



Composition dependence of ternary Pt–Ni–Cr catalyst activity for the methanol electro-oxidation reaction

Min Ku Jeon, Paul J. McGinn*

Department of Chemical and Biomolecular Engineering, University of Notre Dame, 178 Fitzpatrick, Notre Dame, IN 46556, United States

ARTICLE INFO

Article history:

Received 28 April 2009

Received in revised form 5 June 2009

Accepted 8 June 2009

Available online 17 June 2009

Keywords:

Methanol electro-oxidation

Direct methanol fuel cell

Electrocatalyst

Cyclic voltammetry

Chronoamperometry

Combinatorial chemistry

ABSTRACT

Various compositions of binary and ternary Pt–Ni–Cr alloys were investigated as catalysts for the methanol electro-oxidation reaction (MOR). Among the binary (Pt₂₈Ni₇₂/C and Pt₂₈Cr₇₂/C) and ternary Pt–Ni–Cr catalysts (Pt₂₈Ni₃₆Cr₃₆/C, Pt₂₂Ni₃₉Cr₃₉/C, Pt₃₃Ni₃₁Cr₃₆/C, and Pt₃₃Ni₃₆Cr₃₁/C) examined, the Pt₂₈Ni₃₆Cr₃₆/C composition exhibited the highest MOR mass activity (4.42 A g_{cat.}⁻¹) in the as-prepared version, which was higher than the 3.58 A g_{cat.}⁻¹ value of the PtRu/C catalyst after 60 min of chronoamperometry testing. The order of mass activity for the MOR was Pt₂₈Ni₃₆Cr₃₆/C > Pt₃₃Ni₃₆Cr₃₁/C > Pt₂₂Ni₃₉Cr₃₉/C > Pt₃₃Ni₃₁Cr₃₆/C > Pt₂₈Cr₇₂/C > Pt₂₈Ni₇₂/C, which was slightly changed to Pt₂₈Ni₃₆Cr₃₆/C > Pt₂₂Ni₃₉Cr₃₉/C > Pt₃₃Ni₃₆Cr₃₁/C > Pt₃₃Ni₃₁Cr₃₆/C > Pt₂₈Cr₇₂/C > Pt₂₈Ni₇₂/C after a conditioning process. The effect of anodic conditioning was also studied. A combination of X-ray diffraction, cyclic voltammetry, and chronoamperometry experiments revealed that the conditioning process caused dissolution and an oxidation state change of metallic Ni and Cr₂O₃ in the binary catalysts. The higher MOR mass activities of the ternary catalysts compared to the binary ones is attributed to co-alloying of Ni and Cr, leading to exposure of more Pt on the catalyst surface without reducing specific activities of the catalysts. The results of this study also correlate well with a prior ranking of catalytic activity of the same compositions in the form of thin film catalysts that we processed and evaluated by a high-throughput combinatorial approach [J.S. Cooper, M.K. Jeon, P.J. McGinn, *Electrochem. Commun.* 10 (2008) 1545–1547].

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Methanol electro-oxidation reaction (MOR) catalysts are under intensive study for direct methanol fuel cells (DMFCs) application. Unlike other types of fuel cells which use hydrogen as an anode reactant, DMFCs use methanol as the anode fuel. The use of liquid fuel allows for easy fuel handling and reduced re-fueling time. These merits make DMFCs a promising alternative for lithium-ion batteries for portable applications [1]. Although the performance of DMFCs has been strongly improved during the last two decades, DMFCs still suffer from low catalytic activity of the anode and cathode catalysts, and methanol cross-over from the anode to the cathode electrode.

Initially, Pt was employed as the MOR catalyst in DMFCs, but a rapid decrease of activity was observed because of poisoning by intermediate CO [1]. CO tolerance was significantly improved by introducing a Pt–Ru alloy catalyst [2–5]. Pt–Ru is still widely used, but a desire for greater MOR activity and reduced costs have led to a continued search for alternative catalysts. Most researchers

have focused on Pt–Ru based catalysts [6–8] including PtRuFe [9,10], PtRuNi [11,12], PtRuCo [13–15], PtRuW [14–17], and PtRuMo [16,18] to achieve both improved MOR activity and reduced costs. However, recent reports on the performance degradation of DMFCs show that dissolution of Ru occurs during long-term operation [19,20] and that the dissolved Ru crosses through the membrane and are reduced on the cathode electrode resulting in performance decrease [21,22]. Thus more research on Ru-free MOR catalysts is desirable. There are only a limited number of reports on Ru-free MOR catalysts, with promising results being reported in Pt–Co, Pt–Ni, Pt–Fe [23], Pt–Pb [24–26], Pt–Ni–Cr [27–29], and Pt–Co–Cr [30] alloy systems.

Previously, we investigated ternary Pt–Ni–Cr alloys as candidate catalysts for the MOR via a thin film combinatorial method and followed this with an examination of powder versions of the best catalyst compositions [27–29]. It was shown that Pt₂₈Ni₃₆Cr₃₆ composition exhibits satisfactory performance for the MOR that was comparable to that of a PtRu/C catalyst. A thin film combinatorial method is a powerful tool to explore many compositions quickly, but it needs to be complemented by other studies because the synthesis and characterization methods used in the combinatorial libraries are different from conventional techniques used for powder versions of catalysts as typically employed in fuel cells [31,32].

* Corresponding author. Tel.: +1 574 631 6151; fax: +1 574 631 8366.
E-mail address: mcginn.1@nd.edu (P.J. McGinn).

In our earlier Pt–Ni–Cr catalyst study [27], we used multi-target sputtering to synthesize multi-layers of Pt, Ni, and Cr. The multi-layers were annealed to form homogeneous alloys and then characterized simultaneously in a multichannel multielectrode analyzer. The follow-up powder version of the best thin film catalyst composition was synthesized by a chemical reduction method and then characterized by conventional methods such as cyclic voltammetry (CV) and chronoamperometry (CA) experiments. In that study only the best thin film composition was examined. Hence it is natural to consider a range of powder compositions around the best thin film composition to investigate if the different synthesis/characterization techniques yield different optima and provide further validation of the thin film approach. Differences between powder and thin film performance might arise due to differing surface properties such as composition or the oxidation states of Ni and Cr.

Thus the present study examines if the best composition identified via a thin film combinatorial approach is also the best among a range of powder compositions. Various compositions of ternary ($\text{Pt}_{28}\text{Ni}_{36}\text{Cr}_{36}$, $\text{Pt}_{22}\text{Ni}_{39}\text{Cr}_{39}$, $\text{Pt}_{33}\text{Ni}_{31}\text{Cr}_{36}$, and $\text{Pt}_{33}\text{Ni}_{36}\text{Cr}_{31}$ compositions) and binary ($\text{Pt}_{28}\text{Ni}_{72}$ and $\text{Pt}_{28}\text{Cr}_{72}$) catalysts from the Pt–Ni–Cr systems were synthesized and characterized. In addition, the effect of an anodic conditioning process was also investigated. The conditioning process was previously introduced in thin film library studies to improve the MOR activity [14]. The activity improvement was subsequently also observed in powder versions of a Pt–Ni–Cr catalyst [29] indicating that the conditioning process is beneficial to achieve higher MOR activity.

2. Experimental methods

2.1. Catalysts synthesis

All the Pt–Ni–Cr catalysts were synthesized by a conventional NaBH_4 reduction method [33]. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, NiCl_2 , and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as Pt, Ni, and Cr precursors, respectively. The precursors were dissolved in a mixture of de-ionized (DI) water and isopropyl alcohol (80:1 volume ratio). Carbon support (Vulcan XC 72R) was added to the mixture. The mixture was sonicated and stirred for 30 min to achieve homogeneous mixing. 0.2 M NaBH_4 solution was added to the mixture as a reducing agent. Previously, we have shown that the amount of reducing agent, NaBH_4 , affects catalytic properties of the PtNiCr catalysts [28], and the highest MOR activity was observed when 50 times the stoichiometric amount of NaBH_4 was applied. In this study, the amount

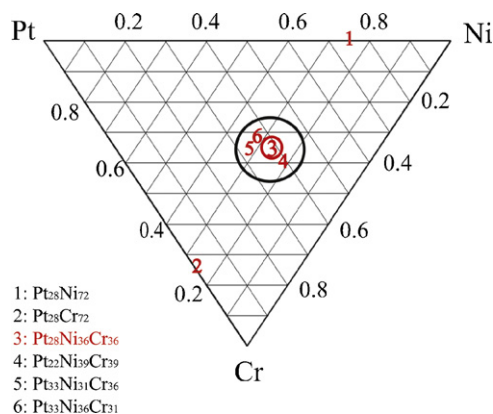


Fig. 1. Map of the synthesized catalyst compositions: $\text{Pt}_{28}\text{Ni}_{72}/\text{C}$, $\text{Pt}_{28}\text{Cr}_{72}/\text{C}$, $\text{Pt}_{28}\text{Ni}_{36}\text{Cr}_{36}/\text{C}$, $\text{Pt}_{22}\text{Ni}_{39}\text{Cr}_{39}/\text{C}$, $\text{Pt}_{33}\text{Ni}_{31}\text{Cr}_{36}/\text{C}$, and $\text{Pt}_{33}\text{Ni}_{36}\text{Cr}_{31}/\text{C}$. The circled composition range investigated in this study was identified as the region of highest activity in thin film screening [27]. Point '3' is the composition $\text{Pt}_{28}\text{Ni}_{36}\text{Cr}_{36}$, which showed the highest MOR activity in the thin film library.

of 0.2 M NaBH_4 solution was fixed as 50 times the stoichiometric amount for all samples except for the Pt/C and PtRu/C catalysts. The mixture was further stirred for 1 h to complete the reduction reaction. All reactions were performed at room temperature. The final mixture was filtered and washed with DI water. The resulting powder was dried at 100 °C in an oven overnight. Total metal loading was adjusted to 20 wt.% of the total catalyst mass. The synthesized catalysts were named according to their composition so, for example, $\text{Pt}_{28}\text{Ni}_{36}\text{Cr}_{36}/\text{C}$ represents a molar ratio of Pt:Ni:Cr of 28:36:36. Synthesized ternary and binary catalyst compositions are: $\text{Pt}_{28}\text{Ni}_{36}\text{Cr}_{36}/\text{C}$, $\text{Pt}_{22}\text{Ni}_{39}\text{Cr}_{39}/\text{C}$, $\text{Pt}_{33}\text{Ni}_{31}\text{Cr}_{36}/\text{C}$, $\text{Pt}_{33}\text{Ni}_{36}\text{Cr}_{31}/\text{C}$, $\text{Pt}_{28}\text{Ni}_{72}/\text{C}$, and $\text{Pt}_{28}\text{Cr}_{72}/\text{C}$. A composition map is shown in Fig. 1. Pt/C and $\text{Pt}_{50}\text{Ru}_{50}/\text{C}$ ("PtRu/C") catalysts were also synthesized by the same method for comparison except that the amount of 0.2 M NaBH_4 solution differed (5 times of stoichiometric amount was applied as it was determined to be the best ratio for PtRu/C [33]). Previously obtained results for these compositions are used in this study [28].

2.2. Structural and electrochemical characterization of the catalysts

Structural characteristics of the catalysts were measured by X-ray diffraction (XRD) over a 2θ range of 20–80° in a step scan mode (0.02° step size and 0.5 s duration time for each step).

For electrochemical analysis, working electrodes were prepared by the thin film method [34]. The catalysts were dispersed in a mixture of DI water and 5 wt.% Nafion ionomer solution. The dispersion was sonicated to achieve homogeneous mixing and then a small amount of the dispersion was dripped on a glassy carbon electrode (3 mm dia., BAS Co., Ltd., MF-2012). After drying in the air, 5 wt.% Nafion ionomer solution was dripped on the catalyst layer to stabilize it. Electrochemical testing was performed in a beaker-type three electrode cell. Pt mesh and saturated calomel electrode were employed as the counter and reference electrodes, respectively. MOR activities were measured via chronoamperometry (CA) tests by keeping the working electrodes at 0.6 V (vs. reversible hydrogen electrode, RHE) for 1 h. All potentials in this paper were converted into RHE scale.

2.3. Conditioning process

Before the conditioning process, the catalysts were rapidly annealed in a tube furnace at 900 °C for 5 min under H_2/Ar (5.2 mol.% H_2) flow to get a higher degree of alloying, with rapid insertion under atmosphere achieved using an external magnetic coupling device. This condition is very close to the previously reported annealing process employed for the Pt–Ni–Cr combinatorial library (900 °C for 5 min under vacuum) [27]. The conditioning process was performed by potential cycling between –0.06 and 1.34 V (vs. RHE) for 10 cycles at a scan rate of 10 mV s^{-1} and 60 °C. Cyclic voltammetry (CV) was measured by potential cycling between 0 and 1.2 V (vs. RHE) for 3 cycles before and after the conditioning processes. The MOR activities were also measured before and after the conditioning processes by the CA tests mentioned above. The 900 °C annealed catalysts were denoted by adding "–900" after their initial name (for example, " $\text{Pt}_{28}\text{Ni}_{36}\text{Cr}_{36}/\text{C}-900$ ").

3. Results and discussion

3.1. Pt–Ni and Pt–Cr binary catalysts

Fig. 2 shows the XRD results of binary $\text{Pt}_{28}\text{Ni}_{72}/\text{C}$ and $\text{Pt}_{28}\text{Cr}_{72}/\text{C}$ catalysts before and after the 900 °C annealing process. Results for pure Pt are also included for comparison [28]. In the $\text{Pt}_{28}\text{Ni}_{72}/\text{C}$ and

Download English Version:

<https://daneshyari.com/en/article/1294022>

Download Persian Version:

<https://daneshyari.com/article/1294022>

[Daneshyari.com](https://daneshyari.com)