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SPIM Thèse de Doctorat

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école doctorale sciences pour l'ingénieur et microtechniques UNIVERSITÉ DE TECHNOLOGIE BELFORT-MONTBÉLIARDA

Long term performance prediction of proton exchange membrane fuel cells using machine learning method



SPIM Thèse de Doctorat

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école doctorale sciences pour l'ingénieur et microtechniques UNIVERSITÉ DE TECHNOLOGIE BELFORT-MONTBÉLIARD

THESE présentée par

Yiming WU

Pour obtenir le Grade de Docteur de l'Université de Technologie de Belfort-Montbéliard

Spécialité : Génie Electrique

Long term performance prediction of proton exchange membrane fuel cells using machine learning method

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Le 13 décembre 2016

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Abstract

The environmental issues, especially the global warming due to greenhouse effect, has become more and more critical in recent decades. As one potential candidate among different alternative "green energy" solutions for sustainable development, the Proton Exchange Membrane Fuel Cell (PEMFC) has been received extensive research attention since many years for energy and transportation applications. The PEMFC stacks, can produce electricity directly from electrochemical reaction between hydrogen and oxygen in the air, with the only by–products of water and heat. If the hydrogen is produced from renewable energy sources, this energy conversion is 100% eco–friendly. The PEMFCs are getting more and more attention because they are considered as potential candidates of clean energy solution in the near future. Besides, the PEMFCs contain no moving parts in the structures, this feature ensures both compactness and reliability of fuel cell systems. Thus, the PEMFCs are especially considered to be used in transportation applications such as hybrid or electrical vehicles.

However, the relatively short lifespan of PEMFCs operating under non steady-state conditions (for vehicles for example) impedes its massive use. The accurate prediction of their aging mechanisms can thus help to design proper maintenance patterns of PEMFCs by providing foreseeable performance degradation information. In addition, the prediction could also help to avoid or mitigate the unwanted degradation of PEMFC systems during operation. In this thesis, we have proposed a novel data driven approach to predict the performance degradation of the PEMFC using improved relevance vector machine method.

In chapter 1, we briefly introduced the theoretical description of the PEMFC during operation. Then followed an extensively detailed illustration on impacts of operational conditions on PEMFC performance. We also discussed the degradation mechanisms on each components of PEMFC. At the end, the different approaches of PEMFC performance prediction in the literature are briefly introduced.

In chapter 2, we proposed a performance prediction method using an improved Relevance Vector Machine (RVM), the prediction results based on different training zones from the

Abstract

historical data were thoroughly discussed and compared with the prediction results using conventional Support Vector Machine (SVM).

The predictions are fairly acceptable based on different training zones. However, all of the prediction were using fixed kernels, which would impede the prediction performance of proposed method. In chapter 3, we further introduced a self-adaptive kernel RVM prediction method. At the same time, the design matrix of the RVM training was also modified in order to acquire higher precision during prediction. The prediction results are illustrated and discussed in the end.

Apart from the proposed data driven approach, two physical degradation prediction models focused on the platinum dissolution on catalyst layer and its precipitation in the membrane were also briefly introduced in APPENDIX I. and II.

In summary, this dissertation mainly discussed the analysis of the PEMFC performance prediction using advanced machine learning methods.

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NOMENCLATURE

Abbreviations

ABC	Advanced Battery Consotium
AC	Alternating current
AFC	Alkaline Fuel Cells
ANFIS	Adaptive Neuro Fuzzy Inference System
ARIMA	Autoregressive Integrated Moving Average
DC	Direct current
DOE	Department of Energy (The United States)
ECM	Equivalent circuit model
ECSA	Electrochemistry Surface Area
EIA	Energy Information Administration
EIS	Electrochemical Impedance Spectroscopy
EKF	Extended Kalman Filter
ESN	Echo State Network
GDL	Gas diffusion layer
HOR	Hydrogen oxidation reaction
ICE	Internal combustion engines
IEO	International Energy Outlook
MAPE	Mean absolute percentage error
MCFC	Molten Carbonate Fuel Cells
MEA	Membrane electrode assembly
ORR	Oxygen reduction reaction
PAFC	Phosphoric Acid Fuel Cells
PEMFC	Proton Exchange Membrane Fuel Cells
PSA	Perfluorocarbon-Sulfonic Acid
PTFE	Polytetrafluoroethylene
RMSE	Root mean square error

RSVAR	Regime Switching Vector Autoregressive
RUL	Remaining useful life
RVM	Relevance Vector Machine
SOFC	Solid Oxide Fuel Cells
SOH	State of health
SVM	Support Vector Machine

Symbols

а	Activity of species
ac	Electrode specific area
α_i	Constrain factor
$\beta_{1,3}$	Butler-Volmer transfer coefficients for reactions 1 and 3
С	Concentration of species
γ	Surface energy
$D_{\rm Pt}$	Platinum atoms distribution coefficient
δ	Kernel width
$\delta_{membrane}$	Membrane thickness
$\delta_{n=1}$	Kronecker delta
Е	Potential
Ec	Activation energy on cathode
F	Faraday constant
G	Gibbs free energy
θ	PtO coverage
Н	Enthalpy
i	Current density
i _{limit}	Limiting current
io	Exchange current density
J	Flux of platinum atoms
K ₂	Equilibrium constant for reaction 2
<i>k</i> (.,.)	Kernel function

<i>k</i> _{1,2,3}	Rate constant of reactions 1, 2, 3
k _{ij}	Aggregation rate constant
Lc	Platinum loading
Γ	Number of moles of active sites per unit of platinum area
λ	Pressure coefficient
μ_{bulk}	Bulk chemical potential
μ_{particle}	Particle chemical potential
n	Number of electrons involved
N(.,.)	Normal distribution
Р	Pressure
R	Ideal gas constant
R_i	Total cell internal resistance
<i>rate</i> _{1,2,3}	Reaction rate of reactions 1, 2, 3
r	Particle diameter
S	Entropy
σ	Standard deviation
Т	Temperature
t _i	Measured value
U _{eq}	Bulk equilibrium potential
$\mathbf{U}_{particle}$	Particle equilibrium potential
U _{PtO}	PtO equilibrium potential
Vact	Activation losses
V _{conc}	Concentration losses
V _m	Molar volume
Vohmic	Ohmic losses
Voutput	Output voltage
w	Weight vector
ω	PtO-PtO interaction energy
$\Phi(\mathbf{x})$	Design matrix
ϕ_i	<i>i</i> th column of design matrix
<i>x</i> _i	Time point
\hat{y}_i	Predicted value

Subscripts

aq	Aqueous solution
g	Gaseous
02	Oxygen
Pt ²⁺	Platinum ions
Pt	Platinum
PtO	Platinum (II) oxide
ref	Reference
S	Solid

GENERAL INTRODUCTION

In last few decades, the environmental issues have become more and more serious than ever, massive use of the fossil fuels in the society have resulted to a variety kinds of problems, such as air pollution, global warming, which would have huge impact on the environment. According to the report of U.S. Energy Information Administration (EIA), the International Energy Outlook 2016 (IEO 2016) Reference case, world energy-related CO₂ emissions will increase from 32.3 billion metric tons in 2012 to 35.6 billion metric tons in 2020 and to 43.2 billion metric tons in 2040 [1]. This is an amount of predictable 40% of increase in carbon dioxide emission. It may not happen if different countries around the world would take this into serious consideration.

In these decades, the world has been facing the increase of global energy demand, the surging prices of the fossil fuels, and the growth of air pollution with the increasing emission of the greenhouse gases. All of these have tremendously pushed us forward in the research and development of renewable energy field. The fuel cell has been one of the most promising clean energy solutions to provide the electrical energy in the stationary or mobile application.

The fuel cell is an electrochemical energy conversion device which is completely environmental friendly if the hydrogen (*i.e.* the fuel) is produced 100% from renewable energy. Zero emission of carbon dioxide, high energy density, and without using the fossil fuels make it a very promising energy solution in the future. Specifically, comparing with battery energy sources, the inherent energy density of fuel cells is significantly higher, as shown in Fig. 1, which compares the specific energy (energy per unit weight) of current deep discharge lead acid (Pb-A) batteries, nickel metal hydride (NiMH), Lithium Ion battery, the US ABC (Advanced Battery Consortium) goal with the specific energy of a proton exchange membrane fuel cell (PEMFC) plus compressed hydrogen storage tanks. Two hydrogen pressures are shown: 35 MPa and 70 MPa with fiber wrapped composite tanks. The 70 MPa hydrogen tanks weigh more than the 35 MPa tanks due to the requirement for extra fiber wrap to provide the needed strength [2].



Fig. 1 The specific energy of hydrogen and fuel cell systems compared to the specific energy of various battery systems

According to different operation conditions and types of electrolyte, there are different types of fuel cells in mobile, transport and stationary application:

- Proton exchange membrane fuel cells (PEMFC)
- Alkaline fuel cells (AFC)
- Phosphoric acid fuel cells (PAFC)
- Molten carbonate fuel cells (MCFC)
- Solid oxide fuel cells (SOFC)

A brief summary of these different kinds of fuel cells is illustrated in TABLE 1. The idea of fuel cell was firstly discovered and introduced in 1838 by the Swiss scientist Christian Friedrich Schönbein. At the meantime, an independent discovery of Sir William Robert Grove also made contributions to the early time of the fuel cell development. However, the first time a fuel cell was implemented to real application can be dated back to 1939, by the British engineer Francis Thomas Bacon. In the early 1960s, General Electric developed a fuel cell system and it was practically used in the US space program, the Gemini Program. Since then, we could see the use of the fuel cells as the energy sources in the Apollo Missions of NASA, and more recently, of the automobiles, submarines and tractors.

TABLE 1

Fuel Cells	Electrolytes	Operating Temperature	Fuels	Advantages	Disadvantages
PEMFC	Proton conducting Polymer	40 – 90 °C	H ₂	Low temperature Quick start up	Expensive Vulnerable to impurities
AFC	КОН	60 – 200 °C	H_2	Cheap Cathode reaction faster	Vulnerable to impurities
PAFC	Phosphoric acid	200 °C	H2	Tolerance to the fuel impurities	Low performance Long start time
MCFC	Molten Carbonate	650 °C	CH4, H2, CO	No precious metal needed for catalyst Fuel flexibility	Low performance Long start time High temperature
SOFC	Solid Oxide	800 – 950 °C	CH4, H2, CO	No certain choices of catalysts Fuel flexibility Solid electrolyte	Prolonged start time due to high temperature

TYPES OF FUEL CELLS

Nowadays, there have been more and more areas using the PEMFC. Comparing with other kinds of fuel cells, PEMFC holds several advantages such as low operating temperature (<80°C), solid electrolyte (no leakage) and quick start-up. It can be implemented in the areas of transportation, electronics, aerospace, and also stationary applications. Regarding to the mobile use, the PEMFC could be used in many means of transportations: cars, buses, bicycles, aircraft, ships or submarines.

In most of the cases, the PEMFC is coupled with other energy providers such as batteries or super capacitors. In these years, many prototypes of PEMFC buses and cars have already been proposed, and more and more hydrogen stations are emerging all around the world.

However, the PEMFC is still relatively a new technology for most of the people all over the world. Its usage is still limited. Some people would fear from the hydrogen related technology simply because of its flammable and combustible properties. This may cause danger in some cases.

Apart from this, the PEMFC is still expensive for industrial application indeed. TABLE 2 shows the PEMFC system cost in the US from 2010 to 2015 according to the reported statistics from the Department of Energy (DOE) in 2015 [3]. Its commercial unfriendly is partly because of the fabrication cost of the proton exchange membrane or the nano platinum particles, which is the main component of the catalyst layer in the PEMFC.

Characteristic	Units	2010	2011	2012	2013	2014	2015
Gross stack	kW	87.9	89.25	88.2	89.4	92.8	88.2
power							
Stack	%	55	55	55	57	55	53
efficiency							
Cell voltage	V	0.676	0.676	0.676	0.695	0.672	0.661
Air							
stoichiometric		2.5	1.5	1.5	1.5	2	1.5
ratio							
Stack inlet	atm	1.69	3	2.5	2.5	2.5	2.5
pressure							
Stack exit	°C	85	90	82	92	95	94.1
coolant							
Total PGM	mg/cm ²	0.15	0.186	0.196	0.153	0.153	0.142
loading							
MEA areal	kW/°C	833	1110	984	692	834	746
power density							
Q/Tb	kW/°C	1.66	1.52	1.78	1.37	1.45	1.45
System cost	\$/kWnet	51	49	47	55	55	53

Table 2

System design parameters and system cost from 2010 to 2015 evaluated at rated power

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GENERAL INTRODUCTION

Moreover, its relatively lower durability also impedes it from massive usage in our daily life. For instance, the current announced lifetime of PEMFC in transportation applications is about 2500 h. In order to be competitive on the market, fuel cell systems should have the durability similar to current internal combustion engines (ICE) systems, while the identified durability target is of 5000 h (equivalent to 300,000 km of driving) with less than 10% loss of performance [4].

In other words, the poor durability of PEMFC is a problem and challenging task that need to overcome. There are many factors that could influence the long term durability of PEMFC. Its different operating conditions would also have different impacts on the fuel cell stack itself. And usually, the degradation phenomena are coupled together, making them extremely hard to be separated and identified. Therefore, in order to extend the lifetime of PEMFC, one need to understand:

- What could impede its performance?
- What are the degradation mechanisms in detail?
- How the observed performance would change during its degradation during long term operation?

In this thesis work, we illustrated first the degradation mechanisms of PEMFC in detail with literature review (chapter 1). We then proposed a mathematical way to macroscopically identify the fuel cell stack performance degradation (chapter 2, 3). Microscopically, we attempted to model the degradation of the electrochemistry catalyst surface area (ECSA) in the fuel cell stack (APPENDIX I. & II.), specifically of the platinum particles. In general, this thesis is organized as follow:

In chapter 1, the PEMFC principles are introduced with theoretical descriptions of the PEMFC. It is well-known that the performance of the PEMFC stack could be significantly impacted and deviated from the output performance by different operation conditions. We specifically illustrate in this chapter the impacts of performance from different operation conditions. The degradation mechanisms are also extensively detailed in terms of different components. In the end, we introduced the topic of PEMFC prognostics with literature review. The main scientific contributions of this thesis are presented in chapter 2 and 3. In chapter 2, we proposed the PEMFC stack performance prediction using feature extended relevance vector machine (RVM). Firstly, the mathematical formulation of RVM was illustrated, then the proposed RVM method is implemented on the performance prediction using two datasets of performance degradation measured from consecutive operation in 400 h. The results have been thoroughly discussed and compared with the prediction results from conventional methods using Support Vector Machine (SVM).

In chapter 3, the performance prediction using self-adaptive kernel RVM is proposed and analyzed. Specifically, this is proposed to enhance the prediction performance by automatically choosing the most proper kernel width during the prediction process, especially in an on-line prediction environment with different training zone. In this chapter, we firstly introduce what the kernel trick is, then the proposed self-adaptive kernel relevance vector machine has been illustrated and developed, followed by the description of the prediction implementation process. In the end, the prediction results acquired from different training sets and different prediction conditions have been extensively demonstrated and compared with both the SVM and the original RVM.

In the last chapter, the contributions of this thesis are concluded, and the future works of this thesis are proposed.

In the appendix, the first two appendixes are about the physical modelling of platinum dissolution on the catalyst layer and its precipitation in the membrane. The third appendix represents the list of publications from this thesis work.

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CHAPTER 1. GENERALITIES on PEMFC and DEGRADATION

The PEMFC can produce electricity directly from electrochemical reaction between hydrogen and oxygen in the air, with the only by–products of water and heat. If the hydrogen is produced from renewable energy sources, this energy conversion is 100% eco–friendly. The PEMFCs are getting more and more attention because they are considered as potential candidates of clean energy solution in the near future. Besides, the PEMFCs contain no moving parts in the structures, this feature ensures both compactness and reliability of fuel cell systems. Thus, the PEMFCs are especially considered to be used in transportation applications such as hybrid or electrical vehicles.

1.1 General description of PEMFC and systems

When we were saying the PEMFC, it could be referring to the PEMFC single cell or the PEMFC stacks. Typically, a PEMFC stack is consisted of up to dozens or even hundreds of single cells in order to get the needed power. These identical single cells are electrically connected in series to form a PEMFC stack. For example, the 1.2kW Ballard NEXA stack that we used in our test cases is composed of 47 single cells.

1.1.1 PEMFC structure

Fig. 1-1 shows a typical layout of a single cell of a PEMFC [5][6]. During its operation, the hydrogen is supplied to the anode side and the air (oxygen) is

supplied to the cathode side. The hydrogen and oxygen are then diffused through the gas diffusion layer to the catalyst layer on each side. At anode catalyst layer, the hydrogen molecules are disassociated to protons and electrons with the presence of platinum catalyst. The protons then migrate through the humidified polymer electrolyte (membrane) from the anode side to the cathode side, while at the same time the electrons are conducted through the external circuit from anode to cathode to form the electrical current. Finally, at the cathode catalyst layer, the protons, the electrons and the oxygen molecules are combined to form water and heat as byproduct.



Fig. 1-1 Layout of a single cell of PEMFC

From a structural point of view, each single cell is composed by:

1. Polymer electrolyte membrane

The polymer electrolyte membrane (or the proton exchange membrane) in a cell is responsible for conduction of protons, separation of reaction gases, and electrical insulation of the electrodes. The polymer electrolyte allows the single cell operating with a very thin membrane while still withstanding high pressures, resulting in low ohmic losses and facilitate the proton conduction across the membrane.

The membranes used in the PEMFCs are a kind of ionomers, which contains a large portion of polymers ions, usually the sulphonic end groups. The hydrophilic ionic end groups are the keys to enable the transporting of protons across the membrane. Several types of membranes were used before, but now the perfluorosulfonic acid (usually abbreviated as PFSA in the literature) membranes are widely used in the PEMFC. It is more commonly known as the NafionTM type membrane. The structure of the PFSA could provide on one hand, the stability in the acid environment which is caused by the hydrogen ions within itself, and also at the meantime, the ability to provide the pathway for the hydrogen ions diffusing from the anode to the cathode. For today's PEMFCs, its thickness does not exceed 25 microns in general [7]. When the membrane absorbs water, the water molecules would tend to agglomerate and form the clusters on the hydrophilic end groups of the PFSA, then these water clusters could provide the pathways for the protons travelling from anode to cathode. The membrane would have higher proton conductivity with higher water uptake.

Normally, the membrane would be regarded as properly functioned if it can endure in these two environments. Firstly, physically, it should be intact to be a separation between the pressurized gases in anode and cathode, with nearly no gases crossover. Moreover, it should be chemically stable in some harsh conditions which are the results of the activity of catalysts, temperature fluctuations, extremely high temperatures or the attacks from the oxidative radicals originally formed from the H_2O_2 . Specifically, the radicals are produced either from the incomplete chemical reactions between the hydrogen and oxygen on the cathode, or in the membrane, where they are created on surface of the precipitated platinum particles. So based on all of these, in general, the ideal membrane for the PEMFC stack should have excellent proton conductivity, high chemical and thermal stability, mechanical strength, flexibility, nearly zero gas permeability, low cost and availability.

In the literature, [8] has been addressed different types of membranes used in the application of the PEMFC stacks. It allows us to be acknowledged of those different kinds of membranes, and also their properties and the degradation related information. In fact in a fuel cell, its lifetime is strongly

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related to its membrane durability [9]. We have to acknowledge the aging mechanisms that are involved in the membrane performance degradation. However, the degradation mechanisms of membrane are hard to be separated and identified because the membrane degradations could be caused by many operation factors. The impacts of these factors on membranes are usually coupled together. Therefore, the research on membrane degradation mechanisms still remain a challenging task.

2. Catalyst layers

The electrodes of a PEMFC single cell are the two thin catalyst layers located on both sides of the polymer electrolyte membrane. All the electrochemical reactions take place at the catalyst layers. In fact, the conventional catalyst layer is majorly composed of platinum nanoparticles supported by carbon surface with a mixture of controlled amount of ionomer. The carbon surface in this layer would give way for both platinum dispersion and electron conductivity. The ionomer, which in principle provides the structural integrity of the catalyst layer, contains many discrete hydrophilic and hydrophobic fields for the reactants and protons to access to the active sites of platinum nano particles, in which the reactions could happen. As shown in Fig. 1-1, the hydrogen oxidation reaction takes place on the active sites of catalyst layer on the left side (the anode side), and the oxygen reduction reaction takes place on the right side (the cathode side).

3. Gas diffusion layer (GDL)

The layer between the catalyst layer and bipolar plate is the gas diffusion layer (GDL). There are mainly two kinds of GDLs: the nonwoven carbon paper and woven carbon cloth. It allows the hydrogen and oxygen (or air) in the flow field channels of bipolar plates from both sides of the cell diffusing into the catalyst layers, where the electrochemical reaction would happen. Specifically, the modes of diffusion of reactants passing through the compressed GDL could be divided as the diffusion and convectiondiffusion. These depend on the geometry of the pores of GDL and the channel design of flow field channels in the bipolar plates.

The GDL is usually treated hydrophobic with coating of Polytetrafluoroethylene (PTFE) for effective transportation of liquid water and reactive gases. The hydrophobic characteristics of GDL is very important to the water management of the whole cell. The proportion of hydrophilic and hydrophobic areas on surface of GDL would tremendously influence the efficiency of gas and water transportation [10]. The PTFE treatment on porous of GDL facilitates the water management of the catalyst layer and the membrane. It could allow water vapor diffusing within the pores of itself along with the reactant gases, thereby ensuring a sufficient humidity environment in the membrane. In addition, it helps at the meantime to be able to evacuate the liquid water produced on the cathode side of each cell, and thereby prevents the water from blocking the pores to the active sites. Moreover, GDL are electrically connected to the catalyst layer and the bipolar plates. This could ensure the transfer of electrons between the active sites and the bipolar plates.

In PEMFC, the GDLs are usually functioning under the environment of high compressive stress. So the GDL should function properly in circumstances of the plastic or elastic deformations, and provide sufficient air permeability under compression.

The GDLs along with the catalyst layers are usually fabricated on both sides of the membrane to form the Membrane Electrode Assembly (MEA). The catalyst layer along with the GDL on each side of MEA could be regarded as two electrodes. Each electrode is electrically insulated from each other by the membrane.

4. Bipolar plates

The bipolar plates are essential to supply the reaction gases to the electrodes with the flow field channels on their surface. Besides, the bipolar plates are also essential for multiple cell configurations for its ability of electrically connection with different cells in series. Moreover, they can structurally support the cells in a pressed and compact configuration, making it more reliable during operation. Among all of these, the abilities of collecting reactant gases and allowing them diffusing into the electrodes are the most important functions of the bipolar plates. In fact, the design of the flow field channels in the bipolar plates is crucial for the efficiency of gas diffusion. Different designs have been discussed in [11].

The bipolar plates should have these characteristics: high electrical conductivity, high corrosion resistance, high mechanical strength, low electrical or thermal contact resistance, low permeability of reactant gases and also, low friability [12], [13]. To fulfill these requirements, a variety kinds of material of bipolar plates (either metal, composite or graphite) are qualified to be fabricated to bipolar plates. The researches would always need to balance the anti-corrosion ability and the contact resistance of the bipolar plates material. They need to choose those with higher anti-corrosion ability with lowest resistance. Usually, higher anti-corrosion of a material would lead to higher contact resistance.

In order to acquire sufficient electric power output, the cells are connected in series in configuration as shown in Fig. 1-2.



Fig. 1-2 Typical layout of a PEMFC stack

From this figure we could see, for each cell, it is the two halves of bipolar plates that compress the MEA in a compact configuration to form each of the single cell. In fact, the hydrogen and oxygen are supplied to each side of the bipolar plates, then the reactant gases in the flow field channels could diffuse to the anode or cathode of each cell to make the electrochemical reactions possible during PEMFC operation.

1.1.2 PEMFC system

The PEMFC stack would always need auxiliaries to functionally provide electricity. The whole system containing the stack and auxiliaries is called a PEMFC system Fig. 1-3. Generally, the auxiliaries could be categorized as 5 subsystems:

- Reactant supply subsystem
- Heat management subsystem
- Water management subsystem
- Power conditioning subsystem
- Power management subsystem



Fig. 1-3 Typical layout of a PEMFC system

1. Reactant supply subsystem

Generally, the reactant supply subsystem is consisted of hydrogen and air supply subsystem.

The objective of the hydrogen supply subsystem is to control the hydrogen pressure and flow rate in the anode. Generally, the hydrogen supply subsystem is consisted of a pressurized hydrogen tank connected to the anode through a pressure reduction valve and a pressure control valve. Sometimes the anode is working under a dead-end mode, which means the hydrogen outlet is closed and all hydrogen supplied in the channels is consumed in the fuel cells. The hydrogen outlet is periodically opened for purging by the purge valve in the anode outlet in order to let out the produced water, accumulated impurities or the nitrogen diffused from the air in the cathode side. When the anode is working under a flow through mode, the hydrogen would flow back to the hydrogen inlet from the outlet by a recirculation pump device.

The air supply subsystem is usually composed of an air compressor or a blower which could inject the pressurized air to the cathode from the environment. Its objective is to supply air with certain flow rate to ensure the proper functioning of the PEMFC stack. The pressure is regulated by a pressure valve at cathode circuit outlet. Usually the cathode side is pressurized up to 2.5 bar in order to acquire higher output power. However, this power increase from stack level should be balanced with the power needed for the compressor on a system level.

2. Heat management subsystem

The heat management subsystem is consisted of the stack cooling system and the reactant heating system. In fact, the general optimized zone of PEMFC operation temperature would be around 60 - 80 °C. So the effectiveness of a heat management subsystem is strongly correlated to the performance of a PEMFC system. In some cases, the byproduct of heat would be reused, either for the heating of the reactant gases at inlet or other purposes.

3. Water management subsystem

Water management in the PEMFC system is very important to maintain the PEMFC working in an efficient profile. Proper water management can prevent the PEMFC stack or system from unwanted degradation. Water is produced on the cathode side from the oxygen reduction reaction. However in some cases, for example in a high current output profile, the amount of water produced on cathode side would be too much and it could influence the performance of the PEMFC by blocking the GDL. In some other cases, in a low current output profile, the PEMFC, especially the membrane would be dehydrated if the reactant gases are not properly humidified. This would also impact the performance of the PEMFC. Therefore, the water management subsystem is very important because its effectiveness is strongly correlated with the PEMFC performance. Detailed illustrations could be referred to subsection 1.2.1. In most of the cases, the water management is done by active or passive interchange humidifiers between the reactant gas inlets and outlets, from which the humidity of the reactant gases can be regulated, and also the excessive water on the electrodes can be removed.

The water management is a challenging task, because the relative humidity levels in different components of PEMFC are coupled and could be influenced by the operation conditions such as the temperature and the load variation. Moreover, the humidification level could influence the performance of the PEMFC due to the changing of the reactant stoichiometry. That is to say, the optimal humidity level may not be compatible with an efficient flux level of the reactant gases in order to best fulfill the load demand.

Generally, there are three ways for reactant humidification:

a. Gas bubbling:

The method of gas bubbling is usually used in a laboratory environment, rather than in a commercial application. The gases would be bubbling through a water tube in a regulated temperature. In this case, the humidity level of the reactant gases would be influenced and controlled by the temperature. However in some cases, the liquid water would be present in the reactant gases after humidification.

b. Direct vapor injection:

This is usually done by injecting the moisture mist into the reactant gases. In order to improve the humidification quality, a heat source would be used to produce the fine water vapor. The humidification level is controlled solely by the amount of injected moisture.

c. Water exchange through permeable material:

The permeable material such as a NafionTM membrane would be brought to use in this case. On one side of the membrane, the liquid water would flow through the surface of the membrane, and the reactant gases would circulate on the other side of the membrane, and get humidified by the diffused water through the membrane. The humidification level of reactant gases can be controlled by the temperature of the water flow.

4. Power conditioning subsystem

The voltage of each single cell of PEMFC stack could be influenced by a variety kinds of operation parameters, such as the gas humidification level, gas flow rate and stoichiometry, stack temperature distribution, membrane hydration level, current density, etc. So the output voltage of PEMFC stack need to be regulated before being supplied to the load demand.

The power conditioning subsystem is usually composed of DC/DC or DC/AC regulators. The DC/DCs or DC/ACs coupling with transformers could on one hand extend the output voltage range of the PEMFC stack, and also ensure the electric isolation between the load and the stack. In many cases, the regulated output voltage could be used either by the load or the

system auxiliaries, which means there would be more than one regulators conditioning the PEMFC output in the system.

5. Power management subsystem

In fact, the power management subsystem is rather an integration of PEMFC system into power generation system. The power management subsystem is usually set up in an operation environment where there are also other energy output or storage devices such as super capacitors, or battery packs. If no other energy sources included, the full load would be supplied by the PEMFC stack, hence there would be no need to include power management module in this condition. However if there are other energy sources in the system, *e.g.*, a hybrid or electrical vehicle case, it is necessary to implement a power management subsystem inside and distribute the output power when needed.

1.1.3 PEMFC operation principles and functioning layers

Basically, the produced electricity from a functioning PEMFC is transferred from the released chemical energy from the electrochemical reactions happened on the electrodes. In the PEM fuel cell, it would be composed of two half-electrochemical reactions on each of the electrodes:

At the anode:

$$2\mathrm{H}_2 \to 4\mathrm{H}^+ + 4\mathrm{e}^- \tag{1-1}$$

At the cathode:

$$0_2 + 4H^+ + 4e^- \rightarrow 2H_20$$
 (1-2)

Overall:

$$2\mathrm{H}_2 + \mathrm{O}_2 \to 2\mathrm{H}_2\mathrm{O} \tag{1-3}$$

The *enthalpy*¹ of this global reaction is the difference between the enthalpy of products and the reactants, so:

$$\Delta H = H_{H_2O} - H_{H_2} - \frac{1}{2}H_{O_2} = -286kJ$$
(1-4)

The negative sign in here means this amount of energy is released in this reaction, so for this exothermic reaction, 286kJ of energy is released per mole of H_2 consumed during the overall reaction. The premise for this amount of released enthalpy is that we assume the water is released in liquid form at 25°C under the atmospheric pressure condition.

However, not 100% of the enthalpy can be converted into electricity. A certain amount of enthalpy is inherent cannot be converted into work, *i.e.*, only part of the 286kJ being released per mole H₂ consumed during operation may be transferred to electricity. This part of energy is the *Gibbs free energy*² Δ G, where,

$$\Delta G = \Delta H - T \Delta S \tag{1-5}$$

 Δ S, the entropy, is the irreversible losses during the electrochemical reaction, T is the reaction temperature in the cell. Δ S would change with different operating conditions: the temperature and the pressure of the reactants. From [14], the Gibbs free energy out of the total available energy in the overall reaction is valued as -237.34kJ per mole hydrogen consumed at 25°C under the atmospheric pressure condition. Here same as the enthalpy, the negative sign means this amount of energy is being released during reaction.

¹ Enthalpy is a measurement of energy in a thermodynamic system. It is the thermodynamic quantity equivalent to the total heat content of a system. It equals to the internal energy of the system plus the product of pressure and volume.

² The greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition [106].

The electrical work is the product of charge and potential, the theoretical potential that could be driven from this energy is:

$$E_{\text{standard}} = \frac{-\Delta G}{nF} = \frac{237.34 \text{kJ/mol}}{2 \cdot 96485 \text{As/mol}} = 1.23 \text{V}$$
(1-6)

F is the faraday constant, valued as 96485 (C/mol), n stands for the number of electrons involved in the overall reaction per mole of hydrogen being consumed. The 1.23V is the voltage getting from the standard condition. In fact, electrochemically, the potential the electrodes could provide would be deviated from 1.23 V if it is not working in the standard condition:

$$E = E_{\text{standard}} - \frac{RT}{nF} \ln(\frac{a_{H_2O}}{a_{H_2} \cdot a_{O_2}^{0.5}})$$
(1-7)

where a stand for the activity of different species. However in most of the cases, the fuel cell would have different losses during operation, and that would usually lead to a much lower power supply comparing with this value. Generally, the losses [5] can be categorized to three parts:

1. Activation losses

The activation losses are due to the electrode kinetics in order to provide continuous electrical current by giving necessary activation energy during the electrochemical reaction. The losses happened at both anode and cathode side, while the losses on the cathode are much higher than the anode side. This is because the hydrogen oxidation reaction happened on the anode side is much easier than the oxygen reduction reaction,

Basically, the activation loss could be deduced from the Tafel equation on the electrodes, and may have the formulation of:

$$V_{act} = \frac{RT}{\alpha F} \ln(\frac{i}{i_0})$$
(1-8)
where α is the transfer coefficient, i is the current density, and the i₀ is the exchange current density on the electrode. It may be in a form of [5]:

$$i_{0} = i_{0}^{\text{ref}} a_{c} L_{c} \left(\frac{P_{O_{2}}}{P_{O_{2}}^{\text{ref}}}\right)^{\lambda} \exp\left(-\frac{E_{c}}{RT}\left(1 - \frac{T}{T_{\text{ref}}}\right)\right)$$
(1-9)

 i_0^{ref} is the reference exchange current density, a_c is the electrode specific area, L_c is platinum loading on the catalyst layer, P_{O_2} and $P_{O_2}^{ref}$ are the actual and reference oxygen partial pressure in cathode, λ is the pressure coefficient, E_c is the activation energy on cathode for oxygen reduction reaction on catalyst, T and T_{ref} are actual and reference temperature, respectively. From a degradation point of view, for a long term operation PEMFC, the exchange current density would drop due to the platinum loss on catalyst layer. As shown in eq. (1-9), the a_c would drop over time when operating under different conditions.

2. Ohmic losses

The ohmic losses are caused by the resistance either to the flow of the ions in the proton electrolyte membrane, or of the electrons in the electrically conductive parts in the fuel cell such as the bipolar plates, GDL, etc. This amount of losses is linearly proportional to the current because the resistance of each electrically conductive components are nearly constant during operation, it could be formulated as:

$$V_{ohmic} = iR_i \tag{1-10}$$

Here the R_i is the total cell internal resistance. The R_i would increase during long term operation and cause the increase of ohmic losses of PEMFC over time.

3. Concentration losses

The concentration losses are usually happening when the reactant gases are consumed rapidly. Due to the diffusion limitation of different gases in the GDL and bipolar plates, the pressure on the reaction site is different with the reactant pressure in the flow field channel. This happens especially during the higher output current condition, in this circumstance, the real pressure at reaction sites would drop considerably comparing with the reactant pressure in the flow field channel. Usually, the concentration loss could be empirically expressed as:

$$V_{\text{conc}} = \frac{\text{RT}}{\text{nF}} \ln(\frac{i_{\text{limit}}}{i_{\text{limit}} - i})$$
(1-11)

Where the i_{limit} stands for the limiting current density. It is the amount of current density the electrode can provide at most due to the diffusion limitation from the flow field channel to the electrode surface.

These three voltage losses happened on each cell would considerably influence the output performance of the PEMFC stack. They are dominated in zone I, II, III in Fig. 1-4, separately.



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Fig. 1-4 Polarization curve of PEMFC

As shown from this figure, the output voltage of the PEMFC stack would be:

$$V_{\text{output}} = E - V_{\text{act}} - V_{\text{ohmic}} - V_{\text{conc}}$$
(1-12)

1.1.4 Subsection summary

In this subsection, we have briefly introduced the generalities and principles of PEMFC and systems. In fact, the V_{output} in eq. (1-12) is indeed highly dependent to the PEMFC operation conditions. In order to optimize the performance of a PEMFC stack, many operation parameters need to be controlled such as the temperature, stoichiometry or flow rate of reactant gases, the water environment in the stack etc. The inadequate control of these operating factors would lead to performance drop of PEMFC. In next subsection, we would like to introduce those operation conditions which could influence or hinder the output performance of the PEMFC stacks.

1.2 Impacts of operating conditions on the PEMFC performance

The output performance of the PEMFC could be strongly influenced by its operating conditions. Most of the performance variations of the PEMFC are due to poor working conditions. We would like to illustrate this topic on different operating conditions: the insufficient water management, poor temperature management, gas starvation, the fuel contaminations and the load cycling.

1.2.1 Insufficient water management

The water management in the PEMFC can greatly impact its output performance. In a PEMFC, water can be either carried into the fuel cell through the humidified reactant gases, or produced at the cathode side during electrochemical reactions. The reactant gases are pre-humidified before supplying to the anode, then the water would be diffused into the membrane and by this way, secure the sufficient proton conductivity of the membrane. On the cathode side, the oxygen reduction reaction produces the water as well.

There's nothing else in the PEMFC could be more paradox than water management. A good water management strategy is crucial to secure the performance of the PEMFC. On one hand, the protons could not diffuse through the polymer membrane from anode to cathode side without the presence of water. While on the other hand, water could block the flow field channels of bipolar plates or the porous in the GDL, and impede the reactions in the fuel cell. This could lead to the local reactant starvation in the fuel cells during operation. Moreover, the excessive water could result a much more humidified environment. The components in the fuel cell such as the bipolar plates, or the GDL would suffer from the corrosions in this excess water environment. In other words, the excessive water will accelerate the aging of GDL and bipolar plates due to its ability to introduce the corrosion environment. It aggregates the degradation of the GDL and the bipolar plates. Therefore, the water management in the fuel cell is very important during normal application.

Basically, the insufficient water management could lead to the flooding on the electrodes or the membrane dehydration.

1.2.1.1 Flooding of the electrodes

The flooding of the electrodes could happen both at the anode and the cathode side.

1. Flooding at the cathode side:

Usually the flooding at the cathode side is much more common than at the anode side. This is because the water is produced during the reaction in the fuel cell at the cathode side, and also, the protons travelling from the anode side would drag the water molecules from the anode side to the cathode side, cause the cathode flooding. In this process, the water dragging phenomenon is called the electro - osmosis. The flooding on the cathode side could impede the mass transportation within the GDL. This could particularly

create hindrance preventing the oxygen from reaching the reaction sites. In some extreme cases, this blockage of the pores in the GDL could cause the local oxygen starvation. Due to the blockage, the oxygen would flow in other channels. This could lead to the pressure imbalance in the flow field channels and cause the performance drop of the PEMFC stack [15]. The cathode flooding is usually happening under higher current densities. He *et al.* [16] demonstrated a specific experiment showing the output voltage of a single cell would drop from 0.9V to 0.3V when the cathode is flooded from 1.5 kPa to around 3 kPa. Usually the cathode flooding could be mitigated from purging the cathode. As what has been mentioned before, the GDL in the PEMFC should all have the PTFE coating treatment on its surface. So the portion of the hydrophobic pores in the GDL are somehow directly correlated with the maximum power of the PEMFC stack. Because when the stack is operating in a high current profile, the hydrophobic pores are of crucial to let out the water produced on the cathode.

Moreover, the excessive water existing in the cathode would lead to the corrosion on the bipolar plates during long term operation. The dissolute or dissolved particles from the corrosion sites on the bipolar plates could block the pores of the GDL, and the particles could also even diffuse into the membrane and cause a decrease of the proton conductivity of the membrane. Both of this could cause the performance drop of a PEMFC stack.

2. Anode flooding

The anode flooding is not common in a properly functioned PEMFC stack. However, under some certain cases, the anode would also suffer from flooding and cause same consequences as the cathode flooding. Generally, the flooding on the anode side of the fuel cell is often happening when the stack is operating under a relatively low current density. In a low current working profile, the electro - osmosis would not be enough to balance the water environment in the anode, due to low flux of protons travelling from the anode to the cathode in the membrane. This kind of anode flooding could happen especially when the anode is fueled with hydrogen of high hydration state. Furthermore, an improper injection of water into the anode may also cause the anode flooding.

1.2.1.2 Membrane dehydration

The dehydration is usually happening on the anode side of the fuel cell due to the electro-osmosis in the membrane. The protons could drag the water molecules to the other side of the membrane, and cause the difference of water content between two sides of the membrane. Even though the water replenishment by back diffusion is physically favored, the anode could still suffer from the dehydration during operation especially when operating under high current densities or being supplied with low humidified fuels [17].

The decreasing water content in the membrane could cause the low proton conductivity of the membrane. This would result the performance drop during operation. From the experiment of [18], Büchi *et al.* observed a PEMFC during 1200 hours' consecutive operation under no humidification conditions on the anode side. The current density dropped from 170 to 130 mA/cm² at the constant output potential at 0.61V. It is possible that the performance could be recovered from the rehydration process on the anode side. However, long term membrane dehydration would result the irreversible performance degradation. The membranes which are operating under dry conditions would always suffer from the brittleness or cracks within itself. The increasing amount of cracks would surely increase the amount of the gas crossover between the electrodes. The crossed over gases would react on the dissolute platinum particles inside the membrane, and lead to the creation of the pinholes. These pinholes would in turn cause more amount of gas crossover. This is a main phenomenon of degradation existing in the membrane.

1.2.2 Poor temperature management

The poor temperature management in the PEMFC stacks could cause the performance drop or degradation during long term operation. In normal applications, the performance of the PEMFC stack increases with temperature in the operation range under 80°C. However, it could drop considerably under the freezing conditions [19]. And the performance drops also when working under an elevated temperature (>80°C) [20], [21]. Therefore, when we are saying the poor temperature management, it could lead to the sub-zero temperature condition or an elevated temperature condition.

1.2.2.1 Sub-zero condition

In the fuel cell, the most common temperature related condition that could cause the performance drop or degradation is the sub-zero working condition, or the freezing condition.

A non-operating PEMFC stack would encounter damages within itself if the stack is exposed in the freezing environment for a long time. This damages are always caused by the ice formation originated from the residual water contained in the membrane. The density difference of ice and liquid water in the membrane could cause the membrane volume change during the temperature changing around zero. The changing of the volume could lead to the excessive mechanical stress within the membrane. This stress could cause the degradation of the catalyst layer and also the membrane.

Specifically on the catalyst layer, the platinum particles are attached on the carbon substrate, the freeze/thaw cycles could cause the frequent volume change of the membrane, the mechanical stress changing with the melting water could reduce the physical stability of the attachment of platinum particles. The particles and the carbon substrate could dissolute with the melting water and diffused and precipitated in other part of the cell.

Moreover for the membrane, He *et al.* [22] demonstrated a comparative study testing the difference impact on different membranes during a sub-zero condition. The results showed the volume change due to ice formation is strongly related with the water content and membrane thickness. For two membranes having been fully hydrated before sub-zero test, the NafionTM 117 membrane is much thicker than the NafionTM 112 membrane after this freezing test. Physically, the sub-zero or cycling around 0 °C condition could create the cracks inside the membrane, and this could

increase the amount of crossover between the electrodes. The pinholes could be formed during the operation and in turn cause more cracks inside the membrane and cause the performance drop of the fuel cell stack. However, it is interesting that for those cells which were completely dried after operation, Kim *et al.* [23] shows that no physical damage could be observed in the membrane or on the catalyst layer during freezing.

1.2.2.2 Elevated temperature condition

Sometimes the engineers would tend to keep the PEMFC stack working under higher temperatures (>100°C) for some reasons. Firstly, the electrochemical reactions would have higher reaction kinetics at higher temperature. Also, higher temperature could make the PEMFC have more tolerance to the impurities in the fuels. Which means in this circumstance, the impact of CO poisoning could be reduced, and this can lead to more robustness of the PEMFC stack when supplying with hydrogen with lower quality.

However, the elevated temperature could cause the performance drop or long term degradation in the fuel cell. What is most important in here is that elevated temperature could increase the degradation rate of the catalyst layers. The platinum particles would be more energetically unstable in a high temperature environment at the cathode side. This way, the nano platinum particles would tend to agglomerate together in order to have lower chemical potential³. This aggregation process or the Ostwald ripening phenomenon, could cause the loss of ECSA and cause the potential drop during long run.

Furthermore, the elevated temperature could cause the unwanted reaction happening on the cathode side. The oxygen molecules would split to two oxygen atoms excited by the high temperature environment with high potential in the cathode side. This way the carbon substrate could react with the atoms to form the carbon dioxide or the carbon monoxide within the cell. That means the elevated temperature could increase the carbon corrosion rate in the catalyst layer, or even influence the carbon structure in the GDL.

³ All systems tend to have lower chemical potentials.[107]

The proton conductivity could be reduced also due to elevated temperature operation conditions, especially when supplying with the non-properly prehumidified fuels. The reduced proton conductivity could increase the ohmic losses in the membrane and cause the performance drop for the whole stack.

1.2.3 Gas starvation

Gas starvation in the fuel cell means the inadequate supply of fuels or oxygen (air). This would always cause the fuel cell working under a sub-stoichiometric operational conditions. The gas starvation could cause the potential drop so the performance drop of the fuel cell. Usually the gas starvation in the fuel cell could cause some undesired facts happening on both electrodes. At the cathode side when supplying with oxygen the fuel cell should produce water. However, in a gas starvation condition, hydrogen could be detected to release from the cathode side from this reaction:

$$2H_{(aq)}^{+} + 2e^{-} \rightarrow H_{2(g)}$$
 (1-13)

while on the anode side, the oxygen could be released from:

$$2H_2O_{(aq)} \to O_{2(g)} + 4H_{(aq)}^+ + 4e^-$$
(1-14)

In some cases, the CO_2 could also be detected and the following reaction could happen on the cathode side:

$$C_{(s)} + 2H_2O_{(aq)} \rightarrow CO_{2(g)} + 4H_{(aq)}^+ + 4e^-$$
 (1-15)

From these several reactions, one could see the gas starvation could reverse the gas composition at each electrode, that is, produce hydrogen at the cathode side and the oxygen at the anode side. Apart from this reactant gases reverse phenomenon, the carbon support is oxidized and consumed due to the gas starvation at the anode side, this could lead to the long term degradation of the electrodes.

The gas starvation is generally caused by the cold start-ups or the insufficient water management. In both cases the water or the ice could block the pores in the gas diffusion layer and prevent the reactant gases from reaching the reaction sites. The imbalanced flow field channel design or sudden load rising could also lead to the gas starvation, and cause the performance degradation of the fuel cell.

1.2.4 Contamination

Contamination could cause the performance drop of the fuel cell. Usually, the contamination could be defined as the impurities coming inside of the fuel cell along with the fuels. In some cases, the impurities could also be found originally from the components within the cell. After all, the impurities of the contamination usually include the CO, NO_x , SO₂, catalyst particles and the metallic ions.

The contamination could strongly influence the performance of the membrane and the electrodes.

For the membrane, the protons could be prevented from being attached on the PFSA end groups due to the contamination of the impurities such as the ammonium or alkaline metal ions. This phenomenon could severely cause the performance degradation of the fuel cell due to elevated ohmic resistance. In some extreme cases, the contamination could cause the dehydration at the cathode side due to low electro-osmosis inside the membrane, which would then cause the lower exchange current density and lower output performance [24].

Moreover, for the electrodes, the contamination is usually caused by the carbon monoxide on the anode side. This contamination process is called the CO poisoning. The CO is introduced to the cell originally with the hydrogen if the hydrogen is reformed from the hydrocarbons. The mechanism of the CO poisoning is that, the molecules of CO could be attached to the platinum particles on the catalyst layers and cause an extremely decrease of the ECSA. In this process, the hydrogen is unable to reach the covered reaction sites on the catalyst layers due to the high coverage of CO, and this could lead to the decrease of the output performance. However, the CO poisoning is recoverable and reversible. The influence of CO poisoning could be mitigated by simply introducing some air into the anode side, and the attached CO molecules would be burned and transformed to CO_2 with the air bleed [25].

1.2.5 Load cycling

The load cycling could cause the platinum agglomeration on the catalyst layer and lead to decrease of the ECSA. This phenomenon is called the ECSA shrinking. In fact, during the ECSA shrinking, it is the number of potential cycling that influences and decreases the ECSA in the fuel cell at the cathode side [26]. The more the potential cycles, the more ECSA degradation would be. Moreover, in normal operations (<1V), the peak value of the potential cycling also plays an important role on ECSA aging. The higher the potential cycles, the faster the ECSA would degrade.

In the PEMFC stack, the load cycling could only influence the catalyst layer on the cathode side, because the platinum particles could only dissolute on higher potentials [27]. The potential on the interface of membrane and cathode is much higher than the potential on the anode side. So the cathode catalyst layer is much more vulnerable than the layer on the anode side to the load cycling.

In fact, it is interesting that higher cathode potential (>1V) during cycling could also create PtO layer on surface of the platinum particles. This oxide layer formed in higher potential could in turn prevent the platinum particles from dissolution into the membrane. In the covering process, the covering rate of PtO is proportional to the potential, higher potential would cause faster covering rate of PtO on surfaces of platinum particles.

Specifically, this ECSA related degradation is also illustrated in APPENDIX I. The readers are kindly referred to APPENDIX I. for more detailed information. We only take into account the creation of the monolayer of PtO and dissolution of platinum particles which are influenced by the changing of the potential.

Apart from the ECSA degradation, the potential cycling could also lead to the carbon corrosion on the catalyst layer or the GDL.

1.2.6 Subsection summary

In this subsection, we collected the detailed information about the impacts on PEMFC performance from different operation conditions. Specifically, some of them could cause severe degradation on the PEMFC stack. In the next subsection, we would like to illustrate the degradation in detail regarding to different components in the PEMFC stack.

1.3 PEMFC degradation mechanisms of different components

During normal operation, the PEMFC components are subject to the aging phenomena, so they can degrade or fail to function, thus causing the PEMFC degradation or failure. Therefore, it is very important that the degradation mechanisms to be thoroughly and profoundly studied and understood. In fact, the degradation mechanisms of components in a fuel cell are usually influenced by each other, so cannot be simply separated. However, in order to make it clear and readable for the readers, it is better to illustrate the different mechanisms on each component separately.

1.3.1 Causes and effects of PEMFC degradation

Electrochemical reactions in the PEMFCs are not perfect, different kinds of degradation could happen during fuel cell operation [28]. Generally, most of the degradations take place in GDL, catalyst layer and polymer membrane. In the GDL, the major degradation phenomenon is carbon corrosion. The GDL is usually made of carbon paper or cloth. In most cases the carbon corrosion is the result of high humidity and/or potential (load) cycling of the PEMFC [29]–[31]. Furthermore, the platinum (catalyst) dissolution or reorganization (sintering) in the catalyst layer are also commonly considered as critical factors influencing long–term performance of PEMFC. The platinum particles are attached on the surface of carbon support or substrate in electrodes, so they are vulnerable when carbon structure starts to degrade. Besides, the platinum particles sintering can be commonly observed under

load cycling and/or operating conditions such as high humidity or high temperature[32], [33]. For the polymer membrane, it is believed that the chemical attacks caused by hydroxyl (OH[•]) and hydroperoxyl (OOH[•]) radicals initiate the membrane degradation. These radicals are stemmed from hydrogen peroxide (H_2O_2) which is formed due to either contamination of fuels or gas crossover. The chemical attack along with the transient operating conditions results to polymer structure degradation and modification of membrane properties [34]–[37]. In conclusion, different major degradation mechanisms and causes can be summarized in TABLE 1-1.

TABLE 1-1

CAUSES & EFFECTS OF PEMFC PERFORMANCE DEGRADATION

	Carbon corrosion	Platinum loss	Membrane degradation	Structural stress
Electrical potential	Cycling potential	High or cycling potential	Potential cycling	
Humidity	High	High	Low or cycling humidity	
Load	Cycling load	Low or Load cycling	Cycling load	
Temperature	High	High	High	Freezing or cycling condition
Impurities			Impurities in the fuel	

1.3.2 PEMFC degradation components

In this section, we would like to introduce the degradation phenomena of different components separately in the fuel cell in detail.

1.3.2.1 Membrane degradation

In most of the literature reviews, the membrane degradation could be separated to chemical degradation, mechanical degradation and thermal degradation. In [7], Gittleman *et al.* presented a slightly different classification: the chemical degradation, mechanical degradation and the crossover related damage. In this thesis work, the degradation of the membrane would be illustrated based on these three aspects.

1. Chemical degradation

Chemical degradation is recognized as a major limit of the lifetime of the polymer membrane. The chemical degradation of the membrane is characterized as thinning of the membrane and the emission of HF, CO_2 and H_2SO_4 during operation. A reduced thickness of the membrane initiates the gas crossover and would lead to the mechanical fragility of the membrane. Basically, it is attributed to the actions of species of aggressive radicals that are formed during operation of the stack, along with the poisoning of the polluted species.

The radicals could attack the vulnerable links of the polymer structure. The perfluorocarbon-sulfonic acid ionomer (PSA) is the essential material for the membrane because of their high chemical stability. It should be chemically and mechanically stable in the fuel cell environment. However, perfluorinated materials are not inert during operation of the stack during long term operation. The chemical degradation is caused by direct attacks of the polymer by radical species leading to the decomposition of the membrane. The reactive species such as hydroxyl (OH \cdot), the hydro peroxyl radicals (\cdot OOH) and hydrogen peroxide (H₂O₂) are the major species responsible for attacks to the membrane. The radical attack phenomenon is discussed in [7], [34], [37]–[39].

The oxidative environment on the cathode side and the anode reductive environment imposes an unstable membrane condition, which could accelerate the membrane chemical degradation. The operation of the PEMFC with relatively low humidity and higher potential could also increase the chemical degradation rates.

Moreover, the chemical degradation of the membrane is accelerated by poisoning species. These species include the cations of Fe^{3+} , Cu^{2+} etc, which are thought to be produced from the peripheral metallic pipes or equipment. The membrane is particularly vulnerable to the presence of these cations because their ability of attachment to the end groups in the polymer electrolyte, would reduce the place for the attachment of the protons in the membrane, and this phenomenon would cause the decrease of the conductivity of the membrane and so to the output voltage of the whole stack.

2. Mechanical degradation

Usually the mechanical degradation is caused by the cyclic working conditions. When the membrane swells and shrinks with the humidity or temperature cycling, the membrane would be subject to mechanical degradation, specifically in this case, called the hydrothermal fatigue. This kind of degradation would cause small pinholes in the membrane and would result in the increase of the gas crossover rate from both sides of the membrane.

Furthermore, the accumulation of the catalyst particles would also create local stress in certain part of the membrane, *i.e.*, the Xo plane. It is thoroughly discussed in the references [31], [40]. In fact, even if during the ordinary operation condition, the Pt particles would tend to diffuse into the membrane. Specifically, the Pt particles on the cathode side would dissolved into the membrane because the involved dissolution reaction is favored in higher potential. Those dissolved platinum ions can be reduced by the hydrogen crossed over from the anode side, and accumulate in a certain region (the Xo plane) in the membrane where the concentration ratio of the crossed over hydrogen or oxygen is favored (Appendix II).

3. Crossover related damage

In a PEMFC, the crossover means that the hydrogen or the oxygen could penetrate within the membrane to reach the reaction sites on the other electrode. The crossed over reactant gases could react with each other either on the electrodes or inside the membrane.

The reactions happened on electrodes with the crossover gases involved would not be considered as the electrochemical reaction, rather than, a chemical combustion reaction. Therefore, this part of the reactants supplied to the fuel cell is considered to be wasted during the crossover. Because a PEMFC would be considered to be an energy converter only when the electrons driven by the converter are coming through an external circuit, rather than being simply wasted on the electrodes.

Moreover, the crossover of the reactant gases in the membrane would cause the gases reacting inside the membrane on surface of the precipitated platinum particles. This combustion reaction would cause severely damage to the membrane and in turn result more crossover through the membrane.

In the literature, several researches [41], [42] have reported the exponentially increasing profile of crossover through the membrane aging over time.

1.3.2.2 GDL degradation

Like other degradation components, the GDL degradation would also have impacts on the fuel cell stack performance during aging through operation time. As what has been mentioned before, the GDL layer is usually made of carbon paper or cloth, majorly compressed between the bipolar plates and MEA in each cell. It is an important component in the PEMFC which is responsible of providing path for transporting, diffusion of the reactants from the bipolar plates to the reaction sites, while at the same time, let out the byproduct water in case the droplets would block the porous through which the reactant gases pass.

In this thesis work, the GDL degradation would be illustrated from the aspects of chemical degradation and the physical degradation, in detail:

1. Chemical degradation

The chemical properties of the GDL would change over time. Specifically, the GDL would loss the hydrophobicity during aging. Generally, the GDL is coated with PTFE treatment on the surface during fabrication. The PTFE is widely used as the coating for the non-stick pans, known as the Teflon pans. This coating would make the GDL have the advantages of high hydrophobicity and operating temperature, extremely low coefficient of friction, fair abrasion resistance and good chemical resistance.

However, the gradual transition from hydrophobic to hydrophilic always occurs over time. The aging tests reported by [38] showed that the hydrophobicity would increase with operating temperature, while decrease over time. When the PTFE coating separates from the carbon cloth, the binding forces of the fibers decrease and this can create hydrophilic surfaces on the GDL. During long term operation, the reactant gases would be blocked by the water droplets from reaching the reaction sites due to the increasing amount of hydrophilic surfaces.

2. Physical degradation

The physical degradation is always regarded as the change of the physical properties. This is mainly due to the carbon corrosions, which would mechanically lead to the change of structural completeness of the GDL, and also cause the unbalanced force distribution from the membrane or the bipolar plate.

Carbon corrosion is always involved in the physical degradation of the GDL. It is well known that the carbon is thermodynamically unstable on the cathode side, where the potential is much higher than the equilibrium potential for the carbon oxidation reaction (0.207V) [43]. More specifically, the carbon corrosion would tend to occur in the start-stop operations when the air is presented on the anode side, which would cause potential elevation, and in turn increase the carbon corrosion rate on the cathode side of the fuel cell [44]–[46].

Moreover, the fuel starvation would also induce the carbon corrosion [47]. The carbon corrosion could cause the cracks or separation on the GDL layer, this could mechanically lead to the structural change of the GDL, and also cause the unbalanced distribution of force either from the membrane or the bipolar plate. All of these outcomes would consequently cause the change of the electric or thermal resistance of the GDL layer.

1.3.2.3 Catalyst layer degradation

The catalyst is majorly consisted of nano platinum particles, ranging from diameters of 2~5 nm. Those small particles would tremendously change the performance of the PEMFC stack if properties of the tiny particles would change. According to [48], the platinum particles would be hardly affected by the dissolution, oxidation or agglomeration on the anode side. However, the platinum particles on the cathode side are somewhat not stable due to the higher potential environment. This higher potential would cause an oxidative environment in which the platinum particles would be oxidized to platinum ions then dissolved into the membrane. This would result a decrease of the ECSA of the catalyst layer over time. Usually it can be resulted from the cyclic working conditions, such as the potential cycling or temperature cycling operation profile.

Generally, the catalyst degradation is identified as these three phenomena:

- Dissolution and diffusion of platinum particles through the ionomer, redeposition on other platinum particles and form larger particles (Ostwald ripening), diffusion through membrane to create the platinum band (Xo plane).
- Generating oxidative species that would cause the degradation of the membrane. These species would always include the hydrogen peroxide (H₂O₂), hydroxyl (•OH) or hydroperoxyl (•OOH) radicals (usually happened on the platinum particles precipitated in the membrane).

 Reversible or irreversible adsorption of pollutants from the air, reactants or other degraded components.

In this thesis work, we would specifically illustrate the Ostwald ripening, which is involved in the catalyst degradation and would cause the ECSA reducing.

The Ostwald ripening is an observed phenomenon in solid (or liquid) solutions which describes the evolution of an inhomogeneous structure over time. The phenomenon was first described by Wilhelm Ostwald [49] in 1896. When a phase precipitates out of a solid, energetic factors will cause large precipitates to grow, drawing material from the smaller precipitates, which shrink. In other words, in an inhomogeneous environment, the size of larger particles tends to increase while the size of the smaller ones tends to shrink. This process is shown in Fig. 1-5.



Fig. 1-5 Ostwald ripening processes

This thermodynamically-driven spontaneous process occurs because larger particles are more energetically stable than smaller particles. This is due to the internal pressure is reversely proportional to the radius of the particles. It stems from the fact that the molecules on the surface of a particle are energetically less stable than the ones already well ordered and packed in the interior. Large particles, with their lower surface to volume ratio, results in a lower energy state, which means they would have a lower surface energy. As all chemical system tries to lower its overall energy, molecules on the surface of a small (energetically unfavorable) particle will tend to detach and diffuse through solution and then attach to the surface of larger particle. Therefore, the number of smaller particles continues to shrink, while larger particles continue to grow. In the fuel cell environment, the platinum particles would have this kind of phenomena especially when the particles are on the surface of the cathode side catalyst layer or in the membrane. This is happening because the higher potential in the cathode side would excite the platinum particles to an unstable state, they tend to dissolve from the reaction site once the potential is favored. As for the platinum particles in the membrane, they tend to precipitate and agglomerate in the membrane due to the oxidative reaction with the H_2 crossed over from the anode side.

On one hand for the Ostwald ripening on the cathode side, the ECSA would be reduced over time with the increasing size of the platinum particles. While on the other hand in the membrane, the Ostwald ripening would cause the platinum precipitation in the membrane. This would lead to the mechanical degradation of the membrane, which would create small pinholes and accelerate the gas crossover from both sides of the membrane.

1.3.2.4 Degradation on bipolar plates, gaskets, and others

In the literature, we only find two articles which have addressed the degradation of bipolar plates [13], [48]. From these two papers, three mechanisms are involved:

- Long term corrosion due to the acid environment of bipolar plates would cause the production of unwanted cations, and this would seriously influence the durability of the membrane and catalyst layers;
- The long term corrosion would create a resistive surface layer leading to a high ohmic contact resistance;
- 3. Deformations or fractures would happen on the plates. These are due to cyclic working conditions such as the temperature cycling, which would cause the unbalanced temperature distribution in the bipolar plates.

Apart from the bipolar plates, the stacks are compressed by the gaskets and seals. The degradation of these components is still unknown. Some causes and effects are illustrated in [13]. The acidic environment and the thermal stress can affect the compression force the gaskets would provide. In some cases, the materials could be dissolute or dissolved in this acidic environment. Their migration and precipitation in the electrodes could affect the hydrophobicity of the GDL and probably poison the catalysts and membrane. Moreover, traces of decomposition products can be found in the MEA during long term operation. At present, no degradation model of this component has been proposed in the literature.

1.3.3 Subsection summary

In this subsection, the degradation mechanisms on different components of the PEMFC stack have been thoroughly illustrated along with related literature review. One could find the degradation mechanisms in a fuel cell are usually influenced by each other. This coupling characteristics could make the degradation of the fuel cell more complicated than what it seems to be on each component. From this subsection, it's clear that the degradation of PEMFC is always accelerated when working under non steady–state, and this is the key that impedes its durability, so to its massive use. The accurate prediction of their aging mechanisms can thus help to design proper maintenance patterns of PEMFCs by providing foreseeable performance degradation information. In addition, the prediction could also help to avoid or mitigate the unwanted degradation of PEMFC systems during operation. In next subsection, we would like to introduce the PEMFC prognostics.

1.4 State of art on PEMFC prognostics

Generally, prognostics means the prediction of the future performance of one or more components by assessing the extent of deviation or degradation of a system from its expected normal operating conditions [50]. With the help of performance prediction, the engineer would have information about when the system or a component would no longer perform an intended function. In many works in the literature, the performance prediction is always correlated to the prognostics, which involves the remaining useful life (RUL) prediction. In this thesis work we are talking about the performance prediction of PEMFC. It means the prediction, or forecast of the long term performance variation of the fuel cell stack by evaluating the acquired historical data.

Basically in the research area of engineering control, the approaches of prognostics could be divided to three categories, the data driven, model based and the hybrid approaches. The articles available in the literature have always addressed approaches on these three categories.

1.4.1 Data driven approaches

The data driven approaches are based on the monitored and acquired historical data. The engineer would need to use the data driven methods to extract the degradation or behavior features from the acquired data. The historical data can be trained and then a RUL or the performance variation could be predicted. As a matter of fact, most of the researches about the prognostics are about the data driven approaches. There are Bayesian probabilistic related works [51]–[55], neuro network related works [56]–[60], kalman filter related works [61], or just simple regression tools related works [62]. These approaches do not require analytical models of the system degradation, and are relatively simple to implement, and usually calculation friendly. However, they sometimes would have low accuracy during prediction thus the models would get results deviated from the actual behavior of the system. Therefore, the data driven approaches represent a compromise, or a balance between the applicability and accuracy.

1.4.2 Model based approaches

The model based approaches require the construction of a physical dynamic model representing the system behavior, and integrating the degradation phenomenon (mainly the phenomenon of fatigue, wear or corrosion) whose evolution could be modeled [63]–[68].

Generally this kind of methods could provide more accurate prognostic results than the two other approaches. However they have some major drawbacks. On one hand, the physical dynamic model is hard to build because usually the degradation mechanisms are difficult to be analytically described. On the other hand, if the physical degradation model is acquired, the model usually would be hard to be implemented in the *in-situ* prognostic situation, where the fast and efficient prognostic model is always favored. Moreover, the physical dynamic model of one system or component is sometimes lack of generality with the others, which means the degradation model would be hard to be implemented on other components or systems. Therefore, the application range of model based approaches are relatively restricted.

1.4.3 Hybrid approaches

The hybrid methods of prognostic are usually a kind of approach which is a mixture of the model based approaches with data driven approaches. The information of the data part and the physical model part of a system is exchanged during the prognostic process. Specifically, there are two major ways of hybrid approaches: the series configuration or the parallel configuration.

The series configuration is usually identified as a model based prognostic approach, while some of the unobservable parameters in the physical dynamic model are estimated or predicted by some data driven methods. This kind of prognostic approach is addressed in [69].

A so-called parallel configuration is to combine the output of a physical model with that of a data driven approach to provide an overall output. This kind of approach is somewhat similar to the data fusion like method, where the output result of two models are fused to provide a global prognostic result. In the literature, these articles have been addressing this topic of area [70], [71].

1.4.4 Literature review on PEMFC prognostics

The PEMFC stack is an energy converter with too much complexity inside. The interchange and influence between different parameters and different operating conditions would make it somewhat difficult to isolate the interested parameters. In other words, the high complexity of the fuel cell stack could make it difficult to

implement accurate prognostics. The main limitations of prognostics now in PEMFC are:

- 1. Data acquiring level (difficult to monitor some interested parameters without interruption);
- 2. Prognostic level (no universal standard in PEMFC prognostics);
- 3. Validation level (the aging mechanisms on auxiliaries maybe ignored).

For the prognostic approaches used on topic of PEMFC prognostics, there haven't been too much articles in these years addressing this research topic:

A particle filter framework based PEMFC prognostic was proposed in [72]. The main contribution of this work was to use the particle filter to achieve the RUL prediction of two fuel cell stacks. The model was configured with three state models (linear model, logarithm model, and the exponential model). All of these three models were tested and compared. The results showed the prediction with logarithm model would have the best prognostic performance (RUL prediction error of 90h in a 1000h case). However, as the knowledge of the author, sometimes the particle filter would have the issue of particle depletion during functioning, usually the particle filter would need much data in order to acquire good prediction result.

Morando *et al.* [73] proposed an Echo State Network (ESN) approach to achieve the PEMFC prognostics. The data of stack output voltage was used by the author to predict the output performance degradation of the PEMFC stack. The ESN is a rapid learning approach, the prognostics was finished with the direct and parallel structures. However, it would be requiring configuration of some training parameters regarding to the prediction algorithm. And different preset parameters could cause inconsistency between different prediction results.

Silva *et al.* [74] proposed a data driven approach which could be used to predict the voltage variation of two PEMFC stacks. The Adaptive Neuro Fuzzy Inference System (ANFIS) prediction proposed in this paper could be used as the online prognostic. In this paper, the author divided the training data of aging voltage to two components, the normal aging part and the external perturbations. However, the prediction using ANFIS is based on slow iterative learning steps. The

computational time would increase with the size of data. Besides, the ANFIS is a soft computing approach. The complexity of the training algorithm is directly dependent on the amount of experimental data and the number of initialize parameters.

Vianna *et al.* [75] proposed a regression based approach to estimate the EIS (Electrochemical Impedance Spectroscopy) impedance of a PEMFC stack. The linear regression method and a higher order polynomial regression were brought to use in the prediction problem. The training was from 0-515h with the fitted impedance values. The results were validated with the experimental data with respect to the impedance measured on four different frequencies in different times: 5.18Hz, 505Hz, 50MHz and 789MHz in 685h, 823h and 991h. The results showed higher prediction accuracy with the linear regression in this impedance prediction case. This may be due to there's not too much portion of non-linear degradation components in the impedance changing profile over time.

Hochstein *et al.* [76] mainly illustrated the algorithm of Regime Switching Vector Autoregressive (RSVAR). Generally, this algorithm could usually be used to model the changing dependency structures of multivariate time series. In the end the author briefly introduced a prognostic case of a constant output PEMFC stack, with the datasets containing a variety kinds of parameters such as the stack voltage, current, inlet/outlet temperature for the fuels, etc... The prediction result was promising. However, this algorithm would need different operational parameters and measurable data during training and predicting. Usually it would need a large dataset if one would demand a good prediction result.

Kimotho *et al*. [77] proposed a PEMFC prognostic of a PEMFC stack using particle filter framework. In this paper, the author introduced the "self-healing factor" into the prediction case. The self-healing means the output performance of the PEMFC stack would be recovered automatically after the measurement of data every certain amount of time during aging. The predictive result was good with the introduced self-healing factor during prediction.

Kim *et al.* [78] proposed an Equivalent Circuit Model (ECM) approach to predict the impedance aging over time of two PEMFC stacks. Basically for a normal ECM description of a PEMFC stack in [78], the model would contain 10 parameters. The author simplified the model to a 4-parameter-model in order to lower the complexity. However, whether it is reasonable or not is somewhat questioned, because some of those parameters were not supposed to be fixed or constant for this simplified model. In fact, at the knowledge of us, the double layer capacity is strongly related to the ECSA and would drop over time. However, this parameter was set to be fixed and pruned from the prognostic model.

Lechartier et al. [79] illustrated two model based approaches on the PEMFC stack performance degradation prediction. A Butler-Volmer equation based static model was used to predict the degradation tendency of the polarization curve. And an equivalent circuit model was also brought to use to form a dynamic model to predict the EIS impedance degradation tendency during long term operation. Both of the models were tuned with nonlinear regression to fit the aging of the PEMFC stack. The prognostic results were promising, while its generality on other stacks is questioned because the models were tuned only based on the tested PEMFC stack. Bressel et al. [80] proposed an observer based prognostic model for PEMFC using the Extended Kalman Filter (EKF). The observer was used to estimate the time varying parameter and derivative which can represent the aging of the cell. The developed method provided good prediction results on voltage degradation under different load conditions. The RUL prediction was also provided and showed its effectiveness. Moreover, it's interesting that the author indicated that the exchange current density would remain unchanged during long term operation for more than 1000 hours.

All of the reviewed articles in literature have been listed in TABLE 1-2 for better review.

TABLE 1-2

Prognostics	Methods being used	Monitored	Vear	Reference
category	Wiethous being used	parameter	I Cal	
Data driven	Particle Filter	Stack voltage	2013	[72]
Data driven	Echo State Network	Cell voltage	2014	[73]

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Data driven	Adaptive Neuro Fuzzy Inference	Stack voltage	2014	[74]
Data driven	Regression	EIS Impedance	2014	[75]
Data driven	Switching Vector Autoregressive	Stack voltage	2014	[76]
Data driven	Particle Filter	Stack voltage	2014	[77]
Hybrid	Equivalent Circuit Model	EIS Impedance	2015	[78]
Model based	Equivalent Circuit Model	Polarization curve / EIS Impedance	2015	[79]
Data driven	Extended Kalman filter	Stack voltage	2016	[80]

The characteristics of each research work are described in TABLE 1-2. From this table we could see the data driven method is more popular than the other two. This is because on topic of PEMFC prognostics, the data driven methods are more practical than others in most cases. Moreover, the stack voltage was mostly being used. This is due to the stack voltage is the most accessible parameter one could measure for the sake of state of health or output performance monitoring, especially in a constant operation profile.

However, for most of the data driven approaches in the literature, each of the work may have one or more of limitations as listed below:

- 1. High computational demand;
- 2. Need large dataset during training;
- 3. Lack of validation in variation load conditions;
- 4. Generalities on different stacks in different conditions.

In order to overcome the limitations, in this thesis work, we would like to propose a data driven prediction method based on a machine learning method: Relevance Vector Machine (RVM). All the prediction works in this thesis based on RVM would need at most 100 historical data of stack voltage aging, and also the computation is fast (<1s for training / prediction for each study case described in chapter 2; for each prediction step on each time point described in chapter 3). Moreover, this method is also brought to use to predict the voltage variation in a dynamic load condition in chapter 3 (PM 200 case). The generalities are demonstrated based on different implementations on different stacks working under different conditions, with different training zones (3 different training zone in chapter 2, and recursively changing training zone in chapter 3).

The detailed illustration on our proposed RVM prediction method would be introduced in next two chapters.

1.4.5 Subsection summary

In this subsection, we mainly illustrated the state of the art of the PEMFC prognostics, three prognostics approaches: the data driven, model based and the hybrid approaches have been briefly illustrated. In the end, a detailed literature review based on the listed articles has been presented.

1.5 Summary

In this section, we firstly introduced the principles of the PEMFC, then a detailed demonstration on the topic of the degradation mechanisms of PEMFC has been thoroughly given. In the end, we briefly introduced the prognostics approaches addressed in the literature. In the next chapter, we would like to propose a PEMFC performance prediction method using Relevance Vector Machine.

CHAPTER 2. PEMFC PERFORMANCE PREDICTION USING FEATURE EXTENDED RELEVANCE VECTOR MACHINE

The performance of PEMFC stack is strongly influenced by the operating conditions, which may cause performance variation or degradation. However, the structural and physical complexity of PEMFCs still make the accurate prediction of the stack performance a great challenge today.

2.1 Research background

As what has been mentioned in last chapter, the PEMFC stack performance prediction can be categorized into model–based, data–driven and hybrid prediction approaches. Generally speaking, the model–based method provides the prediction or performance evaluation based on specific physical model of one component or the whole stack. The data–driven approach stands for the methodologies evaluating the performance degradation by analyzing the historical data related to the degradation with machine learning or data mining based solutions. The hybrid prediction approach is achieved by combining physical and data-driven model into PEMFC degradation evaluation. From a fairly practical point of view on prognostic scenario of PEMFC, the data driven approaches are usually easy to deploy, and computational friendly when predicting the non-linear trends in the PEMFC performance degradation. However, it should be noted that, the observed non–linear

PEMFC PERFORMANCE PREDICTION USING FEATURE EXTENDED RELEVANCE VECTOR MACHINE

fuel cell performance degradation curve (Fig. 2-1) is caused by multiple complex electrochemical phenomena during fuel cell operation and is highly dependent on operation conditions. Thus, it is difficult to find a simple pattern to represent and predict the observed non–linearity. This feature more or less limits the effectiveness of classic mathematical regression solutions such as linear least square regression. Fig. 2-1 shows an example of measured output performance variation and degradation of a single cell in an 8kW, 96–cell PM 200 PEMFC stack. (data measured under cyclic load (between 0.30 and 0.97A/cm²) and start/stops operation conditions (two start/stops per hour) over 400 hours).



Fig. 2-1 Fuel cell measured voltage degradation during operation for an 8 kW, 96 cells PEMFC stack

From this figure, we could see the degradation curve contains high portions of nonlinearity, which cannot be correctly represented by conventional linear regression approaches. Consequently, the non-linear regression methods are thought to have potential to cope with the fuel cell non-linear aging prediction problem.

Although we have found that the non-linear regression methods have been successfully used in the literature for Lithium-ion battery performance degradation modeling and prediction [81]–[83], there have been only few papers in the literature

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[72], [74], [84] that discussed the fuel cell aging / degradation modeling and prediction using non–linear regression approaches.

Among different non-linear regression methods, the vector machines have shown their great interest in classification or regression problems. The vector machines have several advantages: it is defined as a convex optimization problem (no local minima), making it an efficient method. Moreover, vector machines can always deal with large datasets without problems of over fitting whenever they are in classification or regression use. In a PEMFC degradation context, the output voltage is one of the easiest parameters we could acquire to reflect the performance degradation. We would have a huge amount of data for a long term operated PEMFC. In this circumstances, we proposed in this thesis a novel approach to predict PEMFC non-linear performance degradation trend based on the voltage degradation using Relevance Vector Machine (RVM).

Before looking into the performance prediction of PEMFC stack using RVM, we need at first know what the vector machine is, or, what the machine learning is.

Machine learning is a subfield of computer science that "gives computers the ability to learn without being explicitly programmed" [85]. It usually involves providing rules between the input and output of data using predefined learning algorithms. Basically, machine learning could help us to build the mathematical relationship between inputs and outputs when the model of the system in interest is hard to be acquired.

Machine learning tasks can be typically classified into three broad categories, depending on the nature of the learning "signal" or "feedback" available to a learning system.

1. Supervised learning

The supervised learning corresponds to the determination of a mapping function from the input to output of the dataset which are given by the "supervisors". With this learned model, the computer could get the output of an arbitrary data once the input is provided. (Vector machines, etc...)

2. Unsupervised learning

The unsupervised learning means the computer program is given with a group of inputs without outputs. The program need to find the "hidden patterns" within the group of inputs. (Clustering, etc...)

3. Reinforcement learning

The reinforcement learning means the computer program need to interact with the environment and the program need to be enhanced all the way from the beginning to the end. (Chess game, etc...)

The learning task using vector machine is a kind of supervised learning. It always copes with finding the mapping function from the inputs to the outputs of the given data. In this work of PEMFC stack performance prediction, the vector machine could be used to find the hidden function between the operation time and the measured stack voltage. The vector in here denotes the inputs that are used to create the learned model after training, which means the prediction results from this learned model are balanced by these inputs (vectors) from the historical dataset.

Generally speaking, the vector machine could be further divided into two counterparts, the Support Vector Machine (SVM) and the Relevance Vector Machine (RVM). The SVM was introduced much earlier than the RVM. The concept of SVM was firstly introduced by Vladimir N. Vapnik and Alexey Ya. Chervonenkis in 1963. It was then modified in 1992, by Bernhard E. Boser, Isabelle M. Guyon and Vladimir N. Vapnik. They suggested a way to create a nonlinear classifier by applying the kernel trick to maximum-margin hyperplanes [86]. The current standard incarnation (soft margin) was proposed by Corinna Cortes and Vapnik in 1993 and published in 1995 [87].

The RVM approach uses Bayesian based filtering framework that could provide at the same time the predictive results and also the corresponding confidence intervals. This feature is particularly useful when dealing with non–linear and uncertain prediction problems [88]. The RVM was firstly introduced by Tipping *et al.* [88]–[91] around 2001, and has the identical functional form with the Support Vector Machine (SVM). It should be noted that, RVM and SVM are both kernel function

based methods and are both efficient when coping with non-linear regression and prediction problems. However, the RVM shows some advantages than SVM.

- 1. RVM is capable of providing predictions with confidential intervals, that is, the probabilistic prediction, while SVM cannot;
- 2. Unlike SVM, RVM doesn't have limitations on choosing kernel functions during training even though both RVM and SVM are kernel based data driven approaches. Indeed, the kernel functions are completely not compatible in SVM if they couldn't meet the Mercer's criteria, which means, for an arbitrary kernel function k(x, y), it has to fulfill Mercer's condition for all square functions g(x):

$$\iint k(x,y)g(x)g(y)dxdy \ge 0 \tag{2-1}$$

 RVM could give much sparser model in general than SVM after training, which indicates much lower computational demand during regression or classification. This advantage makes the RVM particularly suitable for real time prognostic applications.

Different applications of RVM could be found in the literature. He *et al.* [92] used the RVM to get a model which can predict the Zinc coating weights in cold rolling strip hot-dip galvanizing. The result indicated a superior accuracy in prediction, the main thing discussed in this work was how to implement RVM with a novel type of kernel function. RVM was also brought to use to estimate the component aging crack growth which was characterized by Paris-Erdogan model in [93]. The results were compared with other data-driven approaches, and showed higher accuracy and lower computational demand of RVM. Li *et al.* [94] forecasted the state of health (SOH) of Lithium battery using RVM implementation, and the results were then compared with that of SVM and Autoregressive Integrated Moving Average (ARIMA), which proved the effectiveness of RVM and its potential to be applied to online battery monitoring and prognostics. Zhou *et al.* [95] proposed an online

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learning and training strategy of RVM on predicting the remaining useful lifetime (RUL) of lithium battery which also showed relatively good performance of RVM. In [96], relevance vectors obtained during RVM training were brought to be used to form a three-parameter model to forecast the RUL of lithium battery. Barré *et al.* [97] proposed a real-time method predicting the state of health (SOH) and remaining useful life (RUL) of lithium-ion battery in electric vehicles based on RVM.

The relevance vector machine has been increasingly used in the prognostics work. However at the best knowledge from the author, the relevant vector machine has never been used in the area of PEMFC performance degradation prediction.

2.2 Performance prediction with feature extended RVM

In this subsection, we would like to introduce the PEMFC stack performance prediction using the featured extended relevance vector machine. Basically, the extended feature means each input is extended comparing with the original RVM during training and prediction, in order to get higher effectiveness during training using historical data.

2.2.1 The original RVM explained

Traditionally, when we have a group of measured data set (x_i, t_i) (i = 1, 2, ..., n) sampled from an unknown linear function y(x), it can be fitted by a function $\hat{y}(x)$:

$$\hat{y}(x) = (w_1 x_1 x + w_2 x_2 x + \dots + w_n x_n x) + w_0$$

= $\phi(x) w$ (2-2)

where $\boldsymbol{\phi}(\boldsymbol{x}) = [1, x_1 x, x_2 x, ..., x_n x], \boldsymbol{w} = [w_0, w_1, ..., w_n]^T$. However, if the data set are sampled from a non-linear function, we can firstly use a transformation method (through the kernel function) to map the non-linear data set to a higher

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dimensional space, in which the initial non-linear relationship of data can be transformed to linear one, so that they can be fitted using linear regression in that higher dimensional space. The kernel function, usually expressed in the form of k(a, b), represents the inner product of a and b in higher dimensional space. Thus, we can substitute each $x_i x (i = 1, 2, ..., n)$ in (2-2) with $k(x_i, x)$, which indicate the inner product of x_i and x in higher dimensional space.

Therefore, equation (2-2) can be rewritten in its general form as:

$$\hat{y}(x) = \sum_{i=1}^{n} w_i k(x, x_i) + w_0$$
(2-3)

Generally, a RVM regression problem can be expressed to find the most probable weight vector **w** to fit with the training data set (x_i, t_i) (i = 1, 2, ..., n):

$$\widehat{\mathbf{y}} = \mathbf{\Phi}(\mathbf{x})\mathbf{w} \tag{2-4}$$

where:

$$\boldsymbol{\Phi}(\boldsymbol{x}) = [\boldsymbol{\phi}_{1} \quad \boldsymbol{\phi}_{2} \quad \dots \quad \boldsymbol{\phi}_{n+1}]$$

$$= \begin{bmatrix} 1 & k(x_{1}, x_{1}) & k(x_{1}, x_{2}) & \dots & k(x_{1}, x_{n}) \\ 1 & k(x_{2}, x_{1}) & k(x_{2}, x_{2}) & \cdots & k(x_{2}, x_{n}) \\ 1 & k(x_{3}, x_{1}) & k(x_{3}, x_{2}) & \cdots & k(x_{3}, x_{n}) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & k(x_{n}, x_{1}) & k(x_{n}, x_{2}) & \dots & k(x_{n}, x_{n}) \end{bmatrix}$$

$$(2-5)$$

$$\hat{\boldsymbol{y}} = [\hat{\boldsymbol{y}}_{1}, \hat{\boldsymbol{y}}_{2}, \dots, \hat{\boldsymbol{y}}_{n}]^{\mathrm{T}}$$

 $\Phi(\mathbf{x})$ is the design matrix which is created by Gaussian kernel functions $k(x_i, x_n) = exp(-\frac{\|x_i - x_n\|^2}{2\delta^2})$. We assume that there is a Gaussian noise ϵ_i , which could be regarded as the observation error, associated to each measured t_i compared to \hat{y}_i , where $\epsilon_i \sim N(0, \sigma^2)$, *i.e.*:

$$t_i \sim N(\hat{y}_i, \sigma^2) \tag{2-6}$$

For the derivation needs later on, the likelihood of *n* pairs of training set (x_i, t_i) could be expressed as:

$$P(\boldsymbol{t}|\boldsymbol{x}, \boldsymbol{w}, \sigma^2) \sim \prod_{i=1}^{N} N(\hat{y}_i, \sigma^2)$$

$$= (2\pi\sigma^2)^{-\frac{N}{2}} exp\left(-\frac{1}{2\sigma^2} \|\boldsymbol{t} - \boldsymbol{\Phi}\boldsymbol{w}\|^2\right)$$
(2-7)

In RVM method, the weight vector \boldsymbol{w} is in the following form:

$$P(w_i|\alpha_i) \sim N(0, \alpha_i^{-1}) \tag{2-8}$$

In which α_i^{-1} can be seen as a constrain factor to individual weight value w_i . Many of w_i in weight vector \boldsymbol{w} would be deleted from weight vector because those α_i^{-1} would be too small during training.

The posterior probability over all the parameters mentioned before could be expressed as:

$$P(\boldsymbol{w}, \boldsymbol{\alpha}, \sigma^2 | \boldsymbol{t}) = P(\boldsymbol{w} | \boldsymbol{t}, \boldsymbol{\alpha}, \sigma^2) P(\boldsymbol{\alpha}, \sigma^2 | \boldsymbol{t})$$
(2-9)

In RVM, we are trying to find which combination of $\boldsymbol{w}, \boldsymbol{\alpha}, \sigma^2$ may maximize $P(\boldsymbol{w}, \boldsymbol{\alpha}, \sigma^2 | \boldsymbol{t})$. Regarding the first part after the equal sign in (2-9), based on Bayes' Rule, we have:

$$P(\boldsymbol{w}|\boldsymbol{t},\boldsymbol{\alpha},\sigma^2) \sim N(\boldsymbol{m},\boldsymbol{\Sigma})$$
(2-10)

In here the m and Σ are the expectation and variance of the normal distribution of vector w respectively, with:

$$\boldsymbol{m} = \sigma^{-2} \boldsymbol{\Sigma} \boldsymbol{\Phi}^T \boldsymbol{t} \tag{2-11}$$
$$\boldsymbol{\Sigma} = (diag(\boldsymbol{\alpha}) + \sigma^{-2} \boldsymbol{\Phi}^T \boldsymbol{\Phi})^{-1}$$
(2-12)

$$\sigma^{-2} = \beta \tag{2-13}$$

For the second part of the right hand side of (2-9):

$$P(\boldsymbol{\alpha}, \sigma^2 | \boldsymbol{t}) \propto P(\boldsymbol{t} | \boldsymbol{\alpha}, \sigma^2) P(\boldsymbol{\alpha}) P(\sigma^2) \propto P(\boldsymbol{t} | \boldsymbol{\alpha}, \beta)$$
(2-14)

In RVM method, the objective is thus to find α and β that could maximize the marginal likelihood:

$$P(\boldsymbol{t}|\boldsymbol{\alpha},\boldsymbol{\beta}) = \int_{-\infty}^{\infty} P(\boldsymbol{t}|\boldsymbol{w},\boldsymbol{\beta}) P(\boldsymbol{w}|\boldsymbol{\alpha}) \mathrm{d}\boldsymbol{w}$$
(2-15)

It is feasible to use the maximum–likelihood estimation to evaluate α and β in (2-15). The logarithm of the marginal likelihood is:

$$\mathcal{L}(\boldsymbol{\alpha}) = log P(\boldsymbol{t}|\boldsymbol{\alpha}, \boldsymbol{\beta}) = log \int_{-\infty}^{\infty} P(\boldsymbol{t}|\boldsymbol{w}, \boldsymbol{\beta}) P(\boldsymbol{w}|\boldsymbol{\alpha}) d\boldsymbol{w}$$

$$= -\frac{1}{2} [nlog 2\pi + log |\boldsymbol{C}| + \boldsymbol{t}^{T} \boldsymbol{C}^{-1} \boldsymbol{t}]$$
(2-16)

where,

$$\boldsymbol{C} = \sigma^2 \boldsymbol{I} + \boldsymbol{\Phi} \boldsymbol{A}^{-1} \boldsymbol{\Phi}^T \tag{2-17}$$

The most probable α which can maximize (2-15) can then be calculated when:

$$\frac{\partial \mathcal{L}(\boldsymbol{\alpha})}{\partial \alpha_i} = 0 \ (i \in \{1 \dots n+1\}) \tag{2-18}$$

In general, the α and β have the following form:

$$\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \dots \alpha_{n+1})^T; \ \alpha_i = \frac{1 - \alpha_i \Sigma_{ii}}{m_i}$$
(2-19)

$$\beta = \frac{n - \sum_{i=1}^{n+1} (1 - \alpha_i \Sigma_{ii})}{\|\boldsymbol{t} - \boldsymbol{\Phi}\boldsymbol{m}\|^2}$$
(2-20)

The final value of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ which maximize $P(\boldsymbol{t}|\boldsymbol{\alpha},\boldsymbol{\beta})$ can be determined iteratively from properly chosen initial values. In (2-19) and (2-20), both of \boldsymbol{m} and $\boldsymbol{\Sigma}$ can be calculated from (2-11) and (2-12). Once the convergence criteria is met, the final converged values of $\boldsymbol{\alpha}_*, \boldsymbol{\beta}_*$ correspond to the maximum of $P(\boldsymbol{w}, \boldsymbol{\alpha}, \sigma^2 | \boldsymbol{t})$. Then, the final values of \boldsymbol{m}_* and $\boldsymbol{\Sigma}_*$ can be determined from $\boldsymbol{\alpha}_*$ and $\boldsymbol{\beta}_*$. Finally with all of these parameters we can make the prediction of \hat{t}_{new} from new input x_{new} :

$$\hat{t}_{new} \sim N(\hat{y}_{new}, \hat{\sigma}_{new}^2) \tag{2-21}$$

$$\hat{y}_{new} = \boldsymbol{m}_*^{\ T} \boldsymbol{\phi}(x_{new}) \tag{2-22}$$

$$\hat{\sigma}_{new}^2 = \beta_*^{-1} + \boldsymbol{\phi}(x_{new})^T \boldsymbol{\Sigma}_* \boldsymbol{\phi}(x_{new})$$
(2-23)

As we can see in (2-21), the RVM prediction holds the probabilistic feature with confidence intervals accompanying with the prediction results.

2.2.2 Feature extended RVM

In original RVM regression cases, *n* pairs of successive degradation data should be denoted as stack output voltage $\mathbf{t} = [t_i, t_{i+1}, ..., t_{i+n-1}]^T$ and their corresponding operation time points $\mathbf{x} = [x_i, x_{i+1}, ..., x_{i+n-1}]^T$. *n* represents the number of training points, *i.e.*, $(x_i, t_i), (x_{i+1}, t_{i+1}), ..., (x_{i+n-1}, t_{i+n-1})$. However, in this section, the vector \mathbf{x} is expanded to an $n \times 10$ matrix which can be expressed by:

$$\boldsymbol{x} = [\boldsymbol{x}_{i}, \boldsymbol{x}_{i+1}, \dots, \boldsymbol{x}_{i+n-1}]^{T} = \begin{bmatrix} x_{i-9} & x_{i-8} & \cdots & x_{i+n-10} \\ x_{i-8} & x_{i-7} & \cdots & x_{i+n-9} \\ \vdots & \vdots & \cdots & \vdots \\ x_{i} & x_{i+1} & \cdots & x_{i+n-1} \end{bmatrix}^{T}$$
(2-24)

The reason why we expand the time points \mathbf{x} to a matrix is, we perceive that in an aging data prediction case, each measured value t_i (stack output voltage) should not be only related to its corresponding measured time point x_i , but also to the historical events (thus previous time points). Specifically, in here we choose the time points vector $\mathbf{x}_i = [x_{i-9}, x_{i-8}, ..., x_i]^T$ which comprises 9 successive time points preceding x_i , as the attributes or feature vector corresponding to each t_i . Comparing to the original (x_i, t_i) data pairs, this novel approach using modified expansion formation of (\mathbf{x}_i, t_i) ensures the RVM training taking the historical numerical events into fully consideration. Specifically, each time point x_i should be scaled to [0,1] before the formation of \mathbf{x} in order to ensure both high effectiveness and accuracy of the model during training process.

With the expended structure of matrix \mathbf{x} , the design matrix could be formulated as what is shown in (2-5) with Gaussian kernel function. Favorable starting points of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ should be chosen to initiate the re-estimation process until the converged values of $\boldsymbol{\alpha}_*, \boldsymbol{\beta}_*$ are reached which can maximize the posterior in (2-15). Actually most of the weight elements can be pruned, because during this iteration, most of the elements in $\boldsymbol{\alpha}_*$ would be infinity. The pruning of those element results from (2-8) which clearly shows an infinite α_i indicates a zero peaked w_i . After this iteration process, one can calculate the prediction result with the sparse weight vector \boldsymbol{m}_* given a new input of \boldsymbol{x}_{new} . Specifically, the predictive result is subject to a normal distribution over the predictive value $\hat{y}_{new} = \boldsymbol{m}_*^T \boldsymbol{\phi}(\boldsymbol{x}_{new})$ with the variance of $\hat{\sigma}_{new}^2 = {\boldsymbol{\beta}_*}^{-1} + {\boldsymbol{\phi}}(\boldsymbol{x}_{new})^T \boldsymbol{\Sigma}_* {\boldsymbol{\phi}}(\boldsymbol{x}_{new})$. The associated confidential intervals can thus be demonstrated as two curves determined by deviation of $[-3\hat{\sigma}_{new}, +3\hat{\sigma}_{new}]$ based on \hat{y}_{new} , which indicate a 99.7% confidence level. In order to make it simple and clear, the different training steps of the proposed RVM algorithm are shown in the flow chart in Fig. 2-2.



Fig. 2-2 Flow chart of RVM training steps

2.2.3 Implementation

By applying the above mentioned RVM method, two experimental output voltage aging data sets of two identical PEMFC stacks (1.2 kW Ballard NEXA commercial PEM fuel cell stacks) for 400 h operation under two different working conditions were used. Specifically, the corresponding fuel cell operation conditions of two experimental degradation data sets are listed below in TABLE 2-1.

During the experimental tests, the fuel cell voltage output is measured and logged every ten minutes (thus 6 data points per hour). It has to be mentioned that, before applying to the model, the original measured data have been down-sampled during data post-processing to eliminate too similar or unreliable measurement data points. As shown in Fig. 2-3, degradation data plotted in (a) are composed of 104 successive measurements of the stack working under current of 30 A at 35 °C, while the other was measured under a stack current of 36 A at 40 °C and consists of 92 data points. For both data sets, we choose at first the measured points between 0 h

and 240 h for RVM training and evaluate the predictive results with the remaining data between 240 h and 400 h.

TABLE 2-1

TWO DIFFERENT OPERATION CONDITIONS DURING EXPERIMENTS

Stack configuration					
Fuel cells type	PEMFC dead-end mode				
Cell numbers	47 cells				
Fuel supply	99.99% dry H ₂ @1.2 bar				
Air supply	Air blower				
Cooling	Air fan cooled				
Operation conditions - First experimental test (Fig. 2-3a)					
Operation time	400 hours				
Operation temperature	35 °C				
Operation current	30 A				
Output power range (aging)	960 W (0h) - 885 W (400h)				
Air supply flow rate	55.75 slpm				
Measurement base sampling rate	1 measure point / 10 minutes				
Operation conditions – Second experimental test (Fig. 2-3b)					
Operation time	400 hours				
Operation temperature	40 °C				
Operation current	36 A				
Output power range (aging)	1098 W (0h) - 990 W (400h)				
Air supply flow rate	62.39 slpm				
Measurement base sampling rate	1 measure point / 10 minutes				





Fig. 2-3 Two data sets of training and remaining data

We've been acquiring two data sets of performance degradation of a PEMFC stack operating under different conditions. For each of them, the data measured between 0 and 240 hours were selected as the training set, and the rest in 240h – 400h were used to verify the accuracy of the points predicted by the improved RVM method proposed in this paper. *i.e.*, for each of the training set, one mathematical RVM model could be obtained. The trained RVM model results between 0h – 240h (training zone) correspond thus to the RVM regression results, and model results after 240h (prediction zone) correspond to the forecasted results. In our cases, the prediction results are given between 240h and 400h, which indicate a forecast horizon of 160h. Specifically, the prediction curve from the trained RVM model could be obtained as shown in Fig. 2-4. The RVM model parameters ($m_*, \Sigma_*, \alpha_*, \beta_*$) are deduced from the training steps shown in Fig. 2-2.



Fig. 2-4 Prediction curve calculation of trained RVM model

where $(x_s, x_{s+1}, ..., x_{end})$ stand for the time points from 0h to 400h, \hat{y} stands for the predictive value and $[\hat{y} - 3\hat{\sigma}, \hat{y} + 3\hat{\sigma}]$ indicate the confidential interval of 99.7% as explained in the last section. The $(x_s, \hat{y}_s), (x_{s+1}, \hat{y}_{s+1}), ..., (x_{end}, \hat{y}_{end})$ indicate the predictive values (blue line), while the $(x_s, \hat{y}_s + 3\hat{\sigma}_s), (x_{s+1}, \hat{y}_{s+1} + 3\hat{\sigma}_{s+1}), ..., (x_{end}, \hat{y}_{end} + 3\hat{\sigma}_{end})$ and $(x_s, \hat{y}_s - 3\hat{\sigma}_s), (x_{s+1}, \hat{y}_{s+1} - 3\hat{\sigma}_{s+1}), ..., (x_{end}, \hat{y}_{end} - 3\hat{\sigma}_{end})$ represent the upper and lower limit of the confidential interval, respectively, of the predictive results (pink lines) calculated by the proposed modified RVM algorithm.

Moreover, in order to highlight the superiority of the proposed method, the results are also compared with the ones obtained from SVM training using the same training set and forecast horizon.

2.2.4 Prediction results

2.2.4.1 Prediction with training zone before 240 hours

The performance prediction results from the condition of 30A 35°C and the 36A 40°C are shown in Fig. 2-5, all of these prediction results are based on the training zone from 0h -240h. the prediction curve (blue curve) plotted in each of the figures can be separated to two parts, the plotted curve before 240h can be regarded as the regression result because this is within the training set, while the plotted curve after 240h are the predictive result. The pink curves in all the figures stand for the error bars of $[-3\sigma, +3\sigma]$.





Fig. 2-5 Voltage drop trends prediction for two data set (240h)

As shown in Fig. 2-5, the performance of RVM can be clearly demonstrated. From (a) and (c), the forecasted curves are showing their conformity with the dropping tendency of the points remaining in the validation zone. Specifically, in (a) we can see a good agreement between remaining and prediction around 250h even with the presence of a sharp voltage drop. Besides, from (a) and (c) in Fig. 2-5 the confidence intervals predicted by the proposed RVM method are presented to show their effectiveness, because most of the remaining points have been included in the predicted interval.

Additionally, the comparisons of data regression errors of RVM and SVM methods under both working conditions are shown in TABLE 2-2. Specifically, the mean absolute percentage error (MAPE), root-mean-square error (RMSE), coefficient of determination (R^2) and number of vectors are compared between the proposed RVM and the classic SVM.

MAPE =
$$\frac{1}{n} \sum_{i=1}^{n} \frac{V_i - \hat{y}_i}{V_i}$$
 (2-25)

RMSE =
$$\sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - V_i)^2}{n}}$$
 (2-26)

$$R^{2} = 1 - \frac{\sum_{i=1}^{n} (V_{i} - \hat{y}_{i})^{2}}{\sum_{i=1}^{n} (V_{i} - \overline{V_{i}})^{2}}$$
(2-27)

where, \hat{y}_i stands for the predicted voltage;

 V_i stands for the measured voltage;

 $\overline{V_l}$ stands for the mean value of the measured voltage;

n stands for the number of points we are interested.

For MAPE and RMSE, smaller values indicate lower error and thus better prediction. Values of R^2 indicate how well the statistical models fit pairs of data. The values range from 0 to 1 and larger values indicate better fits (1 represent perfect fit). Number of vectors accounts for the mathematical complexity of the model given by RVM and SVM. Smaller number of vectors indicate less complexity of models and lower computational demand, thus in turn leads to faster of computation.

TABLE 2-2

	RVM	SVM	RVM	SVM
	30A 35°C	30A 35°C	36A 40°C	36A 40°C
MAPE	0.0044	0.0054	0.0068	0.0067
RMSE	0.1751	0.2022	0.2244	0.2263
R^2	0.9153	0.8896	0.9296	0.9224
Number of vectors	3	11	3	8

ERROR ASSESSMENT (240H)

From this table, we can see the RVM can achieve better performance than SVM. Besides, RVM holds the advantage of providing prediction results with confidence intervals which is not the case for SVM method.

Comparing with the predictive results in published previous work, the MAPE and RMSE of predicting result in this paper using newly proposed design matrix formation is 30% and 15% percent less than that presented in [98] respectively. It should be noted that the data set measured under 30A 35°C shows more non-linear characteristics than the data set of 36A 40°C, and this precision improvement indicates the potential ability of RVM prediction when dealing with non-linear prediction case.

2.2.4.2 Prediction with longer training zone

In order to thoroughly evaluate the performance of the proposed RVM comparing to SVM, more prediction results acquired from different training intervals are compared and evaluated.

In addition to the previously used 0 to 240h training interval, the data between 0 to 300h and 0 to 350h of each voltage data set are also chosen as the new training sets for the validation purpose of both RVM and SVM methods. As what is expected, the performance of RVM in predicting the voltage drop trends is still better than

SVM in the two later cases, as shown in Fig. 2-6, Fig. 2-7, TABLE 2-3 and TABLE 2-4.









Fig. 2-6 Voltage drop trends prediction 30A 35°C

TABLE 2-3

ERROR ASSESSMENT 30A 35°C

20 4 25%	RVM	SVM	RVM	SVM
50A 55 C	300h	300h	350h	350h
MAPE	0.0050	0.0054	0.0038	0.0054
RMSE	0.1847	0.1892	0.1534	0.2071
R ²	0.9014	0.8778	0.9334	0.8842
Number of vectors	3	5	4	6









Fig. 2-7 Voltage drop trends prediction 36A 40°C

TABLE 2-4

26 A 40°C	RVM	SVM	RVM	SVM
30A 40 C	300h	300h	350h	350h
MAPE	0.0069	0.0070	0.0064	0.0069
RMSE	0.2258	0.2312	0.2175	0.2309
R ²	0.9250	0.9189	0.9402	0.8896
Number of vectors	3	11	3	13

ERROR ASSESSMENT 36A 40°C

From the figures and obtained error analysis, it could be clearly demonstrated that the proposed modified RVM method can achieve better accuracy comparing to SVM method. Nearly all the values of MAPE and RMSE getting from RVM of different training sets are smaller than those getting from SVM. And for R^2 , all values getting from RVM are closer to 1 than those from SVM. This indicates better fitting of RVM than SVM. Most of the remaining points in the approach of RVM are included in the confidence intervals which SVM could not provide. Besides, the numbers of vectors given from models of RVM are much smaller than the numbers of vectors given from SVM. This proves the models given by RVM are much sparser than SVM, and this can reduce the computational demand during prediction. Moreover, with the results coming from different training intervals, the influence of the number of training data on the performance of RVM and SVM can also be evaluated. For the proposed RVM method, we can see the MAPE of the results predicted from training length of 240 h, 300 h, 350h under condition 30A and 35 °C are 0.0044, 0.0050, and 0.0038, respectively. Thus, it seems that, a longer training data set doesn't necessarily improve the precision of prediction results provided by the proposed RVM method. Once the training length is more than a certain value (threshold), the prediction precision will no longer be highly dependent on the training length. This non-synchronized phenomenon between expansion of training length and improvement of prediction accuracy is also reflected from the values of RMSE, R^2 .

Prediction with extremely limited training zone 2.2.4.3

In addition, in order to highlight the extended prediction capacity of proposed modified RVM method compared to classic SVM method, the fuel cell output voltage aging prediction is also processed with the data sets of 36A 40°C. The training zone of this prediction only contains very few training data. In Fig. 2-8 shows the prediction results with the training length limited only to first 50 hours. It could be seen from the figures that, due to the extremely limited amount of training data, both predictions are not highly accurate especially when the predict time is far from the first 50h.



Fig. 2-8 Voltage drop trends prediction 36A 40°C (50h)

200 Operation time [h]

300

400

100

However, under this extreme condition, the results obtained from the proposed modified RVM is obviously better than SVM because the RVM prediction couldn't show its conformity with the remaining sets until 200 more hours, which is much longer than that of SVM. This proves RVM has the potential to get a fairly acceptable result even when the acquiring data are extremely limited at hand.

2.2.5 Subsection summary

According to the aging data specialty in the cases of data prediction, the formulation of the feature extended RVM was introduced. The implementation of the proposed RVM was then presented for the prediction of the voltage degradation trends from two experimentally measured data sets (from two 1.2 kW NEXA fuel cell stacks). In order to highlight the advantages of using the proposed RVM method, the obtained results were also compared with the ones obtained from a classic Support Vector Machine (SVM) method. The results obtained from different conditions are then compared and discussed thoroughly. It can be concluded that, both the predictive results coming from RVM and SVM were indicated to have good agreements with the measured data points. However, the prediction accuracy of RVM is better than that of SVM, especially in certain conditions when the training data are extremely limited. The models getting from RVM are much sparser than that from SVM which can also reduce the computational demand for prediction applications. Furthermore, the confidence intervals of RVM were also proved to have good effectiveness which classic SVM cannot give. What's more, comparing with the results of original RVM, the results of the feature extended RVM are higher. In conclusion, the proposed modified RVM method has been proved to be a nice option of predicting the performance degradation of PEMFC stacks.

2.3 Summary

In this section, we firstly introduced the background of the topic on PEMFC stack performance degradation prediction. Then the formulation and implementation process of the feature extended RVM was fully illustrated, and the implementation

process of the proposed RVM training and prediction was demonstrated. The results were compared with the results getting from SVM with different training zone. The prediction performance of the proposed RVM is promising in comparison with SVM. Moreover, comparing with the results of original RVM, the results of the feature extended RVM are more accurate. In general, the prediction results of this feature extended RVM method were good and would have the potential to be used in the PEMFC performance prediction.

Generally, in the RVM training problem, or a vector machine training problem, the prediction results getting from constant kernel width using extended feature RVM are good enough. However, the kernel width is usually a critical parameter for vector machines, and could influence the prediction results. Therefore, it is reasonable to have a self-adaptive kernel approach during prediction, and this would make the prediction algorithms smarter, and more optimized. In this chapter, we would like to introduce a self-adaptive kernel RVM in the PEMFC performance prediction case. The prediction capacity of this newly proposed method would be thoroughly demonstrated with different data from different stacks under different operation conditions.

Before looking into the self-adaptive kernel prediction, firstly we need to know what the kernel trick is.

3.1 What is the kernel trick?

Let's assume there is a group of points $(P_1, P_2, ..., P_n)$ on the *xoy* plane as shown in Fig. 3-1. In a common sense of a regression problem, the target is usually to find a function, or a curve which would best fit the points. However, it is sometimes hard to find a proper function if there are too much non-linearity within the hidden function of this group of points. With the kernel trick, one could possibly solve this non-linear regression problem easily by mapping those points with non-linearity

feature at lower dimensional space into higher dimensional space, in which the relationship among those mapped points become less non-linear at higher dimension. The kernel function, usually expressing in the form of $k(P_i, P_j)$, represents the inner product of $\psi(P_i)$ and $\psi(P_i)$ in higher dimensional space. As what has been shown in this figure, those points on xoy plane could be easily fitted after mapping into the higher dimensional space.

Generally, the RVM regression problem usually deals with finding a proper prediction function that could best fit the given group of data.



 $\hat{y}(x) = (w_1 x_1 x + w_2 x_2 x + \dots + w_n x_n x) + w_0$ (3-1)

Fig. 3-1 The kernel trick explained

The kernel trick could help us deal with the regression problem in a higher dimensional space. With the help of kernel function, the regression equation could be modified to:

$$\hat{y}(x) = \sum_{i=1}^{n} w_i k(x, x_i) + w_0$$
(3-2)

In fact, there are plenty of choices of kernel functions. Such as the linear kernel, polynomial kernel, Gaussian kernel, exponential kernel etc. In this thesis work, we choose the Gaussian kernel in all of the vector machine trainings. The Gaussian kernel:

 $k(P_i, P_j) = exp(-\frac{\|P_i - P_j\|^2}{2\delta^2})$ (3-3)

where δ is the kernel width, this value denotes the sparsity between the mapped points in the higher dimensional space. It is reasonable to consider that the points would be better fitted in a sparser distributed condition. So this value is of importance during the regression or prediction problems.

3.2 Prediction implementation using self-adaptive kernel RVM

Before introducing the self-adaptive kernel RVM, something need to be done with the iteration process of the RVM algorithm. As what have been mentioned in last section, generally in RVM method, the objective is to find the α and β that could maximize the marginal likelihood:

$$P(\boldsymbol{t}|\boldsymbol{\alpha},\boldsymbol{\beta}) = \int_{-\infty}^{\infty} P(\boldsymbol{t}|\boldsymbol{w},\boldsymbol{\beta}) P(\boldsymbol{w}|\boldsymbol{\alpha}) \mathrm{d}\boldsymbol{w}$$
(3-4)

It is feasible to use the maximum–likelihood estimation to evaluate α and β in (3-4). The logarithm of the marginal likelihood is:

$$\mathcal{L}(\boldsymbol{\alpha}) = \log P(\boldsymbol{t}|\boldsymbol{\alpha}, \boldsymbol{\beta}) = \log \int_{-\infty}^{\infty} P(\boldsymbol{t}|\boldsymbol{w}, \boldsymbol{\beta}) P(\boldsymbol{w}|\boldsymbol{\alpha}) d\boldsymbol{w}$$

$$= -\frac{1}{2} [n\log 2\pi + \log |\boldsymbol{C}| + \boldsymbol{t}^{T} \boldsymbol{C}^{-1} \boldsymbol{t}]$$
(3-5)

where,

$$\boldsymbol{C} = \sigma^2 \boldsymbol{I} + \boldsymbol{\Phi} \boldsymbol{A}^{-1} \boldsymbol{\Phi}^T \tag{3-6}$$

The most probable α which can maximize (3-4) can then be calculated when:

$$\frac{\partial \mathcal{L}(\boldsymbol{\alpha})}{\partial \alpha_i} = 0 \ (i \in \{1 \dots n+1\}) \tag{3-7}$$

The original RVM method intends to differentiate (3-7) directly. However, it would be computationally expensive to get the result of α afterwards. Thus, some additional modifications could be done from (3-5).

For instance, *C* can be further decomposed as:

$$C = \sigma^{2} I + \sum_{m \neq i}^{n+1} \alpha_{m}^{-1} \boldsymbol{\phi}_{m} \boldsymbol{\phi}_{m}^{T} + \alpha_{i}^{-1} \boldsymbol{\phi}_{i} \boldsymbol{\phi}_{i}^{T}$$

$$= C_{-i} + \alpha_{i}^{-1} \boldsymbol{\phi}_{i} \boldsymbol{\phi}_{i}^{T}$$
(3-8)

In this way the C is separated to two parts, the first part is completely independent of α_i (namely C_{-i}) while the rest is a function of α_i . This way, equation (3-5) can be expressed as:

$$\mathcal{L}(\boldsymbol{\alpha}) = \mathcal{L}(\boldsymbol{\alpha}_{-i}) + \mathcal{L}(\boldsymbol{\alpha}_{i}) \tag{3-9}$$

where:

$$\mathcal{L}(\boldsymbol{\alpha}_{-i}) = -\frac{1}{2} [n \log(2\pi) + \log|\boldsymbol{C}_{-i}| + \boldsymbol{t}^{T} \boldsymbol{C}_{-i}^{-1} \boldsymbol{t}]$$

$$\mathcal{L}(\boldsymbol{\alpha}_{i}) = \frac{1}{2} [\log \alpha_{i} - \log(\alpha_{i} + \boldsymbol{\phi}_{i}^{T} \boldsymbol{C}_{-i}^{-1} \boldsymbol{\phi}_{i}) + \frac{(\boldsymbol{\phi}_{i}^{T} \boldsymbol{C}_{-i}^{-1} \boldsymbol{t})^{2}}{\alpha_{i} + \boldsymbol{\phi}_{i}^{T} \boldsymbol{C}_{-i}^{-1} \boldsymbol{\phi}_{i}]$$
(3-10)

By applying the above-mentioned method, the α_i can be isolated from the log marginal likelihood $\mathcal{L}(\alpha)$ in (3-5). Therefore, the most probable α_i is the one when the gradient of $\mathcal{L}(\alpha)$ with respect to α_i equals to zero:

$$\frac{\partial \mathcal{L}(\boldsymbol{\alpha})}{\partial \alpha_i} = \frac{\partial \mathcal{L}(\alpha_i)}{\partial \alpha_i} = \frac{\alpha_i^{-1} S_i^2 - (Q_i^2 - S_i)}{2(\alpha_i + S_i)^2} = 0$$
(3-11)

where:

$$S_i = \boldsymbol{\phi}_i^T \boldsymbol{C}_{-i}^{-1} \boldsymbol{\phi}_i; \quad Q_i = \boldsymbol{\phi}_i^T \boldsymbol{C}_{-i}^{-1} \boldsymbol{t}$$
(3-12)

From (3-11) it shows that the log marginal likelihood $\mathcal{L}(\alpha)$ can reach its unique maximum under following two circumstances:

$$\alpha_{i} = \frac{S_{i}^{2}}{Q_{i}^{2} - S_{i}} \quad \text{when } Q_{i}^{2} > S_{i}$$

$$\alpha_{i} = +\infty \quad \text{when } Q_{i}^{2} \le S_{i}$$
(3-13)

During the fitting process, $Q_i^2 \leq S_i$ indicates that ϕ_i and w_i should be set to zero because in this case, only when $\alpha_i = +\infty$ the log marginal likelihood could reach its maximum. However from (2-8), w_i is limited to zero when $\alpha_i = +\infty$. So this indicates w_i does not play the role of weight in this model and need to be pruned. During the process,

$$\sigma^{2} = \beta^{-1} = \frac{\|\boldsymbol{t} - \boldsymbol{\Phi}\boldsymbol{m}\|^{2}}{n - \sum_{i=1}^{n+1} (1 - \alpha_{i} \Sigma_{ii})}$$
(3-14)

As soon as we get the final value of α and β , we can calculate the m and Σ . The predictive value t_{new} can then be obtained in the form of normal distribution:

$$t_{new} \sim N(\hat{y}_{new}, \sigma_{new}^2) \tag{3-15}$$

$$\boldsymbol{\phi}(x_{new}) = \begin{bmatrix} 1 \ k(x_1, x_{new}) \ k(x_2, x_{new}) \ \dots \ k(x_n, x_{new}) \end{bmatrix}$$
$$\hat{y}_{new} = \boldsymbol{\phi}(x_{new})\boldsymbol{m}$$
$$\sigma_{new}^2 = \sigma^2 + \boldsymbol{\phi}(x_{new})^T \boldsymbol{\Sigma} \boldsymbol{\phi}(x_{new})$$

It should be noted that, during the process of deducing α_i , many weight elements w_i are set to zero and thought to basically ensure the mathematical sparsity of the predictive model.

In this chapter, the performance prediction would involve two case studies. The first one would be about the performance prediction using 4 datasets measured from four identical NEXA stacks under four different operation conditions. The second one would use a dataset measured from a PM 200 stack operating under variable condition (road test).

- *Case study 1*: 1.2 kW Ballard NEXA commercial fuel cell stacks (47 cells) working under four different operation conditions. (4 data sets)
- *Case study 2*: 8 kW PM 200 PEMFC stack (96 cells) working under mobile/dynamic application. (1 data set)

All of the five data sets are the experimentally measured fuel cell stack output voltage values during about 400 to 450 hours of continuous fuel cell operation, and each of them contains around 100 data points. Specifically, the 4 data sets from the 1.2 kW Ballard NEXA stacks were measured and post–processed under steady–state operation conditions of 12A 30°C, 30A 35°C, 36A 40°C and 44A 40°C respectively. The data set of the PM 200 stack was measured under a cyclic load output condition with a current density profile varies between 0.30–0.97 A/cm², and two start/stops per operation hour. The detailed operation conditions and the V–I characteristics (polarization curves) of the measured NEXA and PM 200 fuel cell stacks are listed in TABLE 3-1 and illustrated in Fig. 3-2 respectively.

TABLE 3-1

	Test case 1	Test case 2	Test case 3	Test case 4	Test case 5
Stack type	NEXA				PM 200
Air supply	Air blower + filter				
Operating hours	400 h				
Number of cells	47				96
Operation mode	Dead–end mode				Recirculation mode
Cooling	Air fan cooled				DI–Water / Glycol
Fuel supply	99.99% dry H ₂ @1.2 bar				99.99% dry H ₂ @1.5 bar
Air stoichiometry	4.2	2.2	2.0	2.0	1.7
Stack temperature	30°C	35°C	40°C	44°C	58°C
Stack current density	0.08A/cm ²	0.20A/cm ²	0.24A/cm ²	0.30A/cm ²	0.30A/cm ² – 0.97A/cm ² (cyclic)

OPERATION CONDITIONS OF NEXA AND PM 200 FUEL CELL STACKS



Fig. 3-2 V-I characteristics for NEXA and PM 200 PEMFC stacks

For a given fuel cell stack and operation conditions, we have N data points in one data set, which can be expressed in the form of $(x_1, t_1), (x_2, t_2), ..., (x_i, t_i), ..., (x_N, t_N)$. x_i represents the sampling time and t_i represents the corresponding stack output voltage measured at time x_i . The index N denotes the total number of data points in each data set.

With *s* initial training points (x_1, t_1) , (x_2, t_2) , ..., (x_s, t_s) , the RVM model is trained first to calculate the corresponding weight vector \mathbf{w}_s . Then the values of the new voltage \hat{y}_{s+1} at new time point x_{s+1} can be predicted from the trained model. When the system reaches time x_{s+1} , the newly measured voltage t_{s+1} is added into the updated data set (x_1, t_1) , (x_2, t_2) , ..., (x_{s+1}, t_{s+1}) , and the RVM model is trained again to get the new weight vector \mathbf{w}_{s+1} to predict \hat{y}_{s+2} at time point x_{s+2} . The same sequence is repeated for \hat{y}_{s+3} , \hat{y}_{s+4} ...etc. That is to say, for *N* training points, we need to train and predict iteratively for (N - s) times (i.e., (N - s)times one–step–ahead predictions) to get the prediction result $[\hat{y}_{s+1}, \hat{y}_{s+2}, ..., \hat{y}_N]$. This iterative dynamic training method can ensure a higher prediction accuracy. It has also to be noted that, even the RVM model need to be re–trained at each time point in our proposed algorithm, the training time with a given data set is relatively short (less than 1 s in our cases with up to 100 data points). Thus, it can be seen as an on-line prediction method. The proposed RVM training steps are developed in detail hereafter:

1. Creation of the design matrix $\Phi(x)$

As shown in (2-5), the design matrix is composed by one bias column $[1, 1, ..., 1]^T$ and *s* kernel columns for *s* training data points. This kind of kernel dominated design matrix can achieve relatively higher regression precision in highly non–linear circumstances. However, the voltage degradation feature of the fuel cell contains also linear tendencies comparing to the pure non–linear data sets. Thus, in order to have better fitting results, the original RVM design matrix is modified in here with additional linear columns. That is to say, in addition to the *s* kernel columns and one bias column, the modified design

matrix $\Phi(\mathbf{x})$ can be created by appending *s* extra columns to the original design matrix using values of $x_1, x_2, ..., x_s$, as shown in (3-16).

$$\boldsymbol{\Phi}(\boldsymbol{x}) = [\boldsymbol{\phi}_{1} \ \boldsymbol{\phi}_{2} \ \dots \ \boldsymbol{\phi}_{s+1} \ \boldsymbol{\phi}_{s+2} \ \dots \ \boldsymbol{\phi}_{2s+1}]$$

$$= \begin{bmatrix} 1 & k(x_{1}, x_{1}) & \dots & k(x_{1}, x_{s}) & x_{1} & x_{2} & \dots & x_{s} \\ 1 & k(x_{2}, x_{1}) & \dots & k(x_{2}, x_{s}) & x_{1} & x_{2} & \dots & x_{s} \\ 1 & k(x_{3}, x_{1}) & \dots & k(x_{3}, x_{s}) & x_{1} & x_{2} & \dots & x_{s} \\ \vdots & \vdots \\ 1 & k(x_{s}, x_{1}) & \cdots & k(x_{s}, x_{s}) & x_{1} & x_{2} & \dots & x_{s} \end{bmatrix}$$

$$(3-16)$$

Consequently, the corresponding weight vector w is also modified by adding s weight elements for the s newly appended columns. Also s more hyperparameters of α_i should be introduced into the training process. With the proposed modification, the linear part in the data sets could be better predicted with the help of the newly added s more weight elements. It should also be noted that all the x_i , which represent the different time points during fuel cell aging test in a time value range of [0, 400] (hours), are needed to be proportionally normalized to [0, 1] before creating the design matrix in order to get higher regressive accuracy.

2. Acquisition of the proper weight vector \boldsymbol{w}

To start the RVM model training, we can randomly choose a column vector ϕ_i from the design matrix, using (3-13), the α_i can thus be calculated from:

$$\alpha_i = \frac{\|\boldsymbol{\phi}_i\|^2}{\frac{\|\boldsymbol{\phi}_i^T \boldsymbol{t}\|^2}{\|\boldsymbol{\phi}_i\|^2} - \sigma^2}$$
(3-17)

While other $\alpha_k (k \neq i)$ are set to infinity, it is then possible to calculate the S_i and Q_i using (3-8) and (3-12). The rule applied here is, if $Q_i^2 - S_i^2 > 0$, update α_i , else if $Q_i^2 - S_i^2 < 0$, set this ϕ_i column in the design matrix to zero

and the α_i to infinite. We can thus calculate all the $Q_j^2 - S_j^2$ (j = 1, 2, ..., 2s + 1) using the same method with ϕ_j choosing from columns of $\Phi(x)$ to see if they are positive or negative. The negative values indicate that the corresponding ϕ_j and α_j should be ruled out from the mathematical model, while the α_j can be updated when the corresponding $Q_j^2 - S_j^2$ are positive. At the same time, we can use (3-14) to update the σ^2 . With the final updated values of α , σ^2 and $\Phi(x)$, the proper weight vector w can then be deduced from m using (2-11) and (2-12), as shown in Fig. 3-3 This diagram illustrates the different calculation steps in detail to determine the proper weight vector w.



Fig. 3-3 Calculation flow chart for deducing vector w

3. Adaptive kernel of δ

The Gaussian kernel function in the design matrix $\Phi(x)$ is expressed as $k(x_i, x_n) = exp(-\frac{\|x_i - x_n\|^2}{2\delta^2})$. The δ , which is called the kernel width, plays an important role in linear or non-linear regression of RVM method and its value should be carefully tuned. If it is overestimated, the exponential will behave almost linearly and the higher-dimensional projection will start to lose its non-linear feature. On the other hand, if it is underestimated, the predictive curve would be sensitive to noise in the training data which could lead to the over fitting problem. In this paper, an innovative method of self-adaptive kernel is proposed to overcome the above-mentioned problems. The proposed adaptation steps are summarized as follow:

For those data sets having been finely normalized in [0, 1], the most proper kernel width is located in [0, 10], we randomly choose *a* values from this zone to form a group of adaptive candidates $(\delta_1, \delta_2, ..., \delta_a) \in [0, 10]$. Each δ_i can be used to create a unique $\Phi(\mathbf{x})$.

Each of the $\Phi(x)$ based on *s* training sets can help to deduce a proper weight vector w_s which is peaked in m_s as detailed in the second step. The adaptive kernel width is proposed as the expression of:

$$\delta_{adaptive} = \arg\min_{\delta \in [0,10]} (\hat{y}_s - t_s) \tag{3-18}$$

where:

$$\hat{y}_{s} = \boldsymbol{\phi}(x_{s})\boldsymbol{m}_{s}$$

$$\boldsymbol{\phi}(x_{s}) = \begin{bmatrix} 1 \ k(x_{s}, x_{1}) \ k(x_{s}, x_{2}) \ \dots \ k(x_{s}, x_{s}) \ x_{1} \ x_{2} \ \dots \ x_{s} \end{bmatrix}$$
(3-19)

Once $\delta_{adaptive}$ is acquired, the $\Phi(x)$ creating from $\delta_{adaptive}$ is chosen as the design matrix, and its deduced w_s is chosen as the most probable weight vector corresponding to these *s* data points training set.

It should be noted that higher values of a indicate higher precision of the prediction results. Because a higher value of a would lead to bigger kernel

candidates of $(\delta_1, \delta_2, ..., \delta_a) \in [0, 10]$, thus makes it more possible to find an adaptive kernel which is very close to the most proper kernel for prediction. In our case, we choose a = 100.

4. Prediction

After acquiring the most probable weight vector w_s , with the s initial training data, we can calculate the predictive result of $\hat{y}_{s+1} = \boldsymbol{\phi}(x_{s+1})\boldsymbol{m}_{s+1}$ with a confidence interval of $[-3\sigma_{s+1}, +3\sigma_{s+1}]$, which indicates 99.7% confidence level. We have mentioned at the beginning of this section that it would take us N - s training iterations to get all the predictive results for $[\hat{y}_{s+1}, \hat{y}_{s+2}, ..., \hat{y}_N]$:

$$\hat{\mathbf{y}}_{predict} = [\hat{y}_{s+1}, \hat{y}_{s+2}, ..., \hat{y}_N]$$

$$= [\boldsymbol{\phi}(x_{s+1})\boldsymbol{m}_{s+1}, \boldsymbol{\phi}(x_{s+2})\boldsymbol{m}_{s+2}, ..., \boldsymbol{\phi}(x_N)\boldsymbol{m}_N]$$

$$\hat{\mathbf{y}}_{upper \ limit}$$

$$[(\hat{\alpha}_{s+1}, \hat{\alpha}_{s+2}), (\hat{\alpha}_{s+2}, \hat{\alpha}_{s+2}), (\hat{\alpha}_{s+2}, \hat{\alpha}_{s+2}), (\hat{\alpha}_{s+2}, \hat{\alpha}_{s+2})]$$
(3-20)

$$= [(y_{s+1} + 3\sigma_{s+1}), (y_{s+2} + 3\sigma_{s+2}), ..., (y_N + 3\sigma_N)]$$

$$= [\phi(x_{s+1})m_{s+1} + 3 \times (\sigma_{s+1} + \phi(x_{s+1}))^T \Sigma_{s+1} \phi(x_{s+1}), \qquad (3-21)$$

$$\phi(x_{s+2})m_{s+2} + 3 \times (\sigma_{s+2} + \phi(x_{s+2}))^T \Sigma_{s+2} \phi(x_{s+2}), ...$$

$$\phi(x_N)m_N + 3 \times (\sigma_N + \phi(x_N))^T \Sigma_N \phi(x_N)]$$

 $\widehat{y}_{lower \ limit}$

$$= [(\hat{y}_{s+1} - 3\sigma_{s+1}), (\hat{y}_{s+2} - 3\sigma_{s+2}), ..., (\hat{y}_N - 3\sigma_N)]$$

$$= [\phi(x_{s+1})m_{s+1} - 3 \times (\sigma_{s+1} - \phi(x_{s+1}))^T \Sigma_{s+1} \phi(x_{s+1}), \qquad (3-22)$$

$$\phi(x_{s+2})m_{s+2} - 3 \times (\sigma_{s+2} - \phi(x_{s+2}))^T \Sigma_{s+2} \phi(x_{s+2}), ...$$

$$\phi(x_N)m_N - 3 \times (\sigma_N + \phi(x_N))^T \Sigma_N \phi(x_N)]$$

where $\phi(x_{s+1})$ denotes the corresponding design vector for the prediction of \hat{y}_{s+1} from *s* data points training data sets, expressed as:

Above illustrated the mathematical modifications of proposed RVM accompanied with the detailed steps of implementation.

3.3 Results and discussions

In order to verify experimentally the effectiveness and the validity of the proposed modified RVM approach, the method is applied to each test case. It has to be noted that, the results presented in 3.3.1, 3.3.2 and 3.3.3 correspond to the single–step–ahead prediction results or comparisons with the proposed modified RVM and SVM, original RVM (*i.e.* the corresponding prediction time is about 4 hours). Multi–step–ahead prediction (up to 20 hours) is presented in 3.3.4.

3.3.1 **RVM** prediction results

3.3.1.1 Case Study 1

In this case, four experimental output voltage degradation data sets of a 1.2 kW PEMFC stack (Ballard NEXA commercial fuel cell stack) for 400 h continuous operation under different working conditions are presented. The data sets are used to train the modified RVM model, and the predicted results are then compared with the measured ones in order to validate experimentally the prediction method proposed in this paper. For each of the data sets, we impose in this study the initial

number of data points s = 15, which indicates the first 15 data points are selected to initiate the prediction. By applying the previously developed RVM method, the model predicted results are shown and discussed hereafter.









Fig. 3-4 RVM predictive results under four different conditions with s=15 (NEXA stack)

In Fig. 3-4, the experimental voltage degradation data points tested under four groups of operating currents and temperatures are marked as red crosses in all four figures. They show the measured data sets $(x_1, t_1), (x_2, t_2), ..., (x_N, t_N)$ are distributed in a time interval of [0h, 400h], where $x_1, x_2, ..., x_N$ represent the sampling time and the $t_1, t_2, ..., t_N$ represents the corresponding measured stack output voltage. The RVM model predicted results are presented in green lines, starting from data point s + 1, noted as $(x_{16}, \hat{y}_{16}), (x_{17}, \hat{y}_{17}), ..., (x_N, \hat{y}_N)$. In

addition, two blue dotted lines in each figure indicate the upper/lower limit of the prediction confidence interval. As mentioned before, this confidence interval are bounded by both lining up $(x_{16}, \hat{y}_{16} + 3\sigma_{16}), (x_{17}, \hat{y}_{17} + 3\sigma_{17}), \dots, (x_N, \hat{y}_N + 3\sigma_N)$ and $(x_{16}, \hat{y}_{16} - 3\sigma_{16}), (x_{17}, \hat{y}_{17} - 3\sigma_{17}), \dots, (x_N, \hat{y}_N - 3\sigma_N)$. The $\pm 3\sigma$ in Gaussian distribution indicates a 99.7% confidence interval.

It can be seen clearly from Fig. 3.4 that, the proposed RVM method with improved design matrix and adaptive algorithm can accurately predict both voltage degradation tendency and voltage values from the data sets. The deduced confidence intervals are also effective to cover most of the data.

3.3.1.2 Case Study 2

In order to demonstrate the capability and effectiveness of the prediction of the proposed RVM method on different fuel cell stacks, another experimental voltage aging data set from an 8 kW PM 200 PEMFC stack (96 cells) working under mobile/dynamic application is also trained in this section. The RVM model training process remains the same. The prediction is also initiated with an initial number of data points s = 15.

The prediction results of a single cell (the middle cell in 96 cells stack) voltage degradation are illustrated in Fig. 3-5. The green line represents the RVM model predicted results, and the two blue dotted lines indicate the confidence interval of the prediction. The measured data points are drawn as red crosses (same with before). Fig. 3.5 clearly shows again that, the predicted results from the proposed RVM method can precisely follow the trend of the non–linear experimental data set with a great accuracy.



Fig. 3-5 Single cell voltage prediction results for mobile application with s=15 (PM 200 stack)

3.3.2 Proposed modified RVM vs. SVM

In order to show the advantages and effectiveness of the proposed RVM method in predicting the voltage degradation of PEMFC, the results from the support vector machine (SVM) method using same training data sets are presented in this section (same adaptive kernel), and they are compared with that of the proposed RVM method.

Using the same five data sets implemented by the improved RVM method before, the predictive results of classic SVM method are presented in Fig. 3-6. It is clear to see from the figures that, the SVM method can give fairly good prediction results of fuel cell voltage degradation at the beginning of fuel cell operation time. However, in some cases, when the operation time passes 300h, the prediction results from SVM become unacceptable, especially in the cases of 44A 40°C of NEXA (Fig. 3-6d) and PM 200 mobile operation (Fig. 3-6e), from which the prediction results after 300h begin to slightly deviate from the data set, and the deviation remains until the end of prediction.










Fig. 3-6 Predictive results of SVM with s = 15

In order to show in detail the effectiveness of predictions of RVM and SVM over the entire fuel cell operation time interval, three types of error analysis—Mean Absolute Percentage Error (MAPE), Root Mean Square Error (RMSE) and Coefficient of Determination (R^2) — are conducted and discussed in the following. Unlike the MAPE or RMSE, larger values of R^2 indicate better fittings (usually $0 < R^2 \le 1$). By applying the MAPE, RMSE and R^2 error analysis, the analysis results for RVM and SVM methods over fuel cell operation time range are illustrated in Fig. 3-7 and 3-9, respectively, for all five experimental data sets. The MAPE, RMSE or R^2 getting from RVM and SVM methods under the same fuel cell operation conditions (four conditions of NEXA stack and one mobile condition of PM 200 stack in total) are plotted with the same color, while the solid lines stand for RVM results and dotted lines stand for SVM results.

The MAPE results are presented in Fig. 3-7, it can be seen clearly from the figure that, the MAPE of RVM is smaller than that of SVM under all five operation conditions. Especially for the mobile condition of 8 kW PM 200 stack, the MAPE of RVM results is nearly 40% less than that of SVM results. Moreover, the MAPE of SVM predicted results for NEXA data sets under 36A 40°C and 44A 40°C are both slightly deviated upward through time, which means the accumulated prediction errors are relatively higher using classic SVM method when training with

larger amount of data. In contrast, the MAPE of improved RVM method under all five conditions are much more consistent than SVM.

The RMSE is scale–dependent, which means if data sets are not scaled into same range, it may lead to different magnitude of RMSE. This is the reason why the RMSE, either of RVM or SVM, for prediction of PM 200 stack is around 10 times higher than that of data sets from NEXA stack. In order to clarify this difference, the RMSE results for PM 200 stack under mobile condition is labelled on the right axis while the rest of RMSE results from NEXA stack under four different operation conditions are labelled on the left axis using different scales. It can be concluded again from the Fig. 3-8 that, comparing with the RMSE results from SVM, the RVM shows stronger capability on maintaining high precision when predicting after training relatively larger amount of data. Moreover, the RMSE results from NEXA stack under 36A 40°C and 44A 40°C using classic SVM method increase through time, while the RMSE results using modified RVM method remain stable for the entire fuel cell operation time range.

At last, the R^2 results under different conditions are shown in Fig. 3-9. The dotted and the solid lines represent the results from SVM and modified RVM, respectively. Generally, a higher R^2 indicates a better fitting. In addition, if compared among different data sets, a lower R^2 value indicates a more random or non–linear feature of the data set compared with the others. It can be seen from Fig. 3-9 that, for both of RVM and SVM, we have $R^2_{36A 40^\circ C} \approx R^2_{44A 40^\circ C} > R^2_{30A 35^\circ C} > R^2_{PM200} >$ $R^2_{12A 30^\circ C}$. This observation indicates the data sets measured from 12A 30°C for NEXA stack is the most non–linear one, while the data from 44A 40°C or 36A 40°C are least fluctuated comparing with other data sets. Furthermore, from this figure we can see that the R^2 of improved RVM method are always higher than that of classic SVM method for all 5 experimental data sets, which indicate the proposed RVM method shows clearly better fitting results.



Fig. 3-7 MAPE comparison



Fig. 3-8 RMSE comparison



Fig. 3-9 R^2 comparison

3.3.3 Proposed modified RVM vs. original RVM

Furthermore, in order to highlight the prediction accuracy improvements of the proposed self-adaptive kernel RVM method compared to the original RVM in the case of PEMFC aging prediction, the MAPE and RMSE comparison between the results of the two methods have been given in Fig. 3-10a and Fig.3-10b respectively for both fuel cell stacks (NEXA and PM 200) under different operation conditions in the range of 0 - 400h. The shallow grey bars denote the errors of modified RVM and the dark grey bars indicate the errors obtained from the original RVM method. In both MAPE and RMSE comparison cases, a better prediction performance of our proposed method are demonstrated. The results show the modified RVM could achieve at least 15% of accuracy improvement in all tested cases, and could achieve nearly 60% improvement on the MAPE or RMSE errors in some specific cases compared with the original RVM method.

Moreover, the voltage degradation prediction results of all the five data sets from both the modified RVM and the original RVM have been illustrated from Fig. 3-11 to Fig. 3-15. It can be seen clearly from these figures that, the modified RVM has more advantage on presenting the non–linear part of the degradation data during

prediction (*i.e.* predicted values are fluctuated more dynamically with the observed tendencies of the datasets).



Fig. 3-10 MAPE and RMSE comparisons with original RVM





Fig. 3-11 Comparison between proposed modified RVM and original RVM (NEXA 12A 30°C)

For the results of Fig. 3-11, the linear columns have been added into the design matrix, however it seems the prediction improvement is not significant with the appending linear columns in this condition. The improvement of this prediction case (better trend tracking) from the self-adaptive kernel RVM is due to the adaptive kernel. The result getting from the constant kernel (original RVM) make the

prediction curve around 300 hours a little "flat". In Fig. 3-11a the prediction curve around 300 h seems to perfectly predict those data.



Fig. 3-12 Comparison between proposed modified RVM and original RVM (NEXA 30A 35°C)

For results of Fig. 3-12, this couple of comparison is similar with the predicting case shown in Fig. 3-11, from 250 hours to 350 hours, the prediction results from modified RVM is enhanced. This better trend tracking is mainly due to the kernel

changing during prediction, which in turn optimizes the prediction results in this region.



Fig. 3-13 Comparison between proposed modified RVM and original RVM (NEXA 36A 40°C)

As what are shown in Fig. 3-13, the data points of 36A 40°C is the most linear datasets in all tested 5 datasets. Even the original RVM could provide a good prediction. Not to say the prediction results getting from the self-adaptive kernel RVM. It can basically capture all the variation tendencies during prediction.



Fig. 3-14 Comparison between proposed modified RVM and original RVM (NEXA 44A 40°C)

In this two prediction results in Fig. 3-14, the results from original RVM are not very accurate in the prediction in the region from 250-300 hours. Comparing to the original one, the prediction results of modified RVM is more accurate. The kernel width of the modified RVM would change during the prediction case, and make the prediction algorithm have the ability of automatically choose the optimized kernel to deploy the prediction algorithm in different situations.





Fig. 3-15 Comparison between proposed modified RVM and original RVM (PM200)

In Fig. 3-15, the predicted results from the modified RVM are better than the original one, especially from 250-300 hours. The prediction results of the modified RVM also fixed several "predicted peaks" (inaccurate predictions) in the result of the original RVM prediction by introducing the self-adaptive kernel.

3.3.4 Multi-step-ahead prediction analysis of the selfadaptive RVM method

As indicated, the results presented in the previous section correspond to the single– step–ahead prediction. The proposed modified RVM method has also the capability to provide multi–step–ahead prediction results, which will be discussed here. It should be noted that, from our test data sets, the time interval between two data points is around 4 hours. Thus, one prediction step could be considered as 4 hours ahead in time.

In order to demonstrate the capability of multi–step–ahead prediction of our modified RVM method in a general way, multi–step–ahead predictions with 4 different prediction times (2 steps to 5 steps) for all tested fuel cell operation conditions have been performed. The obtained corresponding prediction errors (MAPE and RMSE) are presented in TABLE 3-2 and 3-3 for the prediction results in the time range of 0 - 400h.

As mentioned previously, the time interval between 2 data points is around 4 hours in our test cases. Thus, the results of 1 to 5 step–ahead prediction correspond to a forecast time of 4 hours to 20 hours respectively. It can be seen clearly from the tables that, the accuracy of the prediction decreases when the prediction time increases. However, the 5–step–ahead predictions of the proposed modified RVM are still acceptable in all 5 tested cases if compared with the single–step–ahead prediction results from the original RVM method.

TABLE	3-2
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	12A	30A	36A	44A	
	30°C	35°C	40°C	40°C	PM 200
	(NEXA)	(NEXA)	(NEXA)	(NEXA)	
1-step	0.0049	0.0058	0.0062	0.0057	0.0041
2-step	0.0057	0.0054	0.0075	0.0064	0.0059
3-step	0.0056	0.0062	0.0087	0.0080	0.0075
4-step	0.0055	0.0065	0.0101	0.0089	0.0083
5-step	0.0072	0.0075	0.0113	0.0105	0.0090

MAPE ON MULTI-STEP-AHEAD PREDICTION OF THE MODIFIED RVM

TABLE 3-3

	12A	30A	36A	44A	
	30°C	35°C	40°C	40°C	PM 200
	(NEXA)	(NEXA)	(NEXA)	(NEXA)	
1-step	0.2138	0.2282	0.2247	0.1985	3.5753
2-step	0.2510	0.2168	0.2727	0.2443	4.3814
3-step	0.2545	0.2353	0.3305	0.2959	5.6659
4-step	0.2629	0.2589	0.3707	0.3378	6.3731
5-step	0.3090	0.2928	0.3979	0.3926	7.0437

RMSE ON MULTI-STEP-AHEAD PREDICTION OF THE MODIFIED RVM

In addition, the results comparison from single-step-ahead and 5-step-ahead predictions (4 hours and 20 hours, respectively) are given in figures from Fig. 3-16 to Fig.3-20. It can be seen from these figures that, the 5-step-head prediction results can always represent correctly the non-linear fuel cell voltage degradation feature.





Fig. 3-16 Multi-step-ahead prediction comparison (NEXA 12A 30°C)

In Fig. 3-16, the results from 5-step-ahead prediction is a little left behind around 225 and 275 hours, however in most of the prediction time, the 5-step-ahead prediction could provide nearly the same results with the 1-step-ahead prediction. However, both of the prediction results at the beginning around 75-100 hours are less accurate, this may be due to lack of the training set at the beginning of the prediction.





Fig. 3-17 Multi-step-ahead prediction comparison (NEXA 30A 35°C)

In Fig. 3-17, it seems each of the prediction results is no difference with each other. Both of them could provide good prediction except for the region within 200-250 hours in which the prediction results are a little elevated than the real measured data. However in most of the cases, the prediction results and confidence intervals can provide effective prediction results.





Fig. 3-18 Multi-step-ahead prediction comparison (NEXA 36A 40°C)

In Fig. 3-18, both of the prediction results can prove the good prediction performance, and the confidence intervals are almost containing all the datasets. The result of 5-step-ahead prediction is a little legged behind in some certain time points. However, it seems the 5-step-ahead prediction profile didn't influence its prediction effectiveness in this prediction case.





Fig. 3-19 Multi-step-ahead prediction comparison (NEXA 44A 40°C)

For the prediction results shown in Fig. 3-19, both predictions have a lower accuracy from 175 - 200 hours range. Around 260 and 350 hours the prediction are also less accurate. However in most of other regions, the prediction results are of high accuracy especially in the regions of 100-150 hours and 200-250 hours.





Fig. 3-20 Multi-step-ahead prediction comparison (PM 200)

The 1-step-ahead prediction could provide prediction results with high accuracy in Fig. 3-20. The 5-step-ahead prediction is a little left behind due to much more fluctuated distribution of the points (the data is trained in the unit of mV, not in V, so numerically more fluctuated). However, most part of the prediction results are acceptable without any problem. The predictions of both cases didn't do the prediction of the last point in the RVM program because it's located outside of our pre-set prediction range (450 hours for all datasets).

3.3.5 Subsection summary

In this subsection, we provided an extensively detailed demonstration and discussion of the prediction results from self-adaptive kernel RVM. It can provide better prediction results comparing with the SVM and the original RVM. Moreover, it could still achieve a fairly acceptable prediction accuracy at multi–step–ahead prediction (up to 20 hours in our cases). Comparing with the SVM or original RVM methods in one-step-ahead prediction, the proposed self-adaptive kernel RVM in multi-step-ahead prediction could provide similar prediction accuracy with a much longer forecast time (4 hours vs. 20 hours in our cases).

3.4 Summary

In this section, the self-adaptive kernel RVM has been proposed for the use of PEMFC performance degradation prediction. At the beginning, the kernel trick has been briefly introduced, then the proposed non–linear mathematical approach of Relevance Vector Machine has been developed and illustrated thoroughly, followed by a detailed description of algorithm implementation process. Compared with conventional RVM formulation, two enhancements of the proposed RVM method are proposed and complied:

- Comparing with the all kernel function based design matrix in conventional RVM approach, the design matrix proposed in this paper was extended by appending with non-kernel columns in order to acquire both linear and nonlinear features from the fuel cell degradation data during training;
- 2. An innovative adaptive kernel width determination algorithm, which can iteratively choose the most effective kernel width value from different training data set, has been proposed in order to make training or learning process more intelligent and effective.

The advanced self-adaptive approach of RVM is trained and implemented using experimental voltage degradation data from two different kinds of PEMFC stacks (Ballard NEXA (1.2 kW) / PM 200 (8 kW)). The predicted results of this improved RVM method show great agreements with the experimental results under different operation conditions. In order to demonstrate the effectiveness of the proposed method, the error assessments of prediction results have also been compared with that of SVM method. The results analysis convincingly showed that, the proposed modified RVM could achieve better performance than SVM approach. In general cases, the errors of RVM are 30% - 40% less than that of SVM, specifically in terms of the MAPE and RMSE. Moreover, the prediction results from the proposed modified RVM method are also compared with the results from original RVM. The comparison results indicated clearly that, the proposed modified RVM could achieve higher accuracy and shows higher potential to follow observed non-

linearity. Furthermore, comparisons and discussion between single–step–ahead and multi–step–ahead prediction from the proposed modified RVM are also provided. The results show that the modified RVM can still achieve acceptable prediction accuracy in multi–step–ahead prediction, which could provide up to 20 hours forecast time for proper maintenance planning of the studied fuel cells.

In conclusion, this advanced self–adaptive approach of RVM was demonstrated to have good accuracy and effectiveness to predict the performance variation or degradation of PEMFC systems.

CONCLUSION and PERSPECTIVES

Nowadays, the relatively short lifetime of the PEMFC has been a common issue that impedes it from massive use. Good understanding of PEMFC degradation mechanisms along with accurate prediction model of PEMFC performance loss would clearly facilitate the ability of researchers to overcome this issue. In this thesis, we illustrated a detailed state of the art of degradation mechanisms of PEMFC, as well as a novel data-driven model for long term performance prediction using an improved relevance vector machine (RVM) approach. Specifically in this thesis, we presented:

- An extensively detailed illustration of degradation mechanisms of PEMFC regarding to the impacts from the operation fallacies. The major operation fallacies considered are: the insufficient water management, poor temperature management, gas starvation, fuel contamination and load cycling. The influences were detailed and specifically demonstrated;
- A detailed degradation mechanisms description on different components of PEMFC stack. The degradation mechanisms have been thoroughly illustrated with literature review based on different PEMFC composing components: the membrane, catalyst layers, GDL and bipolar plates;
- 3. PEMFC performance prediction model on two datasets from two stacks using feature extended RVM. The formulation of original RVM has been fully addressed at first, the feature extended RVM was then proposed and illustrated. In the prediction case with two Ballard NEXA 1.2 kW stacks, the proposed RVM could achieve better prediction performance regarding to different prediction results of conventional SVM with different prediction zone;

4. An updated self-adaptive kernel RVM is further proposed to predict the performance of the PEMFC stack based on the datasets of five stacks. The prediction results have been thoroughly compared with the SVM, and the original RVM. From the provided results, it can be concluded that the proposed self-adaptive kernel RVM can achieve better performance compared with other two methods. Moreover, the prediction performance was validated and discussed for multi-step-ahead prediction cases. The results demonstrated that, the proposed updated self-adaptive kernel RVM has clearly its potential to be used in the PEMFC performance prediction.

The future works of this thesis is firstly to do more research regarding to the prediction of the PEMFC performance degradation using self-adaptive RVM, while involves other physical parameters than output voltage. In this thesis, we accomplished the prediction using these five datasets at hand, however, we didn't have the degradation information about the polarization curves or the dynamic operation parameters of the PEMFC stack in the 400 to 450 hours of continuous operation. So we planned to finish this part in the future with the diagnostics of PEMFC once we could have the more detailed dynamic operation information.

Moreover, we would like to complete the physical modelling of the PEMFC performance degradation. Apart from the performance prediction in PEMFC using machine learning method proposed in this thesis, a physical model would be a good counterpart or supplement of our work. In our proposed data driven approach, we only macroscopically take into consideration of the performance drop through time. A physical model of the PEMFC performance degradation would help us microscopically and quantitatively look inside of its degradation mechanisms. This would lead to higher accuracy, and also more effective without the need for training. Physically, for each of the single cell in a stack, it's consisted of the catalyst layers, membrane, GDL and bipolar plates. The degradation of the first three components are more critical than the bipolar plates on influencing the performance of a stack. Respectively, the platinum loss, membrane degradation and carbon corrosion are the most critical issues in each of them. We have been working on the research of

platinum loss and membrane degradation. For the carbon corrosion modelling, we will focus on it after finishing the first two modelling cases.

The preliminary models have been illustrated in the appendix I. and II. Specifically, the appendix I. is about the platinum dissolution, and the appendix II. is mainly about the platinum precipitation in the membrane.

However, based on these two models, we couldn't provide substantial prediction results until now, because both of them are still preliminary models. We are lack of some values of critical parameters in the Pt loss modelling case, or still need the modelling on radical attacks in the membrane degradation case. However, more efforts would make it possible for us to finish these future modelling works.

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APPENDIX I. PLATINUM DISSOLUTION

The dissolution of the nano Platinum particles plays an important role which influences the long term performance of the PEMFC stack. The nano Pt particles are the main constituents of both the catalyst layers on the anode and the cathode side. The dissolution of Pt particles would cause the decreasing of the electrochemistry surface area (ECSA).

As what have been mentioned before, the electrochemical reactions take place in fuel cells on each of the electrode is:

At the anode:

 $2H_2 \rightarrow 4H^+ + 4e^-$

At the cathode:

$$0_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Overall:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The electrochemical reactions happened in the fuel cell would only take place on the reaction sites, known as tripe contact zone. Namely, the membrane, the void and the nano Pt particles. The membrane provides the path for the protons to travel from or to the reaction sites. The void allows the gases to reach the reaction sites. The nano Pt particles would play as a role of catalyst of the electrochemical reactions, from where the electrons detached from the hydrogen molecules would travel through the platinum particles and carbon substrate to produce the electric current.



Fig. a-1 Triple contact zone

The ECSA is proportional to the number of the reaction sites. It is obvious that the smaller the platinum particle is, the more number of the platinum particles would be either in contact with the membrane and the reactant gases. This would directly lead to more reaction sites on the catalyst layer, and so lead to higher ECSA. So in here, the size of the platinum particles is a core factor that determines the value of ECSA.

Generally, three chemical reactions would be involved in the platinum dissolution phenomena: [32]

$$Pt_{(s)} + H_2O_{(aq)} \leftrightarrow PtO_{(s)} + 2H_{(aq)}^+ + 2e^- (U_{eq1} = 0.98V)$$
 (Reaction 1)

$$PtO_{(s)} + 2H_{(aq)}^{+} \leftrightarrow Pt_{(aq)}^{2+} + H_2O_{(aq)}$$
 (Reaction 2)

$$Pt_{(s)} \leftrightarrow Pt_{(aq)}^{2+} + 2e^{-} (U_{eq2} = 1.188V)$$
 (Reaction 3)

According to the Pourbaix diagrams of platinum [99], there are some other ionic species of platinum with higher oxidation states. However, they are not expected to be significant on the electrodes of PEMFC. The equilibrium potential of the two electrochemical reactions are indicated from the Pourbaix diagram and listed behind each of the reaction.

For any of the electrochemical reactions, it is possible to use the Butler-Volmer equation to deduce the reaction rate once the equilibrium potential is acquired. However, in the scenario on the surface of the platinum particle, the equilibrium potential is deviated from the value reported from Pourbaix diagram. This is due to the curvature of each platinum particles, which could cause the equilibrium potential deviated from the reported value (the reported value is tested and measured from the bulk platinum, whose surface is a flat plane).

In order to solve this issue, the Gibbs-Thomson equation could be used to physically and geometrically describe the amount of the deviation of the equilibrium potential on surface of the particles from the bulk material.

From the Gibbs–Thomson equation [100], the chemical potential of the nano platinum particle is inversely proportional to its size:

$$\Delta \mu = \mu_{\text{particle}} - \mu_{\text{bulk}} = \frac{4\gamma V_{\text{m}}}{r}$$
(a-1)

Here γ is the surface energy, V_m is the molar volume of the particle, *r* is the diameter of the particle. μ_{particle} and μ_{bulk} are the chemical potential of the nano platinum particles and bulk platinum, respectively.

So the equilibrium potential would decrease with the increasing of particle size:

$$\Delta U = U_{eq} - U_{particle} = \frac{\Delta \mu}{nF} = \frac{4\gamma V_m}{rnF}$$
(a-2)

where *n* is the number of electrons involved in the interested electrochemical reaction. U_{eq} and $U_{particle}$ are the equilibrium potential of bulk platinum and nano platinum particles, respectively. Based on the Butler-Volmer equation, the rate of reaction 1 is [32]:

$$rate_{1} = k_{1} \left[\exp\left(-\frac{\omega\theta}{RT}\right) \exp\left(\frac{n_{1}(1-\beta_{1})F}{RT}\left(E - U_{eq1} + \Delta U_{PtO}\right)\right) - \theta(10^{-PH})^{2} \exp\left(\frac{-n_{1}\beta_{1}F}{RT}\left(E - U_{eq1} + \Delta U_{PtO}\right)\right) \right]$$
(a-3)

Where the k_1 stands for the rate constant of reaction 1, the ω is the PtO-PtO interaction energy, θ stands for the PtO coverage on the surface of the platinum particles. β_1 is the Butler-Volmer transfer coefficient, E is the electrode potential.

R, T, F is the ideal gas constant, electrode temperature, and the Faraday constant, respectively.

Before looking into the reaction 2, we need to consider reaction 3 first. The rate of the reaction 3 could be deduced as:

$$rate_{3} = k_{3} \max(0, (1 - \theta)) \left[\exp\left(\frac{n_{3}(1 - \beta_{3})F}{RT} \left(E - U_{eq3} + \Delta U_{Pt}\right)\right) \right] - \left(\frac{c_{pt^{2+}}}{c_{pt^{2+}_{ref}}}\right) \exp\left(\frac{-n_{3}\beta_{3}F}{RT} \left(E - U_{eq3} + \Delta U_{Pt}\right)\right)$$
(a-4)

where the k_3 is the rate constant of reaction 3, β_3 is the Butler-Volmer transfer coefficient for reaction 3, $c_{pt^{2+}}$ is the concentration of the platinum ions in contact with the electrode, the $c_{pt^{2+}_{ref}}$ is its reference concentration.

As now for the reaction 2, its reaction rate can be deduced as [32]:

$$rate_2 = k_2 \left(\theta (10^{-\text{PH}})^2 - \frac{c_{\text{pt}^{2+}}}{K_2} \right)$$
 (a-5)

Here the k_2 stands for the rate constant of reaction 2, and K_2 is the equilibrium constant which could be deduced from:

$$K_2 = \exp\left[\frac{F}{RT} \left(n_3 (\mathbf{U}_{\text{eq3}} - \Delta \mathbf{U}_{\text{Pt}}) - n_1 (\mathbf{U}_{\text{eq1}} - \Delta \mathbf{U}_{\text{PtO}}) \right) \right]$$
(a-6)

So now we obtained the rate of reactions regarding to the platinum dissolution phenomenon, however, the material balance equations are also required to describe the platinum dissolution.

Firstly, the diameter of the particle size could be deduced from the reaction 1 and the reaction 3. In both of these reactions, the platinum could be formed and precipitated through the reverse reaction of each of them. That is to say the molecules of PtO could be transformed back to the platinum atoms on surface of the nano particles from the reverse reaction of the reaction 1. At the meantime, the

platinum ions could also be reduced to platinum atoms and precipitated on the platinum particles from the reverse reaction of reaction 3.

The size of the platinum particles could thus change with the rates of both electrochemical reactions mentioned above, and the relationship could be illustrated as:

$$\frac{dr}{dt} = -(rate_1 + rate_3)V_{\rm m_{Pt}}$$
(a-7)

Here, the $V_{m_{Pt}}$ is the molar volume of platinum. The assumption of this equation is that the platinum is transformed from PtO or precipitated from ions only on surfaces of the existing platinum particles, rather than creating new particles. Here are two reasons for this assumption:

- For the pathway of platinum atoms transformed from the molecules of PtO, the PtO is originally created from the atoms of platinum on surface of platinum particles with the reaction 1 once the potential is favored. Then the PtO is covering on surface of the nano platinum particles. So it is reasonable to assume the PtO could be reduced back to the surface platinum atoms of the nano particles;
- 2. For the pathway of the precipitation of platinum from the platinum ions, it is possible that if we only look inside of the reaction equation, the reverse reaction of reaction 3 may have chances to create some new nano platinum particles with the agglomeration of produced platinum atoms. However, it is not electrochemical favorable. As what has been mentioned from eq. a-1, the chemical potential of smaller particles would be higher than the bigger particles. That is to say, the smaller ones are less energetically stable than the bigger ones. Therefore, the pathway of creating new platinum particles from agglomeration of platinum atoms is not energetically favorable, the platinum atoms produced from the reverse reaction of reaction 3 is much more possible precipitating on the surface of other nano platinum particles, and their sizes, get increased as consequence.

The coverage of the PtO could be calculated from this equation:

$$\frac{d\theta_{\rm PtO}}{dt} = \frac{rate_1 - rate_2}{\Gamma} \tag{a-8}$$

where the Γ referred to the number of moles of active sites per unit of platinum area. It is assumed to be constant and could be tested and calculated from a specific charge of 220 μ C/cm² [101] through the electrode cyclic voltammetry test regarding to the hydrogen adsorption. In here, the PtO is produced from the reaction 1 and the reverse reaction of reaction 2.

The balance for the platinum ions is:

$$\frac{dc_{Pt^{2+}}}{dt} = a_c(rate_2 + rate_3)$$
(a-9)

where a_c in here is the specific surface area of the electrode, which stands for the area of the platinum particles per volume electrode.

Summary

In this part, we mainly focused on the platinum dissolution based on three involved reactions. Generally, the platinum dissolution would be influenced by their sizes, interface potential and also the PtO coverage on their surface. The model should have its effectiveness on providing a reasonable predictive results on platinum dissolution and particle size variation over time if the electrode potential is indicated. The particle size variation in here would either cause the change of the activation losses of the PEMFC output performance or the ECSA on the electrodes. However, in order to further finish and validate this model, we need to be acknowledged of the values of some critical parameters. For example, we don't acquire a validated value of the specific surface area (a_c) on electrode. Missing this parameter would lead to an unreliable description on the concentration of the platinum ions, and so to the dissolution or regeneration of the platinum atoms on

surface of the nano particles. In our future work, we can to do some related tests in order to acquire this critical data.

Moreover, it is rather practical to deduce the specific surface area from the electrode platinum loading. The specific area can be calculated with the number of platinum particles per volume electrode and their size distribution. A reliable size distribution of the platinum particles would be 2-5nm [102]. However, we still need to further acknowledge the relationship between the numbers of platinum particles per volume electrode with the platinum loading. This issue would be thoroughly understood in our future work with more literature reviews.
APPENDIX II. PLATINUM PRECIPITION MODEL in MEMBRANE

The platinum ions dissolved from the surface of the electrode, would tend to diffuse into the membrane. In the membrane, the ions would meet the hydrogen crossed over from the anode side of the fuel cell. Then it would be reduced to the platinum atoms and may precipitate in the membrane. Generally, the precipitation would be divided to two stages, the first stage would be the uniform distributed precipitation, and the second stage would be the precipitation in the certain area (Xo plane) in the membrane [103].

1. The first stage precipitation

In this stage of precipitation, the platinum ions dissolved from cathode would diffuse into the membrane and be reduced to the platinum atoms by the crossed over hydrogen in the membrane:

$$Pt_{(aq)}^{2+} + H_2 \rightarrow Pt_{(s)} + 2H_{(aq)}^+$$
 (Reaction 4)

The reduced platinum atoms in the membrane are much smaller than the size of the water clusters in the membrane, so it is reasonable to assume the diffusion coefficient of the reduced platinum atoms D_{Pt} for diffusion in the membrane is the same with the diffusion in the bulk water. So the diffusion time of the small reduced platinum atoms reducing through the membrane would be:

$$t_{\rm diffusion} = \frac{\delta_{\rm membrane}^2}{D_{\rm Pt}}$$
(a-11)

The reduced platinum atoms would be uniformly distributed in the membrane. In fact, for a membrane of NafionTM 112, the membrane would have a thickness of 50μ m, with the $D_{Pt} = 10^{-6}$ cm²s⁻¹, the diffusion time for the platinum atoms through the membrane would be 25s. Comparing with the time scale of the precipitation of the platinum in the membrane, it is much shorter and could be neglected. So it is reasonable to assume that the precipitated platinum atoms would have a uniform distribution in the membrane. The uniformly distributed platinum atoms would agglomerate in the membrane. According to the Smoluchowski equation [104], the concentration of the agglomerated platinum particles in the membrane would be:

$$\frac{dc_{nPt}}{dt} = \frac{1}{2} \sum_{i+j=n} k_{ij} c_{iPt} c_{jPt} - c_{nPt} \sum_{i=1}^{\infty} k_{in} c_{iPt} + J\delta_{n=1}$$
(a-12)

Where the c_{nPt} represents the concentration in the membrane bulk of the platinum particles which contain n platinum particles. δ is the Kronecker delta, J represents the flux of platinum atoms. The k_{ij} stands for the aggregation rate constant between particles containing *i* atoms and *j* atoms:

$$k_{ij} = 4\pi (D_{iPt} + D_{jPt})(r_{iPt} + r_{jPt})$$
(a-13)

$$D_{i\rm Pt} = \frac{D_{\rm Pt}a_{\rm Pt}}{r_n} \tag{a-14}$$

Here, the D_{iPt} and D_{jPt} stands for the diffusion constant of small particles containing *i* or *j* platinum atoms, respectively. The *r* stands for the diameter of the platinum particles.

This aggregation reaction stands for the aggregation of the platinum particles in the membrane. Specifically, the aggregation rate of *n*-atom particles equals to the creating rate of aggregation from other particles, and minus the consuming rate due to aggregation to other particles.

2. The second stage precipitation

The size of the platinum particles in the membrane are thought to be uniformly increased in the membrane. This is due to the diffusion time $t_{diffusion}$ of the platinum atoms in the membrane is quite small comparing with the time scale of hours of the precipitation, and this could cause a relatively uniform distribution of the platinum atoms, which would precipitate on the nano particles. The critical diameter of the platinum particles in the membrane is 2.5nm [103]. The reaction of the crossover gases in the membrane: the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) would start to be non-trivial on the surfaces of the platinum particles when they are beyond the critical size. This means the water would be formed on surface of those "big enough" platinum particles until the hydrogen or the oxygen is depleted in the vicinity of the platinum particles.

This is critical to the platinum precipitation in the membrane because the platinum ions diffused from the cathode side couldn't be transformed to atoms in certain part of the membrane, where the hydrogen are consumed completely. The overall reaction of the HOR and ORR in the membrane is:

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

Two moles of hydrogen would be consumed by one mole of oxygen on surface of the platinum particles. So it is fairly reasonable to assume that the platinum particles tend to precipitate at the location where the flux of oxygen is half of the flux of the hydrogen. [105] This is called the Xo plane, where the platinum particles start to precipitate in the membrane of a long term degradation PEMFC. From the Xo plane to the cathode side, the hydrogen would be depleted because of the HOR on the surface of platinum particles bigger than the critical size (2.5 nm). In this region the platinum ions couldn't be reduced to atoms until they reach the Xo plane, where they precipitate.

The following table lists the parameters for the models of the platinum dissolution and precipitation [32][103]. In fact, more critical parameters are still needed for the validation use, and also, for the evaluation of the compatibility of the listed parameters in the proposed models.

TABLE A-1

PARAMETERS

Parameter	Value	Unit
<i>k</i> ₁	1.36e-11	$mol cm^{-2} s^{-1}$
$\beta_{1,3}$	0.5	
$ ho_{ m Pt}$	21.45	g cm ⁻³
M _{Pt}	195	g mol ⁻¹
ω	30000	J mol ⁻¹
$\gamma_{ m Pt}$	2.37e-04	J cm ⁻²
γ _{PtO}	1e-04	J cm ⁻²
$C_{\rm pt_{ref}^{2+}}$	1e-03	mol cm ⁻³
$ ho_{ m PtO}$	14.1	g cm ⁻³
M _{PtO}	211	g mol ⁻¹
k ₂	3.2e-24	$mol cm^{-2} s^{-1}$
k ₃	3.4e-13	$mol cm^{-2} s^{-1}$
Г	2.18e-09	mol cm ⁻²
a _{Pt}	1.4	Å
D _{Pt}	1e-05	$cm^2 s^{-1}$

Summary

In here, we presented a preliminary model on the platinum precipitation in the membrane. In this model, the precipitation could be divided into two stages. The first one is a homogeneous stage during which the platinum atoms precipitate uniformly in the membrane. In the second stage, the inhomogeneous precipitation would mainly take place in the Xo plane after the particle sizes are beyond the critical size in the membrane.

However, this work is only a preliminary model, based on which we need to further complete this model in order to quantify the degradation of the membrane due to the platinum precipitation. This degradation is mainly caused by the radical attacks created on the precipitated platinum particles. The description of radical attacks in this model could be further completed by introducing the concentration profile of the hydrogen and oxygen crossed over in the membrane into the model. This is because the creation rate of the radicals of hydroxyl and hydroperoxyl are related to the concentration of the crossover gases in the region of the platinum precipitation. We need to do more work regarding to this in the future with more specific literature review on this topic of research.

APPENDIX III. PUBLICATIONS

INTERNATIONAL JOURNALS

- Wu, Y., Breaz, E., Gao, F., & Miraoui, A., A Modified Relevance Vector Machine for PEM Fuel Cell Stack Aging Prediction, *IEEE Transactions on Industry Applications*, Volume 52, Issue 3, pp. 2573 – 2581, 2016, DOI: 10.1109/TIA.2016.2524402;
- [2] Wu, Y., Breaz, E., Gao, F., Paire, D., & Miraoui, A., Nonlinear Performance Degradation Prediction of Proton Exchange Membrane Fuel Cells Using Relevance Vector Machine, *IEEE Transactions on Energy Conversion*, Volume: PP, Issue: 99, 2016, DOI: 10.1109/TEC.2016.2582531.

INTERNATIONAL CONFERENCES

- [1] Wu, Y., Breaz, E., Gao, F., & Miraoui, A., "Prediction of PEMFC stack aging based on Relevance Vector Machine", *IEEE Transportation Electrification Conference and Expo. (ITEC)*, Dearborn, MI, Jun. 14–17, 2015 (oral);
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- [3] Zhou, D., Wu, Y., Gao, F., Breaz, E., Ravey, A., Miraoui, A., "Degradation Prediction of PEM Fuel Cell Stack Based on Multi-Physical Aging Model with Particle Filter Approach", *IEEE Industry Applications Society annual meeting*, Portland, OR, Oct. 2-6, 2016 (oral).