0 MPa (0.01, 0.05, 0.1, 0.4, 0.7, 1, 1.3, 1.5 and 2 MPa). Set points were maintained for minimum 3 hours and maximum 8 hours for equilibrium point, where there is no more weight change and gas pressure kept constant. Equilibrium were considered to have

reached when at constant pressure no further weight change was observed throughout time (weight

change rate <0.001 mg/h). Then , the recorded absorption data( $m_{BAL}$ ) was adjusted with the buoyancy effect acting on the sample and the sample container as follows[153,154]:

$$m_{bal,corr} = m_{bal} \rho + \rho_g V_{s+c}$$
 Equation 4-35

This buoyancy corrected mass  $(m_{bal,corr})$  is the mass of the sample container  $(m_c)$  and the mass of the sample with absorbed gas (m = mass of sample + mass of CO<sub>2</sub>). Then, the mass of the sample with absorbed gas is determined by subtracting the mass of the empty sample container from this (m =  $m_{bal,corr} - m_c$ ), the mass of absorbed gas is calculated by subtracting the mass of reactivated sample from the mass of sample with absorbed gas  $(m_{co2} = m - m_s)$ , and the molar fraction of gas absorbed is determined as follows[153]:

$$X_{CO2} = \frac{m_{CO2}/M_{CO2}}{m_{s/}M_{IL}}$$
 Equation 4-36

where  $M_{CO2}$  the molar masses of  $CO_2$  and  $M_{IL}$  is molar masses in the ionic liquid.

The solubility of gas in the liquid can be evaluated by The Henry's law constant, as shown in Equation [154]:

$$K_{H} = \lim_{X_{CO2} \to 0} \left( \frac{P}{X_{CO2}} \right)$$
 Equation 4-37

The diffusion coefficient of the ionic liquid was measured by the gas absorption in the ionic liquid container filled in predetermined liquid level height (L). [152] Moya et. al [153,154] and Gonzales-Miquel et. al. [154] evaluate the recoded data using a simplified mass diffusion process model based on is applied to understand kinetics of the system. In this experiment, the kinetics and thermodynamics of  $CO_2$  in ionic liquid by applying a mass diffusion model that reported by Shiflett and Yokozeki [152] using different apparatus. The gas diffusion and solubility measurements were performed with a Gravimetric High Pressure Sorption Analyzer (ISOSORP GAS LP-flow, Rubotherm) with magnetic suspension balance (MSB) as shown in Figure 4.11.

The Rubotherm sorption analyzer can be operated in dynamic mode with continuous gas dosing flow and equipped with automated and precise computer control of temperature and pressure. This apparatus capable to conduct the experiment in the range from room temperature up to 150 °C. The resolution of the mass reading is 0.01 mg with a standard deviation) of  $\pm 0.03$  mg and an uncertainty <0.002%. The operating pressure range between  $10^{-6}$  bar and 30 bar and the gas is flowing through the sealed sample container with predetermined time. The weight difference as results of the gas absorption is achieved after

the gas flow is stopped and the container is lifted to a freely suspended state by the magnetic suspended balance and weighed.





# 4.5.4.4. Bubble Columns and Gas Absorption Method

This technique is used by Sada et al [156] to determine the solubility and diffusivity of  $CO_2$  in molten NaNO<sub>3</sub>, at 350°C and eutectic mixture of LiCl (58 mol %)-KC1 (42 mol %) at 450°C and 530°C were analyzed on the basis of the film theory for mass transfer with chemical reaction in the aqueous phase. The experiment is conducted by introducing preheated carbon dioxide (superpure grade, 99.96% and free from water) through the bubbling tube into the absorber (4 different inner length; 4,6,8 and 10 cm) inside the furnace as shown in Figure 4.12 at a constant flow rate for a predetermined time.

The CO<sub>2</sub> bubble shape, movement and frequency in the bubbling tube were recorded using 16-mm movie films for visual calculation. The infrared carbon dioxide analyzer (Shimadzu, Type URA-2s) recorded the carbon dioxide concentration in the eluted gas from bubbling nitrogen through the bubbling tube. Then, the data of carbon dioxide absorbed in the salt was obtained by graphical integration of the concentration of carbon dioxide multiplied by the flow rate of eluted gas.

The carbon dioxide balance gives

$$V\frac{dC}{dt} = K_L \dot{a}(C^* - C)$$
 Equation 4-38

Integration of equation 4.42 gives

$$V \ln \frac{C^*}{C^* - C_t} = K_L a' t$$
 Equation 4-39

Where  $K_La$ 'is the volumetric coefficient of liquid-phase mass transfer, C is the absorbed carbon dioxide concentration at time t and C<sup>\*</sup> is the value of C in equilibrium with 1 atm of carbon dioxide. The  $K_La$ 'value was determined from the slope of a V ln C<sup>\*</sup>/(C<sup>\*</sup> - C<sub>t</sub>) vs. t plot for each run. For the estimation of diffusion coefficient,  $K_La$ ' is plotted against the length of the absorber tube, H, as shown in Figure 4.13. The slope of the straight line is present in Equation 4.44

$$\lambda = 4nr \sqrt{\frac{\pi h D_L}{U_b}}$$
 Equation 4-40

Thus, the diffusion coefficient can be obtained



$$D_L = \frac{\lambda^2 U_b}{16\pi n^2 r^2 h}$$
 Equation 4-41

Figure 4-12 a) Absorber b) Schematic diagram of experimental setup [156].

Further mathematical explanation is described on Sada's work [126,156,157]. The experiment results shown in Table 3.3 shows that the diffusion coefficient NaNO<sub>3</sub>, at 350<sup>o</sup> C was higher than those of the eutectic mixture at 450 and 530<sup>o</sup> C. Higher diffusivity of carbon dioxide in molten NaNO<sub>3</sub> might be related to bulky shape of the NO<sub>3</sub><sup>-</sup> ion. Interestingly, these values of the gas diffusivity are in the same order as the self- diffusion coefficients of ions in molten salts. For example, the self-diffusion coefficient of Na<sup>22</sup> in NaNO<sub>3</sub> at 365 <sup>o</sup>C is 2.53 x 10<sup>-5</sup>.

Factors that have to be considered that affect the accuracy of the experimental data are the state of the liquid film on the tube wall around the rising bubble. The movement of a slug is governed by bouyancy, viscosity, and surface tension. The effects due to gas viscosity and inertia can be considered to be negligible in the experiments when surface tension ( $\sigma$ , g/s<sup>2</sup>) dominated with Eotvös number ( $N_{\varepsilon \ddot{o}}$ ) calculation smaller than 3.37, as shown in equation 4.42.

$$N_{\varepsilon \ddot{o}} = \frac{g d^2 (\rho_t - \rho_g)}{\sigma} < 3.37$$
 Equation 4-42

Where d is diameter of tube (cm),  $\rho_t$  is liquid density, and  $\rho_g$  is gas density.



Figure 4-13 Values of K<sub>L</sub>a' plotted against tube length. [126,156,157]

System	Т	<i>U<sub>b</sub></i> (cm/s)	H (cm)	r (cm)	n (1/s)	Diffusivity of
	(°C)					CO <sub>2</sub> (cm <sup>2</sup> /s)
NaNO <sub>3</sub> ,	350	29.8	2.13	0.235	0.075	2.53 x 10⁻⁵
LiCI-KC1 (58mol %- 42 mol %)	450	27.3	2.21	0.236	0.083	1.32 x 10 <sup>-5</sup>
LiCI-KC1 (58mol %- 42 mol %)	530	30.2	2.26	0.234	0.087	1.70 x 10 <sup>-5</sup>
Water	20	27.1	2.1	0.237	0.083	1.86 10 <sup>-5</sup>

Table 4-2 Observed Values for diffusivity in molten salt[126,156,157]

A number of solubility and diffusion coefficient determination techniques in molten salt have been identified in this chapter. Further investigation in experimental technique selection for  $CO_2$  diffusivity in molten salts will be explained in Chapter 9.

# **Chapter 5**

# 5. Research Issues

As described in the literature review, a vital factor to increase energy efficiency in Hall-Héroult cell is in predicting and understanding bubble behaviour. Investigations have been conducted for measuring bubble resistance and determining factors that affect bubble behaviour using in-situ measurements in Hall-Héroult cells, measurements in laboratory-scale cells and physical models. However, there are still matters of debate regarding the bubble nucleation behaviour. The main reason for this is the CO/CO<sub>2</sub> gas transport mechanism on the underside of anode and its correlation between gas diffusion, anode and bath properties is not yet fully understood. Hence this research will use experimental techniques to measure the diffusion coefficient of CO<sub>2</sub> in porous anode and molten salt, in conjunction with the measurement of properties of anodes materials. Theoretical values for these diffusion coefficients will be calculated for comparison.

There are number of techniques available to measure gas diffusion coefficients and to carry out the material characterisation. However, there are also gaps in knowledge that should be addressed for CO/CO<sub>2</sub> diffusion in aluminium electrolysis, namely:

- There are very limited studies and experimental data for diffusion coefficient of CO<sub>2</sub> in porous anode carbons. A previous study by Golovina [1] has measured the CO2 diffusion coefficient in coal at a temperature ranging from 273 to 873 K where the diffusion transfer is not complicated by chemical reactions. Investigation of the diffusion behaviour above this temperature is important especially in the Hall-Héroult cell operating temperature (960°C).
- 2. Few studies [22][62][64] have mentioned the effect of carbon monoxide formation on the underside of an anode in aluminium electrolysis. However, further study on the influence of Borduard reaction in gas transport mechanism in relation on bubble nucleation is required.
- 3. There are several anode carbon characterization techniques proposed, with a comparison between each technique and their correlation with porous solid diffusion processes has not been addressed.
- 4. Study on the solubility and the diffusivity value of CO<sub>2</sub> in molten salts at the typical temperatures of electrolysis (~960 °C) have been studied in the past by Rolin [2] and Vetyukov and Acquah [3] but there are some doubts about these values and they need to be verified independently.
- 5. There are no modelling studies in the literature quantifying the fluid flow, mass transfer and porosity in the anode carbon for diffusion experiment using finite element analysis.

In the present study, the following questions are to be addressed:

- Is it possible to characterize anode porosity as basis measurement for diffusion experiment?
- Do the anode properties affect the diffusion process?
- Is it possible to measure diffusion coefficient without being affected by convective flow?
- What are the factors responsible for the gas diffusion process?
- What is the relative importance of CO<sub>2</sub>/CO diffusion process on bubble nucleation?

The approach used in this thesis was to first characterize the anode properties. MIP, Image analysis using optical microscopy and CT was selected to produce complete porosity result from the sample species. The relationship between porosity and anode physical properties such as density, permeability and anode reactivity have been described in Chapter 6.

In the following step of the study, experimental studies were performed to investigate the diffusion coefficient with different anode sample. Porous alumina sample was selected as comparison to anode sample due to its homogenous porous structure and inertness to react with carbon dioxide producing carbon monoxide gas. This included development of experimental apparatus to carry out diffusion experiment in porous solid with analytical techniques to characterise the concentration results from mass spectrometer. Chapter 7 describes this experimental investigation and the theoretical predictions for diffusion in anode materials.

The issue on the independency of the experiment results to temperature in particular with relation on convective flow and porous geometry has been approached by FEM using COMSOL Multiphysics software. The details of this study have been described in Chapter 8. In Chapter 9, prediction of diffusion coefficient and experimental work in molten salt also has been carried out for data comparison with results. Conclusion and recommendations are presented in Chapter 10.

# **Chapter 6**

# 6. Anode Porosimetric Study

## 6.1. Introduction

This chapter describes the anode characterization carried out to study the pore size distribution, impact of different process parameters and anode properties such as density, permeability and reactivity. Though the effect of process parameters such as binder percentage, temperature mixing, aggregate size has been investigated in the past, it is not clearly understood how the porosity forms and the impact on anode reactivity. Therefore, in the present work, the coarse porosity was investigated using x-ray computed tomography, the mid-range porosity using optical microscopy, and the finest porosity using mercury intrusion porosimetry. These methods were combined to gain a deeper understanding of porosity and how this affects anode quality and the potential for energy savings.

## 6.2. Materials and Methods

## 6.2.1. Pilot Anode Materials

The experiments conducted using pilot anodes were produced at Hydro PMT Årdal under supervision of Lorentz Petter Lossius. Anode material test series were produced with different coke types and partly added butts (recycled used anodes) with different mixing temperature  $(T_{mix})$  and different pitch content (% pitch) as shown in Table 6.1. The pilot anodes were characterized using ISO methods that are considered as standard at Hydro. The density measurement followed ISO 12985-1:200. Hydro in-house method comparable to ISO 15906:2007 was used for permeability.  $CO_2$  and air reactivity were tested using in-house method comparable to ISO 12989-1 that will described in chapter 6.2.7. Raw material coke with high open porosity and sample with typical over-pitching porosity is also measured to identify the porosity distribution. The porosity of the sample will be compared using Image Analysis (IA), X-ray Computerized Tomography (CT) and Mercury Intrusion Porosimetry (MIP)

Sample	T <sub>mix</sub>	% pitch	Coke
P71	200	14.4	А
P77	220	14.4	А
P82	240	14.4	А
J19	200	13.5	В
J24	200	17.0	В
L26	200	13.6	С

#### Table 6-1 Sample test and variability

# 6.2.2. Bulk Density and Apparent Porosity Determination with Water Intrusion Porosimetry

The sample was cut in cube-sized with the largest linear dimension of about 2 cm and dried at  $110 \pm 5^{\circ}$  C for at least 2 hours in the oven. After the samples have been cooled to room temperature, they were weighed to determine the dry test piece mass (m<sub>1</sub>). The sample is placed inside the bulk density and apparent porosity testing machine XQK-03 as shown in Figure 6.1 under vacuum for at least 15 minutes in order to ensure that all the air has been removed from the open pores. The vessel was disconnected from the vacuum pump and the immersion liquid (water) was progressively introduced. The test pieces were covered by about 20 mm of water after 3 minutes. Reduced pressure is maintained for 30 min, then the pump was switched off and the vessel was opened. The test piece remained covered by the immersion liquid throughout the impregnation for at least 30 minutes to ensure that the water penetrated into all the open pores until removed for subsequent weighing.

The mass of the immersed test piece  $(m_2)$  was determined by weighing a suspended test piece completely immersed in a quantity of the liquid, contained in a beaker by a thin thread from the load pan suspension point of a balance and as shown in Figure 6.2. The sample was removed from liquid and excess liquid was immediately removed by quickly rolling the test piece over a damp linen cloth saturated by the water. The samples were immediately weighed in air to ensure that evaporation of the water does not lead to any appreciable loss in mass during the weighing operation, the mass of the soaked test piece  $(m_3)$  was obtained. After all the mass data collection was completed, the bulk density (d) and open porosity were calculated using the equations 6-1 and 6-2.

$$\rho_b = \frac{m_1}{m_3 - m_2} x \rho_w \qquad \qquad \text{Equation 6-1}$$

Apparent porosity  $=\frac{m_3-m_1}{m_3-m_2}x100$ 

Equation 6-2



Figure 6-1 Immersed test piece mass weighing in the scale



Figure 6-2 Bulk density and apparent porosity testing machine XQK-03.

## 6.2.3. Mercury Intrusion Porosimetry Method

Prior to the analysis, the same samples from hydrostatic method were dried at  $200^{\circ}$  C under vacuum for 24 hours to remove moisture in pore spaces and then cooled to room temperature (~23 °C) in a desiccator. The samples were weighed before loading into the penetrometer as shown in the Figure 6.3.



Figure 6-3 Penetrometer with sample for MIP

During an MIP test, each sample underwent two analyses: at low-pressure and high-pressure. The applied pressure is proportional to the radius of the entrance of the pores. In addition, the volume of intruded mercury is recorded. The highest pressure produced by Micromeritics AutoPore IV 9510 as seen in Figure 6.4 is 41.3 MPa, and the pore throat diameter corresponding to this pressure according to Washburn equation is about 6 nm. The largest pore throat diameter recorded by MIP is about 300  $\mu$ m under low-pressure analysis. The samples were evacuated to 50  $\mu$ mHg (6.7 Pa). Equilibration time (the minimum time duration to achieve a stable mercury level before moving on to the next pressure value) was chosen to be 50 seconds.



Figure 6-4 Micromeritics AutoPore IV 9510

The low-pressure measurement steps consist of cell evacuation, filling with mercury and intrusion. The sample was weighed and put in a 15 cm<sup>3</sup> cell penetrometer then the cover was sealed by grease and tightened. The penetrometer containing the sample was installed horizontally in the mercury porosimeter. The air was evacuated from sample cell until a pressure of 5 MPa was obtained. The open end of cell stem was submerged under mercury and argon gas above the mercury forcing the liquid into the stem to fill the voids around the sample. The pressure was gradually increased to 500 MPa to intrude the mercury column in the cell stem was used to calculate the intruded volume (pore volume). Then the penetrometer was transferred to the high-pressure chamber. The pressure was progressively increased to and the intruded volume was recorded during the high-pressure measurement. At this point, depressurization starts, and pressure was gradually decreased to extrude the mercury.

## 6.2.4. Anode Porosity Measurement Using Optical Microscopy

Core samples with 30mm diameter were impregnated with fluorescent epoxy which will emit light from the pores under ultraviolet light under microscope. Sample preparation consists of using a vacuum embedding device, epoxy curing overnight, cutting/grinding with high performance cutter Secotom -15/-50 and polished to be prepared for optical microscopy, polishing and cleaning. Anode samples were analysed using a high-end microscope and computer equipped with motorized stage controller. The systematic movement allows the generation of a series of adjacent images that are combined to a contiguous high-resolution image as shown in Figure 6.5. The porosity of the sample will be measured by converting the images into a binary image and analysed using the program ImageJ. This program is

developed at the National Institutes of Health as open source software written in Java, which allows it to run on Linux, Mac OS X and Windows, in both 32-bit and 64-bit modes [20].



Figure 6-5 Image analysis clockwise [65]

a) the recursive order the frames are acquired, b) Frames 1-4 are merged, c) Frames 1-4, 5-8, 9-12 and 13-16 are merged d) Frames 1-16, 17-32, 33-48 and 46-94 are merged

# 6.2.5. Pore volume with X-ray Tomography

X-ray computed tomography (CT) was used to investigate qualitatively the pore distribution and structure on surface and interior of the anode samples. The CT was performed using a X-TEK XT H225 ST instrument. Settings for the imaging were 135 kV and 150  $\mu$ A. The sample was penetrated by an X-ray point source (cone beam) and scanned in small increments the entire 360° rotation as illustrated in Figure 6.6. The image is captured by a square detector, digitized and stored on a computer. The images were exported as a stack of 2000 single 2D images sliced in the XY (transverse) direction and post processed in ImageJ.



Figure 6-6 The  $\mu$ CT principle [75]

#### 6.2.6. Impurity levels

The impurity content was characterized using X-ray fluorescence (XRF) spectroscopy and Inductively coupled plasma atomic emission spectroscopy (ICP-OES) in CSIRO Clayton. For ICP-OES sample preparation, 0.1g of each sample underwent microwave digestion with nitric acid and peroxide and the resulting solutions (with undigested solids) were made to volume. Later the solutions were filtered to collect the undigested solids and the undigested solids were treated a 2<sup>nd</sup> time with nitric and peroxide to produce second volume of resulting solutions (with solids). Both the first and second extract solutions for XRF procedure, the samples were transferred to a proprietary loose powder cup fitted with a 6um high purity polypropylene film. The samples were then analysed using a Bruker proprietary semi-quantitative scanning calibration. The data was processed to account for the carbon matrix is shown in Table 3.

#### 6.2.7. Reactivity Measurement

Air and CO<sub>2</sub> reactivity tests were performed using in-house methods developed and conducted at Hydro Aluminium similar to ISO 12989-1 and ISO 12988-1, respectively the apparatus consists of five fused silica tube furnaces (gold coated), which can be run in parallel. A sketch of a furnace is given in Figure 6.7. The sample is placed in a standard size platinum wire mesh basket (Ø 20 mm, height 50 mm) which is mounted on a sample holder inside the furnace. The sample holder is connected to a balance. To ensure a satisfactory temperature regulation, the thermocouple controlling the furnace temperature is mounted into the coke aggregate. The reactivity of sample is measured by weight loss of the sample due to reaction inside the apparatus.





#### 6.3. Results and Discussion

## 6.3.1. Anode Density and Porosity

The density and porosity are important properties of the carbon anode. These properties are directly related to anode consumption and the anode's mechanical properties to withstand the high temperature process. Reduced porosity and permeability will result from higher density that should extend the operational life of the anode. However, excessive density will lead to poor thermal shock resistance and fracturing of the anode upon first use in an electrolysis cell [8]. Figure 6.8 shows the similar density results between volumetric approach and MIP. L26 has the largest standard deviation due to the inhomogeneity of the sample that will be explained in the next section. Results from anode carbon samples show good agreement from both methods. The sample J19 has the lowest density and highest porosity. It showed that the density is inversely proportional to the percent porosity, as shown in Figure 6.9.









## 6.3.2. Pore Size distribution

The plot of incremental intrusion volume versus pore entrance diameter provides the indication of where the majority of pore diameters are concentrated. Figure 6.10 shows the comparison of the pore size distribution according MIP, IA and CT. These results demonstrate that MIP systematically generates a lower pore size range and mostly peaked in the range of 1 to 8  $\mu$ m. These size distribution results for anode carbon are in good agreement with the results obtained from Sadler and Algie [62] and Engvoll [63]. The main reason of the different results between MIP, IA and CT are based on the physical basis of the measurement and different measurable pore size ranges.

The basis of the MIP measurement is changes in the mercury intrusion volume corresponding to the applied pressure according to Washburn equation, which relates to pore connectivity and external surface. The smallest open pore size depends on the maximum pressure while the largest measurable pore size is dependent on the height of the sample, which determines a minimum head pressure. On the other hand, Image analysis and the CT technique are based on measurements of the maximum diameter of each pore, and is limited by the smallest image resolution, at 10  $\mu$ m. Direct comparison between these three methods was obtained by analysis in the overlapping pore size distribution around 10 to 100  $\mu$ m.

Besides the pore size limitation, it is found that the MIP measurement pore size results peaks around 25 µm corresponds to the CT measurement peaks around 100 µm. The reason for this shift is that the CT measures each pore's maximum diameter, while Hg measures its minimum diameter (diameter of pore entrance). This different interpretation of pore size is attributed as "ink bottle effect" [158]. However, the IA results does not show a similar peak when compared with the CT results and difficult to prove this effect. In this case, both the optical image analysis and the CT analysis uses a similar algorithm for separating clustered pores. The technique is termed watershed segmentation and is based on an erosion of pore features until one point is left, and then a conditional iterative growth that avoids joining features [67].

The direct correlation between pore size distributions for these techniques was difficult due to their limitations. Figure 6.11 showed that porosity obtained from MIP are larger than porosity obtained from image analysis technique. These findings indicate that MIP is fundamental to represent smaller pores that are undetected using IA and CT. Despite less accuracy in the overlapping range than IA due to over estimation of crack as porosity, CT was useful for meso to macro porosity and offers a non-destructive test that enables the comparison for the same samples within a reasonable time and cost.



Figure 6-10 MIP, IA and CT pore size distribution



Figure 6-11 Porosity comparison from each technique

#### 6.3.3. The Inhomogeneity of Samples

The computerized analysis in IA and CT are also useful tools for pore classification. The parameters for pore image analysis are based on porosity, aspect ratio, mean diameter, porosity density and micro crack is shown in Figure 6.12 shows the image comparison between IA and CT. The image analysis is a combination of 192 images that has adequate contrast for analysis even though the lower contrast in IA caused by fluorescence epoxy quite faint at this scale. Since the CT data has a lower resolution, the results tend to merge several nearby pores (clusters) due to the lack of resolution, resulting in larger apparent pore sizes.

Figure 6.13 and 6.14 depicts the inhomogeneity and the structural components in the samples. The porosity of the baked samples originates from unfilled coke porosity, cracks and interparticle voids and release of pitch volatiles develop during production. Some of this excess porosity can be avoided by good control and design of mixing and baking furnace [159]. Sample J19 and J24 have no butts addition in contrast to sample L26 and P82. In this picture red represents low sulphur coke with circular pore inside, purple represents high sulphur coke (dense) and blue represents anode butts (full structure inside)



Figure 6-12 Comparison between CT results (upper image) and IA results (lower image)



Figure 6-13 Pore classification on CT Image for sample J19, J24 and P82.



Figure 6-14 CT Image for L26 sample

a) Porous area b) Dense area c) Bath material d) Foamy carbon e) High sulfur coke f) Low sulfur coke g) Anode butts (full structure inside)

# 6.3.4. Anode reactivity and permeability

Air and  $CO_2$  reactivity and permeability of anodes are commonly used to compare the quality of anodes prepared under different conditions. In the electrolysis cells,  $CO_2$  is released at the anode during electrolysis which can react with the anode to form CO gas. Similarly, air can diffuse through the cell cover and react with the anode. These reactions increase the anode consumption. In addition, increasing anode permeability increases the diffusion of both  $CO_2$ and air in to the interior of the anode, consequently, increasing the extent of the reaction. Therefore, the anode quality improves as permeability, and the resulting reactivity, decreases.

Figure 6.15 illustrates the permeability data using MIP measurements and air permeability measurements. Both the mercury and the permeability measurements show a similar trend with air permeability, with four times larger values for air permeability compared with mercury permeability. The differences between mercury and air permeability are due to the impact of the compressibility of the mercury phase and the sample, as well as the fact that mercury

might not be able to access some of the micro-pores that gas can access, due to the relatively higher molecule size of mercury compared to air [53]. Furthermore, at elevated fluid pressure, mass transfer occurs between the mercury liquid phase and its mercury vapour phase to reach equilibrium, while no mass transfer occurs during the air permeability measurement since a single phase is used [160].

The anode reactivity comparison is shown in Figure 6.16. The results show that J19 has the highest CO<sub>2</sub> reactivity as this sample has the highest permeability and largest pore size, allowing for a larger accessible surface for carbon reduction to take place. Interestingly, the air reactivity of J19 is the lowest among all the samples. This behaviour may be associated with impurities in the anode, and the reactive pore size being larger than the active pore size for anode reactivity as mentioned in Chevarin's work [161]. However, the active pore size for anode reactivity from previous research [162] range in several order of magnitude, this discrepancy on anode reactivity is likely caused by lack of consideration of impurities in their study.

Suriyapraphadilok et al [19] have previously measured the amount of inorganic material by inductively coupled plasma (ICP). When this chemical analysis is carried out on the anode samples in this work, a very high iron content in this sample (J19) is measured and other major inorganic contents are found to be sulphur, sodium, aluminium, and calcium. Furthermore, Houston and Øye [20] indicated the level of reactivity in  $CO_2$  and air of chars (or cokes) made from lignite followed the order of Na > K > Ca > Fe. These inorganic elements are well known as catalysts for  $CO_2$  oxidation.



Figure 6-15 Permeability data



Figure 6-16 Anode reactivity

These results are consistent with the findings of Walker and Raats [21], in that the sodium level had the strongest catalytic effect for the carboxy reaction despite the presence of other catalytic metals. The sodium content can be improved by proper arrangement in the anode recipe related to cleanliness of anode butts and amount of anode butt addition [21]. Comparatively, vanadium content also adversely affects the air reactivity of the anode [163]. The impurities content of the samples are shown in Table 3. J19 has the least amount of sodium and vanadium content. It is not clear yet whether low vanadium and sodium content are associated with the low air reactivity behaviour observed for samples. Further work using more samples and factorial design analysis is required to clearly identify the key relationship between porosity and anode reactivity.

Sample	Ca	Fe	К	Na	Ni	S	V
	%	%	%	%	%	%	%
P71	0.0053	0.02	< 0.002	0.01	0.01	0.87	0.01
P77	0.0088	0.02	< 0.002	0.02	0.01	1.30	0.01
P82	0.0072	0.03	< 0.002	0.01	0.01	1.40	0.02
J-19	0.0065	0.04	< 0.002	< 0.01	0.02	1.10	0.01
J-24	0.0084	0.03	< 0.002	< 0.01	0.02	1.10	0.01
L-26	0.0082	0.04	0.001	0.02	0.01	1.97	0.02

Table 3 Chemical properties of the investigated anode sample.

## 6.3.5. Anode pore structure and Anode Reactivity

Optimum petroleum coke density and porosity for appropriate binder interaction is required to ensure good electrical conductivity and mechanical strength. Anode surface with pores having diameters in the 1 to10  $\mu$ m range are accessible to oxidation by air and CO<sub>2</sub> gas unless blocked in some manner [162]. Sadler and Algie [62] proposed two models in their study to clarify role of binder microcracking in reaction porosity development. The theoretical requirement for carboxy sub-surface oxidation is the combination of sufficient surface area for reaction and adequate gaseous mass transport rates. The first tree pore model in Figure 6.17 showed that fine porosity is not significant due to mass transport limitation in Knudsen diffusion while larger porosity does not have adequate surface area. The most reactive is intermediate size of porosity because it provides sufficient CO2 flow yet small enough to provide surface are to react. However, this tree pore model is not consistent with their experimental results and did not describe the actual anode pore structure.

An alternative pore structure is proposed in Figure 6.18. This model showed the porosity caused by volatile released within the binder matrix between coke particles and lined with binder carbon. The binder film surrounding coke particles will contain fine pores and microcracks that resulted from evaporation and shrinkage of binder around filler particles as they expand during baking. This microcracks and fine porosity will be a major site of active surface area. The direct connection of feeder pores with microcracks and fine porosity will provide adequate surface area for the reaction. As the surface area are gasified; the binder shrinkage microcracks will be enlarged by sub surface oxidation eventually lead to carboxy attack on the binder carbon. This behaviour was observed an increase on volume of large pores near electrolytic surface. The model confirms that reducing anode permeability by decreasing the size and volume of the volatile release porosity will reduce sub-surface oxidation by lowering the rate of gas flow to the active surface area. Subero [164] suggests the concentration of pores between 0.5 and 15  $\mu$ m on coke materials should be as low as possible to minimise CO<sub>2</sub> reactivity.

Chevarin et al [165] quantify the role of porosity in anode gasification. The most active pores size for  $CO_2$  gasification determined by mercury porosimetry is in the order of 20 to 40 µm. They differentiate factors for anode gasification of anode into internal and external factors. The consumption of the particles through their inside porosity defined as internal gasification while the carbon consumption either from the external surface of particles or from the very large pores connected to the surface defined as external gasification. The experimental results showed that low contribution of internal reaction to overall gasification is due to mass transport limitations in the small pores while external gasification from external surface of the particles

as well as the open pores with entrance diameter larger than a critical size are the principal pores responsible for  $CO_2$  reaction. Therefore, pores size larger than the critical size should be avoided in order to reduce the  $CO_2$  reaction of anodes. These results are consistent to those reported by Boero [166] that suggest when the pore size was higher than 40 µm mass transfer between anode and carbon dioxide is controlled by viscous flow and related to anode permeability

Fischer and Perruchoud [18] differentiated the pore size influence on the anode internal reaction. The authors suggested that the small pore sizes generate most of the internal pore volume and are well connected to the exterior surface of the particles by the feeder pores (transitional and macropores). Thereafter, the reactant gas (e.g., air or  $CO_2$ ) can rapidly diffuse and reacts with the active surfaces and anode permeability is influenced by pores size larger than 50 µm. An implication of high permeability is an increase on anode reactivity. Other experimental by study Chevarin et al [161] suggested that the most active pores size for air reactivity ranged between 0.1 and 40 µm. This pore size range should ideally minimize to decrease air reactivity of anodes by adjusting the anode manufacturing process.

The model confirms that reducing anode permeability by decreasing the size and volume of the volatile release porosity will reduce sub-surface oxidation by lowering the rate of gas flow to the active surface area as explained in previous chapter. The current technology used to fabricate anodes will, however, invariably result in a network of open, interconnected pores. Possible ways of reducing this porosity, and hence anode permeability, are: the use of slower heating rates during baking to reduce the rate of volatile release, a change in the size of the finest coke particles in the aggregate, by maximising the packing of the pitch wetted aggregate, optimisation of the pitch level, or by increasing the coking value of the binder pitch.

Reducing the surface area of the binder film is an alternative way of reducing sub-surface oxidation. Binder coke porosity, particularly shrinkage cracks, is central to the mechanism of internal attack. There are several possibilities for reducing this porosity, and hence anode active surface area. Binder shrinkage cracks could possibly be reduced by the selective addition of partially calcined filler coke to the aggregate. This coke will shrink with the binder during baking and lessen the shrinkage/expansion process that produces the microcracks. There is also some evidence that a lower porosity binder carbon may be achieved with the use of additives to the pitch. Heavier (i.e. higher softening point) binder pitches are being used. These pitches have higher coking values and will shrink less during baking. This should reduce shrinkage cracking, and possibly the size of volatile release pores. Modifications to existing anode production equipment are required to use these pitches.



Figure 6-17 Tree Model of Anode Pore Structure [62]



Figure 6-18 Anode pore structure [62]

#### 6.4. Conclusions

Porosity measurements from MIP, IA and CT are compared and the advantages and limitations of each technique are discussed. The combination of the different techniques gives valuable insight to understanding anode porosity. MIP measures pore sizes that cannot be detected using image analysis-based measurement and also detects pore connectivity. IA using optical microscopy offers better resolution for pore sizes of 10 to  $100\mu m$ , when compared to CT methods and can be used for pore classification. CT is a non-destructive test that measure larger pores in the range 50 to  $1000 \mu m$  as shown in Figure 6.19.



Pore Diameter vs Measurement Techniques

This research also linked the porosity with anode physical properties such as density, permeability and anode reactivity. Sample J19 with least pitch content showed the highest porosity, permeability and  $CO_2$  reactivity but the lowest air reactivity. This behaviour may be associated with active pore size for air reactivity and impurity content. J19 has large volume of pore size larger than 40  $\mu$ m and the least amount of sodium and vanadium content. A different approach and sample selection is required to be able to examine further the relationship between impurities, porosity and reactivity.

Figure 6-19 The measurement range for pore size using MIP, IA and CT.

# Chapter 7

# 7. Investigations of Gas Transport Mechanisms in Porous Anodes

## 7.1. Introduction

In the current investigation, a novel approach has been taken to investigate gas transport mechanisms and bubble nucleation behaviour on the underside of porous anodes. Einarsrud et al [41] proposed there are two possibilities of the gas path, namely transport through pores in the anode or through the bath. However, there are limited measurement data for gas diffusion in both media and limited data for the correlation between anode and bath properties such as composition, porosity, and permeability of anode material. This data would play an important role in understanding the bubble nucleation behaviour and consequently allow for possible energy efficiency improvements. The purpose of this study is to measure the diffusion rate of  $CO_2$  in a porous carbon anode by performing anode characterization using Mercury Intrusion Porosimetry (MIP) and porous solid gas diffusion measurements. The results will lead to further understanding of gas diffusion behaviour in relation to the anode porosity characteristics.

## 7.2. Materials

In order to ascertain the effect of pore properties on the mass transport characteristics, samples from three different anode production batches (L26, L44, L51) from Hydro Aluminium AS and a standard porous alumina sample from ICT international were investigated. The anode carbons were characterized for physical and chemical properties at Hydro Aluminium, PMT Laboratory Årdal. These samples were specifically selected to represent a wide range of open porosity as indicated by the permeability.

# 7.3. Experimental Procedure

# 7.3.1. Anode Characterization

Three samples of each material were tested by mercury intrusion porosimetry (MIP) to obtain the pore characterization. During a MIP test, each sample underwent two analyses: at lowpressure and high-pressure. The entrance radius of the pores was proportional to the applied pressure, and the volume of intruded mercury is recorded as pressure is applied. The highest pressure produced by Micromeritics AutoPore IV 9510 is 45 MPa, and the pore throat diameter corresponding to this pressure according to the Washburn equation was about 6 nm. The largest pore throat diameter recorded by MIP was about 100  $\mu$ m under low-pressure analysis. Therefore, the pore size range measurable by MIP is from 6 nm to 100  $\mu$ m. The Standard Test Method for Determination of Pore Volume and Pore Volume Distribution of Soil and Rock by MIP was carried out by following ASTM D4404 - 84(2004)

#### 7.3.2. Diffusion Experiment with Infrared Analyser

The main component of the apparatus was a reduction furnace (Labec, Australia), a smaller cylinder tube with the internal diameter 15.88 mm and the length 500mm made of alumina silicate covered with refractory blanket to fix the position inside a bigger alumina tube with the internal diameter 35mm and the length 1000mm. The heating element was made from Kanthal A1 wire element winding, a ferritic iron-chromium-aluminium alloy (0.23Cr, 0.058 AI, balance Fe), which was surrounded to the alumina tube furnace and controlled by Eurotherm 3216 PID type controller. The thermocouple used in this experiment was a type-K thermocouple (chromel-alumel) which had temperature range of -180 to 1300 °C. The temperature profile was measured inside the tube furnace in order to find the isothermal zone. At 960 °C, an isothermal zone can be achieved between 25 and 35 cm position with the fluctuation of  $\pm 1^{\circ}$ C.

The porous sample was mounted in the end of smaller tube with high temperature carbon paste Pelco ® and cured it overnight at 65°C. The sample location was positioned in the midway along the bigger alumina tube length. The alumina silicate tube reaction vessel was chosen because the thermal coefficient is only slightly different when compared with the anode carbon ( $\alpha_{al}$  =5.30 x 10<sup>-6</sup>/K while  $\alpha_c$  =3.5.to 4.5 x 10<sup>-6</sup>) hence in the operation at high temperature, both materials was expanded to a similar extent and disjointing can be avoided.

In the initial experiments, an infrared analyser connected with computer was employed to measure the carbon dioxide concentration in the outlet flow of the diffusion rig. The concentration data of carbon dioxide was recorded by a computer using software *modbuspol*. Analysis and calculation from a concentration versus time graph was used for determining the diffusion coefficient. The existing diffusion coefficient experiment shown in Figure 7.1. Preliminary experiments employed a 3 cm sample thickness with three different  $CO_2$  flow rate (0.3,0.4, 0.5 l/min) and three different pulse times (2,5,10 second) at room temperature.

Argon gas flow rate was 0.3 l/min. The flowmeter was set up for respective gases was utilized with accuracy  $\pm 5\%$  of 65 mm scale. This flowrate was selected as the minimum requirement for the infrared analyser and this resulted in only small pressure differences between inlet (1047  $\pm$  5 millibar) and outlet (1045  $\pm$  5 millibar). This preliminary experiment aimed to find the most optimum pulse time and CO<sub>2</sub> flowrate that will be used for the diffusion coefficient experiment. The experimental data obtained for the effect of pulse duration and effect of CO<sub>2</sub> flow rate in diffusion rig is shown in Figure 7. 2 and Figure 7.3. The concentration of carbon dioxide in volume percentage is plotted against time as shown in Figure 7.2, Figure 7.3 and Figure 7.4.



**IR Analyser** 

Figure 7-1 Pictures of equipment used in diffusion experiments with infra-red analyzer.



Figure 7-2 Concentration of CO<sub>2</sub> with 2 second of pulse and different flow rates




From this experimental data, it was shown that the minimum pulse time and the slowest flow rate produced more repeatable results. However, because the concentration that is measured in the preliminary experiment reaches more than 40% volume  $CO_2$ , which exceeds the sensitivity range of the analyser at (20% volume), the data cannot be used for the diffusivity coefficient calculation. In further experiments, a shorter pulse of gas and the use of a mixture of  $CO_2$  and argon gas was used to overcome the issue with the sensitivity range of the analyser. The major limitations of this IR analyser were found to be the large time lag due to the slow response time of the instrument (25 to 45 seconds) and poor repeatability as shown in Figure 7.4. Therefore, modification of the experimental setup was required to produce more accurate results. The steps taken to solve the research problem is summarised in Table 7.1



Figure 7-4 Graph concentration vs % volume of CO<sub>2</sub> with 2 second of pulse

Table 7-1 Research problems	in the diffusion	experiment System	and Actions Taken.
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Problem	Actions Taken		
Gas Leakage	New secure gas line and regulator was		
	applied to the system		
Instrument lag-time and detection limit	Mass spectrometer utilized as the gas		
	analyser		
Repeatability of results	Automated valve was employed		
Conduct experiment in higher temperature	Protective pipe and water cooling was		
and the carbon monoxide formation.	installed in junction with gas analyzer		

# 7.3.3. Diffusion Experiment with Mass Spectrometer

The diffusion experiment rig was modified by replacing the infrared analyser with a mass spectrometer. This analyser has a response time of only 200 ms. The experimental rig configuration as shown in Figure 7.5 consists of an argon and carbon dioxide gas cylinder

system, both gases with purity of 99.9995%. The apparatus was the same as the IR experiment with modification being the use of the mass spectrometer as the gas analyser. The argon gas was drawn from a pressurized cylinder via a dual-stage regulator and needle valve to the inlet of rotameter while a digital vacuum meter is utilized for inlet and outlet pressure monitoring.

This experiment was conducted in a high-temperature tube furnace with an operation temperature of up to 960°C. The anode carbon for sample was cut using a carbide saw to have the same diameter as the inner diameter of an alumina silicate tube (15.88 mm) and with a 3 cm thickness. Samples were placed securely at the end of the tube using PELCO® high temperature carbon paste applied into the outer diameter surface of the sample and inner tube to be coherent. Simultaneously, argon gas is circulated into the furnace to monitor gas leakage and to sweep away other gases to avoid side reactions with the carbon anode at the higher temperatures utilised in these measurements.



Figure 7-5 Schematic Diagram Experimental Setup

A computer-controlled mass spectrometer was employed to measure the carbon dioxide concentration in the outlet flow of the diffusion rig. The concentration data of carbon dioxide was recorded by the computer software *Quadera*. Analysis and calculation of a concentration versus time graph used for determining the diffusion coefficient.

Experiments to measure the carbon dioxide diffusion coefficient were conducted at various temperatures from 25°C, 400°C, 600°C, 700°C, 800°C, 900°C, and 960°C equal to 298 to 1233 K. The first three temperatures are set to compare with the previous results from work by Golovina et al.[1] The highest temperature experiment is at 960°C, which is the typical operation temperature of a Hall-Héroult cell. After conditioning the porous material under

continuous argon gas flow to achieve the condition of zero concentration of carbon dioxide, the porous solid was set to the experimental temperature. Once thermal equilibrium was achieved, the carbon dioxide valve was opened at constant flow rate (under the fixed temperature) for a predetermined time.

The output result from the mass spectrometer was a concentration versus time data graph. Data sampling from this device is 5 Hz, where the time is measured from the initial carbon dioxide detection until the carbon dioxide has been saturated and not changed in the concentration ( $B_{\infty}$ ). Three different flow rates (0.075 l/min, 0.1 l/min, 0.125 l/min) were used in the experiments for each sample to ascertain the effect of pressure.

# 7.4. Results and Discussion

#### 7.4.1. Diffusion Mechanism Based on Anode Characterization

Results from MIP method are shown in the Table 7.2 with the range of porosity between 15-20%. MIP measurements for each sample were carried out in triplicate to evaluate the repeatability of the measurement. Ideally, a repeatability test should be carried out on the same test piece of sample. However, this is not possible in the case of the MIP test because the sample is contaminated with mercury after the MIP test. As a result, three representative samples from the same anode block were used to check the repeatability. For anode L44, we obtained the porosity as  $18.10 \pm 3.18$  %; for anode L26, the porosity was  $17.86 \pm 1.3$ % for L51  $18.71 \pm 1.9$ % and porous alumina with  $35.33\% \pm 0.6$ %. Considering the inherent heterogeneity of carbon anode, the spread of results (variance) is acceptable and the repeatability of the MIP measurement verified.

The MIP instrumental error was monitored by calibration measurements using a reference material of porous alumina. The variance in results for the porous alumina was much lower than that for the carbon anode samples. The instrument error was deemed to be negligible compared to the variation due to the heterogeneity of the carbon samples.

Materials	Porosity	Average Pore	Permeability	Tortuosity factor	
	(%)	Diameter (µm)	(nPm)		
L44	18.01	5.16	0.057	2.15	
L26	17.86	5.06	0.104	2.14	
L51	18.71	9.48	0.898	2.19	
Porous Alumina	35.33	1.89	0.024	2.07	

Table 7-2 Anode characterisation results from MIP

Anode tortuosity was obtained from the MIP data. Tortuosity is the ratio between the actual distance travelled between two points and the minimum distance between the same two

points. Higher values of tortuosity imply that fluids need to navigate through more tortuous pathways in order to migrate from one location to another within the carbon anode. The tortuosity factor is the ratio of tortuosity to constriction and is commonly used in the research area of heterogeneous catalysis, where the manner in which pores interconnect can have a profound effect on the accessibility of reactants to the active sites and on the removal of products.

Dullien [167] has shown that if the pore structure is characterized in sufficient detail, a reasonably accurate prediction of the tortuosity factor can be made. However, this requires a detailed knowledge of the pore shape as well as pore size distribution. The tortuosity factor is a dimensionless factor that characterizes the efficiency of diffusion of fluids through a porous media. Porosity measurements using another technique (image analysis) using optical microscopy and x-ray tomography showed that different average pore sizes result in different tortuosities.[168] The anode characterization results from MIP will be used in the next section for measuring theoretical diffusion coefficients as this technique measured the open porosity which can be accessed by fluids. This is considered the more realistic or relevant porosity to the flow of gas through the porous anode.

The plot of incremental intrusion volume versus pore entrance diameter provides an indication of where the concentration of pore diameter lies and a clear indication of the size distribution. The incremental pore volume distribution versus pore entrance diameter was shown in Figure 7.6 and 7.7. From the graph, it can be seen that most of the measured porosity on carbon anodes (L26, L44, and L51) are located in the range of 1 to 10  $\mu$ m with few different peaks while the porous alumina pore size distribution is concentrated with single high intrusion volume in the range of 1 to 5  $\mu$ m.

The possible explanation for the different size distribution between carbon anode samples and porous alumina lies in the production of the sample. Anode carbon is made by approximately 65 % petroleum coke, 20% anode butts and 15% pitch that makes the pore size non-uniform. Furthermore, Azari et al [169] concluded that the optimum mixing time and temperature improve the distribution of coke, pitch and porosity and penetration of binder matrix, leading to enhanced anode density. The synthetic porous alumina is normally produced via a production process similar to that of baked carbon (forming, impregnation, sintering) but an additional process step is required using uniform powdered alumina as the starting material. The green body was sintered at 1520°C for 2 hours to obtain porous alumina ceramic material with a uniform distribution of pores. [170] Therefore the pores characteristic in alumina ceramic is more uniform in shape and size, whereas those of the porous carbon are more irregular in shape and not so interconnected as in porous alumina. The Knudsen number is a dimensionless number that will be used to predict the diffusion mechanism in the porous solid. The Knudsen number is evaluated using average pore size and the gas mean free path as shown in Equation 7-1. For a significant broad range of pore sizes, the proper mean pore diameter is given by the volume averaged value.[171] Therefore,  $d_{pore}$  is determined from the MIP results using the following equation:

$$d_{pore} = \frac{\sum_{do=0.1\mu m}^{dn=110\mu m} V_i d_i}{\sum_{do=0.1\mu m}^{dn=110\mu m} V_i}$$
Equation 7-1



Figure 7-6 Incremental pore volume distribution in anode a) L26 b) L44 c) L51



Figure 7-7 Incremental pore volume distribution in Porous alumina.

The contribution of molecular and Knudsen diffusion mechanism can be estimated by examining the manner in which ( $D_{eff}$ ) varies with either pressure or temperature. For example, a plot of reciprocal coefficients obtained at a single pressures and various temperatures should be a horizontal line with respect to pressure if the mechanism is pure Knudsen flow, a straight line with a positive slope going through the origin if the mechanism is normal diffusion, and finally a straight line with an appreciable intercept occurs if a combined mechanism exists.[172] The contribution of each mechanism can be estimated by the Bosanquet equation shown equation 7-2. The combined coefficient for carbon dioxide (the measured effective coefficient) would be given by the relationship as follows:

$$\frac{1}{D_{eff}} = \frac{1}{D_m} + \frac{1}{D_k}$$
 Equation 7-2

The Knudsen number calculation derived from average pore sizes obtained from MIP for the diffusion in porous solid experiment temperature range used (298-1233 K) is illustrated in Figure 7.8. The Knudsen number obtained from MIP for L51 indicated pure molecular diffusion would likely dominate. For sample L44, L26 and porous alumina, the calculated Knudsen number is in the transition regime (0.1<Kn<10) in which both Knudsen diffusion and molecular diffusion are taken into account rather than assuming which mechanism is controlling. The line intercept for combined mechanism in sample L26 and L44 occurred in the temperature above 600° C and porous alumina mechanism started change in the temperature 200 °C.



Figure 7-8 Knudsen number Estimation

# 7.4.2. Diffusivity Measurement and Pressure Difference

The gas transport mechanism consists of advective and diffusive components as described in Chapter 4. When pressure is applied on an incompressible fluid, the velocity of the fluid will change. The fluid accelerates or decelerates depending on the relative direction of pressure with respect to the flow direction. This is because applying pressure on the fluid has caused momentum movement in that direction. Minimizing the pressure difference will be a key aspect to determine the diffusion mechanism where net transport of matter in a system is by random molecule motion not forced by convective flow. [84].

The gas diffusion coefficients in the porous samples were determined using gas flow behaviour and measuring the concentration of the gas in the outlet stream via mass spectroscopy. Preliminary experiments were carried out to find the relationship between obtained diffusion coefficient and the different gas flowrates which corresponding have varying pressure differences. Five different flowrate range (0.075, 0.1, 0.125, 0.2 and 0.3 L/min) were used in the temperature range from 25°C to 600°C where the diffusion mechanism is not complicated by a chemical reaction. A flow rate less than 0.075 L/min was difficult to apply because it was not enough flow through the sample to be detected by the analyser. These preliminary experiments showed that pressure difference linearly correlated with diffusion coefficient in Figure 7.9 a to d. Therefore, the diffusion coefficient obtained in this experiment considered as apparent diffusion coefficient (D<sub>ap</sub>) since the diffusion coefficient in porous media fundamentally should not vary with pressure difference. The relationship between experiment results and convective flow (combination of diffusive and advective transport mechanism) will be explained in the next chapter.



Figure 7-9 Plot of pressure and diffusion coefficient a) 25°C b) 200°C c) 400°C d) 600°C The other contributing factor in the selection of the flowrate is the Reynolds number that defines the flow regime. Fluid viscosity causes the flow of a real fluid to occur under two different conditions or regimes: that of laminar flow and that of turbulent flow. The concept of a critical Reynolds number is applied to the flow of any fluid in cylindrical pipes, in order to predict that the flow will be laminar if Re<2000 and turbulent if Re>4000. In high Reynolds number flows there are regions with unstable velocity gradients and chaotic vortical (3dimensional) motion develops. The chaotic motion involves unsteady (chaotic) motion transversal to the main (time averaged) velocity. This induces transport of momentum between the different layers of the time averaged fluid flow and disrupting the diffusion mechanism. It was shown on Figure 7.10 that the turbulence regime occurs in flowrates between 0.2 L/min and 0.3 L/min. Therefore, to ensure the flow in the experimental temperature were in laminar state, flow rates of 0.075, 0.1, 0.125 L/min were selected as flowrate variables in the experiment.

The diffusion coefficient,  $D_{tr}$  (t), derived from this transient state measurement, is obtained from curve fitting the Equation 7.3 to data of normalized concentration (B(t)) obtained by experimental work. The curve fitting was carried out using Matlab. The equation was derived by analogy from thermal diffusion with B(t) being diffusing gas flow, d is sample thickness and t is diffusion time.[173] The solid line represents the theoretical curve fitted to the experimental data (points) by varying D<sub>tr</sub> as a parameter. The flow chart of the experimental sequence is provided in Appendix A.

$$\frac{B(t)}{B_{\infty}} = 1 + 2\sum_{m=1}^{\infty} (-1)^m \exp\left[-D_{tr}\left(\frac{m\pi}{d}\right)^2 t\right] \qquad \text{Equation 7-3}$$

Porous alumina was selected as standard material due to its homogenous pores size as shown previously in the Figure 7.6 and no chemical reaction with CO<sub>2</sub> gas. Therefore, it was shown in Figure 7.11 porous alumina has better curve fitting compare to the carbon anode sample (L51) shown in Figure 7.12. The pressure difference and diffusion coefficient was plotted in Figure 7.13, where the effective diffusion coefficient is determined by linearly extrapolating to zero pressure difference. The linear extrapolation was fitted to the experiment results since the diffusion coefficient in porous media fundamentally should not depend on pressure difference. Measured diffusion coefficients at 960° C are summarized in Table 7.3.



Figure 7-11 Time dependence of CO<sub>2</sub> gas penetration through porous alumina sample.



Figure 7-12 Time dependence of CO<sub>2</sub> gas with different flow rate in anode sample L51.



Figure 7-13 Example of Diffusion coefficient determination by zero pressure difference at different temperature for sample L51 at 600 ° C

Sample	Measured Diffusion Coefficient (m <sup>2</sup> /s <sup>-1</sup> )
Porous Alumina	1.47E-06
L44	4.60E-06
L26	4.93E-06

7.89E-06

Table 7-3. Measured Diffusion Coefficient at 960° C

# 7.4.3. Diffusivity at Elevated Temperature

L51

Experimental results for each sample at elevated temperatures were obtained as shown in Figure 7.14. The solid lines represent the theoretical curve of Equation 7-3 fitted to the experimental data. The blue regions are where the Bourduard reaction took place and the inside rectangle is where the mechanism shift occurred. The two diffusion coefficients, theoretical diffusion and measured diffusion coefficient were shown to be in the same order of magnitude; however, it is seen that there is different behaviour at higher temperatures.

There are several possible reasons for this behaviour, firstly is the diffusion mechanism has shifted from molecular diffusion into mixed diffusion. The effective diffusivity  $D_{eff}$ , is proportional to  $T^{3/2}$  when molecular diffusion dominates, and proportional to  $T^{1/2}$  for the case of diffusion governed by the Knudsen mechanism. <sup>[18]</sup> Molecule-wall collisions become more significant at low pressure and small pore diameters. The molecules collide with the wall more often than between them because the free path of gas is restricted by the geometry of the void space.<sup>[6]</sup> The measured diffusion coefficient in sample L51 showed a similar trend with the

theoretical calculation based on pure molecular diffusion in the experimental temperature range (293.15 to1233.1 K). The measured diffusion coefficient of L26 and L44 starts to deviate when compared to theoretical values after 700°C while the measured diffusion coefficient of porous alumina exhibit large differences after 200°C when the mechanism shifted from molecular to mixed diffusion, as shown in the blue rectangle in Figure 7.14.

Secondly, the carbon dioxide concentration detection decreased as the chemical reaction between  $CO_2$  and anode carbon formed carbon monoxide gas as shown in blue rectangle represent the area when the Bourduard reaction take place above 600°C in Figure 7.14. The results for sample L51 have the best fit to the theoretical calculation in this region compared to other samples. The other possibility is the measured diffusion coefficient is affected by pressure difference related to permeability and fluid flow. The effect of permeability and the chemical reaction on the diffusion behavior will be further explained in the next section.



Figure 7-14 Diffusion coefficient for each sample

# 7.4.4. Effect of Chemical Reaction and Pore Size on Diffusion Coefficient

At elevated temperatures, during the diffusion experiment,  $CO_2$  diffuses to the anode and reacts with carbon resulting in oxidation to form CO gas. This reaction is called Boudouard reaction and proceeds significantly above 600°C according to Equation 7-4 :

$$CO_2 + C = 2 CO$$
 Equation 7-4

The Boudouard reaction could be influenced by the CO<sub>2</sub> mass transport inside the anode pores at 960°C. [162]·[166] The carbon monoxide concentration in sample L51 was increased from at 25 °C and 960°C in mass spectrometer with background subtraction as shown in Figure 7.15 while porous alumina in Figure 7.16 has lower value carbon monoxide concentration increase. The chemical reaction in the anode depends on the impurity levels and the degree of anode graphitisation while the mass transport would be influenced by porosity and tortuosity governed by anode permeability.

Previous studies has investigated the  $CO_2$  flow in the anode pores could be associated with the pore size. According to Sadler [62] and jointly with the results from Boero [166], the viscous flow could take place when the pore size was superior to 40 µm and related to the anode permeability. This result is obtained by measuring pore size distribution using mercury porosimetry. At higher temperatures as  $CO_2$  burnt away, the fine carbon structure resulting in higher permeability and changing diffusion behavior. [70] Another approach by Engvoll[63] ,using image analysis in scanning electron microscopy, confirmed that the majority of the pores in industrial anodes had a size of at least 5 µm similar with the results observed in Figure 7.17. This graph also showed that the measured diffusion coefficient correspondence linearly with the average pore size obtained from MIP. The relationship between average pore size and the diffusion mechanism already explained in the section 7.4.1



Figure 7-15 CO gas evolution in the experiment in anode carbon



Figure 7-16 CO gas evolution in the experiment in porous alumina



Figure 7-17 Measured diffusion coefficient for each sample at 960°C compared to the average pore size.

# 7.4.5. Correlation of Gas Diffusivity with Permeability

Flow of fluid has a great significance in the diffusion of gases in porous solids and permeability is a fundamental property, which describes the fluid flow in the porous medium. In recent years, there has been an increasing interest in relating the influence of pore structure to flow properties. Air and CO<sub>2</sub> reactivity and permeability of anodes are commonly used to compare the quality of anodes prepared under different conditions. The permeability of the anode carbon is affected by anode precursor material composition, mixing time and baking temperature in

anode production [66]. Azari et al [174] studied the influence of mixing time and temperature on the pore volume and pore size in the paste before compaction. They reported the optimum mixing variables to obtain the minimum paste porosity.

The results of permeability for each sample previously are summarized in Table 7.2. The porous alumina sample has the lowest permeability, pore size and measured diffusion coefficient while in contrast sample L51 has the highest average pore size, permeability and measured diffusion coefficient. The logarithmic relationship between permeability and diffusivity are closely related with a correlation coefficient value of  $R^2 = 0.9208$ . These results indicate an increasing trend of diffusivity with the increase of permeability, as shown in Figure 7.18. The most likely correlation between low permeability and low diffusion coefficient is the accessibility and interconnection of the pores. Lower permeability sample will restrict the gas flow to diffuse through the porous media. Further work using more samples and factorial design analysis is required to clearly identify the key relationship between porosity and diffusion mechanism.



Figure 7-18 Measured diffusion coefficient for each sample at 960°C compare to the anode permeability

# 7.5. Conclusions

A study on diffusion in porous solids was conducted using anode materials with different permeability and compared with a porous alumina sample to investigate the effect of Boudouard reaction on anode diffusivity. The measured diffusivity was compared with theoretical calculations based on average pore size obtained from Mercury intrusion porosimetry (MIP). The values of the diffusion coefficients obtained have the same order of

magnitude (10<sup>-6</sup> cm<sup>2</sup>/s) as those calculated by the well-known formulas for diffusion coefficients and experimental results from Golovina's experiment.

The study found the diffusion coefficient not significantly effected in higher temperature can be explained by the diffusion mechanism having shifted from molecular diffusion into mixed diffusion. It was affected by interaction between gas molecule and the pore wall and change of this behaviour with change in temperature. Furthermore, pressure differences related to the permeability may reduce the diffusion coefficient and chemical reaction between carbon dioxide and anode carbon formed carbon monoxide gas. Anodes with lower average pore sizes and permeability are preferable reducing the CO<sub>2</sub> gas diffusion, minimizing the anode consumption and bubble nucleation in aluminium production. A different approach on sample selection, anode characterization technique, simulation and modelling is required to be able to examine further the relationship between porosity, diffusion and permeability.

# **Chapter 8**

# 8. Simulation and Modelling of mass transfer in porous solid using COMSOL Multiphysics.

# 8.1. Introduction

In this chapter, another approach has been developed to explain the issue regarding the convective flow and mass transfer in the experimental results. The mass transfer of CO<sub>2</sub> gas in the carbon anode are space and time-dependent problems and are usually expressed in terms of *partial differential equations* (PDEs) that cannot be solved with analytical methods. Instead, a numerical method can approximate the PDEs based on discretization methods in Finite element method (FEM). In this chapter, COMSOL Multiphysics is used as a numerical software package to study the constitutive relation between permeability and anode properties of a porous medium at different temperatures.

# 8.2. Finite Element Analysis

Numerical methods are used to determine approximate solutions for the majority of complex engineering problems due to its flexibility as an analysis tool. There are three techniques for numerical solution; namely the finite difference method (FDM), finite volume method (FVM) and finite element method (FEM). [175] The FEM in general is based on discretization of the domain into small cells called elements for function approximation and the weighted residuals are evaluated for error measurement. [175,176]

A schematic of the FEM implementation is shown in Figure 8.1. Firstly, PDEs are derived from conservation laws of physical principles, such as conservation of mass, energy, and momentum. Boundary constraints or initial conditions was used to solve the equations. The amount of substance (gas) per unit area of time in these conservation laws are typically composed of advection and dissipation or diffusion. [81] The dissipative process which energy is transformed from some initial form to some final form is given by a constitutive relation, such as the viscous stress for Newtonian fluids, Fourier's law of thermal conduction, and Fick's law of diffusion. [81] The finite element formulation started when the partial differential equations must be restated in an integral form called the weak form. The approximate solutions from weak form does not require continuity, reduces the spatial derivative order by 1, and its boundary is included in the formulation.[177]

The finite element method is constructing a finite set of global basis functions in a function series. When the finite element method is adapted to the geometry the results are a grid of basis function call a mesh.[178] The nature and number of unknowns at each node decide the variation of a field variable within the element.

The next step is to determine the matrix equations that express the properties of individual elements. Combination of the matrix equations represents the physics-related nodal solutions of the problem. The resulting set of algebraic equations are solved to obtain the nodal values of the variable then solution can quantified and visualized. [81][179]



Figure 8-1 Finite element method implementation in COMSOL[81]

One of the most important features of finite element methods is that they are based on unstructured grids. (Finite difference methods use structured grids.) This means that FEM has high adaptability for complex geometries. However, there are few criteria that needs to be satisfied in order to optimise computational costs and produce exact solutions such as: [81]

- Consistent discretization with the analytical problem and convergence of the solution.
- The convergence of the solution is uncompromised by small perturbations.
- Value of a nodal variable has to lie between the neighbouring discrete nodal values
- Equal inflow and the outflow through the control volume for a given period of time.

Numerical solution methods using FEM in COMSOL Multiphysics version 5.3a were chosen for explaining the diffusion and convective term on porous solid in this study for two reasons. First, COMSOL Multiphysics has features to allow the coupling of physical phenomenon, in this case fluid flow and transport of diluted species in a porous media. Secondly, COMSOL Multiphysics is a versatile software package that is able to solve the system with stationary or time dependent mode in one, two and three dimensions.

#### 8.3. COMSOL Multiphysics software

The method for modelling and simulating can be split into five steps as shown in Figure 8.2. Firstly, the geometry of the sample is determined to represent the domain under study and assign the material properties to the domain. Two dimensions design selected in order to have a reasonable computational cost. Then, physical environments of the problem under investigation are generated by assigning the underlying physics. Chemical species transport was chosen as the PDE of the simulation. Parameter and domain values of porous samples was selected. Furthermore, boundary conditions for the axis symmetry, continuity and flux were also defined.

The discretization was using physics-controlled mode. The mesh is adapted to the current physics settings in the model. Time dependent solver for computing the solution of single set of algebraic equations for all the involved physical models. This study type is also used for optimization problems which are constrained with a time dependent PDE problem in a single iteration scheme which is repeated until convergence is reached. The result of the simulation was processed to visualize the surface plot and concentration profile.



Figure 8-2 Steps in COMSOL simulation

#### 8.3.1. Material data

The material used for the porous domain was anode carbon. Due to the fact that anode carbon was made with variability of raw material and production settings materials, the values of anode carbon porosity and permeability was collected from anode characterization described in the previous chapter. The fluid used in this simulation was carbon dioxide the properties of which have already been defined in COMSOL.

### 8.3.2. Geometry and Mesh

The accuracy of simulation solution was linked to the mesh size. As mesh size decreases towards zero (leading to a model of infinite size), the calculation gets closer to the exact solution for the equations. However, since it was limited by finite computational resources and time, the results will be approximated within representation of the geometry and functional representation of the domain. The goal of simulation, therefore, is to minimize the difference ("error") between the exact and the approximated solution, and to ensure that the error is below some accepted tolerance level that will vary from project to project based on design and analysis goals.[180] Three different mesh size detail will be used to shown the effect of mesh in this simulation as shown in Table 8.1 and illustrated in Figure 8.3.

Statistics	Extremely fine	Normal	Extra coarse
Mesh vertices	3358	376	75
Numbers of element	6498	680	120
Minimum element quality	0.6922	0.6397	0.7432
Average element quality	0.9529	0.9394	0.8989
Element area ratio	0.3462	0.396	0.5346

Table 8-1	Statistics	of mesh	selection
-----------	------------	---------	-----------

There were two different geometries will be used in this gas transport in porous solid investigation. These are described in section 8.5. The study was limited to 2D due to computational costs. The different geometries were studied to distinguish the effect of simple block geometry and block geometry with porous boundaries. The mesh comparison was shown in Figure 8.3. The rectangle sample has 1.5 cm diameter and 3 cm length with mesh area 4.5 cm<sup>2</sup> replicated from the diffusion experiments described in Chapter 7.



Figure 8-3 Mesh comparison a) extremely fine b) normal c) extra coarse

#### 8.4. Model Definition and Settings

#### 8.4.1. Fluid Flow

The model used the Brinkman equation to calculate convective mass transfer through the porous media. In COMSOL, the Brinkman equation belongs to the subsurface flow module. Pressure and Darcy velocity described in Chapter 4 were the dependent variables in Brinkman equation. This interface also features a function that combines turbulent flow with a porous media domain to improve the stability of the simulation. The combination of continuity and momentum equations govern the flow of the porous media as shown in equation 8-1 and 8-2. [180][181]

$$\frac{1}{\epsilon_{\rho}}\rho\frac{\partial \mathbf{u}}{\partial t} + \frac{1}{\epsilon_{\rho}}\rho(\mathbf{u}\cdot\nabla)\mathbf{u} = \nabla \cdot \left[-\rho\mathbf{I} + \mu\frac{1}{\epsilon_{\rho}}(\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathsf{T}}) - \frac{2}{3}\mu\frac{1}{\epsilon_{\rho}}(\nabla\cdot\mathbf{u})\mathbf{I}\right] - \left(\mu\kappa^{-1} + \beta_{\mathsf{F}}|\mathbf{u}| + \frac{Q_{\mathsf{m}}}{\epsilon_{\rho}^{2}}\right)\mathbf{u} + \mathsf{F} + \rho\mathbf{g}$$

Equation 8-1

$$\rho \nabla \cdot (\mathbf{u}) = Q_{\rm m}$$
 Equation 8-2

Where  $\mu$  (kg/ms) is the dynamic viscosity of the fluid, **u** (m/s) is the velocity vector,  $\rho$  (kg/m<sup>3</sup>) is the density of the fluid, *p* (Pa) is the pressure,  $\varepsilon_p$  is the porosity,  $\kappa$  (m<sup>2</sup>) is the permeability tensor of the porous medium, and  $Q_m$  (kg/m<sup>3</sup>·s) is a mass source or mass sink Influence of gravity and other volume forces can be accounted for via the force term **F** (kg/m<sup>2</sup>·s<sup>2</sup>). [180][181]

#### 8.4.2. Transport of Diluted Species in Porous Media

Simulation of gas transport mechanisms of chemical compounds in porous media were provided in COMSOL Multiphysics interface. The physics used was transport of diluted species in porous media under the chemical engineering module. This phenomenon included diffusion and fluid flow in porous media with assumption that the chemical species are dilute and the material properties such as density and viscosity assumed to be the same as solvent. The equations used are: [182]

$$P_{1,j}\frac{\partial c_i}{\partial t} + P_{2,j} + \nabla \cdot \mathbf{\Gamma}_i + \mathbf{u} \cdot \nabla c_i = R_i + S_i$$
 Equation 8-3

$$P_{1j} = (\epsilon_p + \rho k_{Pj})$$
 Equation 8-4

$$P_{2,i} = (c_i - \rho_P c_{P,i}) \frac{\partial \epsilon_P}{\partial t}$$
 Equation 8-5

$$\mathbf{N}_i = \mathbf{\Gamma}_i + \mathbf{u}c_i = -D_{\mathbf{e},i}\nabla c_i + \mathbf{u}c_i \qquad \text{Equation 8-6}$$

$$D_{e,i} = \frac{\varepsilon_p}{\tau_{r-i}} D_{F,i}$$
 Equation 8-7

where  $c_i$  is concentration,  $\Gamma_i$ , is the diffusive flux,  $R_i$  is reaction rate,  $S_i$  is source,  $D_{e,i}$  is effective diffusion,  $D_{F,i}$  is molecular diffusion and tortuosity of the i-th species [i= 1, 2].

#### 8.4.3. Boundary Conditions and Parameters

Boundary conditions selection is substantial for accurate simulation. The selected boundary conditions for convective diffusion in porous media are:

BOUNDARY CONDITION	DESCRIPTION
$c = c_0$	Concentration
$-\mathbf{n} \cdot (-D\nabla c + c\mathbf{u}) = N_0$	Flux
$\mathbf{n} \cdot (-D\nabla c + c\mathbf{u}) = 0$	Insulation/Symmetry
$\mathbf{n} \cdot (-D\nabla c) = 0$	Convective flow
$\mathbf{n}_1 \cdot (-D \nabla c + c \mathbf{u})_1 = \frac{D}{d} (c_1 - c_2)$	Thin boundary layer
$\mathbf{n}_2\cdot (-D\nabla c+c\mathbf{u})_2=\frac{D}{d}(c_2-c_1)$	
$n \cdot (N_1 - N_2) = 0$	Continuity
$-\mathbf{n} \cdot (\mathbf{N}_1 - \mathbf{N}_2) = N_0$	Flux discontinuity

Table 8-2 Boundary conditions [180]

Concentration for the boundary condition was  $c_0$  in the equation which was user-specified concentration. Diffusive Flux in the equation for the flux condition,  $N_0$  is an arbitrary user-specified flux expression. Flux discontinuity boundary condition represents a discontinuity in the mass flux across a border between parts in an assembly. This is the default boundary condition on interior boundaries and pair boundaries that not applicable to exterior boundaries. [180][181][182] Specific boundaries in each segment is provided in Appendix C.

Different parameters were employed in this simulation to verify the effect of convective flow on the gas transport mechanism in porous media in the previous diffusion experiment such as porosity, permeability, and mass transfer. The parameters are summarized in Table 8.3.

Porosity input was obtained from anode characterization using Mercury Intrusion porosimetry. The porosity for anode carbon was ranged from 18% to 25%. Another factor that also considered was the pore size of the anode carbon. The diffusion coefficient and maximum concentration was collected from the diffusion experiments described in Chapter 7. Operating temperature and permeability also varied to investigate transport mechanism and the temperature dependency of  $CO_2$  gas.

Name	Unit	Description
D	m²/s	Diffusion coefficient
c_max	mol/m³	Peak initial concentration
Por	-	Porosity
Perm	m²	Permeability
Т	K	Operating temperature

Table 8-3 Simulation parameters

# 8.5. Results and Discussions

Two different geometries at three different temperatures were studied with the same physics for simulating the gas transport mechanism in the anode block. The first model will be a simplified anode carbon block investigating the convective flow and its behaviour with different temperature and permeability. The second model used randomized pore geometry for anode carbon predicting fluid flow behaviour with the pore as restriction.

#### 8.5.1. Pressure Difference in Different Temperature

The correlation between higher maximum concentrations in higher temperature mainly contributed by higher pressure difference. The verification of this simulation is shown in the Figure 8.4. The comparison of simulation results using different mesh selection showed negligible difference and independence from mesh sizes, therefore normal mesh was selected for further simulation. The mass flow rate was selected at 0.1 liter/minute for this simulation as inlet boundary condition. The information of maximum concentration and outflow pressure in three different temperatures (25, 600 and 960 °C) was obtained from the diffusion experiment of sample L51 in chapter 7. Variables used in the simulation is presented in Table 8.4. The pressure contour comparison for three different temperature in the same geometry are shown in Figure 8.5 to 8.7.





Symbol	Unit	Temperature (°C)		
		25	600	960
D	m²/s	4e-6	5.2e-6	7.89e-6
c_max	mol/m³	0.004	0.005	0.008
<b>Outflow Pressure</b>	Pa	101375	101525	102125
Por	-		0.187	
Perm	m <sup>2</sup>		5.4e-12	

Table 8-4 Variables in model 1







The pressure difference was set to be constant throughout the diffusion process. At the start, pressure in the inlet was highest in all temperature to allow the gas penetrated to the porous sample. The red colour represents the highest pressure and blue colour represents lowest pressure in the sample. The simulation results show consistent pressure behaviour across the distance when higher temperature directly proportional with higher pressure. The fluid flow from highest pressure in the inlet and decreased over the distance to the outlet with highest inlet pressure was at 960° C and lowest at 25°C. The effect of this pressure effect to the concentration change will be explored in the next section.

#### 8.5.2. Surface Concentration Profile in Different Temperature

The COMSOL simulation illustrate how the concentration changed with time across the geometry with the maximum concentration determined from the experimental results in the previous chapter. For all the simulations there were taken screenshots of the main window where it is possible to observe how the concentration develops. On the right side of the main window there is placed a colour chart showing the colours that the various concentrations are representing. The blue region represents lower concentration and gradually to the red region that represents highest concentration.

The screenshots were taken from various time steps during the simulation. The concentration change in the first 20 seconds become most critical state in the beginning of the process. The surface concentration profile changed with time (0, 25,100, 200 and 300 second) for different temperatures are presented in Figures 8.8 to 8.10.



Figure 8-8 Surface concentration at 25°C



Figure 8-9 Surface concentration at 600°C



Figure 8-10 Surface concentration at 960°C

In the simulation at 25 °C, the CO<sub>2</sub> concentration interface starts penetrating the inlet less than 5 mm, after 1 second the interface has moved slightly to 1 cm. At 5 seconds the concentration throughout the sample increase and is almost uniform with some lighter blue area observed in the middle section of the sample. The concentration was already saturated at 25 seconds and unchanged until the simulation finish at 300 seconds with maximum concentration at  $3.59 \times 10^{-3}$  mol/m<sup>3</sup>. At 600°C, the concentration interface in the beginning slightly larger the previous temperature and the concentration movement is faster. It was observed at 1 second that the concentration already changed throughout the sample with green area represent the maximum concentration achieved at  $4.81 \times 10^{-3}$  mol/m<sup>3</sup> then move towards the end of sample at 5 seconds. At 25 seconds, the concentration was decreased and saturated at  $4.5 \times 10^{-3}$  mol/m<sup>3</sup>

The maximum concentration archived at 960°C was higher and the movement was faster than in the lower temperature. Due to higher pressure difference, at 1 second the concentration close to uniform state of the concentration and at 5 seconds the concentration increase as the darker shade of red was observed in the middle section of the sample with maximum concentration obtained at 8.33 x10<sup>-3</sup> mol/m<sup>3</sup>. At 25 seconds, the concentration decrease slightly and saturated at 8.07 x10<sup>-3</sup> mol/m<sup>3</sup> until the simulation time finish. The comparison between the simulation and experimental results will be discussed in the next section.

#### 8.5.3. Simulations and Experimental Comparison

In the outlet, concentration was monitored with time and the simulation result will be compared with experimental result. Same behaviour on steep concentration change in three different temperature was identified. The simulation at 25°C show the maximum concentration at 0.00369 mol/m<sup>3</sup> or 5.42% higher than the saturation concentration of experimental results as illustrated in Figure 8.11. The highest concentration in simulation obtained after 10 seconds and stabilise to the same saturation concentration with experimental results after 20 seconds.



Figure 8-11 Curve fitting from COMSOL and experimental results L51 at 25°C

Maximum concentration in simulation at 600°C was 0.00492 mol /m<sup>3</sup> or 9.33% higher than the saturation concentration of experimental results as illustrated in Figure 8.12. The highest concentration was reached after 8 seconds and decreased to saturation concentration in 10 seconds. The simulation on 960 °C reached the maximum concentration after 5 seconds at 0.0092 mol /m<sup>3</sup> or 8.7% higher than the saturation concentration of experimental results as illustrated in Figure 8.13. The concentration was stabilised into saturation concentration in 5 seconds. The concentration changed showed from figure 8.11 to 8.13 it can be concluded that higher simulation temperature caused shorter period of time to reach higher concentration. Furthermore, the simulation at 960 °C showed the closest comparison to the experimental results.



Figure 8-12 Curve fitting from COMSOL and experimental results L51 at 600°C



Figure 8-13 Curve fitting from COMSOL and experimental results L51 at 960°C

The shape difference between the two curves presented in Figure 8.11 to 8.13 could be caused by a number of reasons. Firstly, the assumption of homogenous pores in the simulation. In reality, the anode carbon used in the experiment has a wide variety of pore sizes and not all are interconnected. The closed volume in the sample would restrict the gas flow and cause delayed and dispersed gas detection.

Secondly, the peak concentration shape was caused by gas permeability in the sample. The simulation was setup with different permeability input while the other variable was fixed at 960°C. The results of permeability comparison on the first 50 second is shown in Figure 8.14. Interestingly, the simulation with lowest permeability had the smoothest curve and suggest that diffusion is more dominant in the gas transport mechanism. This result provides additional support for the case that gas diffusion in the anode is a mixture of diffusion and convective flow.



Figure 8-14 Permeability comparison

The simulation study provides further insight on the gas transport mechanism in porous media. The results suggest that the diffusion coefficient obtained in the experiment were dependent on temperature due to the nature of convective flow with higher temperature above 600°C and affected by extra pressure build up caused by the Bourduard reaction. It is really difficult to measure pure diffusion coefficient without a pressure difference and convective flow affecting the outcome. This suggest that previous results by Golovina[1] in measuring carbon dioxide

diffusion coefficient in porous coal had underestimated the effect of fluid flow in diffusion experiment.

# 8.5.4. The Impact of Pore Size and Further Development,

The other variable that was not considered in the previous simulation was pore size and closed volume in the porous material. Therefore, randomized porous geometry was made to simulate fluid flow in the anode block with closed volume as shown in Figure 8.15. A simplified 2D from cross section shown in Fig 8.15. was used to provide another insight on the impact of pore size on gas transport mechanism due to computational limitations.



Figure 8-15 Randomized porous anode block

Pressure difference across the porous sample at 960° was simulated in Figure 8.16. The pressure difference was set to be constant throughout the diffusion process. The red colour represents the highest pressure and blue colour represents lowest pressure in the sample. Highest pressure was shown near the inlet to allow the gas penetration into the sample. However, the pressure direction was not as uniform in the previous model as illustrated in Figure 8.7. The fluid flow from highest pressure in the inlet and decreased over the distance with the pressure slightly increasing near the pore boundary.

The surface concentration profile change with time is provided in Figure 8.17 and 8.18. The screenshots of surface concentration profile change were taken from various time steps during the simulation (0, 50, 200 and 300 second) and showed few differences with the solid block model. The  $CO_2$  concentration interface start penetrating the inlet less the 5 mm. At 50 seconds the concentration already saturated in 0.061 mol/m<sup>3</sup> and remain unchanged until the simulation time finish. However, the residual concentration is left surrounding the pore boundary and even after reaching its maximum concentration detection at 300 seconds.



Figure 8-16 Pressure difference in porous geometry at 960°C



Figure 8-17 Surface concentration of porous geometry at 960°C





The concentration was monitored with time in the outlet and compared with experimental result as shown in Figure 8.19. A steep concentration change at 960°C was observed. The simulation show the maximum concentration at 0.0076 mol/m<sup>3</sup> or 5.6% lower than the saturation concentration of experimental results. The highest concentration in simulation obtained after 5 seconds and stabilised into the saturation concentration at in 0.061 mol/m<sup>3</sup> after 9 seconds. The simulation with porous geometry showed significant lower saturation concentration and narrow maximum concentration peak is compared with Figure 8.13.



Figure 8-19 Curve fitting from porous block simulation and experimental results L51 at 960°C

The non-uniformity in pressure and concentration in the experimental work and modelling is explained by illustration in Figure 8.20. This figure shows schematically a trajectory of a random gas molecule (solid circle) diffusing in the pore space with the white area representing a pore and the rectangle block as the grain/ sample material. In the beginning, the gas molecule rarely hits the grain (grey area) when the gas molecule travel at  $t_1$ , so that the diffusion occurred nearly equal with bulk diffusion in free space. As time passes and the collision between gas molecule and grain/ pore wall develops, the pressure and concentration around the pore boundary area was increase as this phenomena observed previously in Figure 8.16 to 8.18.[183]

The pore boundary also added geometry restriction that increasing time of the molecule reach the gas outlet, thus reducing the maximum concentration gas detection at 300 s. At 960 C, the gap of maximum concentration between simulation and experimental result became larger

due to higher collision rate in higher temperature. Further improvement in data collection and pore representation with variety of pore size would be needed to determine how the pore size affects the fluid flow and gas transport mechanism in porous solid.



Figure 8-20 Schematics of random walk in porous media. [183]

# 8.6. Conclusions

COMSOL Multiphysics was used FEM to determining solutions for gas transport mechanism in porous media. In general, the simulation work shown the convective flow also affecting the gas diffusion coefficient measurement. The apparent lack of temperature dependency is likely to be a consequences of convective flow effect. Lowering permeability, will result in gas transport mechanism dominated by diffusion. The evidence from this model suggests that with lower permeability, the gas transport mechanism is dominated by diffusion. The simulation using porous geometry predicted lower maximum concentration compared to experimental results due to pressure, concentration inhomogeneity around the pore boundaries.
# **Chapter 9**

## 9. Investigation of the Gas Transport Mechanism in Molten Salt

#### 9.1. Introduction

This chapter explains the modelling and experimental methodologies for studying gas transport mechanism in the molten salt. The solubility and diffusion coefficient of  $CO_2$  in cryolite obtained from previous literature is very low compared to the diffusion coefficient in porous solid. Therefore, theoretical prediction was utilized to estimate the value of diffusion coefficient prior the experiment. The first methodology used was thermo-gravimetric analysis for  $CO_2$  gas absorption in a cryolite sample suspended in a microbalance. The next methodology was to use a mass spectrometer to measure  $CO_2$  desorption in cryolite.

#### 9.2. Modelling of Diffusion Coefficient in Liquid

Diffusion is a transport process relevant to many fields in the natural sciences and engineering. It is also an important parameter in predicting the rate of absorption of a solute into a solvent. There are many studies and techniques which have been proposed to measure  $CO_2$  in various liquids. However, diffusivity measurements of  $CO_2$  in molten salts at high temperature are limited. [23] [184]

The techniques to predict diffusion coefficient rely on some correlative corrections broadly classified into two philosophies. Firstly is that the hydrodynamic, viscosity of solvent causes resistance on a moving particle in continuum flow. Hence, the particle size must be significantly larger than the molecules in the liquid matrix. The second approach is the kinetic theory, where collision between diffusing molecule and solvent counter the diffusivity. However, the later approach is not well developed for a non-ideal gas and gives inaccurate predictions without corrections. [184][185]

The first approach will be discussed further in this chapter. The estimation of diffusion coefficient in liquid is far more difficult and heavily dependent on the correlations between material properties [184][185] One of the most common basis to measure diffusion coefficient in liquid is the Einstein-Stokes formula with the accuracy around 20%. [186] This equation describes the diffusion of Brownian particle in a quiescent fluid at uniform temperature. Brownian particle defined as spherical particle with a diameter of the order of several  $\mu$ m denoted by m. The amount collection (N) of Brownian particles is a large number (in the order of 10<sup>13</sup> for instance) and suspended in a fluid with assumption of these particles is identical to the others. The collective motion of each Brownian particle due to the impacts by molecules of the fluid is called diffusion.

The friction has to be calculated when Brownian particle moving in a fluid. *Stokes friction* used if the fluid is liquid, given by: [187]

$$eta = rac{6\pi r}{m}\eta$$
 Equation 9-1

The mobility of Brownian particle as frictional velocity per unit force was represented as quantity of  $1/m\beta$  in Equation 9.2.

$$D = \frac{kT}{m\beta}$$
 Equation 9-2

The Stokes-Einstein formula for Brownian particles in liquid shown in Equation 9.3, by inserting Equation 9.1 to 9.2

$$D = \frac{kT}{6\pi r\eta}$$
 Equation 9-3

Where k is the Boltzmann constant,  $\eta$  is the viscosity of the liquid, r is the radius of the spherical particle and T is the temperature.

Sutherland [188] proposed another modification of  $6\pi$  to  $4\pi$  in Einstein-Stokes formula. This modification is for diffusing particles size equal to the solvent in slipping boundary condition shown in Equation 9.4. Alternatively, the absolute rate theory proposed that diffusion is determined as a rate process. [189] Glasstone et al [189] suggested the numerical coefficient value of 2 instead of  $6\pi$  as shown in Equation 9.5. Comparison on diffusion coefficient of CO<sub>2</sub> in cryolite calculated by Einstein-Stokes, Sutherland and, Glasstone modification will be discussed in the next section.

$$D = \frac{kT}{4\pi r\eta}$$
 Equation 9-4

$$D = \frac{kT}{2r\eta}$$
 Equation 9-5

#### 9.3. Theoretical Prediction of Diffusion Coefficient in Molten Salt

Theoretical prediction using three different formulas (Einstein-Stokes, Sutherland and, Glasstone modification) was compared to the experimental results from the previous researchers. This comparison determined the formula selected as the basis of diffusion coefficient value in molten salt. The experimental diffusivity data of CO<sub>2</sub> in different solvents compared with calculated diffusivities using different formulas is shown in Figure 9.1. It can be seen as an order of magnitude approach, both Einstein-Stokes and Sutherland equations work well for the case of water when compared with Sada eta al's experimental results [156]. In contrast, the verification of theoretical prediction for cryolite is difficult to verify due to the experimental difficulty in handling cryolite and difficulty in working at the higher temperatures.



Figure 9-1 Comparison between theoretical calculation and experimental results.

There are a few factors that can affect the accuracies of the theoretical calculation. First is the radius size of the solute and solvent. All the predictions used the solute as  $CO_2$  with the variation being the solvent (i.e. water, NaNO<sub>3</sub> or cryolite (NaAlF<sub>6</sub>)). The diagram shown the overlapped between theoretical calculation and previous experimental results due to the magnitude of the y-axis. Previous experimental result for the  $CO_2$  diffusion coefficient in molten salt have a wide range of values. The Glasstone equation overestimates the diffusivity with almost three and four times higher in the water and NaNO<sub>3</sub>. The Sutherland modification equation appears to work better with 30.54% higher value in the water and 21.69 % lower value in NaNO<sub>3</sub> compare to Einstein-Stokes equation with 53.7% and 48.67% lower value in the water and NaNO<sub>3</sub> respectively.

The Sutherland equation worked when solute particle was relatively smaller or the same size when compared with the solvent molecule. This phenomenon can be rationalized on the assumption that some of the solvent was slipping past the surface of solute molecule. The other factor is different viscosities of the different solvents. The viscosity increases from water <NaNO3< cryolite. Prediction for water was fairly accurate compared with the prediction for cryolite. It is known that the dissolution of a gas in a liquid also affected by its viscosity, density, and surface tension of the liquid. The previous experimental results from Rolin[48] gave broad range of result from  $10^{-9}$  to  $10^{-12}$  m<sup>2</sup>/s while Vetyukov and Acquah [190] measured cryolite with 20 wt% alumina saturated by CO<sub>2</sub> was between  $10^{-11}$  to  $10^{-12}$  m<sup>2</sup>/s. Lack of comprehensive

data in gas diffusion coefficient in cryolite implies the measurement was complicated and difficult to obtained accurate results. Therefore, Sutherland equation was use to predict cryolite diffusivity with values obtained is in  $2.74 \times 10^{-9}$  m<sup>2</sup>/s at 960°C. The diffusion coefficient prediction showed that the diffusion coefficient in molten salt is few magnitudes lower than diffusion coefficient in porous solid. The next step is to design and verify this value experimentally.

#### 9.4. Experimental Technique Selection

The summary of techniques for measuring diffusion and solubility in molten salts is presented in table 9.1 to 9.2. and discussed in Section 4.4.3. It shown in the table below, the experimental parameters, the limitations and advantages for each technique. In particular, the electrochemical approach is comparably fast, optimum where the values of diffusion coefficient are small (approximately  $10^{-6}$  to  $10^{-8}$  cm<sup>2</sup>s<sup>-1</sup>) and stable at high temperatures. However, electrochemical techniques meet difficulty on CO<sub>2</sub> gas reduction to ion species. The diffusion species must be electroactive to be sensed by electrochemical approach and the oxidation or reduction of the species must be possible within the potential span of stability of the solvent system. Furthermore, the experimental diffusion data is frequently affected by electrode reaction and the effective area of working electrode. [23].

Another approach for measuring the gas solubility and diffusivity are non-electrochemical methods. The principle of bubble columns and gas absorption methods used by Sada et al. [156] This method is based on monitoring the bubble properties (velocity, frequency and dimension) and CO<sub>2</sub> concentration absorbed in molten salts. The material selection for the see-trough container in this experiment assemblies is a critical requirement due to the corrosive nature of cryolite. Quartz container as alternative material had change in colour and less see-trough after approximately one-hour contact with cryolite that not suitable for experiment.

The other alternative method to choose is based on interpretation of pressure decay data from gas absorption in the molten salt. However, to implement this method, an excellent sealing system is required, and a sensitive pressure transducer is also required to produce accurate results. The gravimetric method allows determination of the solubility and diffusivity simultaneously using a simplified mathematical model. The gravimetric apparatus is also equipped with an automated system to control various temperature and pressures with small standard deviation and uncertainty in order to obtain reliable kinetic data. This technique was selected to measure the diffusion coefficient in this chapter and is further explained in the next sections.

	Electrochemical Method							
No	Method	Materials	Temperature	Working	Advantages	Limitation	Diffusion Coefficient value (m <sup>2</sup> /s)	Ref
	Chrono-	Graphites and glassy carbon in alumina-	(1000		Enables to attain kinetics and mechanisms information in a single	Difficulty of CO <sub>2</sub> gas		1001
1	amperometry	Dissolved	1283	Atmospheric	It can be used when the technique of oxidative voltammetry fails because of fouling of the electrodes	Determination of the transition time	2.2 X 10 <sup>-3</sup>	[39]
2	Chrono- potentiometry	alumina in molten cryolite	1293	Atmospheric	Enables to measure higher concentrations.	Difficulty of CO <sub>2</sub> gas redox reaction	1.5 x 10 <sup>−9</sup>	[41]
3	Rotating disk electrode (RDE)	Dissolved alumina species in the NaF-AIF <sub>3</sub> eutectic	1023	Atmospheric	Surface concentration of reactants and products can be controlled through changes in the rotation rate	Difficulty on maintaining controlled atmosphere over the melt under rotation. Difficulty of CO <sub>2</sub> gas redox reaction	1.8 to 2.2 x 10 <sup>-10</sup>	[44]
4	Rotary ring disk electrode (RRDE)	Compact gold- molybdenum electrode in cryolite-based electrolytes	1273	Atmospheric	Highly sensitive and specific technique for mechanistic or related studies in cryolite- based melts.	Expensive apparatus and material Difficulty of CO <sub>2</sub> gas redox reaction	3 x 10 <sup>-9</sup>	[46]

# Table 9-1 Summary of electrochemical diffusion coefficient techniques

Non	Non-Electrochemical Method							
No	Method	Materials	Temperature (K)	Working Pressure	Advantages	Limitation	Diffusion Coefficient value (m²/s)	Ref.
5	Bubble Columns and Gas Absorption Method	CO <sub>2</sub> into NaNO3, LiCl- KCl, Pure Water	293 - 803	Atmospheric	Simple data interpretation Operated in atmospheric pressure	Solubilities data required Complicated apparatus set-up See through container which can stand corrosiveness of cryolite	1.86 -2.53 x10 <sup>-9</sup>	[53]
	Transient Thin-Liquid-	CO <sub>2</sub> into bmim][Tf2N]), ([pmmim][Tf2N]), ([bmpy][Tf2N]), ([bmpy][Tf2N]), ([perfluoro- hmim][Tf2N]),			Enables one to determine the Henry's law constant and the diffusivity simultaneously. CO <sub>2</sub> absorption measurements could be repeated several times with the same sample	Excellent sealing system is required Operate until 2 bar It needs vacuum system Excellent sealing system is required It needs stirring It requires larger sample		
6	Film Method	([bmim][BF4])	283 - 323	1-2 Atm	in the calculation <ul> <li>Simple</li> <li>data</li> </ul>	than Hou's experiment	2.9-10.3 x10 <sup>-9</sup>	[49]
7	Gravimetry	CO <sub>2</sub> into : [bmim][PF6] [bmim][BF4] emim][NTf2], [omim][NTf2],	283.15- 348.15 293-323 298.15 323.15	0.01-19. 738 Atm 1- 20 bar 1- 20 bar	<ul> <li>interpretation</li> <li>Automated system</li> <li>Operated in high temperature and pressure</li> </ul>	<ul> <li>Expensive Apparatus</li> <li>Excellent sealing system is required</li> </ul>	2.4 -7.8 x10 <sup>-10</sup> 0.42-7.63 x10 <sup>-10</sup> 0.12 - 2 x10 <sup>-10</sup>	[15 2] [15 3,1 54] [15 4]

# Table 9-2 Summary of non-electrochemical diffusion coefficient techniques

#### 9.5. TGA Microbalance System

#### 9.5.1. Sample preparation

The raw materials for these experiments were cryolite ( $Na_3AlF_6$ ), calcium fluorite ( $CaF_2$ ), aluminium fluoride ( $AlF_3$ ) and alumina ( $Al_2O_3$ ) powders. Cryolite was obtained from Alfa Aesar with 99.95% purity.  $CaF_2$ ,  $AlF_3$  and  $Al_2O_3$  was obtained from Sigma Aldrich and had a purity of more than 99% and the particle size less than 325 mesh. They were dried for 24 hours and mixed via tumbling in a glass jar with 10 mm in diameter alumina ceramic balls.

#### 9.5.2. Experimental Setup

The thermogravimetric apparatus was built and designed in CSIRO as shown in Figure 9.2. The system consists of two chambers with associated twin furnaces where one reactor is the sample, and the other is platinum counterweight to minimise the effects from drag and buoyancy forces acting on the sample. They are identical in length with minimal bends to maintain uniform and equal gas flow in each reactor. The induction furnaces are controlled using R-type (platinum/platinum rhodium) thermocouples. K-type thermocouples are inserted into the base of the reactors to reach just below the sample to monitor the sample temperature.

The microbalance has mass capacity of 10g and accuracy of  $\pm 10 \ \mu$ g. Gas flow was controlled via rotameters utilized with accuracy  $\pm 5\%$  of 65 mm scale and the pressure of the system is controlled via a valve in the exhaust gas line. An afterburner was positioned where the exhaust gas enters the duct system to ignite excess reactive gas. Laminar flow was maintained at certain temperatures, aided by the vortex breaker in the base. The vortex breaker consists of a cross piece of steel and was inserted in the base of the inner reactor to eliminate the continuance of the gas flow and ensure laminar flow conditions as the gas enters the inner reactor.

#### 9.5.3. Experimental Procedure

This experiment was conducted at temperatures of up to 960°C. A blank measurement of the crucible without sample was performed in the TGA in order to determine the mass and the volume of the sample container with flowing  $CO_2$  gas. This result will be the base line to compare to the measurement with cryolite sample inside the crucible. The gas introduced from the top of the furnaceA vortex breaker consisting of a cross piece of steel was inserted in the base of the inner reactor. The contact surface is on the top of the crucible (it is open crucible) and the absorption takes place inside the crucible. The cryolite sample was weighed and the density of the sample inside the crucible was determined theoretically based on the chemical composition. The left furnace reactor was raised and the crucible was placed at the hook inside the heat zone of the furnace. Simultaneously, argon gas is circulated into the furnace to monitor gas leakage and to sweep away other gases to avoid side reactions with the sample.

The furnace was then heated up at a rate of 200 °C/h. Once the set temperature was reached,  $CO_2$  gas was flown continuously during the experiment with flow of 0.3 l/min. After flowing the gas into sample, small amount of gas will start dissolving into the ionic liquid with a constant pressure at a given temperature, and after a sufficient time it will reach a thermodynamic equilibrium, that is determined by the solubility limit of the gas in the molten salt at the given T and P. [152] When the desired reaction time was achieved, the reactant gas was switched off simultaneously as the inert gas was switched on, followed by halting the computer acquisition program.

This mass change due to CO<sub>2</sub> absorption was recorded and analysed using Cahn-developed software connected to balance inside the furnace. At the beginning of the run the balance was tared to begin the output with a zero mass and time so the mass loss/addition could be plotted. Programs can be set up to record anywhere between once every second to once every hour. The choice of programming can either be for a specified number of points or for a specified time and recording can be halted at any time. In this study, programs were generally set to acquire a mass reading every one second and for a length of time well in excess of actual reaction time.

A mathematical model based on a simplified mass diffusion process is applied to understand the time-dependent behaviour of gas dissolving in liquid. In this experiment, a flat-bottom sample container filled with molten salt at a certain liquid level height (L). The experimentally measured quantity at a specified time is the total concentration (mass per unit volume) of dissolved gas in the molten salt. This space-averaged concentration at a given time,  $\overline{C}$ , can be calculated from the equations: [152][154]

$$C = \frac{1}{L} \int_{0}^{L} C_{0} dz$$
Equation 9-6
$$\bar{C} = C_{s} \left[ 1 - 2 \left( 1 - \frac{C_{o}}{C_{s}} \right) \sum_{n=0}^{\infty} \frac{\exp -\lambda_{n}^{2} D_{t}}{L \lambda_{n}^{2}} \right]$$
Equation 9-7

Where C is the concentration of gas dissolving in the liquid as a function of time, t, and vertical location, z. L is the depth of molten salt in the container (estimated for each case using the mass of the sample and the corresponding density value previously determined theoretically and  $C_0$  is the initial concentration of the dissolving gas at each temperature and pressure. D is the diffusion coefficient that is assumed to be constant. Although the last equation contains an infinite summation, only the first few terms are sufficient in practical applications. Fitting the experimental data to this equation by nonlinear regression, the saturation concentration, Cs, and the diffusion coefficient, D, were determined for each T, P set-point [154].



Figure 9-2 TGA laboratory setup [191]

## 9.5.4. Experimental Results

A preliminary experiment was performed with an empty crucible as a baseline for comparison with the cryolite sample where mass change data monitored and saved in the software for data analysis. The result of experiment once the cryolite sample was put into the crucible was that the mass change become unstable as shown in Figure 9.3. The expected mass change in cryolite sample was smaller than the noise in the mass change detection in the microbalance. The noise of the mass change results was cause by temperature fluctuations in the furnace and turbulence flow when gas adsorb and react with sample. A few improvements can be made for the TGA experiments. Larger sample sizes would help to ensure mass change of  $CO_2$  is detectable. An improvement in the controller of heating system could ensure the intended temperature was stable and not interfering the weighing process in the apparatus.

The problems encountered with TGA required a change in experimental approach and apparatus. The desorption method using the mass spectrometer was consequently investigated. The induction tube furnace has a larger capacity for cryolite sample (up to 300 g), utilises a more reliable temperature controller and continuously monitored for gas absorption and desorption during reaction.



Figure 9-3 Mass change from TGA experiment

#### 9.6. Absorption and desorption with Mass Spectrometer system

#### 9.6.1. Experimental Setup and Procedure

The final technique that was attempted is based on an absorption and desorption method to measure diffusion. This experiment consisted of two gas cylinders, a furnace and mass spectrometer as shown in Figure 9-4. The horizontal tube furnace with 11.5cm in diameter and 38 cm depth is controlled using a K-type thermocouple on the bottom of the furnace. Thermocouple K was inserted into the top of the furnace to reach just top of the sample to monitor the sample temperature. Gas flow was controlled via rotameters with accuracy  $\pm 5\%$  of 65 mm scale and the pressure of the system is controlled via a valve in the exhaust gas line. Argon gas from the bottom of furnace was flow throughout the experiment while the upper inlet-controlled argon gas and carbon dioxide gas interchangeably.

Preliminary experiment in lower temperature using nitrogen in water at low temperature was conducted before using cryolite sample for technique verification. Nitrogen used in the water because CO<sub>2</sub> can react with the water to form carbonic acid and change the acidity of water. The volume of the sample was calculated based on sample density and sample weight. Then the height of sample was obtained from volume and diameter of crucible.

The experiment started when Argon gas entered the furnace until the environment inside the furnace was saturated with argon. Once the set temperature was reached, the top inlet gas was changed into gas  $CO_2$  with flow of 0.3 l/min for determined time and volume. Simultaneously, argon gas was circulated into the furnace to monitor gas leakage and to

sweep away other gases to avoid side reactions with the sample. The furnace was then heated up at a rate of 200 °C/h. After flowing the gas into sample, small amount of gas will start dissolving into the ionic liquid with a constant pressure at a given temperature, and after a sufficient time it will reach a thermodynamic equilibrium. The  $CO_2$  gas inlet was closed and argon gas with same amount was flown with the same predetermined time and flowrate from  $CO_2$  gas before to swept the  $CO_2$  head volume on the top of the sample. The argon gas top inlet was closed and the amount of  $CO_2$  gas desorbed will be detected and analysed in the mass spectrometer.



Figure 9-4 The schematic diagram of absorption apparatus



Figure 9-5 The furnace for the experiment

The diffusion coefficient as concentration approaches zero,  $D_{\theta}$ , can be calculated from Equation 9.8. Diffusion is often expressed in terms of the time at which half of the equilibrium migrant has penetrated the sheet or membrane, ( $M_t/M_{\infty}$ =0.5) is designated as  $t_{1/2}$ .

$$D = -\frac{0.049.l^2}{t_{1/2}}$$
 Equation 9-8

Therefore, if the half-time of absorption or desorption process is observed experimentally, the value of *D*, assumed constant, can be determined. [192]

#### 9.6.2. Experimental results

Three different saturation time (15 min, 30 minute and 1 hour) and the volume of water (10, 20 and 50 cm<sup>3</sup>) of sample in crucible become the variation of the experiment. Half time sorption measured experimentally where  $C_{max}$  is the maximum concentration with  $t_{max}$  is the time to reach the maximum concentration. The  $t_{1/2}$  is the time to reach half of maximum concentration as depicted in Figure 9.6. The results shows when the saturation time is only 15 minutes, nitrogen is not fully absorbed and is not detectable.



Figure 9-6 Depiction of  $t_{1/2}$  measurement

The results of this preliminary experiment and comparison with Sada's experimental result is shown in Table 9.3. However, the different mass of sample resulted in different thickness in the crucible and did not give satisfactory and replicable results. The least thickness of water layer in the crucible gave full saturation with the gas and from the entire water while it is difficult to determine how deep the gas diffusion is absorbed in the water with more sample/ layer thickness. Another challenge for this experiment was due to the low solubility of nitrogen in

liquid and large head volume of the furnace make the change of the concentration after absorption negligible and difficult to control. Further improvement in reducing head volume space and observable experiment on how deep the diffusion occur using see through container, and colour mark such as dye or fluorescent ink can make this experimental technique more reliable. However, it is difficult to do this improvement using cryolite sample due the limited materials that withstand cryolite corrosiveness and high operating temperature.

Volume	Sample	Solubility	Saturatio	t <sup>1/2</sup>	Experimental	% error
(cm³)	Thickness	(mol/	n Time (s)	(s)	Diffusion Coefficient	with Sada's
	(cm)	cm³)			(cm²/s)	Experiment
10	0.26	0.149	900	-	-	-
			1800	187	1.78E-05	4.30
			3600	170	1.95E-05	4.84
20	0.52	0.298	900	-	-	-
			1800	317	4.19E-05	125.27
			3600	235	5.65E-05	203.76
50	1.30	0.745	900	-	-	-
			1800	396	0.00021	1027.31
			3600	420	0.000198	962.85

Table 9-3 Experimental results from absortion method inn water at 25°C

An alternative experimental technique that could be used is the pressure decay technique. Caution must be applied as this technique dealing with high pressure and temperature in completely sealed environment. As is well known, based on previous experimental result from Vetyukov and Acquah [190] and two different technique that have been tried, measurement of diffusion coefficient in cryolite is very difficult to achieve. Therefore, the diffusion coefficient of  $CO_2$  in cryolite (2.74x10<sup>-9</sup> m<sup>2</sup>/s at 960°C) from modelling using Sutherland modification of Einstein-Stokes equation as was used as the basis comparison from diffusion in porous solid. We believe the gas transport for bubble nucleation was controlled by gas flow in porous solid due to significantly slower diffusion coefficient value with several magnitude difference compares to diffusion in porous solid.

#### 9.7. Conclusion

Investigation of the diffusion coefficient in cryolite using modelling and experimental work was conducted in this chapter. Einstein stokes equation and modification using Sutherland and Glasstone approach was applied and compared to experiment results from previous authors.

Sutherland's equation was chosen based on the similarity of the experimental result of CO<sub>2</sub> in water and NaNO<sub>3.</sub> The prediction of CO<sub>2</sub> diffusion coefficient in cryolite at 960°C is  $2.74 \times 10^{-9}$  m<sup>2</sup>/s.

Two different techniques were used to verify this number, but no reliable results were obtained. Measurement using TGA can be improved by using larger sample size, better heating element control. Another technique using absorption and desorption method with mass spectrometer did not gave satisfactory and replicable results. The likely reason for this is due to low solubility of  $CO_2$  in liquid and large head volume of the furnace make the change of the concentration after absorption negligible and difficult to measure. The restriction of experimental technique selection was due to high operating temperature and corrosive nature of cryolite. Therefore, the diffusion coefficient of  $CO_2$  in from modelling using Sutherland modification in Einstein-Stokes equation was used as the basis comparison from diffusion in porous solid.

# Chapter 10

## **10. Conclusions and Further Recommendations**

#### 10.1. Conclusions

In this thesis, anode characterization, diffusion coefficient measurement in porous solid, modelling on COMSOL Multiphysics, attempts on diffusion in molten salt have been carried out for understanding the gas transport mechanism in aluminium electrolysis. The following conclusions can be drawn from the current study

- Mercury Intrusion Porosimetry (MIP) is fundamental to represent smaller pores that are undetected using optical microscopy and X-Ray computerized tomography (CT). Despite less accuracy in the overlapping range than optical microscopy, due to over estimation of crack as porosity, CT was useful for defining meso to macro porosity and offers a nondestructive test that enables a comparison for the same samples within a reasonable time and cost.
- CT and optical microscopy generate microstructure images that can be used for pore classification while MIP data can be used to estimate the porosity, pore entrance size and also quantify pore connectivity.
- The diffusion in porous solid experiment were conducted on anode sample with different permeabilities. The measured diffusivity was compared with theoretical calculation based on average pore size obtained from Mercury intrusion porosimetry (MIP). The value obtained varied from 1.38 x10<sup>-6</sup> m<sup>2</sup>/s to 7.89 x10<sup>-6</sup> m<sup>2</sup>/s over temperature range from 25°C to 960°C. From these results, the values of the diffusion coefficients have the same order of magnitude (10<sup>-6</sup> cm<sup>2</sup>/s) as those calculated by the well-known formula for diffusion coefficients.
- Simulation of gas flow using FEM provides the evidence of convective flow resulting in lack of temperature dependency for the measured diffusion coefficients in anode samples. This simulation suggests that the lower the permeability within the anode matrix, the gas transport mechanism will be dominated by diffusion rather than convective flow.
- Sutherland's formula for diffusion coefficient in molten bath prediction was the closest with the experimental results from previous studies. The cryolite diffusion coefficient at 960°C was predicted in the range 2.74x10<sup>-9</sup> m<sup>2</sup>/s compared to previous experimental results from Rolin[48] in the range from 10<sup>-9</sup> to 10<sup>-12</sup> m<sup>2</sup>/s while Vetyukov and Acquah [190] measured valued between 10<sup>-11</sup> to 10<sup>-12</sup> m<sup>2</sup>/s.
- Two different techniques were attempted to verify this number but no reliable results were obtained. The likely reason for this difficulty is due to low solubility of CO<sub>2</sub> in liquid at high operating temperature and corrosive nature of cryolite.

 The results obtained suggest the gas transport for bubble nucleation is controlled by gas flow in the anode due to slower diffusion coefficient value in cryolite with three order of magnitude difference compare to diffusion in the anode samples.

## 10.2. Limitation and Recommendations

The recommendations suggested for future improvement of this study are as follows

- It would be useful to investigate how the anode production improves anode porosity and reduces permeability. This includes variation of samples with different properties such as wetting properties and coke grain size.
- Further study to improve the experimental techniques for measuring diffusion coefficient in porous solid coupled with mathematical modelling with convective flow effect are considered
- An alternative experimental technique that could be attempted for measuring diffusion coefficient of CO<sub>2</sub> in molten salts is the pressure decay technique. Caution must be applied as this technique would work with high pressure and operating temperature in completely sealed environment.

#### References

- [1] EC Golovina: *Doklady Akademii Nauk CCCR*, 1952, pp. 141–44.
- [2] M. Rolin: Institut National Des Sciences Appliquées de Lyon, 1981.
- [3] M. M. Vetyukov and F. Acquah: *Elektrokhimiya*, 1971, vol. 7, p. 557..
- [4] International Aluminium Institute: *Global Life Cycle Inventory Data for The Primary Aluminium Industry*, London, 2013.
- [5] Gary P Tarcy, Halvor Kvande, and Alton Tabereaux: *JOM*, 2011, vol. 63, pp. 101–8.
- [6] Kaiyu Zhang, Yuqing Feng, Phil Schwarz, Mark Cooksey, and Zhaowen Wang: *Light Met*, 2012, pp. 881–86.
- [7] G Brooks, M Cooksey, G Wellwood, and C Goodes: *Mineral Processing and Extractive Metallurgy*, 2007, vol. 116, pp. 25–33.
- [8] Ove Kobbeltvedt and Bjorn P Moxnes: *Essential Readings in Light Metals, Aluminum Reduction Technology*, 2013, vol. 2, p. 257.
- [9] Jomar Thonstad: Journal of The Electrochemical Society, 1964, vol. 111, pp. 959–65.
- [10] Warren Haupin and Halvor Kvande: *Essential Readings in Light Metals: Aluminum Reduction Technology, Volume 2*, 2000, pp. 160–65.
- [11] Norsk Hydro: *Aluminium, Environment and Society*, Oslo, 2012.
- [12] Donald Picard and Mario Fafard: *Three-Dimensional Constitutive Viscoelastic Model* for Isotropic Materials, INTECH Open Access Publisher, 2011.
- [13] Kai Grjotheim and Halvor Kvande: Introduction to Aluminium Electrolysis: Understanding the Hall-Hérloult Process, Aluminium-Verlag, 1993.
- [14] Warren E Haupin: Journal of The Electrochemical Society, 1960, vol. 107, pp. 232–36.
- [15] Vinicius Pifferl, Ciro Katol Paulo Miotto, Markus Meiei, Raymond Perruchoud, and Peter Sulgei: 2007.
- [16] C Karuppannan and R Prabhakar: Manufacturing Engineering, 2009.
- [17] Sheralyn M Hume, Raymond C Perruchoud, and Werner K Fischer: *JOM*, 1994, vol. 46, pp. 27–31.
- [18] WK Fischer and R Perruchoud: JOM, 1987, vol. 39, pp. 43–45.
- [19] Uthaiporn Suriyapraphadilok, Phillip Halleck, Abraham Grader, and John M Andresen: *Light Metals*, 2005, pp. 617–22.
- [20] GJ Houston and HA \Oye: Essential Readings in Light Metals: Electrode Technology for Aluminum Production, Volume 4, 1985, pp. 290–97.
- [21] PL Walker Jr and Emile Raats: *The Journal of Physical Chemistry*, 1956, vol. 60, pp. 370–72.
- [22] R Farr-Wharton, BJ Welch, RC Hannah, R Dorin, and HJ Gardner: *Electrochimica Acta*, 1980, vol. 25, pp. 217–21.
- [23] George J Janz and NP Bansal: *Journal of Physical and Chemical Reference Data*, 1982, vol. 11, pp. 505–693.
- [24] WE Haupin: Journal of Chemical Education, 1983, vol. 60, p. 279.
- [25] Warren Haupin: JOM, 1991, vol. 43, pp. 28–34.
- [26] T Utigard, JM Toguri, and EW Ip: *Essential Readings in Light Metals: Aluminum Reduction Technology, Volume 2*, 2013, pp. 127–30.
- [27] Philippe Mandin, Rolf Wüthrich, and Hervé Roustan: *ECS Transactions*, 2009, vol. 19, pp. 1–10.
- [28] Vanderlei Gusberti, Dagoberte S Severo, Barry J Welch, and Maria Skyllas-Kazacos: in *Light Metals 2012*, Springer, 2012, pp. 929–34.
- [29] Ernest W Dewing: Canadian Metallurgical Quarterly, 1991, vol. 30, pp. 153-61.

- [30] Graeme A Snook, Katherine McGregor, Andrew J Urban, and Mark A Cooksey: *Electrochimica Acta*, 2009, vol. 54, pp. 4925–32.
- [31] Katherine McGregor, Graeme A Snook, AJ Urban, MR Lanyon, NVY Scarlett, and IC Madsen: 2009.
- [32] AL Perron, LI Kiss, and S Poncsak: *Journal of Applied Electrochemistry*, 2007, vol. 37, pp. 303–10.
- [33] Mark Cooksey: Thesis Auckland University 2012.
- [34] Mark A Cooksey, Mark P Taylor, and John JJ Chen: JOM, 2008, vol. 60, pp. 51–57.
- [35] Morshed Alam, Yos Morsi, William Yang, Krishna Mohanarangam2 Geoff Brooks, and John Chen: *Light Metals*, 2013, pp. 591–96.
- [36] J Zoric and A Solheim: Journal of Applied Electrochemistry, 2000, vol. 30, pp. 787–94.
- [37] H Vogt: Journal of Applied Electrochemistry, 1989, vol. 19, pp. 713–19.
- [38] Harry Marsh: 1989.
- [39] SF Jones, GM Evans, and KP Galvin: *Advances in Colloid and Interface Science*, 1999, vol. 80, pp. 27–50
- [40] Jilai Xue and Harald A Oye: *Light Metals Warrendale*, 1995, pp. 265–71.
- [41] Kristian Etienne Einarsrud, Stein Tore Johansen, and Ingo Eick: *Light Metals 2012*, 2012, pp. 875–80.
- [42] S Fortin, M Gerhardt, and AJ Gesing: *Essential Readings in Light Metals: Aluminum Reduction Technology, Volume 2*, 1984, pp. 385–95.
- [43] John JJ Chen: JOM, 1994, vol. 46, pp. 15–20.
- [44] Alexandre Perron, László I Kiss, and Sandor Poncsak: *Light Metals*, 2005, vol. 565, p. 570.
- [45] Li Xiang Peng, Li Jie, Li Yan-qing, Zhang Heng-qin, and Li Ye-xiang: *Transactions of Nonferrous Metals Society of China Vol 14 (5)*, 2004, pp. 1017–22.
- [46] Subrat Das, Yos Morsi, Geoffrey Brooks, William Yang, and John JJ Chen: *Light Metals* 2011, 2011, pp. 575–80.
- [47] A Solheim, ST Johansen, S Rolseth, and J Thonstad: *Journal of Applied Electrochemistry*, 1989, vol. 19, pp. 703–12.
- [48] Sandor Poncsák and László I Kiss: *Light Metals 2012*, 2012, pp. 773–78.
- [49] Akshaya Jena and Krishna Gupta: in 41st Power Sources Conference, 2005.
- [50] TW Melnyk and AMM Skeet: *Canadian Journal of Earth Sciences*, 1986, vol. 23, pp. 1068–74.
- [51] Herbert Giesche: *Particle \& Particle Systems Characterization*, 2006, vol. 23, pp. 9–19.
- [52] Sari Westermarck and others: 2000.
- [53] Paul A Webb: *Micromeritics Instrument Corp, Norcross, Georgia*, 2001.
- [54] Yuan, Yuehua, and T. Randall Lee. "Contact angle and wetting properties." *Surface science techniques*. Springer, Berlin, Heidelberg, 2013. 3-34.
- [55] Paul A Webb: "Volume and density determinations for particle technologists." *Micromeritics Instrument Corp* 2, no. 16,2001.
- [56] Hillar M Rootare and Carl F. Prenzlow. "Surface areas from mercury porosimeter measurements." *The Journal of physical chemistry* 71, no. 8,1967,pp 2733-2736..
- [57] Shi Ying, Xiao Jinsheng, Pan Mu, and Yuan Runzhang: *Journal of Wuhan University* of Technology-Materials Science Edition, 2006, vol. 21, pp. 22–25.
- [58] Mandelbrot, Benoit B. *The fractal geometry of nature*. Vol. 1. New York: WH freeman, 1982.
- [59] Angulo, R. F., V. Alvarado, and H. Gonzalez. "Fractal dimensions from mercury intrusion capillary tests." In *SPE Latin America Petroleum Engineering Conference*. Society of Petroleum Engineers, 1992.

- [60] Benoit B Mandelbrot: The Fractal Geometry of Nature, WH freeman New York, 1983.
- [61] SC Carniglia: Journal of Catalysis, 1986, vol. 102, pp. 401–18.
- [62] BA Sadler and SH Algie: *Essential Readings in Light Metals: Electrode Technology for Aluminum Production, Volume 4*, 2013, pp. 594–605.
- [63] Marianne Aanvik Engvoll: 2002.
- [64] Donald P Ziegler: Light Metals 2011, 2011, pp. 901–6.
- [65] Stein Rorvik and Harald A Oye: Light Metals 1996, 1996, pp. 561–68.
- [66] Dipankar Bhattacharyay, Duygu Kocaefe, Yasar Kocaefe, Brigitte Morais, and others: *Journal of Surface Engineered Materials and Advanced Technology*, 2013, vol. 3, p. 1.
- [67] Stein Rørvik, Harald A \Oye, and Morten Sørlie: *Light Metals*, 2001, vol. 2001, pp. 601– 7.
- [68] Gao Lin Qiao and Semih Eser: in *Preprints of Symposia-Division of Fuel Chemistry American Chemical Society*, 1997, pp. 933–37.
- [69] S Rorvik, Lorentz Petter Lossius, and HA Oye: in *LIGHT METALS-WARRENDALE*-*PROCEEDINGS*-, 2003, pp. 531–34.
- [70] Tong Chen, Jilai Xue, Guanghui Lang, Rui Liu, Shoulei Gao, and Zengjie Wang: *JOM*, 2017, vol. 69, pp. 1600–1606.
- [71] Richard A Ketcham and William D Carlson: *Computers* \& *Geosciences*, 2001, vol. 27, pp. 381–400.
- [72] Donald Picard, Houshang Alamdari, Donald Ziegler, Pierre-Olivier St-Arnaud, and Mario Fafard: *Light Metals 2011*, 2011, pp. 973–78.
- [73] Donald Picard, Houshang Alamdari, Donald Ziegler, Bastien Dumas, and Mario Fafard: *Light Metals 2012*, 2012, pp. 1283–88.
- [74] Camilla Sommerseth, Rebecca Jayne Thome, Stein Rorvik, Espen Sandnes, Arne Petter Ratvik, Lorentz Petter Lossius, Hogne Linga, and Ann Mari Svensson: *Light Metals* 2015, 2015, pp. 1141–46.
- [75] Stein Rørvik and Lorentz Petter Lossius: in *Light Metals 2017*, Springer, 2017, pp. 1237–45.
- [76] Donald A Nield and Adrian Bejan: in *Convection in Porous Media*, Springer, 2013, pp. 1–29.
- [77] Joseph Kozeny: Sitzungsber Akad. Wiss, 1927, vol. 136, pp. 271–306.
- [78] Tobias Benedikt Hövekamp: *Experimental and Numerical Investigation of Porous Media Flow with Regard to the Emulsion Process*, ETH Zurich, 2002.
- [79] Holdich, R. G., I. W. Cumming, S. Kosvintsev, A. J. Bromley, and G. Stefanini. "Clarification by slotted surface microfilters." *Minerals engineering* 16, no. 2,2003, pp 121-128.
- [80] H. P. G. Darcy: Les Fontaines Publiques de La Ville de Dijon, Victor Dalmont, Paris, pp 1856.
- [81] James Kofi Arthur: 2012.
- [82] Joseph, D. D., D. A. Nield, and G. Papanicolaou. "Nonlinear equation governing flow in a saturated porous medium." *Water Resources Research* 18, no. 4,1982, pp 1049-1052.
- [83] Nield, Donald A., and Adrian Bejan. *Convection in porous media*. Vol. 3. New York: springer, 2006.
- [84] TK Perkins, OC Johnston, and others: *Society of Petroleum Engineers Journal*, 1963, vol. 3, pp. 70–84.
- [85] Weidong He, Jing Zou, Bin Wang, Subramanian Vilayurganapathy, Ming Zhou, Xiao Lin, Kelvin HL Zhang, Junhao Lin, Ping Xu, and James H Dickerson: *Journal of Power Sources*, 2013, vol. 237, pp. 64–73.

- [86] Clifford K Ho and Stephen W Webb: Gas Transport in Porous Media, Springer, 2006.
- [87] S Wilkening: Essential Readings in Light Metals: Electrode Technology for Aluminum Production, Volume 4, 1995, pp. 623–32.
- [88] John Crank: The Mathematics of Diffusion, Oxford university press, 1979.
- [89] William D Callister and David G Rethwisch: *Materials Science and Engineering: An Introduction*, Wiley New York, 2007.
- [90] Edward Allen Mason and AP Malinauskas: *Gas Transport in Porous Media: The Dusty-Gas Model*, Elsevier Science Ltd, 1983.
- [91] R Krishna and JA Wesselingh: *Chemical Engineering Science*, 1997, vol. 52, pp. 861–911.
- [92] RB Evans III, J Truitt, and GM Watson: Supersition of Forced and Diffusive Flow in a Large Pore Graphite, 1961.
- [93] DS Scott and FAL Dullien: AIChE Journal, 1962, vol. 8, pp. 113–17.
- [94] Stephen W Webb and Karsten Pruess: *Transport in Porous Media*, 2003, vol. 51, pp. 327–41.
- [95] Chih-Long Tsai and V Hugo Schmidt: *Journal of Power Sources*, 2011, vol. 196, pp. 692–99.
- [96] R Suwanwarangkul, E Croiset, MW Fowler, PL Douglas, E Entchev, and MA Douglas: *Journal of Power Sources*, 2003, vol. 122, pp. 9–18.
- [97] E Wicke and R Kallenbach: Colloid \& Polymer Science, 1941, vol. 97, pp. 135–51.
- [98] Karel Soukup, Petr Schneider, and Olga \vSolcová: Chemical Engineering Science, 2008, vol. 63, pp. 1003–11.
- [99] O Solcová and P Schneider: Applied Catalysis A: General, 2003, vol. 244, pp. 1–9.
- [100] Josef Valus' and Petr Schneider: Applied Catalysis, 1985, vol. 16, pp. 329–41.
- [101] Koichi Saitoh and Nobuo Suzuki: *Journal of Chromatography A*, 1975, vol. 109, pp. 333–39.
- [102] NA Katsanos, N Bakaoukas, A Koliadima, G Karaiskakis, and A Jannussis: *The Journal of Physical Chemistry B*, 2005, vol. 109, pp. 11240–46.
- [103] S Mohammadi-Jam and KE Waters: *Advances in Colloid and Interface Science*, 2014, vol. 212, pp. 21–44.
- [104] D Butler and DR Williams: in *Encyclopedia of Separation Science*, Elsevier Science Ltd., 2000, pp. 3609–14.
- [105] J Kapolos, N Bakaoukas, A Koliadima, and G Karaiskakis: *Journal of Phase Equilibria and Diffusion*, 2005, vol. 26, pp. 477–81.
- [106] Robert S Brodkey: The Phenomena of Fluid Motions, Courier Dover Publications, 1995.
- [107] R W Mair, G P Wong, D Hoffmann, M D Hurlimann, S Patz, L M Schwartz, and R L Walsworth: *Phys. Rev. Lett.*, 1999, vol. 83, pp. 3324–27.
- [108] Jorg Karger and Douglas M Ruthven: Zeolites, 1989, vol. 9, pp. 267–81.
- [109] JK Jasti and H Scott Fogler: AIChE Journal, 1992, vol. 38, pp. 481-88.
- [110] P Hugo: Developments in Soil Science, 1972, vol. 2, pp. 14–24.
- [111] G. J. Janz: Molten Salts Handbook, Elsevier, 2013.
- [112] K. Kinoshita: *Electrochemical Oxygen Technology*, John Wiley & Sons, 1992.
- [113] Gamsjäger, Heinz, Erich Königsberger, G. Hefter, and R. Tomkins. *Solubility of sparingly soluble ionic solids in liquids*. John Wiley, Chichester, 2003.
- [114] K Koichoro and H Yasuhiko: Trans. JIM, 1988, vol. 29, pp. 417–27.
- [115] Wagner, Carl. "The concept of the basicity of slags." *Metallurgical Transactions B* 6, no.3,1975,405.
- [116] T Förland, H Storegraven, and S Urnes: *Zeitschrift Für Anorganische Und Allgemeine Chemie*, 1955, vol. 279, pp. 205–11.

- [117] D Bratland, K Grjotheim, C Krohn, and K Matzfield: Acta Chem. Scand, 1966, vol. 20, p. 6.
- [118] A. L. Novozhilov, V. N. Devyyatkin, and E. I. Gribova: Russ. J. Phys. Chem. (Eng. Transl.), 1972, vol. 46, pp. 1066–67.
- [119] Borodziński, A., A. Sokołowski, and L. Suski. "Solubility of carbon dioxide, nitrogen, and argon in molten zinc chloride." *The Journal of Chemical Thermodynamics* 7, no. 7 ,1975, pp 655-660.
- [120] Sokołowski, A., and A. Borodziński. "Solubility of carbon dioxide in liquid solutions of zinc chloride in sodium chloride and in potassium chloride." *The Journal of Chemical Thermodynamics* 11, no. 5, 1979, 421-427.
- [121] Bratland, D., K. Grjotheim, C. Krohn, and K. Motzfeldt. "Solubility of CO 2 in molten salts and its influence on current efficiency in aluminum electrolysis." *JOM* 19, no. 10, 1967, pp 13-20.
- [122] Andresen, Rolf E. "Solubility of oxygen and sulfur dioxide in molten sodium sulfate and oxygen and carbon dioxide in molten sodium carbonate." *Journal of the Electrochemical Society* 126, no. 2,1979, pp 328-334.
- [123] Grjotheim, K., P. Heggelund, C. Krohn, and K. Motzfeldt. "On the solubility of carbon dioxide in molten halides." *Acta Chem. Scandinav* 16,1962, pp 689-694.
- [124] Field, Paul E., and William J. Green. "Interactions of gases in ionic liquids. I. Solubility of nonpolar gases in molten sodium nitrate." *Journal of Physical Chemistry* 75, no. 6 ,1971, pp 821-825.
- [125] Sada, Eizo, Shigeo Katoh, Hisao Beniko, Hidehumi Yoshii, and Masanori Kayano.
   "Solubility of carbon dioxide in molten salts." *Journal of Chemical and Engineering Data*25, no. 1 ,1980, pp 45-47.
- [126] Eizo Sada, Shigeo Katoh, Hidehumi Yoshii, Ikuo Takemoto, and Naofumi Shiomi: Journal of Chemical and Engineering Data, 1981, vol. 26, pp. 279–81.
- [127] Bratland, D., and C. Krohn. "On Solubility of Carbon Dioxide in Molten Alkali Nitrates and Alkali Flourides.' Acta Chemica Scandinavia no. 5, 1969, pp 1839.
- [128] R. Berjoan and J. P. Coutures: Rev. Int. Hautes Temp. Refract., 1983, p. 115.
- [129] Yamato, N., and K. S. Goto. "Measurement of solubility of CO2 in Na2O-P2O5-SiO2 ternary melt using a thermobalance." *Journal of the Japan Institute of Metals* 48, no. 10,1984, pp 983-989.
- [130] Pearce, M. L. "Solubility of carbon dioxide and variation of oxygen ion activity in sodasilica melts." *Journal of the American Ceramic Society* 47, no. 7, 1964, pp 342-347.
- [131] Pearce, M. L. "Solubility of carbon dioxide and variation of oxygen ion activity in sodium borate melts." *Journal of the American Ceramic Society* 48, no. 4, 1965, pp 175-178.
- [132] H. Kuwatori T. Kawahara and N. Sano:: Tetsu to Hagane, 1983, vol. 69, p. 974.
- [133] Sosinsky, D. J., M. Maeda, and A. McLean. "Determination and prediction of water vapor solubilities in CaO-MgO-SiO 2 slags." *Metallurgical Transactions B*16, no. 1 ,1985, pp 61-66.
- [134] K. Morinaga S. Sumita and T. Yanagase:: Nippon Kinzoku Gakkaishi, 1982, vol. 46, p. 369.
- [135] Mahieux, J., and G. Ribaud. "Sur Labsorption du Gaz Carbonique dans le Verre en Fussion" Comptes Rendus Hebdomadaires des Seances de L Academie des Sciences" 240, no. 26, 1955, pp 2521-2522.
- [136] H Numata and JO'M Bockris: Metallurgical Transactions B, 1984, vol. 15, pp. 39–46.
- [137] Mysen, Bjorn O., David H. Eggler, M. G. Seitz, and John. R. Holloway. "Carbon dioxide in silicate melts and crystals; Part I, Solubility measurements." *American Journal of Science* 276, no. 4,1976, pp 455-479

- [138] Djokić, Stojan S., Brian E. Conway, and T. F. Belliveau. "A Chronoamperometric Study of Anodic Processes at Various Types of Carbon Anode in Al2 O 3-Na3AlF6 Melts Used in the Electrolytic Production of Aluminum." *Journal of the Electrochemical Society* 141, no. 8,1994, pp 2103-2107.
- [139] Thonstad, J. "Chronopotentiometric measurements on graphite anodes in cryolite alumina melts." *Electrochimica Acta* 14, no. 2, 1969, pp 127-134.
- [140] Shurigin, V. J., and R. M. Yulmetyev. "Kinetics of spin density fluctuations in condensed paramagnets." *Physics Letters A* 135, no. 4-5, 1989, pp 311-314.
- [141] Zurilla, Ronald W., and Ernest Yeager. *Oxygen Electrode Kinetics of Gold*". No TR-23. case Western Reserve Univ Cleveland, Ohio Electrochemistry Research Lab, 1969.
- [142] Frazer, E. J., and J. Thonstad. "Alumina solubility and diffusion coefficient of the dissolved alumina species in low-temperature fluoride electrolytes." *Metallurgical and materials transactions B* 41, no. 3 ,2010, pp 543-548.
- [143] Zambonin, Pier G. "Controlled atmosphere cell for rotating disk electrode voltammetry in fused salts." *Analytical Chemistry* 41, no. 6 ,1969, pp 868-870.
- [144] Stojanovic, Tomislav, Hermann-Josef Gröne, Robert KH Gieseler, Bernd Klanke, Rolf Schlemminger, Dimitris Tsikas, and E. F. Gröne. "Enhanced renal allograft rejection by inhibitors of nitric oxide synthase: a nonimmunologic influence on alloreactivity." *Laboratory investigation* 74, no. 2, 1996, pp 496-512.
- [145] Jiahui Chen, Leslie S Loo, and Kean Wang: *Journal of Membrane and Separation Technology*, 2012, vol. 1, pp. 94–99.
- [146] Morgan, David, Lee Ferguson, and Paul Scovazzo. "Diffusivities of gases in roomtemperature ionic liquids: data and correlations obtained using a lag-time technique." *Industrial & Engineering Chemistry Research* 44, no. 13, 2005, pp 4815-4823.
- [147] Scovazzo, Paul, Ann E. Visser, James H. Davis, Robin D. Rogers, Carl A. Koval, Dan L. DuBois, and Richard D. Noble. "Supported ionic liquid membranes and facilitated ionic liquid membranes." In ACS Symposium Series, vol. 818, pp. 69-87. American Chemical Society, 2002.
- [148] Ying Hou and Ruth E Baltus: Industrial \& Engineering Chemistry Research, 2007, vol. 46, pp. 8166–75.
- [149] Kroon, Maaike C., Alireza Shariati, Marco Costantini, Jaap van Spronsen, Geert-Jan Witkamp, Roger A. Sheldon, and Cor J. Peters. "High-pressure phase behavior of systems with ionic liquids: Part V. The binary system carbon dioxide+ 1-butyl-3-methylimidazolium tetrafluoroborate." *Journal of Chemical & Engineering Data* 50, no. 1 ,2005, pp 173-176.
- [150] Anthony, Jennifer L., Jessica L. Anderson, Edward J. Maginn, and Joan F. Brennecke.
   "Anion effects on gas solubility in ionic liquids." *The Journal of Physical Chemistry B* 109, no. 13 ,2005, pp 6366-6374.
- [151] Moganty, Surya S., and Ruth E. Baltus. "Diffusivity of carbon dioxide in roomtemperature ionic liquids." *Industrial & Engineering Chemistry Research* 49, no. 19 (2010): 9370-9376.
- [152] Mark B Shiflett and A1 Yokozeki: Industrial \& Engineering Chemistry Research, 2005, vol. 44, pp. 4453–64.
- [153] Cristian Moya, Jose Palomar, Maria Gonzalez-Miquel, Jorge Bedia, and Francisco Rodriguez: *Industrial \& Engineering Chemistry Research*, 2014, vol. 53, pp. 13782– 89.
- [154] Maria Gonzalez-Miquel, Jorge Bedia, Concepcion Abrusci, Jose Palomar, and Francisco Rodriguez: *The Journal of Physical Chemistry B*, 2013, vol. 117, pp. 3398–3406.

- [155] http://www.tainstruments.com/wp-content/uploads/IsoSorp.pdf, accessed at 5<sup>th</sup> December 2018
- [156] Eizo Sada, Shigeo Katoh, Hidehumi Yoshii, and Kiyoshi Yasuda: *Journal of Chemical and Engineering Data*, 1980, vol. 25, pp. 341–43.
- [157] Eizo Sada, Shigeo Katoh, Hidehumi Yoshii, and Kiyoshi Yasuda: Industrial \& Engineering Chemistry Fundamentals, 1982, vol. 21, pp. 43–46.
- [158] Cnudde, Veerle, A. Cwirzen, Bert Masschaele, and P. J. S. Jacobs. "Porosity and microstructure characterization of building stones and concretes." *Engineering geology* 103, no. 3-4, 2009, pp76-83.
- [159] Sommerseth, Camilla, Rebecca Jayne Thorne, Arne Petter Ratvik, Espen Sandnes, Hogne Linga, Lorentz Petter Lossius, and Ann Mari Svensson. "The Effect of Varying Mixing Temperatures and Baking Level on the Quality of Pilot Scale Anodes—A Factorial Design Analysis." *Metals*7, no. 3, 2017, pp 74.
- [160] Nooruddin, Hasan A., M. Enamul Hossain, Hasan Al-Yousef, and Taha Okasha. "Comparison of permeability models using mercury injection capillary pressure data on carbonate rock samples." *Journal of Petroleum Science and Engineering* 121,2014, pp 9-22.
- [161] Chevarin, Francois, Ramzi Ishak, Donald Ziegler, Mario Fafard, and Houshang Alamdari. "Evolution of anode porosity under air oxidation: the unveiling of the active pore size." *Metals* 7, no. 3,2017, pp 101.
- [162] Øye, Harald A. "Control of anode consumption during aluminium electrolysis." In Fundamental Issues in Control of Carbon Gasification Reactivity, pp. 573-593. Springer, Dordrecht, 1991.
- [163] Rolle, Jeffery G., and Yen K. Hoang. "Studies of the Impact of Vanadium and Sodium on the Air Reactivity of Coke and Anodes." In *Fuel and Energy Abstracts*, vol. 1, no. 37, p. 8. 1996.
- [164] Subero, José. "Quality of calcined petroleum coke and its influence on aluminium smelting." In *Light Metals 2013*, Springer, Cham, pp. 1085-1088.
- [165] F Chevarin, K Azari, L Lemieux, D Ziegler, M Fafard, and H Alamdari: Fuel, 2016, vol. 178, pp. 93–102.
- [166] Boero, Rey. "Studies on anode reactivity to oxidant gases." *Light Metals 1981*, 1981. 441-458.
- [167] Dullien, Francis AL. *Porous media: fluid transport and pore structure*. Academic press, 2012.
- [168] Epma Putri, Geoffrey Brooks, Graeme A Snook, Stein Rørvik, Lorentz Petter Lossius, and Ingo Eick: in *TMS Annual Meeting* \& *Exhibition*, 2018, pp. 1235–42.
- [169] Kamran Azari, Houshang Alamdari, Gholamreza Aryanpour, Donald Picard, Mario Fafard, and Angelique Adams: *Powder Technology*, 2013, vol. 235, pp. 341–48.
- [170] Zhengwei Nie and Yuyi Lin: Ceramics-Silikáty, 2015, vol. 59, pp. 348-52.
- [171] Z Yu, RN Carter, and J Zhang: Fuel Cells, 2012, vol. 12, pp. 557–65.
- [172] Zhiye Gao: 2014.
- [173] S Satoh, I Matsuyama, and K Susa: Journal of Non-Crystalline Solids, 1995, vol. 190, pp. 206–11.
- [174] Azari, Kamran, Houshang Alamdari, Gholamreza Aryanpour, Donald Ziegler, Donald Picard, and Mario Fafard. "Compaction properties of carbon materials used for prebaked anodes in aluminum production plants." *Powder technology* 246, 2013, pp 650-657.
- [175] Roland W Lewis, Perumal Nithiarasu, and Kankanhalli N Seetharamu: *Fundamentals of the Finite Element Method for Heat and Fluid Flow*, John Wiley & Sons, 2004.
- [176] Kang Lu: 2011.
- [177] Mehrzad Tabatabaian: COMSOL for Engineers, Stylus Publishing, LLC, 2015.
- [178] David Viet Dang Tran: 2013.

- [179] Marco Rovitto, Wolfhard H Zisser, and Hajdin Ceric: in *Physical and Failure Analysis of Integrated Circuits (IPFA), 2015 IEEE 22nd International Symposium on the*, 2015, pp. 434–38.
- [180] COMSOL Multiphysics: COMSOL, AB, 2012, pp. 39-40.
- [181] Emma Persson: Microclimate in a Hygiene, n.d.
- [182] Riani Ayu Lestari: 2010.
- [183] Yoshito Nakashima and Yoshinori Watanabe: Water Resources Research, 2002, vol. 38.
- [184] Shane Cadogan: 2015.
- [185] R Byron Bird: Applied Mechanics Reviews, 2002, vol. 55, pp. R1-R4.
- [186] Bruce E Poling, John M Prausnitz, John P O'connell, and others: *The Properties of Gases and Liquids*, Mcgraw-hill New York, 2001.
- [187] Goran Peskir: Stoch. Models, 2003, vol. 19, pp. 383-405.
- [188] William Sutherland: *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 1902, vol. 3, pp. 161–77.
- [189] Samuel Glasstone, Keith James Laidler, and Henry Eyring: The Theory of Rate Processes; the Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena, 1941.
- [190] Winny Wulandari: 2013.
- [191] Malisja Louella De Vries and others: 2004.
- [192] B Flaconneche, J Martin, and MH Klopffer: Oil & Gas Science and Technology, 2001, vol. 56, pp. 245–59.

## Appendix A

#### **Error analysis**

Error might occur during laboratory experiments and measurement process. The errors can be classified as systematic errors and random errors. Systematic errors are caused by the errors from the measurement apparatus, which might occur due to disturbance during measurement, design of the apparatus, and external effects, such as the effects of environmental changes. Random errors are produced by uncertainties during measurement process. Common influences to random errors are uncertainties during measurement reading on analogue meter, statistical fluctuations, and due to noise.

#### **Errors in Experimental Procedures**

#### Weighing Error

All samples are weighed in six figure balance using he Mettler Toledo digital balance with  $\pm 0.01$ mg weighing accuracy.

#### **Temperature Measurement Error**

The thermocouple used in this experiment was a type-K thermocouple (chromel-alumel) which had temperature range of -180 to 1300 °C with the fluctuation of  $\pm$  1 °C.

#### Flow rate error:

The digital mass flow controller has accuracy ±5% of 65 mm scale

#### Ion detection error:

Few occurrence on lighter gasses tend to show smearing and abrupt jump in MS curve due to lower AMU compared to the heavier carrier gas (argon with 40AMU). Hence, multi runs of the 320 same sample with identical test conditions were performed to observe evolved gas evolution process.

## Experimental Flow chart iteration



## Appendix B

#### Permeability measurement

The first step shown in Figure 1 where threshold pressure  $P_t$  is determined at the inflection point of the cumulative intrusion curve. This inflection point is defined as the highest point in the log differential intrusion curve in porous alumina sample using mercury porosimetry. The cumulative intrusion volume V<sub>t</sub> at threshold pressure (P<sub>t</sub>) is determined as the example shown in Figure 2.





Figure 0-1 Cumulative volume intrusion versus intrusion pressure for Pt determination

Log Differential Intrusion vs. Intrusion Pressure for porous alumina

The next step is to quantify  $V_t$  from data set which was subtracted from each intrusion volume value at each pressure from threshold pressure to maximum pressure. Data points

prior to the threshold pressure are excluded. The hydraulic conductance function or permeability path are measured by the net volume ( $V_c - V_t \text{ in cm}^3$ ) times the diameter cubed (mm<sup>3</sup>) for the corresponding pressure is calculated as a function of pore diameter (µm). Figure 3 shown the pore diameter corresponding to the maximum y-value is L<sub>max</sub>, where the cumulative volume of mercury intruded at this diameter is VL<sub>max</sub>. The fraction S(L<sub>max</sub>) is calculated as the ratio of VL<sub>max</sub>/V<sub>t</sub> and is the fractional volume of connected pore space composed of pore width of size L<sub>max</sub> and larger.



Determination of L<sub>max</sub>

The porosity ( $\phi$ ) of porous solid is 0.355, which can be directly obtained from MIP measurement. Until now all the required parameters in Eq.3-13 are known, and we can calculate the permeability of porous alumina to be 0.2455 mili Darcy. All the other samples were processed to obtain the permeability by the same procedures described above.

# Appendix C

# **COMSOL Multiphysics**

## **Global Definitions**

Parameters

Name	Expression	Value	Description
D2	7.89e-6 [m^2/s]	7.89E-6 m²/s	diffusion coefficient
c_max	0.00807 [mol/m^3]	0.00807 mol/m <sup>3</sup>	peak initial concentration
Por	0.187	0.187	Porosity
Perm	2.87e-12[m^2]	2.87E-12 m <sup>2</sup>	Permeability
T1	1233.15[K]	1233.2 K	Temperature

## Variables

Variables 1

Name	Expression	Unit	Description
c0	c_max*exp(-(x/3[cm])^2)	mol/m <sup>3</sup>	initial concentration

#### Definitions

Selections

left boundary



## left boundary



## right boundary



## Geometry 1

## Units

Length unit	cm
Angular unit	Deg

# Geometry statistics

Description	Value
Space dimension	2
Number of domains	66
Number of boundaries	540
Number of vertices	535

## Materials

# Graphite

**Basic Settings** 

Description	Value				
Relative permeability	{{1, 0, 0}, {0, 1, 0}, {0, 0, 1}}				
Electrical conductivity	{{3e3[S/m], 0, 0}, {0, 3e3[S/m], 0}, {0, 0, 3e3[S/m]}}				
Heat capacity at constant pressure	710[J/(kg*K)]				
Relative permittivity	{{1, 0, 0}, {0, 1, 0}, {0, 0, 1}}				
Surface emissivity	1				
Density	1950[kg/m^3]				
Thermal conductivity	{{150[W/(m*K)]*(300[K]/T), 0, 0}, {0,				
	150[W/(m*K)]*(300[K]/T), 0}, {0, 0,				
	150[W/(m*K)]*(300[K]/T)}}				

## Carbon dioxide

**Basic Settings** 

Description	Value
Dynamic viscosity	eta(T[1/K])[Pa*s]
Ratio of specific heats	1.3
Heat capacity at constant pressure	Cp(T[1/K])[J/(kg*K)]
Density	rho(pA[1/Pa], T[1/K])[kg/m^3]
Thermal conductivity	{{k(T[1/K])[W/(m*K)], 0, 0}, {0, k(T[1/K])[W/(m*K)],
	0}, {0, 0, k(T[1/K])[W/(m*K)]}}

# Brinkman Equations

Equations

$$\frac{1}{\epsilon_{\rho}}\rho\frac{\partial\mathbf{u}}{\partial t} + \frac{1}{\epsilon_{\rho}}\rho(\mathbf{u}\cdot\nabla)\mathbf{u}\frac{1}{\epsilon_{\rho}} = \nabla\cdot\left[-\rho\mathbf{I} + \mu\frac{1}{\epsilon_{\rho}}(\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathrm{T}}) - \frac{2}{3}\mu\frac{1}{\epsilon_{\rho}}(\nabla\cdot\mathbf{u})\mathbf{I}\right] - \left(\mu\kappa^{-1} + \beta_{\mathrm{F}}|\mathbf{u}| + \frac{Q_{\mathrm{m}}}{\epsilon_{\rho}^{2}}\right)\mathbf{u} + \mathbf{F} + \rho\mathbf{g}$$

 $\rho \nabla \cdot (\mathbf{u}) \!=\! \boldsymbol{Q}_{\mathsf{m}}$ 

$$\operatorname{Re}_{\mathsf{w}} = \frac{\rho |\mathbf{u}| \ell_{\mathsf{w}}}{\mu} = \frac{|\mathbf{u}|}{u_{\tau}} \cdot \frac{\rho u_{\tau} \ell_{\mathsf{w}}}{\mu} = u^{+} \ell_{\mathsf{w}}^{+} \quad u^{+} = f(\ell_{\mathsf{w}}^{+})$$
$$\nabla G \cdot \nabla G + \sigma_{\mathsf{w}} G(\nabla \cdot \nabla G) = (1 + 2\sigma_{\mathsf{w}})G^{4}, \quad \ell_{\mathsf{w}} = \frac{1}{G} - \frac{\ell_{\mathsf{ref}}}{2}$$
$$\mu_{\mathsf{T}} = \mu \left( \left( \frac{df}{d\ell_{\mathsf{w}}^{+}} \right)^{1} - 1 \right)$$

Interface settings

Physical model

Settings

Description	Value
Neglect inertial term (Stokes flow)	On
Compressibility	Incompressible flow
Enable porous media domains	On
Include gravity	On
Use reduced pressure	Off
Reference temperature	T1
Reference position, x component	0
Reference position, y component	0
Reference position, z component	0
Reference pressure level	1[atm]

Initial Values 1

Initial values

Settings

Description	Value
Velocity field, x component	0
Velocity field, y component	0
Velocity field, z component	0
Pressure	1[atm]
Compensate for hydrostatic pressure	On
Wall distance in viscous units	br.yPlusinit

Description	Value
Reciprocal wall distance	br.G0
Coordinate system	Global coordinate system



# Boundary condition

Settings

Description	Value
Wall condition	No slip
Translational velocity	Automatic from frame
Sliding wall	Off

## Outlet 1

Selection

Geometric entity level	Boundary
Selection	Boundary 284

# Boundary condition

# Settings

Description	Value
Boundary condition	Pressure
Pressure	102125
Compensate for hydrostatic pressure	Off
Normal flow	On
Suppress backflow	Off

## Transport of Diluted Species in Porous Media 2

Used products

COMSOL Multiphysics CFD Module

Transport of Diluted Species in Porous Media 2

Selection

Geometric entity level	Domain
Selection	Domains 1–66

Equations

$$\mathsf{P}_{1,j}\frac{\partial c_i}{\partial t} + \mathsf{P}_{2,j} + \nabla \cdot \mathbf{\Gamma}_i + \mathbf{u} \cdot \nabla c_i = R_i + S_i$$

 $\mathbf{N}_i = \mathbf{\Gamma}_i + \mathbf{u}_{c_i} = -D_{\mathbf{e}_i} \nabla c_i + \mathbf{u}_{c_i}$ 

Interface settings

Transport mechanisms

Settings

Description	Value
Convection	On
Migration in electric field	Off
Mass transfer in porous media	On
Dispersion	Off
Description	Value
--	-------
Volatilization in partially saturated porous media	Off

# Porous Media Transport Properties 1

Porous Media Transport Properties 1

Selection

Geometric entity level	Domain
Selection	Domains 1–66

Settings

Description	Value
Porous material	Graphite (mat1)
Porosity	User defined
Porosity	Por
Fluid material	Carbon dioxide (mat2)
Fluid diffusion coefficient	User defined
Fluid diffusion coefficient	{{D2, 0, 0}, {0, D2, 0}, {0, 0, D2}}
Effective diffusivity model	Bruggeman model
Coordinate system	Global coordinate system
Temperature	User defined
Temperature	T1

**Initial Values 1** 

Inflow 1



### Selection

Geometric entity level	Boundary
Selection	Boundaries 1, 3

#### Settings

Description	Value
Concentration	c0
Boundary condition type	Concentration constraint

# Outflow 1



### Selection

Geometric entity level	Boundary
Selection	Boundary 284

# Coupled interfaces

Settings

Description	Value
Source	Brinkman Equations (br)
Destination	Transport of Diluted Species in Porous Media 2 (tds2)

### Mesh 1

#### Mesh statistics

Description	Value
Minimum element quality	2.922E-7
Average element quality	0.7874
Triangle	5569
Quad	808
Edge element	1164
Vertex element	535



## Mesh 1

Size (size)

# Settings

Description	Value
Calibrate for	Fluid dynamics
Maximum element size	0.33
Minimum element size	0.0105
Resolution of narrow regions	0.9
Maximum element growth rate	1.4
Predefined size	Extremely coarse

### Study 1

Computation information

Computation time	2 min 20 s
CPU	Intel64 Family 6 Model 78 Stepping 3, 2 cores
Operating system	Windows 7

# Time Dependent

Times	Unit
range(0,0.1,300)	s

# Physics and variables selection

Physics interface	Discretization
Brinkman Equations (br)	physics
Transport of Diluted Species in Porous Media 2 (tds2)	physics

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1



#### Data set: Study 1/Solution 1

#### **Plot Groups**

Velocity (br)





### Pressure (br)



Time=0.7 s Surface: Pressure (Pa)





Time=300 s Surface: Concentration (mol/m<sup>3</sup>) Arrow Surface: Velocity field

#### Comparison plot with experimental results.



# Appendix D

Tabulated results for Diffusion Coefficients of CO <sub>2</sub> in H <sub>2</sub> 0						
T/K	Kb	Н	Rs	D (m <sup>2</sup> s <sup>-1</sup> )	Formula	
293.15	1.38E-	1.00E-	1.65E-	1.30E-09	Einstein Stokes	
	23	03	10			
293.15	1.38E-	1.00E-	1.65E-	1.95E-09	Sutherland	
	23	03	10			
293.15	1.38E-	1.00E-	1.65E-	1.22E-08	Glasstone	
	23	03	10			
Tabulated results for Diffusion Coefficients of CO <sub>2</sub> in NaNO <sub>3</sub>						
T/K	Kb	Н	Rs	D (m <sup>2</sup> s <sup>-1</sup> )	Formula	
623.15	1.38E-	2.36E-	1.65E-	1.17E-09	Einstein Stokes	
	23	03	10			
623.15	1.38E-	2.36E-	1.65E-	1.76E-09	Sutherland	
	23	03	10			
623.15	1.38E-	2.36E-	1.65E-	1.10E-08	Glasstone	
	23	03	10			
Tabulated results for Diffusion Coefficients of CO <sub>2</sub> in Cryolite						
T/K	Kb	Н	Rs	D (m²s⁻¹)	Formula	
1233.15	1.38E-	3.00E-	1.65E-	1.82E-09	Einstein Stokes	
	23	03	10			
1233.15	1.38E-	3.00E-	1.65E-	2.74E-09	Sutherland	
	23	03	10			
1233.15	1.38E-	3.00E-	1.65E-	5.47E-09	Glasstone	
	23	03	10			

# Tabulated Results for CO<sub>2</sub> Diffusion Coefficient