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Fuel cells modelling for power electronic application

Wattana Kaewmanee

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THESE

de

DOCTORAT DE L'UNIVERSITE DE LORRAINE

Spécialité : Génie Electrique

par

Wattana KAEWMANEE



**MODELISATION DES PILES A COMBUSTIBLE DANS UN ENVIRONNEMENT
D'ELECTRONIQUE DE PUISSANCE**



Soutenue publiquement le 08 mars 2012

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Ecole Nationale Supérieure d'Electricité et de Mécanique

Préambule

Ce document présente une partie des travaux de recherche que nous avons réalisés dans le cadre de l'Institut d'Innovation Franco-Thaïlandais (IIFT ou plus communément TFII pour Thai-French Innovation Institute).

Existant depuis 1990, cet institut comprend plusieurs départements (Corrosion, Energie, Métrologie, Productique, Soudure, Technologies électronique et électrique) collaborant chacun avec un ou plusieurs centres techniques ou universités et plusieurs industriels. Pour le département des Technologies électroniques et électriques, c'est l'Institut National Polytechnique de Lorraine (INPL) qui depuis une dizaine d'années nous apporte une aide en parallèle avec le support d'industriels comme Schneider Thailand Limited.

La collaboration avec l'INPL a permis au travers d'un Programme d'Action Intégré (PAI France-Thaïlande 2003-2005) du Ministère des Affaires Etrangères français et de son homologue thaïlandais de développer la formation de Master et de Doctorat ainsi que la recherche dans le domaine du génie électrique. Un Programme Hubert Curien (PHC 2009-2010) est actuellement destiné à développer des travaux de recherche autour de la pile à combustible.

Depuis juin 2005 je suis enseignant au département de formation des enseignants en génie électrique à la faculté des enseignements techniques de l'Université King Mongkut de Bangkok. Mon service d'enseignement est d'environ 20h par semaine.

J'ai commencé mes travaux de recherche sur la pile à combustible en novembre 2008 au sein du laboratoire GREEN. Cette thèse a été effectuée en alternance entre la France et la Thaïlande conformément aux accords et à la bourse que l'ambassade de France m'a accordée. Ma première année de thèse s'est déroulée en France, puis je suis reparti une année en Thaïlande et enfin 6 mois au GREEN afin de finaliser mes travaux. En raison du contexte, ce manuscrit a donc été rédigé en anglais et comporte un résumé étendu en français placé au début de la thèse. Ce résumé reprend l'introduction et la conclusion de la thèse et décrit les divers chapitres qui la composent.

*To my father, Lieutenant Colonel Tanakorn KAEWMANEE,
and to the memory of my mother*

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Abridged Version of the Thesis in French

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Nomenclature

a	activité de l'eau	-
a_i	activité de l'espèce i	-
a_{tube}	diameter du tube de gaz	m
c_i	concentration de l'espèce i	mol/m ³
c_t	concentration du mélange gazeux	mol/m ³
d	distance entre les plaques	m
f_{ij}	facteur de friction	kg/(m ³ · s)
h	hauteur	m
j	densité de courant	A/m ²
$j_{0,anode}$	densité de courant d'échange à l'anode	A/m ²
$j_{0,cathode}$	densité de courant d'échange à la cathode	A/m ²
k_B	constant de Boltzmann	J/K
w	largeur	m
m_i	masse de la molécule de l'espèce i	kg
\dot{m}	debit massique	kg/s
n_{drag}	coefficient électro-osmotique	-
n_{pore}	nombre equivalent de pore	-
$n_{H_2O,diff}^m$	débit molaire	mol/s
p_i	pression partielle de l'espèce i	Pa
t_m	épaisseur de la membrane	m
u_i	vitesse de l'espèce i	m/s
v_i	vitesse moyenne l'espèce i	m/s
x_i	fraction molaire de l'espèce i	-
A_{GDL}	aire de la section transversal d'une GDL	m ²
C	capacité électrique	F
C_{GDL}	capacité equivalente de la GDL	m ³ /Pa
C_H	Capacité de Helmholtz	F
$C_{H_2O,\lambda}^m$	capacité équivalente liée à la teneur en eau	mol/m ²
$C_{H_2O,\mu}^m$	capacité équivalente liée au potentiel électrochimique	mol ² /J
$D_{H_2O,\lambda}^m$	coefficient de diffusion de l'eau dans la membrane	m ² /s
$D_{H_2O,\mu}^m$	coefficient de diffusion de l'eau lié au potentiel électrochimique	mol ² /(J.m.s)
D_{ij}	coefficient de diffusion binaire de Stefan-Maxwell between	m ² /s
D_{ij}^{eff}	coefficient de diffusion effectif	m ² /s
D_{iK}	coefficient de diffusion de Knudsen	m ² /s
E_{OCV}	Tension en circuit ouvert	V
E_r^\ominus	reference potential at the standard state	V

E_r	potentiel réversible	V
EW	masse equivalent de la membrane	kg/mol
F	constant de Faraday	C/mol
J	densité de courant	A/m ²
K_O	facteur géométrique des pore	-
L	longueur	m
$N_{H_2O}^m$	flux d'eau	mol/(m ² · s)
$N_{H^+}^m$	flux de proton	mol/(m ² · s)
N_i	flux molaire de l'espèce i	mol/(m ² · s)
P_{ch}	pression totale au milieu du canal	Pa
P_{sat}	pression de vapeur saturante	Pa
Q	debit volumique	m ³ /s
R	constant des gaz parfait	J/(K · mol)
R_{ch}	résistance hydraulique du canal	Pa · s/m ³
$R_{H_2O,\mu}^m$	résistance équivalente liée au potentiel électrochimique	J · s/mol ²
$R_{H^+}^m$	résistance ionique de membrane	Ω
R_{ij}	résistance équivalente de diffusion de Stefan-Maxwell	kg/(m ⁴ · s)
R_{iK}	résistance équivalente de diffusion de Knudsen	kg/(m ⁴ · s)
RH	humidité relative	%
T	température	K
V_{ch}	volume du canal	m ³
V_{gas}	volume du gaz	m ³

Greek Symbols

α	coefficient de transfert de charge à l'anode	-
β	coefficient de transfert de charge à la cathode	-
ε	porosité du milieu	-
ε_0	permittivité	F/m
ε_r	permittivité relative de la solution	-
η	viscosité dynamique	Pa · s
η	surtension	V
η	distance par unité	-
λ	teneur en eau	-
$\mu_{H_2O}^m$	potentiel électrochimique de l'eau dans la membrane	J/mol
ρ	masse volumique du fluide	kg/m ³
ρ_{dry}	masse volumique de la membrane sèche	kg/m ³
$\sigma_{H^+}^m$	conductivité ionique	S/m
τ	tortuosité du milieu	-

Chapitre 1

Introduction

1.1 Modèles pile à combustible de type PEM (PEMFC)

Le fonctionnement d'une PEMFC est très complexe, un certain nombre de paramètres ou de conditions opératoires affectent ses performances et sa durée de vie. Les modèles de piles permettent de mieux comprendre l'influence de ces paramètres et leur répercussion. Ils ont également pour but de prédire le comportement de la pile à différentes sollicitations.

Le degré de simplification dépend des objectifs et de l'application visés. La pile à combustible est un convertisseur électrochimique, de ce fait sa modélisation est multi-physique. Elle fait intervenir l'électrochimie, la mécanique des fluides, la thermique et le génie électrique. Puisque chaque phénomène dans les PEMFC est fortement couplé à l'autre, chaque type de modèle de PEMFC a quelques intersections avec l'autre, de sorte que, la catégorisation du modèle de pile à combustible n'est pas tout à fait définitive. Les principaux types de modèle PEMFC sont présentés comme suit.

1.1.1 Modélisation EDP

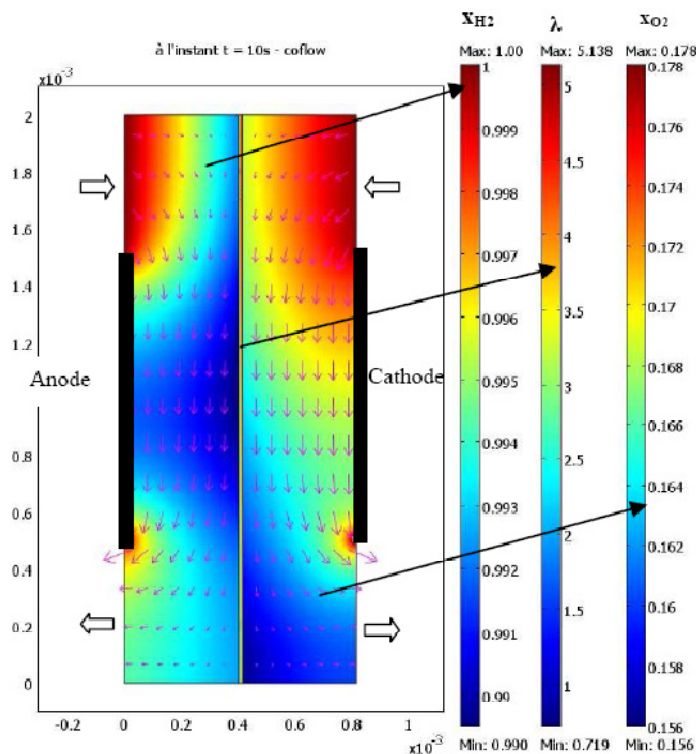


Figure 1-1 Un exemple de résultat de simulation issu de la résolution du modèle EDP [1]

Ce type de modèle repose sur les équations de la physique, qui décrivent les phénomènes réels d'une cellule de pile à combustible [1-11]. Le modèle peut représenter la cellule entière ou juste une partie spécifique [12-15]. Le modèle peut être une, deux ou trois dimensions [16-20] et basé sur des hypothèses différentes, telles que, avec ou sans changement de phases, isothermes ou non isothermes [7, 20-22]. Puisque ce type de modèles est fortement non linéaire et complexe, il est

généralement résolu par la méthode des éléments finis qui exige un temps de calcul assez conséquent [6].

1.1.2 Modèle empirique ou semi-empirique

Le modèle empirique est également connu en tant que modèle comportemental. Le modèle est basé sur le comportement expérimental observé auquel le système réel répond à différents stimuli [23-33]. Les courbes expérimentales sont ensuite approximées à l'aide de fonctions mathématiques de types exponentielle, logarithme, ou polynomiale. L'avantage du modèle empirique est sa simplicité. Le modèle, qui représente la caractéristique statique d'une cellule, peut être juste une équation d'une ligne. Une des équations de caractéristique statiques les plus simples est présentée en [32] où :

$$E = \frac{E_{OCV}}{1 + \left(\frac{I}{I_h}\right)^\alpha} \quad (1-1)$$

Dans cette équation, E_{OCV} est la tension en circuit ouvert, I_h et α sont les paramètres d'ajustement.

Puisque le modèle est développé à partir de la réponse observée de la cellule, le modèle ne fournit pas un lien solide entre les paramètres physiques, par exemple la température de la cellule, l'humidité relative de l'air à l'entrée ou la taille des pores du milieu poreux, et les comportements de la cellule. De nombreux chercheurs tentent de créer un modèle empirique qui intègre certaines des propriétés physiques des cellules. Ce type de modèles est considéré comme un modèle semi-empirique. La volonté d'approximer au plus près le comportement de la pile aboutit à des modèles de plus en plus complexes. La différence entre le modèle semi-empirique et le modèle physique est que le modèle empirique repose toujours sur les données mesurées et les paramètres d'ajustement.

1.1.3 Modèle circuit équivalent

Ce modèle est étroitement lié au modèle empirique. La principale différence est que le lien entre le stimulus et la réponse n'est pas représenté par une fonction mathématique, mais par un circuit électrique [26, 34-50]. Le modèle exige moins de temps de calcul que celui basé sur les phénomènes de transport de masse et de charge (équations aux dérivés partielles). Il intègre également de manière transparente le couplage d'une cellule à un convertisseur de puissance. Ce type de modèle est adapté aux applications en génie électrique.

Dans la littérature, les modèles de type circuit équivalent peuvent être classés en deux grandes catégories. Le premier est le circuit classique où les éléments sont identifiés grâce à la réponse fréquentielle (figure 1-2), [40, 45, 46, 49, 50]. Ce type de modèle se retrouve souvent en électrochimie. L'autre est celui qui reproduit la courbe caractéristique de la pile à combustible [26, 29, 34, 35, 38, 39, 41-44, 47, 48].

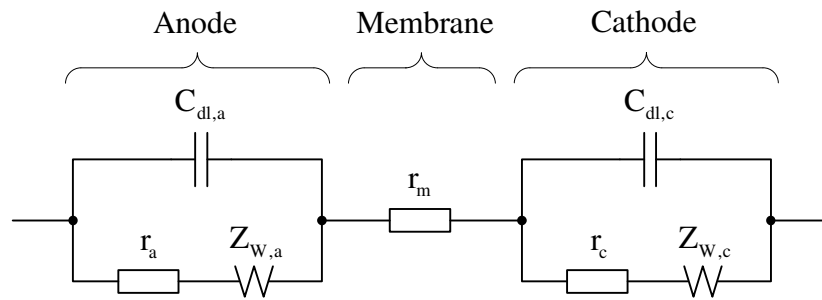


Figure 1-2 Un modèle de circuit électrique équivalent d'une cellule de PEMFC [32]

1.1.4 Modélisation orientée contrôle

Ce type de modèle est développé à des fins de conception de contrôle [26, 29, 49, 51-55]. C'est généralement une version linéarisée du modèle physique autour d'un point de fonctionnement. Le modèle est généralement sous la forme d'équations d'état qui est conforme aux diverses méthodes conventionnelles ou modernes de conception du contrôle.

1.2 Objectif de cette thèse

Les piles à combustible de type PEM sont des sources basses tension à dynamique lente. Le raccordement direct d'une pile à combustible à une charge conventionnelle peut être problématique. Les concepteurs en charge de dimensionner des convertisseurs de puissance destinés à transmettre l'énergie électrique provenant de la pile à la charge sont des électrotechniciens. Afin d'étudier et de vérifier leur conception, ces personnes ont besoin d'un modèle de type PEMFC qui puisse être facilement intégré à leurs nouveaux circuits de puissance. Puisqu'ils ont à simuler le comportement du système pile à combustible / convertisseur et ce pendant un temps incalculable avant d'arriver à obtenir une solution correcte, un des critères de choix du modèle devrait être le temps de calcul.

Les modèles physiques qui sont développées par les électrochimistes ou par les mécaniciens sont difficilement utilisables pour des électriciens. Par ailleurs, ce genre de modèles utilise souvent comme méthode de résolution les éléments finis qui est non seulement gourmande en mémoire et en temps de calcul mais également incompatible avec des simulations de types circuits. C'est pourquoi le modèle de type empirique est préféré par les électriciens.

Le modèle empirique est simple et nécessite un faible temps de calcul. Cependant, l'inconvénient du modèle empirique est l'absence de prise en compte des phénomènes électrochimiques et de transport qui peuvent s'avérer utile dans la conception des circuits de puissance. Par ailleurs, puisque le modèle est basé sur des données mesurées, tous les paramètres physiques de la cellule ne peuvent être ajustés de manière à voir les différentes interactions entre la pile et l'électronique de puissance qui lui ait associée. Le but de ce travail est donc de combler cette lacune. Un modèle de type circuit qui intègre les mécanismes fondamentaux de la PEMFC et qui soit compatible avec des simulations de circuits est ici notre objectif.

Chapitre 2

Modèle de type circuit électrique équivalent

Ce chapitre présente le développement d'un modèle de type circuit équivalent de la pile PEMFC. Nous allons commencer par la mise en place des exigences du modèle en présentant une structure conceptuelle de la cellule. Cela garantit que nous avons la même image de la structure cellulaire dans nos esprits. La prochaine étape est la discussion sur le concept d'échange d'énergie qui sera largement utilisée à travers le chapitre. Nous allons expliciter le modèle de circuit partie par partie en commençant par les canaux, puis la couche de diffusion de gaz et la couche de réaction et en terminant par la membrane. Les modèles de circuit élémentaires ainsi obtenu seront ensuite combinés pour former le modèle mono-cellulaire. Enfin, le modèle de pile à 3 cellules sera présenté.

2.1 Description Physique d'une monocellule

Le modèle est quelque chose qui imite le système réel. La nature du modèle est d'avoir moins de détails que le système réel. Le niveau de simplification, qui a un effet direct sur la complexité du modèle, dépend de l'objectif ou de l'exigence du modèle visé. Alors que, la première étape de la modélisation est d'installer l'exigence et les critères du modèle. Dans cette thèse, nous cherchons à construire le modèle 1D d'une PEMFC qui révèle du comportement des transports de gaz dans les canaux, et dans les couches de diffusion. Le transport de l'eau dans la membrane et la réaction chimique doivent aussi être intégrés dans le modèle. Nous supposons que la température de la cellule est constante et que l'eau dans la cellule est seulement en phase gazeuse.

À partir de ces exigences, nous simplifions le système réel pour devenir une structure conceptuelle comme indiquée sur la figure 2-1. Le modèle d'une pile compose de 3 cellules (ou stack de 3 cellules), qui est notre objectif final, est considéré comme une version étendue de cette structure.

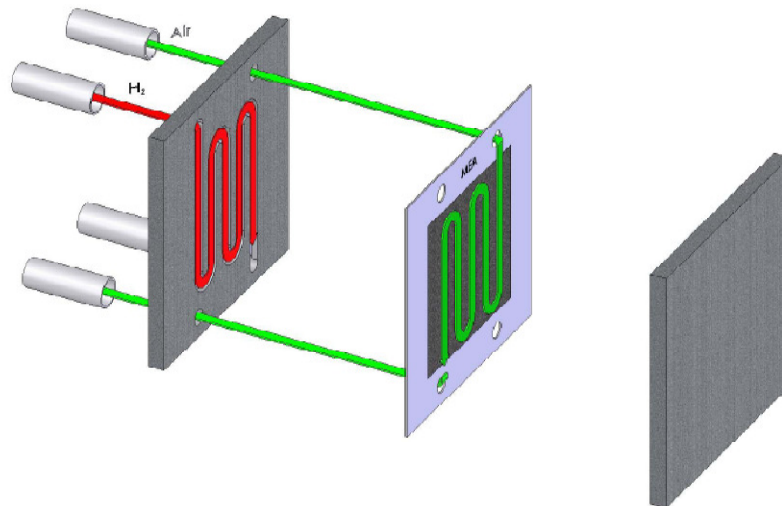


Figure 2-1 Structure d'une PEMFC utilisée dans ce travail

2.2 Analogie de système physique

Le concept d'échange d'énergie est très connu et utilisé dans la modélisation multidisciplinaire [56]. L'énergie circule d'un système à un l'autre via un port d'énergie, comme le montre la figure 2-2. Le transfert d'énergie a deux variables associées, l'une des variables représente le flux d'énergie et l'autre représente l'effort ou la force qui crée le flux. Le produit de ces deux variables est une puissance instantanée, c'est-à-dire la proportion d'énergie transférée via le transfert d'énergie par unité de temps.

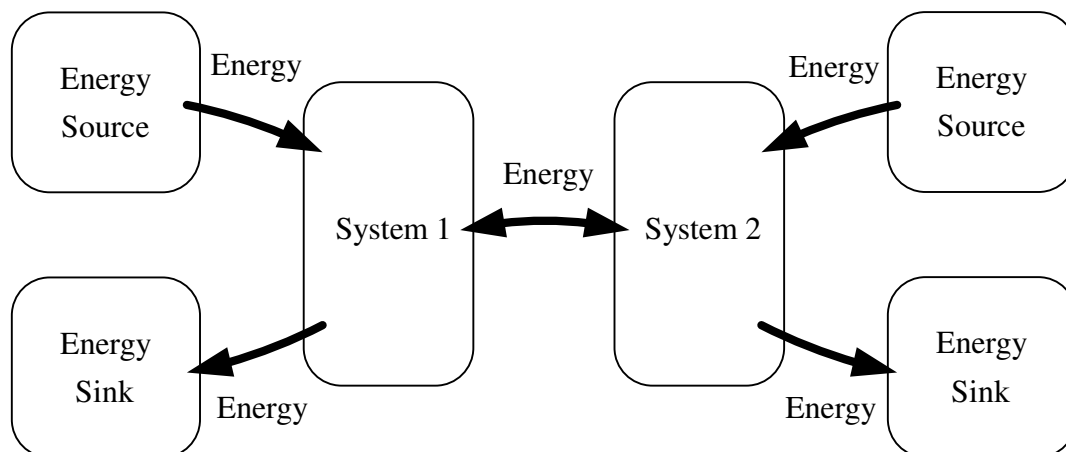


Figure 2-2 Représentation des systèmes physiques en éléments de transfert d'énergie

2.3 Modèle des canaux transportant les gaz

Selon le principe du transfert d'énergie et les variables du système, il est connu que la pression du fluide correspond un effort et le débit volumique à un flux. Le produit de ces deux variables est le travail fourni au système par unité de temps

2.3.1 Élément de dissipation

Dans un circuit électrique, la résistance est considérée comme un élément de dissipation d'énergie qui se traduit par une chute de tension le long de la trajectoire d'écoulement. De la même manière, l'énergie du fluide est également dissipée le long du parcours du fluide ce qui se traduit par une chute de pression dans le canal. Tout comme la loi d'Ohm pour les circuits électriques, la loi de Hagen-Poiseuille [57] décrit la relation entre la chute de pression à travers un canal de fluide, et le débit volumique du fluide, comme suit :

$$\Delta P = R_{ch} \cdot Q \quad (2-1)$$

où R_{ch} représente la résistance hydraulique du canal. Cette valeur dépend des propriétés du canal et du fluide.

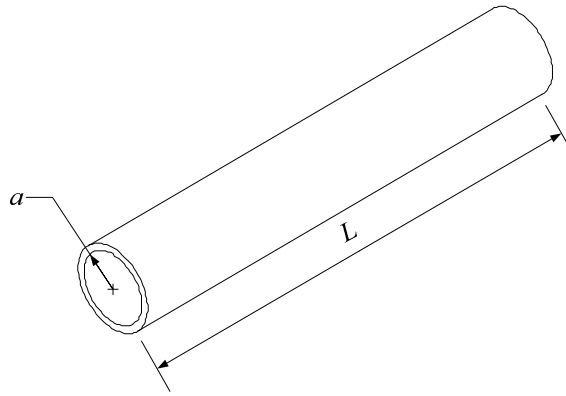


Figure 2-3 Section transversale circulaire d'un canal

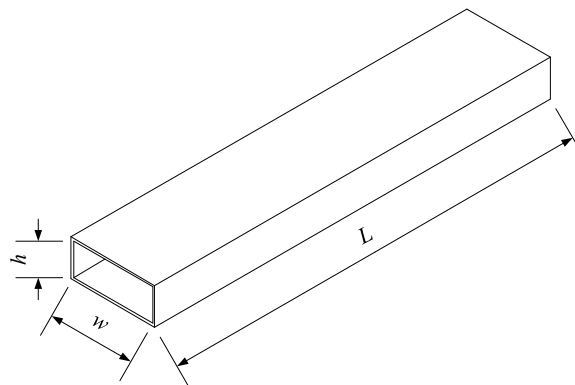


Figure 2-4 Section rectangulaire transversale d'un canal

Pour le système pile à combustible, il existe principalement deux types de canaux d'acheminement des gaz qui sont de sections circulaires ou rectangulaire. Un tube utilisé pour véhiculer les agents oxydants et réducteurs d'un périphérique à un autre sont généralement de section circulaire. Les canaux de section transversale rectangulaire peuvent être trouvés à l'intérieur de certains appareils, par exemple, une plaque distributrice de gaz d'une cellule de pile à combustible.

La résistance hydraulique d'un canal rectiligne circulaire est illustrée en figure 2-3 :

$$R_{ch} = \frac{8}{\pi} \eta L \frac{1}{a^4} \quad (2-2)$$

où a est le rayon, L est la longueur du canal, et η est la viscosité dynamique du fluide.

Pour le canal droit avec section rectangulaire comme le montre la figure 2-4, la résistance hydraulique est :

$$R_{ch} = \frac{12 \cdot \eta \cdot L}{1 - 0.63(h/w)} \cdot \frac{1}{h^3 \cdot w} \quad (2-3)$$

où h et w sont la hauteur et la largeur du canal. La formule est vérifiée pour $w > h$, si $w < h$, on peut faire une rotation du canal pour passer de w à h .

2.3.2 Elément d'accumulation de matière

Dans les systèmes électriques, l'élément de stockage de flux est un condensateur et sa capacité est définie comme suit :

$$C = \frac{d(\text{Charge électrique})}{d(\text{Potentiel})} \quad (2-4)$$

Ainsi la capacité équivalente pour le système de fluide est littéralement définie comme suit :

$$C_{ch} = \frac{d(\text{Volume du gaz})}{d(\text{Pression})} \quad (2-5)$$

Comme nous supposons que les parois des canaux sont rigides, le volume des canaux est constant, et les canaux se comportent comme un réservoir pressurisé. Pour un processus isotherme gazeux, où la température du gaz est constante :

$$\frac{dV_{gas}}{dP} = \frac{V_{ch}}{P} \quad (2-6)$$

Ainsi, la capacité de canal équivalente est définie par :

$$C_{ch} = \frac{V_{ch}}{P} \quad (2-7)$$

2.3.3 Modèle circuit de diffusion d'un gaz pur dans des canaux à section rectangulaire ou circulaire

Pour un canal rectiligne, l'effet capacitif des canaux peut apparaître indépendamment de la direction du fluide. Ainsi, la capacité pour le modèle de circuit devrait être placée au milieu de la résistance estimée du canal [47]. Cela peut être fait en divisant la résistance du canal en deux résistances ; chaque résistance représente la moitié de la résistance du canal (une résistance du canal de l'entrée ou de la sortie au point milieu du canal). Comme le fluide est défini comme un gaz pur, il n'y a qu'une seule pression dans le système et une seule capacité est nécessaire pour représenter la dynamique du système. La capacité équivalente est connectée au pseudo-point milieu comme le montre la figure 2-5. A noter que le même circuit peut être utilisé dans le cas d'un mélange gazeux, si le pourcentage de chaque élément du mélange reste constant le long du tube.

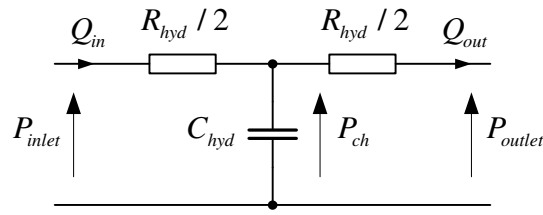


Figure 2-5 Circuit équivalent d'un canal rectiligne

2.3.4 Modèle circuit de canaux de transports à section rectangulaire d'un mélange gazeux

Les gaz qui s'écoulent dans les canaux de pile à combustible de type PEM sont généralement des mélanges gazeux. Du côté cathode, le gaz est le plus souvent de l'air humidifié. Côté anode, bien que l'on alimente en hydrogène pur à l'entrée de la cellule, le gaz à l'intérieur de celle-ci est en réalité un mélange d'hydrogène et de vapeur d'eau qui provient de la diffusion de l'eau de la cathode vers l'anode à travers la MEA. Lorsque le gaz a passé l'entrée du canal, le gaz alimente la couche de diffusion (GDL) via un canal spécial qui s'appelle canal d'écoulement. Le canal d'écoulement a seulement trois parois rigides. La quatrième face correspond à la surface de la couche de diffusion, qui permet le passage des gaz au travers. Chaque espèce du mélange de gaz est consommée ou produite dans le canal à des rythmes différents. Cela affecte clairement le rapport entre chaque espèce dans le canal, en particulier à bas débit. Par conséquent, le modèle essentiel du canal présenté dans la figure 2-5 n'est pas suffisant pour représenter le canal d'écoulement et le canal qui le précède.

Nous allons commencer à développer un modèle de canal plus approprié en tenant compte des canaux côté anodique. Nous supposons que le gaz d'entrée est un mélange d'hydrogène et de vapeur d'eau. Toutefois, avant de démarrer, les deux espèces hydrogène et vapeur d'eau ne sont pas entrées dans le canal, il semble être faux de supposer que le canal est complètement vide, c'est-à-dire sous vide. Dans la plupart des cas, les canaux à l'anode sont généralement remplis d'air ou d'azote avant le démarrage. Deux solutions à ce problème sont : 1) Éviter la période de démarrage en supposant que l'hydrogène est déjà présent dans le canal, 2) introduire la troisième espèce dans le modèle. Dans ce travail, nous supposons que l'azote ne participe nullement à la réaction, un gaz non réactif, et occupe complètement le canal avant de démarrer la cellule.

A partir de des hypothèses que nous avons faites, nous sommes maintenant prêts à poser les équations régissant le modèle du canal à l'anode. Nous considérons en premier lieu que la pression au milieu du canal P_{ch} est défini comme suit :

$$P_{ch} = p_{H_2(ch)} + p_{H_2O(ch)} + p_{N_2(ch)} \quad (2-8)$$

Chaque pression partielle est une conséquence du débit total de chaque espèce et de la capacité du canal. Les relations peuvent s'écrire de la manière suivante :

$$\frac{d}{dt} P_{H_2(ch)} = \frac{Q_{H_2(stored)}}{C_{ch}} \quad (2-9)$$

$$\frac{d}{dt} P_{H_2O(ch)} = \frac{Q_{H_2O(stored)}}{C_{ch}} \quad (2-10)$$

$$\frac{d}{dt} P_{N_2(ch)} = \frac{Q_{N_2(stored)}}{C_{ch}} \quad (2-11)$$

où les débits totaux remplissant le canal s'écrivent :

$$Q_{H_2(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{H_2(in)} - \frac{P_{outlet}}{P_{ch}} Q_{H_2(out)} \quad (2-12)$$

$$Q_{H_2O(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{H_2O(in)} - \frac{P_{outlet}}{P_{ch}} Q_{H_2O(out)} \quad (2-13)$$

$$Q_{N_2(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{N_2(in)} - \frac{P_{outlet}}{P_{ch}} Q_{N_2(out)} \quad (2-14)$$

Comme il est difficile de combiner la dynamique des trois tensions couplées en un seul condensateur, nous essayons de remplacer le condensateur dans le modèle de la figure 2-5 par une source de tension dépendante comme le montre la figure 2-6.

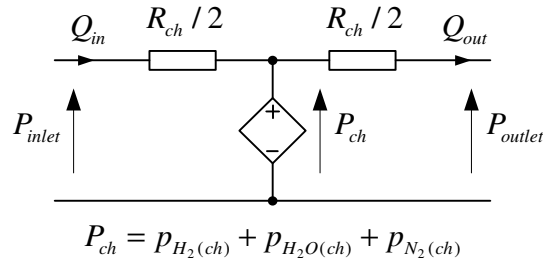


Figure 2-6 Modèle modifié du circuit équivalent du canal

Le débit d'entrée de chaque espèce, est manifestement proportionnel au débit du mélange gazeux entrant, Q_{in} , et la fraction molaire de chaque espèce à l'entrée. Nous supposons que les proportions de chaque espèce constituant le mélange gazeux à l'entrée sont contrôlées par un dispositif externe, et donc la fraction molaire de chaque espèce est constante. Nous pouvons écrire :

$$Q_{H_2(in)} = x_{H_2(in)} \cdot Q_{in} \quad (2-15)$$

$$Q_{H_2O(in)} = x_{H_2O(in)} \cdot Q_{in} \quad (2-16)$$

$$Q_{N_2(in)} = x_{N_2(in)} \cdot Q_{in} \quad (2-17)$$

Puisque la somme de toutes les fractions molaires est égal à un, Q_{in} s'écrit également :

$$Q_{in} = Q_{H_2(in)} + Q_{H_2O(in)} + Q_{N_2(in)} \quad (2-18)$$

et en fonction des pressions comme :

$$Q_{in} = \left(\frac{P_{inlet} - P_{ch}}{R_{ch}/2} \right) \cdot \left(\frac{P_{inlet} + P_{ch}}{2P_{inlet}} \right) \quad (2-19)$$

De la même manière, pour la sortie des gaz :

$$Q_{H_2(out)} = x_{H_2(ch)} \cdot Q_{out} \quad (2-20)$$

$$Q_{H_2O(out)} = x_{H_2O(ch)} \cdot Q_{out} \quad (2-21)$$

$$Q_{N_2(out)} = x_{N_2(ch)} \cdot Q_{out} \quad (2-22)$$

et :

$$Q_{out} = Q_{H_2(out)} + Q_{H_2O(out)} + Q_{N_2(out)} \quad (2-23)$$

Le débit total du gaz en sortie s'écrit :

$$Q_{out} = \left(\frac{P_{ch} - P_{outlet}}{R_{ch}/2} \right) \cdot \left(\frac{P_{ch} + P_{outlet}}{2P_{outlet}} \right) \quad (2-24)$$

Cependant, les fractions molaires de chaque espèce dans le canal ne sont pas nécessairement constantes. Ainsi, nous définissons les fractions molaires de chaque espèce dans le canal de la manière suivante :

$$x_{H_2(ch)} = \frac{P_{H_2(ch)}}{P_{ch}} \quad (2-25)$$

$$x_{H_2O(ch)} = \frac{P_{H_2O(ch)}}{P_{ch}} \quad (2-26)$$

$$x_{N_2(ch)} = \frac{P_{N_2(ch)}}{P_{ch}} \quad (2-27)$$

Les équations dérivées décrivent les mécanismes de transport de gaz dans le canal, et maintenant nous sommes prêts à construire le nouveau modèle de circuit équivalent. Les équations (2-9), (2-12), (2-15), et (2-20) aboutissent au modèle de sous-circuit représenté dans la figure 2-7. De la même manière, les équations (2-10), (2-13), (2-16) et (2-21) conduisent à un modèle circuit représenté en figure 2-8, et les équations (2-11), (2-14), (2-17) et (2-22) au modèle du sous-circuit représenté figure 2-9. Le modèle multi-espèces d'un gaz, sous forme de circuit équivalent de l'ensemble du canal côté anode, se compose des sous-circuits présentés dans les figures 2-6 à 2-9, figure 2-10.

Le même processus peut être appliqué aux canaux côté cathodique. Nous avons simplement changé la première espèce d' H_2 en O_2 . On obtient alors le modèle équivalent du canal d'écoulement (figure 2-11).

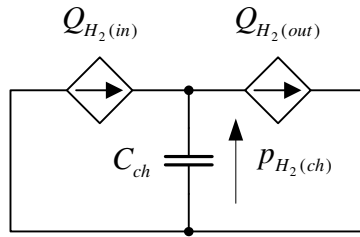


Figure 2-7 Modèle dynamique d'une portion de canal coté H_2

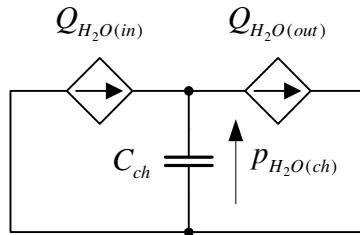


Figure 2-8 Modèle dynamique d'une portion de canal pour la circulation d' H_2O

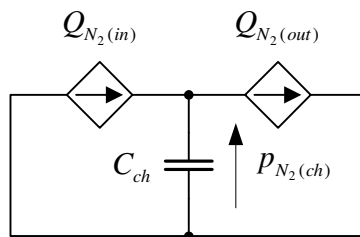


Figure 2-9 Modèle dynamique d'une portion de canal pour la circulation d' N_2

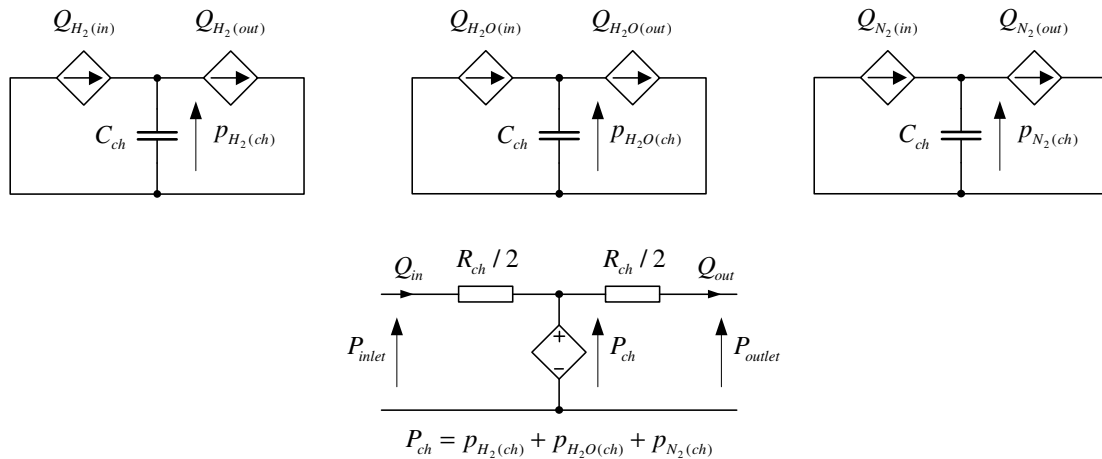


Figure 2-10 Modèle circuit complet d'un canal d'écoulement côté anode

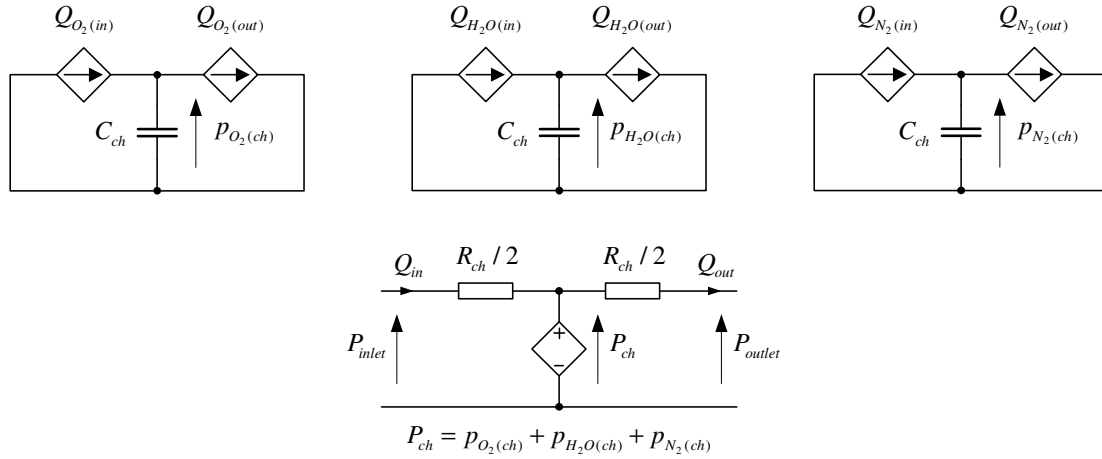


Figure 2-11 Modèle circuit complet d'un canal d'écoulement côté cathode

L'idée du modèle de canal multi-espèces peut être facilement appliquée au canal d'écoulement. Nous avons mentionné plus tôt que le canal d'écoulement est un canal spécial. Ce canal est un petit canal intégré à la surface d'une plaque de graphite et recouvert par la couche de diffusion. Les principales fonctions de ce canal particulier sont d'acheminer le gaz correspondant à la surface de la couche de diffusion de manière uniforme et de recueillir ou de transmettre des électrons à partir ou vers le site de réaction, qui se situe à l'interface membrane couche de diffusion.

La principale différence entre un canal normal et un canal d'écoulement est que d'un côté du canal d'écoulement de champ est une paroi poreuse. La paroi poreuse permet à chaque espèce du mélange gazeux d'entrer ou de sortir du canal en même temps. Ainsi, pour adapter le modèle circuit d'un canal droit à un canal d'écoulement, nous devons modifier les équations (2-12), (2-13) et (2-14) comme suit :

$$Q_{H_2(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{H_2(in)} - \frac{P_{outlet}}{P_{ch}} Q_{H_2(out)} - Q_{H_2(GDL)} \quad (2-28)$$

$$Q_{H_2O(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{H_2O(in)} - \frac{P_{outlet}}{P_{ch}} Q_{H_2O(out)} - Q_{H_2O(GDL)} \quad (2-29)$$

$$Q_{N_2(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{N_2(in)} - \frac{P_{outlet}}{P_{ch}} Q_{N_2(out)} - Q_{N_2(GDL)} \quad (2-30)$$

Le modèle circuit peut être modifié en ajoutant simplement une source de courant pour chaque capacité de canal. La source de courant représente une quantité d'espèce qui sort du canal en direction des couches de diffusion. Le modèle circuit de canal d'écoulement pour l'anode et la cathode est présenté respectivement en figure 2-12 et 2-13.

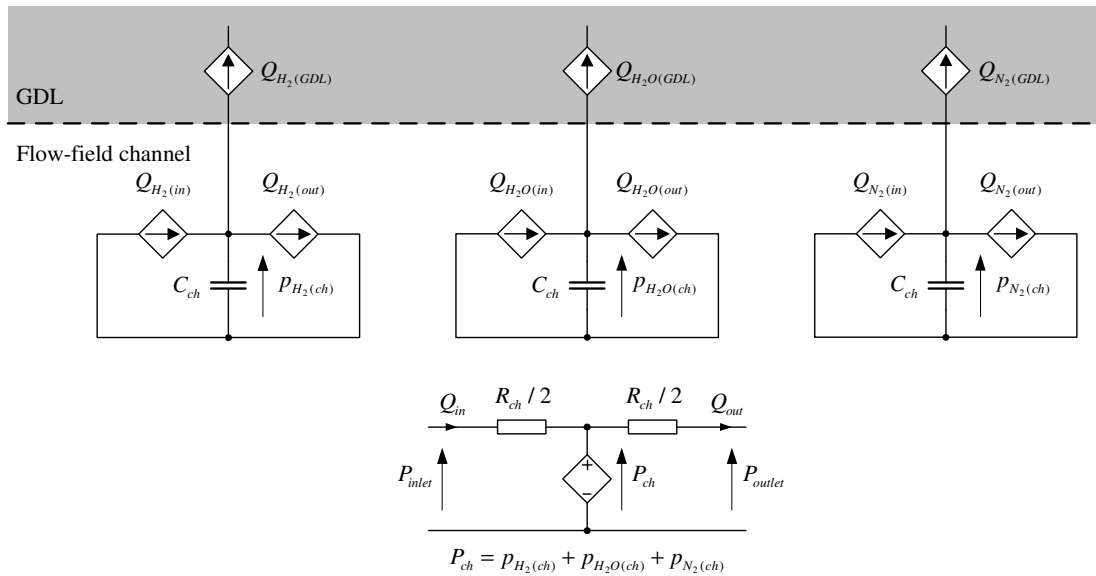


Figure 2-12 Modèle circuit complet d'un canal d'écoulement côté anode

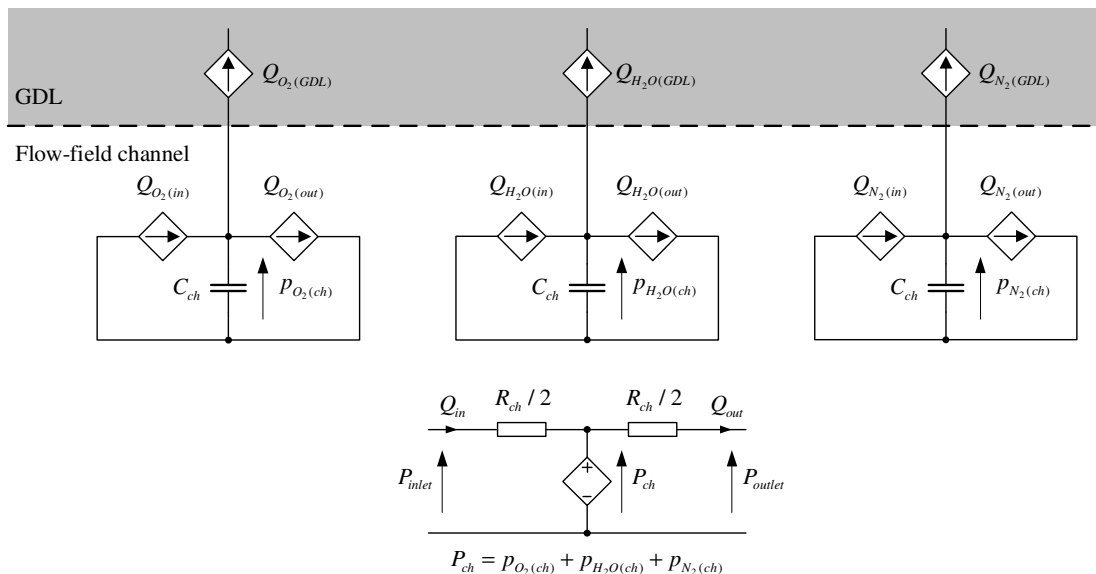


Figure 2-13 Modèle circuit complet d'un canal d'écoulement côté cathode

2.4 Modèle de la couche de diffusion

La couche de diffusion (GDL) est située entre la plaque distributrice de gaz et la couche de réaction. La GDL est faite à partir de matériaux poreux, à travers laquelle les gaz réactifs diffusent. L'intérieur de la GDL est en contact avec la couche de réaction où se produit l'oxydation ou la réduction. Ce paragraphe sera axé d'abord sur la mécanique de diffusion se déroulant dans le GDL, puis sur le modèle de circuit équivalent.

2.4.1 Modèle circuit des couches de diffusion issu de l'équation de Stefan-Maxwell

Maintenant, nous allons établir des circuits à partir de la diffusion de Stefan-Maxwell. Puisque le transport se fait par diffusion, nous supposons que la pression totale le long de la couche de diffusion est constante. La prise en compte du transport convectif sera traitée un peu plus loin.

Selon le concept d'échange d'énergie dans les systèmes physiques, il semblerait que la variable d'effort est la fraction molaire x_i , et la variable de flux est le flux molaire \mathbf{N}_i .

Cependant, le produit de la fraction molaire et du flux molaire est la quantité qui a une autre unité que celle de la puissance. Pour faire une analogie correcte du circuit, il faut sélectionner une paire de variables plus appropriées. Comme nous savons que des processus de diffusion sont impliqués dans le déplacement des molécules du fluide, les variables du système sont censés être la pression et le débit volumique. Ainsi, nous modifions l'équation de Stefan-Maxwell de manière à faire apparaître les variables mentionnées précédemment.

De la forme standard de l'équation :

$$\frac{d}{dz} x_i = \sum_{j=1}^n \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{c_t D_{ij}} \quad (2-31)$$

qui est dérivée de :

$$\frac{d}{dz} p_i = P \sum_{j=1}^n \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{c_t D_{ij}} \quad (2-32)$$

avec :

$$D_{ij} = \frac{P}{f_{ij}} \quad (2-33)$$

et :

$$x_i = \frac{p_i}{P} \quad (2-34)$$

l'équation (2-31) peut être réécrite :

$$\frac{d}{dz} p_i = \sum_{j=1}^n \left\{ f_{ij} \cdot \left(\left(\frac{p_i}{P} \right) \cdot \left(\frac{\mathbf{N}_j}{c_t} \right) - \left(\frac{p_j}{P} \right) \cdot \left(\frac{\mathbf{N}_i}{c_t} \right) \right) \right\} \quad (2-35)$$

Nous avons maintenant la pression partielle qui est la variable d'effort du système cible.

Comme (\mathbf{N}_i/c_t) représente le débit volumique de l'espèce i par unité de surface, le débit volumique du système concerné est obtenu en multipliant les termes par la surface de diffusion comme suit :

$$\frac{d}{dz} p_i = \sum_{j=1}^n \left\{ f_{ij} \cdot \left(\left(\frac{p_i}{P} \right) \cdot \left(\frac{A}{A} \right) \cdot \left(\frac{\mathbf{N}_j}{c_t} \right) - \left(\frac{p_j}{P} \right) \cdot \left(\frac{A}{A} \right) \cdot \left(\frac{\mathbf{N}_i}{c_t} \right) \right) \right\} \quad (2-36)$$

Ou :

$$\frac{d}{dz} p_i = \sum_{j=1}^n \left\{ \left(\frac{f_{ij}}{A} \right) \cdot \left(\left(\frac{p_i}{P} \right) \cdot \left(\frac{A \cdot \mathbf{N}_j}{c_t} \right) - \left(\frac{p_j}{P} \right) \cdot \left(\frac{A \cdot \mathbf{N}_i}{c_t} \right) \right) \right\} \quad (2-37)$$

Le terme $\left(\frac{A \cdot \mathbf{N}_i}{c_t} \right)$ correspond au débit volumique de l'espèce i, ce qui peut être vérifié en considérant ses unités :

$$\text{unit} \left(\frac{A \cdot \mathbf{N}_x}{c_t} \right) = [\text{m}^2] \cdot \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right] \cdot \left[\frac{\text{m}^3}{\text{mol}} \right] = \left[\frac{\text{m}^3}{\text{s}} \right] \quad (2-38)$$

Nous pouvons également modifier la distance de diffusion pour être de valeur unitaire, notée η , où la valeur de base est l'épaisseur de la couche de diffusion, qui est notée l :

$$\eta = (z - z_0) / l \quad (2-39)$$

et où sa dérivée est :

$$dz = l \cdot d\eta \quad (2-40)$$

En substituant la dérivée η dans l'équation modifiée qui devient :

$$\frac{d}{d\eta} p_i = \sum_{j=1}^n \left\{ \left(f_{ij} \cdot \frac{l}{A} \right) \cdot \left(\left(\frac{p_i}{P} \right) \cdot \left(\frac{A \cdot \mathbf{N}_j}{c_t} \right) - \left(\frac{p_j}{P} \right) \cdot \left(\frac{A \cdot \mathbf{N}_i}{c_t} \right) \right) \right\} \quad (2-41)$$

Définissons :

$$R_{ij} = \left(f_{ij} \cdot \frac{l}{A} \right) \quad (2-42)$$

et :

$$Q_x = \left(\frac{A \cdot \mathbf{N}_x}{c_t} \right) \quad (2-43)$$

l'équation précédente devient :

$$\frac{d}{d\eta} p_i = \sum_{j=1}^n \left\{ \frac{R_{ij}}{P} \cdot (p_i \cdot Q_j - p_j \cdot Q_i) \right\} \quad (2-44)$$

Si l'on considère que les pressions partielles sont équivalentes à des tensions et les débits volumiques à des courants, le circuit équivalent est alors celui présenté en figure 2-14.

Nous continuons de modifier le circuit par la théorie de la transformation de source et si nous supposons que la pression totale le long du canal est constante, seules (n-1) équations de Stefan-Maxwell sont indépendantes. Le modèle de circuit de la figure 2-14 peut être simplifié comme indiqué dans la figure 2-15. Un modèle de circuit équivalent pour un système de diffusion de 3 espèces peut être construit par le même procédé.

Puisque les paramètres du circuit dépendent des pressions partielles et que celles-ci ont tendance à changer le long du parcours de diffusion, des circuits équivalents avec des paramètres fixes ne sont valables que si Δp_i est petit. Une solution consiste à diviser la couche de diffusion en sous-couches comme le montre la figure 2-16. Cela permet ainsi de mettre à jour les paramètres du circuit tout au long du parcours de diffusion, et d'obtenir des résultats plus précis.

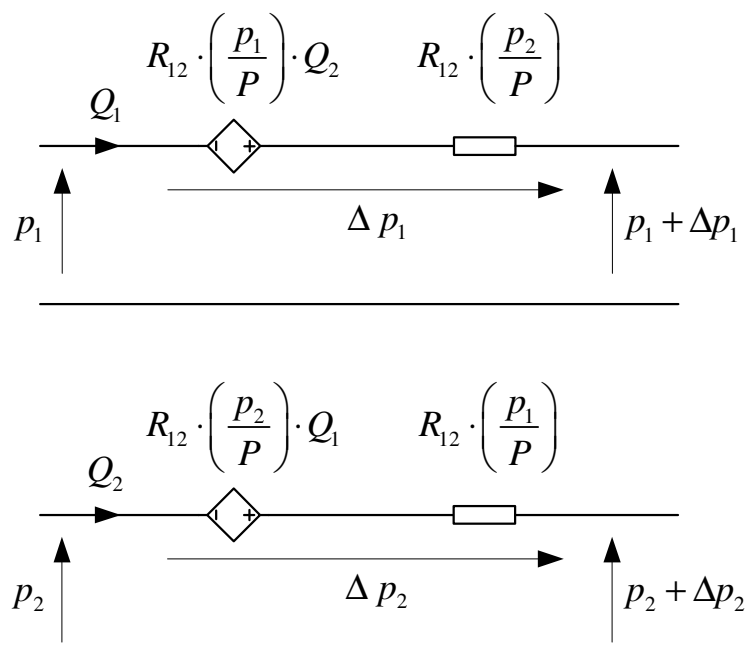


Figure 2-14 Modèle de circuit équivalent issu de la modification de l'équation de diffusion de Stefan-Maxwell

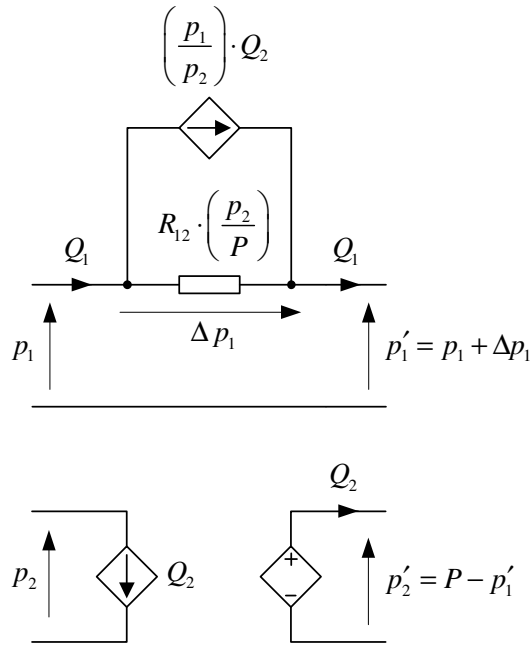


Figure 2-15 Circuit simplifié pour 2 espèces

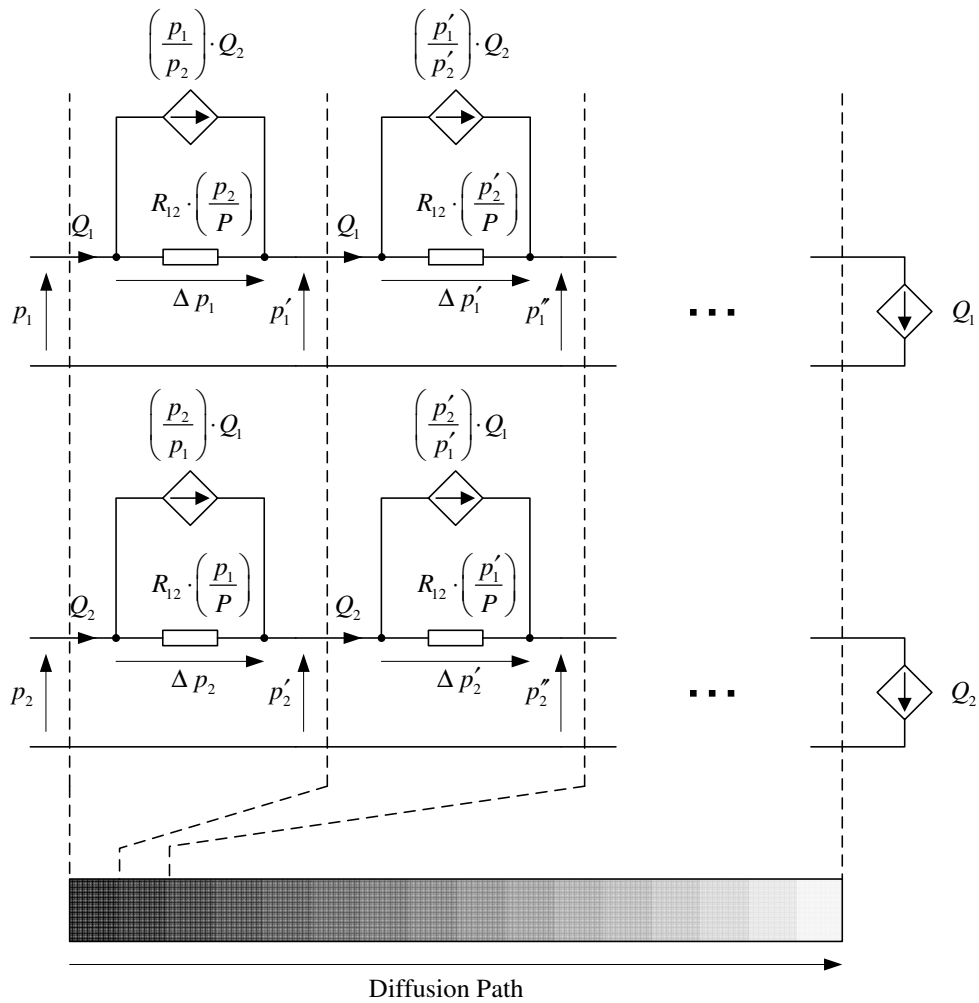


Figure 2-16 Subdivision possible de la couche de diffusion en sous-couches

2.4.2 Elément d'accumulation des matière dans la couche de diffusion

Tout comme pour la modélisation du canal, une capacité équivalente dans les couches de diffusion peut être calculée à partir de l'espace vide lié au volume géométrique, et à la porosité du milieu comme suit :

$$C_{GDL_total} = \varepsilon \frac{V_{GDL}}{P} \quad (2-45)$$

En se reportant au modèle de circuit proposé pour la couche de diffusion qui fractionne celle-ci en plusieurs sous-couches, auxquelles est associé le circuit équivalent et afin de placer la capacité équivalente dans chaque circuit de sous-couche, celle-ci doit être calculée en fonction de la géométrie de la sous-couche. Ainsi :

$$C_{GDL} = \varepsilon \frac{A_{GDL} L_{sub-layer}}{P} \quad (2-46)$$

où A_{GDL} est la section transversale de la couche de diffusion et $L_{sub-layer}$ est l'épaisseur de chaque sous-couche. Le condensateur équivalent peut être placé entre chaque sous-couche comme indiqué en figure 2-17.

2.4.3 Diffusion de Knudsen dans les couches de diffusion

En régime de Knudsen, le transport de gaz est contrôlé par les collisions successives des particules avec la paroi de la couche de diffusion. Autrement dit, les collisions des particules les unes avec les autres n'est pas le processus dominant dans le transport du gaz :

$$\frac{d}{dz} c_i = -\frac{1}{D_{iK}} \mathbf{N}_i \quad (2-47)$$

où c_i et \mathbf{N}_i sont la concentration molaire et le flux de diffusion des espèces, et D_{iK} est le coefficient de diffusion de Knudsen. Le coefficient de diffusion de Knudsen est lié à la vitesse des molécules, et une constante K_o représente la géométrie des pores :

$$D_{iK} = K_o v_i \quad (2-48)$$

La constante K_o est liée à la taille et à la forme des pores. Elle peut être estimée par l'équation (2-49), toutefois, il est préférable de les déterminer de manière expérimentale. :

$$K_o = \frac{2}{3} \frac{\varepsilon r}{\tau} \quad (2-49)$$

La vitesse des molécules se calcule de la manière suivante :

$$\mathbf{v}_i = \sqrt{\frac{8k_B T}{\pi m_i}} \quad (2-50)$$

où k_B est la constante de Boltzmann et égale à 1.38×10^{-23} J/K, T est la température absolue, et m_i est la masse de la molécule de l'espèce i .

2.4.4 Modèle circuit de la diffusion de Knudsen

Puisque le régime de Knudsen suppose aucune collision entre les molécules de gaz, et la quantité de mouvement transférée à la paroi poreuse a tout simplement disparu du système, le modèle de circuit se réduit à une résistance pour chaque espèce. Pour être conforme au modèle de circuit proposé de la diffusion de Stefan-Maxwell, où le débit volumique est équivalent à un courant dans le circuit, nous devons modifier l'équation de diffusion de Knudsen comme suit.

Nous allons commencer avec l'équation de diffusion de Knudsen mentionné, qui est :

$$\frac{d}{dz} c_i = -\frac{1}{D_{iK}} \mathbf{N}_i \quad (2-51)$$

Puisque :

$$c_i = \frac{p_i}{RT} \quad (2-52)$$

avec l'hypothèse que la température dans chaque sous-couche est constante, nous pouvons écrire :

$$\frac{d}{dz} p_i = -\frac{RT}{D_{iK}} \mathbf{N}_i \quad (2-53)$$

En incorporant l'aire de la surface, A , et la concentration molaire total, c_t , dans l'équation (2-53), il vient :

$$\frac{d}{dz} p_i = -\frac{RT}{D_{iK}} \left(\frac{A}{A} \right) \left(\frac{c_t}{c_t} \right) \mathbf{N}_i \quad (2-54)$$

puis :

$$\frac{d}{dz} p_i = -P \left(\frac{1}{D_{iK} A} \right) \left(\frac{\mathbf{N}_i A}{c_t} \right) \quad (2-55)$$

La dernière modification consiste à ramener la dérivée par unité de longueur dans le système d'équations de Stefan-Maxwell par :

$$\eta = (z - z_0) / l \quad (2-56)$$

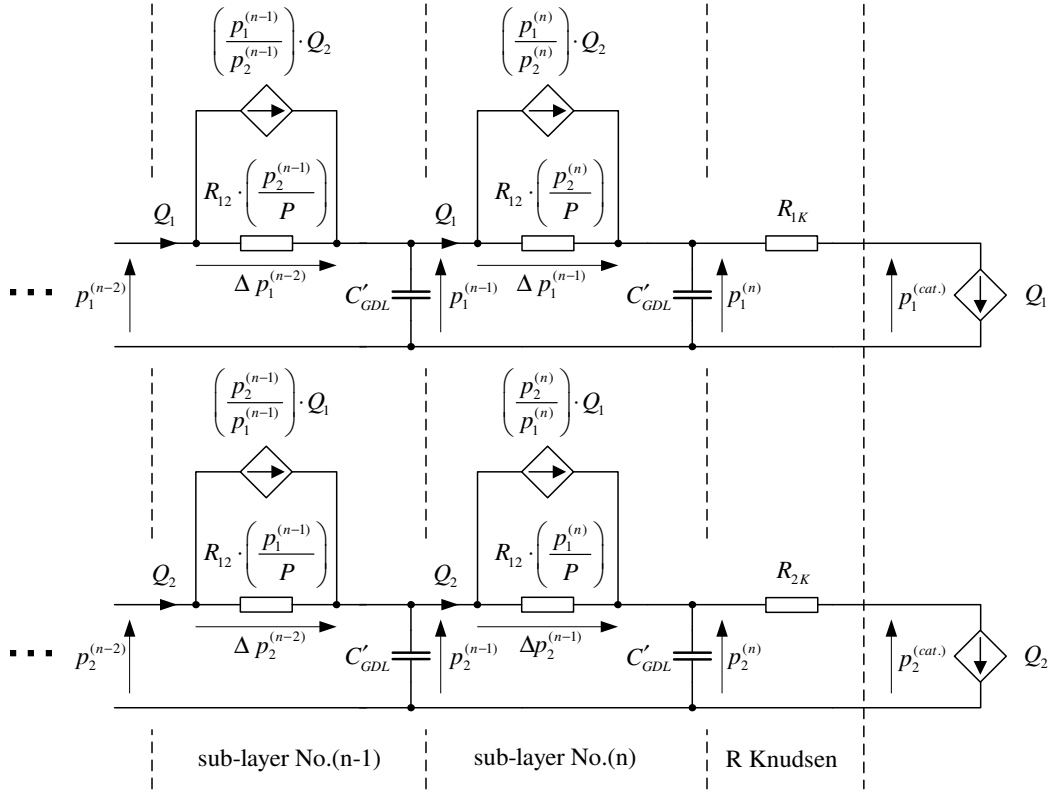


Figure 2-17 Modèle de circuit équivalent de la diffusion de Knudsen avec une résistance

Il en résulte

$$\frac{d}{d\eta} p_i = -P \left(\frac{l}{D_{iK} A} \right) \left(\frac{N_i A}{c_t} \right) \quad (2-57)$$

En comparant les variables du modèle circuit de Stefan-Maxwell, nous définissons :

$$R_{iK} = P \frac{l}{D_{iK} A} = f_{iK} \frac{l}{A} \quad (2-58)$$

où R_{iK} est une résistance équivalente de la diffusion de Knudsen. La valeur effective de la résistance du circuit varie en fonction de la pression totale.

Mason et Evans [58, 59] ont suggéré que les effets des transferts mouvement dans chaque régime devrait être combinés de manière additive, nous plaçons donc la résistance équivalente de diffusion de Knudsen en série avec le circuit de Stefan-Maxwell.

Puisque la couche poreuse est très fine côté couche de diffusion, il conviendrait d'ajouter la résistance équivalente de diffusion de Knudsen en série avec la dernière

sous-couche ou à l'intérieur de quelques sous-couches du modèle de circuit équivalent des couches de diffusion. La figure 2-17 montre le modèle de circuit GDL où la résistance de diffusion de Knudsen équivalente est en cascade avec la dernière sous-couche de circuit.

2.4.5 Combinaison de la diffusion et de la convection dans le modèle circuit de la couche de diffusion

Le modèle de circuit proposé dans le paragraphe précédent ne représente que le transport en mode de diffusion. En d'autres termes, la pression totale est supposée constante le long de la couche de diffusion. La différence de pression totale est considérée comme un moteur pour la convection. La même idée pour le transport de gaz dans un canal d'écoulement, qui est le transport convectif, est appliquée à la couche de diffusion. Le débit volumique de convection dans la couche de diffusion est calculé grâce à la relation suivante

$$Q_{conv} = \left(\frac{P - P'}{R_{conv}} \right) \cdot \left(\frac{P + P'}{2P'} \right) \quad (2-59)$$

Puisque l'information de la résistance hydraulique ou de convection de la couche de diffusion est restreinte, nous approximons la résistance de couche de diffusion par le modèle tubulaire de canal avec une correction de Bruggeman :

$$R_{conv} = \frac{\varepsilon^{1.5}}{n_{pore}} \left(\frac{8}{\pi} \eta L \frac{1}{a_{pore}^4} \right) \quad (2-60)$$

où a_{pore} est le rayon moyen des pores de la couche de diffusion, n_{pore} est le nombre équivalent de pores, calculé à partir de l'aire de la section transversale, A , de la couche de diffusion :

$$n_{pore} = \frac{A}{\pi \cdot a_{pore}^2} \quad (2-61)$$

Le flux de gaz dans ce mode de transport peut être introduit dans le circuit via les sources de courant. Puisque le flux de convection et de diffusion remplissent les mêmes pores de la couche de diffusion, Q_{conv} et Q_{diff} sont regroupés pour charger la même C_{GDL} . La combinaison du débit volumique de diffusion et de convection est considérée comme le débit volumique total.

Un couple de sources courant-tension contrôlées est utilisé pour prévenir l'effet de la différence de pression totale sur les circuits de diffusion. Le circuit équivalent modifié du transport dans la couche de diffusion est présenté dans la figure 2-18. La même idée peut être appliquée pour un système de trois espèces.

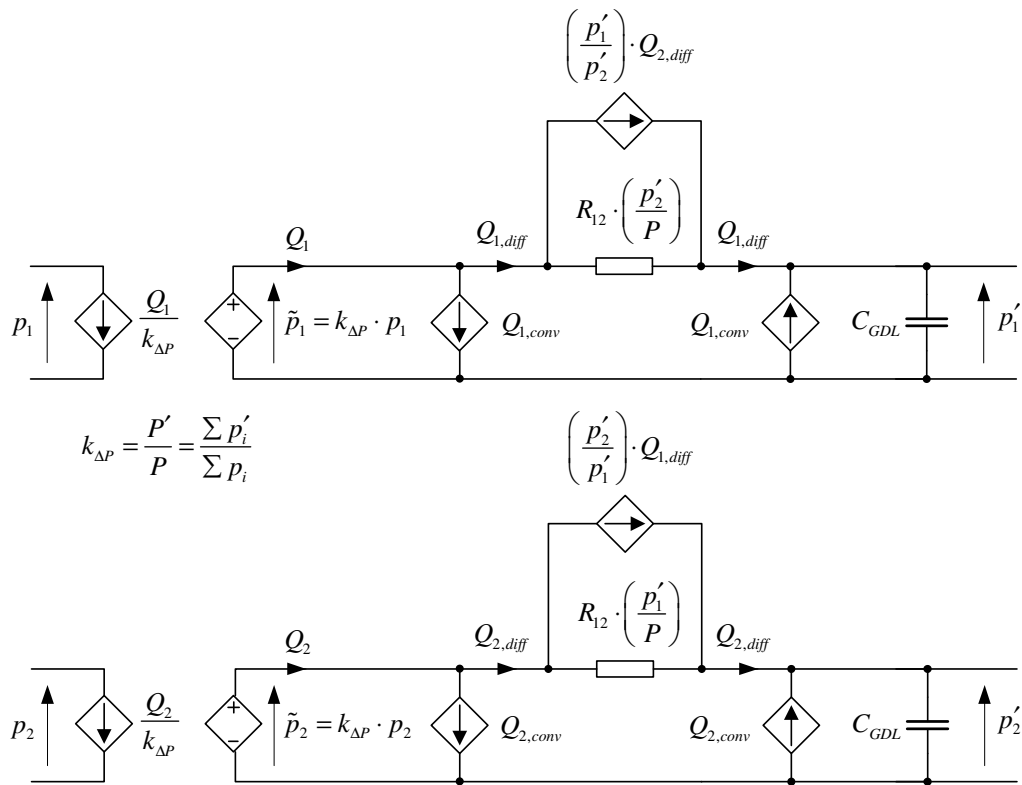


Figure 2-18 Modèle de transport pour un couple d'espèce

2.5 Modèle de la couche de réaction

Les couches de réaction des PEMFC sont des couches minces situées entre la couche de diffusion et la membrane. Les réactions électrochimiques se produisent dans ces couches. Le platine (Pt) est le meilleur catalyseur de l'anode et la cathode pour les PEMFC. Les nanoparticules de platines intégrés à la poudre de carbone sont réparties sur la face intérieure de la couche de diffusion pour former la couche de réaction.

L'hydrogène est oxydé à l'anode (HOR) et l'oxygène réduit à la cathode (ORR).

Les modèles de circuit proposés porteront sur les réactions électrochimiques et l'effet de la capacité de couche double à l'interface membrane-électrodes.

2.5.1 Réaction électrochimique à l'anode

La réaction à l'anode est l'oxydation de l'hydrogène et s'écrit :



Le potentiel thermodynamique ou réversible de la réaction peut être calculé à partir de l'équation de Nernst :

$$E_{r,anode} = E_{r,anode}^{\ominus} + \frac{R \cdot T}{F} \cdot \ln \left(\frac{a_{H_2}^{1/2}}{a_{H^+}} \right) \quad (2-63)$$

où E_r^{\ominus} est le potentiel de référence, dans les conditions standards $E_r^{\ominus} = 0 \text{ V}$ par définition, R est la constante des gaz parfait, T la température, F la constante de Faraday, a_{H_2} et a_{H^+} sont respectivement les activités de l'hydrogène et des protons.

La cinétique de réaction est exprimée par l'équation de Butler-Volmer :

$$j = j_{0,anode} \left(e^{\frac{\alpha F}{RT} \eta} - e^{-\frac{(1-\alpha) F}{RT} \eta} \right) \quad (2-64)$$

où j est la densité de courant, $j_{0,anode}$ est la densité de courant d'échange, α est le coefficient de transfert de charge, et η est la surtension.

2.5.2 Réaction électrochimique à l'anode

La réaction à la cathode est la réduction de l'oxygène et s'écrit :



Tout comme à la cathode, le potentiel réversible s'obtient par :

$$E_{r,cathode} = E_{r,cathode}^{\ominus} + \frac{R \cdot T}{4F} \cdot \ln \left(\frac{a_{H^+}^4 a_{O_2}}{a_{H_2O}^2} \right) \quad (2-66)$$

Ainsi, la cinétique de la réaction est écrite comme suit :

$$j = j_{0,cathode} \left(e^{\frac{\beta 4F}{RT} \eta} - e^{-\frac{(1-\beta) 4F}{RT} \eta} \right) \quad (2-67)$$

où β est le coefficient de transfert de charge pour cette réaction. Notez que les puissances des exponentielles sont multipliées par quatre, ce qui correspond au nombre d'électrons transférés lors de la réaction.

2.5.3 Potentiel réversible de l'ensemble de la cellule

Sachant que la réaction à l'anode et la cathode sont en série, le potentiel réversible de la cellule entière se calcule de la manière suivante :

$$E_r = E_{r,cathode} + E_{r,anode} \quad (2-68)$$

$$E_r = E_{r,cathode}^{\ominus} + E_{r,anode}^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{a_{H_2} a_{O_2}^{1/2} a_{H^+}^2}{a_{H_2O} a_{H^+}^2} \right) \quad (2-69)$$

Puisque $E_{r,anode}^{\ominus}$ est égal à zéro par définition et que la membrane entre la couche de réaction est très fine si bien que les protons se déplacent d'un côté à l'autre en rien de temps, l'équation du potentiel réversible de la cellule se réduit à :

$$E_r = E_r^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}} \right) \quad (2-70)$$

Où :

$$E_r^{\ominus} = E_{r,cathode}^{\ominus} + E_{r,anode}^{\ominus} \quad (2-71)$$

La forme la plus commune de l'équation est :

$$E_r = E_r^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \right) \quad (2-72)$$

qui s'obtient en supposant que les pressions des mélanges gazeux des réactants sont identiques et que tous les gaz impliqués dans la réaction se comportent comme des gaz parfaits.

2.5.4 Effet de double couche aux électrodes

L'effet de double couche est le phénomène à l'interface électrode/électrolyte [60]. Un modèle simple de capacité de double couche est proposé par Helmholtz. Il considère la séparation des charges opposées comme deux couches de charges parfaites [61]. La capacité par unité de surface selon Helmholtz est définie par :

$$C_H = \frac{\epsilon_r \epsilon_0}{d} \quad (2-73)$$

où ϵ_r est la permittivité relative de la solution ϵ_0 permittivité de l'espace vide et d est la distance entre les plaques chargées.

2.5.5 Modèle circuit de la couche de réaction

La séparation des réactions anodique et cathodique introduit l'activité du proton dans la membrane dans les équations de potentiels réversibles à l'anode et à la cathode. En combinant les potentiels réversibles à l'anode et à la cathode, l'activité des protons n'apparaît plus dans l'équation (2-70). Ainsi, nous choisissons d'éliminer l'activité de protons en choisissant un potentiel de référence de nouveau arbitraire :

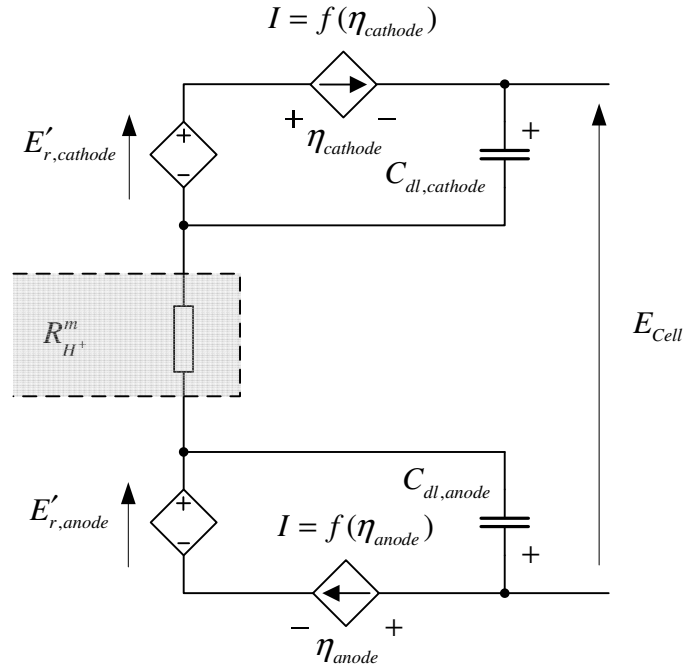


Figure 2-19 Modèle circuit de la couche de réaction (présenté avec la résistance de membrane)

$$E'_{r,anode}{}^{\ominus} = E_{r,anode}{}^{\ominus} - \frac{R \cdot T}{F} \cdot \ln \left(\frac{a_{H_2}^{1/2}}{a_{H^+}} \right) \quad (2-74)$$

$$E'_{r,cathode}{}^{\ominus} = E_{r,cathode}{}^{\ominus} + \frac{R \cdot T}{F} \cdot \ln \left(\frac{a_{H_2}^{1/2}}{a_{H^+}} \right) \quad (2-75)$$

A noter que :

$$E'_{r,anode}{}^{\ominus} + E'_{r,cathode}{}^{\ominus} = E_{r,anode}{}^{\ominus} + E_{r,cathode}{}^{\ominus} = E_r{}^{\ominus} \quad (2-76)$$

En fait, la définition $E_{r,anode}{}^{\ominus} = 0$ ne signifie pas qu'il n'y ait pas de réaction. Bien évidemment, il y a une réaction et il y a un certain niveau de potentiel, mais nous l'avons choisi comme référence de potentiel (0V) :

$$E'_{r,anode}{}^{\ominus} = 0 \quad (2-77)$$

et :

$$E'_{r,cathode}{}^{\ominus} = E_r{}^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}} \right) \quad (2-78)$$

L'activité du proton a été éliminée, et nous pouvons maintenant passer à la modélisation circuit. Le modèle de circuit de la couche de réaction est assez simple [62], puisque le potentiel de la réaction est la somme des potentiels réversibles et des surtensions, Combiné avec l'effet de la capacité de double-couche, le modèle du catalyseur est montré dans la figure 2 -19. Le rôle de la résistance de la membrane, $R_{H^+}^m$, sera discuté dans le prochain paragraphe.

2.6 Modèle de membrane

2.6.1 Modèle mathématique de la membrane

La conductivité ionique de la membrane est l'une des propriétés les plus importantes, elle influe directement sur la caractéristique statique de la pile à combustible. La conductivité ionique de la membrane est essentiellement fonction de la teneur en eau locale et de la température de la membrane. La teneur en eau de la membrane est définie par :

$$\lambda = \frac{[H_2O]}{[SO_3^-]} \quad (2-79)$$

où $[H_2O]$ est la concentration en eau et $[SO_3^-]$ est la concentration en acide sulfonique dans la membrane.

Un autre paramètre important est la conductivité ionique de la membrane. Springer et al [63] ont mené une expérimentation et proposé une corrélation entre la conductivité ionique, $\sigma_{H^+}^m$, la teneur en eau, et la température :

$$\sigma_{H^+}^m = (0.5139\lambda - 0.326) \cdot \exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad \text{for } \lambda > 1 \quad (2-80)$$

Récemment, Fimrite et al [64] propose un nouveau modèle de conductivité de membrane basé sur les phénomènes physiques se déroulant dans la membrane :

$$\sigma_{H^+}^m = \frac{c_i (\varepsilon - \varepsilon_0)^q \left(\frac{1}{D_{12}} + \frac{\lambda}{D_{2M}}\right) F^2}{\lambda \left(\frac{1}{D_{12}D_{1M}} + \frac{\lambda - 1}{D_{12}D_{2M}} + \frac{\lambda}{D_{1M}D_{2M}}\right) RT} \quad \text{for } \lambda > 1.5 \quad (2-81)$$

où ε_0 est le seuil de porosité, D_{12} est le coefficient de diffusion binaire entre les ions hydronium et les molécules d'eau, D_{1M} est le coefficient de diffusion de l'hydronium dans la membrane, D_{2M} est le coefficient de diffusion de l'eau dans la membrane, et q est un paramètre de réglage.

Le modèle de transport de l'eau suggéré par Springer et al [63], nous permet d'estimer le profil de teneur en eau le long de la membrane :

$$N_{H_2O, total}^m = n_{drag} N_{H^+}^m - \left(D_{H_2O, \lambda}^m \frac{\rho_{dry}}{EW} \right) \frac{d}{dz} \lambda \quad (2-82)$$

Dans cette équation, $N_{H_2O,total}^m$ est le flux d'eau dans la membrane, $N_{H^+}^m$ est le flux de protons, $D_{H_2O,\lambda}^m$ est le coefficient de diffusion de l'eau dans la membrane, ρ_{dry} est la masse volumique de la membrane sèche, EW est le poids équivalent de la membrane. n_{drag} est le coefficient électro-osmotique qui représente le nombre de molécules d'eau entraînées par les ions H^+ lors de leur déplacement de l'anode vers la cathode, ce coefficient est environ égal à 1.

Le coefficient de diffusion de l'eau dans la membrane est également fonction de la teneur en eau de la membrane. Springer et al. [63] l'a estimé à :

$$D_{H_2O,\lambda}^m = \exp\left(2416\left(\frac{1}{303} - \frac{1}{T}\right)\right) \times (2.563 - 0.33\lambda + 0.0264\lambda^2 - 0.000671\lambda^3) \quad \text{for } \lambda > 4 \quad (2-83)$$

Le modèle énonce que le flux d'eau totale est composé du flux d'eau électro-osmotique et du flux dû au gradient de concentration de l'eau.

2.6.2 Modèle circuit de la membrane

Le modèle circuit qui représente les mécanismes de transport de l'eau dans chaque sous-couche est décrit par l'équation (2-82) et est représenté dans la figure 2-20. La résistance dans le circuit est définie comme suit :

$$R_{H_2O,\lambda}^m = \left(\frac{EW \cdot \Delta z}{D_{\lambda}^m \cdot \rho_{dry}} \right) \quad (2-84)$$

L'équation (2-82) peut être mise sous la forme suivante, faisant apparaître ainsi le potentiel électrochimique :

$$n_{H_2O,total}^m = n_{H_2O,drag} n_{H^+}^m - \frac{1}{R_{H_2O,\mu}^m} \Delta \mu_{\Delta,H_2O}^m \quad (2-85)$$

où :

$$R_{H_2O,\mu}^m = \frac{\Delta z}{A D_{H_2O,\mu}^m} \quad (2-86)$$

Le modèle circuit de l'équation (2-85) est présenté dans la figure 2-21.

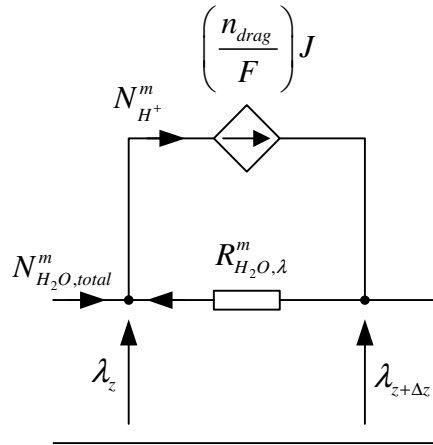


Figure 2-20 Exemple de modèle circuit du transport d'eau dans la membrane

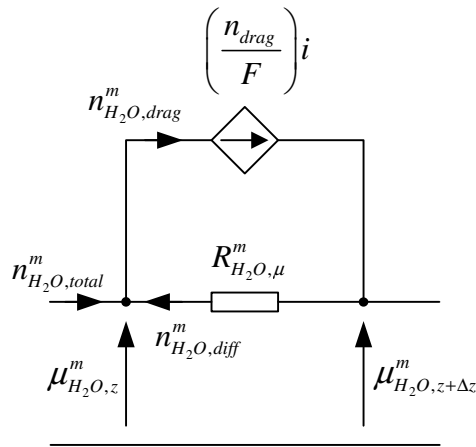


Figure 2-21 Modèle circuit du transport d'eau dans la membrane faisant intervenir le potentiel électrochimique

2.6.3 Élément d'accumulation de matière

La teneur en eau locale d'une petite portion de membrane change selon le déséquilibre entre le flux d'entrée et de sortie d'eau. La capacité associée s'écrit :

$$C_{H_2O,\mu}^m = \left(\frac{\rho_{dry}}{EW} \frac{a}{RT} \frac{d\lambda}{da} \right) \Delta z A \quad (2-87)$$

Le modèle de circuit équivalent de la membrane utilisée dans ce travail est présenté dans la figure 2-22.

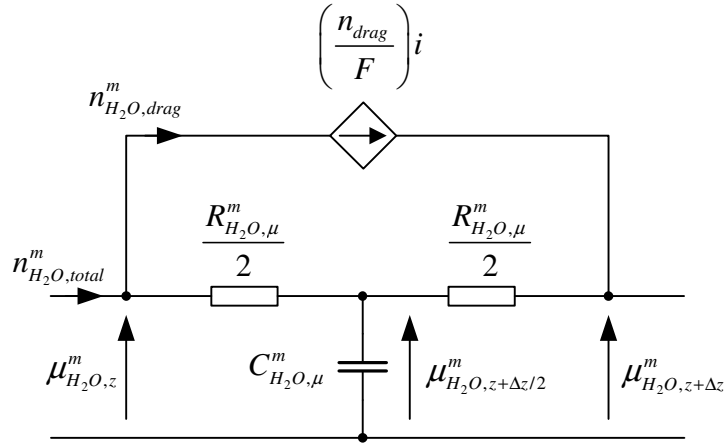


Figure 2-22 Modèle circuit équivalent de la membrane utilisé dans ce travail

2.6.4 Modèle circuit complet de la membrane

Le modèle circuit équivalent, comprenant les conditions aux frontières de la membrane est montré dans les figures 2-23 et 2-24.

Les informations sur le potentiel chimique issues de la simulation du circuit sont utilisées pour calculer la teneur en eau de la membrane. Ensuite, à partir du profil de la teneur en eau, nous déterminons la conductivité ionique de la membrane grâce à l'équation (2-80). La résistance totale de la membrane se calcule de la manière suivante :

$$R_{H^+}^m = \frac{1}{A} \int_0^{t_m} \frac{1}{\sigma_{H^+}^m(\lambda)} dz \quad (2-88)$$

où t_m est l'épaisseur totale de la membrane.

La version discrétisée de la résistance est la suivante :

$$R_{H^+}^m = \frac{1}{A} \sum_{i=0}^n \frac{\Delta z}{\sigma_{H^+}^m(\lambda_i)} \quad (2-89)$$

où λ_i est la teneur en eau dans la sous couche i . Cette résistance totale de membrane est celle utilisée dans la figure 2-19.

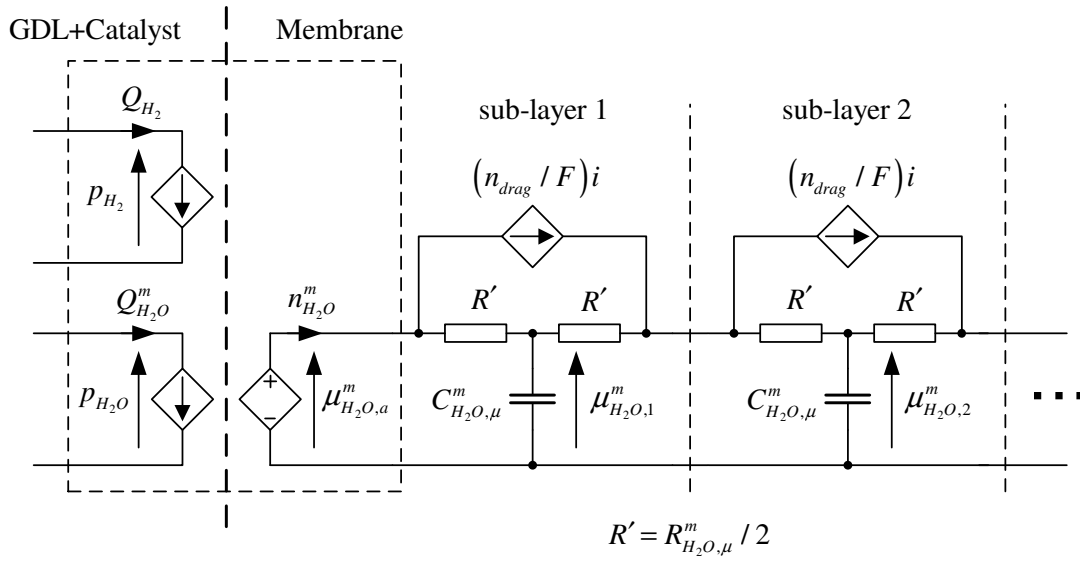


Figure 2-23 Modèle circuit de la membrane comprenant la frontière côté anode

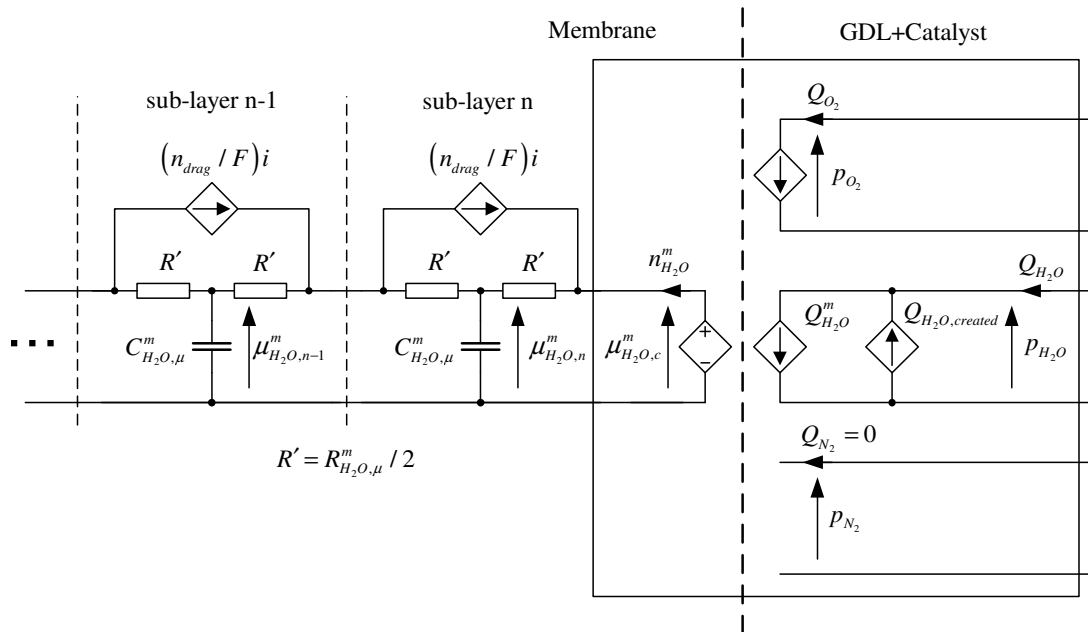


Figure 2-24 Modèle circuit de la membrane comprenant la frontière côté cathode

2.7 Modèle de cellule de PEMFC

Le modèle de cellule unique peut être formé en combinant les canaux de transport de gaz, les couches de diffusion, la couche de réaction et le modèle de la membrane. Le modèle partant de l'anode jusqu'à la membrane est présenté dans les figures 2-25 à 2-27. Le modèle de la cathode est presque un miroir du côté anode. La différence entre l'anode et la cathode ont déjà été discutées. Le modèle de cellule entière est représenté par le schéma présenté dans la figure 2-28.

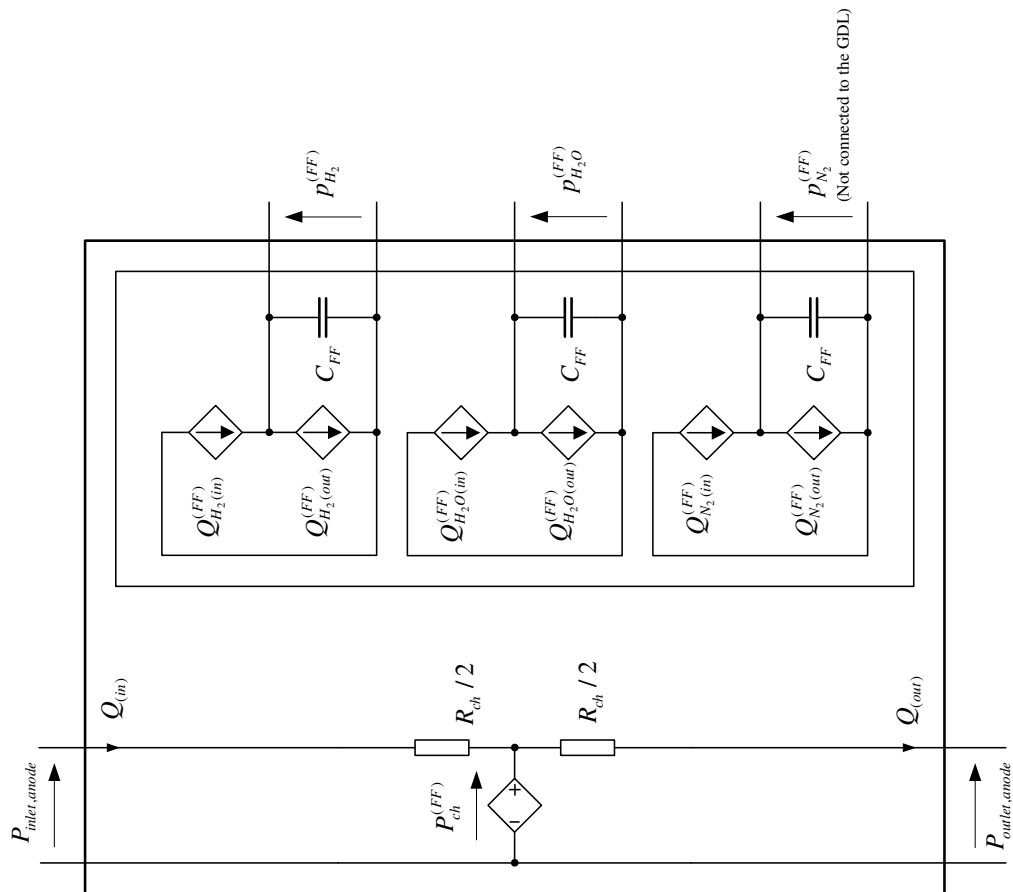


Figure 2-25 Modèle circuit du canal

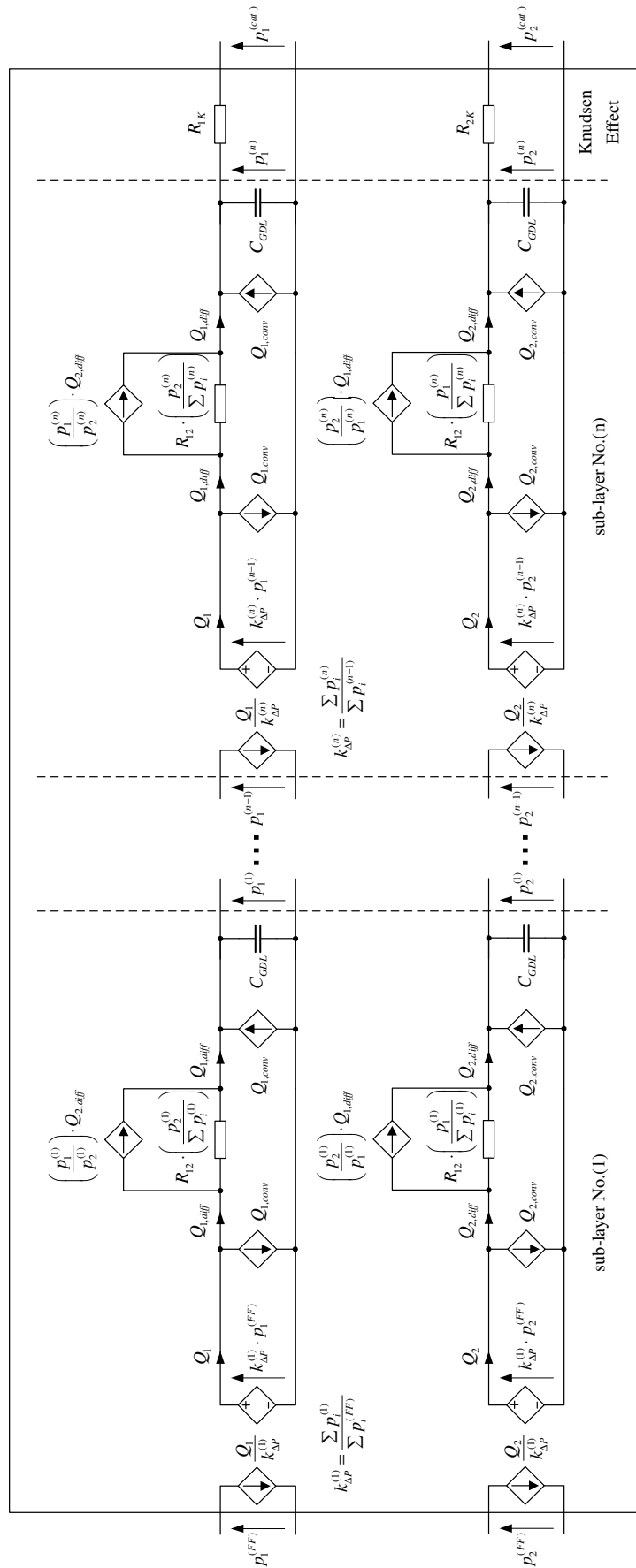


Figure 2-26 Modèle circuit de la couche de diffusion à l'anode

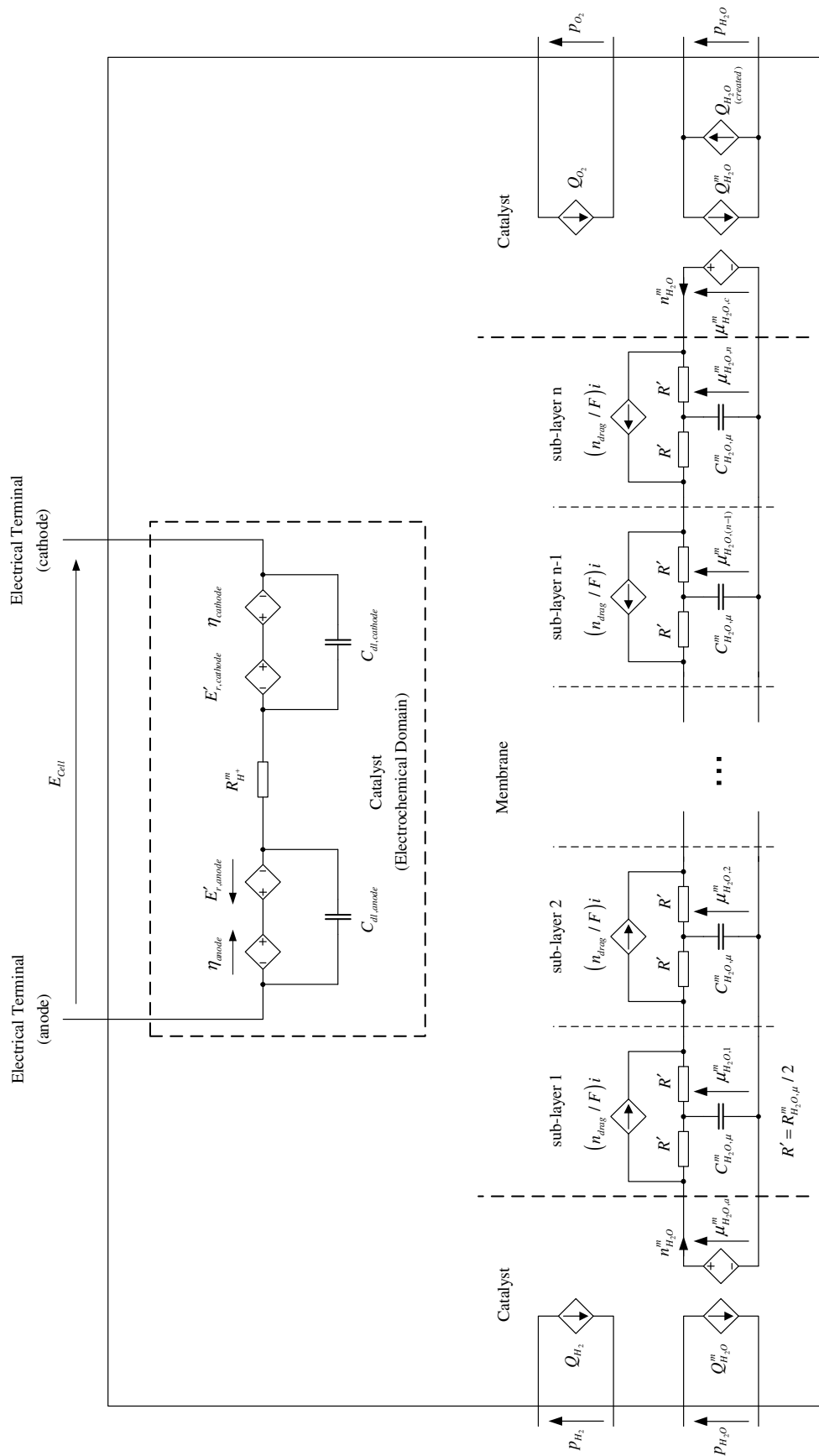


Figure 2-27 Modèle circuit de la couche de réaction et de la membrane

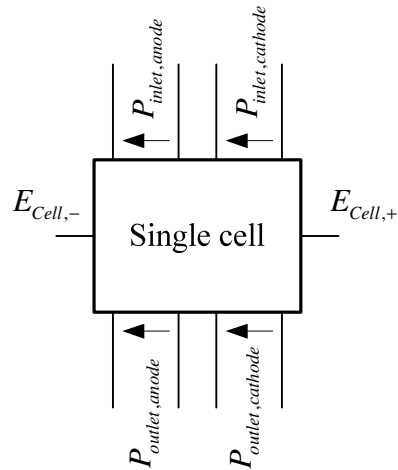


Figure 2-28 Diagramme block représentant le modèle d'une monocellule

2.8 Modèle d'un stack 3 cellules

La structure du stack 3 cellules est présentée dans la figure 2-29. Le modèle de ce stack peut être développé en ajoutant le canal commun aux cellules qui permet une distribution en parallèle des gaz. Le modèle de cette artère principale de distribution est identique à celui des canaux des plaques distributrices de gaz. On peut également tenir compte, dans la modélisation, des tubes acheminant le gaz depuis le détendeur jusqu'à la pile, si nécessaire.

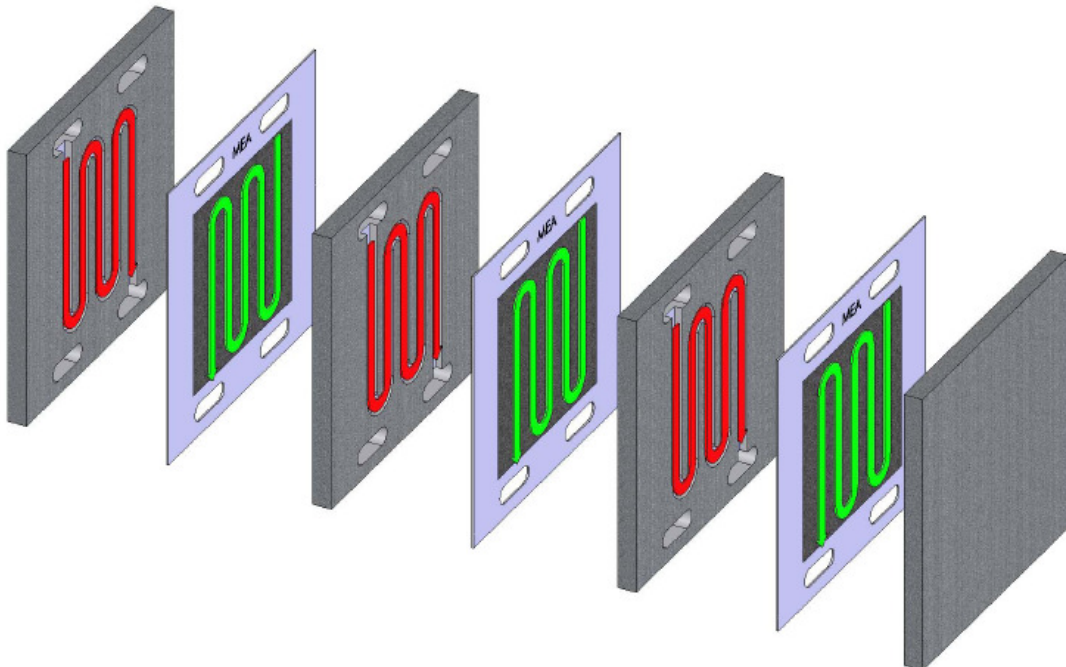


Figure 2-29 Structure d'un stack composé de 3 cellules

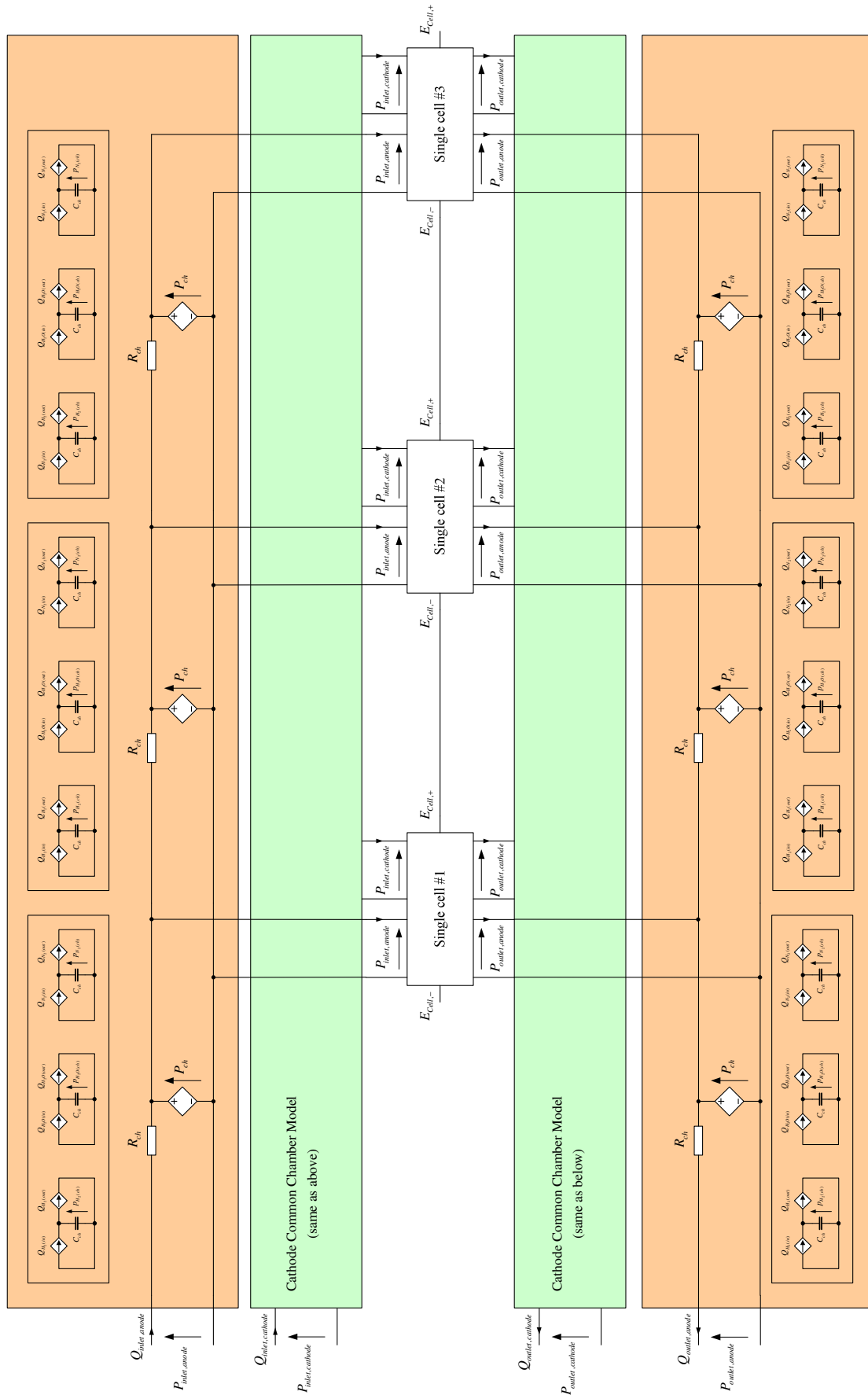


Figure 2-30 Modèle d'un stack composé de 3 cellules

2.9 Conclusion

L'établissement d'un modèle de type circuit d'une pile à combustible type PEMFC a été présenté dans ce chapitre. Ce modèle est basé sur les phénomènes physiques du cœur de pile. Il se compose de résistances non-linéaires et de sources de courant et de tension contrôlées qui sont familières au domaine du génie électrique. Ce modèle est implémentable dans les logiciels usuels du commerce très utilisés en électricité, tels que PSpice®, Saber®, Matlab ® ou d'autres équivalents.

Chapitre 3

Implémentation du modèle et résultats

Ce chapitre présente les résultats de simulation du modèle développé. La simulation est faite sous Matlab/Simulink. La première simulation présente le fonctionnement dynamique de la pile à combustible. La deuxième simulation présente le fonctionnement statique de la pile sous différents débits d'alimentation de gaz. L'effet du réseau de canaux a été également discuté. Le chapitre se termine par la simulation d'un stack de 3 cellules couplé à un convertisseur élévateur.

3.1 Simulation d'une cellule de pile et résultats

La simulation du modèle de cellule unique est présentée dans ce paragraphe. Les paramètres de simulation sont donnés dans les tableaux 3-1 à 3-5.

Table 3-1 Paramètres

Paramètre	Symbole	Valeur
Pression de fonctionnement [Pa]	P	1×10^{-5}
Température [K]	T	333.15
Humidité relative à l'entrée de l'anode [%]	RH_A	10
Humidité relative à l'entrée de la cathode [%]	RH_K	60

Table 3-2 Tubes et artère principale

Paramètre	Symbole	Valeur
Diamètre du tube à l'anode [m]	a_{Tube_A}	2×10^{-3}
Diamètre du tube à la cathode [m]	a_{Tube_K}	5×10^{-3}
Longueur du tube d'alimentation côté anode [m]	$l_{Tube_A_inlet}$	2
Longueur du tube en sortie de cellule côté anode [m]	$l_{Tube_A_outlet}$	2
Longueur du tube d'alimentation côté cathode [m]	$l_{Tube_K_inlet}$	2
Longueur du tube en sortie de cellule côté cathode [m]	$l_{Tube_K_outlet}$	2
Dimension de l'artère principale [m]		
Largeur	$w_{FF_chamber}$	30×10^{-3}
Hauteur	$h_{FF_chamber}$	10×10^{-3}
Longueur	$l_{FF_chamber}$	15×10^{-3}
Dimension du canal simplifié à l'anode [m]		
Largeur	w_{FF_A}	1.5×10^{-3}
Hauteur	h_{FF_A}	1×10^{-3}
Longueur	l_{FF_A}	5
Dimension du canal simplifié à la cathode [m]		

Largeur	w_{FF_K}	41.4×10^{-3}
Hauteur	h_{FF_K}	1.1×10^{-3}
Longueur	l_{FF_K}	150×10^{-3}

Table 3-3 Paramètres des couches de diffusion

Paramètres	Symbole	Valeur
Aire de la section transverse [m ²]	A	100×10^{-4}
Epaisseur [m]	l_{GDL}	200×10^{-6}
Porosité [-]	ε	0.4
Tortuosité [-]	τ	$\varepsilon^{-0.5}$
Coefficient de diffusion [m ² /s]		
entre $O_2 - H_2O$	$D_{O_2-H_2O}^{eff}$	8.285×10^{-6}
entre $O_2 - N_2$	$D_{O_2-N_2}^{eff}$	6.588×10^{-6}
entre $H_2O - N_2$	$D_{H_2O-N_2}^{eff}$	8.894×10^{-6}
Coefficient de diffusion de Knudsen [m ² /s]		
entre H_2	D_{H_2-K}	1.283×10^{-3}
entre H_2O	D_{H_2O-K}	4.295×10^{-4}
entre O_2	D_{O_2-K}	3.222×10^{-4}
entre N_2	D_{N_2-K}	3.444×10^{-4}
Epaisseur de la couche micro-poreuse [m]	l_{MPL}	20×10^{-6}
Nombre de sous couches anode/cathode [-]	$n_{GDL_sub-layer}$	4

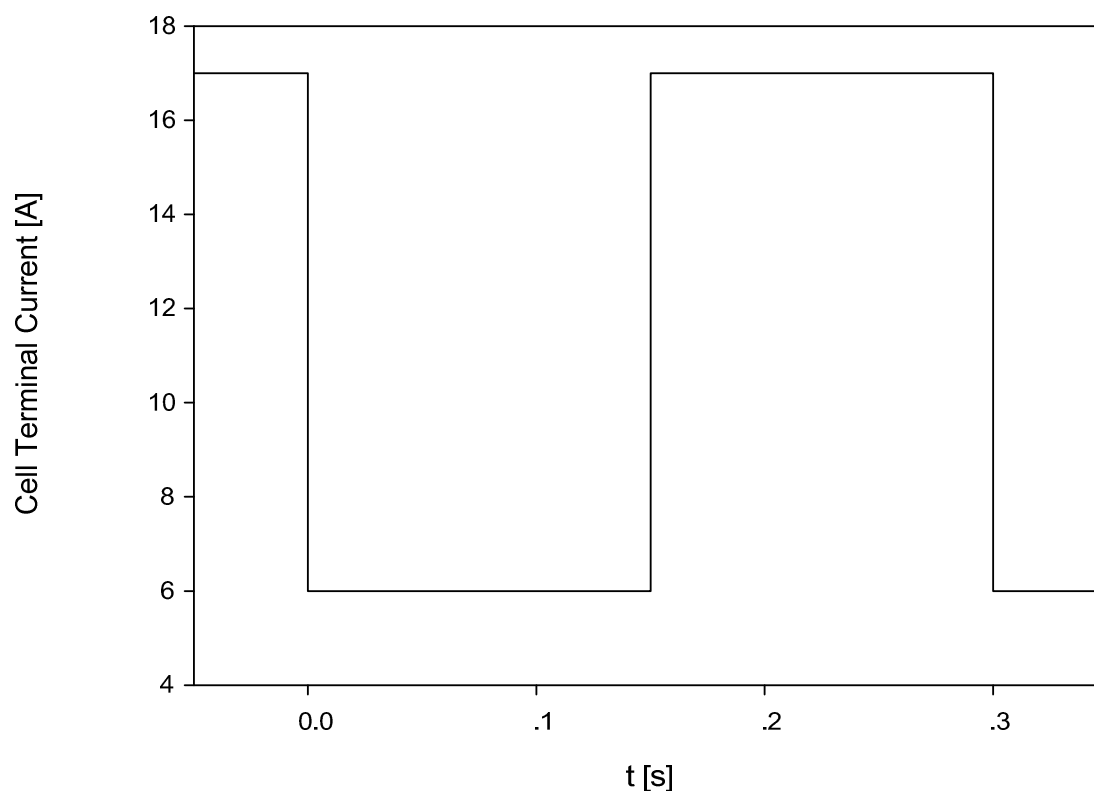
Table 3-4 Paramètres de la couche de réaction

Paramètres	Symbole	Valeur
Courant d'échange à l'anode [A/m ²]	$j_{0,anode}$	35
Courant d'échange à la cathode [A/m ²]	$j_{0,cathode}$	3×10^{-3}
Potentiel en circuit ouvert [V]	E_r^{\ominus}	1.229
Capacité de double couche [F]	C_{dl}	2

Table 3-5 Paramètres de membrane

Paramètres	Symbole	Valeur
Epaisseur de la membrane [m]	l_m	30×10^{-6}
Nombre de sous couches [-]	$n_{membrane_sub-layer}$	4
Masse équivalente (EW) [kg/mol]	EW	1.1
Masse volumique de la membrane sèche [kg/m ³]	ρ_{dry}	1967.2
Coefficient électro-osmotique [-]	n_{drag}	1
Conductivité ionique	$\sigma_{H^+}^m$	Eq.(2-81)
Coefficient de diffusion de l'eau [m ² /s]	$D_{H_2O,\lambda}^m$	Eq.(2-83)

Nous simulons le fonctionnement de la cellule lorsque celle-ci est connectée à une charge contrôlée en courant. La figure 3-1 présente le profil de courant appliqué à la pile. Les résultats de simulation de fonctionnement en régime permanent sont présentés dans les figures 3-2 à 3-13. La tension de cellule calculée est comparée à celle mesurée (figure 3-13).

**Figure 3-1** Courant de charge

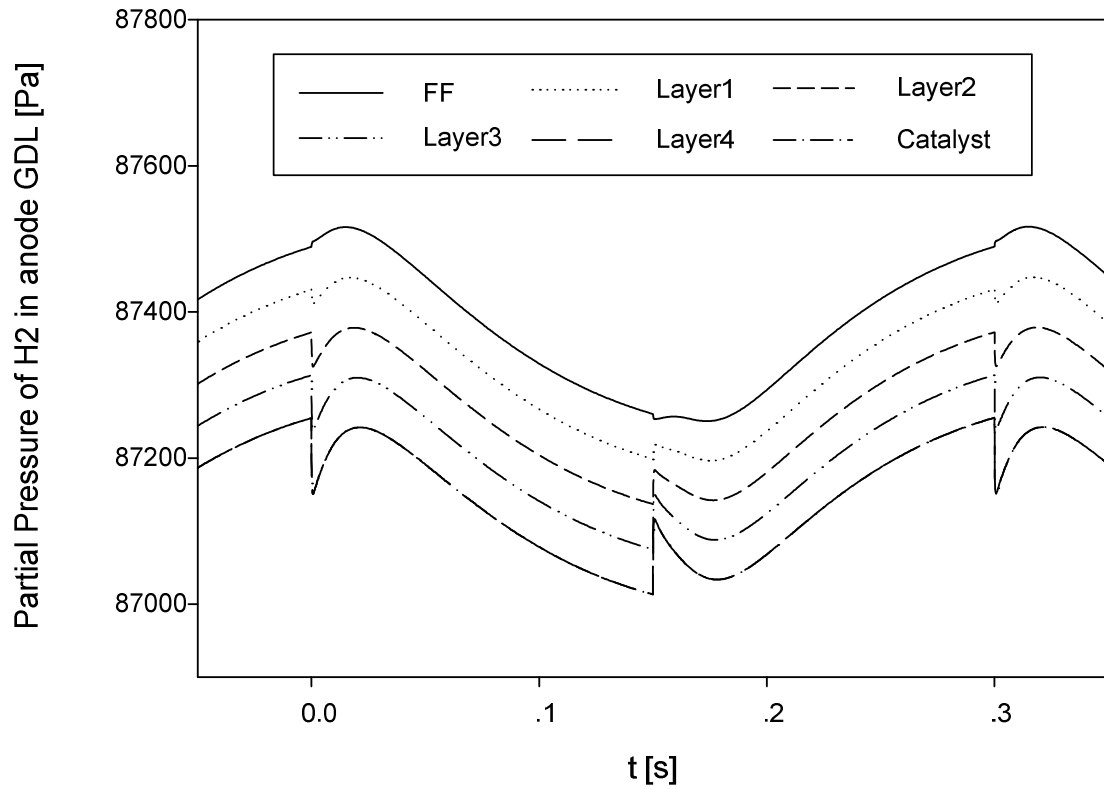


Figure 3-2 Pression partielle de H_2 dans les différentes couches de diffusion à l'anode

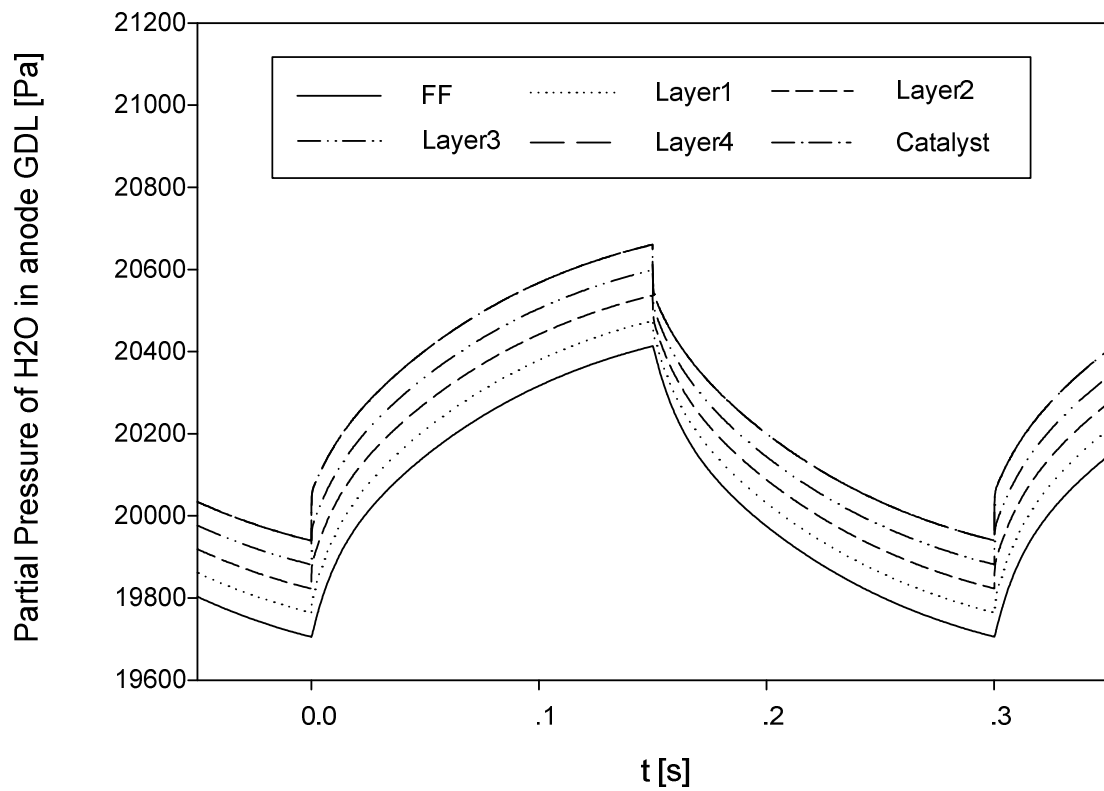


Figure 3-3 Pression partielle d' H_2O dans chacune des sous couches de diffusion à l'anode

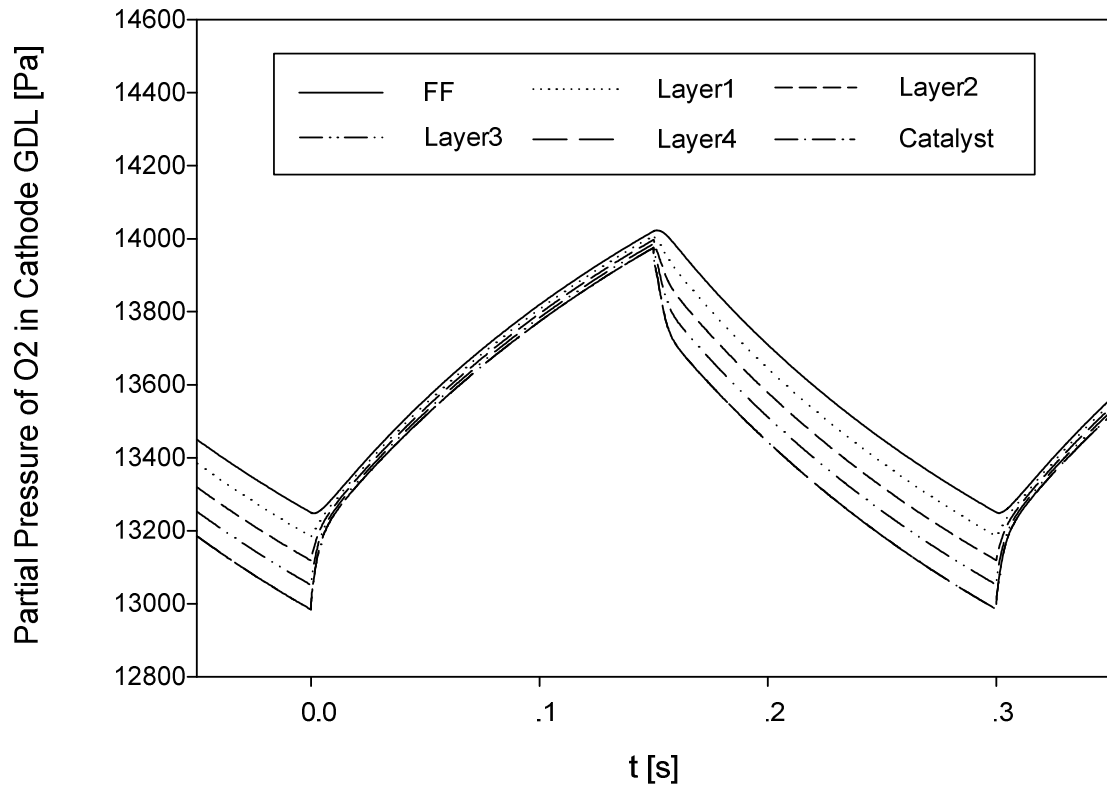


Figure 3-4 Pression partielle d' O_2 dans chacune des sous couches de diffusion à la cathode

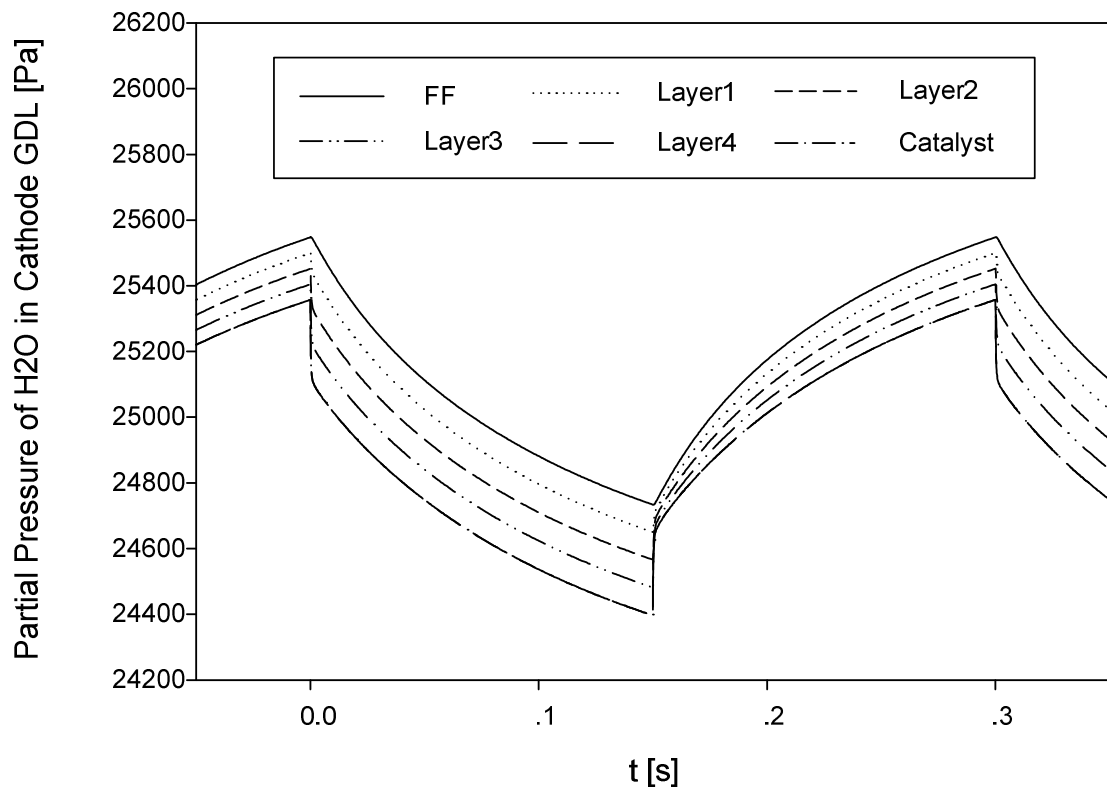


Figure 3-5 Pression partielle d' H_2O dans chacune des couches de diffusion à la cathode

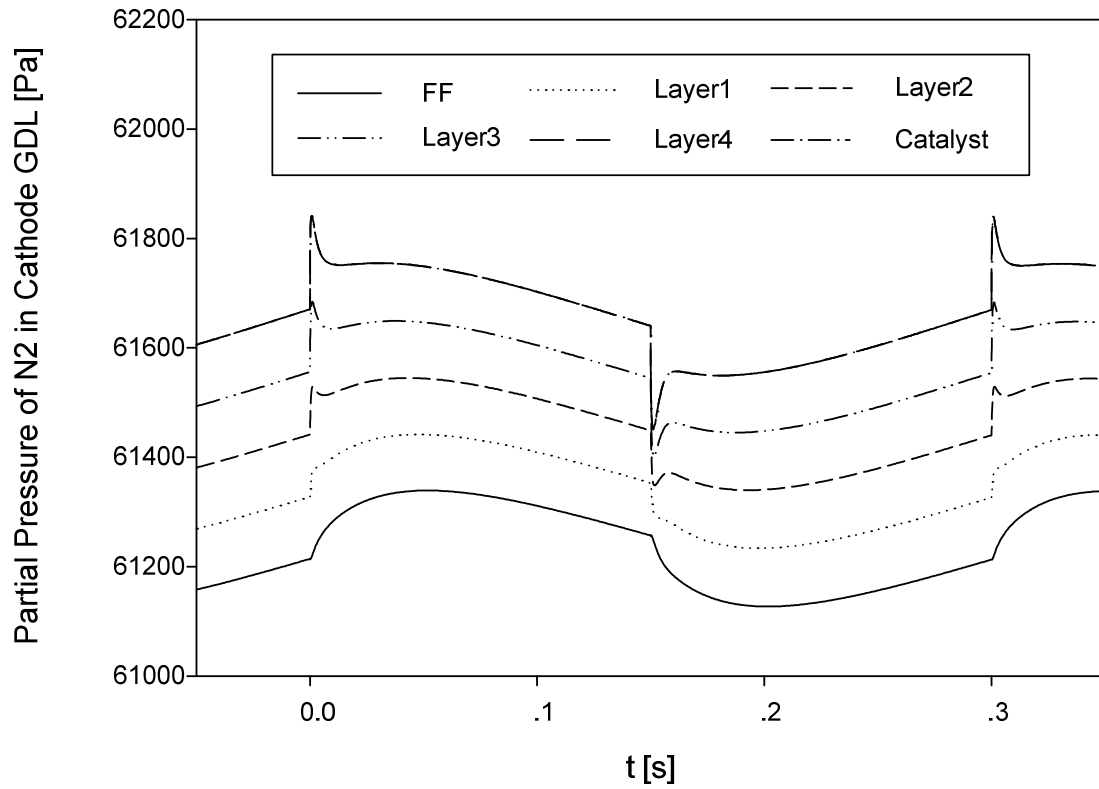


Figure 3-6 Pression partielle de N_2 dans chacune des couches de diffusion à la cathode

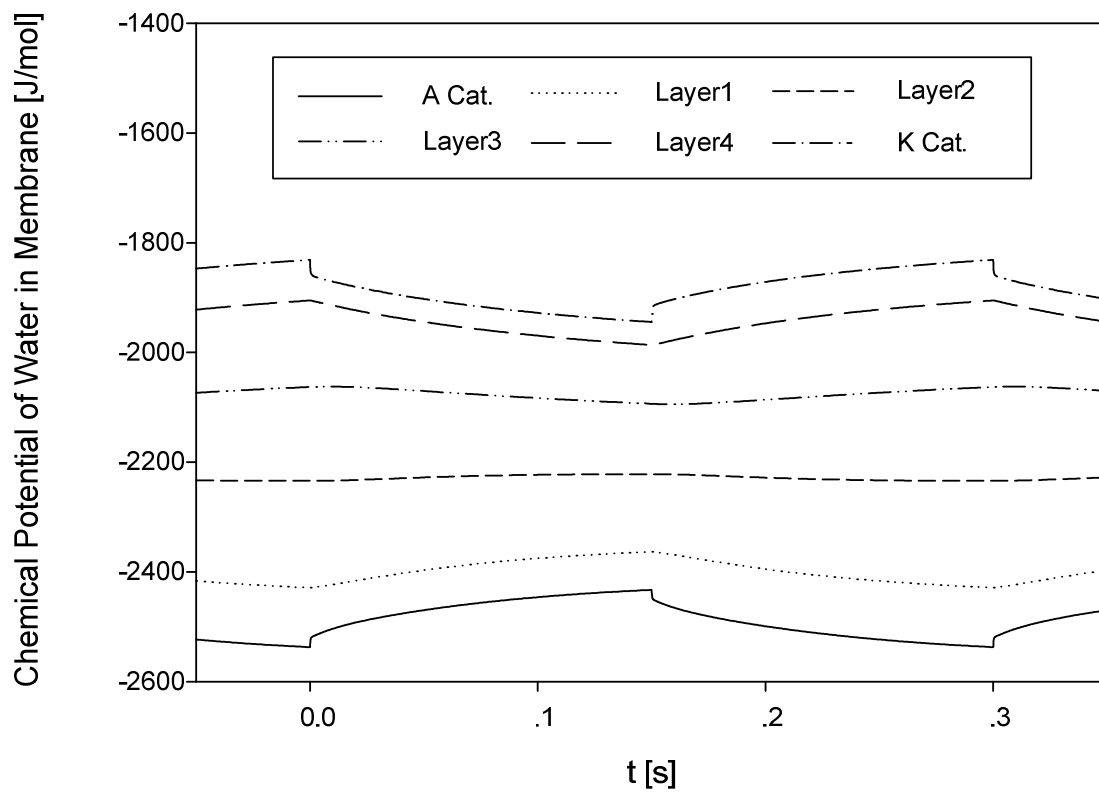


Figure 3-7 Potentiel chimique d' H_2O dans chacune des sous couches

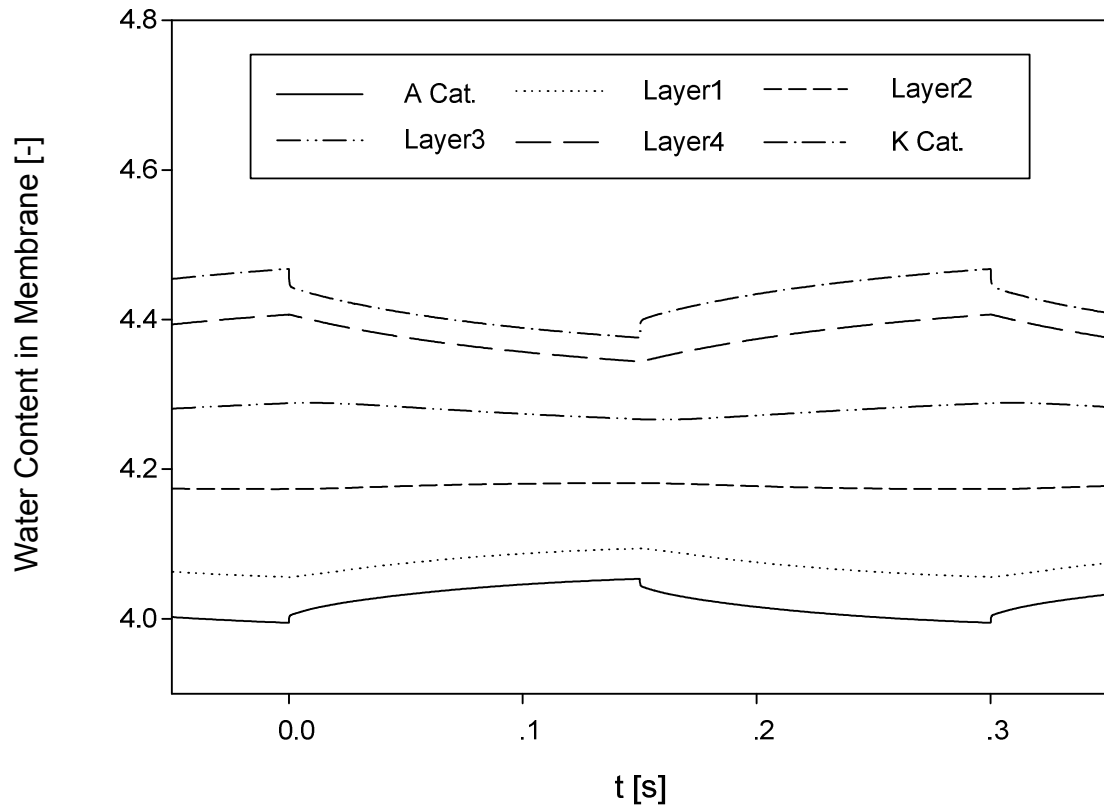


Figure 3-8 Teneur en eau (λ) dans chacune des couches de la membrane

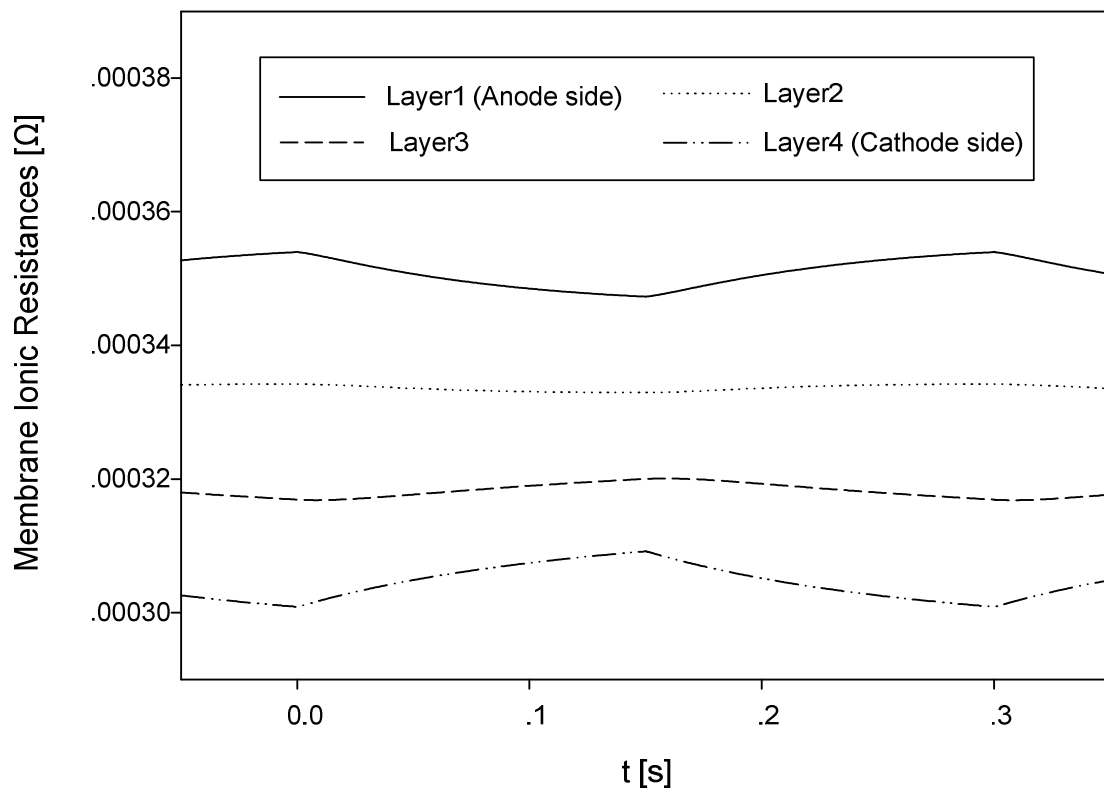


Figure 3-9 Résistance de la membrane

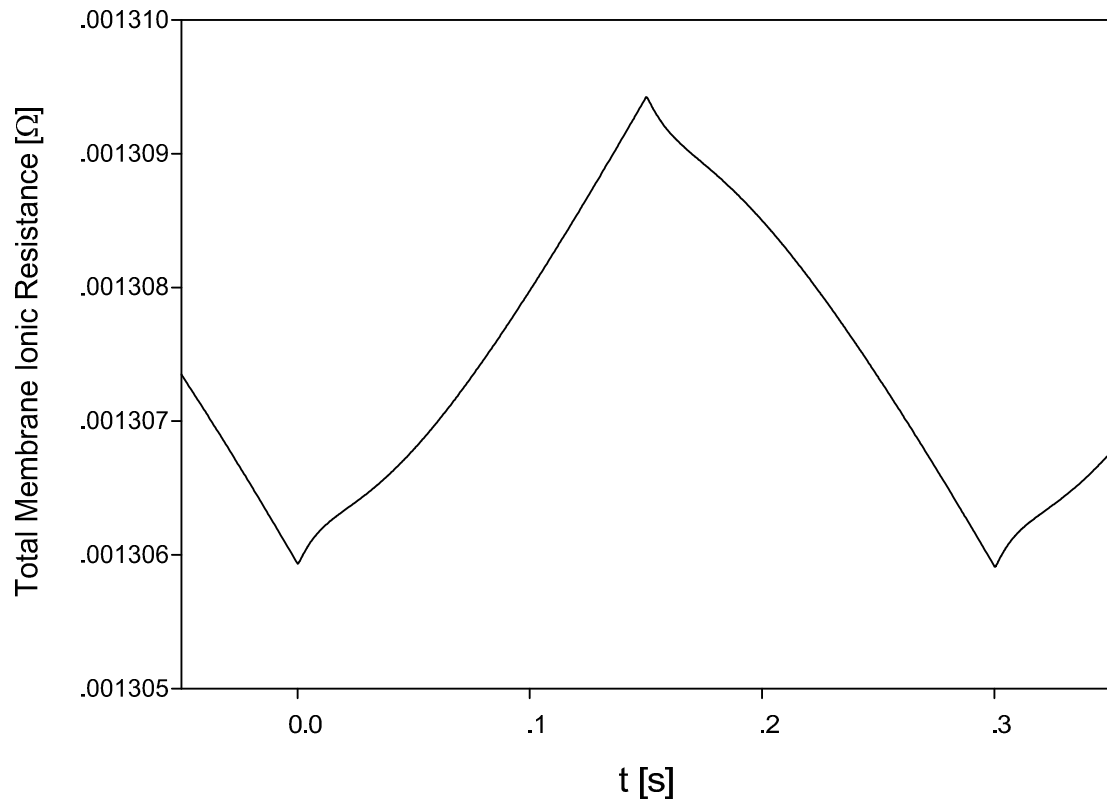


Figure 3-10 Résistance totale de la membrane

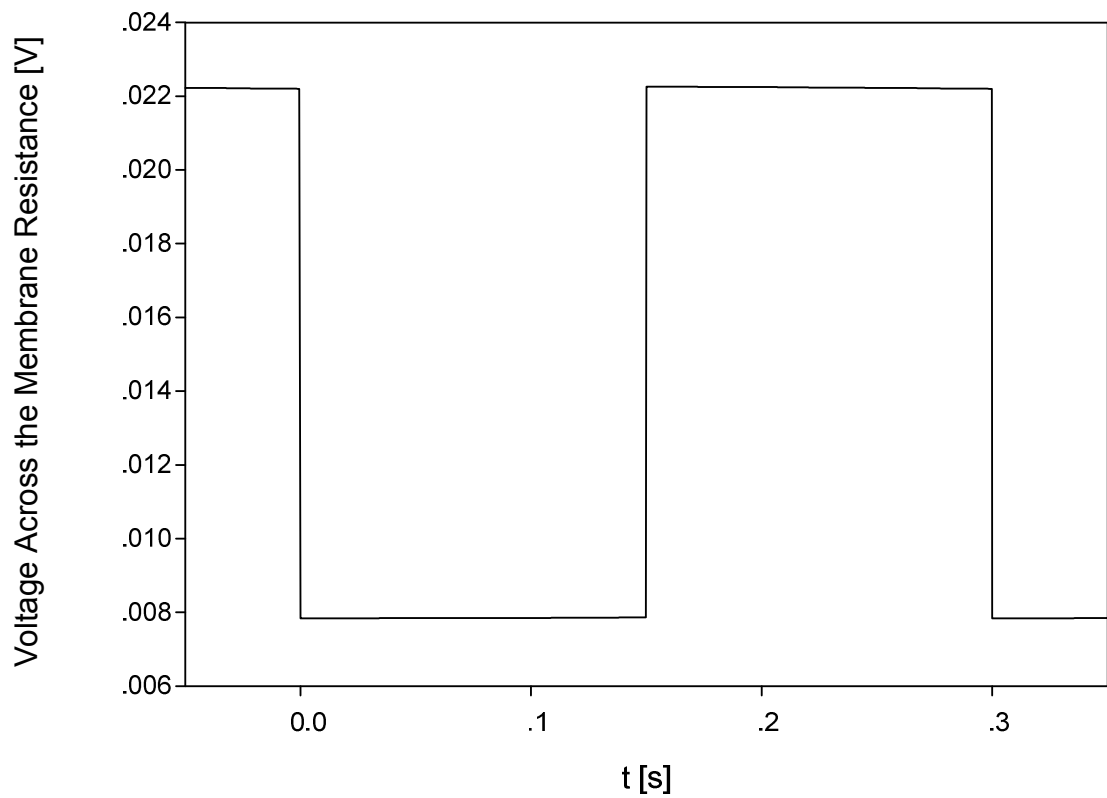


Figure 3-11 Chute de tension dans la membrane

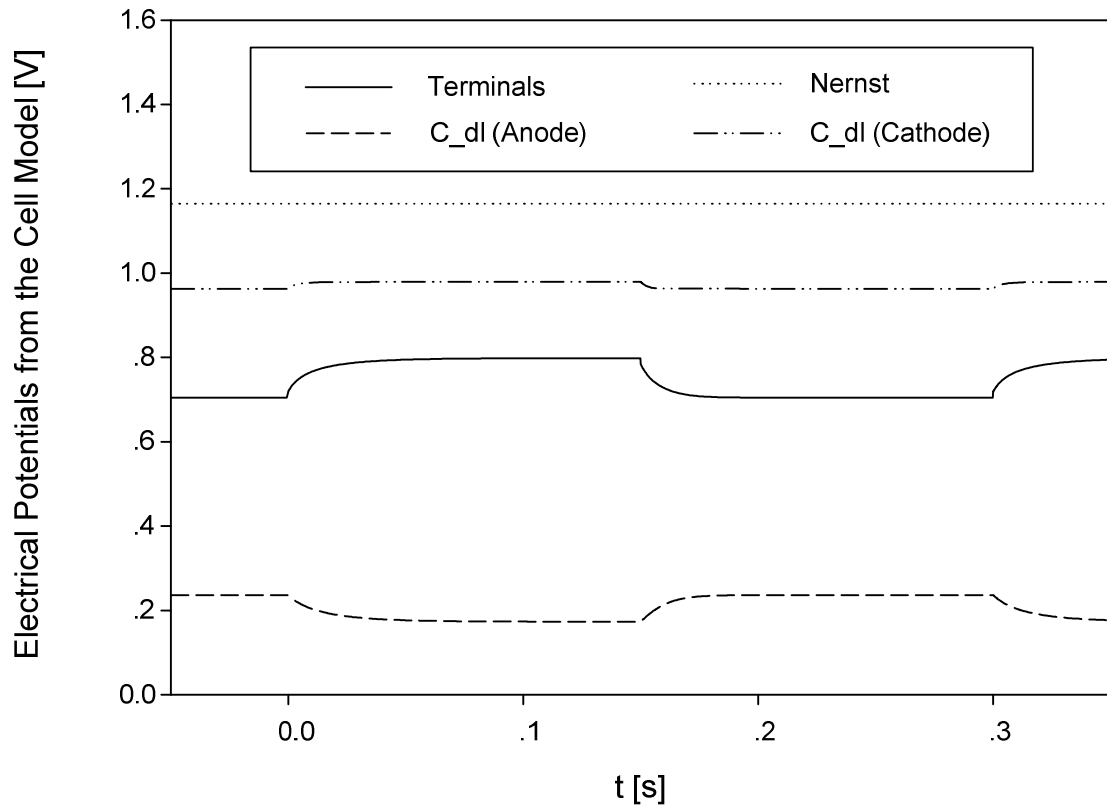


Figure 3-12 Potentiel de cellule

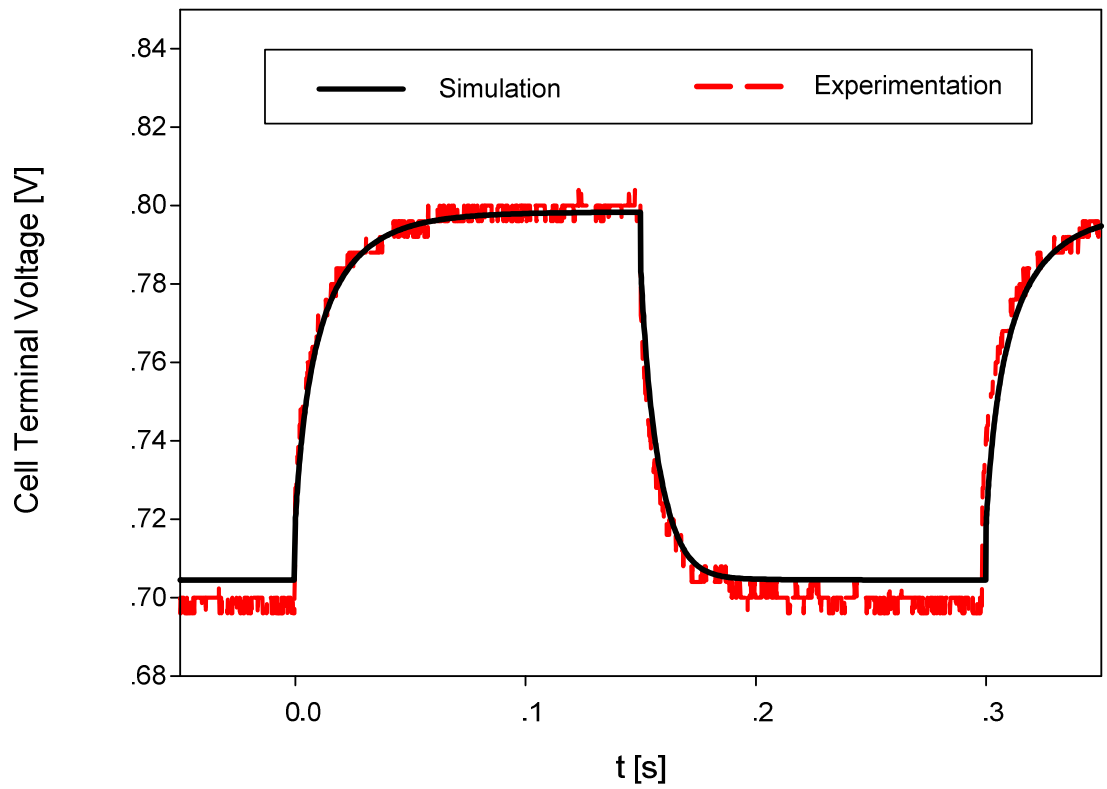


Figure 3-13 Tension de cellule simulée et mesurée

3.2 Caractéristique statique V-I

La courbe statique V-I de la pile à combustible est l'une des informations les plus importantes. La chute de tension de la cellule est due au potentiel d'activation, à la résistance de la membrane et à la perte de concentration. Les pertes dues à l'activation et à la résistance de la membrane sont fixes et très peu modifiables. Les scientifiques qui ne travaillent pas sur l'AME peuvent juste gérer les conditions opératoires de sorte à réduire ces pertes. La perte de concentration, ou la diminution du potentiel de cellule est généralement due à une alimentation en gaz insuffisante. Dans la plupart des cas, le problème survient à la cathode où l'oxygène de l'air est insuffisant pour produire le courant électrique. La consommation des réactifs au niveau du catalyseur est calculée de la manière suivante :

$$Q_{H_2_consumed} = \frac{I_{ref}}{2F} \cdot \left(\frac{R \cdot T}{P} \right) \quad (3-1)$$

$$Q_{O_2_consumed} = \frac{I_{ref}}{4F} \cdot \left(\frac{R \cdot T}{P} \right) \quad (3-2)$$

où I_{ref} est le courant de référence.

Bien que la consommation exacte des réactifs au niveau du catalyseur peut être calculée, la totalité de l'oxygène entrant dans la cellule n'atteint pas le catalyseur, une partie de l'oxygène passe juste par la surface de la couche de diffusion et sort directement de la cellule. Cela implique qu'il y ait suralimentation en gaz. D'une part, cette sous-alimentation en gaz engendre une chute de tension. D'autre part, une suralimentation en gaz est du gaspillage d'H₂ et une perte d'énergie au niveau du compresseur. Il est donc important de déterminer correctement la quantité de gaz d'alimentation.

Ce paragraphe présente la courbe V-I de la cellule du modèle développé. Les paramètres de simulation sont donnés dans le paragraphe précédent et les débits des gaz sont calculés comme suit :

$$Q_{gas_anode} = \zeta_A \cdot \frac{I_{ref}}{2F} \cdot \left(\frac{R \cdot T}{P} \right) \quad (3-3)$$

$$Q_{gas_cathode} = \zeta_K \cdot \frac{1}{0.21} \cdot \frac{I_{ref}}{4F} \cdot \left(\frac{R \cdot T}{P} \right) \quad (3-4)$$

La figure 3-4 présente les courbes de polarisation sous différentes alimentations en gaz.

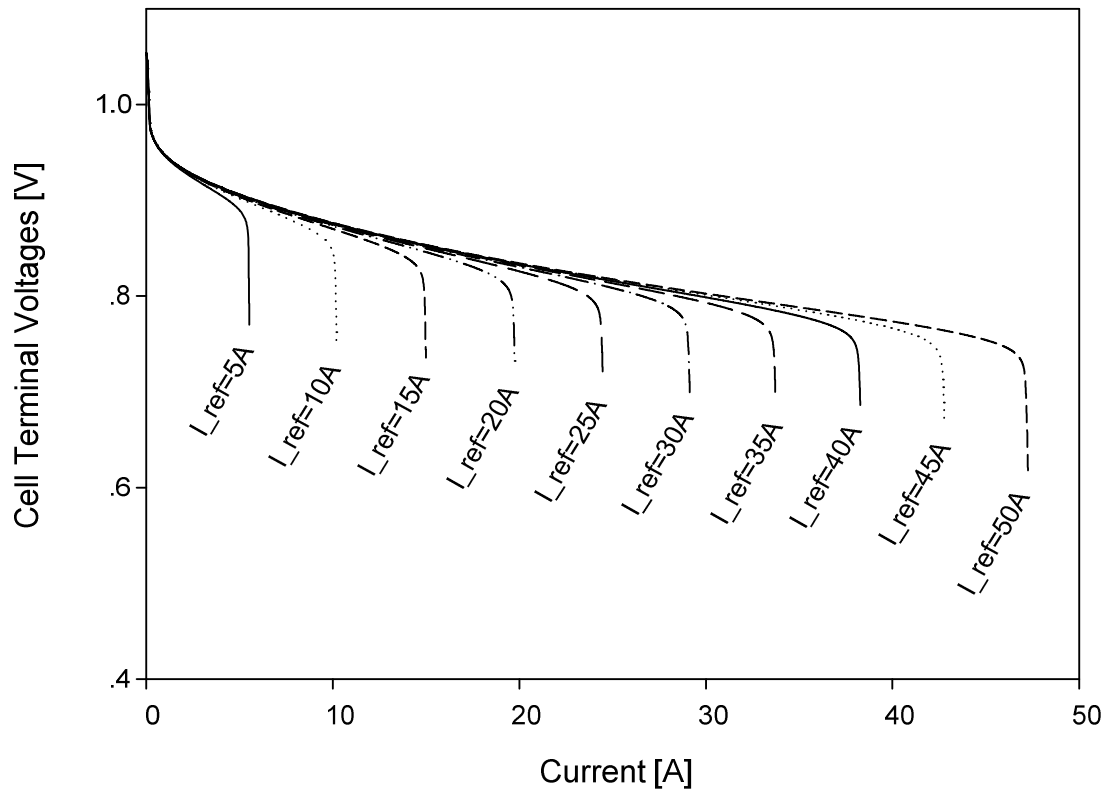


Figure 3-14 Courbes statiques pour différentes alimentations en gaz

3.3 Couplage à convertisseur élévateur

Le modèle développé est destiné à des applications en génie électrique, nous le connectons à un convertisseur. Le convertisseur élévateur est l'une des topologies de base de convertisseur DC-DC. Le convertisseur élévateur est utilisé pour augmenter la tension de sortie de la pile, qui est une source basse tension, à un niveau de tension adapté à la charge. Le schéma du circuit de simulation est présenté dans la figure 3-15. Les paramètres de la pile sont les mêmes que dans la section 3.1. Le convertisseur fonctionne en boucle ouverte avec un rapport cyclique de 70% et la fréquence de commutation est fixée à 5 kHz. Les résultats des simulations sont présentés dans les figures 3-16 à 3-19.

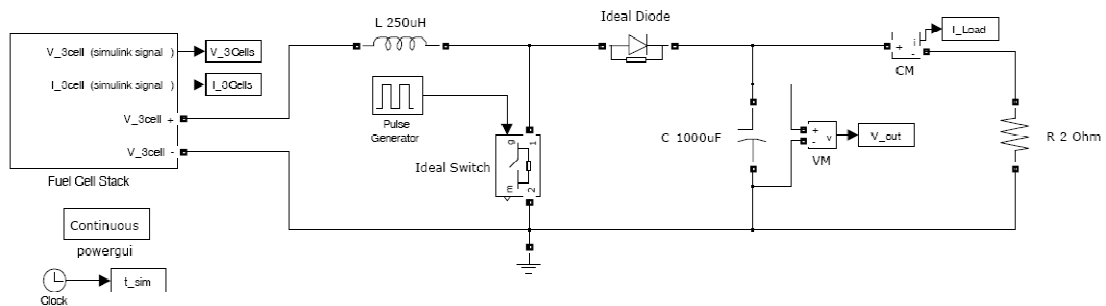


Figure 3-15 Schéma d'une pile de 3 cellules connectée à un convertisseur

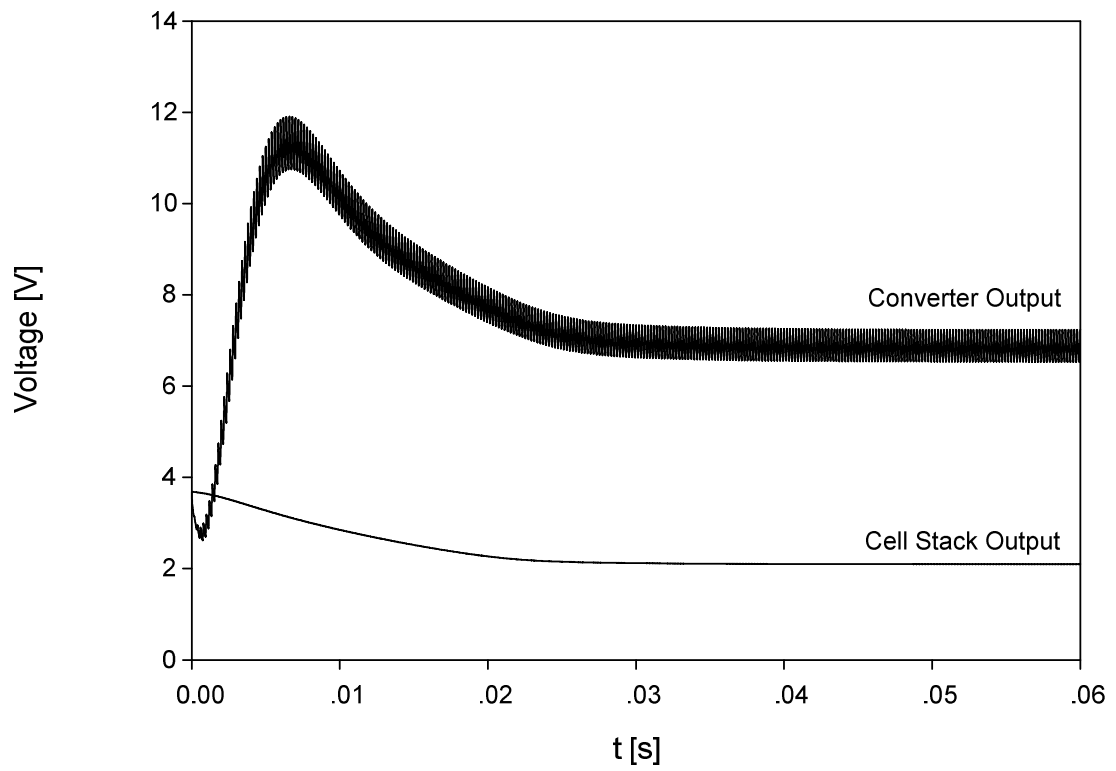


Figure 3-16 Tensions de sortie de pile et du convertisseur

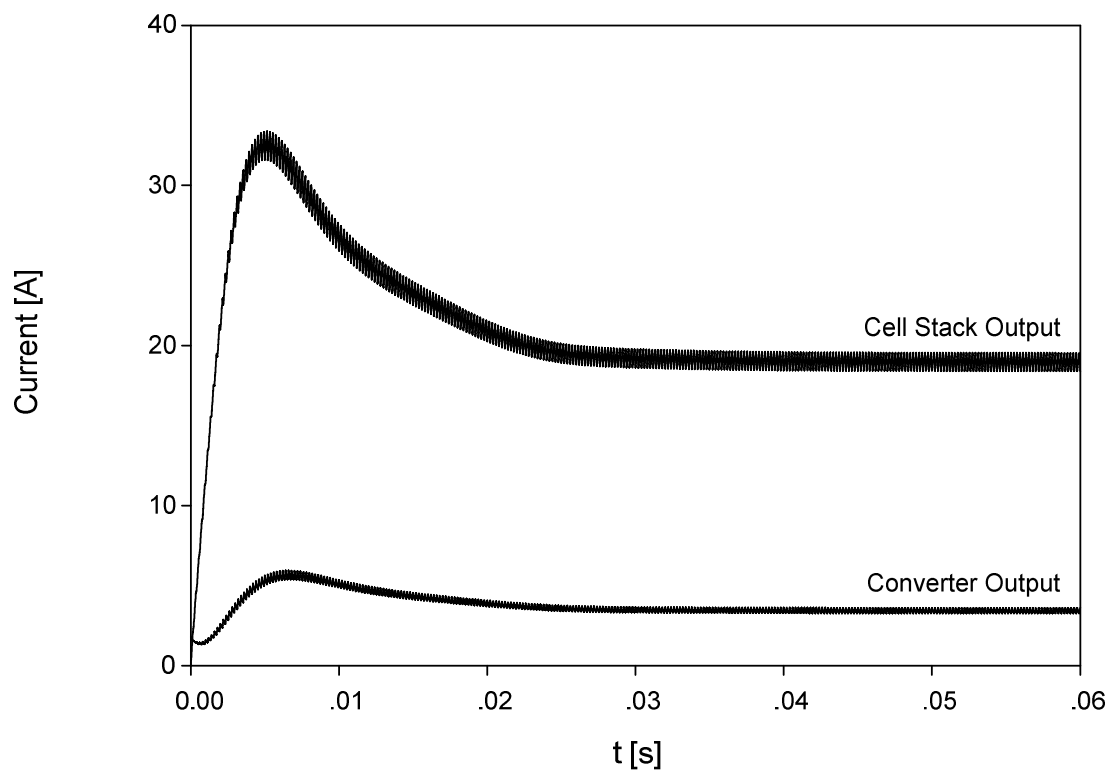


Figure 3-17 Courants de sortie de pile et du convertisseur

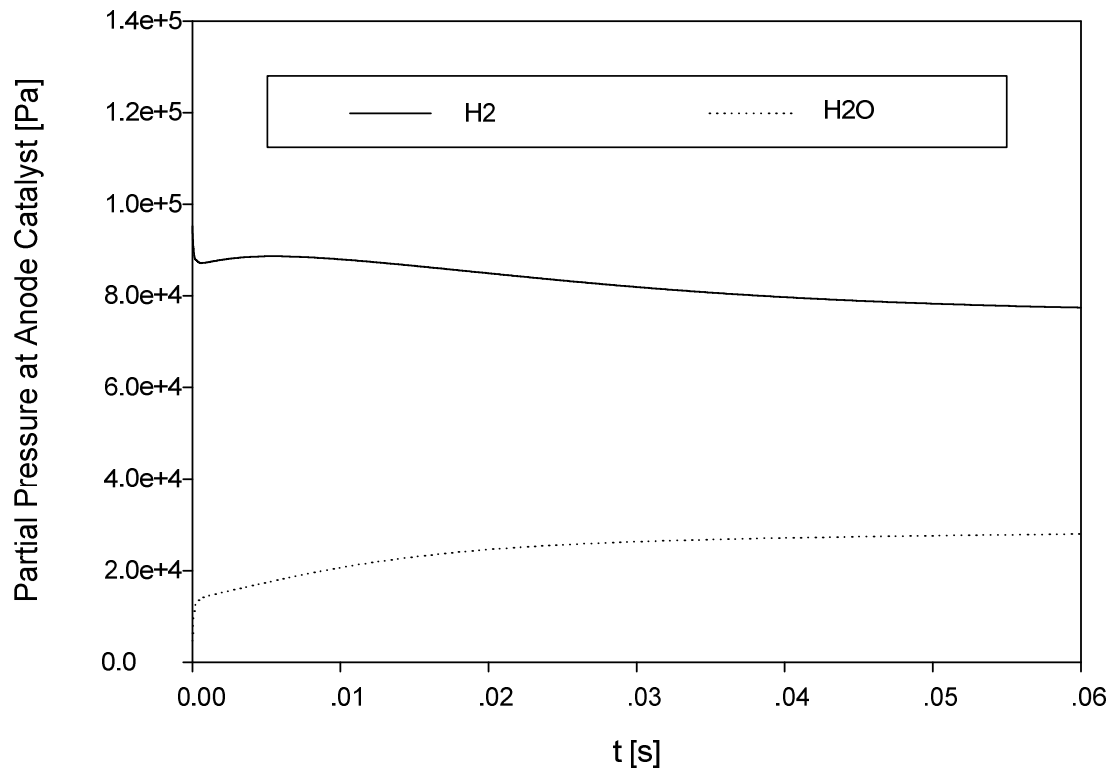


Figure 3-18 Pression partielle de chaque espèce au niveau de la couche de réaction à l'anode

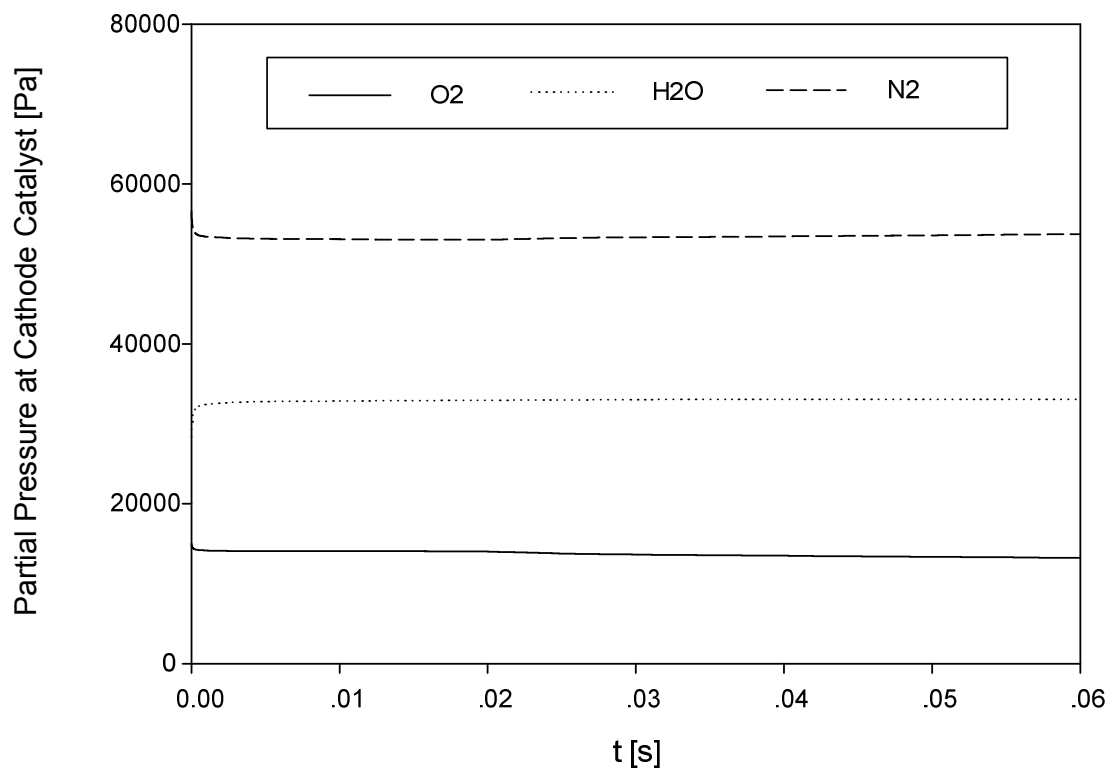


Figure 3-19 Pression partielle de chaque espèce au niveau de la couche de réaction à la cathode

3.4 Conclusion

La mise en œuvre du modèle de circuit équivalent de la pile à combustible a été établie dans ce chapitre. Dans ce travail, nous avons choisi de mettre en œuvre le modèle de circuit sous le logiciel commercial Matlab /Simulink. Le modèle développé fournit une large capacités de simulation, du fonctionnement en statique au dynamique, et permet de nombreux paramètres de réglage. Ceci est possible car le modèle est élaboré à partir des équations physiques. Cette fonctionnalité n'est pas disponible dans la plupart des modèles empiriques. La simulation montre que le modèle développé peut être intégré de façon transparente avec des circuits d'électroniques de puissance. Ce modèle permet d'étudier en détail l'interaction entre les circuits de puissance et la pile à combustible.

Chapitre 4

Conclusion

Ce travail a pour objectif d'établir un modèle approprié pour utilisation en génie électrique. Le modèle recherché doit être en mesure d'intégrer des modèles de circuits d'électronique de puissance et valable sur une large plage de fonctionnement. Le modèle que nous avons établi reste un modèle local et non global ce qui autorise une étude du cœur de pile. Nous avons commencé par étudier les mécanismes de transport dans la pile à combustible. Puisque le modèle est destiné à un usage en génie électrique, il a été intéressant d'utiliser l'analogie des phénomènes de transport de masse et de charge dans le cœur de pile avec l'électricité. Cette analogie est basée sur les transferts d'énergie. L'exigence du faible coût de calcul implique de limiter le modèle à une seule dimension. Nous avons d'abord développé un modèle des tubes de gaz et de canaux pour les systèmes multi-espèces, des couches de diffusion de gaz, des couches de réaction et de la membrane. A ce niveau, nous avons obtenu un nouveau modèle circuit équivalent d'une cellule de pile. Pour la modélisation d'un stack composé de n -cellules, la façon la plus simple d'y arriver, est de multiplier la tension de sortie de la cellule par n (ce que l'on trouve dans la plupart des ouvrages). Cependant, nous avons choisi un modèle de pile qui tient compte du canal commun aux cellules et de la circulation des fluides dans chacune des cellules, ce modèle est plus proche de la réalité. Nous nous sommes limités à un stack de 3 cellules.

Nous avons décidé de mettre en œuvre le modèle sous Matlab / Simulink, logiciel du commerce très utilisé en électricité. Les résultats de simulations ont montré que le modèle est assez fidèle au fonctionnement réel de la pile. La tension de sortie de cellule calculée est en accord avec celle obtenue expérimentalement. L'effet du réseau de canaux entre chaque cellule de la pile a été exploré. Nous avons remarqué que l'effet du réseau de canaux pour une pile de 3 cellules est très faible. L'effet ne peut être très prononcé en raison de la petite taille du stack (3 cellules), D'ailleurs on note des différences de niveau de tension d'une cellule à l'autre dans de plus grand stack (16 cellules) et particulièrement en régime dynamique. Pour prouver que le modèle peut atteindre l'objectif fixé, le modèle de pile de 3 cellules a été connecté à un convertisseur élévateur. Nous avons constaté que la simulation peut être faite sans problème. L'interaction entre la pile à combustible et le circuit convertisseur est bien mise en évidence.

Notre modèle étant élaboré à partir des équations physiques, il ouvre la voie à un large éventail de futurs travaux de recherche. Diverses structures de contrôle peuvent être améliorées grâce à ce modèle. L'étude de l'impédance de la cellule à partir du modèle développé est le sujet premier dans notre liste de travaux futurs.

Section B

Unabridged Version in English

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Glossary of symbols

a	water activity	-
a_i	activity of species i	-
a_{Tube}	gas tube diameter	m
c_i	molar density of species i	mol/m ³
c_t	mixture molar density	mol/m ³
d	distance between the charge plates	m
f_{ij}	friction factor	kg/(m ³ · s)
h	height	m
j	net current density	A/m ²
$j_{0,anode}$	anode exchange current density	A/m ²
$j_{0,cathode}$	cathode exchange current density	A/m ²
k_B	Boltzmann's constant	J/K
w	width	m
m_i	molecular mass of species i	kg
\dot{m}	mass flow rate	kg/s
n_{drag}	water dragged coefficient	-
n_{pore}	equivalent pore holes number	-
$n_{H_2O,diff}^m$	molar transfer rate	mol/s
p_i	partial pressure of species i	Pa
t_m	thickness of the membrane	m
\mathbf{u}_i	velocity of species i	m/s
\mathbf{v}_i	average velocity	m/s
x_i	molar fraction of species i	-
A_{GDL}	cross-section area of the GDL	m ²
C	electrical capacitance	F
C_{GDL}	GDL equivalent capacitance	m ³ /Pa
C_H	Helmholtz's capacitance	F
$C_{H_2O,\lambda}^m$	equivalent capacitance in water content domain	mol/m ²
$C_{H_2O,\mu}^m$	equivalent capacitance in chemical potential domain	mol ² /J
$D_{H_2O,\lambda}^m$	water diffusion coefficient in membrane	m ² /s
$D_{H_2O,\mu}^m$	water diffusion coefficient in chemical potential domain	mol ² /(J · m · s)
D_{ij}	Stefan-Maxwell diffusivity between species i and j	m ² /s
D_{ij}^{eff}	effective diffusion coefficient	m ² /s
D_{iK}	Knudsen diffusion coefficient	m ² /s
E_{OCV}	open circuit voltage	V
E_r^\ominus	reference potential at the standard state	V

E_r	reversible potential at specified state	V
EW	equivalent weight of the membrane	kg/mol
F	Faraday's constant	C/mol
J	current density	A/m ²
K_O	pore-hole geometry factor	-
L	length	m
$N_{H_2O}^m$	water flux	mol/(m ² · s)
$N_{H^+}^m$	proton flux	mol/(m ² · s)
N_i	molar flux of species i	mol/(m ² · s)
P_{ch}	mixture pressure at the middle of the channel	Pa
P_{sat}	saturation pressure of water	Pa
Q	fluid volumetric flow rate	m ³ /s
R	gas constant	J/(K · mol)
R_{ch}	hydraulic resistance of channel	Pa · s/m ³
$R_{H_2O,\mu}^m$	equivalent resistance in chemical potential domain	J · s/mol ²
$R_{H^+}^m$	membrane ionic resistance	Ω
R_{ij}	Stefan-Maxwell diffusion equivalent resistance	kg/(m ⁴ · s)
R_{iK}	Knudsen diffusion equivalent resistance	kg/(m ⁴ · s)
RH	Relative humidifier	%
T	absolute temperature	K
V_{ch}	channel volume	m ³
V_{gas}	gas volume	m ³

Greek Symbols

α	anode charge transfer coefficient	-
β	cathode charge transfer coefficient	-
ε	porosity of the medium	-
ε_0	permittivity of free space	F/m
ε_r	relative permittivity of solution	-
η	dynamic viscosity	Pa · s
η	overpotential	V
η	per-unit distance	-
λ	water content	-
$\mu_{H_2O}^m$	chemical potential of water in membrane	J/mol
ρ	mass density of the fluid	kg/m ³
ρ_{dry}	specific weight of the membrane	kg/m ³
$\sigma_{H^+}^m$	ionic conductivity	S/m
τ	tortuosity of the medium	-

Chapter 1

Introduction

1.1 Why should we work on Fuel Cell Systems?

Energy from fossil fuels has been used for growing and supporting human civilizations for many decades. The use of fossil fuels, i.e., coal, oil, natural gas, transforms the industry, expands the economic, advances the technology, and improves the living standards of people [65-68]. Undoubtedly, the fossil fuels become the vital materials for economics of countries around the world.

The hard truth is that the current civilizations cannot be sustained by the energy from the fossil fuels. This is because the fossil fuels in the world are limited and the use of them results in environmental degradations. Precisely, burning fossil fuels generates toxic gases and carbon dioxide which is regarded as the root of climate change [68-70]. If human ignores this truth, the civilizations will have risk to collapse in the near future.

Scientists around the world are trying to solve the problem by two approaches. The first one is working on the demand side which is to reduce the energy demand and to improve the efficiency [71-73]. The second one is to looking for the new energy sources. The good news is that there are various renewable energy sources [74-77], this kind of the energy sources replenish them self automatically or by a little help from human. The major source of the renewable energy is the sun. The world energy consumption is just a tiny quantity compared to the energy that the sun transmitted to the world.

The current technology like solar cell or wind turbine allows us to convert the renewable energy into electricity. The major problem of electricity from the mentioned sources is that they are not always available during a day. This is the point where the hydrogen and fuel cells enter the scene.

Hydrogen is a gas that can be created from water by electrolysis process. The electrolysis process let water molecules adsorb energy from electricity and detach into hydrogen and oxygen gases. This process can be occurred in the reverse direction, the recombination of hydrogen and oxygen result in water and releasing the adsorbed energy. The simplest way to observe the recombination process is to ignite the hydrogen; the released energy can be seen immediately as the heat from burning.

A modified internal combustion engine which uses hydrogen as fuel can be configured as a prime mover of an electric generator for supplying electricity. This system first converts chemical energy to kinetic energy, and then to electric energy. Since the loss of energy appears in each step of conversions, the total energy loss of using an internal combustion engine with an electric generator is significant. An alternative method to convert chemical energy to electric energy is to use fuel cells. Fuel cells convert chemical energy to electric energy in single step. Fuel cells operate quietly and emit no pollution, so that, they are compatible with the concept of clean energy for the future. One more advantage of the fuel cell and hydrogen system to be addressed here is that hydrogen can be created from the current energy sources like fossil fuel or nuclear energy [69, 78]; this feature allows a smooth transition from the current technology to the future.

The sustainable energy system is the key factor for human living condition in the near future. Although many progresses have been made, there are still many challenges ahead. The mitigation from the oil age is imperative. The difficulty of inventing a new technology does not suggest human to give up, in contrast, it suggest human to make it quickly.

1.2 Preliminary on Proton Exchange Membrane Fuel Cells

The first demonstration of fuel cell was conducted by Sir William Grove in 1839 [79]. The research on fuel cell was very active in 1960 where fuel cells were developed for the NASA's space program. Technology at that time let the Alkaline Fuel Cell (AFC) be the best choice of electrical source on the space shuttle. The first Proton Exchange Membrane Fuel Cell (PEMFC) was developed during this program. The breakthrough of DuPont on Nafion membrane in late of 1960 made the PEMFC more suitable for real world application [80]. The researches on fuel cells have been increased rapidly since 1997 by the awareness of the energy and environmental problems. Various types of fuel cell are available, but PEMFC is seemed to be the most practical among the low temperature types. The applications of the PEMFC ranges from small portable devices to stationary power supplies for resident or industrial use [78, 81].

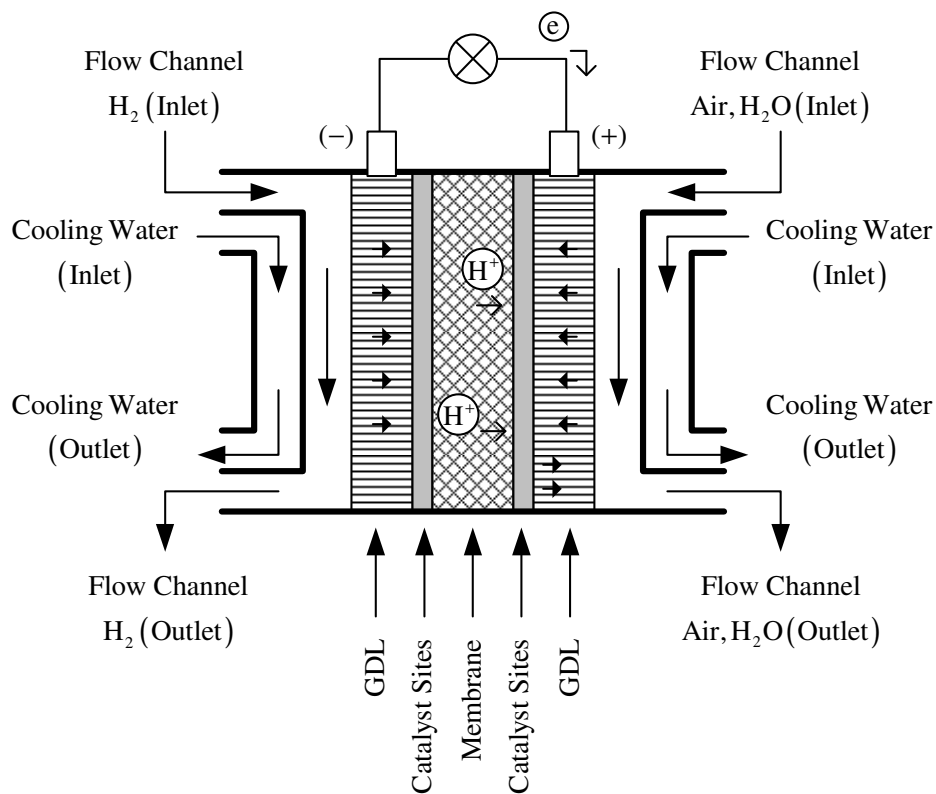


Figure 1-1 The PEMFC structure

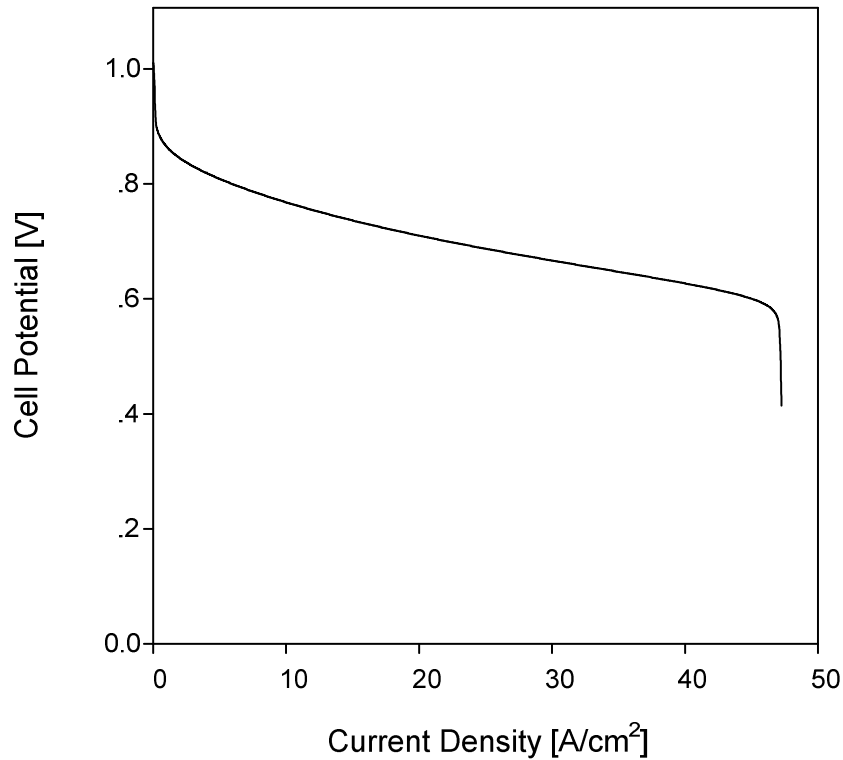


Figure 1-2 Typical V-I characteristic of the PEMFC

The simplified structure of the PEMFC is shown in figure 1-1. The membrane is situated in the middle of the cell. The unique property of the membrane is that the proton can travel across the membrane while the electron cannot.

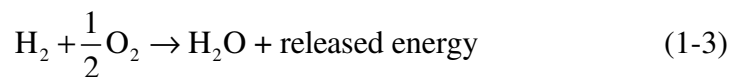
As hydrogen entering the anode side of cell, it will move to the catalyst layer which is at the boundary of the membrane. Here the hydrogen will separate into hydrogen ions (or simply called protons) and electrons. The chemical formula of this reaction is:



Since the membrane is the proton conductor, protons can move directly to the cathode side of the membrane. The electron cannot move through the membrane, it can reach the cathode side only if we provide an external circuit between the anode and cathode sides. The traveling of the electrons through an external circuit is the usable electrical current. As the electrons reached the cathode side, they combine with the protons and oxygen atoms, and result in water. The chemical formula on the cathode side can be written as:



The overall reaction is:



The electrical potential across the cell at open circuit state, E_0 , is related to the released energy by

$$E_0 = \frac{\text{released energy}}{2F} \quad (1-4)$$

where F is Faraday's constant.

For PEMFC the E_0 at the standard state is equal to 1.229 Volt. However, this potential is not observable at the cell terminal. The cell terminal potential is decreased by several factors. To archive more potential, scientists build a cell stack which is a pack of several fuel cells connected together in series. Although a higher potential can be obtained from the cell stack, the connection of the cell stack to the real world load still a challenge. The main problem is that the cell potential changes dramatically when it takes load. The typical V-I characteristic of PEMFC is shown in figure 1-2. Moreover, the dynamic response of the cell is slow and nonlinear [82, 83]. Not much application in the real world demands a constant current. These reasons suggest that a power electronic converter with auxiliary energy storage should be connected between fuel cells and loads [84-88].

1.3 PEMFC Models

The operation of the PEMFC is very complex, a number of parameters or conditions affect its performance and lifetime. The study of cell operations cannot always be done by experimental due to the limit of cost or technology. Models of the PEMFC can be used in place of the real system for studying purpose.

Model is a thing that we use to represent something in real world [89]. The model cannot have details greater than its original. The level of simplification is depending on the objectives and the requirements of the model. PEMFCs are multi-disciplinary devices; various approaches of different scientific fields have been used for studying different phenomena of the cells. Since each phenomenon in the PEMFC is highly coupled with the other, each kind of PEMFC model has some intersection with the other, so that, the categorization of the fuel cell model is quite not definite. The major types of the PEMFC model are presented as follow.

1.3.1 Physical Model

This kind of model relies on the physics equations which describe the real phenomena of the fuel cell [1-11]. The model may represent the whole cell or just a specific part [12-15]. The model is range from 1-dimension to 3-dimensions [16-20] and different assumptions, for example, one or two phase flow, isothermal or non-isothermal, can also be made [7, 20-22]. An example result form a 2-dimension physical model is shown in figure 1-3. Since this kind of models is highly complex and nonlinear, it is usually solved by finite element method which requires a tremendous computational cost [6].

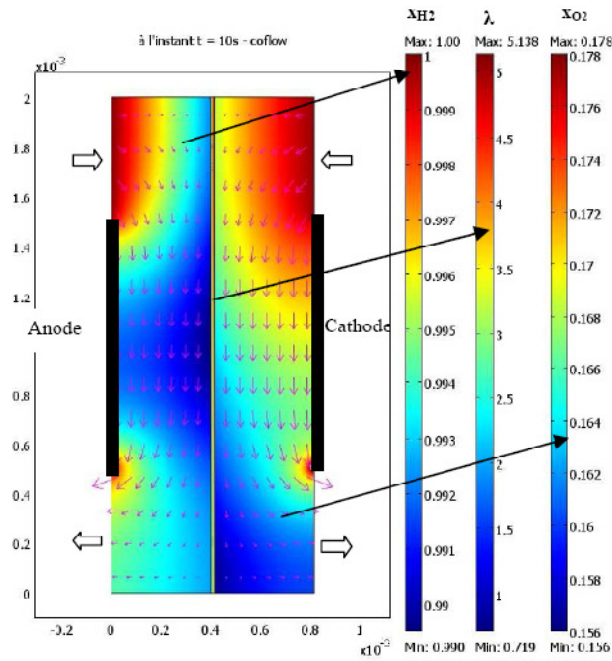


Figure 1-3 An example of simulation result from a PEMFC physical model [1]

1.3.2 Empirical or Semi-Empirical model

The empirical model is also known as the behavioral model. The model is based on the observed behavior which the real system response to the stimulus [23-33]. The mathematical formula, like exponential, logarithm, or polynomial, can be used to provide a link between the stimulus and the responses. The advantage of the empirical model is the simplicity. The model which represents a static characteristic of an observed cell can be just a one line of equation. One of simplest static characteristic equation is shown in [32] where

$$E = \frac{E_{OCV}}{1 + \left(\frac{I}{I_h}\right)^\alpha} \quad (1-5)$$

In this equation, E_{OCV} is the open circuit voltage, I_h and α are the fitting parameters.

Since the model is developed from the observed response of the cell, the model does not provide a solid link between physical parameters, for example the cell temperature, the relative humidity of the air at the inlet, or the pore size of porous media, to the cell behaviors. Many researchers try to create an empirical model which incorporates some physical properties of the cells. This kind of models is regarded as a semi-empirical model. The establishing of physical aspect to the model results in an increasing of model complexity. The different between the semi-empirical model and the physical model is that the empirical model still relies on the measured data and fitting parameters.

1.3.3 Equivalent circuit model

This model is closely related to the empirical model. The main difference is that the link between the stimulus and the response is not represented by a set of mathematical functions, but by an electric circuit [26, 34-50]. The model requires less computational cost than the model that is based on physics equations. An example of PEMFC circuit model is shown in figure 1-4. The PEMFC equivalent circuit model can be integrated seamlessly with a circuit model of a power electronic converter that is connected to the cell's electrical terminals. This kind of model is preferred by electrical engineers.

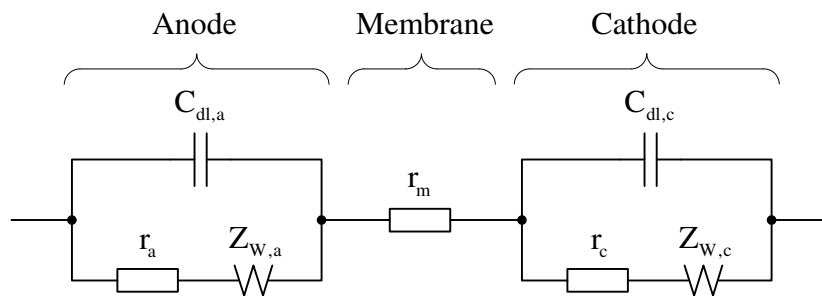


Figure 1-4 An example of PEMFC equivalent circuit model [32]

The equivalent circuit model in literature can be classified into two major categories. The first one is the classical circuit which is based on the response in the frequency domain [40, 45, 46, 49, 50]. This kind of model is well studied in electrochemistry. The other one is the circuit that mimics the characteristic curve of the fuel cell [26, 29, 34, 35, 38, 39, 41-44, 47, 48].

1.3.4 The control oriented model

This kind of model is developed for control design purposes [26, 29, 49, 51-55]. It is usually a linearized version of the physical model at a certain operating point. The model is usually in the form of state equations which conform to various conventional or modern control design techniques.

1.4 The objective of this thesis

As we have mentioned that PEMFCs have a low output voltage level and slow dynamic response. Connecting the fuel cell output directly to the conventional load may result in a serious problem. The responsibility for designing the power electronic converter to transmit electrical energy from the cell output to the load properly belongs to electrical engineers. In order to study and verify their design, electrical engineers need a PEMFC model that can be easily incorporated with their novel power electronic circuits. Since engineers have to simulate their fuel cell/converter system in countless times before they arrive at a good solution, the model of choice should also require a reasonable computational cost.

The physical models which are developed by chemical or mechanical engineers are very difficult for the electrical engineers. Furthermore, this kind of model uses the finite element method which not only requires a high computational

cost, but is also not compatible with circuit simulations. This is why the empirical type of the PEMFC models is preferred by electrical engineers.

The empirical model is simple and requires a little computation cost. However, the drawback of the empirical model is the absent of the internal chemical or transportation mechanics which may useful in the designing of the power electronic circuits. Moreover, since the model is based on the measured behavioral data, scientists or engineers cannot adjust any physical parameter of the cell to see the different interaction between the cell and the power electronic circuits. The aim of this work is to fill this gap. A circuit model which incorporates the fundamental mechanics of the PEMFC and compatible with circuit simulations is the goal of this thesis.

Chapter 2

Equivalent Circuit Models for PEMFCs

This chapter presents the development of an equivalent circuit model of the PEMFCs stack. We begin the chapter with setting up the requirement of the model, then presenting the conceptual structure of the cell. After that we discuss about the energy exchange concept which is used extensively throughout the chapter. The development of the circuit model is presented part-by-part from the channels, the flow-field plate, the gas diffusion layer, the catalyst layer and the membrane, in a step-by-step manner. Then we combine each part together to form the single-cell model. At last, the stack model of 3-cell is presented.

2.1 Physical Description of a Single Cell System

Model is something that mimics a real system [89]. The nature of the model is having less detail than the real system. The level of simplification which affects the complexity of the model is subject to the objective or requirement of the model. In this thesis we aim to construct a one dimension PEMFC model that reveals the gas transport behavior in channels, flow-field plates and the gas diffusion layers. The model must also include the membrane water transport and necessary chemical effects. We assume that the temperature of the cell is constant and the water in the cell is only in gas phase.

From the requirements, we simplified the real PEMFC system to a conceptual structure as shown in figure 2-1. The 3-cell PEMFC stack model, which is our final goal, is considered as an extended version of this structure.

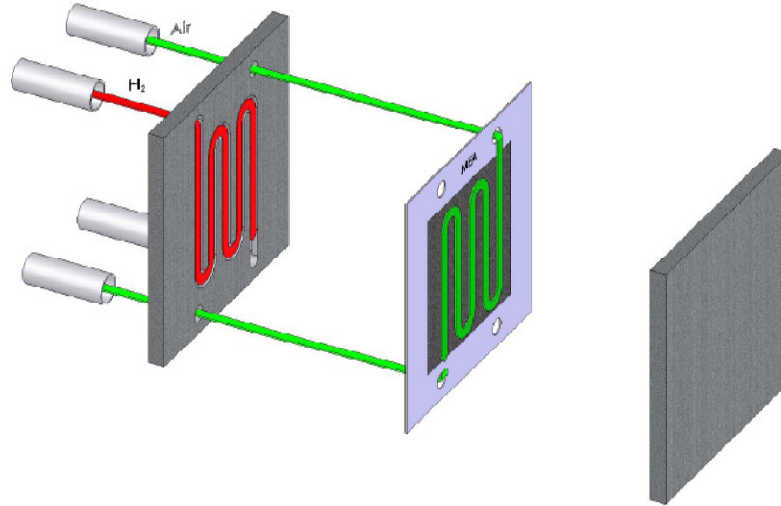


Figure 2-1 The PEMFC conceptual structure of PEMFC used in this work

2.2 Analogy of physical systems

Energy exchange concept is a famous idea used in multidisciplinary modeling [56]. This concept considers each component in a dynamic system as an energy manipulator, as shown in figure 2-2. The energy flows from one system to another system via an energy port. The energy port has two associated variables, where one of the variables represents the flow of the energy and the other one represents the effort or the strength that create the flow. The product of these two variables is an instantaneous power, i.e., the rate that the energy transferred through the energy port per unit time.

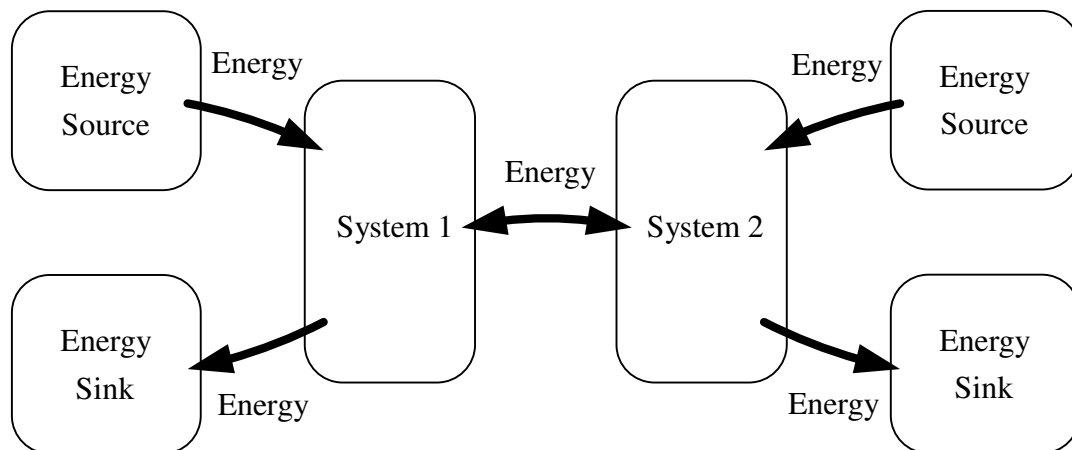


Figure 2-2 Physical systems as energy transfer elements

Two systems in different domain are shown in figure 2-3 and 2-4. The system in figure 2-3 is in electrical domain where the effort is the voltage and the flow is the current. The system in figure 2-4 is in hydraulic domain where the effort is the pressure and the flow is the volumetric flow.

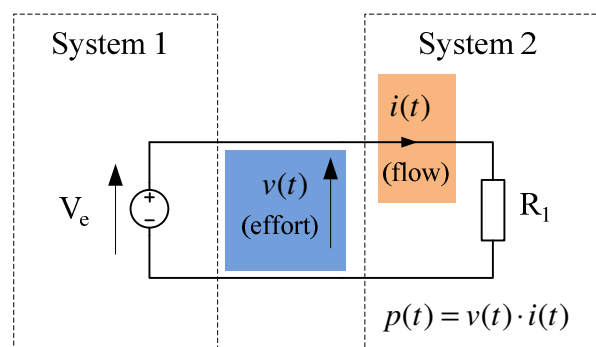


Figure 2-3 Efforts and flows in an electrical circuit

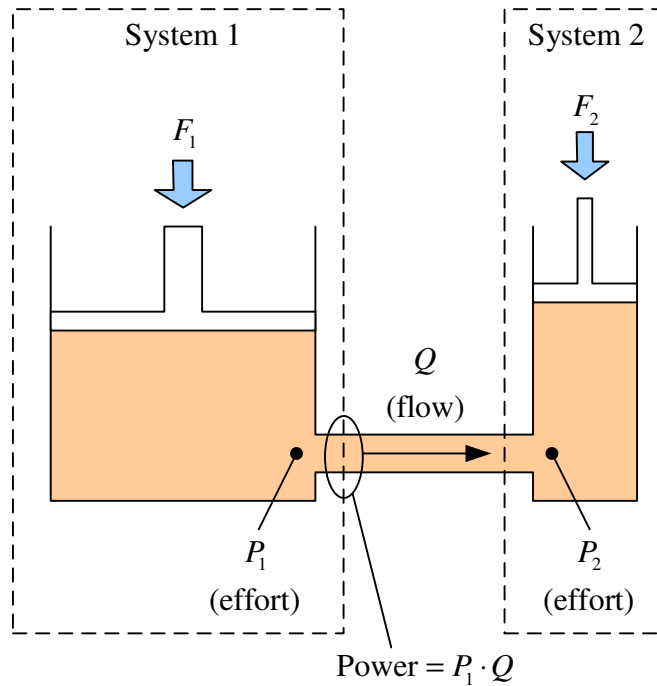


Figure 2-4 Efforts and flows in a hydraulic system

Since energy is appeared in every physical system, the concept provides a proper method to link systems from different energy domains together. Thus we will follow this concept for making an appropriate circuit analogy model of the fuel cell systems.

2.3 Gas Channel Model

2.3.1 Analogy of Fluid Systems

According to the principle of energy transfer and system variables, it is well known that the fluid pressure is an effort and the volumetric flow rate is a flow. The product of these two variables is the work done per unit time on the system.

2.3.1.1 Dissipation Element

In electrical circuit, resistance is considered as an energy dissipating element which results in a dropped voltage along the charge flow path. In the same manner, fluid energy is also dissipated along the fluid flow path which results in a dropped pressure across the channel. As Ohm's law in electrical circuit, Hagen–Poiseuille law [57] describes the relationship between the pressure dropped across a fluid channel, Δp , and the fluid volumetric flow rate, Q , as:

$$\Delta P = R_{ch} \cdot Q \quad (2-1)$$

where R_{ch} represents a hydraulic resistance of the channel. This value depends on properties of the channel and the fluid.

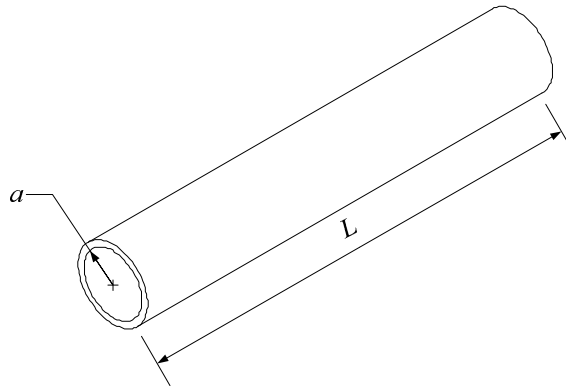


Figure 2-5 A circular cross-section channel

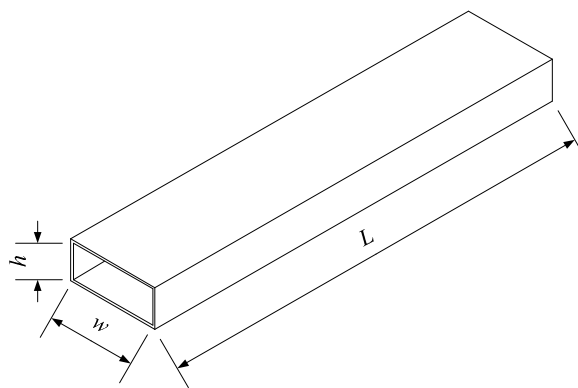


Figure 2-6 A rectangular cross-section channel

For the fuel cell system, there are mainly two kinds of gas channel which are circular and rectangular cross-section channels. A tube used to convey oxidizing and reducing agents from one device to another usually have circular cross-section shape. Rectangular cross-section channels can be found inside of some devices, for example, a flow field plate of the fuel cell.

The hydraulic resistance of the straight circular channel depicted in figure 2-5 is defined as:

$$R_{ch} = \frac{8}{\pi} \eta L \frac{1}{a^4} \quad (2-2)$$

where a is the radius, L is the length of the channel, and η is the dynamic viscosity of the fluid. The dynamic viscosities of the gas used in the PEMFC are presented in table 2-1.

For the straight channel with rectangular cross section as shown in figure 2-6, the hydraulic resistance is described as:

$$R_{ch} = \frac{12 \cdot \eta \cdot L}{1 - 0.63(h/w)} \cdot \frac{1}{h^3 \cdot w} \quad (2-3)$$

Table 2-1 Viscosity of the interested gases at 1 bar (10^5 Pa) [90]

Gas	Viscosity ($\mu\text{Pa} \cdot \text{s}$)	
	300 K	400 K
H_2	9.0	10.9
N_2	17.9	22.2
O_2	20.8	26.1
<i>Air</i>	18.6	23.1

where h and w are the height and width of the channel. The formula requires that $w > h$, in case of $w < h$, a rotation may apply to the channel to switch between w and h .

2.3.1.2 Flow Store Element

In electrical systems, the flow store element is a capacitor and its capacitance is defined as:

$$C = \frac{d(\text{Electric Charge})}{d(\text{Potential})} \quad (2-4)$$

Thus the equivalent capacitance for the fluid system is literally defined as:

$$C_{ch} = \frac{d(\text{Gas Volume})}{d(\text{Pressure})} \quad (2-5)$$

As we suppose that the channel walls of fuel cell systems are rigid, volumes of the channels are constant, and the channels behave like a pressurized tank depicted in figure 2-7. The volumetric flow rate which flow into the closed tank is the inlet flow rate subtracted by the outlet flow rate of the channel.

From the mass conservation principle, the relationship between the flow rate and the tank pressure is

$$\dot{m} = \rho \cdot Q = V_{ch} \frac{d\rho}{dt} \quad (2-6)$$

or

$$\rho \frac{dV_{gas}}{dt} = V_{ch} \frac{d\rho}{dt} \quad (2-7)$$

where \dot{m} is the mass flow rate and ρ is the mass density of the fluid, V_{gas} is the volume of the gas flow into the tank, and V_{ch} is the channel volume.

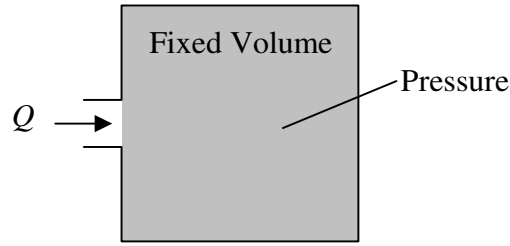


Figure 2-7 A pressurized tank which exhibit a flow store behavior [56]

The relationship between the fluid mass density and the fluid pressure is

$$d\rho = \frac{\rho}{\beta} dP \quad (2-8)$$

For an isothermal gaseous process, where the gas temperature is constant, $\beta = P$. Put (2-8) in (2-7), results in

$$\frac{dV_{gas}}{dP} = \frac{V_{ch}}{P} \quad (2-9)$$

Thus, the description of the equivalent channel capacitance is defined as:

$$C_{ch} = \frac{V_{ch}}{P} \quad (2-10)$$

2.3.2 Circuit Model for Gas Tubes or Straight Channels with Single-Species Gas

For a straight channel, the channel capacitance effect may appear regardless of the direction of the fluid. Thus, the capacitance for the circuit model should be placed in the middle of the evaluated channel resistance [47]. This can be done by dividing the channel resistance into two resistors; each resistor represents a half of channel resistance, i.e. a channel resistance from the inlet or outlet to the middle point of the channel. As the fluid is defined as a pure gas, there is only one pressure in the system and only one capacitance is required to represent the dynamic of the system. The equivalent capacitance is connected at the pseudo-middle point as shown in figure 2-8. Please note that the same circuit can be applied to a mixture gas system if its component ratios are constant along the tube.

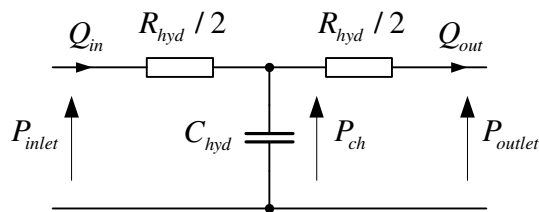


Figure 2-8 An equivalent circuit model of a straight channel

2.3.3 Circuit Model for Gas Tubes or Straight Channels with Multi-Species Gas

Gas in the PEMFC channel is usually a mixture gas. The most common gas on the cathode side is humidified air. Even on the anode side where the pure hydrogen is fed to the cell inlet, the gas inside the fuel cell is actually a combination of hydrogen and the water vapor which diffuses through the MEA from cathode to anode side. As the gas from the supply passed the inlet channel, the gas is fed to the gas diffusion layer (GDL) via a special channel which called a flow-field channel. The flow-field channel has only three rigid walls. The other side of the wall is a surface of GDL, which allows gases to pass through. Each species of the mixture gas is consumed or produced in the channel at different rates. This clearly affects the ratio between each species in the channel, especially at low gas flow rate. As a result, the essential model of the gas channel in figure 2-8 is not sufficient to represent the flow-field channel and the channel prior it.

We shall begin to develop a more suitable channel model by considering the PEMFC anode channel. We assumed that the inlet gas is a combination of hydrogen and water vapor. However, before starting up, where both hydrogen and water vapor have not entered the channel, it seems incorrect to assume that the channel is completely empty, i.e. in a vacuum state. In most cases, the anode channel is usually filled with air or nitrogen before starting up. Two solutions to this issue are: 1) skip the start up period by assume that the hydrogen is already filled in the channel, 2) introduce the third species in the model. In this work, we supposed that nitrogen, a non-reactive gas, is occupied the whole channel before we start up the cell.

From the assumptions we had made, we were now ready to establish the governing equations of the anode channel model. We firstly considered the pressure at the middle of the channel, P_{ch} , which defined as:

$$P_{ch} = p_{H_2(ch)} + p_{H_2O(ch)} + p_{N_2(ch)} \quad (2-11)$$

Each partial pressure is a consequence of the total flow rate of each species and the channel capacitance. The relationships can be written as follow:

$$\frac{d}{dt} p_{H_2(ch)} = \frac{Q_{H_2(stored)}}{C_{ch}} \quad (2-12)$$

$$\frac{d}{dt} p_{H_2O(ch)} = \frac{Q_{H_2O(stored)}}{C_{ch}} \quad (2-13)$$

$$\frac{d}{dt} p_{N_2(ch)} = \frac{Q_{N_2(stored)}}{C_{ch}} \quad (2-14)$$

where the total flow rates are the rates that the gases fill the channel, which are described as:

$$Q_{H_2(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{H_2(in)} - \frac{P_{outlet}}{P_{ch}} Q_{H_2(out)} \quad (2-15)$$

$$Q_{H_2O(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{H_2O(in)} - \frac{P_{outlet}}{P_{ch}} Q_{H_2O(out)} \quad (2-16)$$

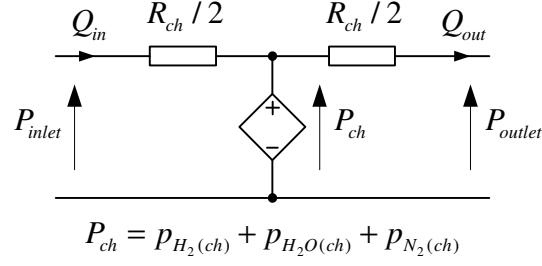


Figure 2-9 A modified circuit for the flow field channel model

$$Q_{N_2(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{N_2(in)} - \frac{P_{outlet}}{P_{ch}} Q_{N_2(out)} \quad (2-17)$$

Since it was difficult to combine the dynamic of three dependent voltages in a single capacitor, we managed to replace the capacitor in the essential model in figure 2-8 by a dependent voltage source as shown in figure 2-9.

The inlet flow rate of each species, $Q_{X(in)}$, is clearly proportional to the inlet mixture gas flow rate, Q_{in} , and the molar fraction of each species at the inlet. We assumed that the gas composite ratio at the inlet is controlled by an external system, thus the molar fraction of each species is constant, and can be written as:

$$Q_{H_2(in)} = x_{H_2(in)} \cdot Q_{in} \quad (2-18)$$

$$Q_{H_2O(in)} = x_{H_2O(in)} \cdot Q_{in} \quad (2-19)$$

$$Q_{N_2(in)} = x_{N_2(in)} \cdot Q_{in} \quad (2-20)$$

Since the sum of all molar fractions is equal to one, the following relation also holds:

$$Q_{in} = Q_{H_2(in)} + Q_{H_2O(in)} + Q_{N_2(in)} \quad (2-21)$$

The inlet gas flow rate was determined by Hagen–Poiseuille law as follow

$$Q_{in} = \left(\frac{P_{inlet} - P_{ch}}{R_{ch}/2} \right) \cdot \left(\frac{P_{inlet} + P_{ch}}{2P_{inlet}} \right) \quad (2-22)$$

In the same manner, for the outlet:

$$Q_{H_2(out)} = x_{H_2(ch)} \cdot Q_{out} \quad (2-23)$$

$$Q_{H_2O(out)} = x_{H_2O(ch)} \cdot Q_{out} \quad (2-24)$$

$$Q_{N_2(out)} = x_{N_2(ch)} \cdot Q_{out} \quad (2-25)$$

and

$$Q_{out} = Q_{H_2(out)} + Q_{H_2O(out)} + Q_{N_2(out)} \quad (2-26)$$

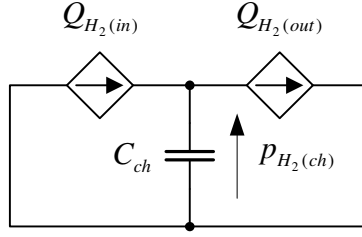


Figure 2-10 A sub-circuit model for H_2 dynamic response in the flow field channel

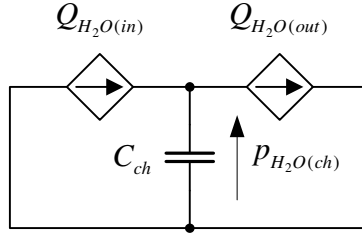


Figure 2-11 A sub-circuit model for H_2O dynamic response in the flow field channel

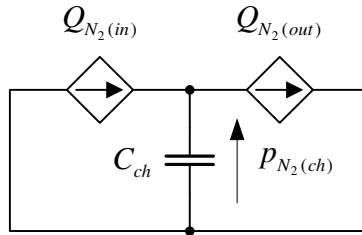


Figure 2-12 A sub-circuit model for N_2 dynamic response in the flow field channel

The gas flow out rate was determined by

$$Q_{out} = \left(\frac{P_{ch} - P_{outlet}}{R_{ch}/2} \right) \cdot \left(\frac{P_{ch} + P_{outlet}}{2P_{outlet}} \right) \quad (2-27)$$

However, the molar fractions of each species in the channel are not necessary to be constant. In other words, they may change from their initial values toward the values at the inlet. Thus, we defined the molar fractions of each species in the channel as:

$$x_{H_2(ch)} = \frac{P_{H_2(ch)}}{P_{ch}} \quad (2-28)$$

$$x_{H_2O(ch)} = \frac{P_{H_2O(ch)}}{P_{ch}} \quad (2-29)$$

$$x_{N_2(ch)} = \frac{P_{N_2(ch)}}{P_{ch}} \quad (2-30)$$

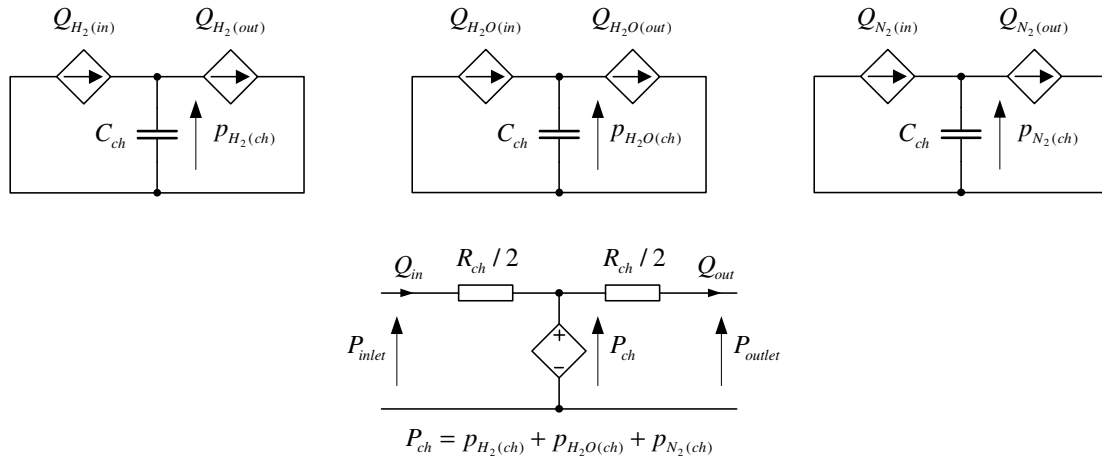


Figure 2-13 A complete circuit model for the anode side flow-field channel

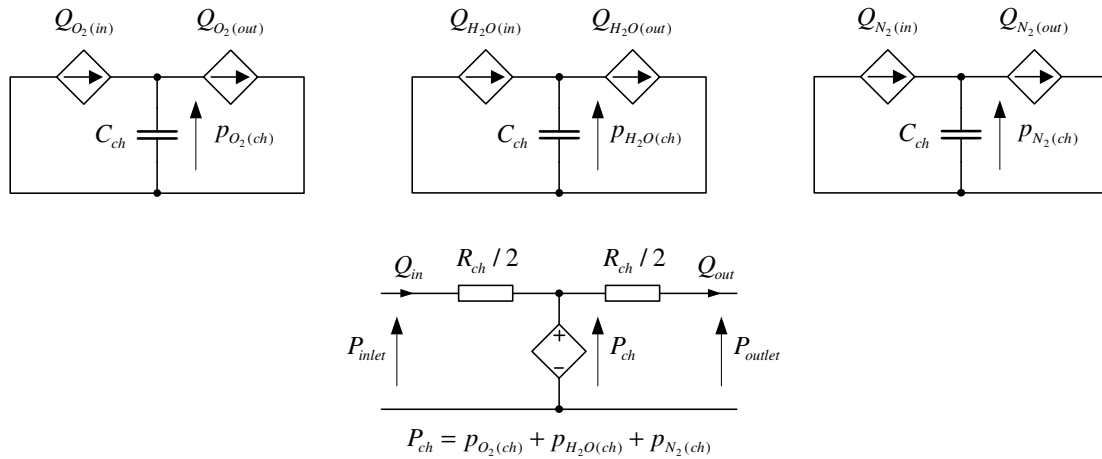


Figure 2-14 A complete circuit model for the cathode side flow-field channel

The derived equations are covering the detail of the gas transport mechanics in the channel and now we were ready to construct the new equivalent circuit model. Equation (2-12), (2-15), (2-18), and (2-23) led to a sub-circuit model shown in figure 2-10. In the same manner, equation (2-13), (2-16), (2-19) and (2-24) led to a circuit model shown in figure 2-11, and equation (2-14), (2-17), (2-20) and (2-25) led to the sub-circuit model shown in figure 2-12. The overall equivalent circuit model of the channel with multi-species gas on the anode side, which composes of the sub-circuits shown in figures 2-9 to 2-12, are depicted in figure 2-13.

The same process was applied to the channel on the cathode side. We merely changed the first species from H_2 to O_2 then we obtained the flow field equivalent channel model as shown in figure 2-14.

The idea of multi-species channel model can be easily applied to the flow-field channel. We mentioned earlier that the flow-field channel is a special channel. The channel is a small canal embedded on a surface of a graphite plate and covered with the GDL. The main functions of this special channel are to deliver the corresponding gas to the GDL surface uniformly and to collect or transmit electrons from or to the reaction site, which situates inside next to the GDL.

The pattern of the canal, which is likely to be found on the anode side, is the parallel-serpentine pattern as shown in figure 2-15. The parallel of direct channels, as shown in figure 2-16, is preferred on the cathode side because it can remove water droplet faster than the serpentine pattern [91].

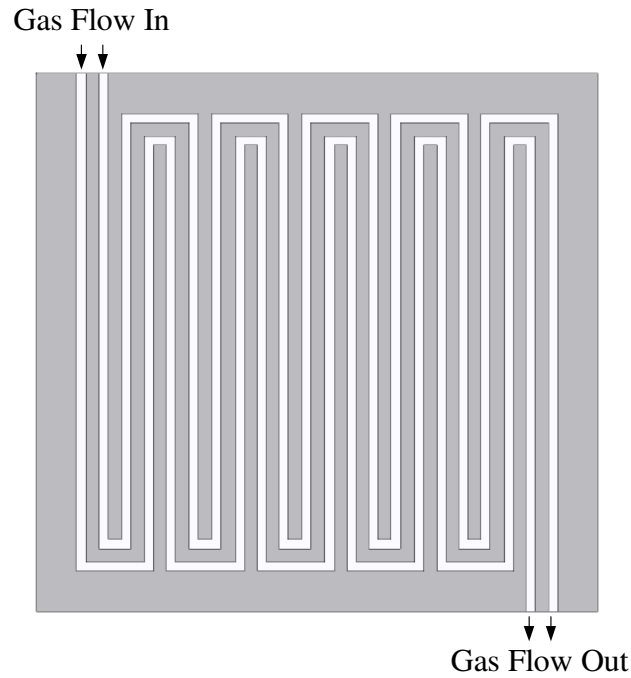


Figure 2-15 Parallel-serpentine pattern of the flow field plate (adapted from [91])

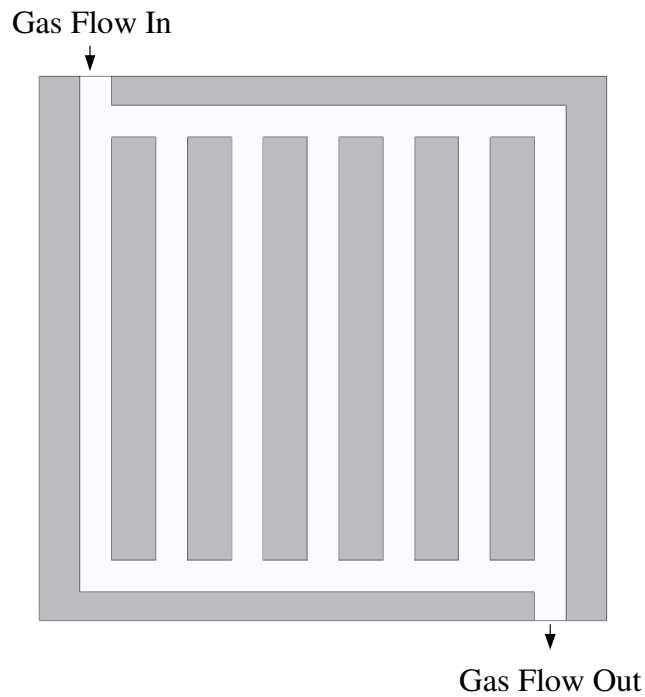


Figure 2-16 Direct parallel pattern of the flow field plate (adapted from [91])

The main difference between normal channel and flow-field channel is that one side of the flow-field channel is a porous wall. The porous wall allows each species of the mixture gas entering or leaving the channel at the same time. Thus, to adapt the circuit model of the normal straight channel to the flow-field channel, we modified equations (2-15), (2-16) and (2-17) as follow:

$$Q_{H_2(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{H_2(in)} - \frac{P_{outlet}}{P_{ch}} Q_{H_2(out)} - Q_{H_2(GDL)} \quad (2-31)$$

$$Q_{H_2O(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{H_2O(in)} - \frac{P_{outlet}}{P_{ch}} Q_{H_2O(out)} - Q_{H_2O(GDL)} \quad (2-32)$$

$$Q_{N_2(stored)} = \frac{P_{inlet}}{P_{ch}} Q_{N_2(in)} - \frac{P_{outlet}}{P_{ch}} Q_{N_2(out)} - Q_{N_2(GDL)} \quad (2-33)$$

The circuit model was modified by simply adding a current source to each channel capacitor. The current sources were used for representing the amount of the corresponding species of gas that leaves the channel into the GDL. The flow-field channel circuit model for anode and cathode sides are shown in figure 2-17 and 2-18, respectively.

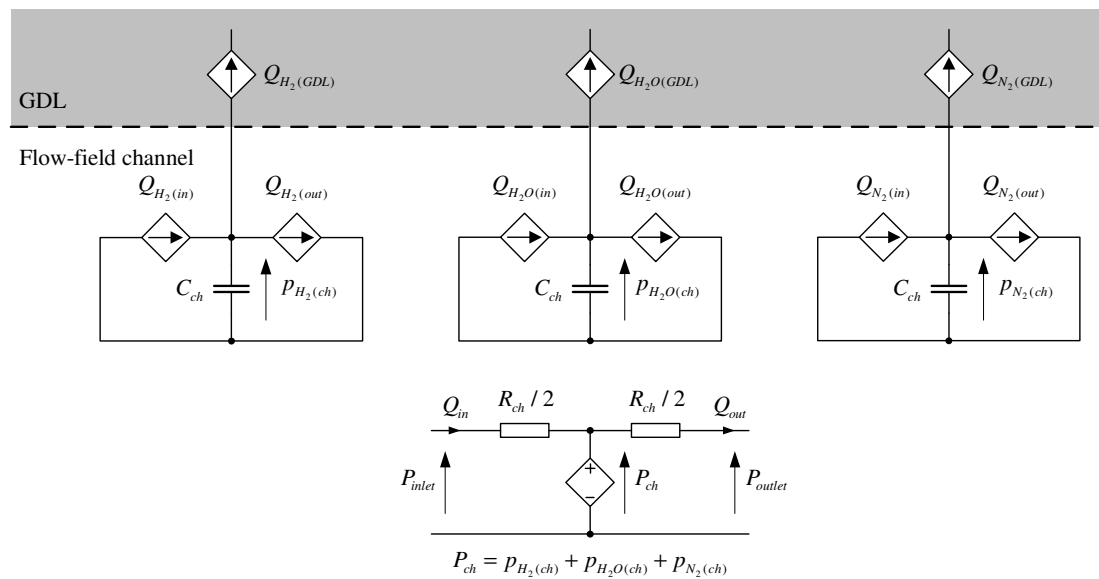


Figure 2-17 A complete circuit model for the anode side flow-field channel

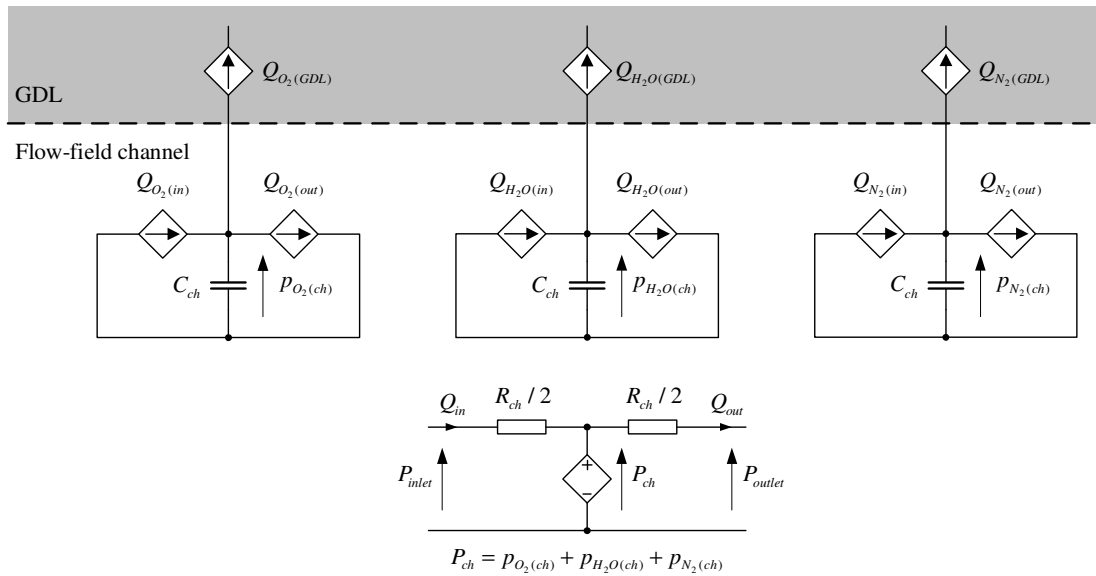


Figure 2-18 A complete circuit model for the cathode side flow-field channel

2.4 Gas Diffusion Layer Model

The gas diffusion layer (GDL) is situated between the flow field plate and the catalyst layer. The GDL is made from porous materials then the reactant gases can diffuse through. The inner side of the GDL is connected to the catalyst layer which the reaction occurred. This section will first focus on the diffusion mechanics which happen in the GDL, and then the equivalent circuit model will be developed.

2.4.1 Physical Description of Gas Diffusion Layers

The most common type of the GDL material is carbon fiber. The fiber can be randomly distributed as paper or woven as cloth. The GDL surface is usually finished with processes that enhance hydrophobic property. The micro structure of the GDL made from carbon paper is shown in figure 2-19.

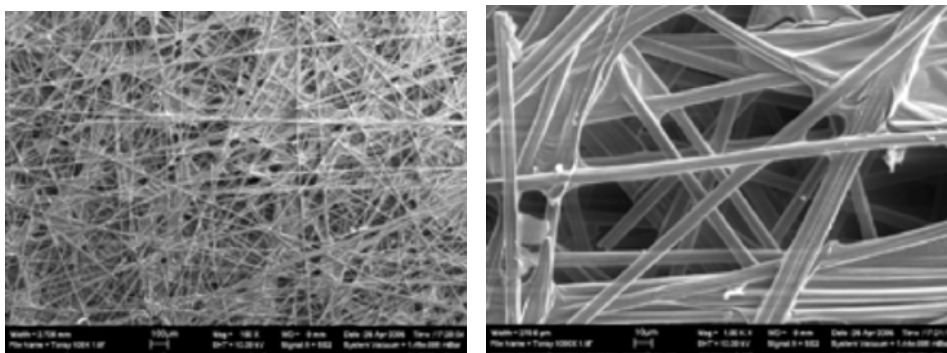


Figure 2-19 SEM image of a commercial GDL [92], (a) 100x, (b) 1000x

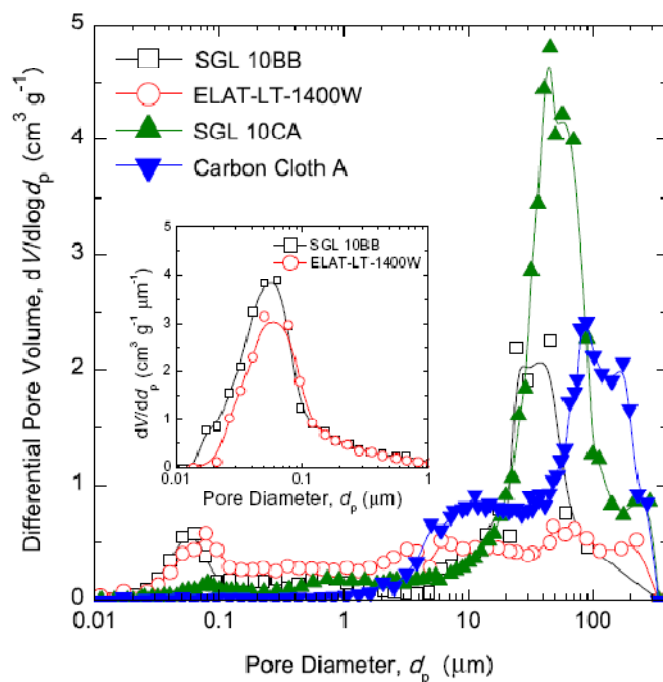


Figure 2-20 Distribution of GDL pore-sizes [93]

From figure 2-19, we can see that the GDL has numerous pore holes and the sizes of the holes are varied. The pore-sizes of the GDL are ranged between 10 nm to 400 μm , as shown in figure 2-20. The extremely small pore sizes are mainly due to the layer of carbon powder at the inner side of the GDL. The carbon powder functions as catalyst supporter. This carbon powder layer also knows as a micro porous layer (MPL).

2.4.2 Gas Transport in Porous Media

Generally, there are three different modes of transport in electrochemical systems, the convection, the diffusion and the migration [91, 94]. More than one transport modes can be occurred simultaneously, the total mass transferred is equaled to the sum of the mass transferred in each mode.

The transport of gas in convection mode is a movement of gas as a bundle which is resulted from external physical forces. In our case, the convection of gas in GDL is resulted from the difference of the total pressure of the gas. Though the pressure of fuel cell system is controlled by the pressure control valve, the pressure in the flow-field channel may slightly different from the pressure control valve due to the hydraulic resistance of the channel between them.

This mode of the transport is the same as the movement of the fluid in the channel that we have discussed before. Thus the same idea of channel model can be applied to the convection model of the GDL. However, one should note that the direction of the flow can be both into and out from GDL and a proper molar fraction should be selected to determine the flow quantity of each species. The effect of the carbon fiber of the GDL to the traveling path will be discussed later.

The transport of gas in the diffusion mode is the transport due to the different of the concentration of each species. The diffusion can take place even though the total pressure along the diffusion path is constant.

The transport in diffusion mode can be classified into several regimes. Each regime has its own theory and characteristics. The theories use in GDL modeling usually fall in one of the two following groups. The first group is the theories that describe the interaction between each molecule of the gas. In this case, the pore size of the GDL is very big compared to the mean free path of the gas then the effect of the porous wall is absent and the collision among the gas species is dominating the diffusion behavior. The most common theories are Fick's and Stefan-Maxwell diffusion laws.

The second group is the theories that describe the interaction between gas molecules and the porous wall. In case of the pore size of the GDL is very small compared to the mean free path of the gas, the collision between the gas molecules and the wall will govern the diffusion behavior. In this case the Knudsen diffusion theory is used.

The migration mode is the transport of particles due to an electric field. Since the charge of the gas is neutral, the migration mode does not affect the transport in the GDL. We also assume that the fluid in the GDL is only in the gas phase.

Table 2-2 Mean free path of Gases (at $P = 1 \times 10^5$ Pa and $T = 298.15$ K) [90]

Gas	Mean Free Path (nm)
H_2	126
N_2	67.6
O_2	73.6
<i>Air</i>	69.1

The pore-size of the GDL varies as shown in figure 2-20. Since the mean free path of the reactant gases, shown in table 2-2, fall in the same order of the pore-size, the diffusion is in a transition regime, i.e., both Knudsen and molecular diffusion regimes are occurred in GDL layers.

2.4.3 Stefan-Maxwell Diffusion

Consider a very small portion of space filled with more than one species of molecules as shown in figure 2-21. An average speed of species i , which diffuse through the space, are not only a function of the partial pressure p_i , but also effected by the other molecules. The Stefan-Maxwell Equation can be used to predict the diffusion behavior of each species in the systems.

The idea of the Stefan-Maxwell equation based on the molecular collisions mechanic is well described in [95], where

$$\left(\begin{array}{l} \text{The sum of the forces} \\ \text{acting on a system} \end{array} \right) \propto \left(\begin{array}{l} \text{The rate of change of the} \\ \text{momentum of the system} \end{array} \right) \quad (2-34)$$

since

$$\left(\begin{array}{l} \text{The sum of the forces acting on} \\ \text{species 1 molecules per unit volume} \end{array} \right) = -\nabla p_1 \quad (2-35)$$

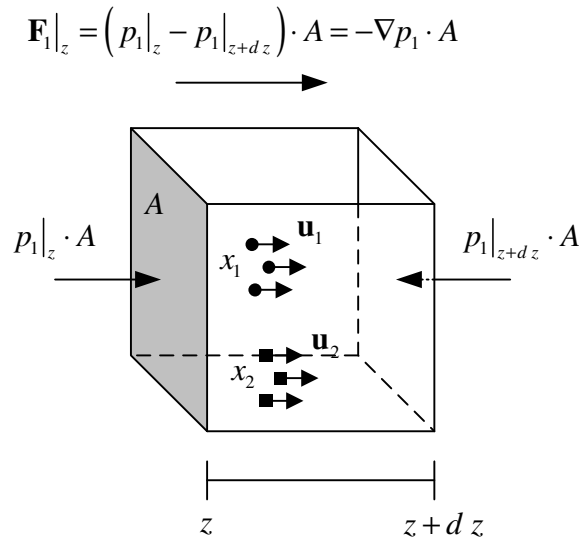


Figure 2-21 The small portion of a space which has a diffusion phenomenon

and

$$\left(\text{The rate of change of the momentum of the system} \right) = \left(\begin{array}{l} \text{The average amount of} \\ \text{momentum transferred} \\ \text{from a molecule of} \\ \text{species 1 to a molecule} \\ \text{of species 2 through} \\ \text{a single collision} \end{array} \right) \cdot \left(\begin{array}{l} \text{The number of} \\ \text{species 1-2 collisions} \\ \text{per unit volume} \\ \text{per unit time} \end{array} \right) \quad (2-36)$$

with

$$\left(\begin{array}{l} \text{The average amount of momentum transferred} \\ \text{from a molecule of species 1 to a molecule} \\ \text{of species 2 through a single collision} \end{array} \right) = \frac{m_1 m_2}{m_1 + m_2} (\mathbf{u}_1 - \mathbf{u}_2) \quad (2-37)$$

and the assumption of

$$\left(\begin{array}{l} \text{The number of species 1-2 collisions} \\ \text{per unit volume per unit time} \end{array} \right) \propto x_1 x_2 \quad (2-38)$$

With those ideas, one can deduce the following relation:

$$-\nabla p_1 \propto (x_1 x_2, (\mathbf{u}_1 - \mathbf{u}_2)) \quad (2-39)$$

or

$$\nabla p_1 = -f_{12} x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2) \quad (2-40)$$

For the convenient, the Stefan-Maxwell diffusivity between species 1 and 2 is defined as:

$$D_{12} = \frac{P}{f_{12}} \quad (2-41)$$

then

$$\nabla p_1 = -P \left(\frac{x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2)}{D_{12}} \right) \quad (2-42)$$

Since $x_1 = p_1/P$ and if the mixture pressure, P , is constant along the diffusion path, one can write

$$\nabla x_1 = -\frac{x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2)}{D_{12}} \quad (2-43)$$

The same idea can be applied to the species 2 and the result is

$$\nabla x_2 = -\frac{x_1 x_2 (\mathbf{u}_2 - \mathbf{u}_1)}{D_{12}} \quad (2-44)$$

For a ternary system which contains 3 species, the equations for the system can be written as follow:

$$\nabla x_1 = -\frac{x_1 x_2 (\mathbf{u}_1 - \mathbf{u}_2)}{D_{12}} - \frac{x_1 x_3 (\mathbf{u}_1 - \mathbf{u}_3)}{D_{13}} \quad (2-45)$$

$$\nabla x_2 = -\frac{x_2 x_1 (\mathbf{u}_2 - \mathbf{u}_1)}{D_{21}} - \frac{x_2 x_3 (\mathbf{u}_2 - \mathbf{u}_3)}{D_{23}} \quad (2-46)$$

$$\nabla x_3 = -\frac{x_3 x_1 (\mathbf{u}_3 - \mathbf{u}_1)}{D_{31}} - \frac{x_3 x_2 (\mathbf{u}_3 - \mathbf{u}_2)}{D_{32}} \quad (2-47)$$

Or one can deduce the equation for the n-species systems as:

$$\nabla x_i = -\sum_{j=1}^n \frac{x_i x_j (\mathbf{u}_i - \mathbf{u}_j)}{D_{ij}} \quad (2-48)$$

where D_{ij} is a diffusion coefficient between species i and j . Onsager's relation suggests that $D_{ij} = D_{ji}$.

However, the above form of Stefan-Maxwell relations is not so convenient because it is difficult to know the average speed of each species. The average speed can be eliminated by the definition of the molar fluxes which is

$$\mathbf{N}_i = c_i \mathbf{u}_i \quad (2-49)$$

where \mathbf{N}_i is the molar flux and c_i is the molar concentration of the specie i .

Substitute the molar fluxes into the developed Stefan-Maxwell relations results in the most useful form, which is:

$$\nabla x_i = \sum_{j=1}^n \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{c_i D_{ij}} \quad (2-50)$$

where c_i is the molar concentration of the mixture.

Note that only $n-1$ of the Stefan-Maxwell equations are independent. This is because the summation of all molar fractions is always equal to one. Thus, the n^{th} concentration gradient is obtained by

$$\nabla x_n = -\nabla x_1 - \nabla x_2 - \dots - \nabla x_{n-1} = -\sum_{k=1}^{n-1} \nabla x_k \quad (2-51)$$

2.4.4 The effect of porous medium to the molecular diffusion

Though the original version of the Stefan-Maxwell equation is developed for diffusion in free spaces, the equation is also valid for diffusion process in porous medium if the pore-size of the medium is much greater than the gas molecular mean free path. This is because one can assume that the molecules collide much more often with other molecules than the porous wall.

However, the present of the porous medium modify the path length and effective area of the diffusion. The effects of porous wall can be brought to the equation via the diffusion coefficient as follow [96]:

$$D_{ij}^{\text{eff}} = \frac{\varepsilon}{\tau} D_{ij} \quad (2-52)$$

In this equation, D_{ij}^{eff} is the effective or corrected diffusion coefficient, ε is the porosity of the medium which equal to the empty volume divided by the overall volume, and τ is the tortuosity of the porous medium.

Another method which is widely used [15, 97], is Bruggeman correction

$$D_{ij}^{\text{eff}} = \varepsilon^{1.5} D_{ij} \quad (2-53)$$

This is equivalent to equation (2-52) with $\tau = \varepsilon^{-0.5}$.

2.4.5 Circuit Model of Gas Diffusion Layers

The first part of GDL equivalent circuit model was developed from the Stefan-Maxwell equation. Since the Stefan-Maxwell equation describes transports in diffusion mode, we could assume that the total pressure along the diffusion path is constant. The effect of the transport in convection mode will be discussed in the later section.

According to the concept of energy exchange in physical systems, it seem that the effort variable is the molar fraction, x_i , and the flow variable is the molar flux, \mathbf{N}_i . However, a product of molar fraction and molar flux is a quantity that has unit different from power. In order to make a proper circuit analogy, we should select a more appropriate variables pair. As we knew that diffusion systems are involved with displacement of fluid molecules, the system variables was expected to be the pressure

and volumetric flow rate. Thus, we modified the Stefan-Maxwell equation into a form that contains the mentioned variables as follow.

From the standard form of the equation:

$$\frac{d}{dz} x_i = \sum_{j=1}^n \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{c_t D_{ij}} \quad (2-54)$$

which is derived from:

$$\frac{d}{dz} p_i = P \sum_{j=1}^n \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{c_t D_{ij}} \quad (2-55)$$

By the definition of:

$$D_{ij} = \frac{P}{f_{ij}} \quad (2-56)$$

and

$$x_i = \frac{p_i}{P} \quad (2-57)$$

equation (2-55) was rewritten as:

$$\frac{d}{dz} p_i = \sum_{j=1}^n \left\{ f_{ij} \cdot \left(\left(\frac{p_i}{P} \right) \cdot \left(\frac{\mathbf{N}_j}{c_t} \right) - \left(\frac{p_j}{P} \right) \cdot \left(\frac{\mathbf{N}_i}{c_t} \right) \right) \right\} \quad (2-58)$$

Now we had the partial pressure which was selected as the effort variable of the target system.

As (\mathbf{N}_i/c_t) represents the volumetric flow rate of specie i per unit area, the volumetric flow rate of the interested system was obtained by multiply the diffusion surface as follow:

$$\frac{d}{dz} p_i = \sum_{j=1}^n \left\{ f_{ij} \cdot \left(\left(\frac{p_i}{P} \right) \cdot \left(\frac{A}{A} \right) \cdot \left(\frac{\mathbf{N}_j}{c_t} \right) - \left(\frac{p_j}{P} \right) \cdot \left(\frac{A}{A} \right) \cdot \left(\frac{\mathbf{N}_i}{c_t} \right) \right) \right\} \quad (2-59)$$

or

$$\frac{d}{dz} p_i = \sum_{j=1}^n \left\{ \left(\frac{f_{ij}}{A} \right) \cdot \left(\left(\frac{p_i}{P} \right) \cdot \left(\frac{A \cdot \mathbf{N}_j}{c_t} \right) - \left(\frac{p_j}{P} \right) \cdot \left(\frac{A \cdot \mathbf{N}_i}{c_t} \right) \right) \right\} \quad (2-60)$$

The term $\left(\frac{A \cdot \mathbf{N}_i}{c_t} \right)$ represents the volumetric flow rate of species i . This can be confirmed by checking their units as:

$$\text{unit} \left(\frac{A \cdot \mathbf{N}_x}{c_t} \right) = [\text{m}^2] \cdot \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right] \cdot \left[\frac{\text{m}^3}{\text{mol}} \right] = \left[\frac{\text{m}^3}{\text{s}} \right] \quad (2-61)$$

We modified the distance of the diffusion to be per-unit value, which was denoted by η , where the base value was the thickness of the diffusion layer, which was denoted by l . We defined the relation of the per unit distance as follow:

$$\eta = (z - z_0) / l \quad (2-62)$$

The derivative of the per unit distance is equal to

$$dz = l \cdot d\eta \quad (2-63)$$

Substituting the derivative of η into the modified equation resulted in

$$\frac{d}{d\eta} p_i = \sum_{j=1}^n \left\{ \left(f_{ij} \cdot \frac{l}{A} \right) \cdot \left(\left(\frac{p_i}{P} \right) \cdot \left(\frac{A \cdot \mathbf{N}_j}{c_t} \right) - \left(\frac{p_j}{P} \right) \cdot \left(\frac{A \cdot \mathbf{N}_i}{c_t} \right) \right) \right\} \quad (2-64)$$

We defined

$$R_{ij} = \left(f_{ij} \cdot \frac{l}{A} \right) \quad (2-65)$$

and

$$Q_x = \left(\frac{A \cdot \mathbf{N}_x}{c_t} \right) \quad (2-66)$$

Then the derived equation became

$$\frac{d}{d\eta} p_i = \sum_{j=1}^n \left\{ \frac{R_{ij}}{P} \cdot (p_i \cdot Q_j - p_j \cdot Q_i) \right\} \quad (2-67)$$

As we considered partial pressures as voltages and volumetric flow rates as currents, the equivalent circuit could be written as shown in figure 2-22.

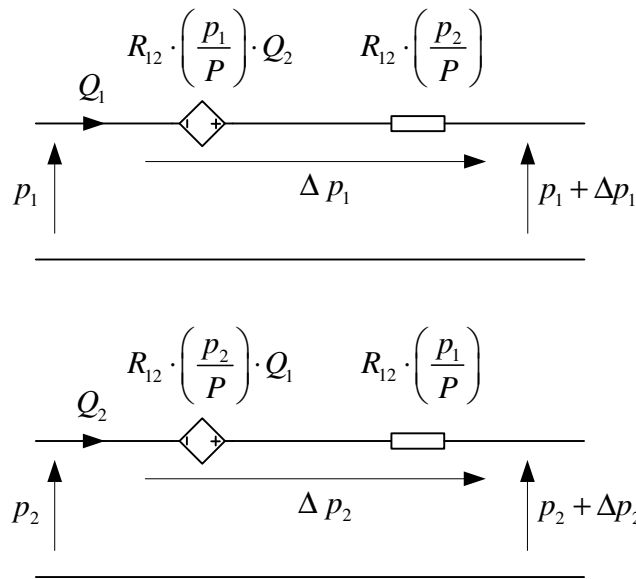


Figure 2-22 A literal circuit model from the modified Stefan-Maxwell equation

We further modified the circuit by source transformation theory. The principle of the theory is shown in figure 2-23 where a voltage source network is transformed to an equivalent current source network. The transformed circuit model is shown in figure 2-24. Note that the new circuit shows a more vivid link between each species than the literal circuit shown in figure 2-22.

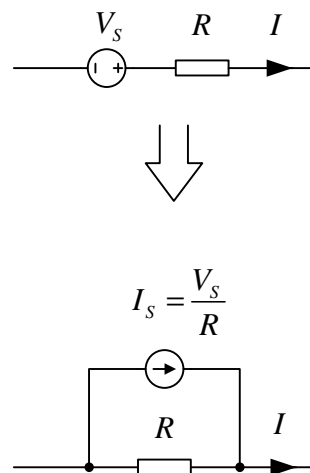


Figure 2-23 Principle of source transformation

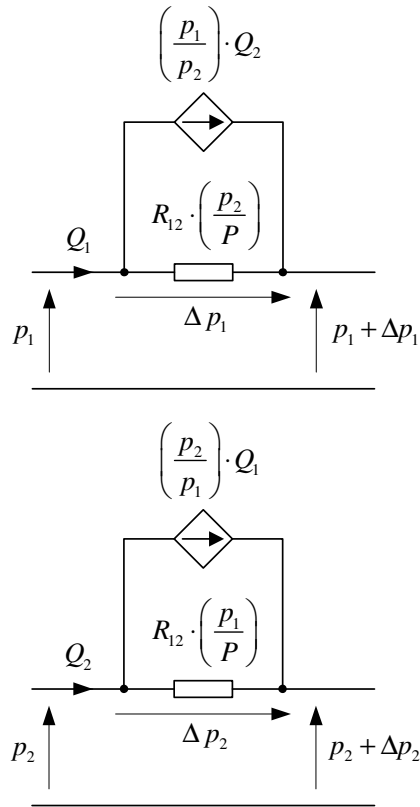


Figure 2-24 A modified equivalent circuit model for 2 species diffusion system

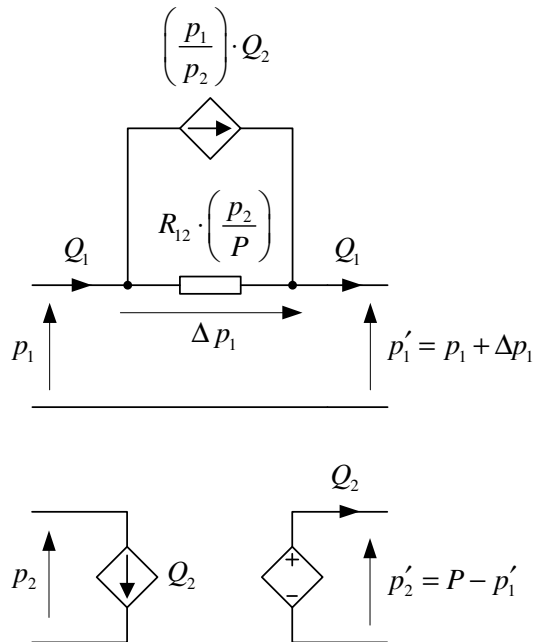


Figure 2-25 A simplified of 2-species circuit by its linear dependent property

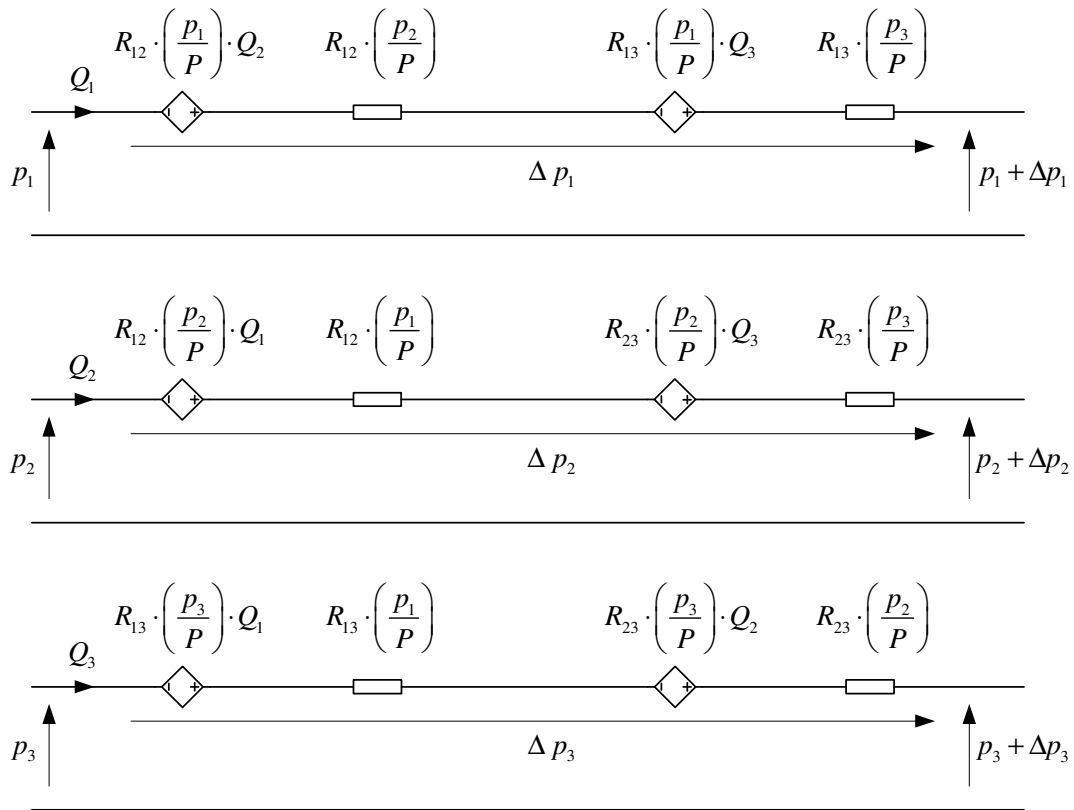


Figure 2-26 A literal circuit model for the 3-species diffusion system

As we assumed that the total pressure along the channel is constant, only $n-1$ equations of Stefan-Maxwell are independent and the circuit model in figure 2-24 was simplified to a circuit model shown in figure 2-25.

In the same manner, a literal and modified equivalent circuit model for 3 species diffusion system are shown in figure 2-26 and 2-27, respectively. The circuit in figure 2-27 is very interesting because it portrays the multi-species Stefan-Maxwell diffusion mechanic in simple but descriptive manner. It can be useful in educational purpose.

A more compact version of the circuit was also developed by reducing the circuit of each species in figure 2-26 to a series of total voltage and total impedance. Then, the source transformation theorem and a little bit manipulation led us to a circuit shown in figure 2-28. Though the circuit parameters are more complex, this circuit is simpler and suited for simulation purpose.

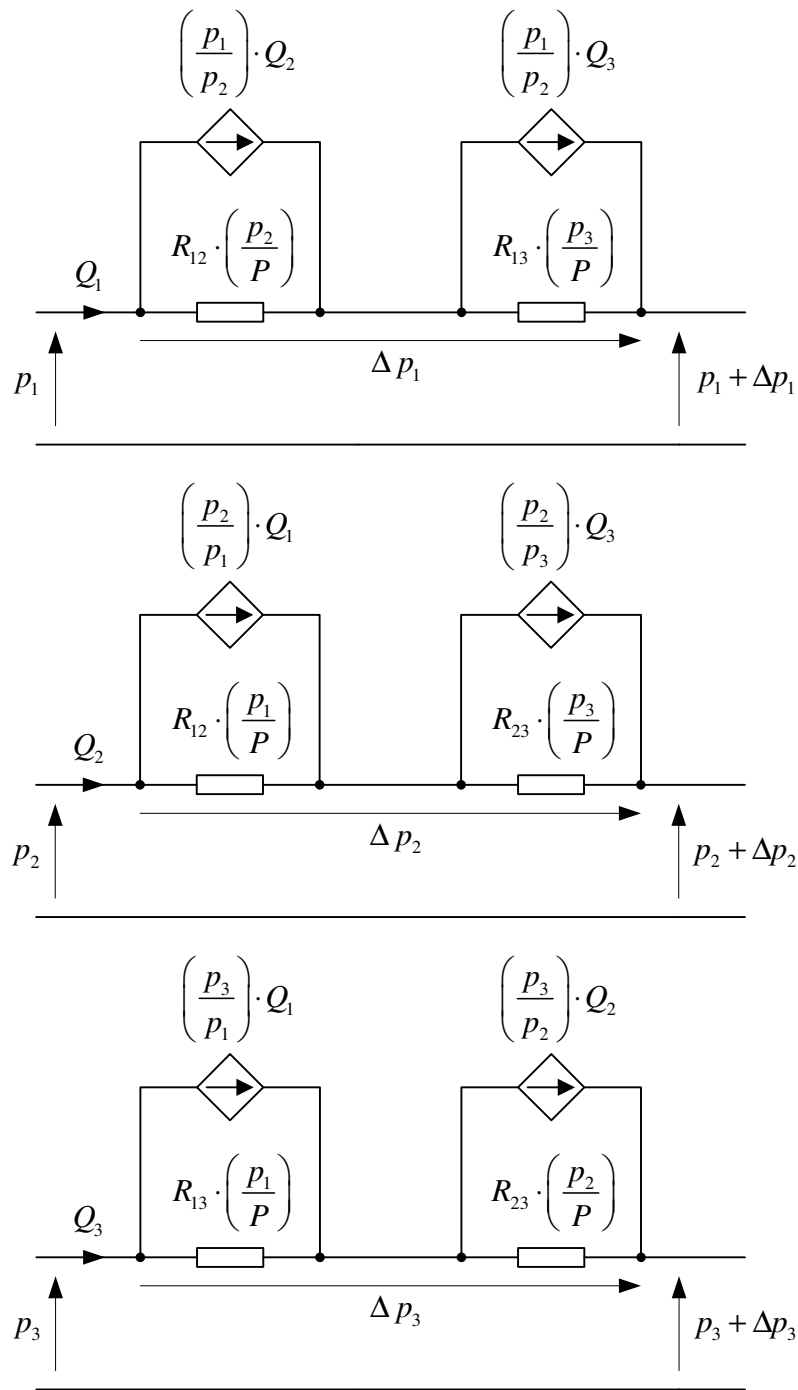


Figure 2-27 A modified equivalent circuit model for the 3-species diffusion system

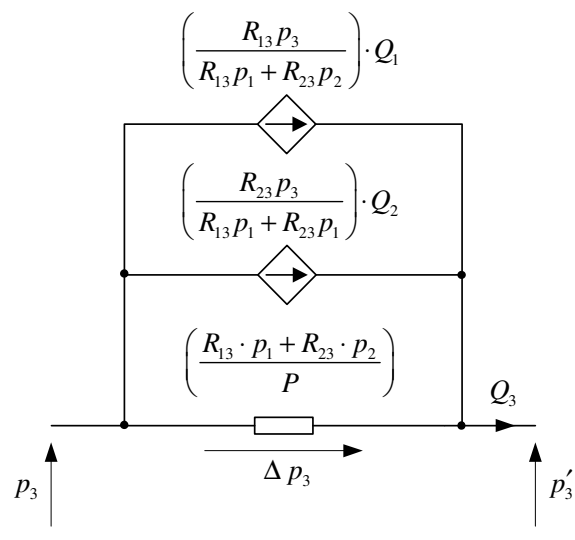
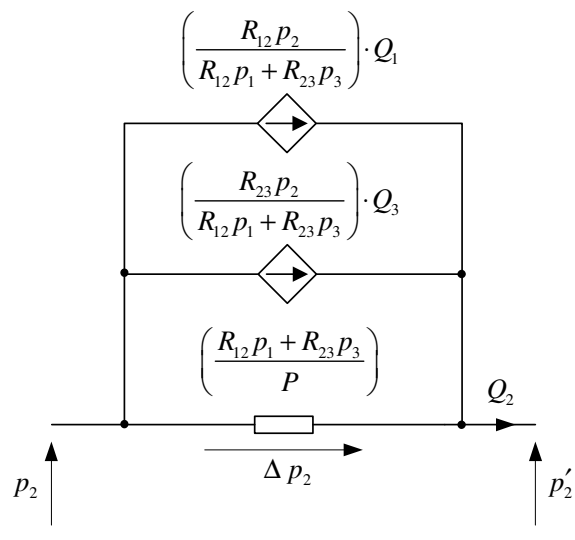
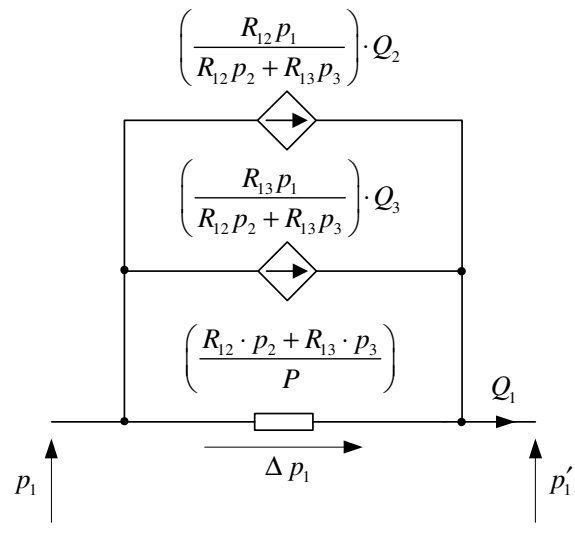


Figure 2-28 A 3-species circuit model modified for simulation purpose

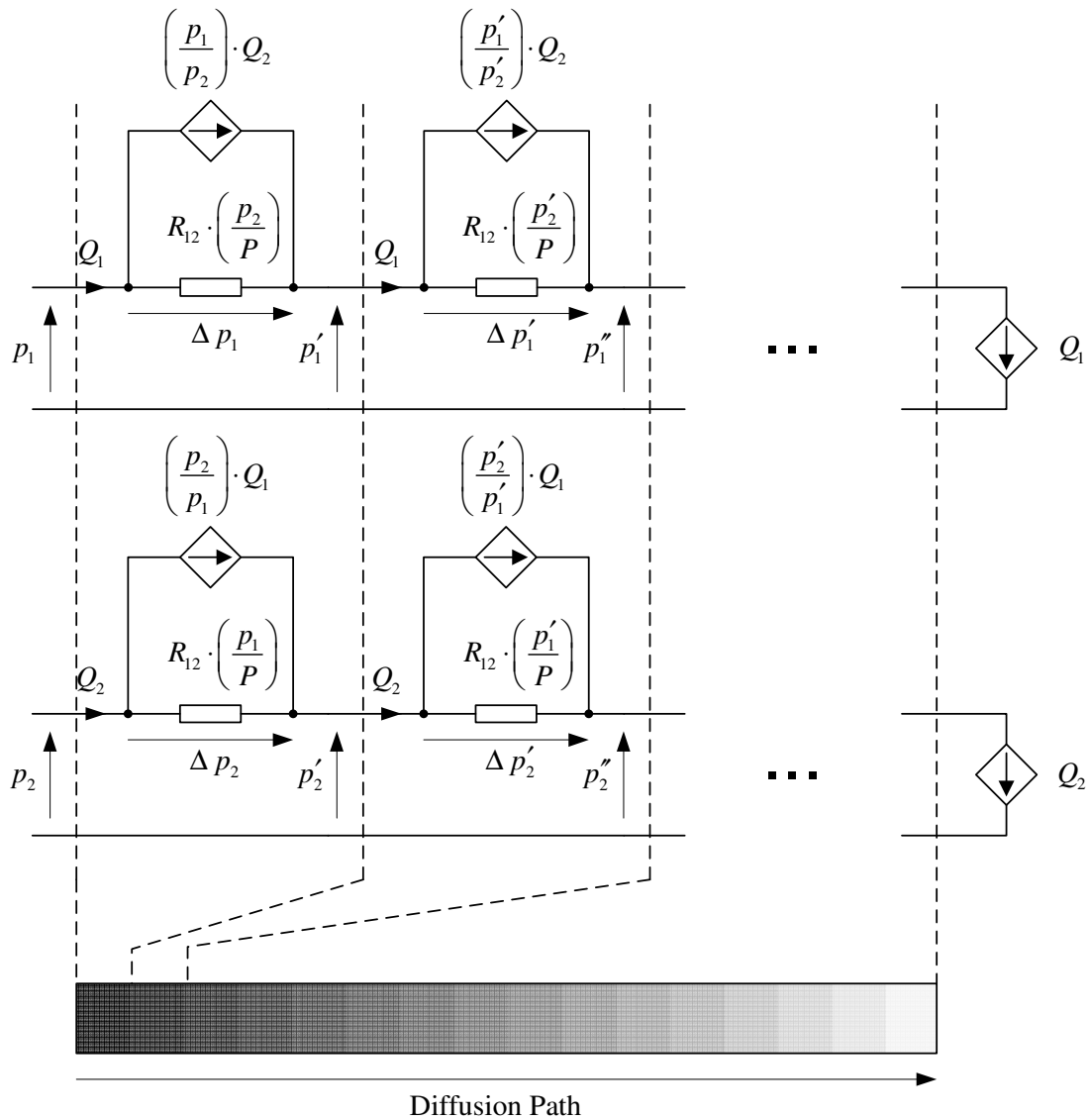


Figure 2-29 An idea of dividing GDL into sub-layer

As circuit parameters depend on partial pressures and the partial pressures are tend to change along the diffusion path, equivalent circuits with fixed parameter are approximately valid if the Δp_i is small. We solved this problem by divide the GDL into sub-layer along the diffusion path as shown in figure 2-29. This allowed us to update the circuit parameters along the diffusion path, and obtained more accurate results.

2.4.6 Flow Store Element of GDL

As in the channel model, a GDL equivalent capacitance was calculated from the empty space which related to geometric volume, V_{GDL} , and porosity, ϵ , of the GDL as follow:

$$C_{GDL_total} = \epsilon \frac{V_{GDL}}{P} \quad (2-68)$$

Refer to the proposed circuit model of the GDL which divides a GDL into several sub-layers, and each sub-layer has the equivalent circuit associated with. To place the GDL equivalent capacitance in each sub-layer circuit, the capacitance was calculated according to the geometry of the sub-layer. Thus,

$$C_{GDL} = \epsilon \frac{A_{GDL} L_{sub-layer}}{P} \quad (2-69)$$

where A_{GDL} is the cross-section area of the GDL and $L_{sub-layer}$ is the thickness of each sub-layer. The equivalent capacitor was placed between each sub-layer as shown in figure 2-30.

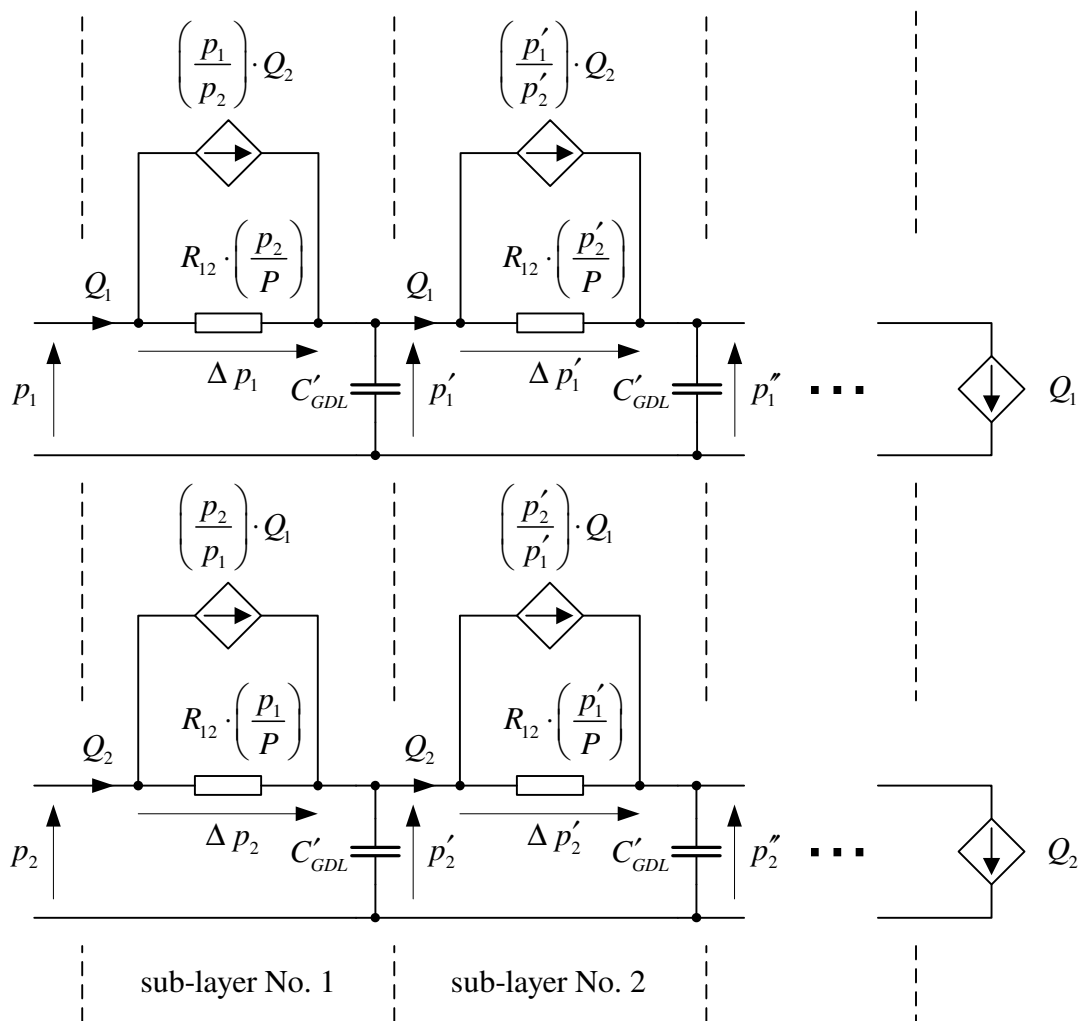


Figure 2-30 GDL circuit model with equivalent capacitance

2.4.7 Knudsen Regime in GDL

The Knudsen regime describes the loss of momentum in molecule when they collide with porous walls. This regime is an inversion of the molecular diffusion regime which the collisions are occurred only among the gas molecules and the momentum of the bulk gas is considered to be constant.

$$\frac{d}{dz}c_i = -\frac{1}{D_{iK}}\mathbf{N}_i \quad (2-70)$$

where c_i and \mathbf{N}_i are the molar concentration and the diffusion flux of species i , and D_{iK} is the Knudsen diffusion coefficient. The Knudsen diffusion coefficient is related to the molecular speed, \mathbf{v}_i , and a constant represent the geometry of the pore-hole, K_o , as:

$$D_{iK} = K_o \mathbf{v}_i \quad (2-71)$$

The constant K_o is related to the size and shape of pore-holes. It can be estimated by equation (2-72), however, it is best to determined by experimentation.

$$K_o = \frac{2}{3} \frac{\varepsilon r}{\tau} \quad (2-72)$$

The molecular speed can be calculated by

$$\mathbf{v}_i = \sqrt{\frac{8k_B T}{\pi m_i}} \quad (2-73)$$

where k_B is Boltzmann's constant which equals to 1.38×10^{-23} J/K, T is the absolute temperature, and m_i is the molecular mass of species i .

2.4.8 Circuit Model of Knudsen Diffusion

Since the Knudsen regime assumes no collision between gas molecules, and the momentum transferred to the porous wall is just disappeared from the system, the circuit model can be simply a resistance for each species. To conform to the proposed circuit model of the Stefan-Maxwell diffusion, which set the volumetric flow rate as a current in the circuit, we modified the Knudsen diffusion equation as follow.

We started with the Knudsen diffusion equation, which is

$$\frac{d}{dz}c_i = -\frac{1}{D_{iK}}\mathbf{N}_i \quad (2-74)$$

Since

$$c_i = \frac{P_i}{RT} \quad (2-75)$$

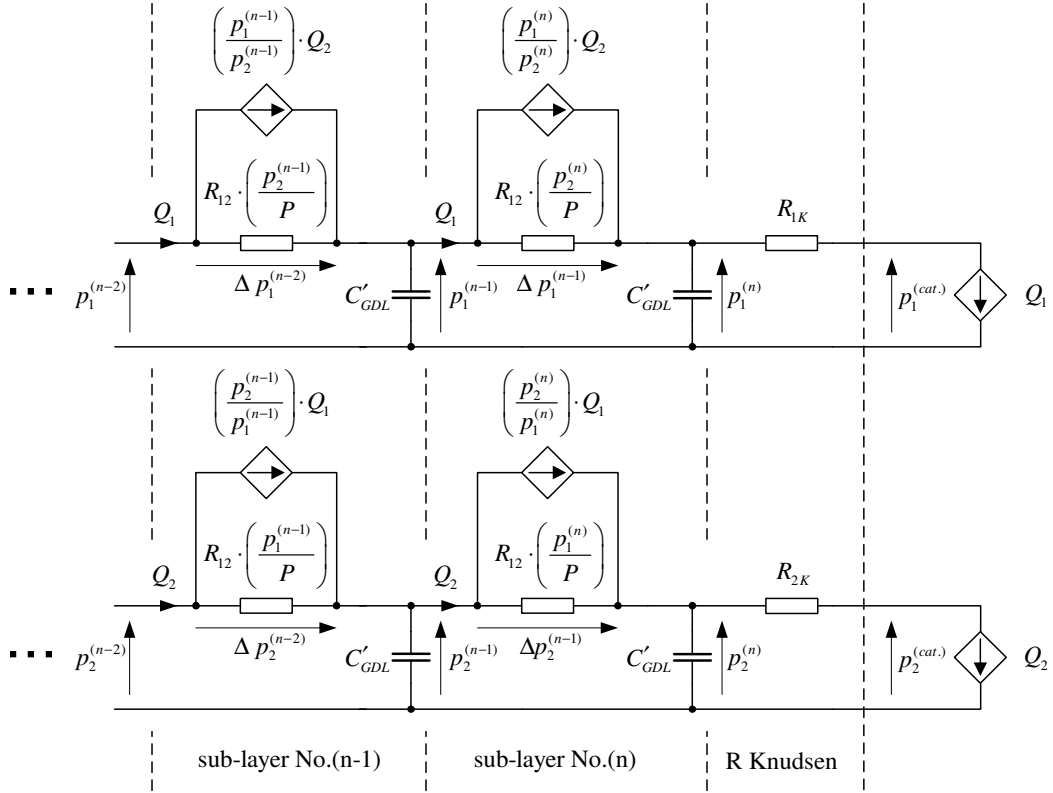


Figure 2-31 The proposed circuit model with Knudsen diffusion equivalent resistance

With the assumption of the temperature in each sub-layer is constant, we could write:

$$\frac{d}{dz} p_i = -\frac{RT}{D_{iK}} \mathbf{N}_i \quad (2-76)$$

We inserted the surface area, A , and the total molar concentration, c_t , into equation (2-76) by

$$\frac{d}{dz} p_i = -\frac{RT}{D_{iK}} \left(\frac{A}{A} \right) \left(\frac{c_t}{c_t} \right) \mathbf{N}_i \quad (2-77)$$

Then

$$\frac{d}{dz} p_i = -P \left(\frac{1}{D_{iK} A} \right) \left(\frac{\mathbf{N}_i A}{c_t} \right) \quad (2-78)$$

The last modification was to change the derivative into per unit length as in the Stefan-Maxwell system, where

$$\eta = (z - z_0) / l \quad (2-79)$$

This result in

$$\frac{d}{d\eta} p_i = -P \left(\frac{l}{D_{iK} A} \right) \left(\frac{N_i A}{c_i} \right) \quad (2-80)$$

Comparing the variable to the Stefan-Maxwell circuit model, we defined Knudsen equivalent diffusion resistance, R_{iK} , as

$$R_{iK} = P \frac{l}{D_{iK} A} = f_{iK} \frac{l}{A} \quad (2-81)$$

where f_{iK} is the fiction factor which equals to P / D_{iK} .

Mason and Evans [58, 59] suggested that the effects of momentum transfers in each regime should be combined additively then we placed the Knudsen equivalent diffusion resistance in series with the Stefan-Maxwell circuit.

As the micro porous layer is a very thin layer at the inner side of GDL, we added the Knudsen equivalent diffusion resistance in series with the last inner sub-layers of the GDL circuit model. Figure 2-31 shows the GDL circuit model where the Knudsen equivalent diffusion resistance is cascaded with the last sub-layer circuit.

2.4.9 The Combination of Diffusion and Convection Mode in GDL Circuit Model

The proposed circuit model in the previous section represented only the transport in diffusion mode. In other words, the total pressure was assumed to be constant along the diffusion path. The same idea for gas transport in a flow-field channel was applied to the GDL transport in convection mode. The total pressure difference is considered as an effort for the transport in convection mode. The convective volumetric flow in GDL was calculated by

$$Q_{conv} = \left(\frac{P - P'}{R_{conv}} \right) \cdot \left(\frac{P + P'}{2P'} \right) \quad (2-82)$$

Since the information of the hydraulic or convective resistance of the GDL is limited, we approximated the GDL resistance by the model of tubular tube channel with Bruggeman correction

$$R_{conv} = \frac{\epsilon^{1.5}}{n_{pore}} \left(\frac{8}{\pi} \eta L \frac{1}{a_{pore}^4} \right) \quad (2-83)$$

where a_{pore} is an average radius of GDL pore holes. The n_{pore} is the number of equivalent pore holes which is calculated from the cross sectional area of the GDL, A , by

$$n_{pore} = \frac{A}{\pi \cdot a_{pore}^2} \quad (2-84)$$

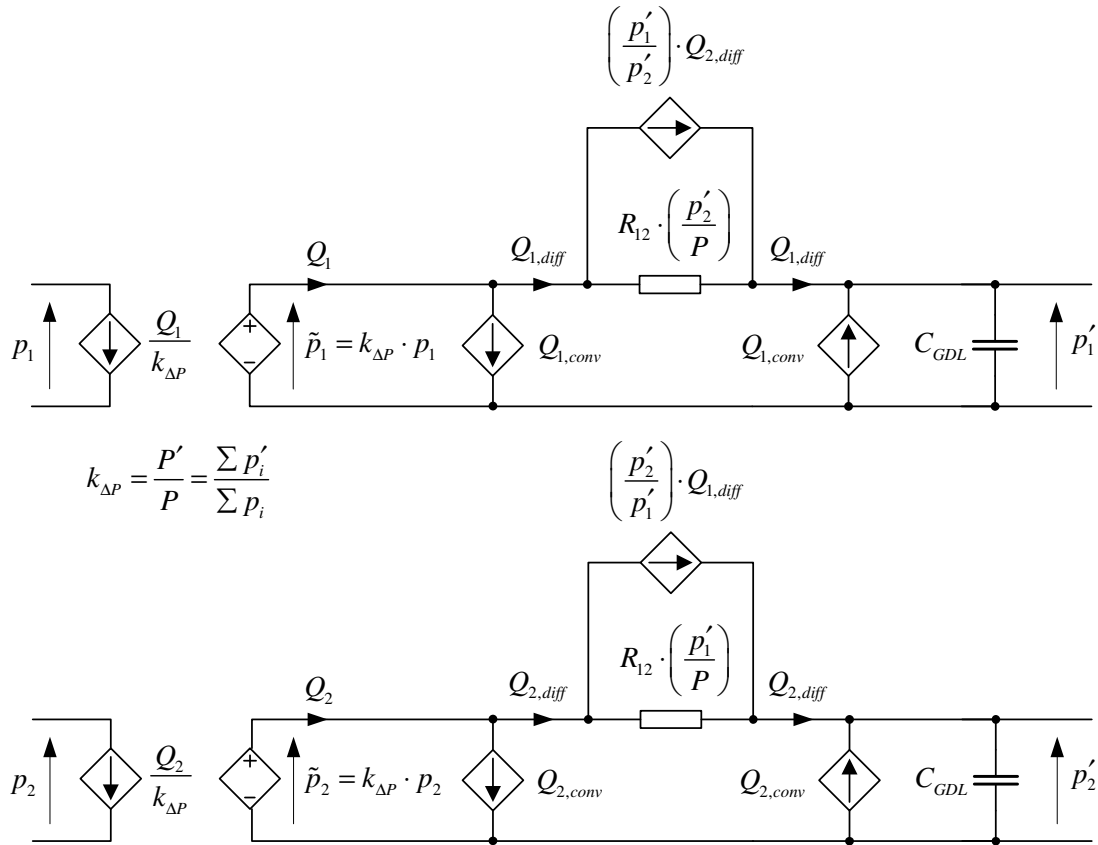


Figure 2-32 The transport model for a 2-species system

The flow of gas in this mode was introduced to the circuit by the current sources. Since the flow of both convection and diffusion fill the same GDL pore space, Q_{conv} and Q_{diff} was combined together to charge the same C_{GDL} . The combination of diffusion and convection volumetric flow was considered as the total volumetric flow.

A pair of current and voltage controlled sources was used to prevent the diffusion circuits from the effect of the total pressure difference. The modified equivalent circuit of the transport in the GDL is shown in figure 2-32. The same idea was applied to the 3 species system.

2.5 Catalyst Layer Model

Catalyst layers of PEMFCs are thin layers between the GDLs and each side of the membrane. The electrochemical reactions of the fuel cell occurred in these layers. Scientists believe that platinum (Pt) is the best catalyst for both anode and cathode sides of PEMFCs. The nanoparticles of platinum embedded on the carbon powders are dispersed on the inner side of the GDL to form the catalyst layer.

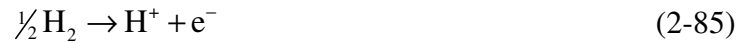
Since there is a membrane in the middle of two catalyst layers, the fuel cell reaction is divided into two sub-reactions. The first one is the hydrogen oxidation

reaction (HOR), which takes place on the anode side, and the second one is the oxygen reduction reaction (ORR), which happens on the cathode side.

The proposed circuit models will cover the electrochemical reactions and the double-layer capacitance effect of both catalyst layers.

2.5.1 Electrochemical Reaction on the Anode Side

The reaction on the anode side is the oxidation of the hydrogen. The reaction's formula is written as



The reversible or thermodynamic potential from the reaction can be predicted from the Nernst equation as:

$$E_{r,anode} = E_r^\ominus + \frac{R \cdot T}{F} \cdot \ln \left(\frac{a_{\text{H}_2}^{1/2}}{a_{\text{H}^+}} \right) \quad (2-86)$$

where E_r^\ominus is the reference potential, at the standard state $E_r^\ominus = 0\text{V}$ by definition, R is the gas constant, T is the temperature, F is the Faraday constant, a_{H_2} and a_{H^+} are the activity of hydrogen and proton, respectively.

The steps of the reaction are as follow [98]:



The subscript ‘‘ad’’ is stand for adsorption which indicates that the atom is adsorbed on the catalyst site. Note that only the last step is an electrochemical reaction, the first and second steps are the adsorption and recombination reaction, respectively.

As water molecule exists at the reaction site, the proton, H^+ , will continue to reacts with the water and result in different hydrate forms of hydrogen ion, for example, hydronium ion (H_3O^+), zundel ion (H_5O_2^+), or eigen ion (H_9O_4^+).

The kinetic of the reaction is expressed by the Butler-Volmer equation as

$$j = j_{0,anode} \left(e^{\frac{\alpha F}{RT} \eta} - e^{-\frac{(1-\alpha) F}{RT} \eta} \right) \quad (2-90)$$

where j is the net current density, $j_{0,anode}$ is the exchange current density, α is the charge transfer coefficient, and η is the overpotential.

2.5.2 Electrochemical Reaction on the Cathode Side

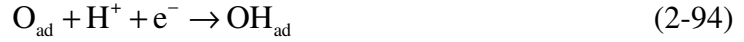
On the cathode side, the reduction of the oxygen is occurred. The reaction's formula is stated as



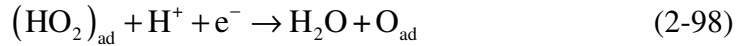
As on the anode side, the reversible potential is obtained by

$$E_{r,cathode} = E_{r,cathode}^{\ominus} + \frac{R \cdot T}{4F} \cdot \ln \left(\frac{a_{\text{H}^+}^4 a_{\text{O}_2}}{a_{\text{H}_2\text{O}}^2} \right) \quad (2-92)$$

There are two proposed reaction steps for this oxygen reduction reaction [99]. The first one is the dissociative mechanism which is for the low current density. The reaction steps are:



The second one is the associative mechanism which is for the high current density. In this case, the reaction steps are:



Both associative and dissociative mechanisms are considered as a four electrons transfer reaction because there are four electrons transferred for each oxygen atom. Thus, the kinetic of the reaction is written as follow

$$j = j_{0,cathode} \left(e^{\frac{\beta 4F}{RT} \eta} - e^{-\frac{(1-\beta) 4F}{RT} \eta} \right) \quad (2-101)$$

where β is the charge transfer coefficient for this reaction. Note that the powers of the exponentials are multiplied by four which is the number of electrons transferred in the reaction.

2.5.3 Overall Cell Reversible Potential

As the reaction on the anode and cathode sides are series together, the reversible potential of the whole cell is calculated by:

$$E_r = E_{r,cathode} + E_{r,anode} \quad (2-102)$$

$$E_r = E_{r,cathode}^{\ominus} + E_{r,anode}^{\ominus} + \frac{R \cdot T}{4F} \cdot \ln \left(\frac{a_{H^+}^4 a_{O_2}}{a_{H_2O}^2} \right) + \frac{R \cdot T}{F} \cdot \ln \left(\frac{a_{H_2}^{1/2}}{a_{H^+}} \right) \quad (2-103)$$

$$E_r = E_{r,cathode}^{\ominus} + E_{r,anode}^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{a_{H^+}^2 a_{O_2}^{1/2}}{a_{H_2O}} \right) + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{a_{H_2}}{a_{H^+}^2} \right) \quad (2-104)$$

$$E_r = E_{r,cathode}^{\ominus} + E_{r,anode}^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{a_{H_2} a_{O_2}^{1/2} a_{H^+}^2}{a_{H_2O} a_{H^+}^2} \right) \quad (2-105)$$

Since the $E_{r,anode}^{\ominus}$ is equal to zero by definition and the membrane between the catalysts layer is very thin, so that, the protons can move from one side to the other by a negligible time, the cell reversible potential equation is reduced to

$$E_r = E_r^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}} \right) \quad (2-106)$$

where

$$E_r^{\ominus} = E_{r,cathode}^{\ominus} + E_{r,anode}^{\ominus} \quad (2-107)$$

The more common form of the equation is

$$E_r = E_r^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \right) \quad (2-108)$$

which obtained by assumed that the mixture pressure of the product and reactant are the same and all gases in the reaction are behaves as an ideal gas.

2.5.4 Double Layer Effect at the Electrode

The double layer effect is the phenomena at the electrode/electrolyte interface [60]. Consider a cross-section of flat electrode carrying some negative charges and submerged in an electrolyte, as shown in figure 2-33. Since the electrode is made from high electronic conducting materials, their charges reside only at the skin of the electrode. The layer of the negative charges attracts the opposite charges in the electrolyte. As the charges in the electrolyte are sheathed by the molecule of solvent, the opposite charges stop in front of the electrode surface and form a positive charge layer. The structure of the two opposite charge layers are much like the structure of the capacitor. The distance between these two layers is in range of some 10^{-10} m, which is extremely small. Thus the capacitance at the electrode interface, or known as double layer capacitance, is very high.

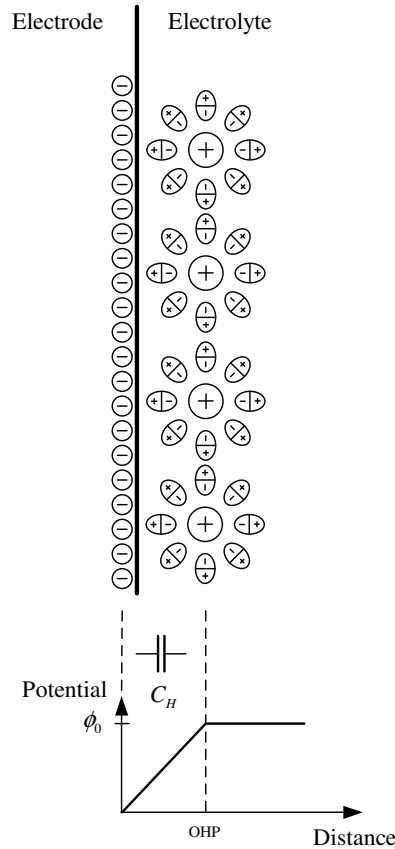


Figure 2-33 Double layer effect modeled by Helmholtz

The straightforward model of the double layer capacitance is proposed by Helmholtz. He considers the separation of opposite charges as two perfect charge sheets [61], as shown in figure 2-33. The capacitance per unit area according to Helmholtz's model is defined by

$$C_H = \frac{\epsilon_r \epsilon_0}{d} \quad (2-109)$$

where ϵ_r is the relative permittivity of solution ϵ_0 permittivity of free space and d is the distance between the charge plates. It should be noted that the distance shown in figure 2-33 is the Outer Helmholtz Plane (OHP). In some case where the negative ion break the solvent shield and moves closer to the electrode, the ion is said to be specifically adsorbed on the electrode surface. The distance between the electrode and the specifically adsorbed ion is called the Inner Helmholtz Plane (IHP). In this work, the double-layer capacitance will be obtained by experimentation.

2.5.5 Circuit Model of the Catalyst layer

The separation of the anode and cathode reactions introduces the activity of the proton in membrane into the anode and cathode reversible potential equations. Equation (2-106) has shown that the activity of the proton will disappear as one combines the anode and cathode reversible potential together. Thus, we chose to eliminate the proton activity by select a new arbitrary reference potential to be:

$$E'_{r,anode}{}^{\ominus} = E_{r,anode}{}^{\ominus} - \frac{R \cdot T}{F} \cdot \ln \left(\frac{a_{H_2}^{1/2}}{a_{H^+}} \right) \quad (2-110)$$

and

$$E'_{r,cathode}{}^{\ominus} = E_{r,cathode}{}^{\ominus} + \frac{R \cdot T}{F} \cdot \ln \left(\frac{a_{H_2}^{1/2}}{a_{H^+}} \right) \quad (2-111)$$

Please note that

$$E'_{r,anode}{}^{\ominus} + E'_{r,cathode}{}^{\ominus} = E_{r,anode}{}^{\ominus} + E_{r,cathode}{}^{\ominus} = E_r{}^{\ominus} \quad (2-112)$$

And in fact the definition of $E_{r,anode}{}^{\ominus} = 0$ is not imply that there is no reaction, of course, there is a reaction and there is some level of potential, but we just choose to name that level as zero volt.

This result in

$$E'_{r,anode} = 0 \quad (2-113)$$

and

$$E'_{r,cathode} = E_r{}^{\ominus} + \frac{R \cdot T}{2F} \cdot \ln \left(\frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}} \right) \quad (2-114)$$

The activity of the proton was eliminated, and now we proceed to the circuit model.

The circuit model of the catalyst layer is quite straightforward [62], as the potential of the reaction is the summation of the reversible and overpotential, then we combined together with the effect of the double-layer capacitance, the model of the catalyst is shown in figure 2-34. The membrane resistance, $R_{H^+}^m$, will be discussed in the next section.

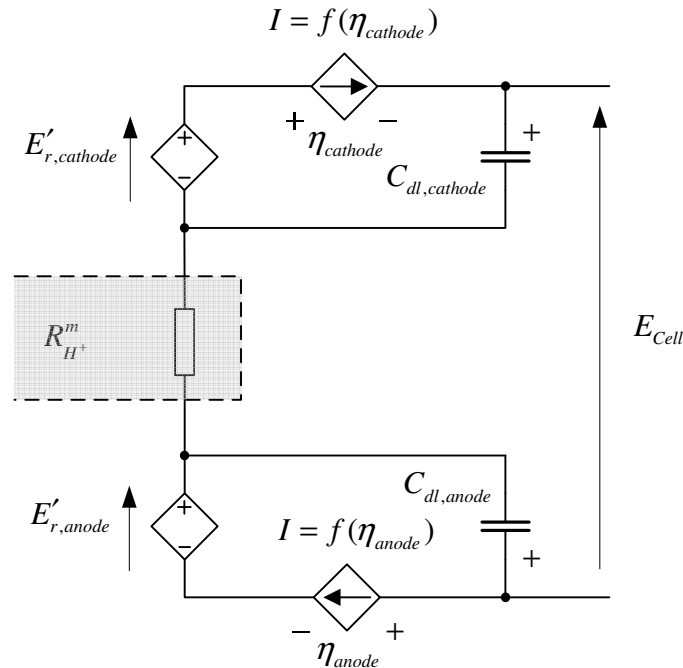
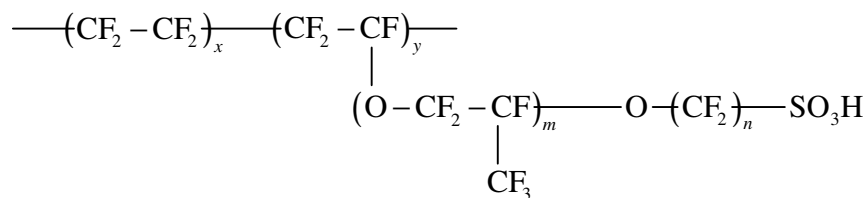


Figure 2-34 The circuit model of the catalyst (shown with the membrane resistance)

2.6 Membrane Model

The most important part of the PEMFC is the membrane. Membranes situate at the middle of the cells, between the anode and cathode catalyst layers. Membranes for PEMFCs are functioned as electrolytes in solid phase. The perfect membrane allows only the protons to diffuse easily from one side to the other. Thus, electrons generated from the oxidation on the anode side are forced to travel to the cathode side via an external circuit. The crossover of the oxygen or hydrogen to the other side of the membrane results in the reduction of efficiency and catalyst degradation, thus, the good membrane may not allow the reactant species to travel through. The chemical stability at the operating condition, the feasibility of excess water removal, and the production cost are also the key features of the good membrane.

At present, the perfluorosulfonic acid (PFSA) membrane is seemed to be the best membrane in the market. The General structure of perfluorosulfonic acid (PFSA) ionomer is shown in figure 2-35.



Nafion ^(R) 117	$m \geq 1,$	$n = 2,$	$x = 5 - 13.5,$	$y = 1000$
Flemion ^(R)	$m = 0, 1,$	$n = 1 - 5$		
Aciplex ^(R)	$m = 0, 3,$	$n = 2 - 5,$	$x = 1.5 - 14$	
Dow	$m = 0,$	$n = 2,$	$x = 3.6 - 10$	

Figure 2-35 The General chemical structure of PFSA membrane [100]

2.6.1 Mathematical Model of the Membrane

The ionic conductivity of the membrane is one of the most important properties. This is because it affects directly to the electrical characteristic curve of the fuel cell. The ionic conductivity of the perfluorosulfonic acid (PFSA) membrane is mainly a function of the local water content and the temperature of the membrane. The water content of the membrane is defined as

$$\lambda = \frac{[H_2O]}{[SO_3^-]} \quad (2-115)$$

where $[H_2O]$ is the concentration of the water molecules and $[SO_3^-]$ is the concentration of the sulfonic acid group of the membrane.

The membrane water contents at the membrane/catalyst interfaces can be evaluated from the water activity, a . The water activity is defined as

$$a = \frac{P_{H_2O}}{P_{sat}} \quad (2-116)$$

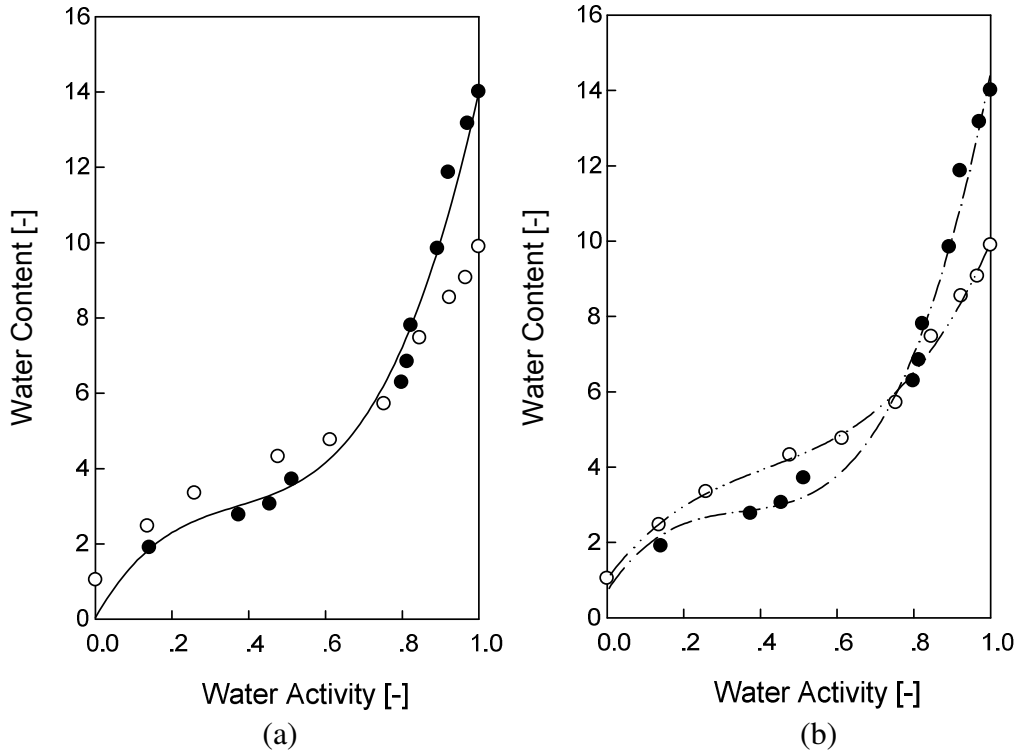


Figure 2-36 The relation of water content and water activity in Nafion® membrane from Springer et al., (a) plot with (2-118), (b) plot with (2-119) and (2-120).

where p_{H_2O} is the partial pressure of the water at the interface, and P_{sat} is the saturation pressure of the water. The empirical expression of the P_{sat} is [63]:

$$\log_{10} \left(\frac{P_{sat}}{101325} \right) = -2.1794 + 0.02953 \cdot (T - 273.15) - 9.1837 \cdot 10^{-5} (T - 273.15)^2 + 1.4454 \cdot 10^{-7} (T - 273.15)^3 \quad (2-117)$$

The temperature, T, is in Kelvin.

The relation between Nafion® membrane water content and surrounded water activity, at 303.15°K (30°C) and 353.15°K (80°C), measured by Zawodzinski et al. [5, 63, 101] are shown in figure 2-30. Springer et al. proposed the empirical model that links the membrane water content at 303.15°K (30°C) to the water activity as follow[63]

$$\lambda_{(30^\circ C)} = 0.043 + 17.81a - 39.85a^2 + 36.0a^3 \quad \text{for } 0 < a \leq 1 \quad (2-118)$$

The more recent research found that the water content in the membrane is hardly reduced less than 1.5 [15]. So that, we proposed the modified empirical models which follow the result of Zawodzinski et al. at 303.15°K and 353.15°K as follow:

$$\lambda_{(30^\circ\text{C})} = 0.6966 + 15.5596a - 40.7848a^2 + 38.9719a^3 \quad \text{for } 0 < a \leq 1 \quad (2-119)$$

$$\lambda_{(80^\circ\text{C})} = 1.0242 + 13.5743a - 23.3770a^2 + 18.7285a^3 \quad \text{for } 0 < a \leq 1 \quad (2-120)$$

Equation (2-119) and (2-120) are plotted to compare with the experimental result in figure 2-36.

Another important parameter is the ionic conductivity of the membrane. Springer et al.[63] conducted experimentation and proposed the correlation between the ionic conductivity, $\sigma_{H^+}^m$, the water content, and temperature as follow:

$$\sigma_{H^+}^m = (0.5139\lambda - 0.326) \cdot \exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad \text{for } \lambda > 1 \quad (2-121)$$

Neubrand et al. [102] presented another version of the membrane conductivity as

$$\sigma_{H^+}^m = (0.0014\lambda^3 + 0.0298\lambda^2 + 0.2658\lambda) \cdot \exp\left[(2640 \cdot \exp(-0.6\lambda) + 1183)\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad (2-122)$$

Recently, Fimrite et al.[64] proposed a new membrane conductivity model that based on physical equation of the membrane as follow:

$$\sigma_{H^+}^m = \frac{c_i (\varepsilon - \varepsilon_0)^q \left(\frac{1}{D_{12}} + \frac{\lambda}{D_{2M}}\right) F^2}{\lambda \left(\frac{1}{D_{12}D_{1M}} + \frac{\lambda - 1}{D_{12}D_{2M}} + \frac{\lambda}{D_{1M}D_{2M}}\right) RT} \quad \text{for } \lambda > 1.5 \quad (2-123)$$

where ε_0 is threshold porosity, D_{12} is diffusion coefficient between hydronium and water, D_{1M} is diffusion coefficient between hydronium and membrane, D_{2M} is diffusion coefficient between water and membrane, and q is fitting parameter.

Springer et al.[63] suggested the water transport model, which let us estimate the water content profile along the membrane, as follow

$$N_{H_2O, total}^m = n_{drag} N_{H^+}^m - \left(D_{H_2O, \lambda}^m \frac{\rho_{dry}}{EW}\right) \frac{d}{dz} \lambda \quad (2-124)$$

In this equation, $N_{H_2O, total}^m$ is the flux of water molecules, $N_{H^+}^m$ is the flux of protons, $D_{H_2O, \lambda}^m$ is the diffusion coefficient of water in membrane, ρ_{dry} is specific weight of the membrane and EW is the equivalent weight of the membrane. The n_{drag} is the water

dragged coefficient which represents the number of water molecule dragged along with H^+ . The model states that the total water flux is composed of the water flux due to the electro-osmotic drag and the flux due to the water concentration gradient. Since the water flux resulted from the concentration gradient usually has opposite direction with the electro-osmotic drag, it also known as back diffusion flux.

The value of n_{drag} , as given with the model, is estimated by:

$$n_{drag} = 2.5 \frac{\lambda}{22} \quad (2-125)$$

This correlation is widely cited in literatures, but in a few years later, the same research team suggested that the value might be over estimated. They proposed another version of water drag coefficient as [103]:

$$n_{drag} = \begin{cases} 0.2\lambda & \text{for } \lambda < 5 \\ 1 & \text{for } 5 \leq \lambda \leq 14 \\ 0.1875\lambda & \text{for } \lambda > 14 \end{cases} \quad (2-126)$$

At last, in 1995, they deduced that n_{drag} is equal to 1 for non-liquid phase water in the membrane [104]. This was confirmed in the work of Ye et al. [105]. They conducted the experimentation and proposed that n_{drag} is constant. Their n_{drag} is equal to 1.07 for Gore® membrane and is equal to 1.1 for Nafion® membrane.

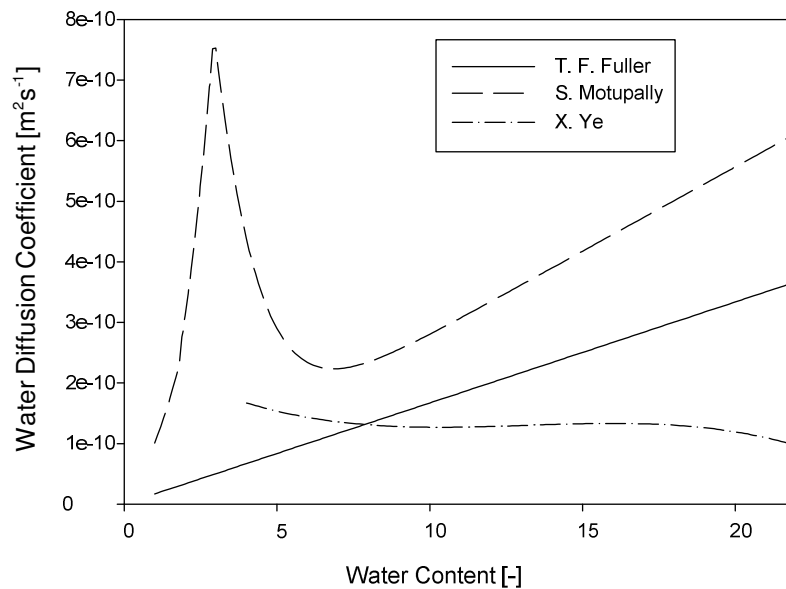


Figure 2-37 Plot of diffusion coefficient

The protons flux link to the current density, J , by Faraday's constant, F , as follow:

$$N_{H^+}^m = \frac{J}{F} \quad (2-127)$$

The diffusion coefficient of water in the membrane is also a function of membrane water content. Springer et al. [63] proposed that

$$D_{H_2O,\lambda}^m = \exp\left(2416\left(\frac{1}{303} - \frac{1}{T}\right)\right) \times (2.563 - 0.33\lambda + 0.0264\lambda^2 - 0.000671\lambda^3) \quad \text{for } \lambda > 4 \quad (2-128)$$

As usual, there are many variation of this coefficient, for example, T.F. Fuller [106] suggested that

$$D_{H_2O,\lambda}^m = 3.5 \cdot 10^{-6} \cdot \exp\left(-\frac{2436}{T}\right) \cdot \frac{\lambda}{14} \quad (2-129)$$

Motupally [107] presented this value in his work as

$$D_{H_2O,\lambda}^m = \begin{cases} 3.1 \cdot 10^{-7} \cdot \lambda \cdot (\exp(0.28\lambda - 1)) \cdot \exp\left(-\frac{2436}{T}\right) & \text{for } \lambda \leq 3 \\ 4.17 \cdot 10^{-8} \cdot \lambda \cdot (1 + 161 \cdot \exp(-\lambda)) \cdot \exp\left(-\frac{2436}{T}\right) & \text{for } \lambda > 3 \end{cases} \quad (2-130)$$

X. Ye et al. [105] proposed the water diffusion coefficient of the Gore-Select membranes as

$$D_{H_2O,\lambda}^m = k \times 10^{-10} \exp\left(2416\left(\frac{1}{303} - \frac{1}{T}\right)\right) \times (2.563 - 0.33\lambda + 0.0264\lambda^2 - 0.000671\lambda^3) \quad \text{for } \lambda > 4 \quad (2-131)$$

where k is scaling factor. The experimental showed that the values of k is scattered mostly in range of 0.3 and 0.7, the value of 0.5 is suggested. It should be noted that water diffusion coefficient of X. Ye et al. is the same as of Springer et al. The only different is the scaling factor k . This indicates that the water diffusion coefficient of water in Gore-Select membranes is about half of the Nafion®. Various water diffusion coefficient models are plotted together in figure 2-37.

2.6.2 Circuit Model of the Membrane

The circuit model which represents water mechanic in each sub-layer can be developed literally from equation (2-124), the result are shown in figure 2-38. The resistance in the circuit is defined as

$$R_{H_2O,\lambda}^m = \left(\frac{EW \cdot \Delta z}{D_{\lambda}^m \cdot \rho_{dry}} \right) \quad (2-132)$$

This model is simple and applicable; however, the principle of energy port is not satisfied in this model. To select a more proper variable pair we investigated the

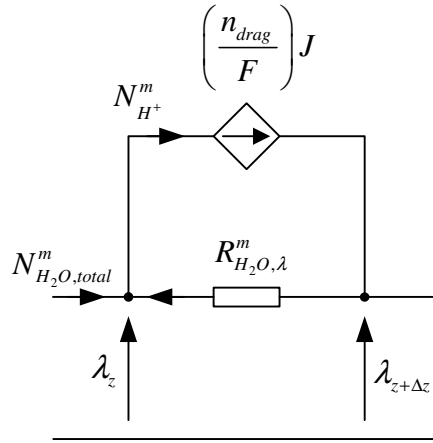


Figure 2-38 An example of circuit model of water transport in the membrane

development of equation (2-124) in Springer et al.'s work and we found that the mechanic of water in the membrane is developed from

$$N_{H_2O, diff}^m = - \left(\frac{D' \lambda}{RT} \frac{\rho_{dry}}{EW} \right) \frac{d}{dz} \mu_{H_2O} \quad (2-133)$$

where D' is intradiffusion coefficient obtained from his experimentation and μ_{H_2O} is the chemical potential of free water in the membrane. The chemical potential of free water is defined by

$$\mu_{H_2O} = \mu_{H_2O}^\circ + RT \ln(a) \quad (2-134)$$

where $\mu_{H_2O}^\circ$ is the chemical potential at the reference state, which is constant. The term $RT \ln(a)$ indicates the changing of the chemical potential due to the temperature and the water activity. We may denote this changing as

$$\mu_{\Delta, H_2O}^m = RT \ln(a) \quad (2-135)$$

By the assumption of T is constant

$$\frac{d}{dz} \mu_{H_2O} = RT \frac{d}{dz} \ln(a) = \frac{RT}{a} \frac{da}{dz} = \frac{RT}{a} \frac{da}{d\lambda} \cdot \frac{d\lambda}{dz} \quad (2-136)$$

The water content is a function of the water activity as shown in (2-118) and its derivative is given by

$$\frac{d\lambda}{da} = 17.81 - 79.7a + 108a^2 \quad \text{for } 0 < a \leq 1 \quad (2-137)$$

And the inverse slope is given by

$$\frac{da}{d\lambda} = \frac{1}{17.81 - 79.7a + 108a^2} \quad \text{for } 0 < a \leq 1 \quad (2-138)$$

Substitute (2-136) into (2-133), results in

$$N_{H_2O,diff}^m = - \left(\frac{D' \lambda}{a} \frac{da}{d\lambda} \right) \frac{\rho_{dry}}{EW} \frac{d\lambda}{dz} \quad (2-139)$$

Then, Springer et al. defined the water diffusion coefficient as

$$D_{\lambda}^m = \left(\frac{D' \lambda}{a} \frac{da}{d\lambda} \right) / (1 + 0.0126\lambda)^2 \quad (2-140)$$

where the factor $(1 + 0.0126\lambda)^2$ is for membrane water swelling effect compensation.

The water diffusion thus become

$$N_{H_2O,diff}^m = -D_{H_2O,\lambda}^m \frac{\rho_{dry}}{EW} \frac{d\lambda}{dz} \quad (2-141)$$

which is the common version that widely used.

To fulfill the need of more proper effort and flow pair, we modified the free water transport equation, shown in (2-141), into another form as

$$\frac{n_{H_2O,diff}^m}{A} = -D_{H_2O,\lambda}^m \frac{\rho_{dry}}{EW} \left(\frac{a}{RT} \frac{d\lambda}{da} \right) \left(\frac{RT}{a} \frac{da}{d\lambda} \right) \frac{d\lambda}{dz} \quad (2-142)$$

This resulted in

$$n_{H_2O,diff}^m = - \left(D_{H_2O,\lambda}^m \frac{\rho_{dry}}{EW} \frac{a}{RT} \frac{d\lambda}{da} \right) A \frac{d}{dz} \mu_{H_2O}^m \quad (2-143)$$

Please note that:

$$\frac{d}{dz} \mu_{H_2O}^m = \frac{d}{dz} \mu_{\Delta,H_2O}^m = RT \frac{d}{dz} \ln(a) \quad (2-144)$$

Thus, equation (2-143) was rewritten as:

$$n_{H_2O,diff}^m = -D_{H_2O,\mu}^m A \frac{d}{dz} \mu_{\Delta,H_2O}^m \quad (2-145)$$

where $D_{H_2O,\mu}^m$ is the water diffusion coefficient in the chemical potential domain, which was defined as:

$$D_{H_2O,\mu}^m = D_{H_2O,\lambda}^m \frac{\rho_{dry}}{EW} \frac{a}{RT} \frac{d\lambda}{da} \quad (2-146)$$

Choosing μ_{Δ,H_2O}^m , which has unit of $J \cdot mol^{-1}$, as an effort, and $n_{H_2O,diff}^m$, which has unit of $mol \cdot s^{-1}$ as a flow, was a perfect choice. The product of these two variables is a rate of energy transferred during the displacement of the water molecules.

We rewrote equation (2-145) in a discrete form as:

$$n_{H_2O,total}^m = n_{H_2O,drag}^m n_{H^+}^m - \frac{1}{R_{H_2O,\mu}^m} \Delta\mu_{\Delta,H_2O}^m \quad (2-147)$$

where

$$R_{H_2O,\mu}^m = \frac{\Delta z}{A D_{H_2O,\mu}^m} \quad (2-148)$$

The circuit model from equation (2-147) is shown in figure 2-39.

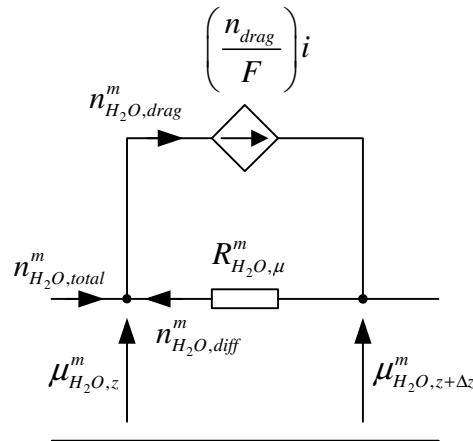


Figure 2-39 The circuit of water transport complied with energy port principle

2.6.3 The Flow Store Element

The local water content of a small portion of the membrane is changing according to the imbalance of the inlet and outlet water flux. The idea under the 1-D model assumption is stated in figure 2-40. The changing rate of the water content is an inverse function of $[\text{SO}_3\text{H}^+]$ sites, which defined as:

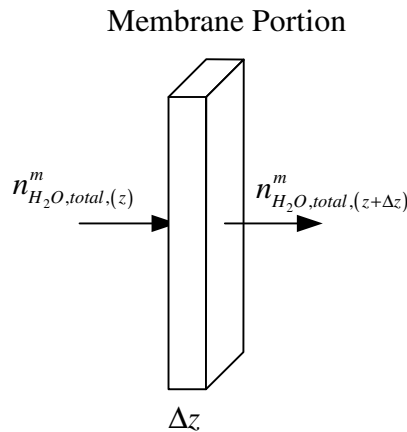
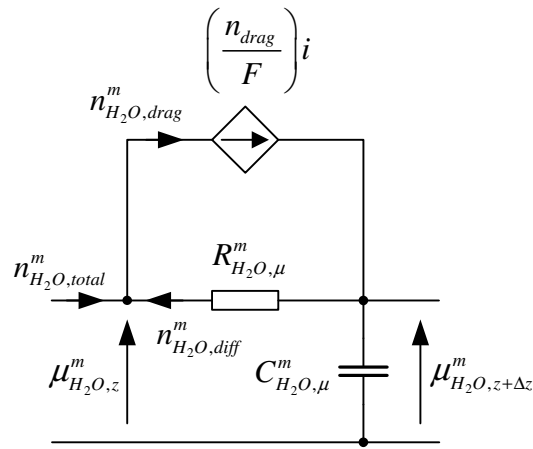


Figure 2-40 The accumulation of water in membrane [108]

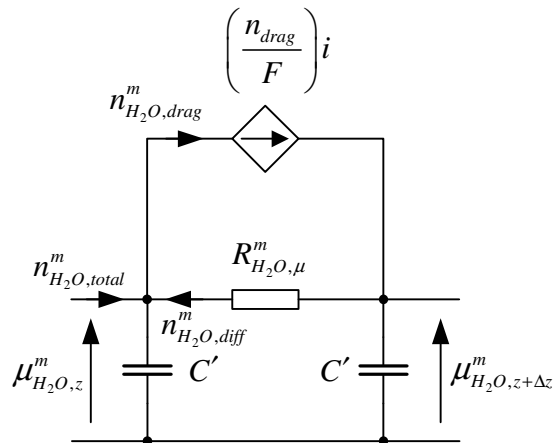
$$\frac{d}{dt} \lambda = -\frac{EW}{\rho_{dry}} \cdot \frac{d}{dz} N_{H_2O}^m \quad (2-149)$$

Note that the ratio of the equivalent weight and the specific weight is the number of $[\text{SO}_3\text{H}^+]$ sites. Equation (2-149) leads us to the definition of the equivalent capacitance in domain of the water content as follow:

$$C_{H_2O,\lambda}^m = \frac{\rho_{dry}}{EW} \Delta z \quad (2-150)$$



(a)



$$C' = \frac{C_{H_2O,\mu}^m}{2}$$

(b)

Figure 2-41 Two examples of placing the equivalent capacitance in the circuit

We rewrote equation (2-149) in the chemical potential domain as follow:

$$\frac{d}{dt} \mu_{H_2O}^m = - \left(\frac{EW}{\rho_{dry}} \right) \left(\frac{RT}{a} \frac{da}{d\lambda} \frac{1}{A} \right) \cdot \frac{d}{dz} n_{H_2O, total}^m \quad (2-151)$$

So that, the capacitance in this domain was defined as:

$$C_{H_2O, \mu}^m = \left(\frac{\rho_{dry}}{EW} \frac{a}{RT} \frac{d\lambda}{da} \right) \Delta z A \quad (2-152)$$

A number of capacitor positions were plausible. Two example of placing the capacitance in the circuit are shown in figure 2-41. It is better to have the circuit in symmetry form, thus, the circuit in figure 2-41 (b) can be a good choice. However, some simulation software considers a capacitor as a voltage source and cannot connect in parallel with another voltage source. So, we arranged the circuit in the form as shown in figure 2-42.

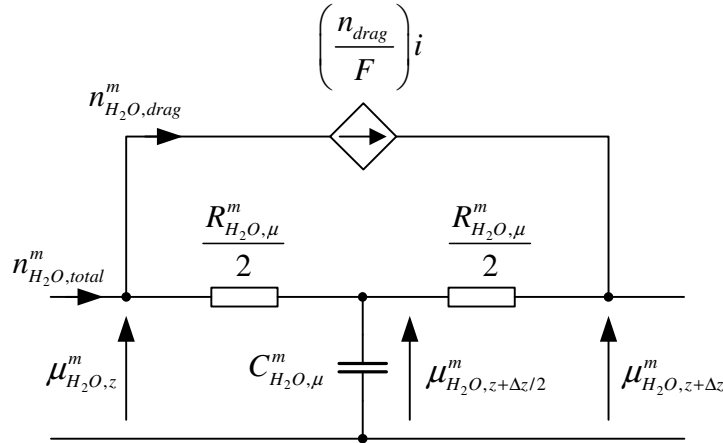


Figure 2-42 The membrane equivalent circuit model used in this work

2.6.4 The Complete Equivalent Circuit of the Membrane

The membrane equivalent circuit model including the mechanic at the boundary on the anode and cathode sides are shown in figure 2-43 and 2-44, respectively.

In simulation process, the chemical potential in each sub-layer were used to calculate the local membrane water contents. Then, the profile of water content was converted to the profile of membrane ionic conductivity via equation (2-121) or other equivalent. The total membrane resistance can be calculated by

$$R_{H^+}^m = \frac{1}{A} \int_0^{t_m} \frac{1}{\sigma_{H^+}^m(\lambda)} dz \quad (2-153)$$

where t_m is the overall thickness of the membrane.

The discrete version, which is more suitable for the data obtained from the circuit simulation, is

$$R_{H^+}^m = \frac{1}{A} \sum_{i=0}^n \frac{\Delta z}{\sigma_{H^+}^m(\lambda_i)} \quad (2-154)$$

where λ_i is the water content in sub-layer i . This total membrane ionic resistance is the value that we referred to in figure 2-34.

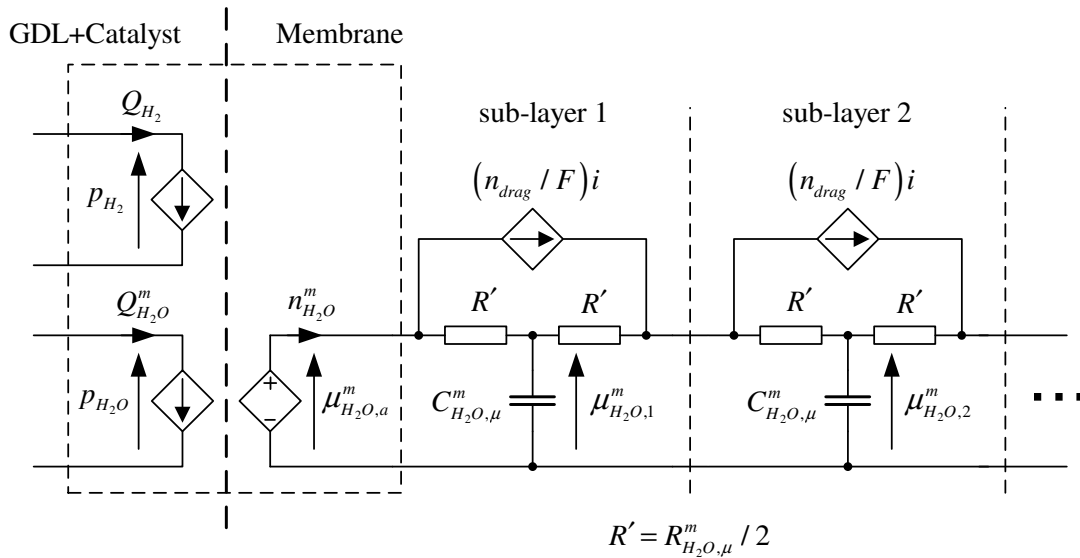


Figure 2-43 The circuit model with the interface on the anode side

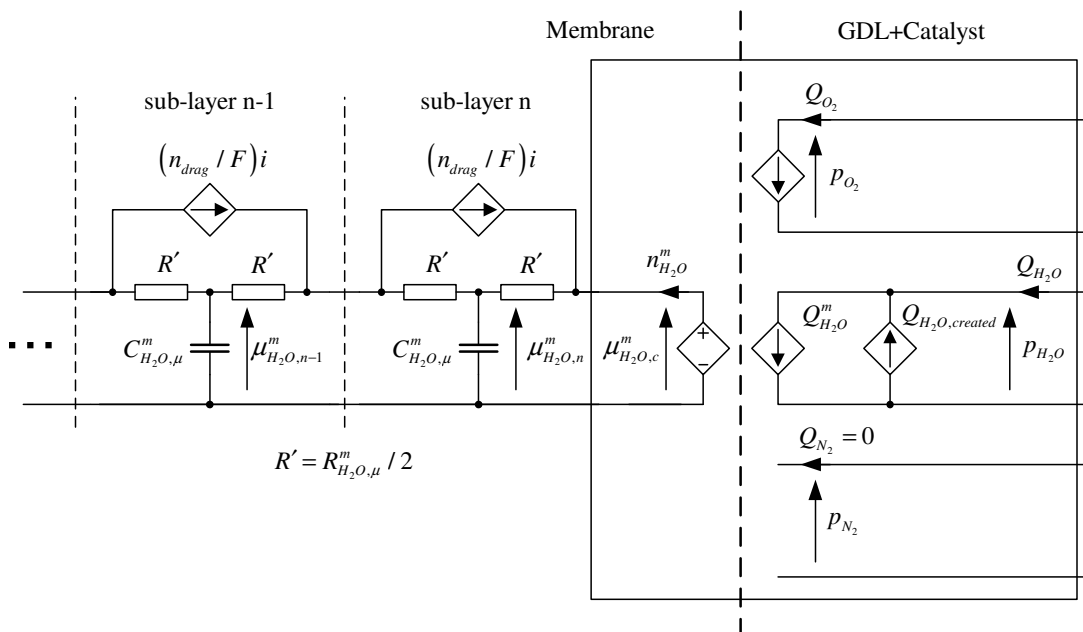


Figure 2-44 The circuit model with the interface on the cathode side

2.7 The Single Cell Model

The single cell model was formed by combining the channel, GDL, catalyst, and membrane models together; the model from the anode flow-field channel to the membrane is shown in figure 2-45 to 2-47. The model on the cathode side is nearly a mirror of the anode side. The different between the anode and cathode side has been discussed while developing the model. The single cell model had five ports for connecting to the environment, four of which are electric equivalent ports that represent the flow-field channel on the anode and cathode sides. The model had one real electric circuit port which was intended to be connected with the electrical circuit components. The whole single cell model is represented by a block diagram shown in figure 2-48.

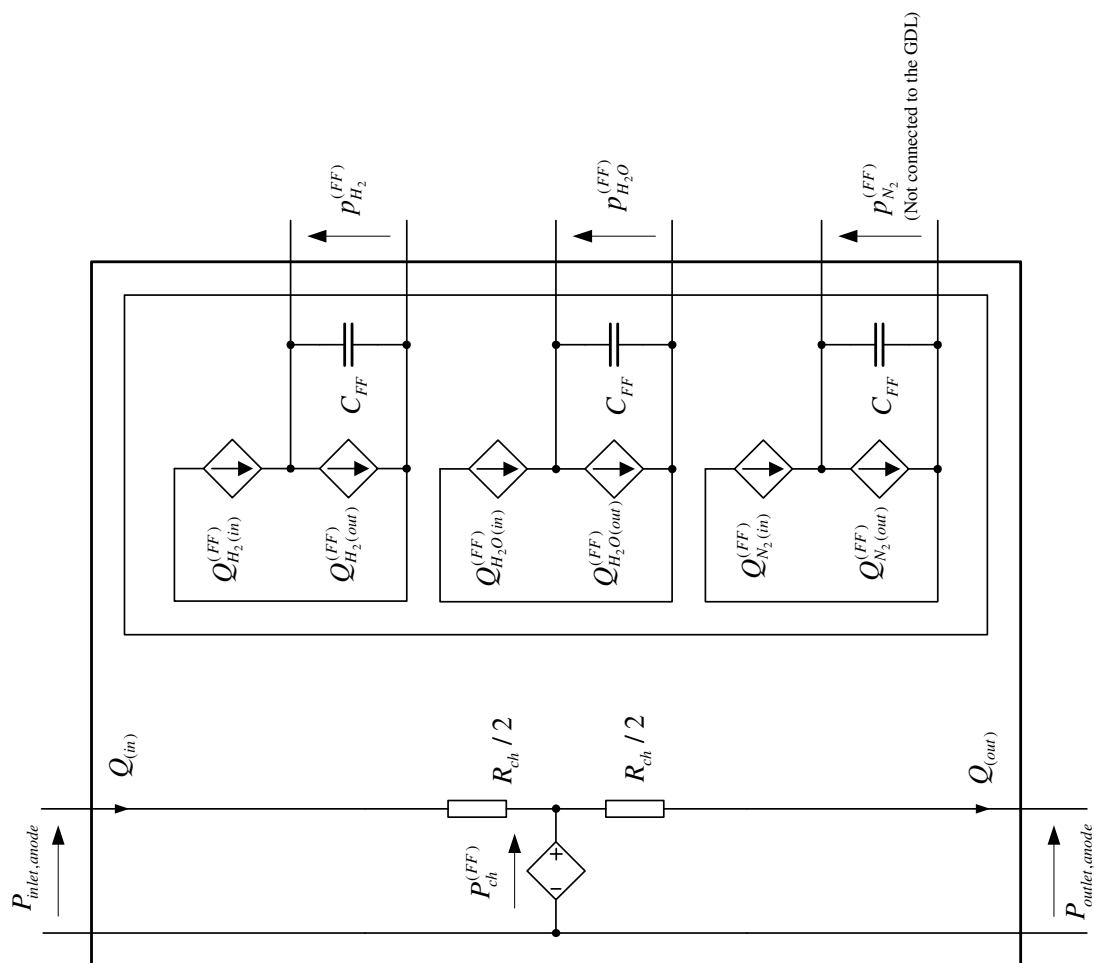


Figure 2-45 The flow-field channel circuit model

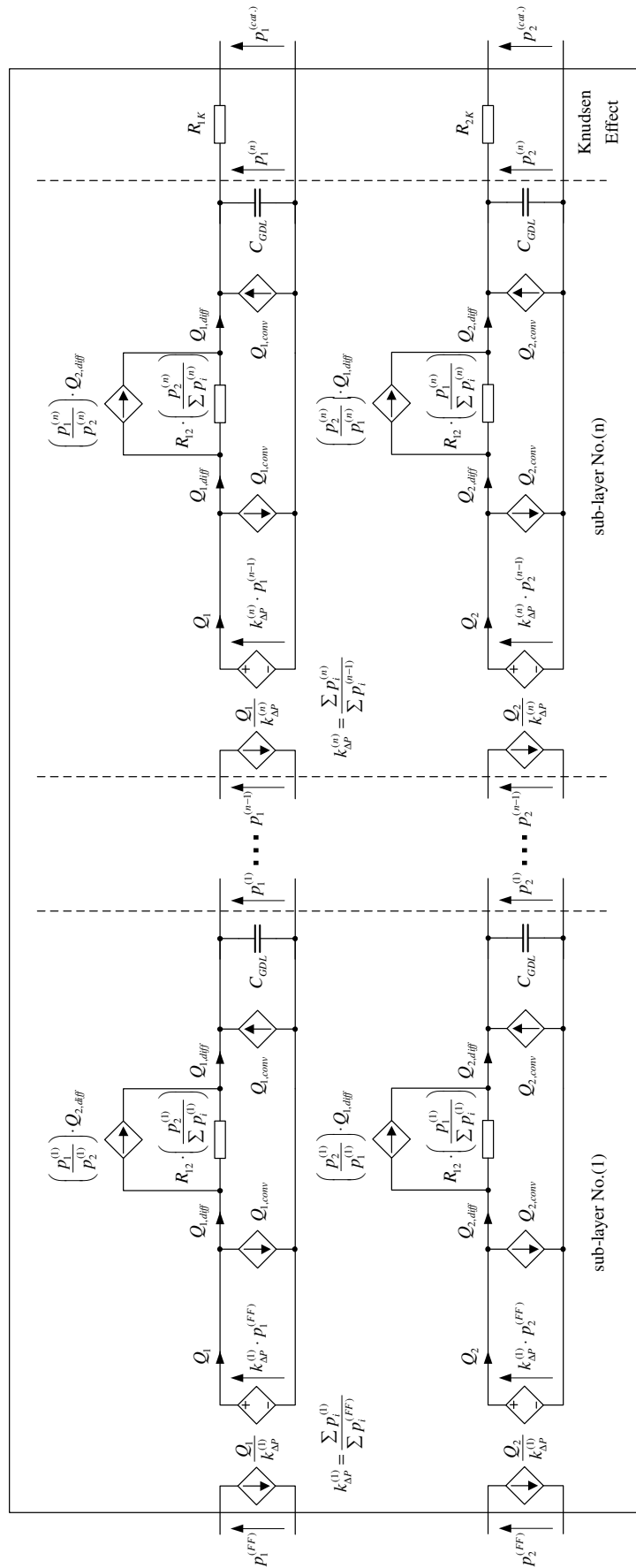


Figure 2-46 The GDL circuit model on anode side

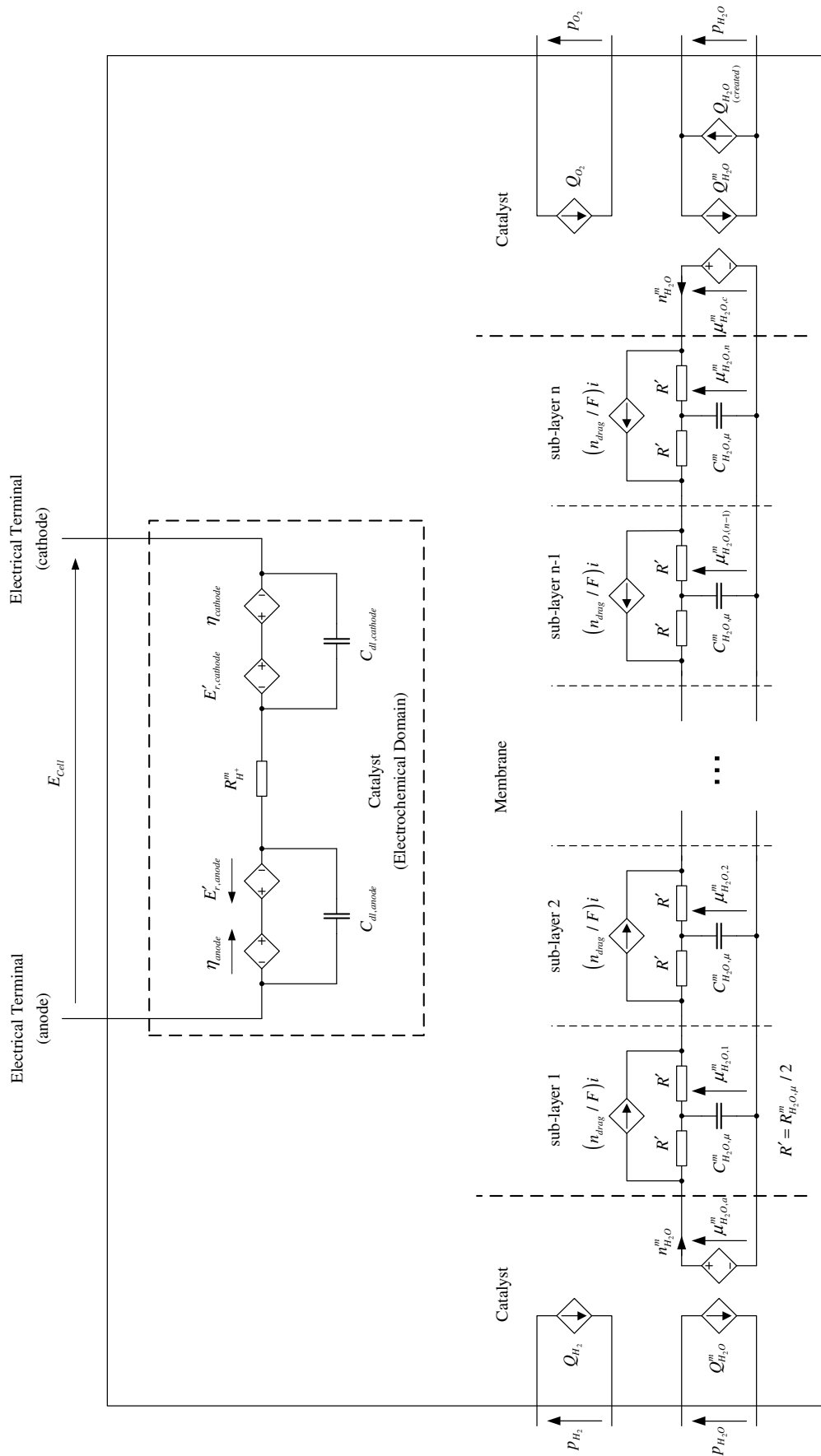


Figure 2-47 The catalyst and membrane circuit model

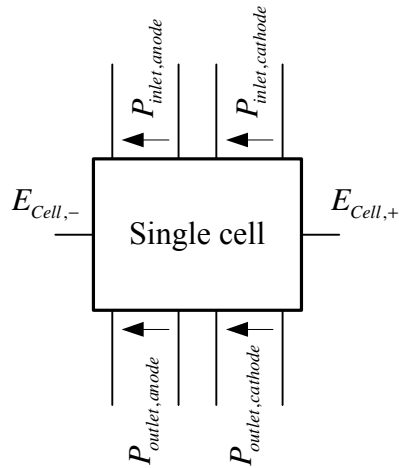


Figure 2-48 Block diagram representing the single cell model

2.8 The 3-Cell Stack Model

The structure of 3-cell stack is shown in figure 2-49. The 3-cell stack was developed by creating the backbone channel model between each single cell model as shown in figure 2-50. The theory used for the backbone channel model was the same as the flow field channel model. The model of the tubes conveying air/fuel from the storages to the cell can be added in the same way if required.

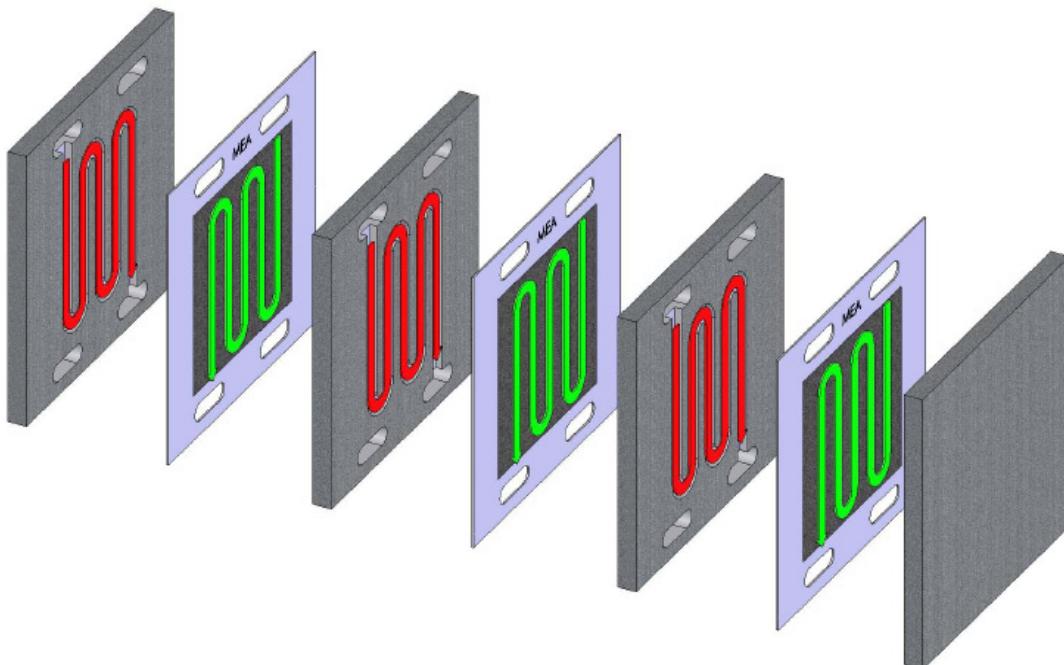


Figure 2-49 The structure of 3-cell stack of PEMFC

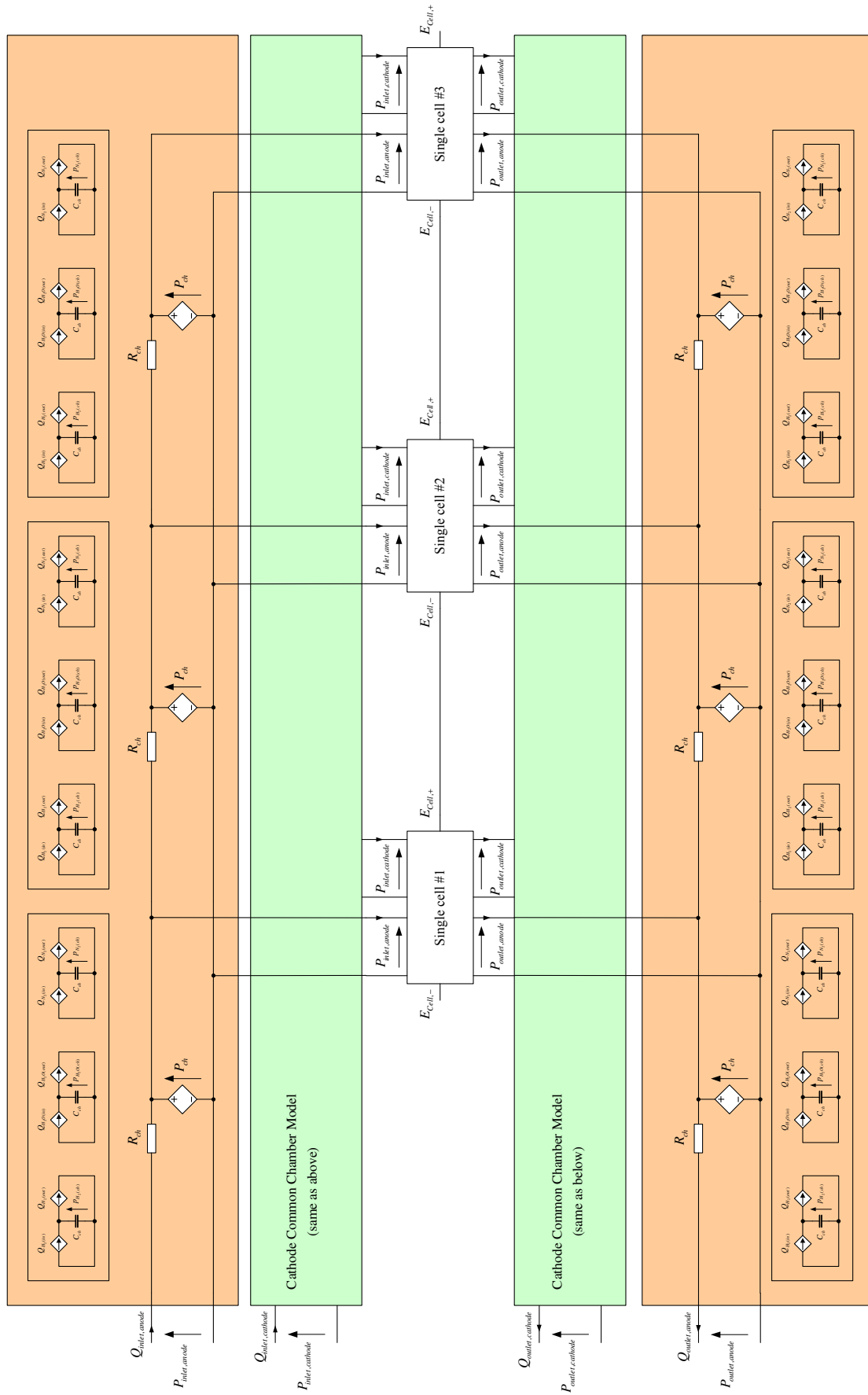


Figure 2-50 The 3-cell stack model

2.9 Conclusion

The development of the PEMFC circuit model has been presented in this chapter. The model was based on its physical equations. The principle of effort and flow was used as guidance in model development. Though the principle introduced some difficulty in modeling process, but it resulted in a systematic model.

The circuit model consisted of nonlinear resistors and controlled sources which are already familiar to electrical engineers. A veteran electrical engineer should be able to implement the model in circuit simulation tools like PSpice®, Saber®, Matlab® or other equivalent.

Chapter 3

Model Implementation and Results

This chapter presents the implementation of the equivalent circuit model of the Proton Exchange Membrane (PEM) fuel cell. The chapter starting with the strategy of using a controlled current source to imitate a nonlinear resistor is stated. Then, the error from the process that divides the gas diffusion layer nonlinear model into several sub-layer local linear models is discussed. After the proper number of sub-layer becomes clear, various simulation results are presented. The first simulation result is the dynamic operation of the fuel cell in steady state. The second simulation is about the static operation with different gas feeding rates. The effect of the channel network also discussed. The chapter ends with the simulation of 3-cell stack with a boost converter.

3.1 Implementation of the PEMFC Equivalent Circuit Model

The proposed PEMFC equivalent circuit model consists of nonlinear resistors, capacitors and controlled sources. The capacitance and controlled sources are available in most of the simulation tools. However, the nonlinear resistor whose resistance is controlled by an external command is seemed to be not available. The simple solution is to use a controlled current source in place of the nonlinear resistor. The current of the controlled source is calculated from its terminal voltage, V_R , divided by the resistance which includes the effect of the control values, as shown in figure 3-1.

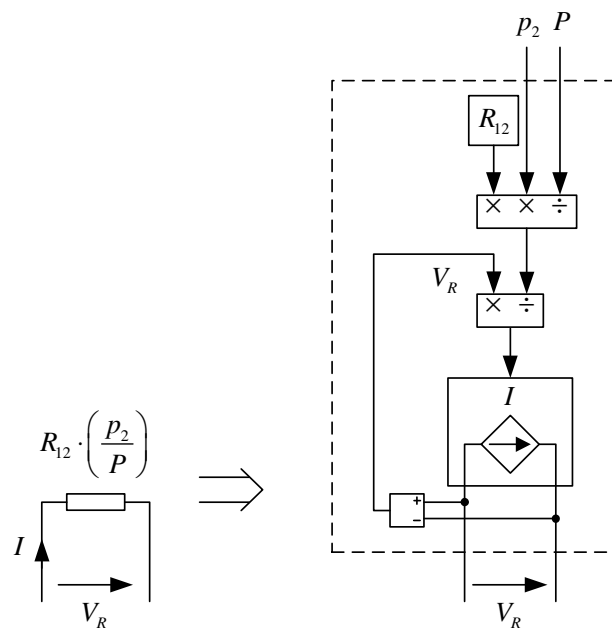


Figure 3-1 An implementation of nonlinear resistor

Beside the well-known circuit simulation tools like PSpice or Saber, Matlab/Simulink is another interesting simulation environment. The major advantage of the Matlab/Simulink over PSpice or Saber is its flexible. Enormous functions are available in Matlab for data analysis and post-simulation processes. This lets Matlab/Simulink be a favorite tool in engineering field for decades. Thus we decided to implement our model on the Matlab/Simulink platform.

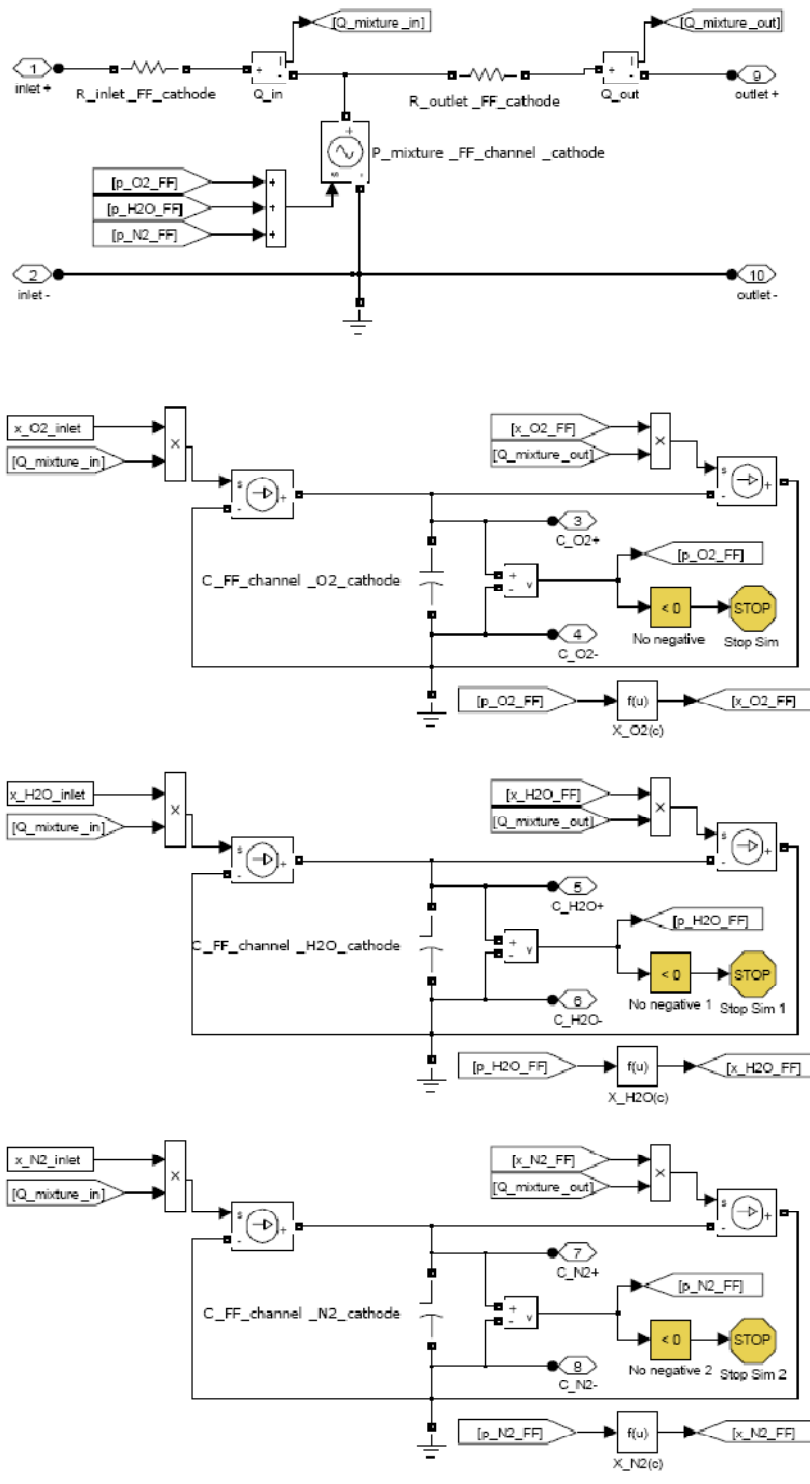


Figure 3-2 The flow-field model implemented by using SimPowerSystems blockset

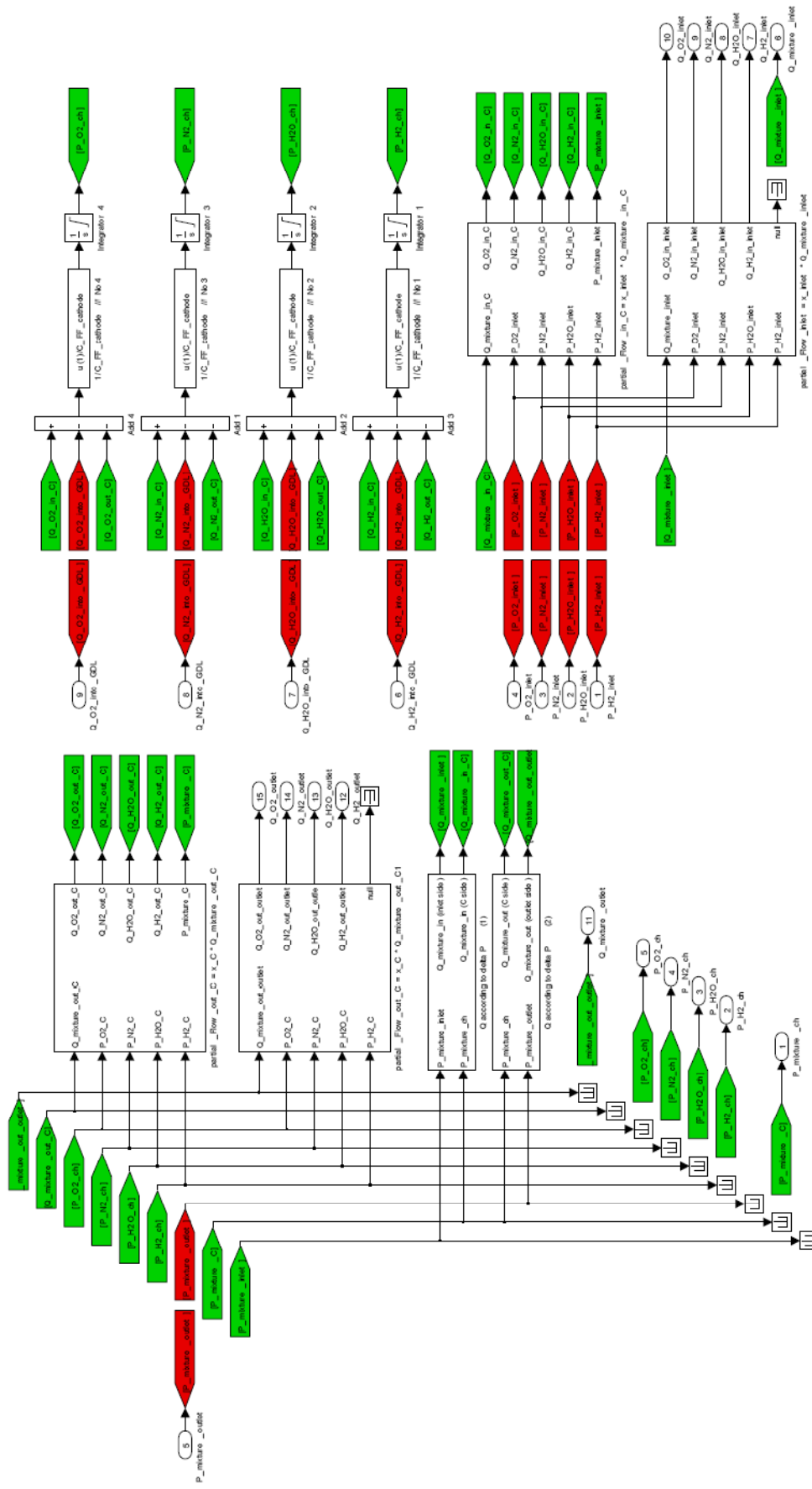


Figure 3-3 The flow-field model implemented by using basic Simulink blocks

A circuit simulation in Matlab/Simulink can be done in several ways. A direct method is to use a SimPowerSystems blockset which allow user to create and simulate a circuit based on electrical component. Another method is to use a basic Simulink blocks which is more common and is preferred by experienced engineers. It should be noted that the basic simulink blocks have been used extensively in power electronic and electric drive simulations. As an example, the model of flow-field channel implemented by using the SimPowerSystems blockset is shown in figure 3-2. The model of flow-field channel, which is extended to 4 species, is implemented by using the basic Simulink blocks is shown in figure 3-3.

3.2 Error from Layer Discretization

Several parts of the proposed model used a discretization technique to convert a mass transport equation to a linear circuit. This method divided the traveling path into a small discrete step and assumes that each step is locally linear. The parameters between each step were assumed to be constants and are updated every cycle of calculation.

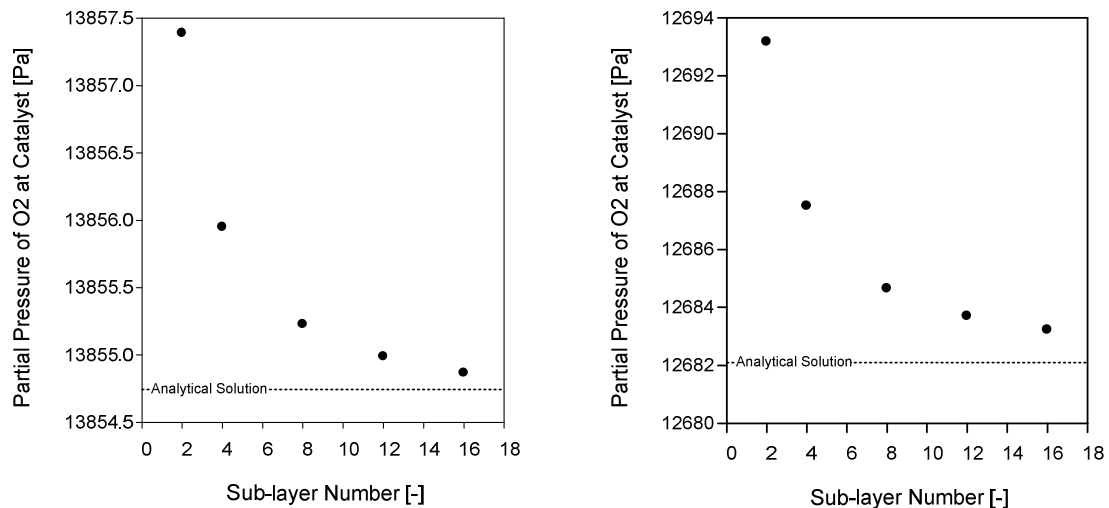
It is obvious that the length of the small discrete step affects the accuracy of the simulation. Decreasing the step length means increasing the sub-layer number and the sub-layer circuit. Higher sub-layer circuit number means higher computational cost. This is why the number of sub-layer should be carefully selected.

Table 3-1 Parameters for GDL discretization effect studying

Parameter	Symbol	Value	
		for 0.5 A/cm ²	for 1 A/cm ²
Temperature [K]	T	353.15	
GDL cross-section area [cm ²]	A	100	
GDL porosity [-]	ϵ	0.4	
Effective Diffusion coefficient [m ² s ⁻¹]			
Between $O_2 - H_2O$	$D_{O_2-H_2O}^{eff}$	8.285×10 ⁻⁶	
Between $O_2 - N_2$	$D_{O_2-N_2}^{eff}$	6.588×10 ⁻⁶	
Between $H_2O - N_2$	$D_{H_2O-N_2}^{eff}$	8.894×10 ⁻⁶	
Partial pressure at flow-field channel [Pa]			
Oxygen	$p_{O_2}^{(FF)}$	15038.784	
Water (gas phase)	$p_{H_2O}^{(FF)}$	28386.741	
Nitrogen	$p_{N_2}^{(FF)}$	56574.474	
Molar flux toward membrane [mol m ⁻² s ⁻¹]			
Oxygen	N_{O_2}	1.295×10 ⁻⁴	2.591×10 ⁻⁴
Water (gas phase)	N_{H_2O}	-2.591×10 ⁻⁴	-5.182×10 ⁻⁴
Nitrogen	N_{N_2}	0	0

Table 3-2 Analytical and simulation results

Sub-layer Number	50 A		100 A	
	p_{O_2} at catalyst [Pa]	Relative Error [%]	p_{O_2} at catalyst [Pa]	Relative Error [%]
Analytical Sol.	13854.5234	-	12681.8232	-
2	13857.3885	0.0206802	12693.1706	0.089477
4	13855.9492	0.0102911	12687.4967	0.044738
8	13855.2282	0.0050875	12684.6474	0.022269
12	13854.9878	0.0033521	12683.6957	0.014765
16	13854.8674	0.0024826	12683.2193	0.011009

**Figure 3-4** The flow-field model implemented by using basic Simulink blocks

In our model, the most critical part which relied on the discretization technique was the cathode GDL. This is because the diffusion of oxygen through the GDL is more difficult than the hydrogen. The membrane model which also relied on the same technique should require less sub-layer number because its physical dimension is thinner than the GDL. Thus, we selected the cathode GDL for studying the effect of sub-layer number on the accuracy of the simulation.

Since the analytical solution of Stefan-Maxwell diffusion systems in steady-state is available, we evaluated the effect of the sub-layer number on the accuracy by comparing the results from circuit model simulation with different sub-layer numbers to the analytical solution.

We set a simple GDL operation by letting the air on the cathode flow-field channel has RH=60%. The oxygen flux flowed toward membrane was calculated from the electrical current density. In this study we let the current density be 0.5 and 1 A/cm². We also assumed that all the produced water diffuses back to the flow-field

channel. The other necessary parameters are shown in table 3-1. The comparative of simulation results with the analytical solution are shown in table 3-2 and figure 3-4.

As one can expect, the simulation result approached the analytical result as we increase the number of GDL sub-layer. However, the relative error of the simulation was somewhat unexpected. Though we divided the GDL into just two sub-layers, the simulation result even at the high current density deviated less than 0.1% from the analytical result. This is because the GDL is very thin; so that, the partial pressure profile along the diffusion path was almost straight and a few sub-layers were enough for an accurate result.

3.3 Single Cell Simulation and Results

The simulation of the single cell model, discussed in section 2.6, with inlet tubes is presented in this section. Parameters used in this simulation are presented in table 3-3. The parameters are intentionally selected to replicate the real structure and the operating point of the cell that we have as much as possible.

Table 3-3 General Parameters

Parameter	Symbol	Value
Fuel cell operating pressure [Pa]	P	1×10^5
Fuel cell Temperature [K]	T	333.15
Relative humidifier of anode inlet gas [%]	RH_A	10
Relative humidifier of cathode inlet gas [%]	RH_K	60

Table 3-4 Tubes and the Common Chambers

Parameter	Symbol	Value
Anode gas tube diameter [m]	a_{Tube_A}	2×10^{-3}
Cathode gas tube diameter [m]	a_{Tube_K}	5×10^{-3}
Anode gas tube length prior the cell [m]	$l_{Tube_A_inlet}$	2
Anode gas tube length after the cell [m]	$l_{Tube_A_outlet}$	2
Cathode gas tube length prior the cell [m]	$l_{Tube_K_inlet}$	2
Cathode gas tube length after the cell [m]	$l_{Tube_K_outlet}$	2
Simplified common chamber dimension[m]		
Width	$w_{FF_chamber}$	30×10^{-3}
Height	$h_{FF_chamber}$	10×10^{-3}
Length	$l_{FF_chamber}$	15×10^{-3}
Simplified anode flow-field dimension [m]		

Table 3-4 Tubes and the Common Chambers (continued)

Width	w_{FF_A}	1.5×10^{-3}
Height	h_{FF_A}	1×10^{-3}
Length	l_{FF_A}	5
Simplified cathode flow-field dimension [m]		
Width	w_{FF_K}	41.4×10^{-3}
Height	h_{FF_K}	1.1×10^{-3}
Length	l_{FF_K}	150×10^{-3}

Table 3-5 GDLs Parameters

Parameter	Symbol	Value
GDL cross-section area [m ²]	A	100×10^{-4}
GDL thickness [m]	l_{GDL}	200×10^{-6}
GDL porosity [-]	ϵ	0.4
GDL tortuosity [-]	τ	$\epsilon^{-0.5}$
Effective Diffusion coefficient [m ² /s]		
Between $O_2 - H_2O$	$D_{O_2-H_2O}^{eff}$	8.285×10^{-6}
Between $O_2 - N_2$	$D_{O_2-N_2}^{eff}$	6.588×10^{-6}
Between $H_2O - N_2$	$D_{H_2O-N_2}^{eff}$	8.894×10^{-6}
Knudsen Diffusion coefficient [m ² /s]		
Between Wall - H_2	D_{H_2-K}	1.283×10^{-3}
Between Wall - H_2O	D_{H_2O-K}	4.295×10^{-4}
Between Wall - O_2	D_{O_2-K}	3.222×10^{-4}
Between Wall - N_2	D_{N_2-K}	3.444×10^{-4}
Thickness of the MPL layer [m]	l_{MPL}	20×10^{-6}
GDL anode/cathode sub-layer number [-]	$n_{GDL_sub-layer}$	4

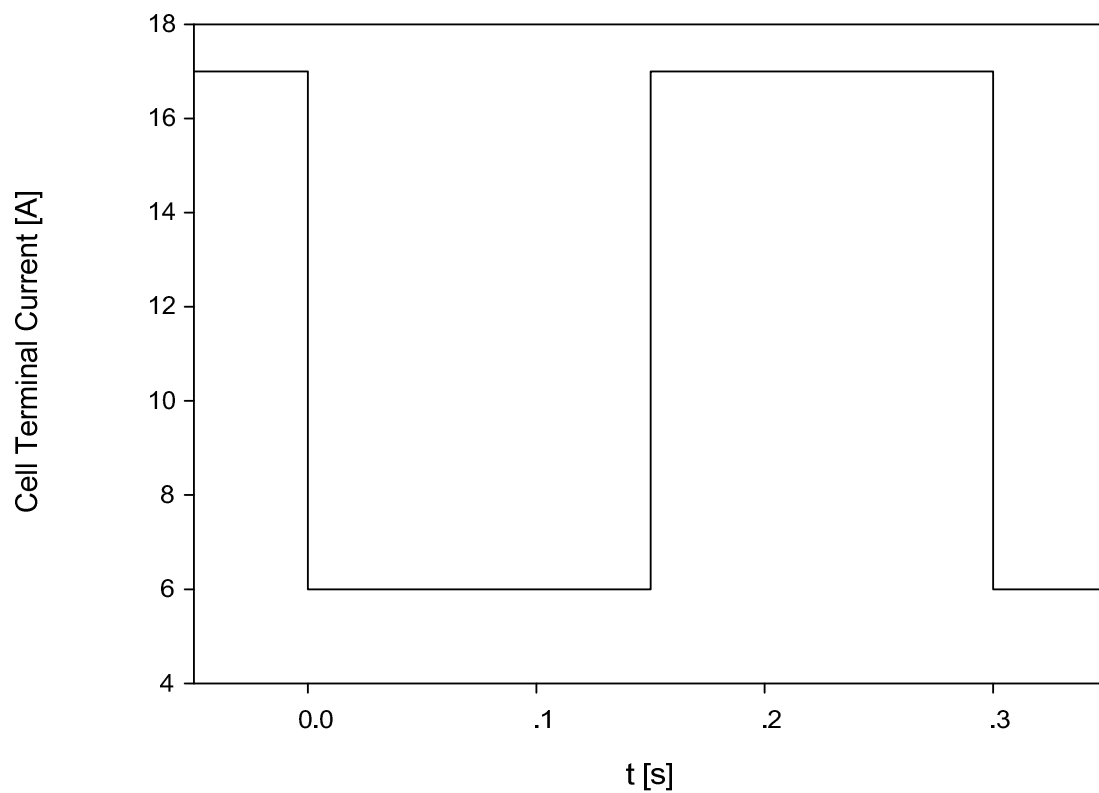
Table 3-6 Catalysts Parameters

Parameter	Symbol	Value
Anode exchange current density [A/m ²]	$j_{0,anode}$	35
Cathode exchange current density [A/m ²]	$j_{0,cathode}$	3×10^{-3}
Cell Reversible potential [V]	E_r^\ominus	1.229
Double layer capacitance [F]	C_{dl}	2

Table 3-7 Membrane Parameters

Parameter	Symbol	Value
Membrane Thickness [m]	l_m	30×10^{-6}
Membrane sub-layer number [-]	$n_{membrane_sub-layer}$	4
Equivalent Weight (EW) [kg/mol]	EW	1.1
Membrane specific weight [kg/m ³]	ρ_{dry}	1967.2
Water drag coefficient [-]	n_{drag}	1
Ionic conductivity	$\sigma_{H^+}^m$	Eq.(2-123)
Water diffusion coefficient [m ² /s]	$D_{H_2O,\lambda}^m$	Eq.(2-128)

We simulated the single cell operation when connected to the current controlled load. The load repeatedly switched the cell current between 6 and 17 A as shown in figure 3-5. In the experimentation process, the current controlled load was realized by an electronic load. The simulation results in steady state operation are shown in figure 3-6 to 3-17. The terminal voltage from the simulation and experimentation are plotted together in figure 3-17.

**Figure 3-5** Load Current drawn from the single cell

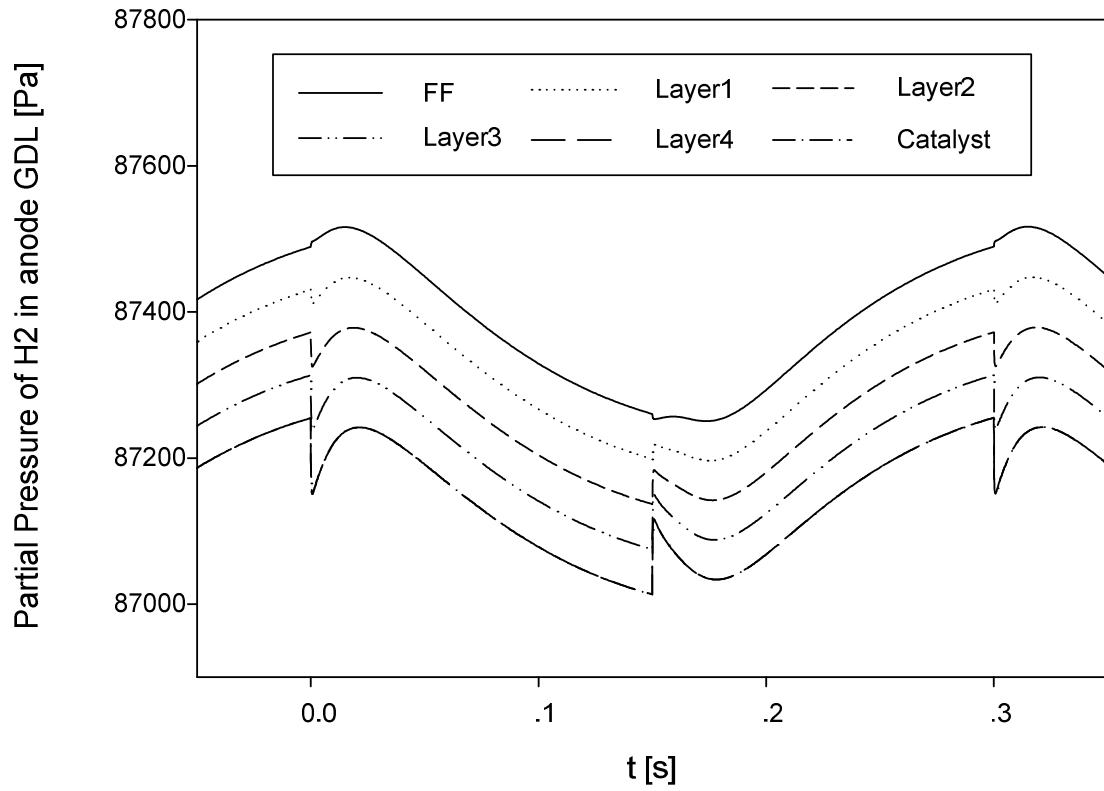


Figure 3-6 Partial pressure of H_2 in each layer of anode GDL

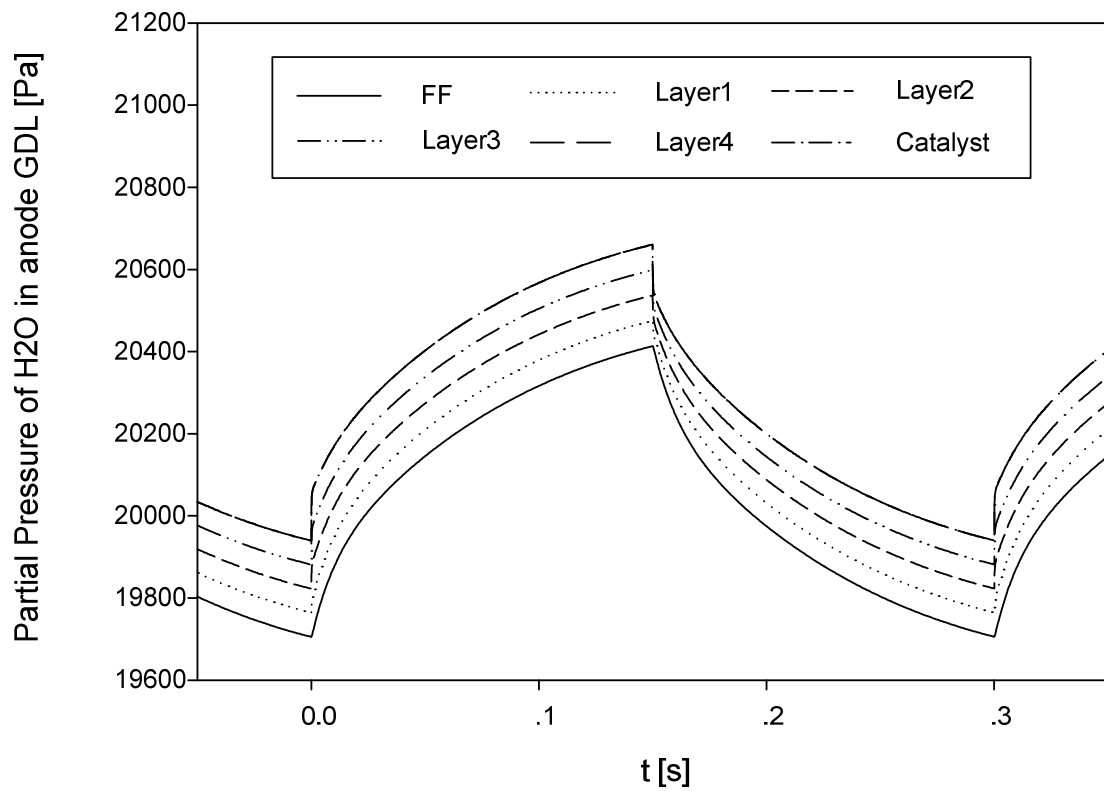


Figure 3-7 Partial pressure of H_2O in each layer of anode GDL

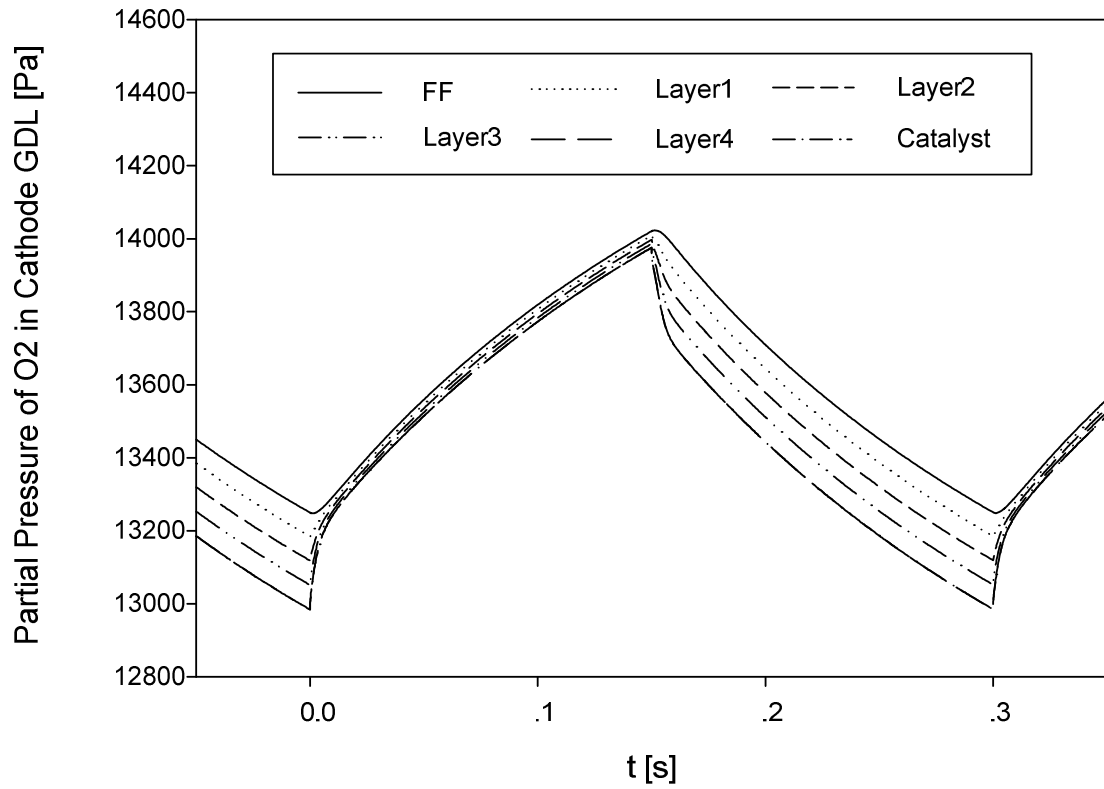


Figure 3-8 Partial pressure of O_2 in each layer of cathode GDL

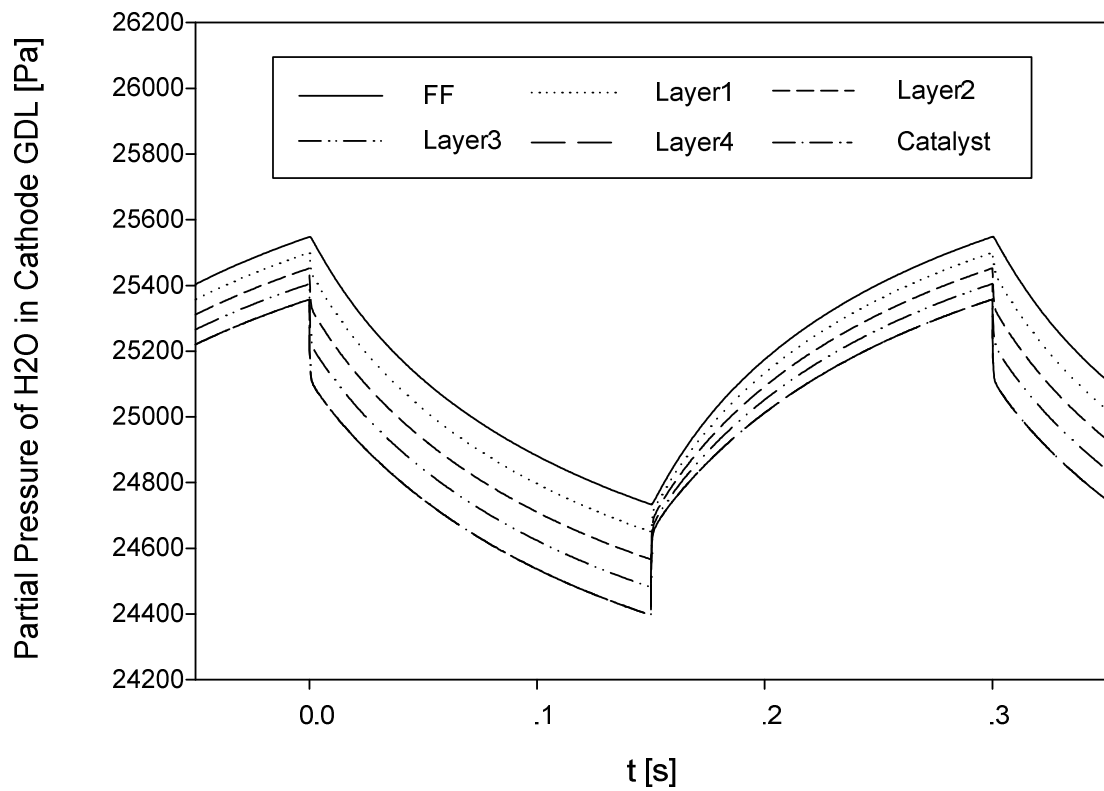


Figure 3-9 Partial pressure of H_2O in each layer of cathode GDL

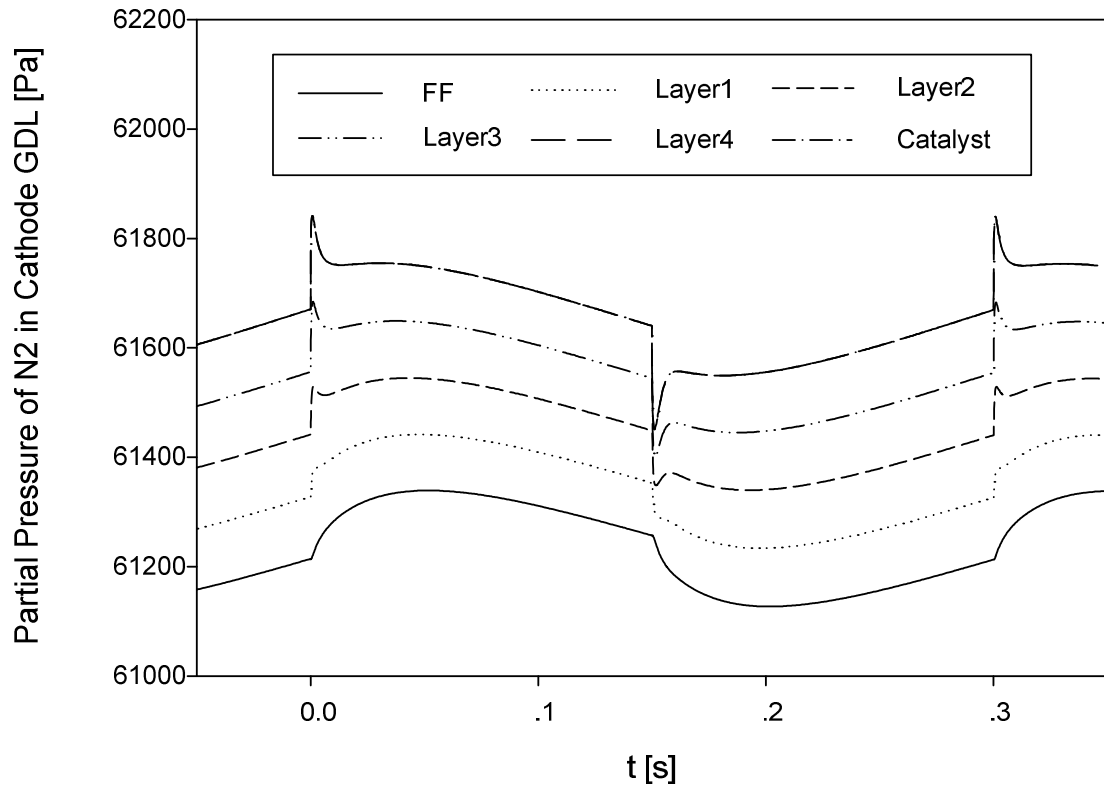


Figure 3-10 Partial pressure of N_2 in each layer of cathode GDL

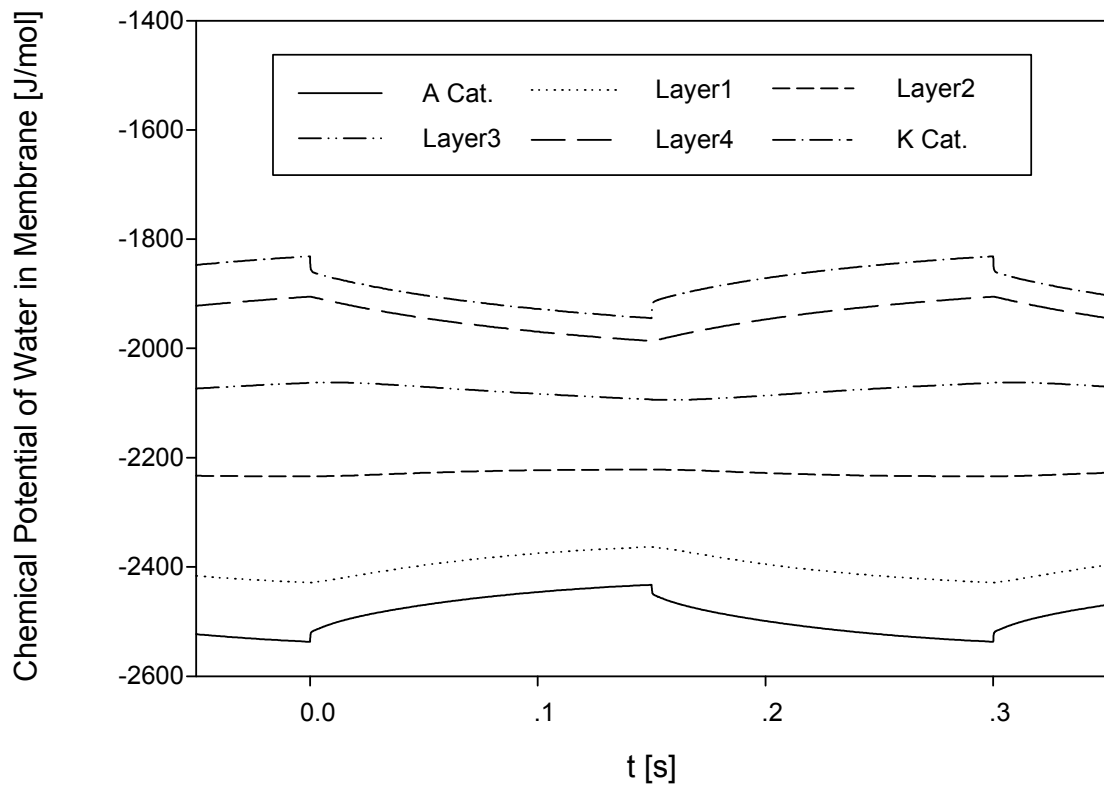


Figure 3-11 Chemical potential of H_2O in each membrane layer

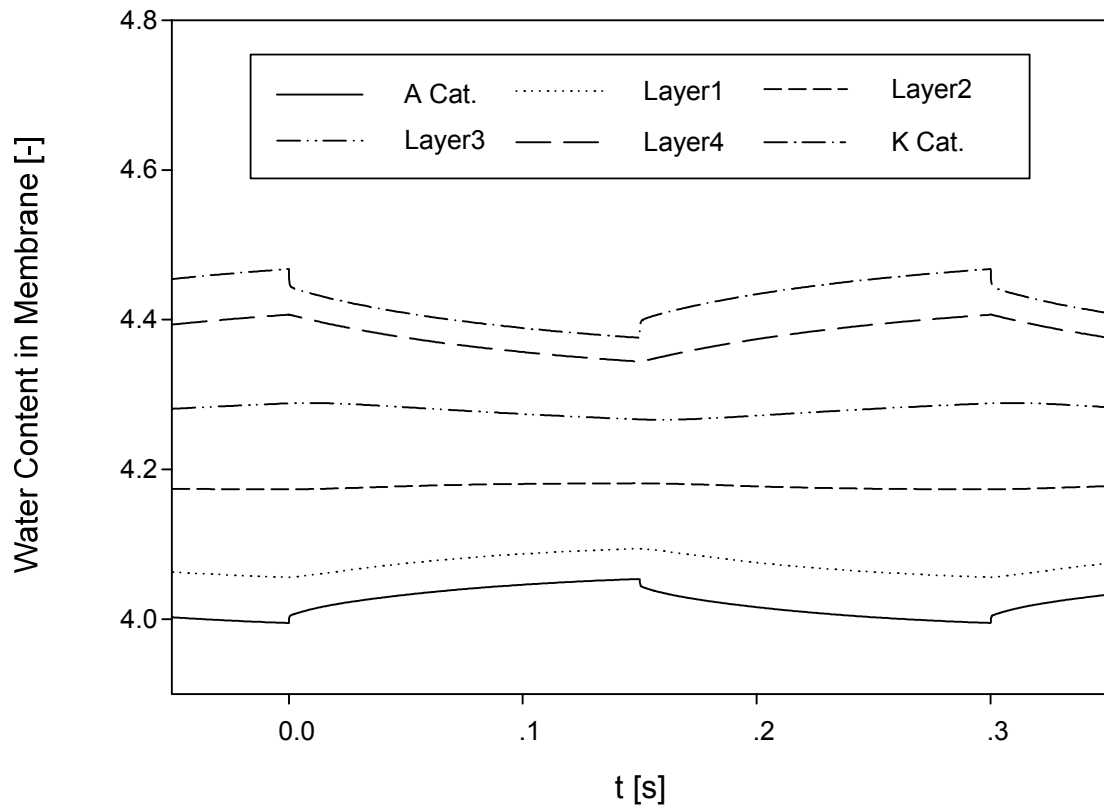


Figure 3-12 Water content (λ) in each membrane layer

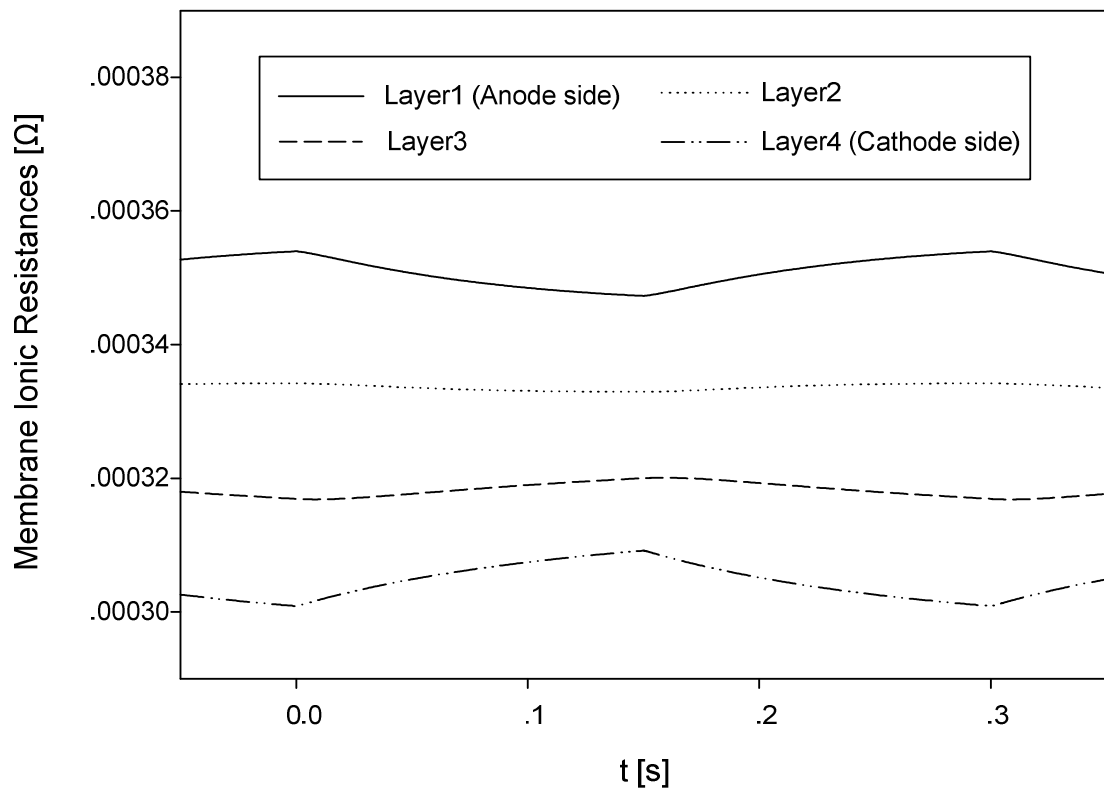


Figure 3-13 Ionic resistance of each membrane layer

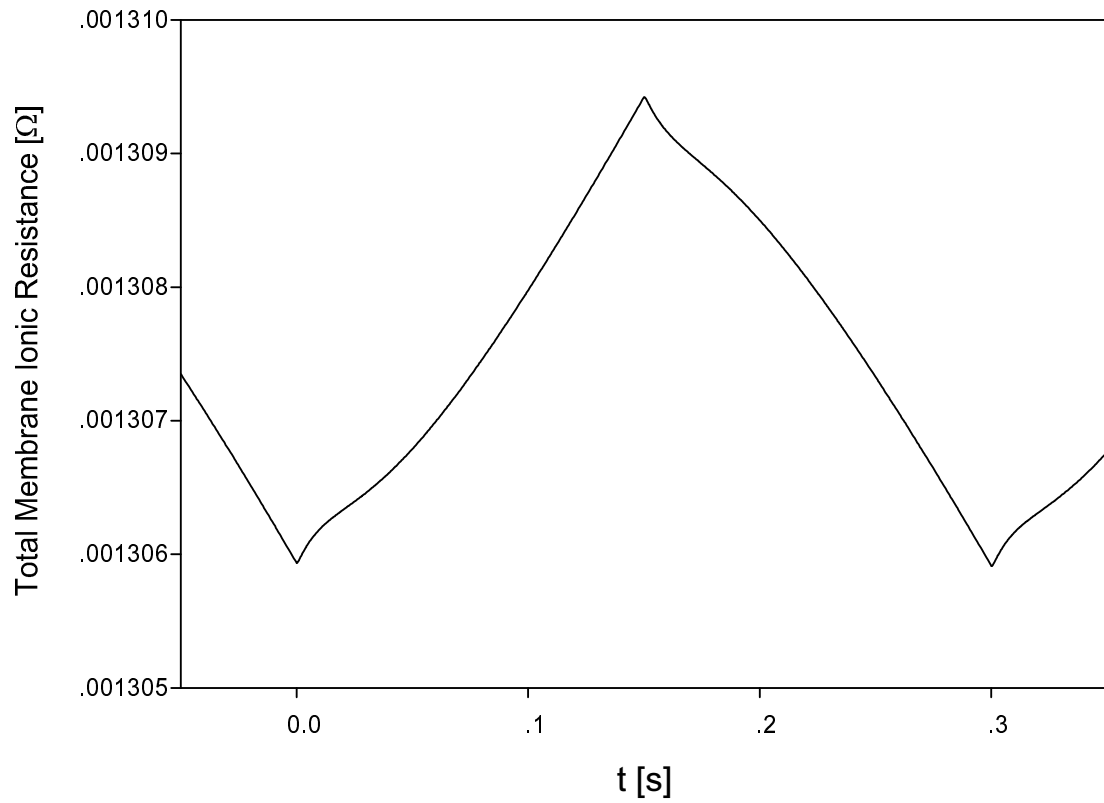


Figure 3-14 Total membrane ionic resistance

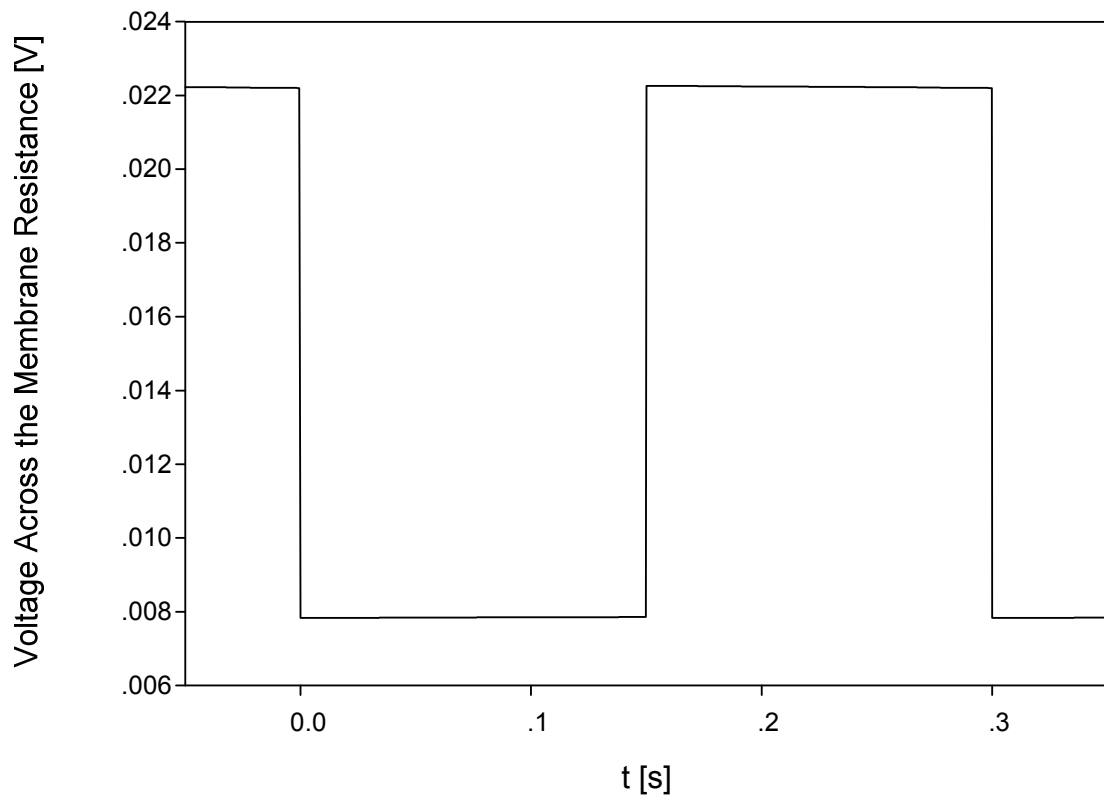


Figure 3-15 Voltage dropped across the membrane

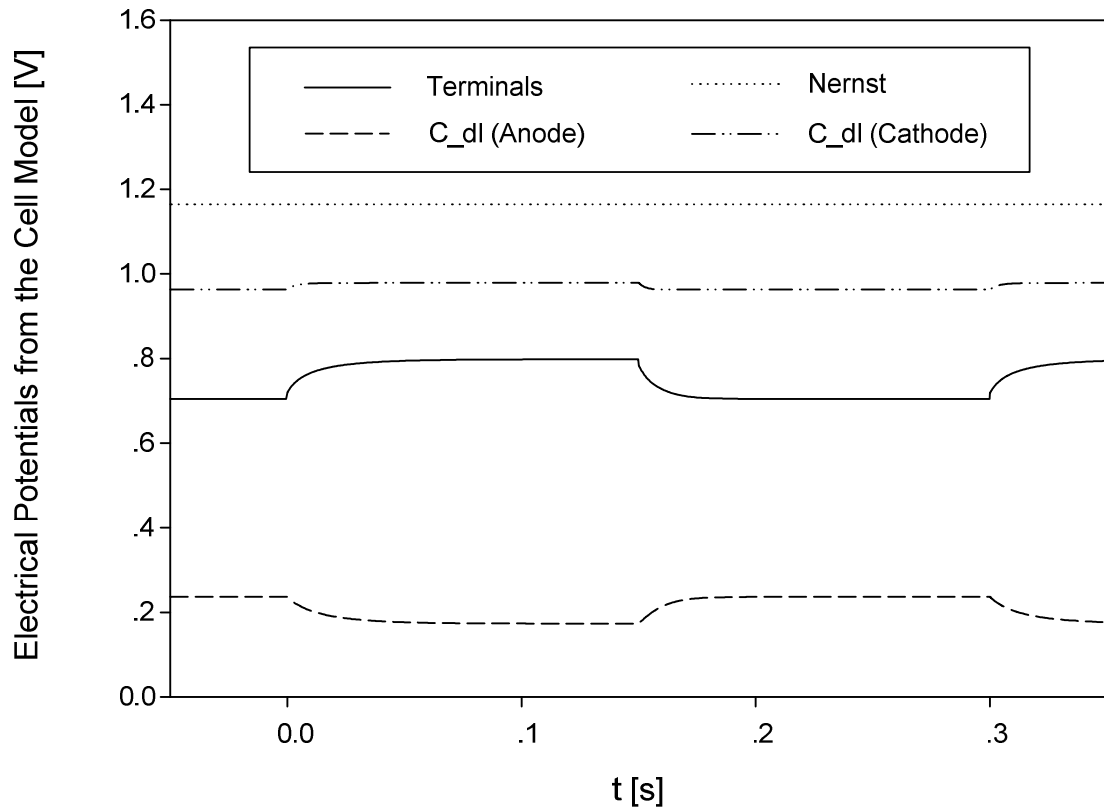


Figure 3-16 Electrical Potentials of the cell

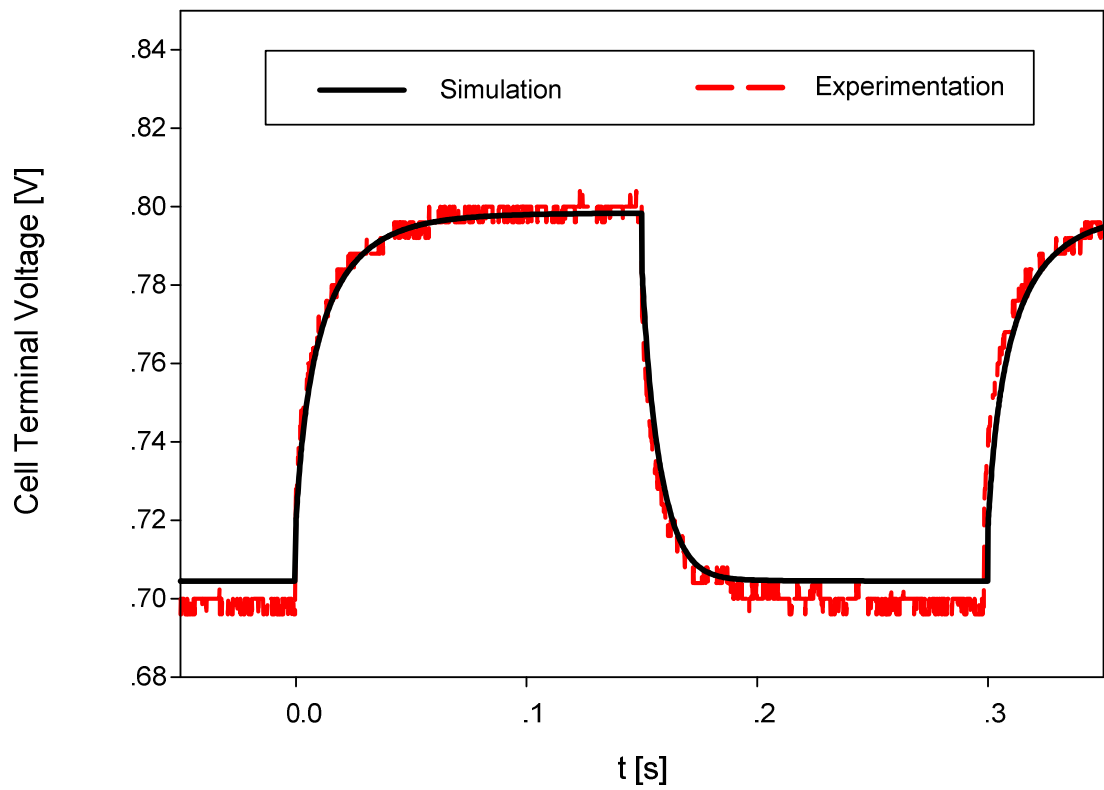


Figure 3-17 Cell terminal voltages from simulation and experimentation

3.4 Static V-I Curves

The static V-I curve of the fuel cell is one of the most important information. The decreasing of the cell potential is due to the activation potential, the membrane resistance and the concentration loss. The loss due to the activation potential and the membrane resistance are seemed to be fixed. Engineers or scientists who are not working with the MEA can do just a few things to reduce these losses. The concentration loss, or the decrease of the cell potential due to the absent of the fuel or oxidant at the catalyst, is related to the fuel and oxidant feeding rates. In most case the problem occurred at the cathode side where the oxygen in the air is insufficient for producing the electric current. The exact consummation rates at the catalyst can be calculated by:

$$Q_{H_2_consumed} = \frac{I_{ref}}{2F} \cdot \left(\frac{R \cdot T}{P} \right) \quad (3-1)$$

$$Q_{O_2_consumed} = \frac{I_{ref}}{4F} \cdot \left(\frac{R \cdot T}{P} \right) \quad (3-2)$$

where I_{ref} is the target electrical current.

Although the exact consummation rates at the catalyst can be calculated, not all the oxygen fed into the cell goes to the catalyst, i.e., some of the oxygen just passes by the GDL surface and goes directly to the cell outlet. This implies that the species feeding rate must be greater than the exact consummation rate. On one hand, too little gas feeding rate causes the potential loss. On the other hand, too much gas feeding rate mean wasting fuel/oxidant and energy at the compressor. The very first duty of a scientist or engineer who designs or operates the fuel cell system is to specify this proper gas feeding rate.

This section shows the single cell static V-I curve from the developed model. The external tubes was not included in this simulation, i.e., we assumed that the gas was fed directly to the flow-field plate. The other simulation parameters were the same as in the previous section. The fuel/oxidant feeding rates were calculated by:

$$Q_{gas_anode} = \zeta_A \cdot \frac{I_{ref}}{2F} \cdot \left(\frac{R \cdot T}{P} \right) \quad (3-3)$$

$$Q_{gas_cathode} = \zeta_K \cdot \frac{1}{0.21} \cdot \frac{I_{ref}}{4F} \cdot \left(\frac{R \cdot T}{P} \right) \quad (3-4)$$

The coefficients 0.8 and 0.21 were added for partial pressure compensation. The ζ_A and ζ_K are the overfeeding factors for the anode and cathode sides, respectively. In this simulation, the overfeeding factors for both sides are equaled to 1. The I_{ref} was fixed for each V-I curved. The simulation results are shown together with the experimental result in figure 3-18. As operating the fuel cell under insufficient fuel/oxidant condition may severely damage the catalyst layer, the experimental in this region was omitted. The experimental result was obtained with a fixed air inlet feeding rate at 5 liter/min.

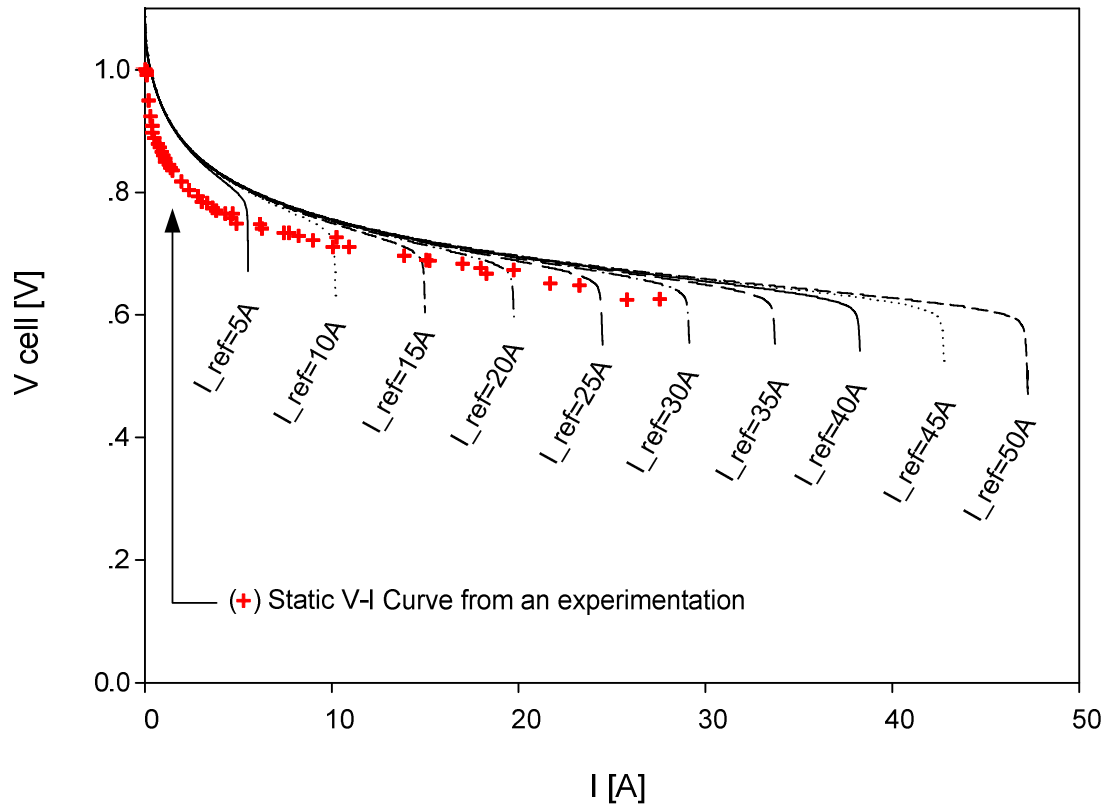


Figure 3-18 Static V-I curve with different gas feeding rates

3.5 Effects of the Channel Network

In the stack system as shown in figure 2-50, the gas inlet of each cell is connected to the common gas chamber. Logically, the cell that closest to the inlet should receive the freshest air and the performance of the cell should be better than the other cell in the same stack. This effect should not be seen easily if the common chamber is well designed and if the stack contains just a few cells. However, in some case where the stack had large number of cell, or several single cell were connected together manually by small and long external tubes, this effect is worth to taking into account.

To see this effect, we simulated the 3-cell stack model with $I_{ref}=30$ A and applied the 80 A of load current to the cell stack. The result is shown in figure 3-19. As expected, we found that the effect of the channel network was very small in a well designed stack; however, the simulation allowed us to zoom in and observed this effect.

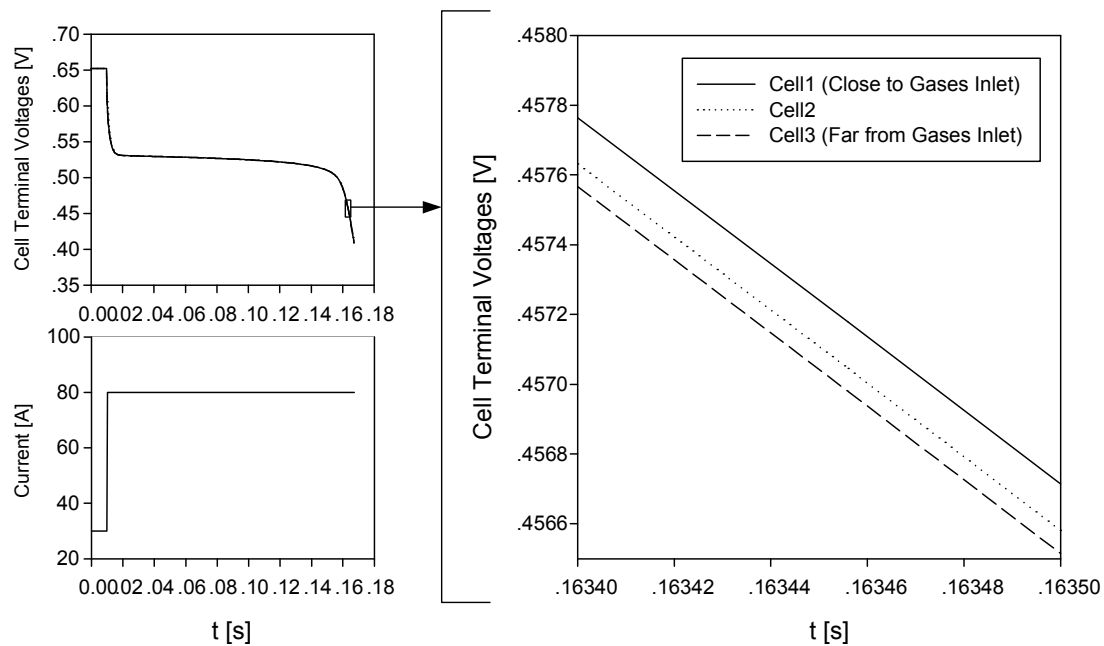


Figure 3-19 Effect of gas channel structure on the cell operation

3.6 Connected with Boost Converter

To demonstrate the capability of the developed model in power electronic applications, the model was connected to the boost converter. The boost converter is one of the basic topology of the dc-dc converter. The boost converter is used to step the cell output voltage, which is usually low, up to a higher level which suited for the load. The circuit components, for example, R, L, C, or diode, were taken from the SimPowerSystems blockset. The schematic of the simulation circuit is shown in figure 3-20. The cell stack parameters were the same as in section 3.3. The converter operated as open-loop with fixed duty cycle at 70% and the switching frequency was set to 5 kHz. The simulation results are shown in figure 3-21 to 3-24.

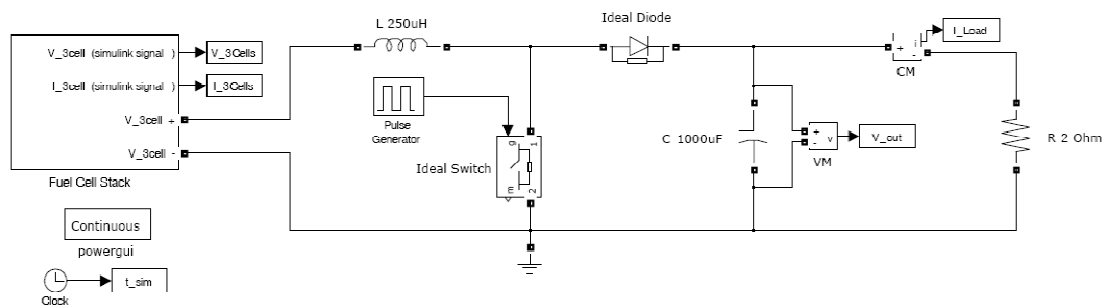


Figure 3-20 Schematic of 3-cell stack connected with the converter in Simulink

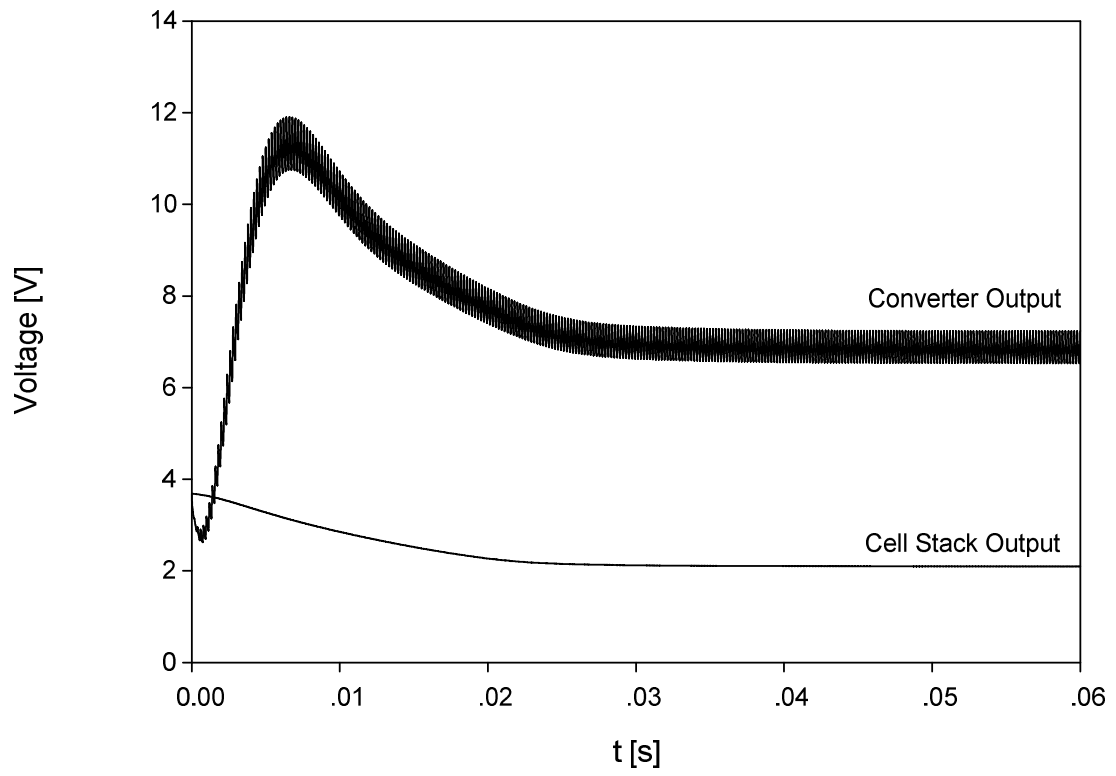


Figure 3-21 Output voltage of the cell stack vs. the converter

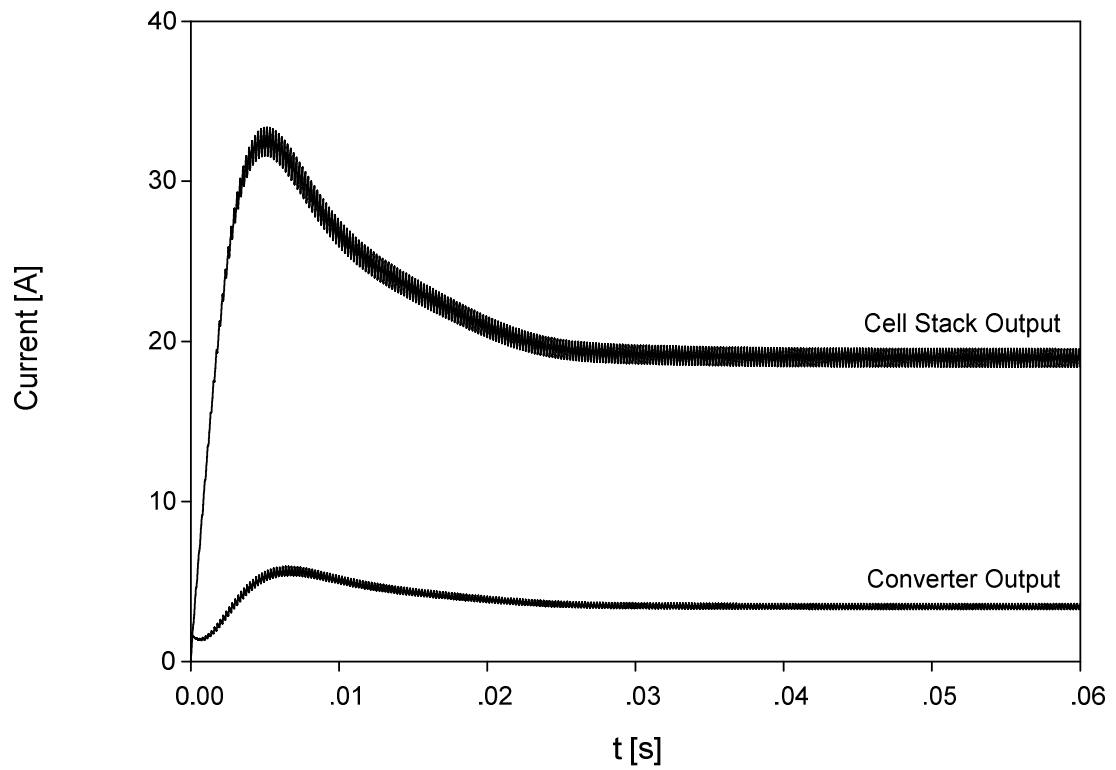


Figure 3-22 Output current of the cell stack vs. the converter

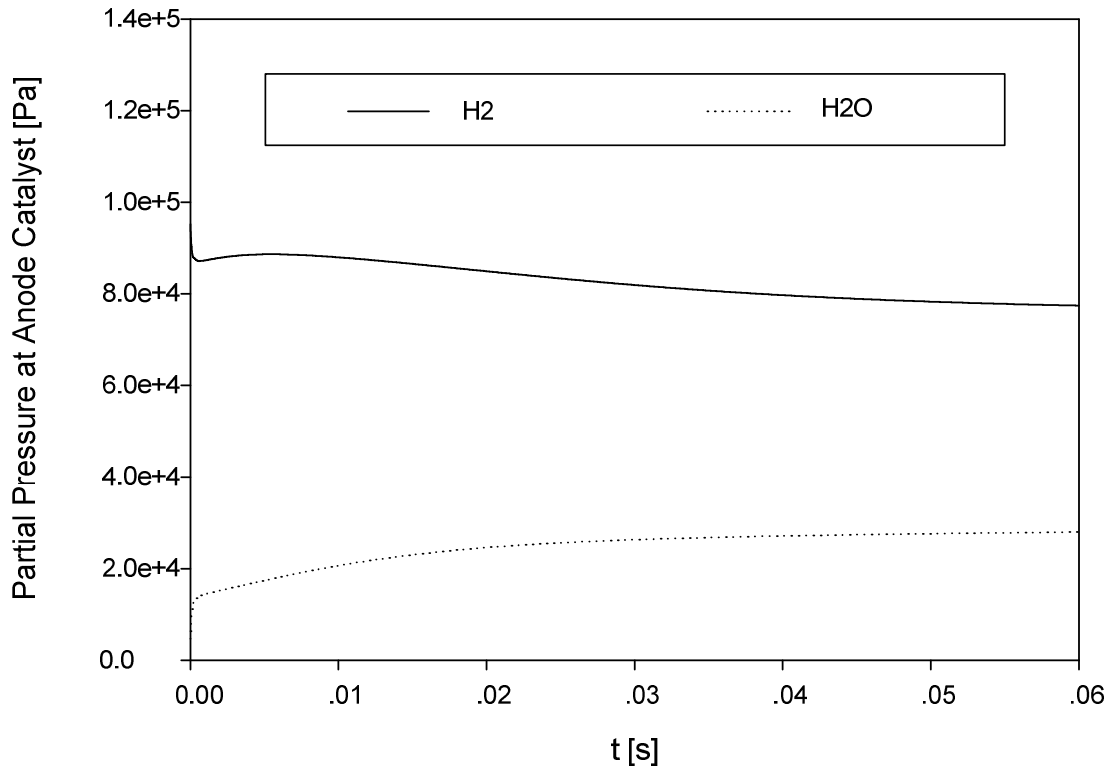


Figure 3-23 Partial pressure of each species at the anode catalyst

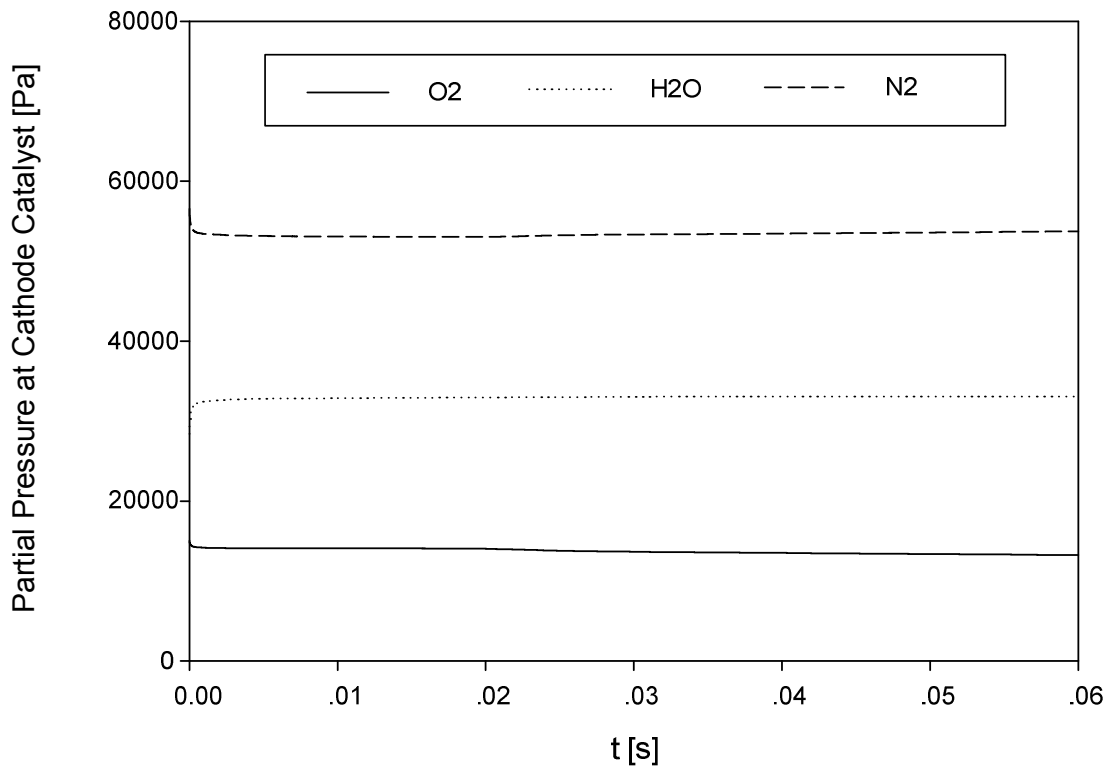


Figure 3-24 Partial pressure of each species at the cathode catalyst

3.7 Conclusion

The implementation of the equivalent circuit model of the fuel cell has been shown in this chapter. There are several choices of the implementation platform, for example, the Saber, the PSpice, or the Matlab/Simulink. In this work, we chose to implement the circuit model on the Matlab/Simulink because it is flexible and common to most scientists and engineers. The anxiety of the discretization error was proved to be less important. The developed model provided a wide range of simulation capability, from static to dynamic operation, and allowed many parameters to be adjusted. This is possible because the model was developed from physical equations. This feature is not available in most empirical models. The simulation showed that the developed model can be seamlessly integrated with the power electronic circuits. This allows scientists and engineers to see the detail interaction between power electronic circuits and the fuel cell in more convenient manner.

Chapter 4

Conclusion

This work is an effort to create a more proper model for electrical engineers. The target model should be able to incorporate with power electronic circuits and give more insight information than the empirical circuit models. We started the thesis by studying the mechanic of the fuel cell. Since the model was expected to be used by electrical engineers, the analogy of cell mechanics to electrical circuits was also our interest. To granites the proper analogy, we introduced the principle of energy port to our model. The requirement of the low computational cost suggested us to limit the model to only one dimension. We first developed a model of gas tubes and channels for multi-species systems, then, proceeded to the gas diffusion layers, the catalysts and the membrane. At this level we obtained a new equivalent circuit model of the single cell system. For the n -cell stack model, the simplest way which can be found in most literature is to multiply the single cell output voltage by n . However, we chose to develop the real 3-cell stack model, i.e., there was 3 independent cells in the system and the effect of common channels between each cell was incorporated.

We decided to implement the model in Matlab/Simulink because it is common to most electrical engineers. The simulation results showed that the model is working well. The internal phenomena of the cell at the specified condition were illustrated. The cell output voltage from the model is well agreed with the experimental result. The effect of the channel network between each cell in the stack had been explored. Although the expected result was obtained, we noticed that the channel network effect to the 3-cell stack operation was very small. This is because the channel parameters that we gave to the model are from the real cell structure which is well designed. Nevertheless, this effect should be magnified in a stack system which has higher cell number. To prove that the model can fulfill the ultimate thesis goal, the 3-cell stack model was connected to boost converter. We found that the simulation can be done without problem. The interaction between the fuel cell and the converter circuit is revealed; the objective of the thesis is accomplished.

Since our model was developed from physical equations, it paved the way to a wide range of future works. Variety of control schemes can be enhanced by this model. The cell impedance from the developed model is the very first topic in our future work list.

Section C

Appendix

The Fuel Test Bench Implemented at the Thai-French Innovation Institute

This thesis is under the TFII Excellent Scholarship Program where the student is required to spend 6 months/year studying in France and the other 6 months/year studying in Thailand. I took this opportunity to construct a new fuel cell test bench at Thai-French Innovation Institute, KMUTNB, Thailand.

The schematic of the test bench is shown in figure A-1. The photos of the implemented test bench are shown in figure A-2 and A-3. The flow rates and pressures are controlled by automatic valves. The valves link to a personal computer for receiving command and display their real-time values. The electronic load is another important part of the test bench. The electronic load composes of 24 modules of the circuit shown in figure A-4. The current rating of the electronic load is about 50A. The photo of the electronic load is shown in figure A-5. The operating of the test bench and an example of the results are shown in figure A-6 and A-7.

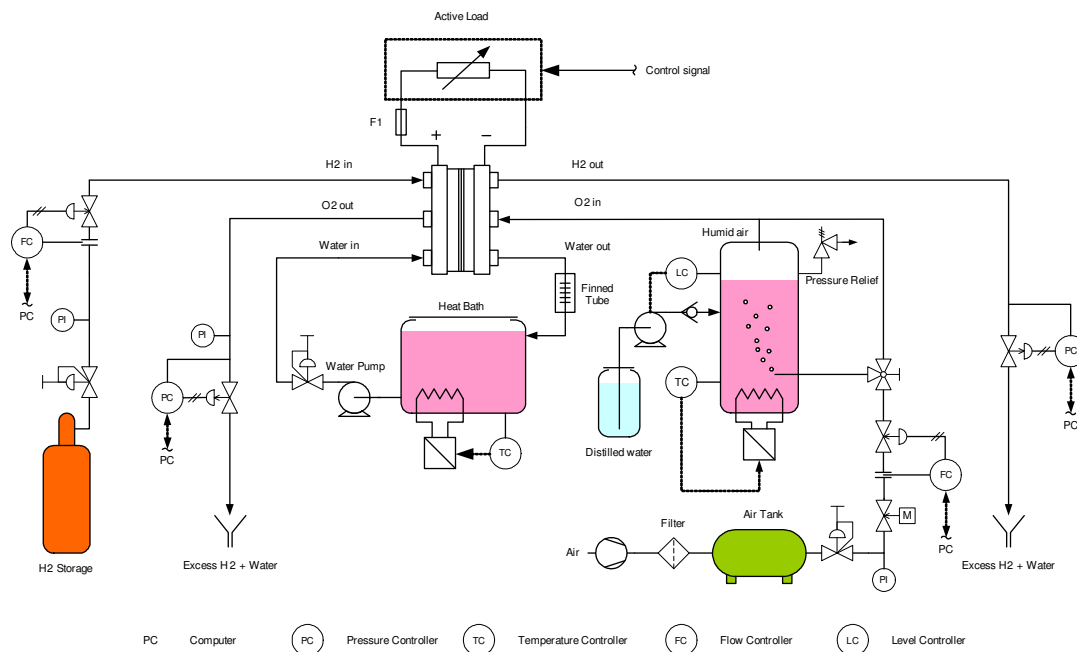


Figure A-1 Diagram of the implemented fuel cell test bench

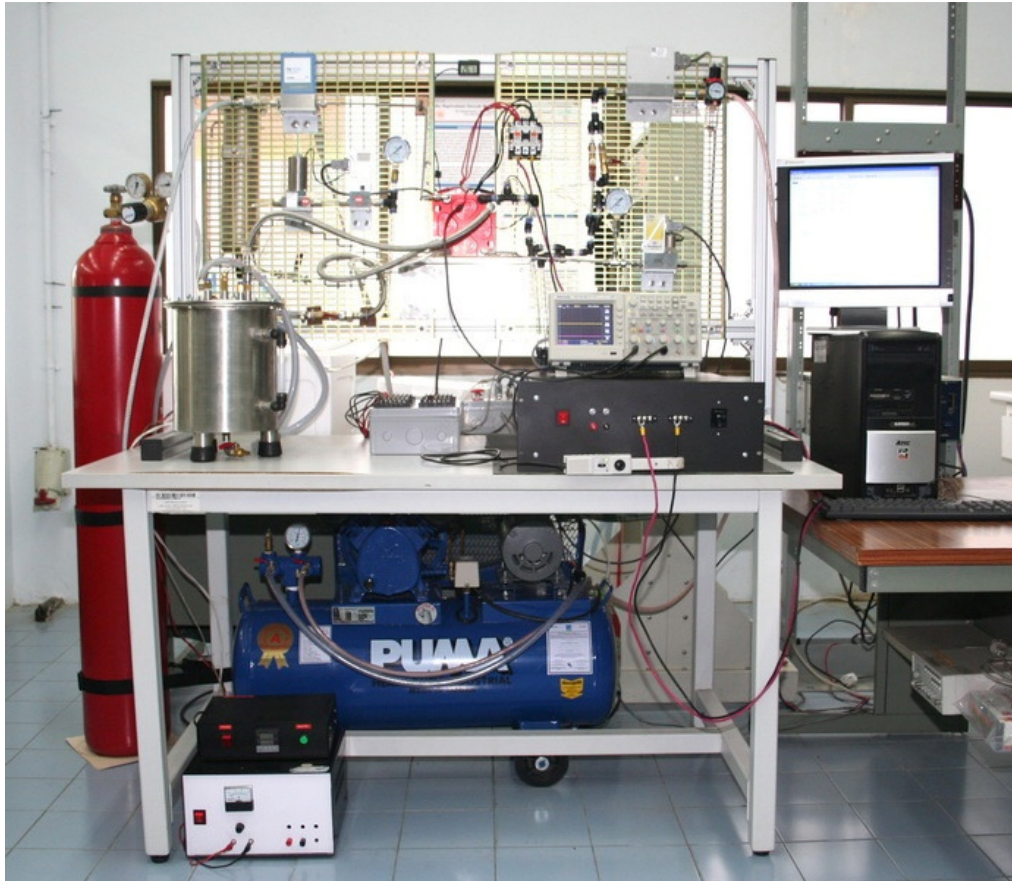


Figure A-2 The implemented fuel cell test bench

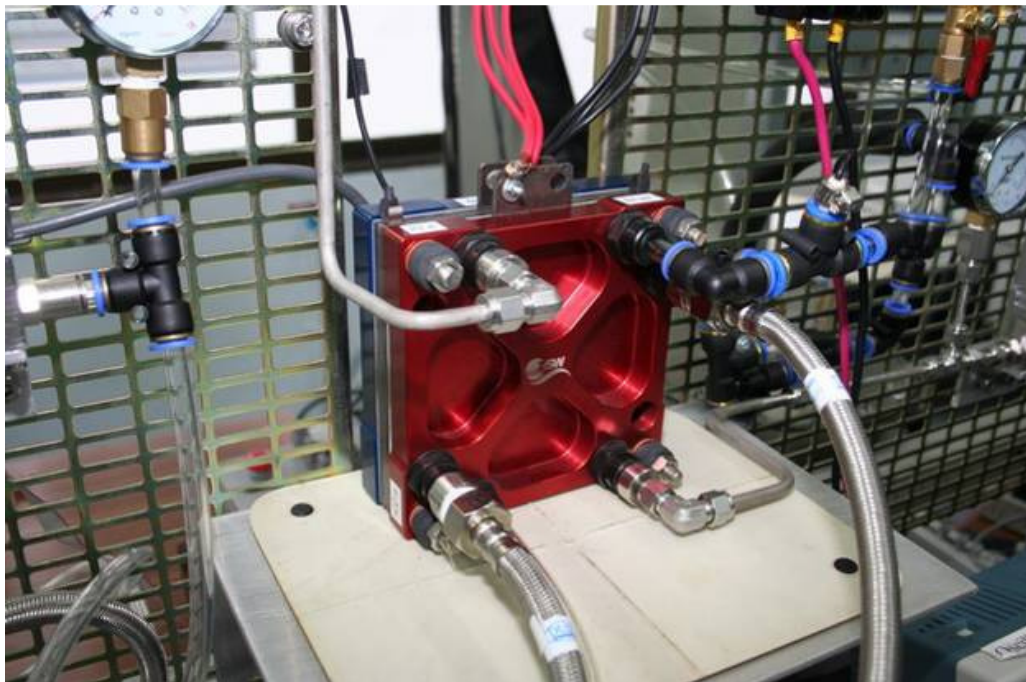


Figure A-3 The single cell installed in the test bench

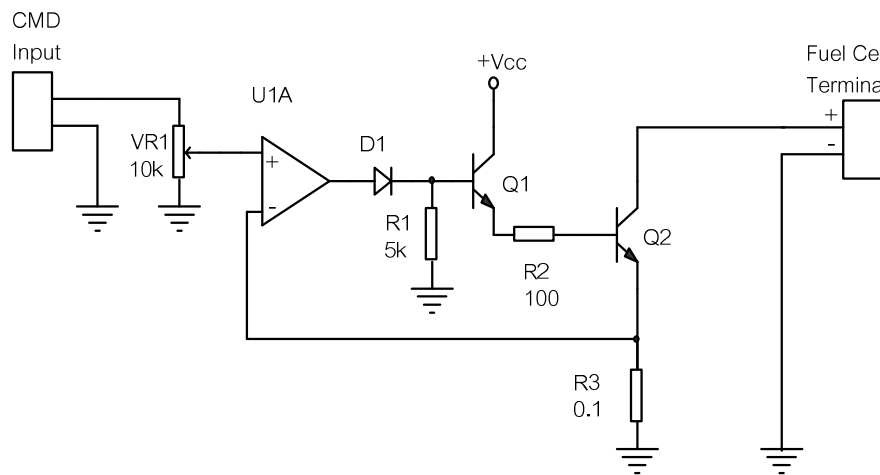


Figure A-4 The circuit of one module of electronic load

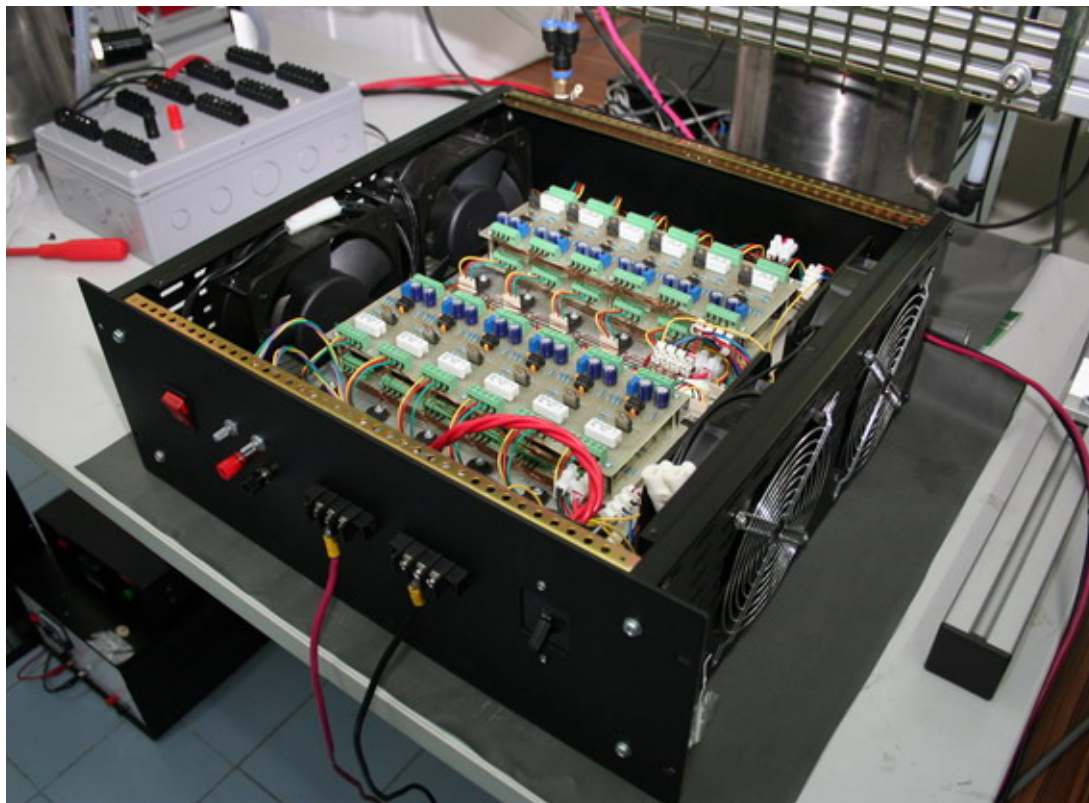


Figure A-5 The electronic load used in the test bench



Figure A-6 The test bench while performing experimentation

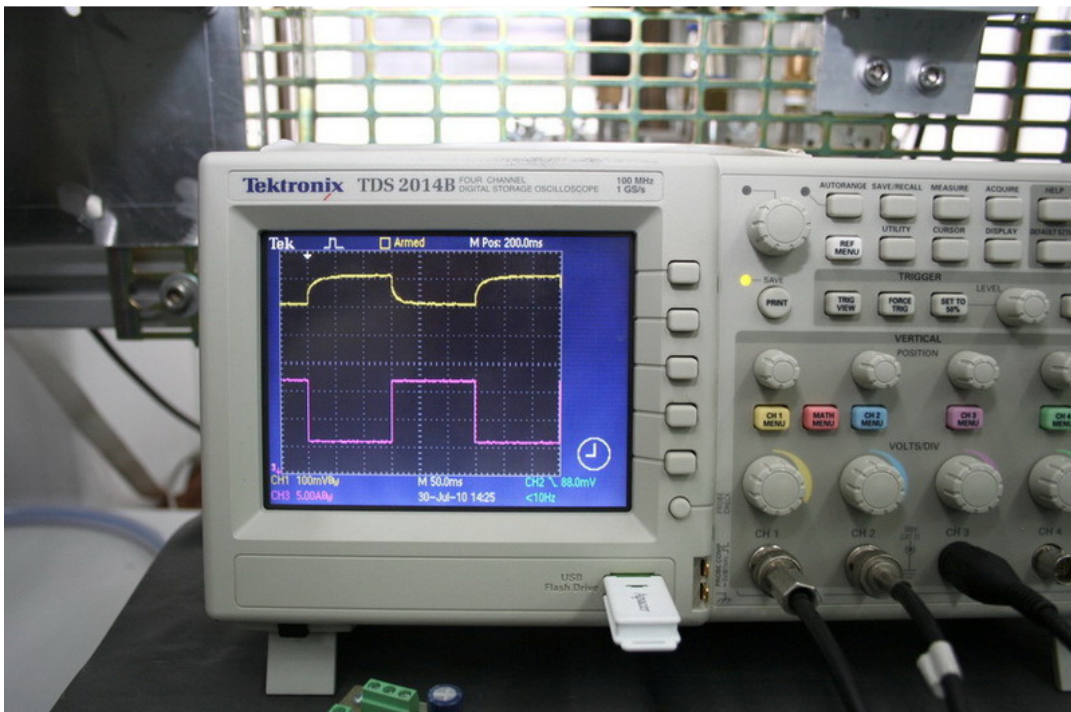


Figure A-7 An example of waveforms obtained from the test bench

Section D

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Résumé

Ce travail présente un modèle de pile à combustible plus approprié au domaine du génie électrique. Le modèle qui en résulte doit être en mesure d'intégrer des circuits électroniques de puissance et de donner des informations plus pertinentes que les modèles empiriques de type circuit. Les phénomènes du cœur de pile à combustible ont été étudiés. Les analogies entre mécanique des fluides et électricité ont été utilisées dans ce travail. Nous avons introduit le principe du flux d'énergie à notre modèle. Ceci garantit l'analogie appropriée entre deux différents domaines de l'ingénierie. L'exigence du faible coût de calcul exige de limiter le modèle à une seule dimension. Nous avons d'abord élaboré un modèle des tubes de gaz et des canaux pour les systèmes multi-espèces, puis, nous avons procédé à la modélisation des couches de diffusion de gaz, de la couche de réaction et de la membrane. A ce stade, nous avons obtenu un nouveau modèle de type circuit équivalent d'une monocellule de pile à combustible. Pour le modèle de pile n -cellule, la façon la plus simple qui peut être trouvée dans la plupart des ouvrages est de multiplier la tension de sortie d'une cellule par n . Toutefois, nous avons choisi de développer le modèle réelle d'un stack comprenant 3 cellules, autrement dit, de modéliser 3 cellules indépendantes et donc de tenir compte de l'effet du canal commun de gaz qui assure la distribution de chacune des cellules d'un stack.

Nous avons décidé de mettre en œuvre le modèle sous Matlab / Simulink, logiciel très utilisé en génie électrique. Les résultats des simulations ont montré que le modèle fonctionne bien. Les phénomènes internes de la cellule sous conditions opératoires spécifiées ont été illustrés. La tension de sortie de cellule à partir du modèle est bien en accord avec les résultats expérimentaux. L'effet du réseau de canal entre chaque cellule de la pile a été exploré. Bien que le résultat escompté ait été obtenu, nous avons remarqué que l'effet du réseau de distribution de gaz d'une cellule à l'autre d'un stack de 3 cellules était moindre. Ceci est dû aux paramètres géométriques du canal que nous avons implanté dans notre modèle qui correspondent à la structure réelle de la cellule, et qui est bien conçu. Néanmoins, cet effet devrait être fortement accentué dans le cas de stack comprenant de nombreuses cellules. Afin de vérifier que notre modèle atteint bien les objectifs visés, l'association d'un stack de 3 cellules et d'un convertisseur est simulée. Nous avons constaté que la simulation se fait sans difficulté et que le modèle autorise l'analyse de l'interaction entre la pile à combustible et le circuit convertisseur; l'objectif de la thèse est donc accompli.

Abstract

This work is an effort to create a more proper model for electrical engineers. The resultant model should be able to incorporate with power electronic circuits and give more insight information than the empirical circuit models. The mechanic of the fuel cell has been studied. The analogies of cell mechanics to electrical circuits were used in this work. We introduced the principle of energy port to our model. This guaranties the proper analogy between two different engineering domains. The requirement of the low computational cost suggested us to limit the model to only one dimension. We first developed a model of gas tubes and channels for multi-species systems, then, proceeded to the gas diffusion layers, the catalysts and the membrane. At this level we obtained a new equivalent circuit model of the single cell system. For the n -cell stack model, the simplest way which can be found in most literature is to multiply the single cell output voltage by n . However, we chose to develop the real 3-cell stack model, i.e., there was 3 independent cells in the system and the effect of common channels between each cell was incorporated.

We decided to implement the model in Matlab/Simulink because it is common to most electrical engineers. The simulation results showed that the model is working well. The internal phenomena of the cell at the specified condition were illustrated. The cell output voltage from the model is well agreed with the experimental result. The effect of the channel network between each cell in the stack had been explored. Although the expected result was obtained, we noticed that the channel network effect to the 3-cell stack operation was very small. This is because the channel parameters that we gave to the model are from the real cell structure, which is well designed. Nevertheless, this effect should be more observable in a stack system which has higher cell number. To prove that the model can fulfill the ultimate thesis goal, the 3-cell stack model was connected to boost converter. We found that the simulation can be done without problem. The interaction between the fuel cell and the converter circuit is revealed; the objective of the thesis is accomplished.