

# Electrodeposited Ni–Pt binary alloys as electrocatalysts for oxidation of ammonia

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## Abstract

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. 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  $1 \text{ mg cm}^{-2}$  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. Electro-oxidation of ammonia is rate-limited by diffusion of  $\text{NH}_3$  towards the electrode surface. The  $\text{NH}_3$  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  $\text{NH}_3$  adsorption and further oxidation. It is demonstrated that fabrication by electrolytic deposition of Ni–Pt binary alloy electrode provides a promising alternative for development of low-cost, high-performance electrocatalyst for electro-oxidation of ammonia.

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**Keywords:** Electrocatalyst; Ammonia oxidation; Ni–Pt binary alloy; Electrolytic deposition

## 1. Introduction

Electro-oxidation of ammonia has been paid particular attention in recent years for production of hydrogen [1–4]. Ammonia is an excellent hydrogen carrier [1]. Liquid ammonia contains 1.7 times more hydrogen and boasts a specific energy density 50% higher than liquid hydrogen for a given volume [2]. Decomposition of ammonia by electro-oxidation technique in alkaline media at low overpotentials is  $\text{NO}_x$  and  $\text{CO}_x$  free with nitrogen and water as products of reaction [5]. Therefore, electro-oxidation of ammonia offers a significant advantage in clean energy supply.

The commonly used electrocatalysts for ammonia electro-oxidation include pure platinum (Pt) and the noble metal-modified Pt electrocatalysts. de Vooy et al. [6,7] investigated the electrocatalytic activities for ammonia oxidation on pure Ru, Pd, Rh, Ir, Pt and Au electrodes. It was found that Pt is the best elec-

trocatalyst. Endo et al. [8–10] fabricated the various Pt matrix binary alloys including Pt–Ir, Pt–Ru and Pt–Cu as electrocatalysts for ammonia oxidation in KOH solution. It was found that addition of Ir and Ru to Pt enhanced the electrocatalytic activity of ammonia, which is probably due to a kind of cooperation with Pt at the surface, whereas Cu–Pt alloy showed almost activity inferior to Pt.

Despite the high electrocatalytic activities of Pt and Pt-matrix binary alloys for ammonia oxidation, the non-affordability of these electrocatalysts limits their application at an industrial scale. Nickel was considered as a potential alternative [11]. However, Despic et al. [12] believed that nickel showed little or no activity to catalyze ammonia electro-oxidation reaction because electrochemically activated Ni surfaces were spontaneously oxidized at potentials obtaining in ammonia solution, and hence lost practically all catalytic activity for anodic oxidation of ammonia. Cooper and Botte [13] reported that there was a high catalytic activity of Raney Ni–Pt electrode for ammonia electro-oxidation in 1 M  $\text{NH}_3$ /5 M KOH solution, but further detail has not been revealed yet. To date, there has been limited work to investigate the fundamentals of pure Ni and

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Ni-noble metal binary alloys as electrocatalysts for ammonia oxidation.

In this work, electrolytic deposition technique was used to fabricate Ni-substrate Pt electrocatalysts, and the electrocatalytic activities of Ni–Pt electrocatalysts for ammonia oxidation were studied by cyclic voltammetry and surface analysis techniques including scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDXA). Furthermore, the cyclic voltammetric behaviors of Ni–Pt electrode with different Pt loading concentrations were compared with those measured on pure Ni and Pt electrodes. The parametric effects, such as ammonia concentration, KOH concentration and temperature, on electrolytic activity of Ni–Pt were investigated. It is anticipated that this work would provide an insight into development of economically affordable, high-performance Ni–Pt electrocatalysts for ammonia oxidation.

## 2. Experimental

### 2.1. Preparation of pure Ni and Pt electrodes

Nickel substrate specimens were cut from a pure nickel plate, which was supplied by Institute of Metal Research, Chinese Academy of Sciences, with the chemical composition (wt%): Co 0.01, C 0.002, Si 0.001, P 0.0001, S 0.0004, Fe 0.003, Cu 0.005, Zn 0.001, As 0.0008, Cd 0.0002, Sn 0.0001, Pb 0.0007, Bi 0.0003, Mg 0.0006 and Ni balance. Each sample was ground to 600 grit emery paper on all faces. The unexposed edges were coated with a masking paint to prevent crevice corrosion between the epoxy mount and electrode. The specimens were embedded in epoxy resin (LECO), with an exposed area of 0.26 cm<sup>2</sup>. The pure Pt electrode with a working area of 0.26 cm<sup>2</sup> was purchased from Pine Research Instrumentation and had a purity of 99.99%. Prior to cyclic voltammogram (CV) measurements, all the electrodes were polished continuously with 9, 3 and 1 μm Al<sub>2</sub>O<sub>3</sub> polishing suspension (BUEHLER), and then cleaned by ethanol and deionized water.

### 2.2. Fabrication by electrolytic deposition of Ni–Pt electrode

The depositing electrolyte was prepared with chemical composition: 65% (v/v) NaOH, 0.2 mM H<sub>2</sub>PtCl<sub>6</sub> and distilled water (ultra-high purity, 18 MΩ). All the chemicals were the analytic grade reagents (Fisher Scientific).

The galvanostatic technique was employed for electrolytic deposition of Ni–Pt binary alloy through a Solartron 1280C electrochemical system, with Ni electrode as cathode and a platinum plate as anode. The depositing current density was 1.25 mA cm<sup>-2</sup>. The fabricated Ni–Pt electrodes with different Pt loading concentrations were prepared by controlling the depositing time. According to Faraday's law, a Pt loading of 0.5 mg cm<sup>-2</sup> required a depositing time of 780 s, and the loading concentrations of 1.0, 2.0 and 3.0 mg cm<sup>-2</sup> corresponded the depositing times of 1560, 3120 and 4680 s at room temperature, respectively.

### 2.3. Measurements of cyclic voltammograms

Measurements of CVs were performed in a three-electrode cell through the Solartron 1280C electrochemical system. Pure Ni or Ni–Pt alloy was used as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The test solutions contained ammonia hydroxide (extra pure, ACRÖS Organics) and KOH (analytical reagent, BDH Inc.) with various concentrations. The CVs were measured at a potential sweep rate of 5 mV s<sup>-1</sup>.

Prior to and during tests, the test solutions were purged with high-purity nitrogen gas (99.999%). All the tests were performed at room temperature with the exception that the effect of temperature on ammonia electro-oxidation was investigated.

### 2.4. Surface characterization of the deposited Ni–Pt binary alloys

The morphology and composition of fabricated Ni–Pt binary alloys were characterized using a Philips XL30 SEM and the coupled EDXA.

## 3. Results

### 3.1. CVs measured on pure Ni, pure Pt and Ni–Pt electrodes in alkaline solutions

Fig. 1 shows CVs measured on pure Ni (A), pure Pt (B) and Ni–Pt with 1 mg cm<sup>-2</sup> Pt loading (C) electrodes in 1.0 M KOH solution without and with 0.1 M ammonia. It is seen that, on pure Ni electrode (Fig. 1(A)), one anodic current peak was observed at about -1.0 V (SCE) in both KOH and KOH + ammonia solutions. The CV measured on pure Pt electrode in KOH solution was similar to those measured on pure Ni electrode. However, when solution contained 0.1 M ammonia, another anodic current peak was observed at a more positive potential of about -0.35 V (SCE). The CVs measured on Ni–Pt electrode were similar to those measured on pure Pt electrode, as shown in Fig. 1(B) and (C). Furthermore, the peak current densities at -0.35 V (SCE) on Ni–Pt electrode was 0.40 mA cm<sup>-2</sup>, which was comparable to 0.41 mA cm<sup>-2</sup> measured on pure Pt electrode.

### 3.2. CVs measured on Ni–Pt electrodes with the various Pt loading concentrations

Fig. 2 shows CVs measured on fabricated Ni–Pt electrodes with different Pt loading concentrations in 1 M KOH + 0.1 M ammonia solution. It is apparent that the peak current density at -0.35 V (SCE) increased with the increasing Pt loading concentration, while the characteristic peak potential was not shifted.

### 3.3. Morphology and composition of the fabricated Ni–Pt electrodes

Fig. 3 shows SEM images of the surface morphologies of pure Ni and Ni–Pt electrodes with the various Pt loading concen-

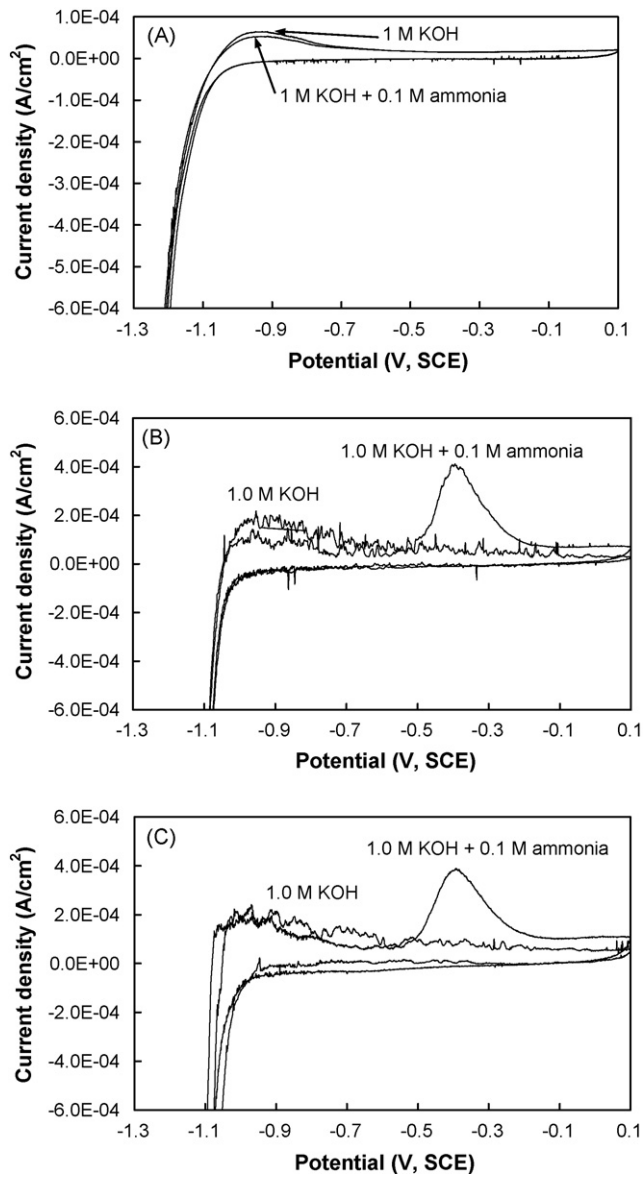


Fig. 1. Cyclic voltammograms measured on pure Ni (A), pure Pt (B) and Ni–Pt (C) electrodes in 1.0 M KOH solution without and with 0.1 M ammonia.

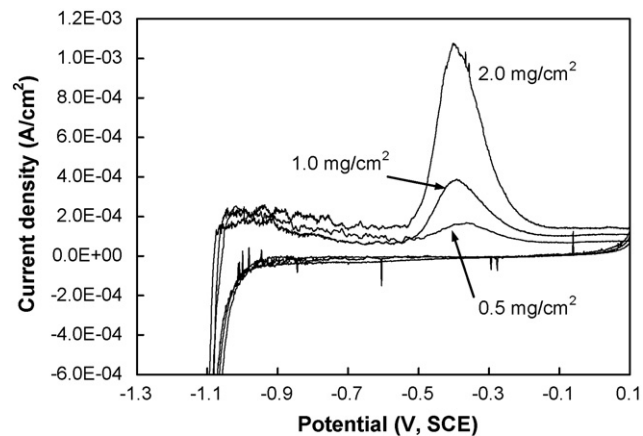


Fig. 2. Cyclic voltammograms measured on Ni–Pt electrode with the different Pt loading concentrations in 1 M KOH + 0.1 M ammonia solution.

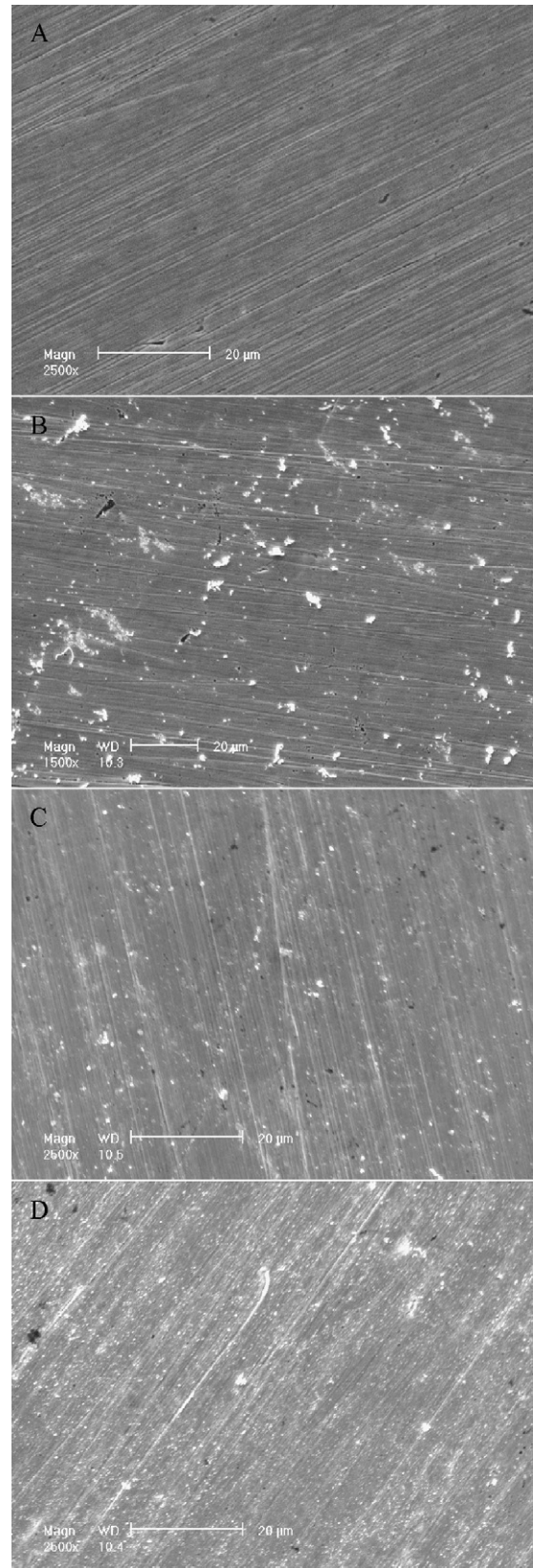


Fig. 3. SEM images of the surface morphologies of pure Ni (A) and Ni–Pt electrodes with the Pt loading concentrations of 0.5 mg cm<sup>-2</sup> (B) and 2.0 mg cm<sup>-2</sup> (C).

Table 1

Chemical compositions (wt%) of the whole electrode and the selected white dots on Ni–Pt electrodes with different Pt loading concentrations

	Whole electrode		Selected white dot	
	Ni	Pt	Ni	Pt
Pure Ni	100	0	N/A	N/A
Ni–Pt (0.5 mg cm <sup>-2</sup> Pt loading)	97.30	2.70	96.81	3.19
Ni–Pt (1.0 mg cm <sup>-2</sup> Pt loading)	95.84	4.16	95.39	4.61
Ni–Pt (2.0 mg cm <sup>-2</sup> Pt loading)	89.76	10.24	89.45	10.55

trations. Compared to pure Ni, a number of white dots were distributed on the surface of Ni–Pt electrode. The density of white dots increased significantly with the Pt loading concentration. Furthermore, with the increasing Pt loading concentration, the dot size decreased. For example, the average diameter of dots was approximately 3–5  $\mu\text{m}$  when the Pt loading concentration was 0.5 mg cm<sup>-2</sup>, while the dots were less than 1  $\mu\text{m}$  (within the scale of nanometer) when the Pt loading concentration was up to 2 mg cm<sup>-2</sup>.

To investigate the deposition of Pt under different Pt loading concentrations, EDXA was performed to measure both the averaged composition of the whole electrode and the composition specific to the selected white dot. EDXA results are summarized in Table 1. It is seen that the total Pt concentration increased with the increasing Pt loading concentration. Furthermore, white dots contained more Pt than the whole electrode.

#### 3.4. Parametric effects on CVs measured on Ni–Pt electrode

Fig. 4 shows CVs measured on Ni–Pt electrode with 1 mg cm<sup>-2</sup> Pt loading concentration in 1.0 M KOH solution with the various ammonia concentrations. It is seen that the peak current density at  $-0.35$  V (SCE) increased with the increasing ammonia concentration. A further observation shows that the increasing amplitude of peak current density from 0.1 to 1.0 M ammonia was much smaller than that for the ammonia concentration increasing from 0.05 to 0.1 M.

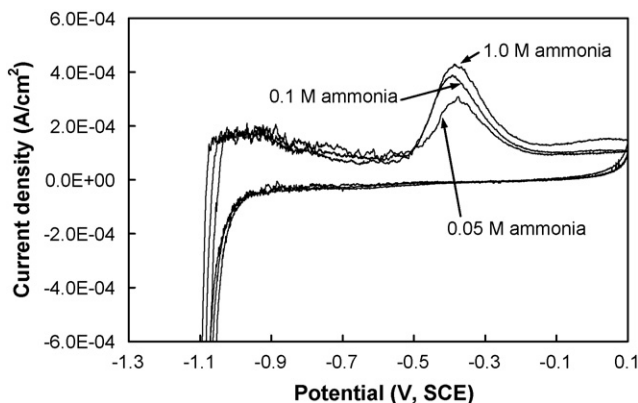


Fig. 4. Cyclic voltammograms measured on Ni–Pt electrode (1 mg cm<sup>-2</sup> Pt loading) in 1.0 M KOH solution with the various ammonia concentrations.

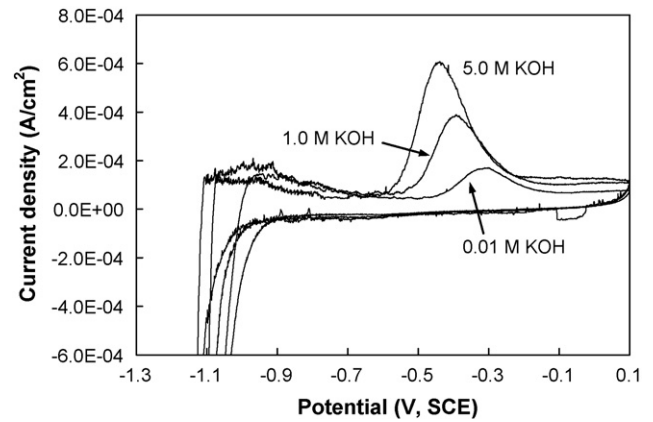


Fig. 5. Cyclic voltammograms measured on Ni–Pt electrode (1 mg cm<sup>-2</sup> Pt loading) in 1.0 M KOH solution with the various KOH concentrations.

Fig. 5 shows CVs measured on Ni–Pt electrode with 1 mg cm<sup>-2</sup> loading concentration in 0.1 M ammonia solution with the various KOH concentrations. It is seen that the peak current density at  $-0.35$  V (SCE) increased with the increasing KOH concentration. Furthermore, the peak potential was shifted negatively when KOH concentration increased.

Fig. 6 shows CVs measured on Ni–Pt electrode with 1 mg cm<sup>-2</sup> loading concentration in 0.1 M ammonia + 1 M KOH solution at different temperatures. Generally, the peak current density at  $-0.35$  V (SCE) increased with the increase in temperature, while peak potential was shifted negatively.

Fig. 7 shows CVs measured on Ni–Pt electrode with 1 mg cm<sup>-2</sup> loading concentration in 0.1 M ammonia + 1 M KOH solution at the various potential sweep rates. It is seen that the peak current density at  $-0.35$  V (SCE) increased with the increasing potential sweep rate, and peak potential remained unchanged.

## 4. Discussion

### 4.1. Cyclic voltammetric behavior of pure Ni, pure Pt and Ni–Pt electrodes in alkaline solutions

The anodic current peaks at about  $-1.0$  V (SCE) observed in all the three electrodes in Fig. 1 are attributed to the oxidation of

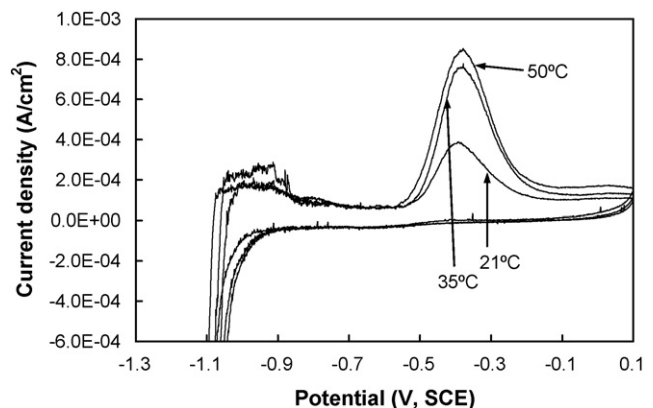


Fig. 6. Cyclic voltammograms measured on Ni–Pt electrode (1 mg cm<sup>-2</sup> Pt loading) in 0.1 M ammonia + 1.0 M KOH solution at the different temperatures.



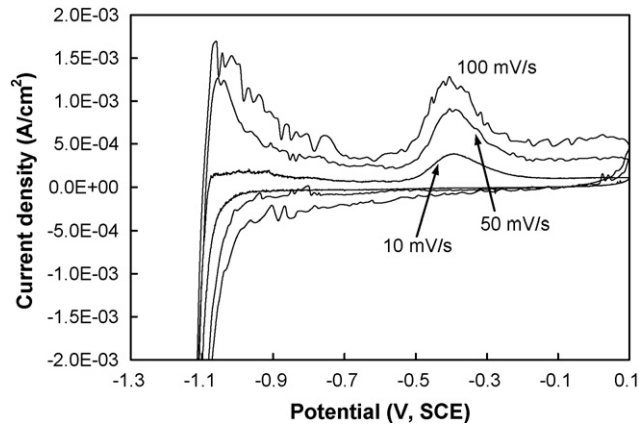


Fig. 7. Cyclic voltammograms measured on Ni–Pt electrode ( $1 \text{ mg cm}^{-2}$  Pt loading) in 0.1 M ammonia + 1.0 M KOH solution at the different potential scanning rates.

hydrogen atoms that are generated during cathodic polarization. Since there is a much lower overpotential for hydrogen evolution reaction on Pt than on Ni, the peak current densities at  $-1.0 \text{ V}$  (SCE) measured on Pt and Ni–Pt electrodes are much higher than that measured on Ni electrode.

The anodic current peaks at  $-0.35 \text{ V}$  (SCE) measured on Pt and Ni–Pt electrodes in ammonia-containing solution are attributed to oxidation of ammonia to  $\text{N}_2$  [14]. Apparently, both pure Pt and Ni–Pt electrodes have high catalytic activity for electro-oxidation of ammonia. Furthermore, a comparison of the peak current density for ammonia oxidation indicates that electrocatalytic activity of the fabricated Ni–Pt electrode with only  $1 \text{ mg cm}^{-2}$  of Pt loading is comparable to that of pure Pt electrode. With the increases in Pt loading concentration, the catalytic activity for ammonia oxidation further increases, as shown in Fig. 2. Therefore, fabrication by electrolytic deposition of Ni–Pt binary alloy electrode provides a promising alternative for development of low-cost, high-performance electrocatalyst for electro-oxidation of ammonia.

The anodic current peak corresponding to ammonia oxidation is not observed on pure Ni electrode no matter if ammonia is contained in the solution, as shown in Fig. 1(A). The lack of catalytic activity of Ni is due to the oxidation of Ni in alkaline solution. It has been acknowledged [15,16] that, in alkaline solution, Ni is oxidized to form two-valence nickel oxides containing  $\text{Ni}(\text{OH})_2$  or  $\text{NiO}$  or both. The oxidized Ni does not have catalytic activity for ammonia oxidation. Thus, the use of nickel as an electrocatalyst for ammonia electro-oxidation is unfeasible.

#### 4.2. Electro-oxidation of ammonia on Ni–Pt electrodes

The mechanism of ammonia electro-oxidation on electrocatalysts, as proposed by Gerischer and Mauerer [17], involves diffusion, adsorption of  $\text{NH}_3$  and then dehydrogenation steps of  $\text{NH}_{3,\text{ads}}$  to  $\text{N}_{\text{ads}}$  as well as the recombination of two  $\text{NH}_{x,\text{ads}}$ , where partially dehydrogenated species of  $\text{NH}_{2,\text{ads}}$  and  $\text{NH}_{\text{ads}}$  are active intermediates to give the final product of  $\text{N}_2$ :

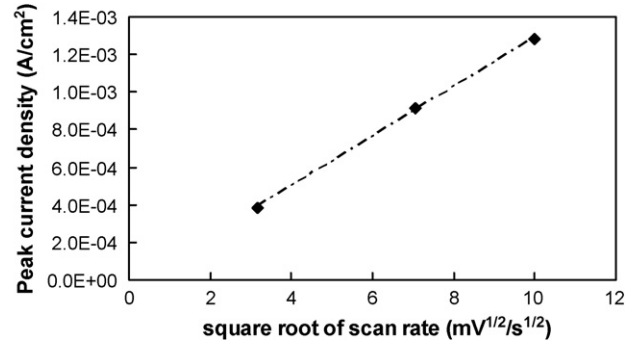
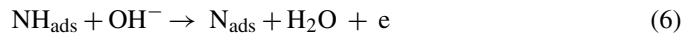
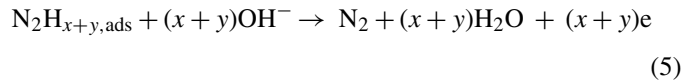
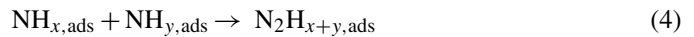
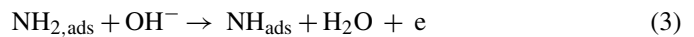
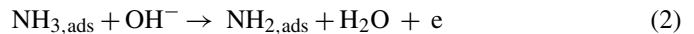


Fig. 8. The peak current density as a function of the square root of potential sweep rate.



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

To determine the rate-limiting step in ammonia electro-oxidation, analysis is performed to investigate the current density response to the potential sweep rate. The increasing anodic current density with potential sweep rate is attributed to the excitation signal by-passing charge-transfer processes during charging of the interfacial capacitance. Furthermore, peak potentials are independent of potential sweep rate, and peak current density follows a linear  $v^{1/2}$  ( $v$ : potential sweep rate) dependence, as shown in Fig. 8, indicating mass-transfer control of ammonia electro-oxidation reaction [18].

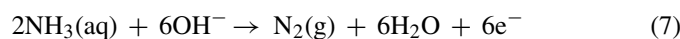
Once diffusing to reach the electrode surface,  $\text{NH}_3$  adsorbs on specific active sites on electrode, i.e., the deposited Pt on Ni–Pt electrode. The morphological observation of the deposited electrode surface by SEM shows that the deposited Pt is distributed randomly on Ni surface and it is not necessary for the whole Ni electrode to be covered completely by Pt. With the increase in Pt loading concentration, more Pt is deposited to generate more active sites for  $\text{NH}_3$  adsorption. Consequently, the oxidizing current density increases. Furthermore, with the increasing Pt loading concentration, there is a more uniform distribution of deposited Pt that is within the range of nano-scale in size, as shown in Fig. 3. The refined Pt particles increase the total surface area of the active sites for  $\text{NH}_3$  adsorption and enhanced ammonia oxidation.

#### 4.3. Parametric effects on electrocatalytic activity of Ni–Pt electrode

This work shows that the increasing ammonia concentration causes the increase in anodic current density at potential typical of ammonia oxidation. Generally, with the increase in

ammonia concentration in the solution, more  $\text{NH}_3$  (aq) will be adsorbed on electrode surface to be oxidized, resulting in the increasing anodic current density. However, adsorption of ammonia on electrocatalyst electrode will achieve a relatively saturation status. The further increase of ammonia concentration will accelerate the adsorption saturation process. Moreover, the intermediates generated during ammonia oxidation, such as  $\text{NH}_{2,\text{ads}}$  and  $\text{NH}_{\text{ads}}$ , could remain on electrode surface and block ammonia adsorption. It is reasonable to assume that the block effect will be significant when the solution contains a high concentration of ammonia. Therefore, peak current density increases significantly when the ammonia concentration in the solution is low, and increases slowly with the further increase in ammonia concentration.

The critical role of KOH 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. Furthermore, the increasing alkalinity can decrease the ammonia oxidation overpotential, shifting the ammonia oxidation potential negatively. Such an essential role of alkalinity can be explained by Nernst equation for reaction (7) that is the combination of reactions (1)–(6) under the constant ammonia concentration and test temperature:



$$\varphi_{\text{NH}_3/\text{N}_2} = \varphi_{\text{NH}_3/\text{N}_2}^0 - \frac{2.303RT}{nF} \log \frac{[\text{NH}_3]^2[\text{OH}^-]^6}{[\text{N}_2]} \quad (8)$$

where  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}$ ),  $T$  the temperature,  $n$  the number of exchanged electrons, and  $F$  is Faraday's constant. It is apparent that the ammonia oxidation potential decreases with the increasing hydroxide ion concentration, i.e., alkalinity of the solution.

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 bulk solution through the diffusive layer to adsorb on electrode surface (mass-transfer effect) or the rapid electro-oxidation reactions (activation effect). Furthermore, the negative shift of peak potential, which can be explained by Nernst equation of ammonia oxidation reaction (7), indicates the favorable condition (the lowered overpotential) for ammonia oxidation.

## 5. Conclusions

Fabrication by electrolytic deposition of Ni–Pt binary alloy electrode provides a promising alternative for development of low-cost, high-performance electrocatalyst for electro-oxidation of ammonia. Electrocatalytic activity of the fabricated Ni–Pt electrode with only  $1 \text{ mg cm}^{-2}$  of Pt loading 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.

Pure Ni does not have catalytic activity for ammonia oxidation due to its oxidation in alkaline solution.

The ammonia electro-oxidation is rate-limited by diffusion of  $\text{NH}_3$  towards the electrode surface. The  $\text{NH}_3$  adsorption occurs at the active spots that are deposited Pt on Ni surface. With the increase of Pt loading concentration, the distribution of Pt is more uniform and the size of Pt particles becomes smaller within the range of nano-scale, which increases the total active area for  $\text{NH}_3$  adsorption.

The ammonia electro-oxidation current increases significantly with the increasing ammonia concentration in the solution, and then increases slowly when ammonia concentration is sufficiently high to fasten the saturation of  $\text{NH}_3$  adsorption on the electrode surface. The role of KOH in ammonia electro-oxidation is to increase the oxidative current density and to decrease over-potential. The increase in temperature could increase the ammonia oxidation current density and decrease over-potential.

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## References

- [1] R.A. Wynveen, *Fuel Cells* 2 (1963) 153–167.
- [2] G. Strickland, *Int. J. Hydrogen Energy* 9 (1984) 759–766.
- [3] S.F. Yin, B.Q. Xu, X.P. Zhou, C.T. Au, *Appl. Catal. A: Gen.* 277 (2004) 1–9.
- [4] F. Vitse, M. Cooper, G.G. Botte, *J Power Sources* 142 (2005) 18–26.
- [5] S. Wasmus, E.J. Vasini, M. Krausa, H.T. Mishima, W. Vielstich, *Electrochim. Acta* 39 (1994) 23–31.
- [6] A.C.A. de Vooy, M.F. Mrozek, M.T.M. Koper, R.A. van Santen, J.A.R. van Veen, M.J. Weaver, *Electrochem. Commun.* 3 (2001) 293–298.
- [7] A.C.A. de Vooy, M.T.M. Koper, R.A. van Santen, J.A.R. van Veen, *J. Electroanal. Chem.* 506 (2001) 127–137.
- [8] K. Endo, Y. Katayama, T. Miura, *Electrochim. Acta* 49 (2004) 1635–1638.
- [9] K. Endo, K. Nakamura, Y. Katayama, T. Miura, *Electrochim. Acta* 49 (2004) 2503–2509.
- [10] K. Endo, Y. Katayama, T. Miura, *Electrochim. Acta* 50 (2005) 2181–2185.
- [11] A. Hu, M. Copper, F. Vitse, G.G. Botte, *Proceedings of the 204th Annual Meeting of the Electrochemical Society, Orlando, FL, October 12–16, 2003*, Abstract 57.
- [12] A.R. Despic, D.M. Drazic, P.M. Rakin, *Electrochim. Acta* 11 (1966) 997–1005.
- [13] M. Cooper, G.G. Botte, *Proceedings of the 205th Annual Meeting of the Electrochemical Society, San Antonio, TX, May 9–13, 2004*, Abstract 676.
- [14] T. Katan, R.J. Galiotto, *J. Electrochem. Soc.* 110 (1963) 1022–1023.
- [15] C.A. Melendres, M. Pankuch, *J. Electroanal. Chem.* 333 (1992) 103–113.
- [16] L. Zhang, D.D. Macdonald, *Electrochim. Acta* 43 (1998) 2661–2671.
- [17] H. Gerischer, A. Mauerer, *J. Electrochem. Chem.* 25 (1970) 421–443.
- [18] C. Gabrielli, M. Keddad, H. Takenouti, V.Q. Kinh, F. Bourelier, *Electrochim. Acta* 24 (1979) 61–65.