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Development of Platinum-Matrix Electrocatalysts for Ammonia Oxidation

by

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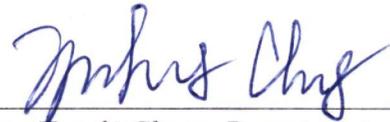
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The undersigned certify that they have read, and recommend to the Faculty of Graduate studies for acceptance, a thesis entitled "Development of Platinum-Matrix Electrocatalysts for Ammonia Oxidation" submitted by Liu Zhou in partial fulfilment of the requirements of the degree of Master of Science.



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Abstract

The ammonia electro-oxidation for production of hydrogen is a promising technology for providing a clean energy source, and simultaneously, controlling ammonia emission into air for environmental sustainability. This work focused on development of high-performance electrocatalysts for ammonia oxidation.

Cyclic voltammetry was used to characterize the electro-oxidation of ammonia and the hydrogen evolution on platinum (Pt) electrode in alkaline solution. The ammonia oxidation reaction mechanism was determined, and the parametric effects, such as ammonia concentration, KOH concentration, electrode rotating speed, temperature, upper switch potential, potential sweep rate and cyclic number, on the electrocatalytic activity of Pt were investigated. Oxidation of ammonia on Pt electrode is controlled by mass-transfer process of ammonia towards the electrode surface. However, the adsorption and desorption of N_xH_y intermediates play important roles in ammonia oxidation and hydrogen evolution. Determination of the ammonia oxidation kinetics depends on a comprehensive consideration of mass-transfer and adsorption/desorption processes. There is an optimal ammonia concentration and KOH concentration to maximize the ammonia oxidation and hydrogen evolution simultaneously. Moreover, the ammonia oxidation current decreases with the increase of electrode rotating speed, resulting from the enhanced detachment of nitrogen-containing intermediates from the electrode surface and, thus, the decreasing amount of the N-H compounds to be oxidized. The ammonia oxidation is accelerated at an

elevated temperature, which is due to either the accelerated diffusion of ammonia from the bulk solution through the diffusive layer to adsorb on the electrode surface (mass-transfer effect) or the rapid electro-oxidation reaction (activation effect). The ammonia electrolytic cell efficiency on Pt could be up to 45%.

In order to further improve the activity of Pt as an electrocatalyst for ammonia oxidation, Pt black electrode was fabricated by electrolytic deposition technique. The electrocatalytic activity and surface morphology of Pt black electrode were characterized by cyclic voltammetry and atomic force microscopy, respectively. Compared with bright Pt, Pt black enhances significantly the electrocatalytic activity for ammonia oxidation. The enhanced activity of Pt black is attributable to both an increased effective surface area of the electrode and an enhanced electron transfer reaction. However, the latter is predominant in the whole ammonia oxidation processes. The electrodeposition parameters affect the electrocatalytic activity of the fabricated Pt black. In particular, there is an optimal depositing potential to maximize the catalytic activity of Pt black. With an increase in deposition time and bath temperature, the electrocatalytic activity of Pt black electrode increases.

It is demonstrated from this research that development of Pt-matrix electrocatalysts improves significantly the ammonia electro-oxidation. It is anticipated that the ammonia electro-oxidation technique provides a promising alternative for development of clean energy supply.

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List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
AFM	atomic force microscope
CV	cyclic voltammogram
DEMS	differential electrochemical mass spectrometry
DFT	density functional theory
GC	glassy carbon
GHG	greenhouse gas
PM	particulate matter
RDE	rotating disk electrode
RRDE	rotating ring-disk electrode
SCE	saturated calomel electrode
SEM	scanning electron microscopy
SERS	surface enhanced Raman spectroscopy
SHE	standard hydrogen electrode
SOFC	Solid oxide fuel cell
e	cell efficiency
F	Faraday's constant
R	gas constant
T	temperature
ΔE	cell voltage
ΔH_{H_2}	lower heating value of hydrogen
ΔH_{NH_3}	lower heating value of ammonia
φ_{NH_3/N_2}	ammonia oxidation potential
φ_{NH_3/N_2}^0	

Chapter One: INTRODUCTION

Increasing greenhouse gas (GHG) emissions worldwide have resulted in a renewed interest in alternative energy technologies such as fuel cells, where hydrogen is the preferred fuel because its use ensures zero GHG emissions. However, switching to the hydrogen energy poses numerous challenges that are related to delivery and storage of hydrogen and catalyst as well as the reactor stability for on-board or on-site generation of hydrogen in an integrated fuel cell system [Yin et al., 2004; Chellappa et al., 2002]. Furthermore, hydrogen generated from hydrocarbon substances, such as, methanol and methane, inevitably includes CO_x ($x = 1,2$) that degrades cell electrode even at extremely low concentrations and introduces the additional source for generation of GHG. It is expected that issues concerning options for hydrogen production, transportation and storage are still to be resolved.

Ammonia is an excellent hydrogen carrier [Wynveen, 1963]. Liquid ammonia contains 1.7 times more hydrogen and boasts a specific energy density 50% higher than liquid hydrogen for a given volume [Strickland, 1984]. Ammonia is also easily condensed at ambient temperature (under 8 bar of pressure), which makes it a good choice for transportation and storage. Furthermore, decomposition of ammonia by electro-oxidation in alkaline media at low overpotentials is NO_x and CO_x free with nitrogen and water as products of reaction [Wasmus et al., 1994]. Therefore, ammonia offers a significant advantage in cost and convenience over pure hydrogen as an alternative fuel for clean energy supply.

On the other hand ammonia is a major pollutant in animal agricultural operation. The trend towards fewer and larger livestock farms has heightened public concern about pollution. Over the past several years, environmental policies related to animal agriculture have switched from the land application of manure to the reduction of air emission from animal waste. Ammonia is by far the most important potential air pollutant. The adverse effects of agricultural ammonia emissions extend to regional, national and global scales. Dramatic increases in atmospheric ammonia emission have been reported in recent years in areas of intensive animal agriculture [Phillips, 1995]. The potential negative impacts of ammonia include eutrophication of surface water, over-fertilization of soils, the decline of aquatic species and serious health problems to humans.

Electrolysis of ammonia for production of hydrogen provides a promising technology for generating a clean energy source, and simultaneously, controlling ammonia emission into air for environmental sustainability. Generally, the ammonia electrolysis depends on development of high-performance electrocatalysts that decreases the over-potential for ammonia oxidation and enhances the hydrogen evolution. This work is aimed at investigating the fundamentals of electrocatalytic oxidation of ammonia on Pt and Pt black electrodes. By developing an advanced understanding of ammonia oxidation process on Pt-matrix electrocatalysts and optimizing the electrocatalyst fabricating parameters and conditions, it is anticipated that, this work will contribute to development of high-performance electrocatalysts for ammonia oxidation and hydrogen generation.

In order to present the above-mentioned work clearly and systematically, this thesis is divided into six chapters, with Chapter 1 giving a brief description of the research background and objectives.

Chapter 2 is a comprehensive review of the electrocatalytic oxidation of ammonia and the electrocatalysts used for ammonia oxidation and hydrogen production. The ammonia electro-oxidation principles were reviewed and the parametric effects on the ammonia oxidation kinetics were analyzed. In addition, the various electro-catalysts for ammonia oxidation and their fabrication techniques were summarized.

Chapter 3 introduced the experimental preparation, the establishment of experiments and the main research approaches as well as result analysis methods employed in this work.

Chapter 4 presents the main results for ammonia electro-oxidation and hydrogen evolution on Pt electrode in alkaline solution studied by cyclic voltammetry. The effects of operating conditions and the electrochemical test parameters, including ammonia concentration, KOH concentration, electrode rotating speed, temperature, upper switch potential, potential sweep rate and cyclic number, on the ammonia oxidation were investigated.

Chapter 5 introduced the fabrication of Pt black electrode by electrolytic deposition technique. The electrocatalytic activity of Pt black electrode was characterized by cyclic voltammetry. Electrodepositing parameters, including depositing potential, temperature and depositing time, were optimized to maximize the electrocatalyst performance. The surface morphology of the fabricated Pt black

electrode was characterized by atomic force microscope (AFM), and the improved catalytic activity of Pt black electrocatalyst was discussed based on determination of the effective surface area and the enhanced electrode transfer reaction.

In the final chapter, the main conclusions were summarized, as well as the recommendations for further work.

Chapter Two: LITERATURE REVIEW

2.1. Physical properties of ammonia

Ammonia (NH_3) is a colorless gas with a pungent odor that is noticeable at concentrations above 50 ppm. It is poisonous if inhaled in great quantities and is irritating to the eyes, nose, and throat in lesser amounts. At normal atmospheric pressure, ammonia has a boiling point of -33.34°C and a freezing point of -77.73°C . It is highly soluble in water, with one volume of water absorbing 1.148 volumes of ammonia at 0°C [Eggen, 1991].

The molecular structure of ammonia is shown in Fig. 2.1. Nitrogen atom and three hydrogen atoms are located in a 3-dimensional space, with an average bond-length of 101.7 pm and bond-angle of 107.8° . The ammonia molecule has a triangular pyramid shape, and belongs to C_{3v} group and the bond energy of N-H bond is 388 kJ/mol. The nitrogen atom in the molecule has a lone electron pair, and ammonia acts as a base, a proton acceptor. This shape gives the molecule an overall dipole moment and makes it polar so that ammonia readily dissolves in water.

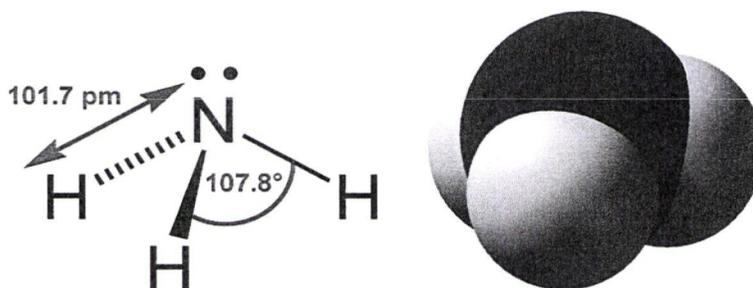


Fig. 2.1. The structure of ammonia

The danger associated with ammonia is that it is explosive when mixed with air in certain proportions, approximately one volume of ammonia to two volumes of air, and is much more so when mixed with oxygen [U.S. Environmental Protection Agency].

2.2. Ammonia emission into air as an environmental pollutant

Ammonia is a major pollutant in animal agricultural operation. Dramatic increases in atmospheric ammonia emission have been reported in recent years in areas of intensive animal agriculture [Phillips, 1995]. Livestock and poultry manure is one of the major sources of ammonia emission. Ammonia is a common by-product of animal waste due to the often inefficient conversion of feed nitrogen into animal product. Nitrogen that is not metabolized into animal protein is excreted in the urine and feces of livestock and poultry where further microbial action releases ammonia into the air during manure decomposition. Inorganic nitrogen in the waste is emitted through several mechanisms including ammonia volatilization, nitrification, denitrification, leaching, and runoff, where ammonia volatilization could generate the highest total loss of nitrogen. In addition, livestock feedlots and cropland spreading also contribute to the significant ammonia emission.

The potential negative impacts of ammonia include eutrophication of surface water, over-fertilization of soils, the decline of aquatic species and serious health problems to humans. Ammonia is typically considered an indoor air quality concern by livestock and poultry producers because the gas often accumulates inside poorly

ventilated animal facilities. Elevated levels of ammonia can have a negative impact on both animal health and production, resulting in reduced body weights in poultry. Furthermore, dramatic increases in atmospheric ammonia emission have been reported in recent years in areas of intensive animal agriculture. The potential negative impacts of ammonia are dramatic. Deposition of atmospheric ammonia can cause eutrophication of surface water, where phosphorous concentrations are sufficient to support harmful algal growth. Nutrient enrichment and eutrophication lead to the decline of aquatic species, including those with commercial values. Sensitive crops such as tomatoes, cucumbers and fruit cultures can be damaged by over-fertilization caused by ammonia deposition if they are cultivated near major ammonia sources. The deposition of ammonia on soils with a low buffering capacity can result in soil acidification or basic cation depletion. In addition to its effects on water, plant and soil systems, ammonia reacts with other compounds to form particulate matter (PM) with a diameter of 2.5 microns or lesser. Several recent community health studies indicate that significant respiratory and cardiovascular problems are associated with exposure to PM.

The trend towards fewer and larger livestock farms has heightened public concern about pollution. Over the past several years, environmental policies related to animal agriculture have switched from the land application of manure to the reduction of air emission from animal waste. Ammonia is by far the most important potential air pollutant. The adverse effects of agricultural ammonia emissions extend to regional, national and global scales.

2.3. Ammonia emission control techniques

Extensive attentions have been paid to control and mitigate the potential negative impacts from ammonia emission in animal agricultural operation [U.S. Environmental Protection Agency]. In US, all states are required to report agricultural ammonia-nitrogen gas emission to the Environmental Protection Agency, and these estimates will be used to in air quality regulations. To respond to this need, the “Partnership in Understanding and Abating Ammonia Emission from Wisconsin Dairy Farms” was created in March 2004. The research performed by the partnership has been focused on reducing ammonia emission by some key management practices, such as remove excess protein from the cow’s diet, improve manure handling and storage, and incorporate manure in the field. The researchers in Minnesota tried to control ammonia emission by developing impermeable covers for the manure storage. Their results showed that the biofilter or biological effect can be more significant than the physical barrier effect since the straw provided larger reduction in gaseous emission than the geotextile cover. The geotextile cover may be useful as a barrier between the manure and the straw, and might also keep the straw from sinking under some specific conditions. In Virginia, researchers developed two different strategies to limit ammonia emission from animal production operations. The pre-excretion strategies manipulate animal diets through the addition of acid-producing phosphorous sources and/or calcium chloride and calcium sulfate to feed so that the amount of nitrogen that ends up in manure can be minimized. The post-excretion strategies include the treatment or

management of manure. One popular method is to apply chemical amendments to manure where animals are housed to reduce ammonia generation. In UK, the Code of Good Agricultural Practice recommends some potential techniques to reduce ammonia emission. It is suggested that the greatest potential to reduce ammonia emission involves measures on land-spreading of manure and slurry and storage. Covering slurry stores using specially manufactured covers could also be the alternative to control ammonia emission.

It is seen from the American and Britain's practices that the ammonia-control technologies can be generally classified into two categories: add-on control devices and pollution prevention techniques. The typical example of the first category is wet scrubber, specifically the packed tower scrubber, which has been successfully used to control ammonia emissions, demonstrating control efficiencies up to 99% [Buonicore and Davis, 1992; Cooper and Alley, 1986]. Condensers are also used to remove ammonia by converting the gas to a liquid.

With respect of the second technology, ammonia recycle, in which the ammonia is retrieved from the exhaust gas stream and returned to the process, is a common pollution prevention method. The recycling method is often used in the manufacture of fertilizers, where ammonia is a feedstock and the implementation of recycling benefits the process in addition to controlling emissions.

In the case of fossil fuel combustion where ammonia is emitted as a result of the controls implemented to reduce nitrogen oxide emissions, careful application of the nitrogen oxide control methods will limit the amount of ammonia that will slip through

the process. With regards to ammonia leakage, good management practices can reduce the amount of ammonia escaped. For those leaks that cannot be prevented, capture devices such as hoods may be used to collect the ammonia gas, which is then conveyed to a control device for treatment [Gomaa and Cindric, 1991; Epperly and Broderick, 1988].

Table 2-1: Control Efficiencies for Wet Scrubbers Applied to Livestock Facilities [Buonicore and Davis, 1992].

Equipment	Percent Reduction	Problems Encountered
Wet scrubber on the exhaust emitted from a swine building	Odor – 88%	Sludge created from collected dust caused difficulties in recirculating the scrubbing water
Wet scrubber	Not given	Problems with spray nozzles clogging when recycled water and biological treatment were used
A cross-flow packed-bed wet scrubber on a big containment building	Ammonia - 8-38% Odor- 82%	None identified
A packed-bed dry scrubber containing zeolite (clinoptilolite) used on a poultry house	Ammonia - 45% at first, but then decreased to 15% in 18 days	None identified
Soil filter system on a swine confinement building	Ammonia – 52%-78% organic constituent - 86%	None identified
0.25-acre sand filter field for air scrubbing on a poultry manure composting operation	Ammonia – 95-99% Odor – 30-82%	None identified

Table 2-1 summarizes the specific application of wet scrubber for ammonia emission in livestock facilities and the individual control efficiencies. It is seen that the performance of wet scrubber depends on the locations and facilities to be applied.

From the comprehensive review of the worldwide practices in ammonia emission reduction in agricultural production, it is apparent that the current work has been focused on improving food and development of physical methods. None of them attempts the value-added processing to transfer the animal ammonia waste into valuable products while reducing the ammonia emission into air.

2.4. Ammonia as a hydrogen source

2.4.1. Basic facts

Ammonia is an excellent hydrogen carrier [Wynveen, 1963]. Liquid ammonia contains 1.7 times more hydrogen and boasts a specific energy density 50% higher than liquid hydrogen for a given volume [Strickland, 1984]. Ammonia is also easily condensed at ambient temperature (under 8 bar of pressure), which makes it a good choice for transportation and storage. Furthermore, decomposition of ammonia by electro-oxidation in alkaline media at low overpotentials is NO_x and CO_x free with nitrogen and water as products of reaction [Wasmus, 1994]. Therefore, ammonia offers a significant advantage in cost and convenience over pure hydrogen as an alternative fuel for clean energy supply.

Some typically developed techniques for conversion of ammonia into hydrogen have been introduced as follows.

2.4.2. Ammonia cracker

Hydrogen can be released from the ammonia molecule by shifting the formation reaction back to the elements [Kordesch et al., 2000]:



The formation reaction of ammonia is exothermic. For the industrial importance of ammonia, its equilibrium data has been available since the beginning of the century for a wide range of temperature and pressure [Larson and Dodge, 1923]. According to this data, the equilibrium of the equation on the right side at temperatures exceeding 500 K (low pressure provided). However this equilibrium is not achieved due to bad kinetic properties and high activation energies. So, an excellent catalyst is necessary, and extensive studies all around the world have already been done based on several different approaches [Yoshida and Sasaki, 1994; Choi and Jung, 1997].

Extensive studies have been conducted at University of Technology of Graz to develop a commercial nickel oxide catalyst (on aluminum oxide), treated with ruthenium salts, which was chosen to make electrically heated tube cracker [Faleschini et al., 2000]. In the cracker, ammonia is converted to nitrogen and hydrogen, and the

higher the temperature, the more ammonia is converted. The upgraded, plate designed reformer is shown in Fig. 2.2. It was heated by burning a hydrogen-enriched gas coming from an alkaline fuel cell and was fitted with ten temperature sensors. One plate like the one shown in the figure could produce enough hydrogen for continuous operation of a 2 kW fuel cell.

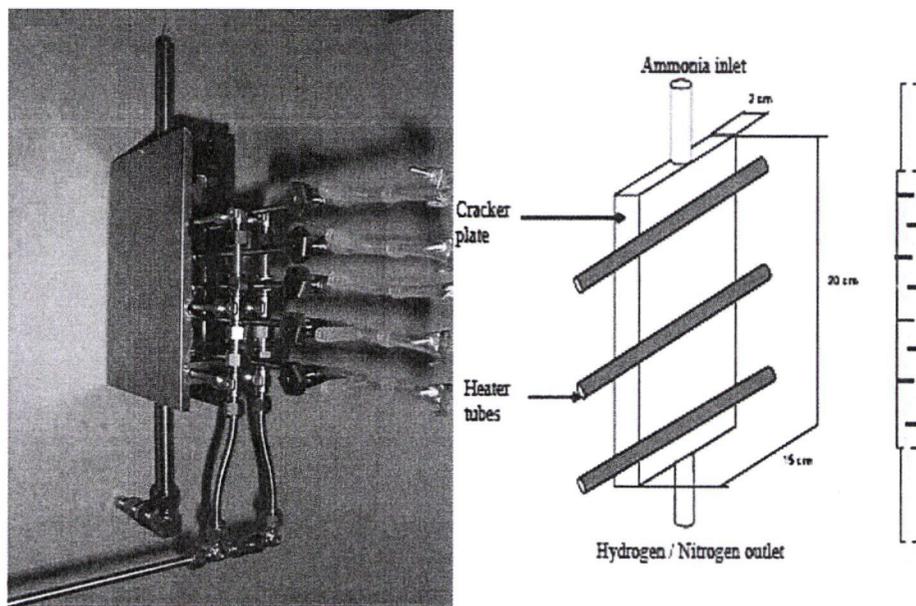


Fig. 2.2. Ammonia Reformer Prototype. This plate-type reformer is heated by hydrogen and supplies hydrogen for a 2 kW fuel cell system [Faleschini et al., 2000]

2.4.3. Ammonia as fuel in solid oxide fuel cells

Solid oxide fuel cells (SOFC) are attractive fuel cell concepts because of their ability to accept a range of fuels, other than pure hydrogen. SOFC conventionally run at temperatures above 500°C (typically 800–1000°C), and one of the advantages of this is that the cracking process, necessary to free the hydrogen from the fuel, and the

generation of electricity can be combined. In other words ammonia may be directly input into the SOFC without any pre-treatment [Wojcik et al., 2003].

The overall reaction for complete combustion of ammonia is



In the solid oxide fuel cell, oxygen is transported through the solid electrolyte (typically yttria stabilized zirconium) from the cathode to the anode.

The desired anodic reaction for ammonia is



The corresponding cathodic reaction is the reduction of oxygen from air:



The structure of a iron-based silver cell is shown in Fig. 2.3. To determine the effectiveness of catalyst in activating ammonia, a comparison in cell performance was made using ammonia and also hydrogen as the fuel. The results obtained on a platinum anode are given in Fig. 2.4, which compares the cell voltage using ammonia as a fuel with that using hydrogen as fuel at the various temperatures. It is seen that ammonia gave quite similar performance to hydrogen. Apparently, ammonia provides a potential

fuel alternative in solid oxide fuel cell applications.

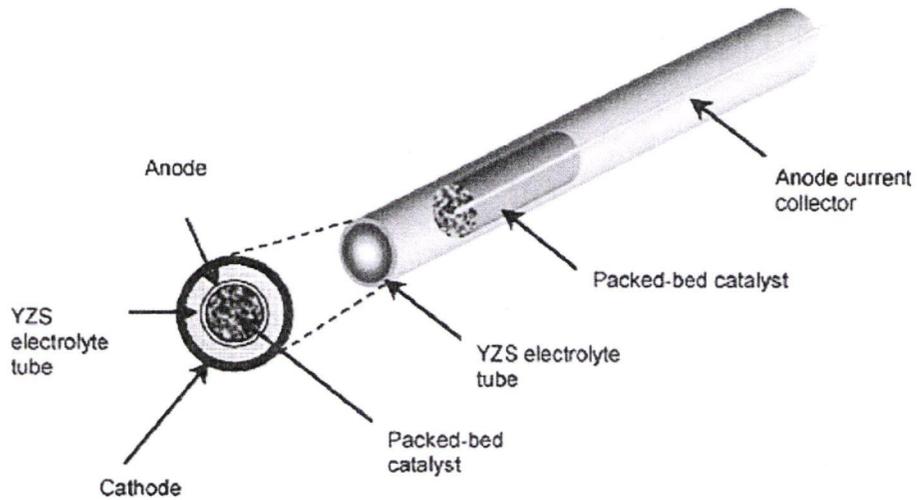


Fig. 2.3. A schematic drawing of the fuel cell structure employed showing the packed bed catalyst in situ in the electrolyte tube [Wojcik et al., 2003].

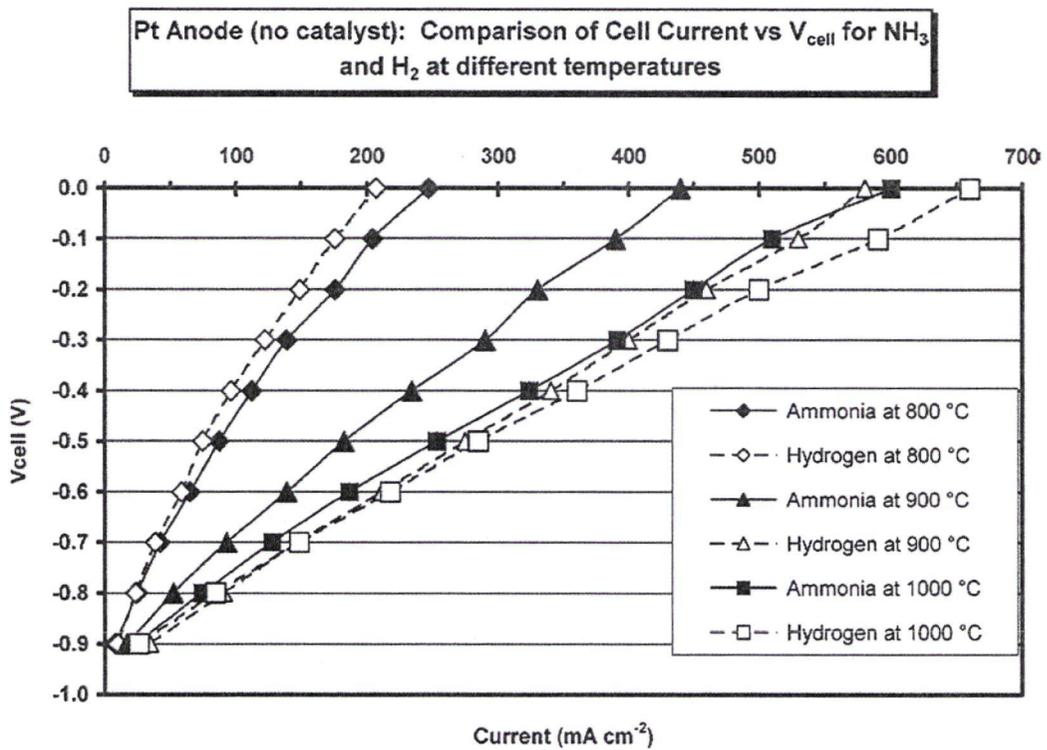
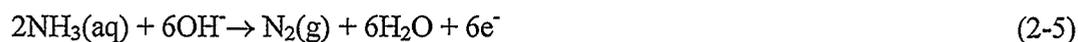


Fig. 2.4. Comparison of ammonia and the equivalent hydrogen fuel at different temperatures in solid oxide fuel cell [Wojcik et al., 2003].

2.5. Ammonia electro-oxidation

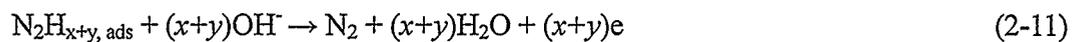
The ammonia electro-oxidation for production of hydrogen provides a promising technology for creating the alternative, clean energy source, and simultaneously, controlling ammonia emission into air for environmental sustainability. The ammonia electro-oxidation reaction can be coupled with the hydrogen evolution reaction for the production of high-purity hydrogen in an alkaline electrolytic cell [Vitse et al., 2005]:



At 25°C the ammonia oxidation potential is -0.77 V (vs. standard hydrogen electrode, SHE), only 0.06 V less negative than the value of -0.83 V (vs. SHE) for hydrogen evolution in alkaline solution [Simons et al., 1969]. Therefore, thermodynamic values are much in favor of the production of hydrogen coupled to the ammonia electro-oxidation compared to hydrogen production by electrolysis of water, for which the theoretical cell voltage is 1.223 V. The advantage of this process is its ease of integration with renewable energy (electricity) sources. Because the energy consumption is low, the cell could operate with renewable energy.

2.5.1. Mechanism of the ammonia electro-oxidation

Electro-oxidation of ammonia to generate nitrogen and water has been investigated not only for fuel cell applications [Oswin and Salomon, 1963; Gerischer and Mauerer, 1970], but also for electrochemical sensing of ammonia [Mishima et al., 1998] and for industrial waste water treatments [Marinčić and Leitz, 1978]. Several mechanisms have so far been proposed for the ammonia oxidation on noble metals such as platinum [Oswin and Salomon, 1963]. A recent study by means of differential electrochemical mass spectrometry (DEMS) [Gootzen et al., 1998] and surface enhanced Raman spectroscopy (SERS) [De Vooy et al., 2001] supported the following mechanism proposed by Gerischer and Mauerer [Gerischer and Mauerer, 1970]:



where $x = 1$ or 2 , $y = 1$ or 2 .

The mechanism involves the dehydrogenation step of $\text{NH}_{3, \text{ads}}$ to N_{ads} and the recombination of two $\text{NH}_{x, \text{ads}}$, where partially dehydrogenated species of $\text{NH}_{2, \text{ads}}$ and

NH_{ads} are active intermediates to give the final product of N_2 .

Despite the various proposed mechanisms describing the ammonia oxidation process, the reaction mechanism of anodic oxidation of ammonia is not yet completely understood, especially for the intermediate and N_2 formation step. For example, De Vooy et al. [De Vooy et al., 2001] have revealed that N_2 is hardly produced on the transition metals which have high affinity for N_{ads} calculated by the density functional theory (DFT) method because the active intermediates are not stable and then N_{ads} is formed at low potential. Endo *et al.* [Endo et al., 2005] used the platinum rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) techniques to investigate the anodic oxidation of ammonia in alkaline solutions. The ammonia oxidation current on the rotating platinum disk was confirmed not to increase but to decrease with increasing the rotation rate at 25°C- 60°C. The in-situ ring electrode detector gave two kinds of signals for the electroactive species transported from the disk electrode engaged in ammonia oxidation; one can be again reduced and another can further be oxidized on Pt ring. These results suggested that at least some of the intermediates involved in ammonia oxidation on Pt may not be strongly adsorbed but be detached from the surface regions.

2.5.2. Electro-catalysts for ammonia oxidation

2.5.2.1. Pure metal electro-catalysts

Metal platinum has been regarded as one ideal electrocatalyst for ammonia oxidation [Endo et al., 2004]. Vidal-Iglesias et al. [Vidal-Iglesias et al., 2003] have investigated the ammonia oxidation using Pt single crystal electrodes and found that Pt could catalytically oxidize ammonia in alkaline solution. Furthermore, it was pointed out that the ammonia oxidation takes place almost exclusively on the (100) surface at Pt, indicating the potential difference of electrocatalytic activities of the various oriented crystalline surfaces on ammonia electro-oxidation.

In addition to Pt, several noble metals have been considered as potential catalysts. De Vooy et al. [De Vooy et al., 2003] studied the electro-activity of ammonia oxidation on platinum, palladium, rhodium, ruthenium, iridium, copper, silver and gold electrodes, and found that the activity in the selective oxidation of ammonia to N_2 is related to the nature of the species at the electrode surface: the electrode is active if NH_{ads} (or $NH_{2,ads}$) is present and deactivates when N_{ads} is present. The potential at which NH_{ads} or N_{ads} is formed is metal-dependent. The observed trend in the strength of adsorption of N_{ads} is $Ru > Rh > Pd > Ir > Pt \gg Au, Ag, Cu$. This trend corresponds well with the trend observed in the calculated heat of adsorption of atomic nitrogen, with Ir being an exception. Platinum is the best catalyst for this reaction because N_{ads} is formed at a higher potential, compared to Ru and Pd, but seems to stabilize NH_{ads} rather well. Gold, silver, and copper do not form NH_{ads} or N_{ads} , and show only an activity when the surface becomes oxidized. Most metals produce oxygen-containing products, like NO and N_2O , at potentials where the surface becomes oxidized.

It has been found [Oswin and Salomon, 1963; Katan and Galiotto, 1963] that significant oxidative current density can be obtained from the oxidation of ammonia on Pt, but this electrode process is far less reversible, with a high anodic overpotential. Apart from the fact that a large anodic overpotential is needed to drive ammonia oxidation reaction, the deactivation of Pt catalyst is rapid at higher current densities [Gerischer and Mauerer, 1970; Vidal-Iglesias et al., 2003]. Therefore, ammonia electro-oxidation requires development of improved catalysts.

The electro-oxidation of ammonia in KOH solution was also reported to be conducted on Pt-black electrode, where a combination of cyclic voltammetry with on-line mass spectroscopy analysis was used to characterize the electrocatalytic activity [McKee, 1969]. It was found that all compounds investigated in this study formed adsorbates on Pt electrode. The adsorbates can be reduced to ammonia and oxidized to nitrogen.

A study on bulk iridium electrodes [Ge and Johnson, 1995] showed that iridium has a quite high electrocatalytic activity toward ammonia oxidation. However, the current densities observed on the catalyst were relatively low (less than 1 mA/cm^2).

There have been reports about the ammonia electro-oxidation on nickel [Cooper and Botte, 2003] and titanium [Vitse et al., 2004] as electrocatalysts. Fig. 2.5 shows the cyclic voltammograms (CV) performance of a $1 \text{ M NH}_3/1 \text{ M KOH}$ solution using the Raney nickel/platinum catalyst. The large peak near -0.2 V on the plot confirms activity of the catalyst on the reaction. The curves shown on the plot are actually the final 5 cycles out of 50 performed by the CV test; this shows the staying activity of the catalyst

after many cycles, and the fact that the curves are so close together may indicate that deactivation by N_{ads} on the catalyst is at a minimum.

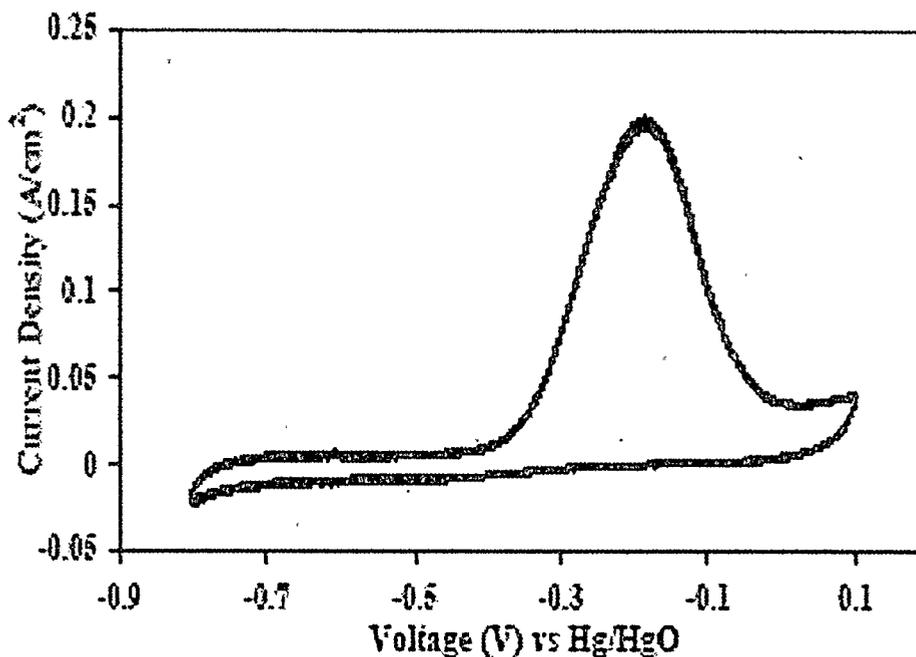


Fig. 2.5. Cyclic voltammetry performance of 1 M NH_3 / 5 M KOH at a scan rate of 10 mV/s on a Raney nickel-Pt electrode at 25 °C [Cooper and Botte, 2003].

Vitse et al. [Vitse et al., 2004] acquired platinum layer with good adherence on titanium substrate and found that with a preliminary anodization of titanium substrate (at 5 V vs. SHE), the amount of platinum deposited was significantly lower and so was the catalytic effect on ammonia (Fig. 2.6). Fig. 2.7 shows that the Ti/Pt electrode is activated by ammonia dissolved in a potassium hydroxide electrolyte. Interestingly, a reduction peak was observed around -0.4 V (SHE), which disappeared as the electrode activation took place. Such peak was more pronounced on pre-anodized Ti/Pt electrodes (Fig. 2.6) and was not observed on platinized platinum substrate.

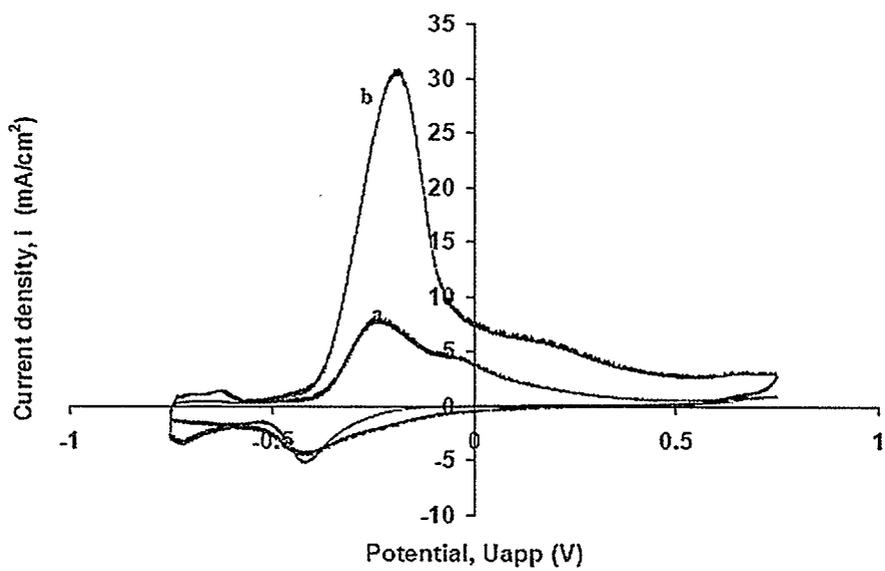


Fig. 2.6. Cyclic voltammety of Ti/Pt electrode in 1M NH₃, 5 M KOH. Sweep rate: 10 mV/s. Reference electrode: Hg/HgO. a- anodization of Ti substrate before deposition, b- no anodization of the substrate [Vitse et al., 2004].

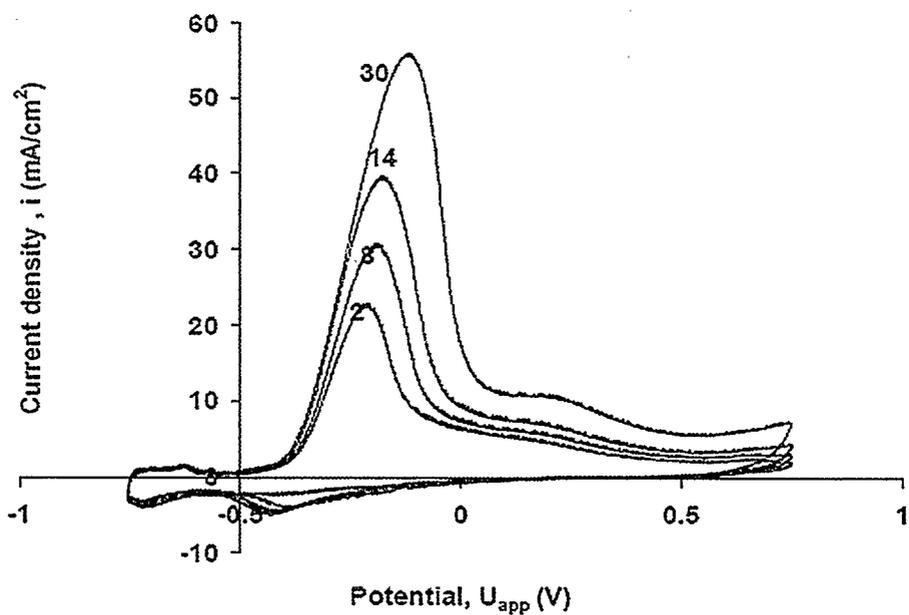


Fig. 2.7. Cyclic voltammety of Ti/Pt electrode in 1M NH₃, 5 M KOH. Sweep rate: 10 mV/s. Reference electrode: Hg/HgO. Acitvation of the electrode with time (2, 8, 14 and 30 cycle) [Vitse et al., 2004].

2.5.2.2. Binary and triple alloy electrocatalysts

Metal alloys, metal oxides and bimetallic or even triple alloy electrocatalysts have been reported to show higher activity towards ammonia oxidation compared to monometallic catalysts. Endo and coworkers [Endo et al., 2004] fabricated various Pt-Me (Me = Ir, Ru, Ni or Cu) binary alloys on a glassy carbon (GC) substrate by thermal decomposition and conducted the cyclic voltammogram measurements to characterize the Pt-Me as electrocatalysts for ammonia oxidation in KOH solutions. It was shown in Fig. 2.8 that, on the solid solutions of $\text{Pt}_{1-x}\text{Ir}_x$ ($0 \leq x \leq 1.0$) and $\text{Pt}_{1-x}\text{Ru}_x$ ($0 \leq x \leq 0.6$), ammonia oxidation began at a lower potential (-0.6 V vs. Ag/AgCl) than on pure Pt by about 0.1 V, indicating the lower energy barrier to overcome for ammonia oxidation on binary alloys than Pt. The saturated current density at a high oxidation potential was apparently higher on $\text{Pt}_{1-x}\text{Ir}_x$ ($x \leq 0.8$) or $\text{Pt}_{1-x}\text{Ru}_x$ ($x \leq 0.4$) than on Pt, indicating a higher electrocatalytic activity of the Pt-Me electrocatalysts than Pt. Furthermore, the results also suggested a positive cooperation of Ir and Ru with Pt in the ammonia electro-catalysis. The reason that Ir and Ru enhance the catalytic activity might be explained by their activity at the dehydrogenation steps of NH_3 at a lower potential, at which ammonia oxidation can never start on the surface of pure Pt. On the other hand, Ni added as a solute to Pt contributed to lower current density with x in $\text{Pt}_{1-x}\text{Ni}_x$ ($0 \leq x \leq 0.7$) and did not lower the starting potential of ammonia oxidation at all. $\text{Pt}_{0.5}\text{Cu}_{0.5}$ and $\text{Pt}_{0.67}\text{Cu}_{0.33}$ alloys showed almost the compatible activity inferior to Pt (Fig. 2.9). Thus, the alloying of Pt-Ni and Pt-Cu will not lead to the significant

improvement in electro-catalytic activity or ammonia oxidation.

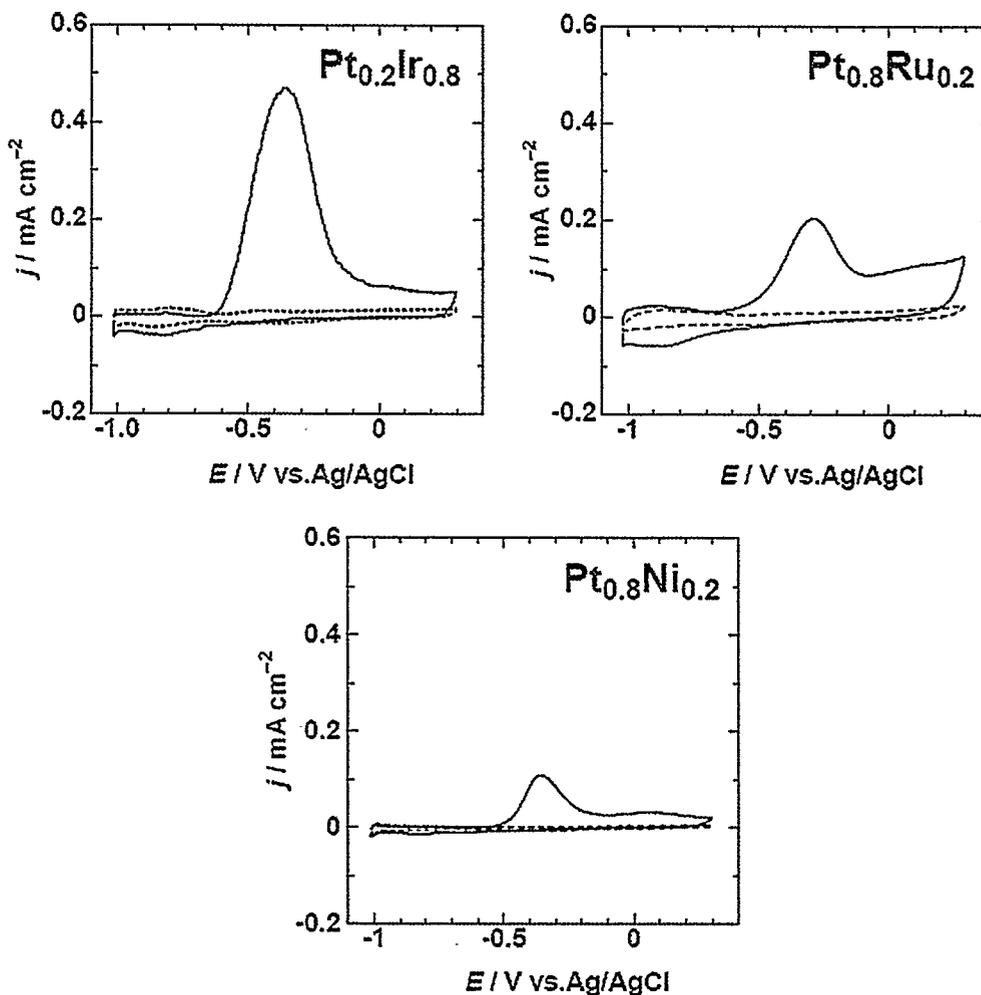


Fig. 2.8. Typical cyclic voltammograms of $\text{Pt}_{0.2}\text{Ir}_{0.8}$, $\text{Pt}_{0.8}\text{Ru}_{0.2}$ and $\text{Pt}_{0.8}\text{Ni}_{0.2}$ in the presence (solid) and the absence (dashed) of $1\text{M NH}_3 + 1\text{M KOH}$ aqueous solution at 25°C . Scan rate: 10mVs^{-1} [Endo et al., 2004].

In addition, co-deposited Pt-Ru electrocatalysts with a low percentage of Ru (15 wt%) have been reported to show a higher activity than platinum black electrode at a lower overpotential [Giner and Moser, 1972]. However, the loading of noble metals used (up to 51 mg cm^{-2}) prohibits the use of such technology from an economical point of view.

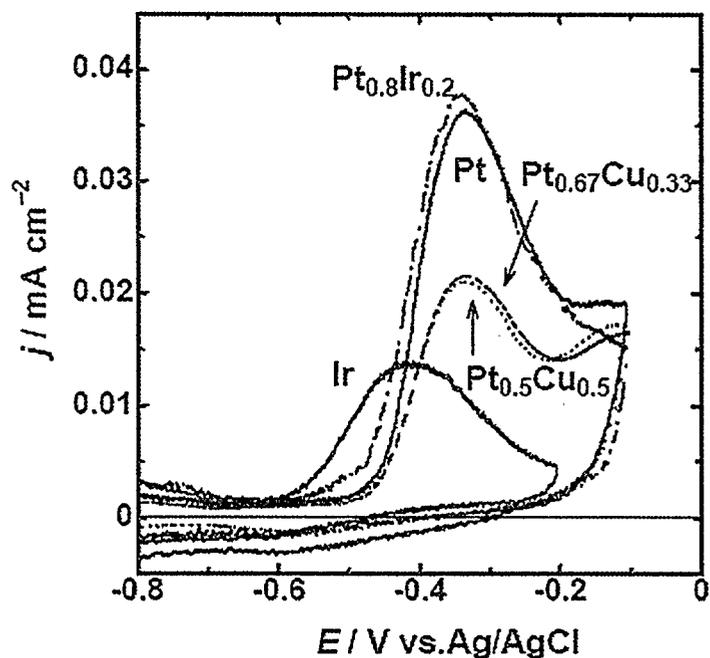


Fig. 2.9. Cyclic voltammograms of Ir, Pt_{0.8}Ir_{0.2}, Pt_{0.5}Cu_{0.5} and Pt_{0.67}Cu_{0.33} electrodes in 0.1M NH₃+1M KOH aqueous solution. Scan rate: 1mVs⁻¹ [Endo et al., 2004].

Vitse et al. [Vitse et al., 2005] used electrolytic deposition technique to prepare low-loading Pt-matrix electrocatalysts for ammonia oxidation. The influence of the electrodeposited secondary metals (Ru or Ir) on the efficiency of the electrolytic cell was investigated. The main results presented in Fig. 2.10 show that Pt–Ir electrocatalyst showed the highest activity toward ammonia oxidation and the lowest cell voltage for ammonia electrolysis. Significant current densities were obtained (above 100 mA/cm²) during electrolysis testing at relatively low metal loading, low cell voltages, and high cell efficiencies. The catalyst stability was also characterized. It is found that the reaction intermediates such as blocking the active surface of electrocatalyst could be reduced back to an active species toward sustainable nitrogen production.

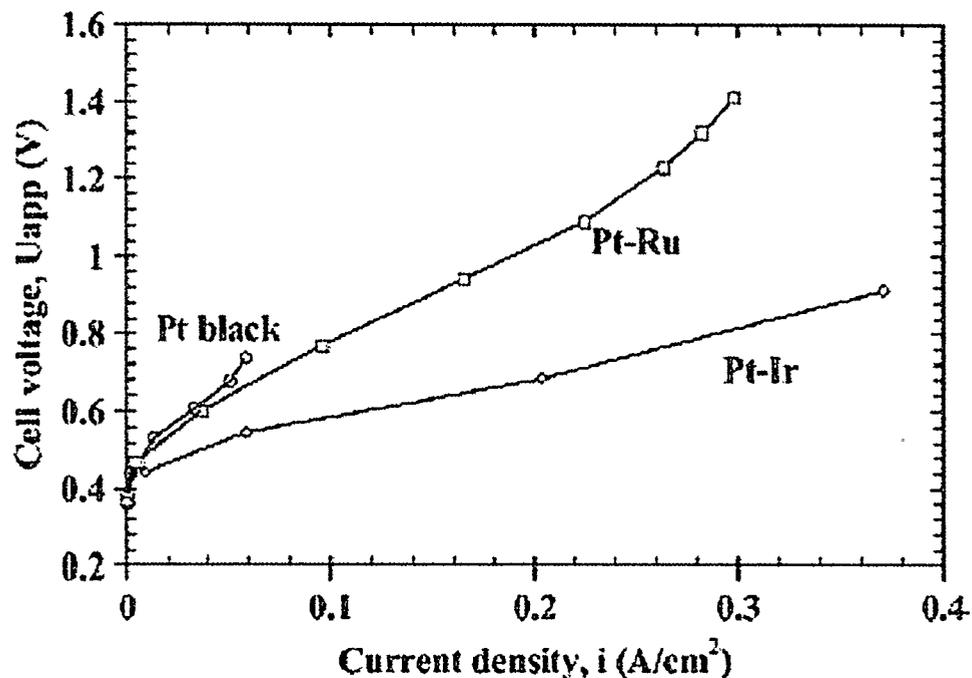


Fig. 2.10. Polarization curves for the ammonia electrolytic cell. Experiments carried out at 60°C in 1M NH₃ and 5M KOH. Cell voltages as low as 0.3V are observed when Pt-Ir is used as an anode [Vitse et al., 2005].

In addition to Pt-matrix binary alloy electrocatalysts, other metals have also been used for ammonia oxidation. Donten et al. [Donten et al., 1997] investigated the electro-oxidation of ammonia at the Ti/TiO₂/RuO₄ electrode using voltammetry, coulometry, potentiometry and numerical simulation. It was found that the major product of electro-oxidation was elementary nitrogen and nitrate was a minor product. NH₄⁺ is not electroactive at the oxide electrode. Since protons are formed in the course of the electrode reaction, incoming ammonia is transformed to NH₄⁺ and therefore the flux of ammonia to the electrode surface is strongly depressed in solutions containing no excess of hydroxide ion. Amines were electro-oxidized to a variety of compounds.

Both ammonia and amines strongly adsorb on the electrode surface. Height of the anodic voltammetric peaks of both ammonia and simple amines was found to be linearly dependent on substrate concentration in a wide milli-molar range.

Electrocatalytic activity of Ni–Pt binary alloy electrodes fabricated by electrolytic deposition for oxidation of ammonia was investigated by cyclic voltammetry and surface analysis techniques [Yao and Cheng, 2007]. The parametric effects, including ammonia concentration, KOH concentration and temperature, on ammonia electro-oxidation on Ni–Pt electrode were investigated. It is found that electrocatalytic activity of the fabricated Ni–Pt electrode with only 1 mg cm^{-2} of Pt loading for ammonia oxidation is comparable to that of pure Pt electrode. With the increases in Pt loading concentration on Ni surface, the catalytic activity for ammonia oxidation further increases. The NH_3 adsorption then occurs at the active spots that are associated with the deposited Pt on Ni surface. With the increase of Pt loading concentration, the Pt distribution is more uniform and the size of Pt particles becomes smaller within the range of nano-scale, resulting in the significant increase of total active area for NH_3 adsorption and further oxidation. Fabrication by electrolytic deposition of Ni–Pt binary alloy electrode could be a promising alternative for development of low-cost, high-performance electrocatalyst for electro-oxidation of ammonia.

2.6. Perspective of ammonia electro-oxidation for production of hydrogen

Electro-oxidation of ammonia to generate hydrogen undoubtedly provides a promising alternative for clean energy supply, and simultaneously, maintains the environmental sustainability. However, commercialization of the technology is facing several technical challenges listed as follows:

Electrocatalysts: It is anticipated that development of high-performance electrocatalysts is essential to commercialization of ammonia oxidation technology. To date, the high electrocatalytic activity and service stability of Pt for ammonia oxidation have not been substituted by other candidate metal electrocatalysts. However, economic consideration drives development of other metal-matrix Pt-modified electrocatalysts, such as Ni-Pt electrocatalyst. Furthermore, optimization of electrolytic deposition condition and parameters will fabricate low-load high-performance electrocatalysts, with the improved size and distribution of secondary metal particles (such as Pt particles) and surface roughness of the electrocatalyst.

Substrate: As discussed, cheap and reliable substrate materials with doping of highly active secondary metal particles ensures the economic competition of the electrocatalysts. In addition to cost, the substrate materials must also be capable of maintaining stability in alkaline solution.

Electrocatalyst fabrication: Electrolytic deposition technique is capable of adjusting the depositing condition and parameters to optimize the property and performance of the fabricated electrocatalysts. The key consideration during electrolytic deposition is to control the nucleation and growth of secondary metal nuclei, ensuring uniformly distributed, nano-scaled electroactive particles formed on the substrate surface.

Chapter Three: EXPERIMENTAL PROCEDURES

3.1. Material and electrode

The platinum rotating disk electrode (RDE) with a radius of 0.25 cm (purchased from PINE Instrument) was used in characterization of electrocatalytic oxidation of ammonia. The RDE was consequently polished with 9 μm , 3 μm , 1 μm and 0.05 μm Al_2O_3 polishing suspension (BUEHLER), and then cleaned by ethanol and deionized water.

3.2. Fabrication of Pt black electrode

Electrolytic deposition technique was used to fabricate the Pt black electrode. A platinum rod with a diameter of 0.13 cm (purity > 99.999%, VWR Chemicals) was soldered to a copper wire and mounted by epoxy (BUEHLER) at 60°C for 90 minutes. The electrode was consequently polished with 9 μm , 6 μm , 3 μm and 1 μm Al_2O_3 polishing suspension (BUEHLER), and then cleaned by ethanol and deionized water.

The bath solution for Pt black electrolytic deposition was prepared with 4 mM H_2PtCl_4 (ACRÖS Organics) + 1 M HCl (analytical reagent, BDH Inc.). During electrolytic deposition, the prepared Pt rod electrode was used as cathode, and pure Pt wire (VWR Chemicals) as anode. The deposition was controlled potentiostatically, with adjustment of depositing potential, temperature and time.

3.3. Solutions

The test solutions for characterization of electrocatalytic activity of Pt and Pt black electrodes were prepared with ammonium hydroxide (extra pure, ACROS Organics), potassium hydroxide (analytical reagent, BDH Inc.) and distilled water (Easy pure RF/UV ultra pure water system, $R > 18 \text{ M}\Omega$), saturated with high-purity nitrogen gas. The concentration of each component was adjusted to investigate the parametric effects.

3.4. Measurements of cyclic voltammograms

Cyclic voltammetry was used to characterize the activity of electrocatalysts for ammonia oxidation. A three-electrode cell (Fig.3.1.) was utilized to measure cyclic voltammograms (CV) through a Solartron 1280C electrochemical system or a PAR Model 263 potentiostat. The platinum RDE or Pt black electrode was used as working electrode, a platinum plate as counter electrode and a saturated calomel electrode (SCE) as reference electrode. CV was measured in ammonia + KOH solutions with the various concentrations. The potential was scanned at a sweep rate of 5 mV/s. The RDE rotation was controlled through a PINE Analytical Rotator system. To investigate the influence of Pt electrode pre-treatment on CV behavior, cathodic polarization of the electrode was applied at -1.3 V for 1 minute and 5 minutes.

Prior to and during tests, the solutions were purged with high-purity nitrogen gas (99.999%). All the tests were performed at ambient temperature with the exception that the effect of temperature was investigated. The temperature of the solution was controlled through an OMEGA LHS-730 series digital hot plate/stirrer.

3.5. Electrolytic cell polarization curve measurements

Ammonia electrolysis tests were performed in a cell containing 1 M KOH + 0.1 M ammonia solution, with Pt or Pt black electrode as anode and a platinum plate as cathode. The electrolytic potential was applied through a Xantrex XDL-56 4P DC Power Supply.

3.6. AFM and SEM characterization

The morphology of the fabricated Pt black electrode was characterized by a NanoWizard atomic force microscope (AFM, JPK Instruments AG, Berlin, Germany). Silicon cantilevers (Type BS-ElectriTap300, Budget Sensors, Sofia, Bulgaria) with a chromium/platinum conductive coating, a resonant frequency of 300 kHz, and a force constant of 40 N/m were used. Images of the sizes 15 x 15 μm and 5 x 5 μm were taken at a line rate of 0.2 Hz and a pixel density of 512 x 512.

The morphology was also observed using a Philips XL30 scanning electron microscopy (SEM).

Chapter Four: CATALYTIC ELECTROLYSIS OF AMMONIA ON PLATINUM IN ALKALINE SOLUTION FOR HYDROGEN GENERATION

Platinum as an effective electrocatalysts was used for electro-oxidation of ammonia and production of hydrogen. The parametric effects were investigated to maximize the ammonia oxidizing current density and, more important, to determine the ammonia oxidation mechanism and kinetics on Pt.

4.1. Parametric effects on electrocatalytic oxidation of ammonia on Pt

4.1.1. Effects of ammonia concentration

Fig. 4.1 shows the anodic (A) and cathodic (B) portions of CVs measured on Pt in 1 M KOH solution with the various ammonia concentrations. It is seen that two anodic current peaks were observed at approximately -0.9 V and -0.38 V (SCE), respectively. Furthermore, with the increase in ammonia concentration, the peak current density at -0.38 V increased continuously. In particular, there was a significant increase in peak current density when the ammonia concentration increased from 0 to 0.1 M. The further increase of ammonia amount to 1 M enhanced the peak current density only slightly. With respects to the influence of the ammonia concentration on peak current density at -0.9 V, there was no apparent change initially. The peak current density decreased when the ammonia concentration reached 1 M.

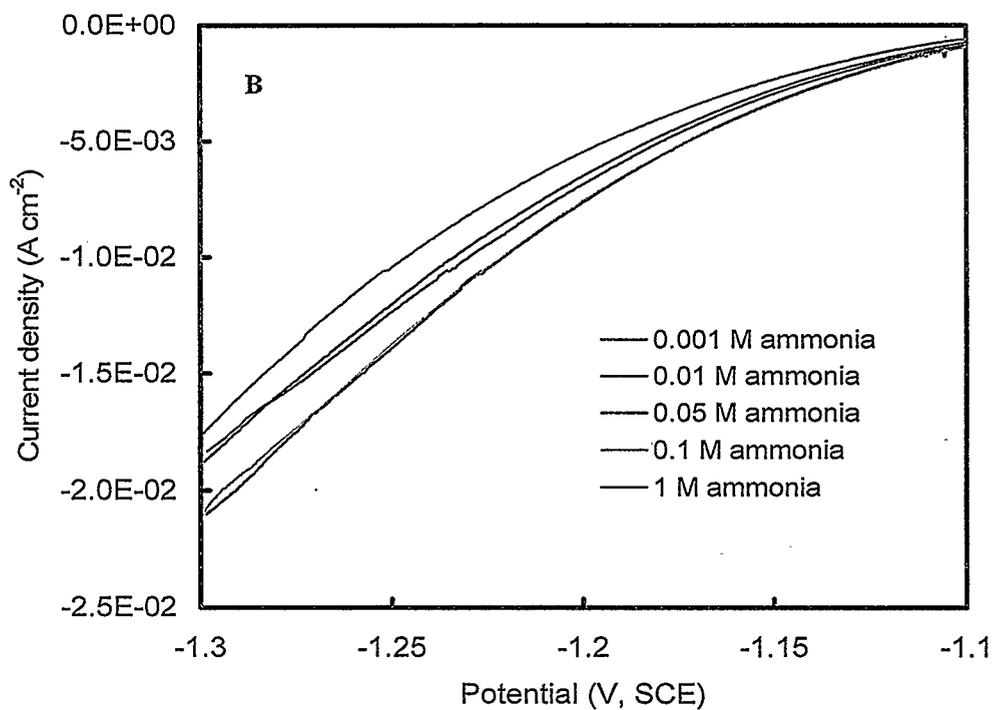
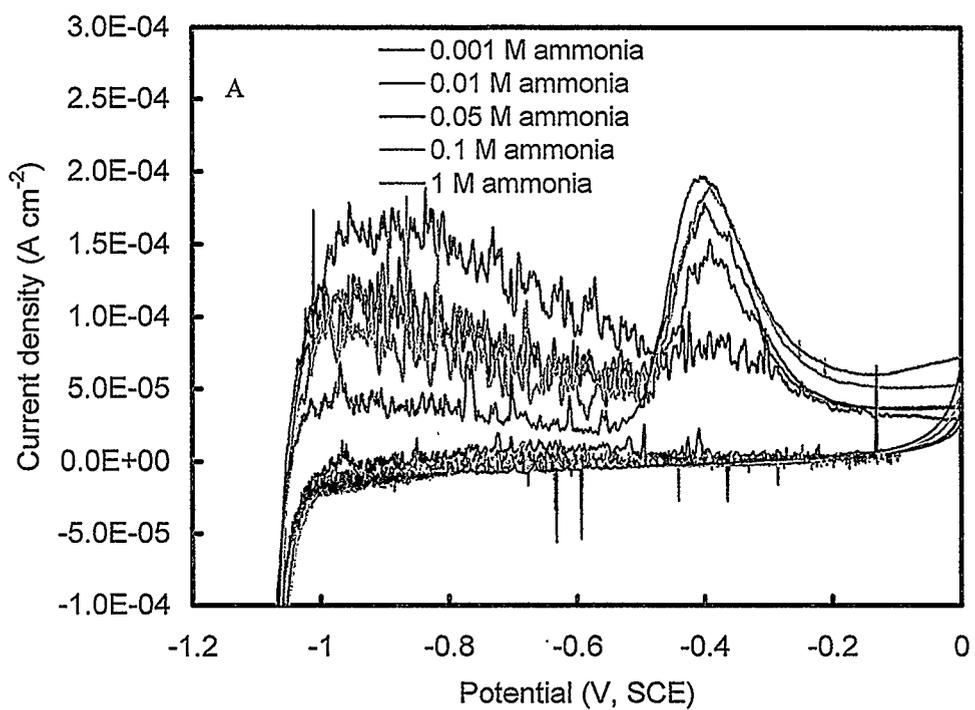


Fig. 4.1. The anodic (A) and cathodic (B) portions of the CVs measured on Pt in 1 M KOH solutions with the various ammonia concentrations.

The mechanism of ammonia electro-oxidation on noble metals, such as platinum, proposed by Gerischer and Mauerer [Gerischer and Mauerer, 1970] involves the dehydrogenation step of $\text{NH}_{3,\text{ads}}$ to N_{ads} and the recombination of two $\text{NH}_{x,\text{ads}}$, where partially dehydrogenated species of $\text{NH}_{2,\text{ads}}$ and NH_{ads} are active intermediates to give the final product of N_2 .

The anodic current peaks at -0.38 V is attributed to the oxidation of ammonia to N_2 [Katan and Galiotto, 1963], while the anodic peaks at about -0.9 V is associated with the oxidation of hydrogen atoms that are generated during cathodic polarization in CV test. The present results show that ammonia can be oxidized effectively on Pt electrode. With the increase in ammonia concentration in the solution, more NH_3 (aq) will be adsorbed on the electrode surface to be oxidized. Thus, the anodic current density increases continuously with the ammonia concentration. When the ammonia concentration reaches a certain content, i.e., 0.1 M in this work, the adsorption of ammonia on Pt electrode will achieve a relatively saturation status. The further increase of ammonia concentration in the solution will not apparently enhance the amount of ammonia to adsorb on electrode for oxidization. Moreover, the intermediates generated during ammonia oxidation, such as $\text{NH}_{2,\text{ads}}$ and NH_{ads} , could remain on the electrode surface and block the ammonia adsorption. It is reasonable to assume that the block effect will be significant when the solution contains a high concentration of ammonia. Therefore, an increase of the ammonia concentration from 0.1 M to 1 M results in unapparent increase in anodic peak current density.

To investigate the effect of intermediates on ammonia oxidation, the cyclic

voltammograms were measured with the various upper switch potentials in 0.1 M ammonia + 1 M KOH solution, as shown in Fig. 4.2. It is seen that another anodic current peak was observed at potential more than 0 V. The cathodic potential shoulders at about -0.7 V were observed for all the curves where the proceeding anodic scans were reversed at potential higher than -0.38 V, suggesting that cathodic current is related either to the reduction or to the desorption of intermediate species such as NH_{ads} and $\text{NH}_{2,\text{ads}}$. On the other hand, the cathodic peak at -0.9 V corresponding to the reduction of other oxidized species such as nitrite anions [Sasaki and Hisatomi, 1970] appears clearly when the potential is set above 0 V.

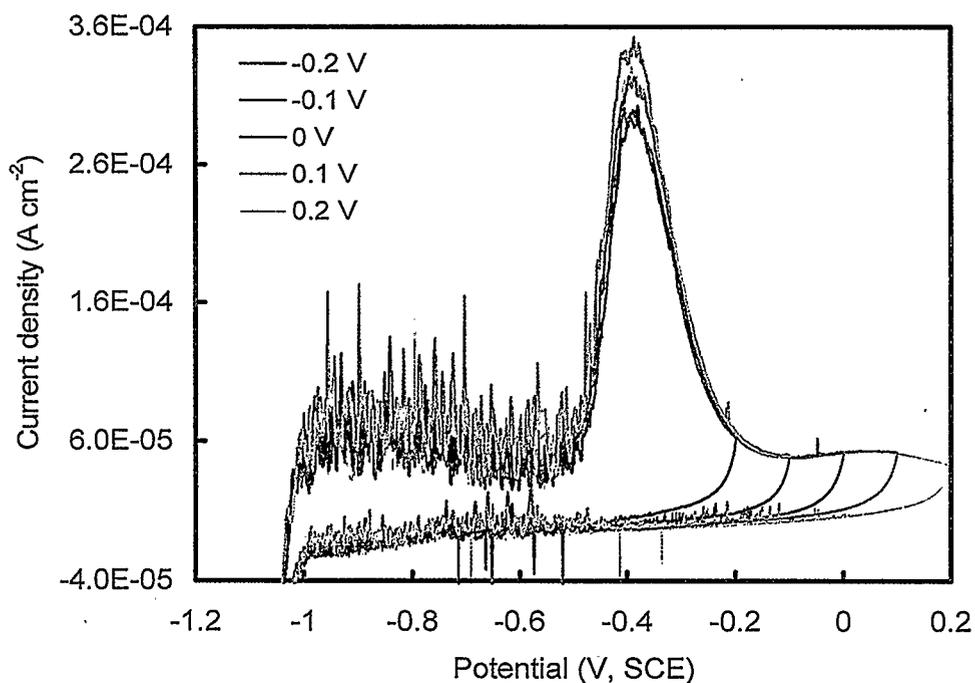


Fig. 4.2. CVs measured on Pt electrode in 0.1 M ammonia + 1 M KOH solution with the various upper switch potentials.

Furthermore, it is seen from Fig. 4.1 (B) that, when the ammonia concentration

increased from 0 to 0.1 M, the cathodic reduction current density increased continuously. When the ammonia concentration reached 1 M, the cathodic current density decreased significantly. It has been acknowledged [Vitse et al., 2005] that electrolysis of ammonia contains the ammonia electro-oxidation reaction coupled with the hydrogen evolution reaction. Analysis of the cathodic reduction portions of CVs provides essential information related to hydrogen evolution mechanism and the parametric effects on generation of hydrogen. Generally, hydrogen evolution in alkaline solution is mainly due to reduction of water. The increasing cathodic reduction current density with the ammonia concentration in Fig. 4.1 (B) indicates that, in addition to water reduction reaction contributing to hydrogen evolution, either the remaining NH_3 or the intermediates (NH_{ads} , $\text{NH}_{2,\text{ads}}$) could be further reduced to generate hydrogen. When the ammonia concentration increased to 1 M, the significant amount of intermediates will remain on the electrode surface to decrease the electro-activity of Pt electrode for hydrogen evolution, resulting in the decrease in cathodic current density.

Analysis of the effects of ammonia concentration on the anodic electro-oxidation of ammonia and cathodic hydrogen evolution shows that an optimal ammonia concentration of 0.1 M is preferential for both ammonia oxidation and hydrogen generation in this work.

4.1.2. Effects of KOH concentration

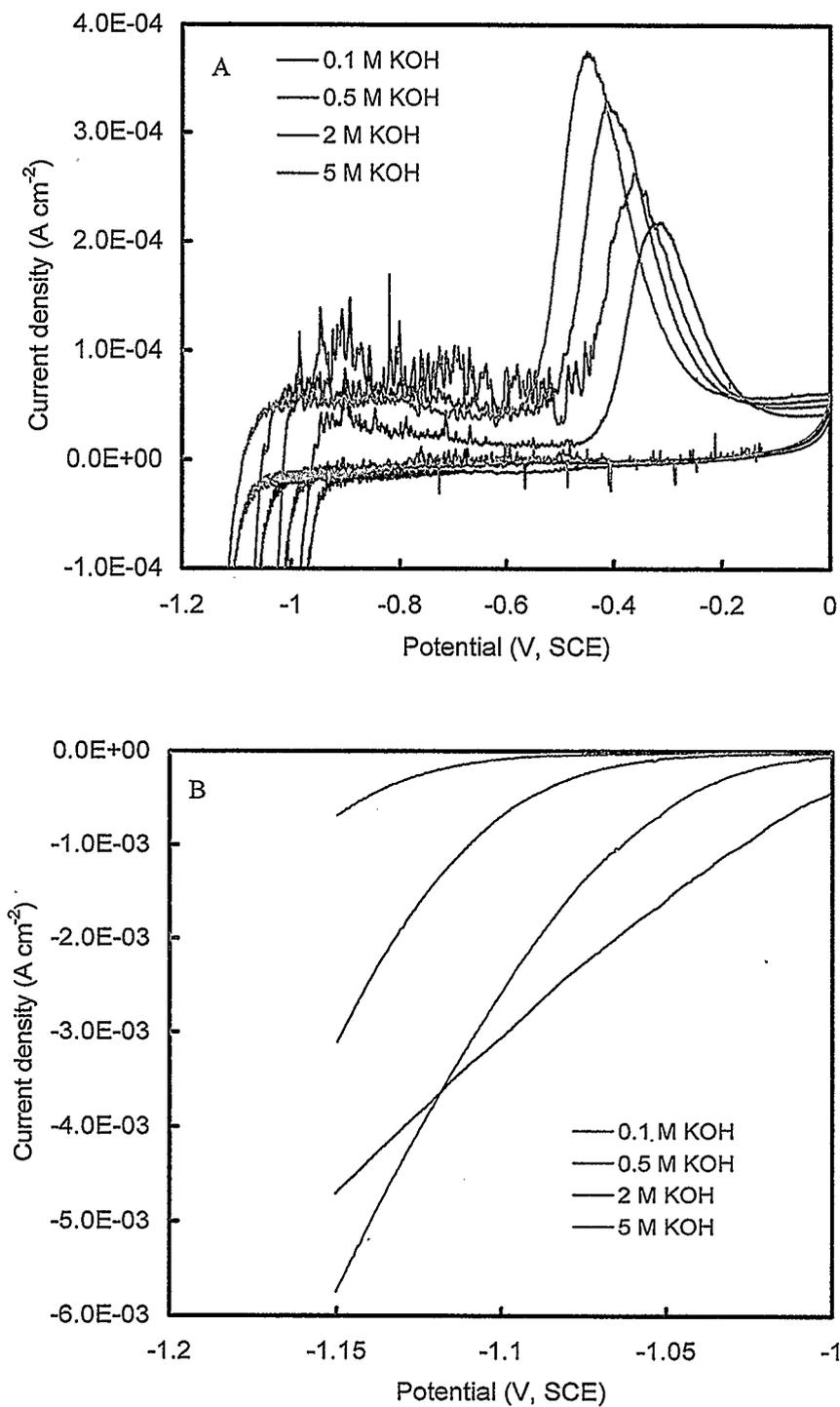
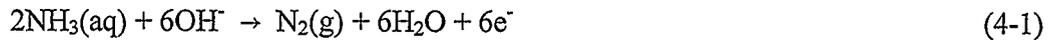


Fig. 4.3. The anodic (A) and cathodic (B) portions of the CVs measured on Pt in 0.1 M ammonia solutions with the various KOH concentrations.

Fig. 4.3 shows the anodic and cathodic portions of the CVs measured on Pt electrode in 0.1 M ammonia with the various KOH concentrations. It is seen that, with the increase in KOH concentration, the peak current density at approximately -0.38 V increased significantly. Furthermore, the increasing KOH concentration shifted the peak potential negatively. When the KOH concentration changed, there was no apparent effect on the anodic current peak at about -0.9 V, which showed frequent fluctuations. Furthermore, the cathodic current density decreased when the KOH concentration increased

The critical role of KOH in ammonia electrolysis is to generate an alkaline environment for ammonia oxidation. The current work shows that, with the increasing KOH concentration (increasing pH value), the ammonia oxidation current density increases continuously. More important, the increasing alkalinity can decrease the ammonia oxidation overpotential, shifting the peak potential negatively. Such an essential role of the solution alkalinity can be explained by Nernst equation for the overall reaction for ammonia oxidation that combines reactions (2-7) to (2-12) under the constant ammonia concentration and the test temperature:



$$\varphi_{\text{NH}_3/\text{N}_2} = \varphi_{\text{NH}_3/\text{N}_2}^0 - \frac{2.303RT}{nF} \log \frac{[\text{NH}_3]^2 [\text{OH}^-]^6}{[\text{N}_2]} \quad (4-2)$$

It is apparent that the ammonia oxidation potential decreases with the increasing

hydroxide ion concentration, i.e., the alkalinity of the solution.

On the other hand, the increase in KOH concentration results in the decrease of cathodic current density for hydrogen evolution, as shown in Fig. 4.3 (B). The result is very straightforward because the increase of solution alkalinity reduces the amount of hydrogen ions for hydrogen evolution, resulting in the decreasing cathodic reduction current density.

Apparently, the role of solution alkalinity in ammonia electro-oxidation is two-fold: enhance the ammonia oxidation current density and decrease the oxidation reaction overpotential, and simultaneously, decrease hydrogen evolution. Thus, an appropriate KOH concentration is essential to the ammonia electrolysis for hydrogen generation.

4.1.3. Effects of electrode rotating speed

Fig. 4.4 shows the anodic and cathodic portions of the cyclic voltammograms of platinum electrode at the various rotating speeds in 0.1 M ammonia + 1 M KOH solution. It is seen that, with the increase in electrode rotating speed, the anodic current peaks at both -0.38 V and -0.9 V decreased. Moreover, the change of the rotating speed of electrode did not alter the peak potential. Moreover, the increase in electrode rotating speed decreased the cathodic current density slightly.

If it is assumed that a diffusion coefficient for ammonia is $2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [Endo et al., 2005; Donten et al., 1997] and the 3-electron oxidation of ammonia, the diffusion

limited current density is approximately 260 mA cm^{-2} at 800 rpm. The actually measured peak current density is much lower, suggesting that the transport of ammonia to the electrode surface does not play a kinetic role, and moreover, that a certain hindering process such as N-intermediate poisoning [Gerischer and Mauerer, 1970] might take place at the platinum surface.

The dependence of anodic peak current density on electrode rotating speed shows a unique feature, that is, the peak current density decreases with the increasing rotating speed of the electrode. Such a phenomenon was also observed by Endo et al. [Endo et al, 2005]. According to Gerischer and Mauerer's mechanism [Gerischer and Mauerer, 1970], electro-oxidation of ammonia to nitrogen experiences the generation of several nitrogen-containing intermediates that will be sequentially oxidized to the final product of nitrogen. With the increasing electrode rotating speed, some of the intermediates may not be adsorbed strongly on the Pt electrode surface but be detached from the electrode. Endo et al. [Endo et al., 2005] used in-situ ring electrode detector to find two kinds of signals for the electroactive species transported from the disk electrode engaged in ammonia oxidation. It was concluded that at least two kinds of intermediate could be detached from the electrode surface. Thus, with the increasing electrode rotating speed, it is reasonable to assume that more intermediates will be detached, resulting in a decreasing amount of N-H compounds to be oxidized on the electrode and thus the decreasing oxidizing current density.

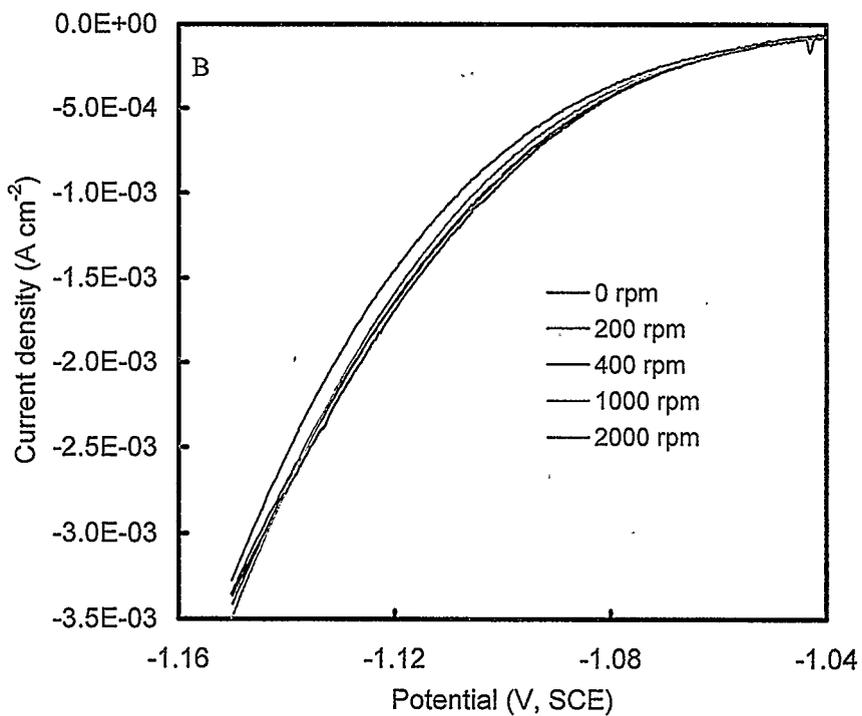
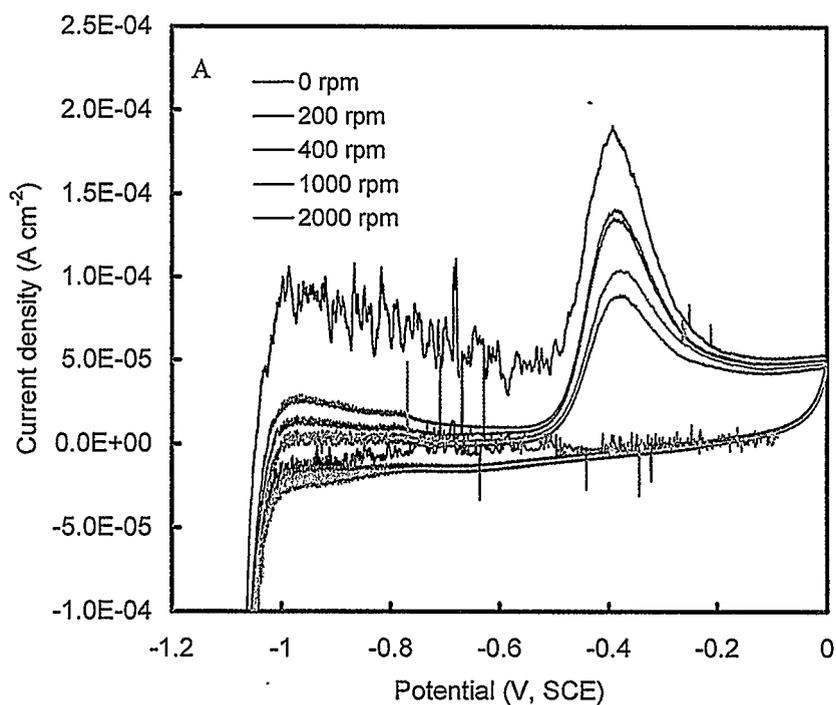


Fig. 4.4. The anodic (A) and cathodic (B) portions of the CVs of Pt electrode at the various rotating speeds in 0.1 M ammonia + 1 M KOH solution.

The increasing electrode rotating speed on hydrogen evolution reaction has a two-fold effect. Detachment of the nitrogen-containing intermediates from the electrode surface reduces the possibility of Pt electrode to be contaminated or poisoned, resulting in the increase of hydrogen evolution. On the other hand, the loss of intermediates that contain hydrogen from the electrode also decreases the total amount of hydrogen to be reduced. Thus, the hydrogen evolution will decrease. The competitive effects due to the increasing rotating speed of the electrode are expected to result in an unapparent change of cathodic current density that is from hydrogen evolution. In this work, the cathodic reduction current density decreases slightly with the increase of electrode rotating speed, indicating that detachment of hydrogen-containing intermediates from the electrode may override the effect of electrode contamination by these intermediates.

4.1.4. Effects of temperature

Fig. 4.5 shows the anodic and cathodic portions of CVs measured on Pt in 0.1 M ammonia + 1 M KOH solution at the various temperatures. It is seen that an elevated temperature enhanced considerably the value of anodic peak current density. Furthermore, the peak potentials were shifted negatively. Similar to the effect on anodic behavior, the increase in temperature resulted in the increase of the cathodic current density.

The ammonia oxidation can be accelerated at elevated temperature since it is observed that the anodic peak current density increases with the increasing temperature.

The enhancement of ammonia oxidation could be due to either the accelerated diffusion of ammonia from the bulk solution through the diffusive layer to adsorb on the electrode surface (mass-transfer effect) or the rapid electro-oxidation reactions (activation effect). Furthermore, the negative shift of the peak potential, which can be explained by Nernst equation of ammonia oxidation reaction (3), indicates the favorable condition (the lowered overpotential) for ammonia oxidation.

Similar to the effect on anodic reaction, the increase of cathodic current density at elevated temperature is also due to the accelerated hydrogen evolution reaction.

Fig. 4.6 shows the CVs measured on Pt electrode in 0.1 M ammonia +1 M KOH solution at the various potential sweep rates. It is seen that the anodic peak current density at about -0.38 V increased significantly with the increasing potential sweep rate, while the anodic current peaks at about -0.9 V increased slightly. The alternation of potential sweep rate did not shift the peak potential. Furthermore, the cathodic reduction current density increased with the scanning rate with the exception of a slight deviation of cathodic curve measured at 1 mV/s.

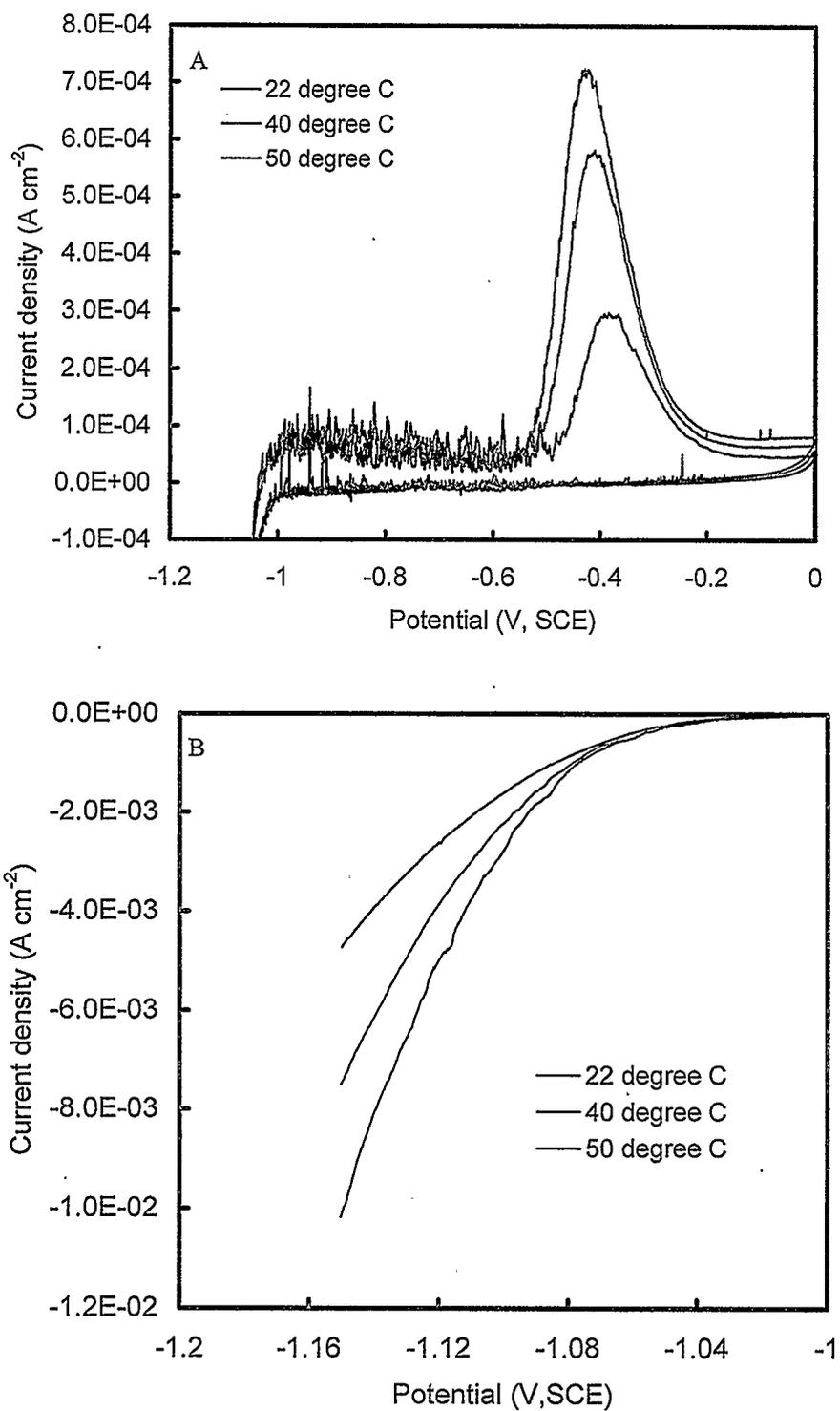


Fig. 4.5. The anodic (A) and cathodic (B) portions of the CVs of Pt electrode at the various temperatures in 0.1 M ammonia + 1 M KOH solution.

4.1.5. Effects of potential scanning rate

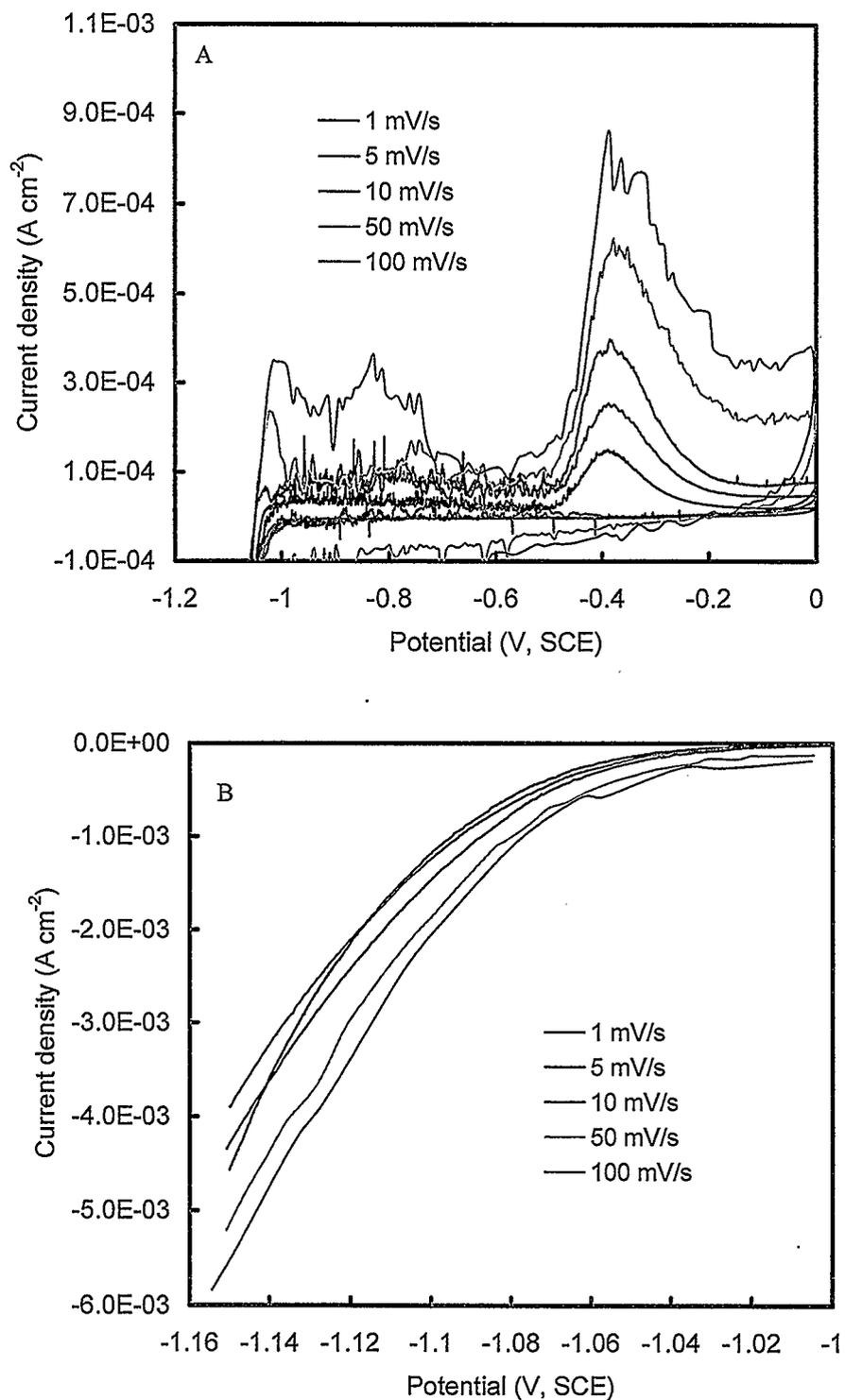


Fig. 4.6. The anodic (A) and cathodic (B) portions of CVs measured on Pt electrode in 0.1 M ammonia + 1 M KOH solution at the various potential sweep rates.

An expression of the current response to the potential sweep rate was given by Gabrielli [Gabrielli et al., 1979]. The increasing anodic and cathodic current density with potential sweep rate is attributed to the excitation signal by-passing charge-transfer processes during the charging of the interfacial capacitance.

Furthermore, the effects of electrode rotating speed on ammonia oxidation current density (Fig. 4.4) show that, although an enhanced mass-transfer of ammonia towards the electrode surface can increase the ammonia oxidation, the side effect of the accompanying adsorption/desorption of N_xH_y intermediates on ammonia oxidation could not be ignorable. A comprehensive consideration of mass-transfer process and the associated adsorption/desorption processes will be essential to determine the ammonia oxidation kinetics and optimize the ammonia oxidation.

4.1.6. Effects of the cyclic number

Fig. 4.8 shows CVs measured on Pt electrode in 0.1 M ammonia + 1 M KOH solution with the different cyclic numbers. It is seen that, after 9 cycles of CV measurements, there was little change of the peak current density at -0.38 V. However, the increase in cyclic number resulted in the decrease of cathodic current density, especially the initial few cycles. When the cycle number increased from 7 to 9, there was little change of the cathodic current density any more.

CV tests with the multiple cycles are aimed at determining the stability and long-term performance of Pt electrocatalyst for ammonia oxidation. The present results

show that the electrocatalytic activity of Pt is still sufficiently high for ammonia oxidation in this system after 20 cycles of tests. In this work, an appropriate ammonia concentration of 0.1 M was selected to ensure that the coverage of electrode by ammonia adsorption is sufficient, while the “poisoning” effect of electrode by nitrogen-containing intermediates is insignificant.

Furthermore, the decrease of cathodic current density with the cyclic number, especially the first few cycles, could be due to the elevated pH nearby the electrode surface by water reduction. It has been analyzed that electrons generated during the ammonia oxidation reaction is consumed by the reduction of water molecules, as shown in reaction (4-3).



The generated hydroxide ions will enhance the local pH. Thus, after the first cycle of oxidation reaction, the decrease in cathodic reduction current is significant due to the enhanced alkalinity of the solution. During the following cycles, the consumption and generation of hydroxide ions nearby the electrode will reach a relative equilibrium, resulting in a relatively stable local pH. Therefore, an unapparent change of the cathodic current density is observed.

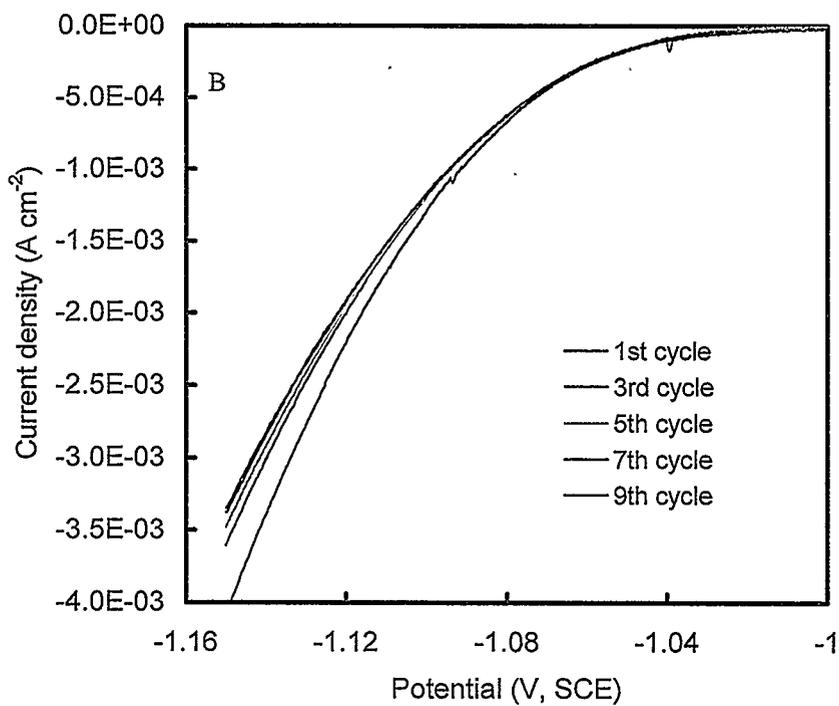
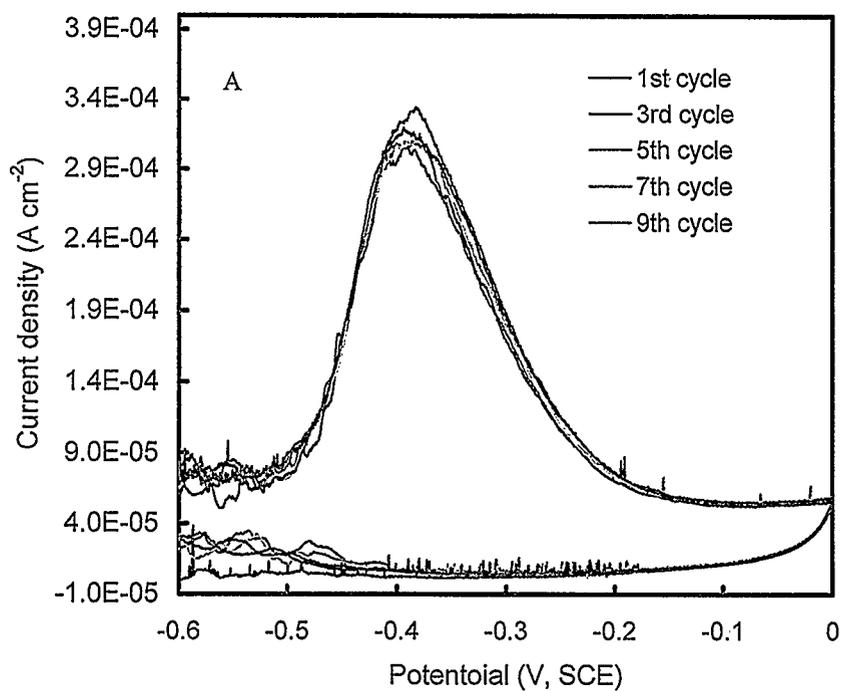


Fig.4.8. The anodic (A) and cathodic (B) portions of the CVs of Pt electrode in 0.1 M ammonia + 1 M KOH solution with the various cyclic numbers.

4.2. Polarization curve for the ammonia electrolytic cell

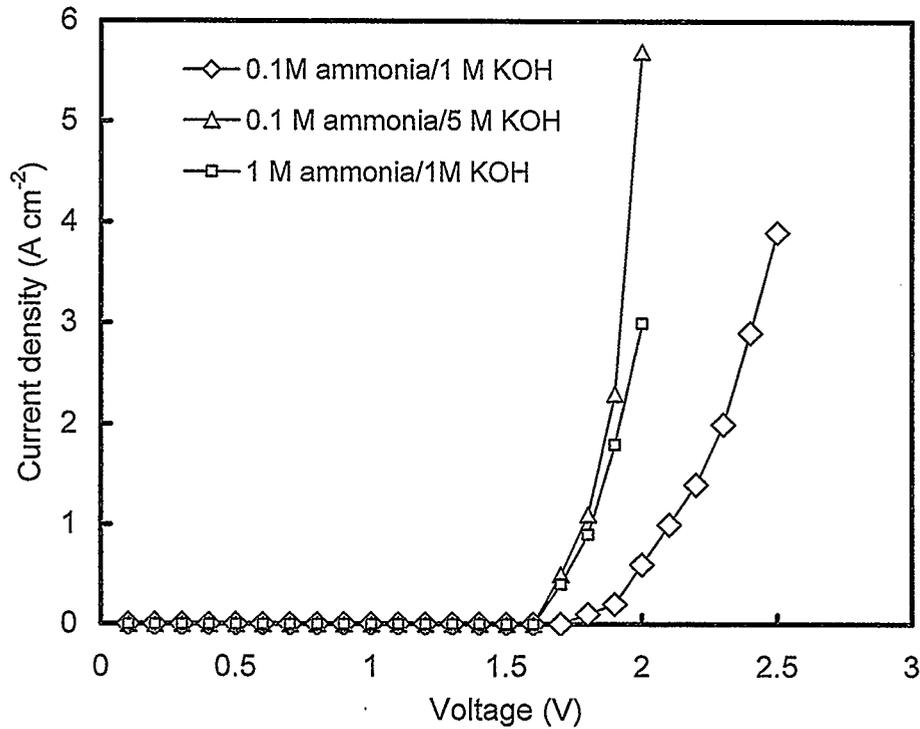


Fig. 4.9. The polarization curves for ammonia electrolytic cells.

Fig. 4.9 shows the ammonia electrolytic cell polarization curves where Pt plates were used as both anode and cathode. It is seen that the threshold applied voltage was 1.6 V for the three solutions. With the increase in ammonia and/or KOH concentration, the cell current density increased significantly.

The present work shows that the threshold voltage for ammonia electrolysis is independent of the solution composition and concentration. It is thus reasonable to assume that the property of electrocatalysts is critical to the threshold voltage value.

The efficiency of the electrolytic cell is essential to the practical application at an industrial scale. The cell efficiency can be expressed as [Vitse et al., 2005]:

$$e = \frac{3 \times \Delta H_{H_2}}{2 \times \Delta H_{NH_3} + 6F\Delta E} \quad (4-4)$$

where ΔH_{H_2} is the lower heating value of hydrogen ($242.7 \text{ kJ mol}^{-1}$), ΔH_{NH_3} is the lower heating value of ammonia ($320.1 \text{ kJ mol}^{-1}$), F is the Faraday's constant, and ΔE is the cell voltage. The efficiency represents the amount of energy that could be obtained by burning the produced gas (lower heating value of hydrogen) divided by the amount of energy required to produce this gas (lower heating value of ammonia plus electrical energy needed to electrolyze ammonia). The value of e as a function of the hydrogen production rate (i.e. anodic current density) is given for the three solutions on Pt electrode in Fig. 4.10. It is seen from Fig. 4.9 that, with the increasing current density, the required electrolytic cell voltage increases. Thus, the cell efficiency decreases, as seen from equation (4-4). The efficiency of ammonia transformation into hydrogen on Pt electrode in 0.1 M ammonia + 1 M KOH solution ranges from 45% at 0.01 A cm^{-2} to 37% at 2 A cm^{-2} . When the ammonia and KOH concentrations increased to 1 M and 5 M, respectively, the cell efficiencies were slightly increased to 47%. Apparently, the change of the solution composition does not improve significantly the electrolytic cell efficiency. It is expected that a significant increase of the cell efficiency could be achieved by developing high-performance electrocatalyst, which will be discussed in the following chapter.

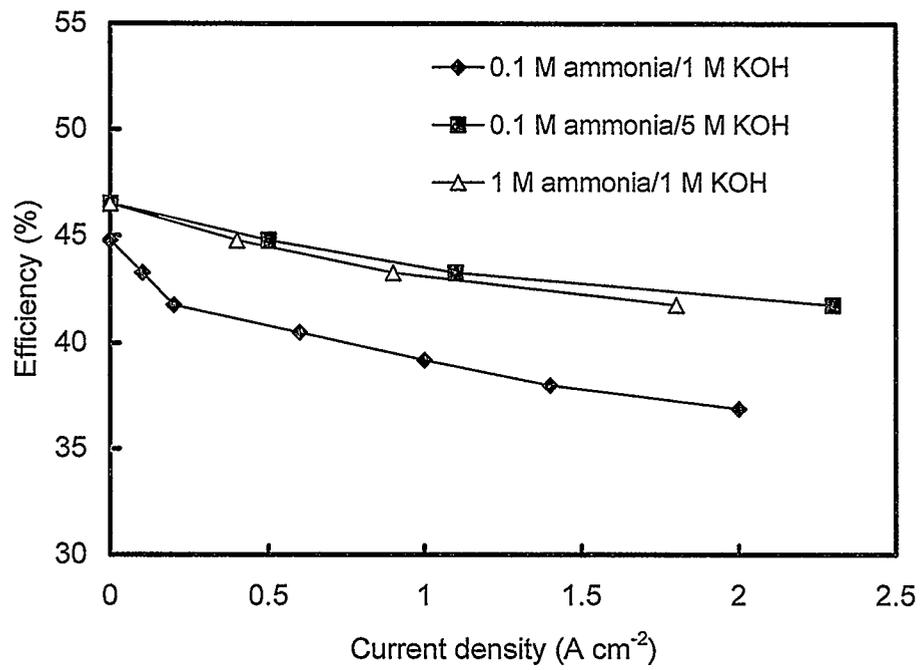


Fig. 4.10. The electrolytic cell efficiency for ammonia electrolysis in the various solutions.

Chapter Five: AMMONIA OXIDATION ON PLATINUM BLACK

5.1. CVs measured on Pt and Pt black electrodes

Fig. 5.1 shows the CVs measured bright Pt and the fabricated Pt black electrodes in 0.1 M ammonia + 1 M KOH solution. It is seen that an anodic current peak was observed at -0.35 V (SCE). In particular, the peak current measured on Pt black of $2.25 \times 10^{-2} \text{ A/cm}^2$ was nearly 45 times higher than that measured on bright Pt of about $5.05 \times 10^{-4} \text{ A/cm}^2$. Furthermore, the cathodic current density was much higher than on Pt black than on bright Pt electrode.

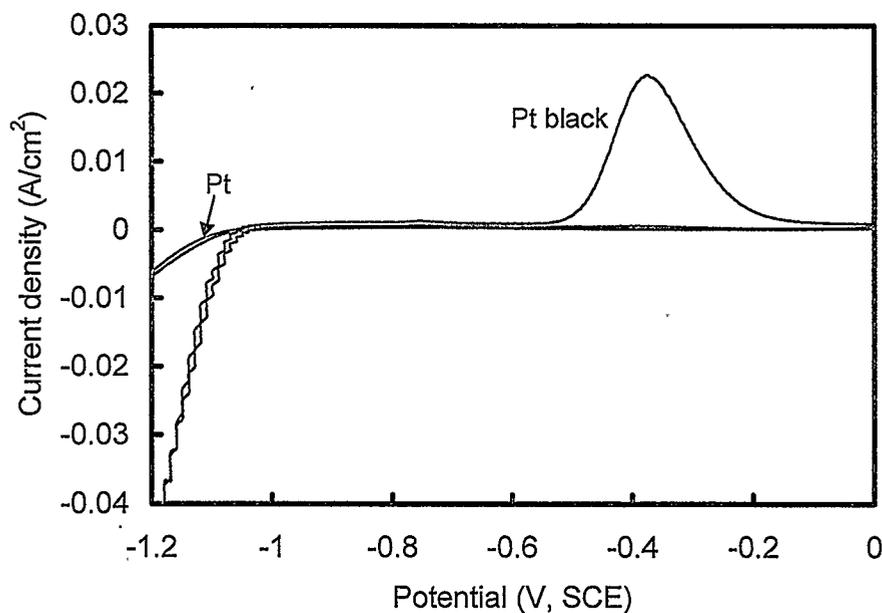


Fig. 5.1. CVs measured on bright Pt and the fabricated Pt black electrodes in 0.1 M ammonia + 1 M KOH solution.

5.2. Cycling on Pt black electrode

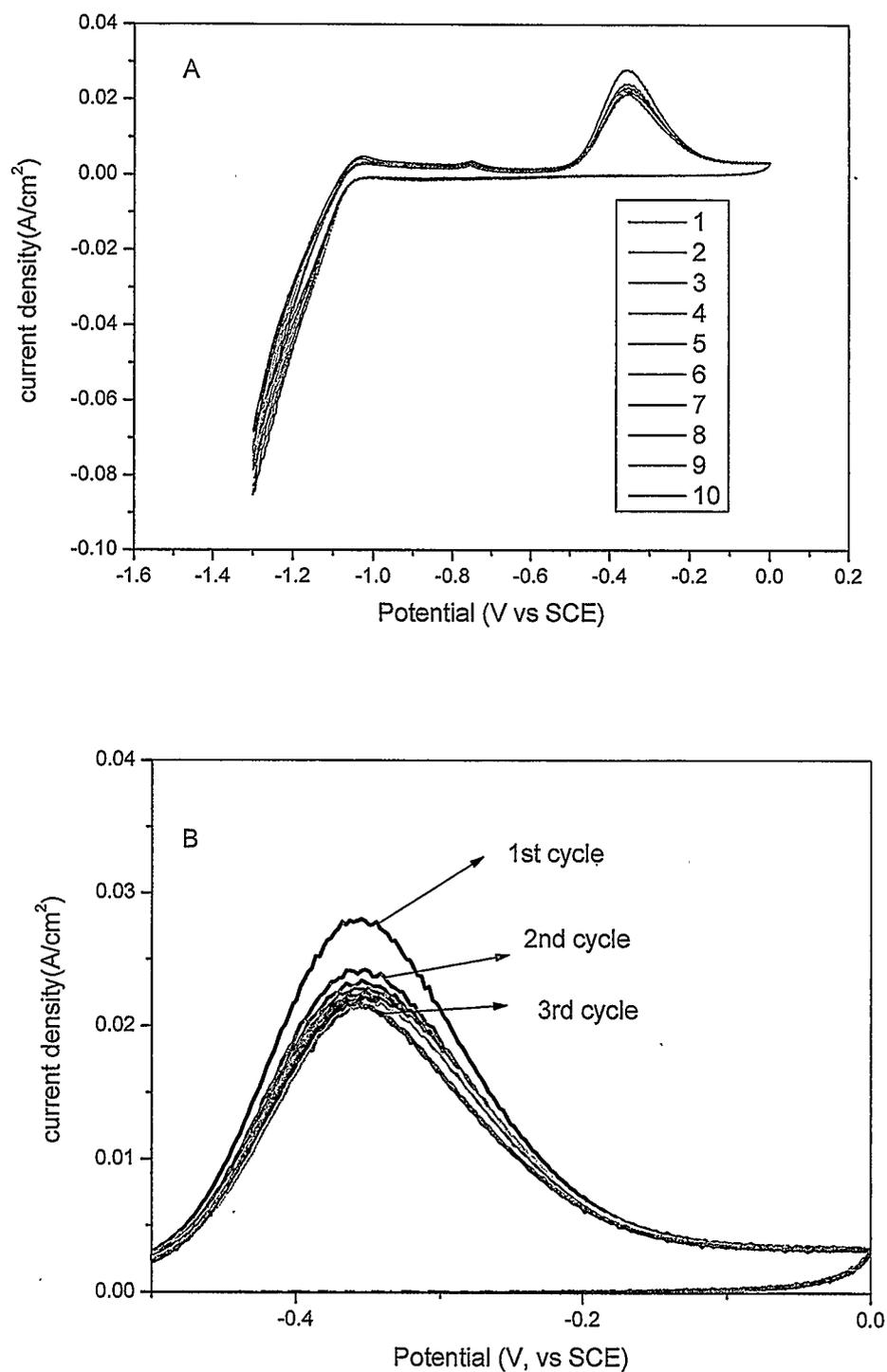


Fig. 5.2. Cycling CVs (A) and (B) measured on Pt black electrodes in 0.1 M ammonia + 1 M KOH solution.

Fig. 5.2 shows the CVs measured on Pt black electrode with the various cycle numbers. It is seen that the ammonia oxidative current density at -0.38 V (SCE) decreased slightly from 0.028 A/cm^2 measured in the first cycle to 0.024 A/cm^2 in the second cycle. Since then, the current density would be relatively stable to the tenth cycle. There was little change of cathodic current density with the cyclic number.

5.3. Effects of electrodeposition parameters on electrocatalytic activity of Pt black electrode for ammonia oxidation

5.3.1. Effects of electrodeposition potential

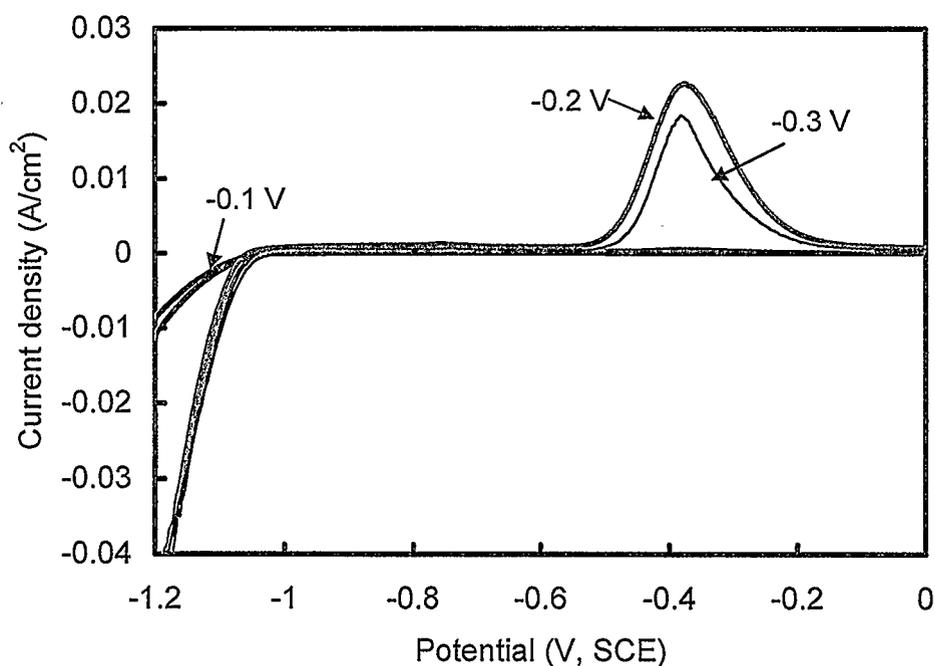


Fig. 5.3. CVs measured on Pt black electrodes fabricated at the various depositing potentials for 20 mins at room temperature.

Fig. 5.3 shows the CVs measured on Pt black electrodes fabricated at the various depositing potentials for 20 mins at room temperature. It is seen that the anodic current

peak at -0.38 V (SCE) measured on Pt-black electrode was dependent on the depositing potential to fabricate the electrode. There was a maximum value of anodic current density when the depositing potential was -0.2 V (SCE). In particular, when the depositing potential was -0.1 V (SCE), the cathodic/anodic polarization behaviors were quite similar to those measured on bright Pt electrode. At -0.3 V (SCE) of depositing potential, accompanying with the decrease of anodic current peak, the cathodic reductive current density decreased as well.

5.3.2. Effects of electrodeposition time

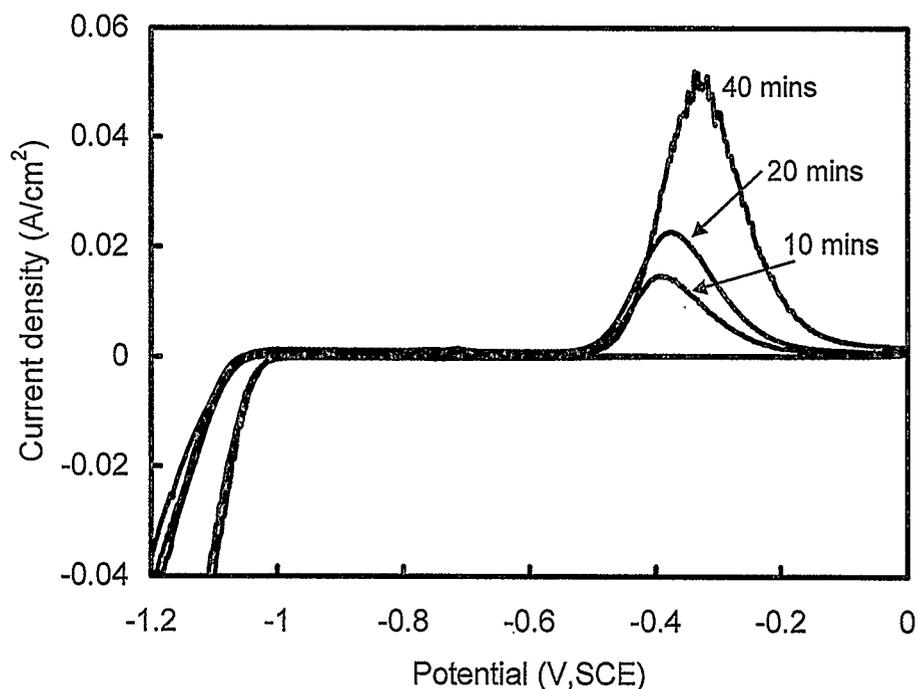


Fig. 5.4. CVs measured on Pt black electrodes fabricated at -0.2 V (SCE) with the various times at room temperature.

Fig. 5.4 shows the CVs measured on Pt black electrodes fabricated at -0.2 V (SCE) with the various times at room temperature. It is seen that, with the increase of

electrodepositing time, both the anodic current peak and the cathodic current density increased.

5.3.3. Effects of electrodepositing temperature

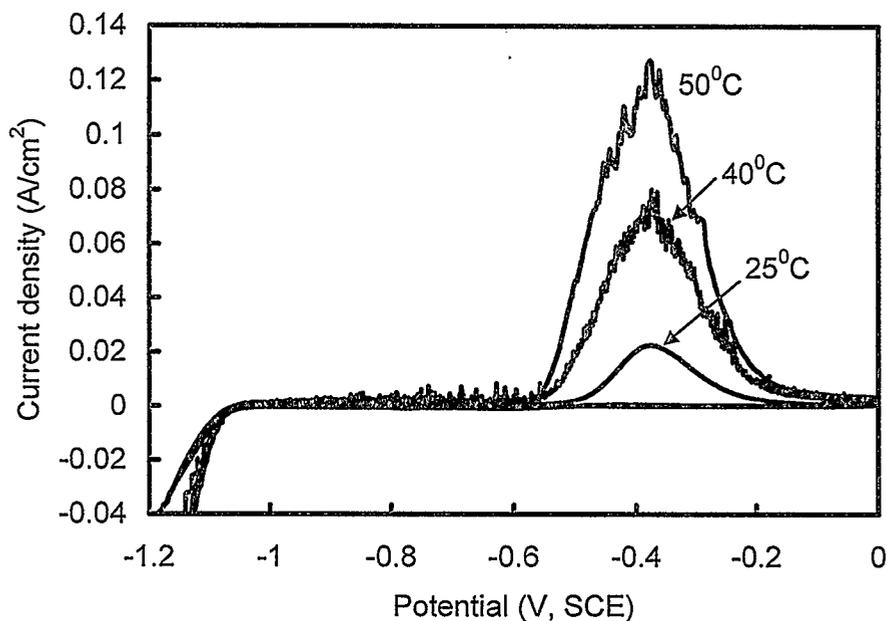


Fig. 5.5. CVs measured on Pt black electrodes which were fabricated at -0.2 V (SCE) for 20 mins at the various temperatures.

Fig. 5.5 shows the CVs measured on Pt black electrodes which were fabricated at -0.2 V (SCE) for 20 mins at the various temperatures. It is seen that the anodic current peaks at -0.35 V (SCE) and the cathodic current density increased with the elevated temperature.

5.4. SEM characterization of Pt black electrodes

With the increase of electrodeposition time, the surface morphology of the fabricated Pt black electrode changed apparently. It can be seen from Fig. 5.6, where the SEM images of bright Pt and Pt black electrodes electrodeposited at 10 minutes and by 20 minutes are presented. The surface roughness increased and the deposited particles grew with the increase of electrodeposition time.

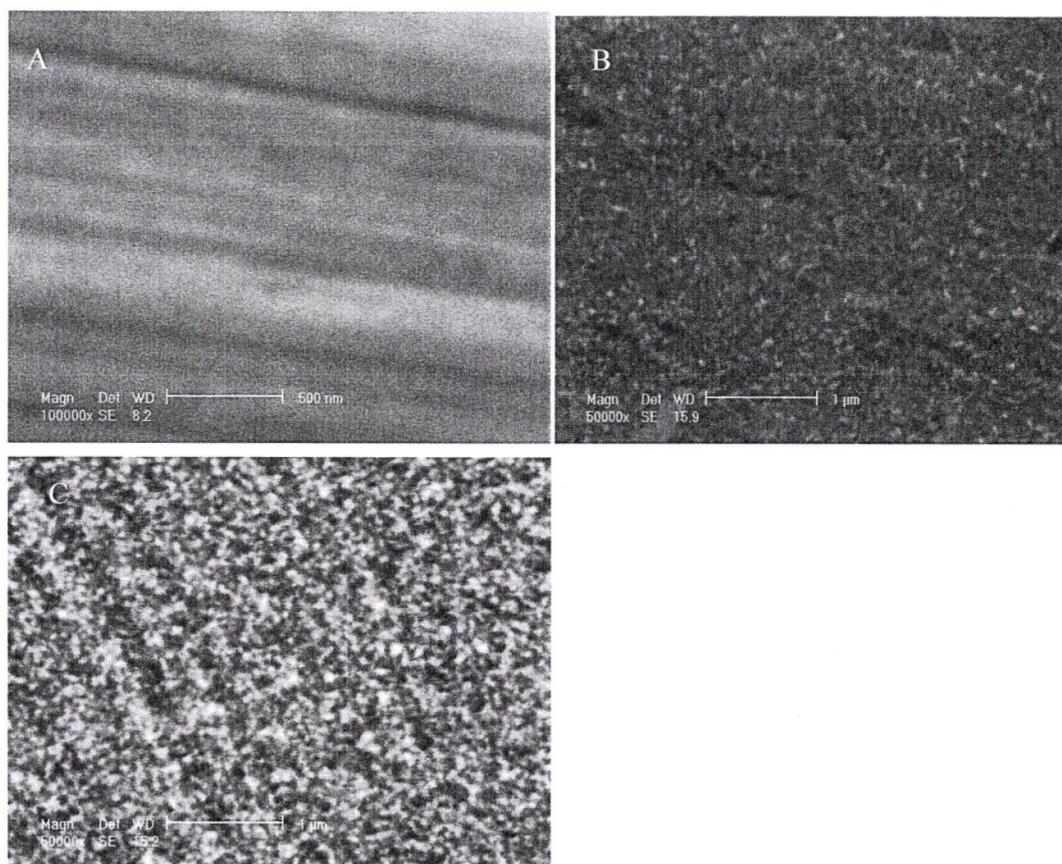
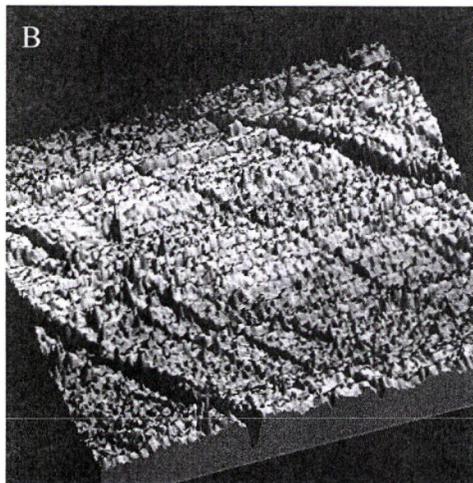
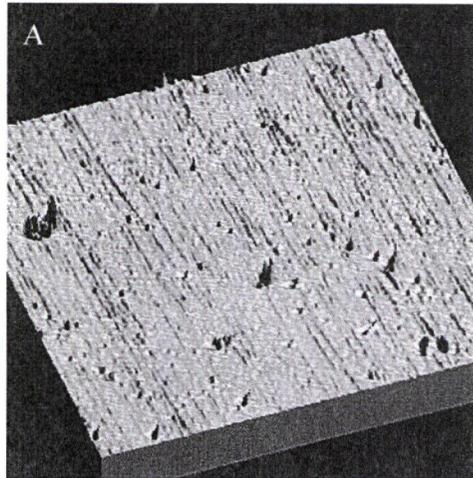


Fig. 5.6. SEM images of (A) Pt bright electrode, (B) Pt black electrode for 10 mins of electrolytic deposition, and (C) Pt black electrode for 20 mins of electrolytic deposition.

5.5. AFM characterization of Pt black electrodes

Fig. 5.7 shows the AFM images of bright Pt and the fabricated Pt black electrodes

with the various depositing times. It is apparent that the surface roughness of Pt black electrode was quite different from that of bright Pt. Furthermore, the AFM images indicate that the shape of Pt nuclei is generally 3-dimensionally conical. At 5 mins of electrodeposition, the Pt nuclei were small, and randomly distributed on the Pt surface. After 10 mins and 20 mins, the Pt nuclei grew and much more additional initiated. After 40 mins of deposition, the island-shaped growth was observed and the Pt surface was completely covered by the deposited Pt.



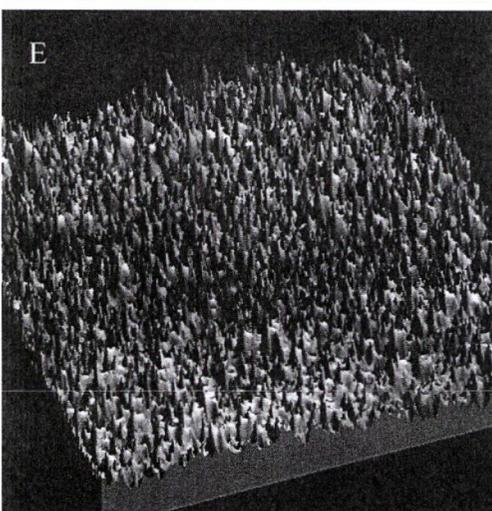
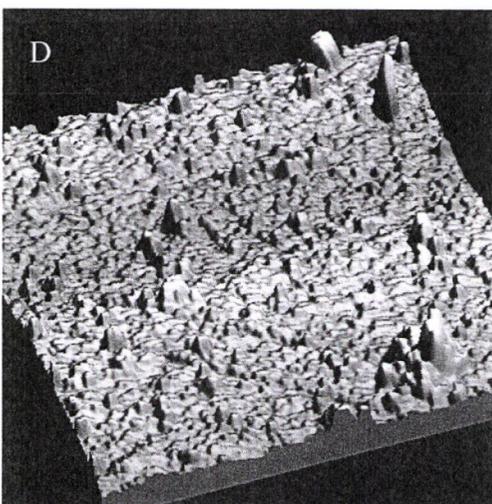
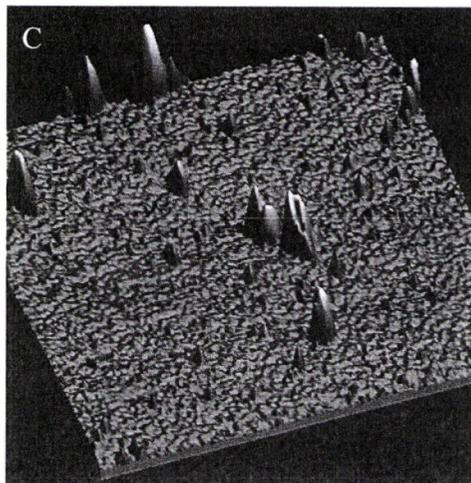


Fig. 5.7. AFM micrographs of Pt electrodes: (A) Pt bright, (B) Pt black 5min, (C) Pt black 10 min, (D) Pt black 20min, (E) Pt black 40min.

5.6. Discussion

The present work shows that, when electrode was deposited at -0.1 V (SCE), the measured CV behavior is identical to that measured on bright Pt electrode, indicating that there exists a threshold potential for electrolytic deposition of Pt. Below the threshold value, reduction of Pt ions will not occur because the required energy barrier is not overcome. The value of threshold potential is dependent on the Pt ion concentration and depositing temperature. Furthermore, the maximum value phenomenon is observed in this work in terms of the dependence of ammonia oxidation current density on the depositing potential of Pt to fabricate Pt black electrode. When the depositing is at -0.3 V (SCE), the energy criterion becomes less important and the Pt depositing layer thickness increases. It is also assumed that, accompanying with the continuous deposition of Pt layer on the previous layer, the Pt film becomes more compact, resulting in decrease in effective surface area. Thus, the catalytic activity of the deposited Pt black electrode decreases. Apparently, there is an optimal cathodic depositing potential, which is essential to maximize the electrocatalytic activity of the fabricated Pt black electrode in the present system.

It is also found in this work that the electrocatalytic activity of Pt black electrode increases with the depositing time. As shown in AFM images reflecting the electrolytic deposition process of Pt black electrode, with the increasing time, there are more Pt nuclei occurring on the electrode and furthermore, the Pt nuclei grow and distribute to the whole electrode surface.

The catalytic activity of Pt black electrode for ammonia oxidation is enhanced when it is fabricated at an elevated temperature. In general, the increase of electrodeposition bath temperature accelerates both mass-transfer of Pt ions from the bulk solution towards the electrode (mass-transfer effect) and the reduction reaction on the electrode surface (activation effect), resulting in the enhancement of electrocatalytic activity of the electrode.

Chapter Six: CONCLUSION AND RECOMMENDATION

6.1. Conclusions from the research work

In this work, the electrocatalytic activity of Pt for ammonia oxidation and hydrogen evolution reactions was studied by cyclic voltammetry. The parametric effects, including ammonia concentration, support electrolyte (KOH) concentration, electrode rotating speed, electrode surface status and temperature, were investigated to determine the ammonia oxidation reaction mechanism and kinetics. Furthermore, electrolytic deposition technique was used to fabricate Pt black electrode for enhancement of the ammonia oxidation reaction activity. Cyclic voltammetry, combined with SEM and AFM surface morphology characterization, was used to determine the mechanism for enhanced electrocatalytic activity of Pt black electrode. The main conclusions from this research include:

(1) Pt as an effective electrocatalyst is capable of catalytically oxidizing ammonia for production of hydrogen in alkaline solution.

(2) There is an appropriate ammonia concentration to maximize the ammonia oxidation and hydrogen evolution reactions simultaneously. The presence of excessive ammonia in the solution may result in nitrogen-containing intermediates remaining on the Pt electrode surface degrading the electrocatalytic activity of Pt.

(3) The role of the solution alkalinity in ammonia electrolysis is two-fold: enhance the ammonia oxidation current density and decrease the oxidation reaction

overpotential, and simultaneously, decrease hydrogen evolution. Thus, an optimal KOH concentration is essential to the ammonia electrolysis for hydrogen generation.

(4) The ammonia electro-oxidation current decreases with the increasing electrode rotating speed due to the enhanced detachment of ammonia from the electrode surface. Moreover, an elevated temperature is beneficial to both ammonia oxidation and the hydrogen evolution.

(5) The cell efficiency for ammonia electrolysis on Pt can be up to 45%. Increasing ammonia and KOH concentrations could increase the electrolytic cell efficiency slightly. A significant improvement of the cell efficiency is dependent on development of high-performance electrocatalysts.

(6) Fabrication by electrolytic deposition of Pt black electrode enhances significantly the electrocatalytic activity for ammonia oxidation and hydrogen evolution. The increase of catalytic activity of Pt black electrode is attributable to both an increased effective surface area of the electrode and an enhanced electron transfer reaction. However, the latter is predominant in the whole ammonia oxidation processes.

(7) The electrodeposition parameters affect the electrocatalytic activity of the fabricated Pt black electrode. In particular, there is an optimal depositing potential to maximize the catalytic activity of Pt black electrode. With the increasing depositing time and bath temperature, the electrocatalytic activity of Pt black electrode increases.

6.2. Recommendations for future work

(1) Fabrication by electrolytic deposition of noble metal-modified Pt-based binary and/or triple alloys as electrocatalysts for ammonia oxidation and production of hydrogen. The candidate secondary metal may include Ir, Ru, Rh, etc. The fabricated electrocatalysts may be dependent on the optimal combination of noble metal components.

(2) Development of cost-effective, high-performance electrocatalysts for ammonia oxidation. One potential alternative is to develop nickel-matrix noble metal-modified electrocatalysts, such as Ni-Pt, Ni-Ir, etc.

(3) Investigation of stability and service life of Pt and Pt-based electrocatalysts in the presence of potential affecting factors, such as oxygen, carbon dioxide, and inorganic salts, which are typically experienced in animal agricultural operation where ammonia emission is a big concern.

(4) Optimize electrolytic deposition conditions and parameters to maximize the electrocatalytic activity of the fabricated electrocatalysts. For example, optimize the nucleation and growth process to ensure uniform distribution of nano-scaled, deposited secondary metal particles.

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