Electrochimica Acta 109 (2013) 433–439

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Tri-metallic transition metal–nitrogen–carbon catalysts derived by sacrificial support method synthesis

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ARTICLE INFO

*Article history:*
Received 24 June 2013
Received in revised form 12 July 2013
Accepted 12 July 2013
Available online 26 July 2013

*Keywords:*
Non-PGM catalysts
Fuel cell
ORR
Cathode
Mixed metals

ABSTRACT

A series of tri-metallic oxygen reduction catalysts derived from pyrolyzed Fe-$M_1$-$M_2$ (where M = Co, Ni, Cu and Mn) and 4-aminoantipyrine (Fe-$M_1$-$M_2$-AAPyr) were prepared using a sacrificial support method (SSM). The influence of the iron interacting with the two transition metals on the catalytic activity of the oxygen reduction reaction (ORR) was investigated. This series of materials was analyzed and characterized by scanning electron microscopy (SEM) and the BET method (BET) in order to establish structural morphology, and rotating ring disk electrode (RRDE) experiments were performed to evaluate catalytic activity. The results were then correlated to one another, thereby establishing a composition to function relationship. Data from the ring current was used to execute a mechanistic study of the materials for the ORR, and it was found that supplementation of the iron with transition metals significantly improved catalytic activity, in addition to decreasing the hydrogen peroxide yield. The most pronounced enhancement of ORR catalysts is when the base transition metal Fe is supplemented with Co as a secondary metal and Cu or Mn are the tertiary metal in the system.

## 1. Introduction

Over the past several years, all major automobile manufactures have revealed programs to power cars with fuel cell systems that utilize hydrogen as fuel. Despite the significant improvements in durability, reduction in size and weight of the fuel cell stack, and membrane enhancement, these cars have remained relegated to prototype status and have not been offered to the public for purchase. The cost of the vehicle is the barrier to the market place that is holding these vehicles back, and it must be reduced in order to satisfy the demand in the market place for them. The largest component cost of the fuel cell system is the platinum that is used in the stacks as electrocatalysts.

Taking into account the scarcity, and therefore the high price of platinum, the catalysts used in an MEA can be substituted with inexpensive, non-precious metal materials in order to drive down the cost. Non-PGM materials have been extensively studied for both anodic [1] and cathodic [2] applications. Literature reviews of the current state of the art of non-PGM cathode catalysts reveals that the activity and durability of these catalysts are approaching that of the industry standard platinum based catalysts.

Non-PGM catalysts can be categorized into three separate groups based upon their synthetic precursors: transition metal chalcogenides (mainly ruthenium, palladium or rhodium selenides) [3–10], heteroatomic nitrogen-containing polymers [11–13], and small nitrogen-containing molecules [14–66]. The later category can be further bisected into coordinated metal macrocyclic compounds as the sole source M–N–C network formation [13–27], and soluble metal salt with nitrogen and carbon rich small molecule co-precursors to the M–N–C network [28–66].

Recent reports from several research groups have demonstrated that bi-metallic Fe-M-N-C catalysts (where M = Co, Cu) are promising materials for facilitating the ORR [11,67–71]. Recently, we performed systematic study on influence of addition of second transition metal to Fe–N–C catalysts [71]. It was shown that bi-metallic non-PGM catalysts generate $H_2O_2$ in significantly lower amounts compared to mono-metallic materials. Furthermore, it was found that alloying of iron with manganese in frame of N—C bonds results in significant improvement of performance. On our best knowledge, there is no published data that addresses the influence of two metals in addition to Fe–N–C catalysts on catalytic activity and hydrogen peroxide production. In the light of our study of bi-metallic catalysts [71] that can lead to further reduction of peroxide yield and possible improve catalytic activity of tri-metallic catalysts.

The present work is devoted to synthesis, characterization, and evaluation of several Fe-$M_1$-$M_2$-N-C materials (where M = Co, Cu, Ni

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http://dx.doi.org/10.1016/j.electacta.2013.07.104

and Mn) comprised of iron to metals ratios of 1:1:1. Further differentiation of this synthetic approach from those reported elsewhere involves templating the carbon support using the SSM, prior developed by our group [72]. The nitrogen-carbon precursor selected was 4-aminoantipyrine, which as we shown to result in materials with both activity and durability approaching those of the current state-of-the-art non-PGM catalysts [73]. We have shown that Non-PGM catalysts of this category are usually displaying a bi-functional mechanism of ORR with M—N moiety being responsible for the first reaction step of $O_2$ reduction to $H_2O_2$, and M—O moiety being involved in the secondary process of $H_2O_2$ reduction to $H_2O$ or, alternatively participate in chemical dissproportionation [21,29]. The importance of the activity and stability of the second reaction site (the $H_2O_2$ reduction one) has been shown to be influenced by the stability of metal nanoparticles and is most likely to be effected by the formation of complex metal oxides with pronounced activity in critical ORR steps [77,78]. Morphological characterizations were then performed on the synthesized catalyst materials by SEM and the BET method, and the reaction kinetics and mechanism of ORR of these materials were then analyzed using the RRDE.

## 2. Experimental

### 2.1. Catalysts preparation

$Fe$-$M_1$-$M_2$-AAPyr catalysts were prepared by wet impregnation of iron, metals, and 4-aminoantipyrine precursors onto the surface of fumed silica (Cab-O-Sil$^{TM}$ EH-5, surface area: ~400 $m^2\,g^{-1}$). A graphic representation of the SSM is depicted in Fig. 1 [71–78]. First, a known mass of silica was dispersed in water by ultrasonication. Then, the aminoantipyrine (4-aminoantipyrine, Sigma–Aldrich) was dissolved in acetone, and the solution was added to silica and ultrasonicated for 20 minutes. Finally, a solution of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, Sigma–Aldrich), and two of those: cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$, Sigma–Aldrich), nickel nitrate ($Ni(NO_3)_2{\cdot}4H_2O$, Sigma–Aldrich), copper nitrate ($Cu(NO_3)_2{\cdot}2H_2O$, Sigma–Aldrich) and/or manganese nitrate ($Mn(NO_3)_2{\cdot}H_2O$, Sigma–Aldrich) were added to $SiO_2$-AAPyr solution and ultrasonicated for 8 hours, where the total metals loading to silica was ~15% by mass. After ultrasonication, the silica and $Fe$-$M_1$-$M_2$-AAPyr solution was dried overnight at $T = 85\,°C$. The resulting solid was ground to a fine powder, and then subjected to heat treatment (HT). The general conditions of the HT were UHP nitrogen (flow rate 100 cc $min^{-1}$), 10 ° $min^{-1}$ temperature ramp rate, and a 3 h pyrolyzation time at 800 °C. Finally, the silica was leached out by means of 20 wt% of HF and resulting powder was washed with DI water until neutral reaction. Final total metals content after washing with HF was found to be ~2–3 wt%.

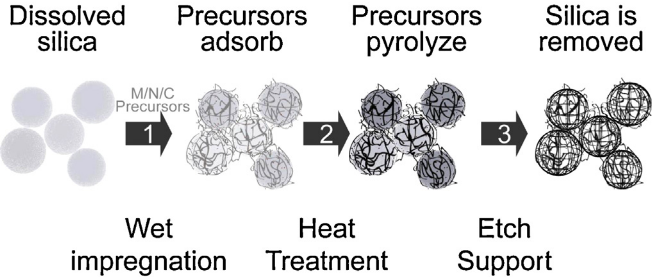

**Fig. 1.** Schematic representation of sacrificial support method (SSM).

The ratio of iron to the other two metals was selected to be 1:1:1, while the mass ratio of $Fe$-$M_1$-$M_2$ to AAPyr was held constant at 1–8, which was found to be optimal of Fe to AAPyr for monometallic catalytic materials [73].

### 2.2. Characterization

All SEM images were generated using the Hitachi S-800 instrument.

The electrochemical analysis of the synthesized material was performed using the Pine Instrument Company electrochemical analysis system. The rotational speed is reported at 1200 rpm, with a scan rate of 5 mV $s^{-1}$. The electrolyte was 0.5 M $H_2SO_4$ saturated in $O_2$ at room temperature. A platinum wire counter electrode and a Ag/AgCl reference electrode were used.

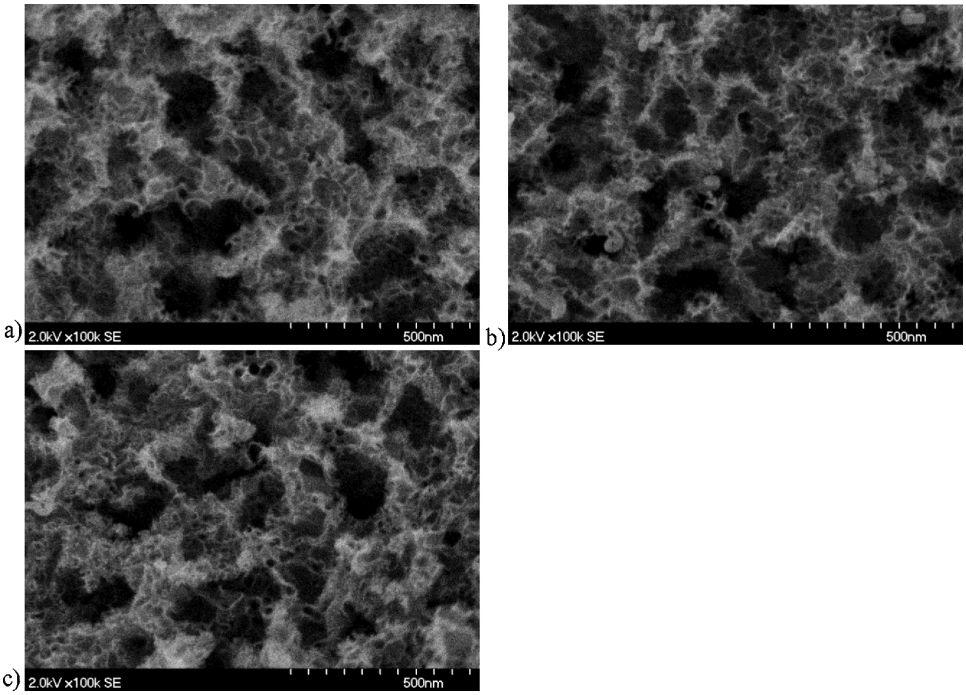

**Fig. 2.** SEM images for $Fe$-$M_1$-$M_2$-AAPyr catalysts (a) Fe-Cu-Ni-AAPyr, (b) Fe-Co-Ni-AAPyr and (c) Fe-Ni-Mn-AAPyr.