



## Oxygen reduction activity of binary PtMn/C, ternary PtMnX/C (X = Fe, Co, Ni, Cu, Mo and, Sn) and quaternary PtMnCuX/C (X = Fe, Co, Ni, and Sn) and PtMnMoX/C (X = Fe, Co, Ni, Cu and Sn) alloy catalysts

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### H I G H L I G H T S

- ▶ Binary alloy PtMn/C is evaluated towards ORR.
- ▶ Ternary PtMnX/C (X = Fe, Co, Ni, Cu, Mo and, Sn) alloys were evaluated towards ORR.
- ▶ Quaternary PtMnCuX/C (X = Fe, Co, Ni, and Sn) alloys were evaluated towards ORR.
- ▶ Quaternary PtMnMoX/C (X = Fe, Co, Ni, Cu and Sn) alloys were evaluated towards ORR.
- ▶ PtMnCu/C, PtMnCuFe/C and PtMnMoCu/C were found to be the best catalysts for ORR.

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### A B S T R A C T

In this study, we evaluated the activity of binary PtMn/C, ternary PtMnX/C (X = Fe, Co, Ni, Cu, Mo and, Sn) and quaternary PtMnCuX/C (X = Fe, Co, Ni, and Sn) and PtMnMoX/C (X = Fe, Co, Ni, Cu and Sn) alloy catalysts towards the oxygen reduction reaction (ORR) in acidic solution. Although all catalysts exhibited improved activities towards the ORR if normalized by the mass of Pt; when they are considered per milligram of total metal only a handful of them illustrated improved activities towards the ORR in terms of onset potential and current intensity determined by cyclic voltammetry with respect to pure Pt/C. PtMnCu/C, PtMnCuFe/C and PtMnMoCu/C were found to be the best catalysts for ORR. In order to gain a better understanding of the pathways of ORR, Pt/C, PtMnCu/C, PtMnCuFe/C and PtMnMoCu/C were further studied using a Rotating Disk Electrode (RDE) and Rotating Ring Disk Electrode (RRDE). Tafel plots and Koutecky–Levich analysis of the data revealed that the activity towards the ORR is better with PtMnMoCu/C followed by PtMnCuFe/C and PtMnCu/C. The estimated average number of the electrons transferred during the ORR process was found to be around 4e<sup>-</sup>. The average percentage of the generated H<sub>2</sub>O<sub>2</sub> reached as high as ~7.5% with PtMnMoCu/C. All these data point to the fact that the pathways of ORR which produce H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O as final products took place. As a final comparison for this series of catalysts, this study also gives a better selection of the catalysts that may preferably be used at the anode for ethanol oxidation or at the cathode for ORR to yield fuel cells with substantial output voltages.

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## 1. Introduction

The fuel cell is a promising alternative to environmentally unfriendly devices that are currently powered by fossil fuels [1,2]. There are various kinds of fuel cells such as polymer electrolyte membrane fuel cell, phosphoric acid fuel cell, alkaline fuel cell, solid oxide fuel cell and direct alcohol fuel cell. Among these, direct

alcohol fuel cells (DAFCs) are considered highly promising power devices due to advantages like: i) simplified liquid fuel storage compared to hydrogen gas storage, ii) low operating temperatures and, iii) easy handling. On the other hand, although all these fuel cells employ different fuels at the anode, all of them use oxygen fuel at the cathode [3,4].

The electrocatalytic reduction of dioxygen (O<sub>2</sub>) at a reasonably low overpotential has been the aim of numerous studies. This reaction plays a very important role in the cathode of fuel cells. Many types of electrocatalysts for O<sub>2</sub> reduction have been investigated either in alkaline or acidic media [5–10]. In regard to this, oxygen reduction reaction (ORR) on noble metal surfaces such as platinum

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(Pt) remains as one of the well-investigated electrochemical processes. However, due to kinetic limitations of the ORR, the cathodic overpotential losses amount to several hundreds of millivolts under typical operation condition of fuel cells [11]. In the last decades efforts were undertaken to optimize the catalyst towards the ORR in order to avoid voltage losses. For that, a variety of binary, ternary and even quaternary Pt alloys catalysts have been investigated for the ORR [12–20]. The results obtained throughout these studies are by no means consistent. For example, when investigating PtCr, PtV, PtCrCo and PtVCo alloys instead of pure Pt, Luczak and Landsman [21–23] found an increase in mass activity by factor of 1.5–2.5 (at 0.9 V) whereas Beard and Ross [24] and Glass et al. [25] noticed no increase in the activity of PtCo and PtCr alloys compared to Pt. As reported by Beard and Ross [24], it is generally assumed that comparison between supported alloys catalysts with respect to pure Pt is difficult. The reason for that has to do first with the metal nanoparticle composition that may promote or not the ORR. Second, the activity of supported metal nanoparticles can also depend on the particle size, shape and distribution on the supporting carbon.

We have previously reported the synthesis, characterization and activity towards ethanol oxidation of a series of binary PtMn/C, ternary PtMnX/C (X = Fe, Co, Ni, Cu, Mo and, Sn) and quaternary PtMnCuX/C (X = Fe, Co, Ni, and Sn) and PtMnMoX/C (X = Fe, Co, Ni, Cu and Sn) alloy catalysts [26–28]. Overall we demonstrated that these catalysts exhibited an enhanced activity towards ethanol oxidation. In the course of this study, we have examined the series of alloy catalysts towards the ORR under the same condition in order to identify the best catalysts that might be of interest to use in cathodes of fuel cells.

## 2. Experimental

### 2.1. Catalyst synthesis

Pt/C, PtMn (19:81)/C, PtMnX/C (X = Fe, Co, Ni, Cu, Mo and, Sn) and PtMnCuX/C (X = Fe, Co, Ni, and Sn) and PtMnMoX/C (X = Fe, Co, Ni, Cu and Sn) alloy catalysts have been synthesized as previously

**Table 1**

Summary of the synthesized catalysts, their compositions determined by ICP as well as the average grain size calculated from X-ray diffraction data using the Debye–Scherrer equation. Table summarized from Refs. [26–28].

Electrocatalysts	Molar ratios measured by ICP				Grain size (nm ± 0.5)	
	Pt	Mn	–	–	Cubic	Tetragonal
Pt/C	100	0	–	–	8.5	–
PtMn/C	19	81	–	–	7.5	–
	Pt	Mn	X	–	Cubic	Tetragonal
PtMnFe/C	18	52	30	–	3.1	–
PtMnCo/C	19	54	27	–	5.0	–
PtMnNi/C	17	48	35	–	6.0	–
PtMnCu/C	17	43	40	–	3.1	–
PtMnMo/C	17	61	22	–	4.5	–
PtMnSn/C	17	44	39	–	8.0	17.0
	Pt	Mn	Cu	X	Cubic	Tetragonal
PtMnCu/C	17	43	40	–	3.5	–
PtMnCuFe/C	31	40	18	11	3.1	–
PtMnCuCo/C	17	46	24	13	4.0	–
PtMnCuNi/C	26	42	20	12	4.0	–
PtMnCuSn/C	24	30	12	34	5.0	17.0
	Pt	Mn	Mo	X	Cubic	Tetragonal
PtMnMo/C	17	61	22	–	4.5	–
PtMnMoFe/C	21	41	24	14	6.0	–
PtMnMoCo/C	12	67	4	17	6.0	–
PtMnMoNi/C	30	48	6	16	6.0	–
PtMnMoCu/C	31	50	4	15	4.5	–
PtMnMoSn/C	14	37	3	46	6.0	26.0

reported [26–28]. Briefly, for the synthesis of PtMn (19:81)/C, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Aldrich) and MnCl<sub>2</sub>·2H<sub>2</sub>O (Aldrich) at the ratio of 23:77 were mixed in ultrapure water (Milli-Q, 18.2 MΩ cm). After 15 min of constant stirring Vulcan XC72R carbon black (Cabot) was added to the solution in an amount to give a total metal content of 20 wt%. PtMn nanoparticles supported on carbon were formed by reduction of the metal precursors with NaBH<sub>4</sub>, which was added as a solid to the mixture in a weight ratio of 3:1 to metals. The resulting mixture was then left under constant stirring over night and the formed supported catalysts were collected via suction filtration, washed thoroughly with ultrapure water, ethanol and acetone and finally dried over night at 80 °C. The ternary alloy catalysts PtMnX/C (X = Fe, Co, Ni, Cu, Mo and, Sn) were prepared using the same procedure by replacing 20% (w/w) of MnCl<sub>2</sub>·2H<sub>2</sub>O (Aldrich) by FeCl<sub>3</sub>·6H<sub>2</sub>O (Gelest Inc.), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma–Aldrich), NiCl<sub>2</sub> (Fluka), CuCl<sub>2</sub>·2H<sub>2</sub>O (Sigma–Aldrich), (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> (Aldrich) or SnCl<sub>2</sub> (Aldrich). The quaternary alloys were also formed following the same procedure by replacing 10% (w/w) of CuCl<sub>2</sub>·2H<sub>2</sub>O (Sigma–Aldrich) in PtMnCu/C by FeCl<sub>3</sub>·6H<sub>2</sub>O (Gelest Inc.), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma–Aldrich), NiCl<sub>2</sub> (Fluka) and, 10% (w/w) of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> in PtMnMo/C by FeCl<sub>3</sub>·6H<sub>2</sub>O (Gelest Inc.), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma–Aldrich), NiCl<sub>2</sub> (Fluka), CuCl<sub>2</sub>·2H<sub>2</sub>O (Sigma–Aldrich) or SnCl<sub>2</sub> (Aldrich).

### 2.2. Materials characterization

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was utilized for quantitative determination of metal content in the catalysts. 5 mg of each catalyst was dissolved in nitric acid (>70%) and left to dissolve for at least 1 week. Afterwards, the solutions were filtered off to separate the supporting carbon from the solution and yield a clear solution for ICP-OES analyses. Standardization was performed with three Pt, Mn and X solutions ranging from approximately 1–20 ppm. These standards contained approximately 2% nitric acid to ensure the complete dissolution and keep both sample and standard matrices equivalent.

Transmission Electron Microscopy (TEM) images were acquired using a Philips CM10 instrument equipped with an AMT digital camera system. Catalysts powders were dispersed in ultrapure water and applied to nickel 400 mesh formvar coated carbon reinforced grids and allowed to dry under air. Grids were then scanned in a Philips CM10 TEM at 100 kV.

Table 1 gathers the list of the synthesized catalysts; their molar ratios determined by ICP and as well as the average grain size of the catalysts nanoparticles estimated from XRD [26–28].

### 2.3. Electrochemical characterization

The electrocatalytic activity of the catalysts towards ORR was measured through the preparation of electrode inks, which were prepared as follows: 11 mg of the synthesized electrocatalyst was dispersed in 500 μL of a mixture of ultrapure water and 2-propanol (1:1 by volume) and the suspension was stirred in an ultrasonic bath for 15 min. 5 μL of the catalysts ink was immobilized onto the surface of either a glassy carbon (GC) electrode (diameter = 3 mm, CH Instruments), rotating disk electrode (diameter = 5 mm, Pine Instruments) and a rotating ring disk electrode which is composed of a platinum ring (7.5 and 8.5 mm inside and outside diameters, respectively) surrounded the glassy carbon disk (diam = 5 mm), and dried at 80 °C for 20 min. Prior to use, the electrodes were first polished with 6, 3 and 1 μm alumina then abundantly rinsed with ultrapure water and acetone. The final loading of metal catalysts on each electrode was 0.30 ± 0.03 mg cm<sup>-2</sup>.

Electrochemical measurements were performed using either a Solartron SI 1286 potentiostat controlled using Corrware software

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