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# Methanol oxidation reaction activity of microwave-irradiated and heat-treated Pt/Co and Pt/Ni nano-electrocatalysts

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## ABSTRACT

Bimetallic Pt nanoparticles were prepared by alloying Pt with the non-noble transition metals, Co and Ni, using a conventional heat-treatment (HT) method and microwave-irradiation (MW). The resulting samples were Pt–Co-HT, Pt–Ni-HT, Pt–Co, MW and Pt–Ni-MW. The aim was to evaluate the electrocatalytic behaviour and surface properties of the materials based on the alloying metal used and the synthesis process. XRD studies of the nanoparticles indicated that alloyed structures were formed for the microwave (MW) synthesized samples, as seen by a decrease in the lattice parameters. Using X-ray photoelectron spectroscopy analysis, surface segregation of Co and Ni occurred (1:4 surface atomic ratio Pt–Co or Ni) for the Pt–Co-MW and Pt–Ni-MW samples. In contrast the heat-treated Pt–Ni catalyst showed Pt surface segregation. Methanol oxidation reaction (MOR) studies revealed an increase in the electrocatalytic activity upon the addition of Co and Ni to Pt when compared to a monometallic Pt catalyst. The presence of oxide and hydroxide alloying metal species is suggested to be the cause of the observed enhancement in the catalytic activity. Overall the Pt–Ni-MW catalyst displayed the best MOR activity and this is attributed to the large amounts of Ni-hydroxide species observed on the catalyst surface. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Recent interest in fuel cells as alternative energy devices have resulted in a substantial increase in their study, especially direct methanol fuel cells (DMFCs) [1–3]. This is because methanol has advantages over hydrogen as a fuel source as it is cheap, is easy to handle, transport and store, and it also has a high theoretical energy density [1,4]. The most commonly

used catalyst in DMFCs is platinum (Pt). However, the use of Pt has drawbacks that include the high cost of Pt [5], as well as the propensity for Pt to be poisoned by carbon monoxide (CO), which is one of the carbonaceous species formed during the methanol dissociation process [6,7]. A general remedy to this problem is to alloy Pt with cheaper transition metals such as nickel [8], cobalt [5], iron [9] and ruthenium [10]. In addition to lowering the overall costs, these metals also increase the CO tolerance of the Pt catalysts.

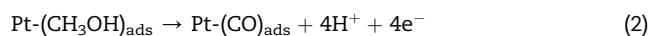
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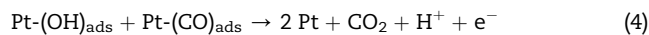
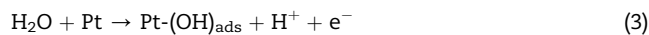
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To achieve further success in the use of Pt-alloy catalysts, it is important to understand the mechanism of CO poisoning in the methanol oxidation reaction (MOR). The first reaction (Eq. (1)) in MOR is methanol adsorption on the catalyst to give Pt-(CH<sub>3</sub>OH)<sub>ads</sub>, which occurs at potentials of around 0.2 V and requires several free Pt binding sites [11]. The Pt-(CH<sub>3</sub>OH)<sub>ads</sub> is then broken down to produce Pt-(CO)<sub>ads</sub> (Eq. (2)) and carbonaceous species such as CO, formic acid and formaldehyde [12]. The dissociation of water then takes place at 0.4–0.5 V on pure Pt electrodes, where the H<sub>2</sub>O molecule acts as the oxygen donor for the reaction. The electro-oxidation of methanol on the platinum electrode occurs as follows:



This adsorbed CO is then removed by the reaction with OH<sub>ads</sub> (Eqs. (3) and (4)), produced by the dissociation of the water molecules [13]:



The overall reaction yields 6e<sup>−</sup> and 6H<sup>+</sup> for each adsorbed molecule of CH<sub>3</sub>OH [7], as well as CO<sub>2</sub>, formed by the surface reaction between the CO- and O-species (from OH) (Eq. (4)). These formed carbonaceous species can block the catalytically active sites and affect the overall efficiency of the catalysts [6,12].

Numerous mechanisms have been proposed to explain the enhancement in the activity of the methanol oxidation reaction (MOR) through the addition of the alloying of transition metals. These include the bifunctional model [14], the ligand model, the synergistic effect model and the oxide formation model [15]. For example, in the bifunctional model, an oxygenated surface is created by H<sub>2</sub>O dissociation at the metal alloy sites which are at lower potentials (0.2 V, NHE) when compared to monometallic Pt sites. This promotes the oxidation of adsorbed CO to CO<sub>2</sub>, decreasing the amount of CO present, thus resulting in the improvement of the metal CO tolerance [16,17]. In the ligand model the alloying metal changes the chemical properties of Pt at the surface, weakening the Pt-CO<sub>ads</sub> bond and minimizing CO poisoning [7,18–20].

The effect of the addition that the alloying metals such as Co [2,5] and Ni [8,14] have on the electrocatalytic activity of Pt is well researched. Paulus et al. [21] studied the catalytic activity of Pt<sub>3</sub>Ni and Pt<sub>3</sub>Co bulk alloy catalysts with emphasis on the alloy surface properties. They found that Pt<sub>3</sub>Co had an improved activity when compared to Pt<sub>3</sub>Ni and Pt alone, though they did not perform CO poisoning studies. The same was also observed by Antolini et al. [2] and Zhang et al. [22] for Pt–Co electrocatalysts, and Kang et al. [3], and Deivaraj et al. [8] for Pt–Ni electrocatalysts in MOR. When Co and Ni atoms

are added to Pt, they modify the Pt (fcc) lattice and improve oxidation reactions by lowering the electron binding energy in Pt [2]. The Co (−0.28 V) and Ni (−0.26 V) redox potentials are very close to each other [23] and are lower than that of Pt (0.73 V) which indicates the higher reduction ability of Pt. These two transition metals possess the ability to enhance the MOR activity by promoting C–H bond cleavage at low potentials [8]. The presence of Co or Ni oxides on the surface also provides an oxygen source for CO oxidation in the bifunctional model.

In the work presented here, we demonstrate the methanol oxidation behaviour of Pt–Co and Pt–Ni nanoparticles synthesized using a conventional synthesis procedure entailing heat-treatment and a microwave-irradiation synthesis process. The aim was to evaluate the role of the synthesis strategies on the production of Pt catalysts alloyed with Co and Ni and to evaluate the activity and resistance to CO poisoning of the new alloys. The atomic ratio of metals used in synthesizing these nanoparticles was 1:1 (Pt: Co/Ni) to reduce the amount and therefore the cost of Pt needed to obtain enhanced catalytic activity.

## Experimental procedure

### Materials

H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (99%), NiCl<sub>2</sub>·6H<sub>2</sub>O (97%), CoCl<sub>2</sub>·6H<sub>2</sub>O (99%), ethylene glycol (EG, ≥99.5%), polyvinylpyrrolidone (MW 40,000, PVP-40), NaBH<sub>4</sub> (95%), isopropanol (99.5+%), Nafion (5 wt%, 45% water) and tetrahydrofuran (THF, 99.9%) were purchased from Sigma Aldrich and used as received without further modification or purification.

### Heat-treatment (HT) synthesis

PVP-40 (500 mg; 0.0125 mmol), CoCl<sub>2</sub> (250 mg; 1.05 mmol) or NiCl<sub>2</sub> (250 mg; 1.05 mmol) and H<sub>2</sub>PtCl<sub>6</sub> (545 mg; 1.05 mmol) were dissolved in THF (10 ml) and stirred for 18 h. NaBH<sub>4</sub> (1.0 M, 10 ml) was added drop wise to this solution to reduce the metal precursors. The mixture was further stirred for 2 h before centrifuging and washing with a 50/50 distilled water/ethanol mixture four times, and then the precipitates were air-dried at room temperature overnight. The resulting powders were heat-treated at 150 °C (Pt–Co) and 200 °C (Pt–Ni) for 4 h to remove low boiling contaminants and capping agents. These samples will be referred to as Pt–Co-HT and Pt–Ni-HT (HT = heat-treatment). For this procedure, platinum nanoparticles were also synthesized without the addition of Co or Ni for comparison.

### Microwave-irradiation (MW) synthesis

PVP-40 (500 mg; 0.0125 mmol), CoCl<sub>2</sub> (250 mg; 1.05 mmol) or NiCl<sub>2</sub> (250 mg; 1.05 mmol) and H<sub>2</sub>PtCl<sub>6</sub> (545 mg; 0.0125 mmol) were dissolved in EG (60 ml) and stirred for 2 h before adding NaOH (1.0 M, 10 ml). The two solutions, which contained Pt:M (M = Co or Ni) in a 1:1 M ratio, were poured into Teflon reaction vessels and irradiated with microwaves in an Anton Paar M300 reactor (temperature = 200 °C, power = 750 W,

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