Contents lists available at SciVerse ScienceDirect





Electrochimica Acta

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

Microgravity effects on the electrochemical oxidation of ammonia: A parabolic flight experiment

Eduardo Nicolau^{a,b}, Carlos M. Poventud-Estrada^{a,b}, Lisandra Arroyo^{a,b}, José Fonseca^{a,b}, Michael Flynn^c, Carlos R. Cabrera^{a,b,*}

^a Department of Chemistry, University of Puerto Rico, Río Piedras Campus, PO Box 23346, San Juan, PR 00931-3346, USA

^b NASA-URC Center for Advanced Nanoscale Materials, PO Box 23346, San Juan, PR 00931-3346, USA

^c NASA Ames Research Center, Bioengineering Branch, Moffett Field, CA 94036, USA

ARTICLE INFO

Article history: Received 12 February 2012 Received in revised form 19 April 2012 Accepted 20 April 2012 Available online 27 April 2012

Keywords: Microgravity Ammonia oxidation Pt nanoparticles Electrocatalysis Parabolic flight

1. Introduction

Experimentation in microgravity imposes a buoyancy-free and thus macroconvection-free environment. Due to this guiescent condition, researchers have shown interest to study under such environment several processes within the fields of biology [1], crystal growth [2], human health [3], nanotechnology [4], and electrochemistry [5]. Within the field of electrochemistry, its impact on energy production is of particular importance. In an effort to find alternative means to generate electrical energy, fuel cells have been proposed with the use of different fuels such as: ethanol, methanol, ammonia and others. Particularly, ammonia has been recently considered as a possible substitute to hydrogen and the next generation fuel due to its high energy density (12.6 MJL^{-1}) , and easiness of storage and transportation [6]. For this reason, several recent investigations have focused on the development of catalysts [7-10] for electrolyzers [11,12], and microreactor [7] applications for the production of hydrogen from ammonia [6,13] or as direct ammonia fuel cells [14].

Tel.: +1 787 76400001x4807; fax: +1 787 756 8242.

E-mail address: carlos.cabrera2@upr.edu (C.R. Cabrera).

ABSTRACT

The diffusion of molecular species through nanoporous systems in microgravity conditions is of interest due to the implications of nanotechnology in aerospace technologies. Herein we present the electrochemical oxidation of ammonia at Pt nanoparticles/nano-supporting electrode systems. The decomposition of ammonia has become of critical importance since it is a common component in aqueous streams. The experiments were carried out in a parabolic flight by using different materials to test the electrooxidation of ammonia. Linear polarization curves were attained in microgravity for all materials. In general, a reduction in catalytic performance of 20–65% was observed.

© 2012 Elsevier Ltd. All rights reserved.

The electrochemical oxidation of ammonia is a mass transfer controlled reaction and this paper describes an assessment of the effects on a linear polarization under microgravity conditions. Water electrolysis also has been proposed as a way to generate hydrogen to be used as fuel in polymer electrolyte membrane fuel cells (PEMFC) and it has been investigated under microgravity conditions. These investigations have shown that the three-phase zone between the electrode, gas bubbles and electrolyte plays a key role in microconvection [15,16]. Kaneko et al. investigated water electrolysis in microgravity by parabolic flight and found that gas bubbles become larger and current densities decreased in microgravity. This suggests that the mass transfer of water molecules to the electrode controls water electrolysis. However, under normal gravity conditions water electrolysis is kinetically limited [17]. When methanol is employed as fuel in a fuel cell under microgravity, a similar effect is observed as when water electrolysis is performed, this is enlargement of gas bubbles and a decrease in overall cell performance [18]. Matsushima et al. indicated that in alkaline solutions, current density is much smaller under microgravity than under terrestrial gravity, and that ohmic resistance increases in microgravity due to the formation of a gas bubble froth layer and as well as an increase in electrode surface blockage by bubbles [15,19]. Iwasaki et al. found that the electrolysis current on the ground reached a steady state faster than that under microgravity conditions. Since the diffusional mass transfer was predominant over the process in microgravity, the characteristic time was longer

^{*} Corresponding author at: Department of Chemistry, University of Puerto Rico, Río Piedras Campus, PO Box 23346, San Juan, PR 00931-3346, USA.

^{0013-4686/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.electacta.2012.04.079



Fig. 1. The Electrochemical Microgravity Laboratory (EML) is comprised of three major components: (a) Teflon custom-made electrochemical cells; each have 5 cavities in total, 3 for the electrodes and 2 inlet valves. (b) Electronics rack (EIR) to control the electrochemical operation and (c) the double contained MakrolonTM box containing the cells built according to NASA specifications for flight.

than that of the process on the ground where macroconvection is predominant [20].

In terms of the ammonia electrooxidation the most accepted mechanism is the one from Gerisher and Maurer where N_{ads} is a poisonous intermediate that blocks the surface while the adsorbed NH and NH₂ species are the active intermediates to finally form nitrogen [21]. The mechanism is as follows:

$$\mathrm{NH}_{3(\mathrm{aq})} \to \mathrm{NH}_{3\mathrm{ads}} \tag{1}$$

$$NH_{3ads} + OH^{-} \rightarrow NH_{2ads} + H_2O + e^{-}$$
(2)

$$NH_{2ads} + OH^{-} \rightarrow NH_{ads} + H_2O + e^{-}$$
(3)

$$NH_{x,ads} + NH_{y,ads} \rightarrow N_2 H_{x+y,ads}$$
(4)

$$N_2H_{x+y,ads} + (x+y)OH^- \rightarrow N_2 + (x+y)H_2O + (x+y)e^-$$
 (5)

$$NH_{ads} + OH^- \rightarrow N_{ads} + H_2O + e^-$$
(6)

Other researchers have proposed alternative mechanisms for this reaction. In 2006 Vidal-Iglesias et al. provided evidence on the formation of an azide anion (N_3^-) in the electrochemical oxidation of ammonia by means of surface enhanced Raman-spectroscopy [22]. In step 5, the $N_2H_{4,ad}$ species are capable of reacting with ammonia in the alkaline medium to produce the azide as follows:

$$NH_3 + N_2H_4 + 70H^- \rightarrow N_3^- + 7H_2O + 6e^-$$
 (7)

The standard potential for this reaction is 0.66 V vs. NHE. The N_3^- species formed in this reaction would react at the potentials where the ammonia oxidation is reported to form $N_2.$

$$Pt + N_3^- \leftrightarrow PtN_3^- \tag{8}$$

$$PtN_3^- + 2H_2O + e^- \leftrightarrow PtNH_2 + 2OH^- + N_2$$
(9)

In 2005 Endo et al. investigated the electrochemical oxidation of ammonia by means of rotating disc electrode. In this research, the formation of intermediate species such as NO_x is proposed, however no experimental evidence was developed [23]. The electrochemical oxidation of ammonia has been recently reviewed and these and other mechanisms are discussed [24].

2. Experimental

2.1. Materials and apparatus

2.1.1. Parabolic flight details

The experiments were conducted using a parpabolic microgravity aircraft. These were conducted as part of a NASA parabolic flight campaign: NASA Minority Institution Flight Week Program at the NASA Johnson Space Center in Ellington Field, Houston, TX. The aircraft used during this campaign was a Boeing 727-200 of the Zero Gravity Corporation. An average gravity of 0.006g was achieved for an average window of 14.5 s in each of the 30 parabolic flights per day. Two days of flights were conducted.

2.1.2. Electrodes preparation

The electrochemical oxidation of ammonia was tested under microgravity by employing electrodes of different composition. In this campaign three different electrodes were used to test the microgravity effects on the electrochemical oxidation of ammonia. These were labeled as: Pt-GCE, Pt/C, and Pt-H₂/C. For the Pt-GCE a glassy carbon electrode was immersed in a three-electrode electrochemical cell containing a 1 mM K₂PtCl₆/0.5 M H₂SO₄ solution with a Ag/AgCl (0.197 V vs. NHE) as a reference and a platinum wire as counter electrode. A HCP-803 potentiostat from Bio-Logic USA was used to cycle the potential between -0.2 V and 1.0 V vs. Ag/AgCl at 300 mV/s for 25 cycles to generate a platinum electrodeposited glassy carbon electrode (Pt-GCE). For the Pt/C electrode 1 mg of 20 wt.% platinum on carbon from Johnson Matthey was weighed and mixed with 200 μL of isopropanol and 8 μL of a 5% wt. Nation^{TM} solution from Sigma-Aldrich. After sonicating and magnetic stirring of this mixture for 2 h, 8 µL were drop-casted over a glassy carbon electrode and left overnight. For the Pt-H₂/C, 500 mg of Vulcan XC-72R were weighed and mixed with 91.78 mg of K₂PtCl₄ and 3.80 mL of a 0.1 M solution of sodium polyacrylate (2100 g/mol, Sigma-Aldrich). Thereafter, this mixture was thoroughly mixed with deionizezed water and placed in a bottom flask under nitrogen atmosphere for 2 h. Then, the mixture was placed under hydrogen gas atmosphere for 2 h to promote platinum reduction [25]. After completing the platinum reduction the mixture was left covered overnight and then it was filtered several times with nanopure water (18.3 M Ω , Barnstead), and subsequently dried at 80 °C for 24 h under vacuum. Then, 1 mg of the resulting catalyst was mixed with isopropanol and NafionTM solution and drop-casted in the same way as for the Pt-Vulcan electrode. The charge under the hydrogen desorption peaks, in presence of a 0.5 M sulfuric acid solution, was calculated and the electrochemical active surface area for each electrode was determined (i.e. 0.14 cm² (Pt-GCE), 1.1 cm² $(Pt-H_2)$ and 1.0 cm^2 (Pt/C)). All of the shelf materials were used as received and without further purification.

2.1.3. Test apparatus

An electrochemical microgravity laboratory (EML) shown in Fig. 1 was constructed by following specific guidelines from NASA. In brief, three independent Teflon made electrochemical cells were placed in a double contained MakrolonTM box. These three electrochemical cells were independently controlled from outside the box via an electronics rack (ER). This electronics rack contained an SP-50 potentiostat from Bio-Logic USA to control the experiments inside the boxes. The three electrochemical cells were fixed to the larger box and all had a silver wire as a pseudo-reference electrode and a platinum wire as the counter electrode. The whole apparatus was fixed via bolts to the airplane and it was designed and made to withstand up to 9g of acceleration in a triple contained environment. An accelerometer was used to monitor gravitational acceleration.

2.2. Ammonia electrooxidation under microgravity

A 1 M solution of NH₄OH (Acros Organics) adjusted to pH 10 with HCl was used to test the electrochemical oxidation of ammonia. The accelerometer was set as a trigger and when 0.02g were achieved the experiment was initiated. To promote ammonia electrooxidation a potential sweep between 0.0V to a final potential of 0.8 V vs. RHE at 40 mV/s was executed. After each parabola, the cells were allowed to equilibrate during the resting period, which usually was around 1–3 min. In this publication potentials were corrected to reflect it as a relative hydrogen electrode (RHE).



Fig. 2. Average of gravitational acceleration as a function of time during parabolic flight.

3. Results and discussion

The main objective of this investigation is to observe the effects on the electrochemical oxidation of ammonia at nanobased electrodes under microgravity; Fig. 2 shows the gravitational acceleration reading during the experiments that confirms the microgravity environment. Previous investigations have demonstrated that ammonia electrooxidation takes place between ca. 0.45 and 0.6 V vs. RHE, where the active intermediates (i.e. NH_{ads} and NH_{2.ads}) are produced to form N₂. More anodic potentials up to a value of ca. 0.8 V vs. RHE is known to form nitrogen adsorbates (N_{ads}). The results of this experiment demonstrated that in a microgravity environment the diffusion of products and reactants to and from the catalyst and inside the pores of the catalyst are affected. Fig. 3 presents the graphical experimental results for an electrode of Pt reduced by the hydrogenation method and supported by Vulcan $(Pt-H_2/C)$. In Fig. 3 the difference in currents when the electrochemical cell is operated under microgravity versus the ground control is shown. At a potential of ca. 0.7 V vs. RHE the electrochemical oxidation of ammonia to nitrogen is clearly presented. From this figure it



Fig. 3. Linear polarization of a $Pt-H_2/C$ electrode in 1 M NH_4OH at pH 10 at 40 mV/s under normal gravity conditions (black line) and microgravity (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



Fig. 4. Schematic representation of the ammonia electrochemical oxidation effect in microgravity and ground.

is noticeable the difference in the ammonia oxidation current when in microgravity vs. the ground control. Thus, when in microgravity the adsorbed ammonia molecules ($\rm NH_{3,ads})$ that occurs between ca. 0.3 and 0.4 V are immediately oxidized when the anodic potential of 0.45 V is reached. In contrast to conditions of normal gravity, the nitrogen molecules that are formed by oxidation of ammonia have insufficient buoyancy to leave the surface readily, and thus block the approach of further ammonia molecules, see Fig. 4. This leads to a significant decrease in the anodic current from the ammonia oxidation. Also from this figure another broad peak at higher potential values (ca. 1.1 V vs. RHE) is observed. This signal has been ascribed to the oxidation of nitrogen adsorbates (N_{ads}) leading to the formation of an "oxynitride" layer, mostly composed of NO_x and N_xO [26,27]. However, in microgravity these adsorbates are more pronounced compared to the ground control. This may be due to the inability of the nanocatalyst to desorb these species under microgravity, perhaps a direct effect of nitrogen (N₂) formation at the three-phase interface at the nanoscale.

A similar pattern was found for the commercial catalyst Pt/C from Johnson Matthey. Fig. 5 presents the electrochemical oxidation of ammonia on an electrode with Pt-Vulcan. At a potential of

0.6 0.5 Ground uG 0.4 Current / mA 0.3 0.2 0.1 0.0 -0.1 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 Potential vs. RHE / V

Fig. 5. Linear polarization of a Pt/C electrode in $1 \text{ M NH}_4\text{OH}$ at pH 10 at 40 mV/s under normal gravity conditions (black line) and microgravity (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

0.7 V vs. RHE one can observe the peak indicating the electrochemical oxidation of ammonia, and at a higher potential of ca. 1.1 V the same broad peak as in Fig. 3 is observed. However, the difference in the current ratio between the ammonia oxidation peak (0.7 V vs. RHE) and the nitrogen adsorbates oxidation peak (ca. 1.1 V vs. RHE) under normal gravity conditions is 0.20, under microgravity is 0.17 and there corresponding ratio (g's/µg's) is 1.176. This is different than the catalyst prepared by the colloidal method (Pt-H₂). For the Pt-H₂/C this current ratio was 0.26 when comparing normal gravity conditions (0.045) against microgravity (0.17). These results suggest that Pt/C-H₂ has a higher affinity for the nitrogen adsorbates and the formation of the oxynitride layer when compared to the Pt/C catalyst.

A third material was tested in microgravity, electrodeposited platinum nanoparticles over a glassy carbon electrode (Pt-GCE). Fig. 6 shows the electrochemical oxidation of ammonia for this material. At a potential of 0.62 V vs. reference one can observe the peak indicating the electrochemical oxidation of ammonia, and at a higher potential of around 1.1 V vs. RHE the signals ascribed to the nitrogen adsorbate oxidation or formation of oxides. The difference between the ammonia oxidation signals and the



Fig. 6. Linear polarization of a Pt-GCE electrode in 1 M NH₄OH at pH 10 at 40 mV/s under normal gravity conditions (black line) and microgravity (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 1

Summary of peak current generated and % performance reduction under normal gravity conditions compared to microgravity.

Electrode	$\rm NH_3$ oxidation peak current density normal gravity ($\mu A cm^{-2}$)	NH_3 oxidation peak current density microgravity ($\mu Acm^{-2})$	% performance reduction in microgravity vs. ground
Pt-H ₂ /C	106	81 ± 2	24
Pt/C	198	112 ± 2	43
Pt-GCE	374	140 ± 3	63

nitrogen adsorbate signals in microgravity and under normal gravity conditions is shown. If the same reasoning as for the previous catalyst is applied here, the ratio between these two peaks under the two different condition results in 0.05. This means that this electrode has a tremendous affinity for the nitrogen adsorbates when in microgravity and perhaps is more prone to poisoning under such conditions.

From the data presented in Figs. 3, 5 and 6 one can notice the difference in current between the ground control and microgravity electrochemical oxidation of ammonia. The results are consistent among all the materials tested in the sense that the absence of gravity negatively affects the current.

To establish a baseline upon which the performance of materials can be compared, Table 1 shows data on ammonia oxidation peak current and peak current average density (μ A/cm²). The table shows that based upon platinum content, Pt-GCE provides a better catalysis since it has a higher current average density over the Pt/C and $Pt-H_2/C$; the latter two are comparable. This difference can be attributed to the fact that platinum was directly electrodeposited in a homogeneous layer on the electrode instead of using a carbon support. However, when these results are compared to the results on the ground experiments, the material that shows the lowest decrease in performance is the $Pt-H_2/C$, followed by Pt/C and Pt-GCE respectively, as shown in Table 1. This result pin points the experimental fact that during linear polarization having Pt nanoparticles within the matrix of a carbon support in a microgravity environment has a positive impact on the movement of electroactive species toward the catalyst. A possible explanation for Pt-H₂ having less of a decrease in performance could be that it was prepared according to a formulation that presumably leads to the formation of platinum nanoparticles with selective domains of (100). Previous investigations have shown that ammonia electrooxidation takes place almost exclusively in the (100) domains [28–30]. Therefore, the fact that Pt-H₂ presents the lowest decrease in performance may be due to a catalyst effect.

4. Conclusions

The results of this research demonstrate a decrease in performance of 20–65% over ground-based controls for the electrochemical oxidation of ammonia. This decrease in current is theorized to be due to the lack of buoyancy driven mixing that occurs in microgravity. In microgravity only diffusional mixing occurs and therefore molecules may be unable to reach the nanocatalyst interface at the same rate as on the ground.

During the first oxidation peak at ca. 0.7 V the formation of N_2 molecule during microgravity conditions creates a stagnant gassurface interaction that avoids ammonia molecules to reach the Pt surface. This situation leads to a significant peak current decrease compared to the ground experiments. On the other hand, during the second oxidation peak an oxynitride layer is formed at the interface of the electrode without the formation of N_2 molecule. This latter peak does not have the effect of microgravity due to the surface chemistry reaction and the oxide adsorbates are no readily

desorbed as presented by Koper et al. [26]. Therefore, no major differences between the microgravity and ground conditions are observed in such an oxynitride layer region.

These findings indicate that significant reductions in electrode performance for ammonia electrooxidation may occur if catalyst design measures are not taken in consideration to mitigate these microgravity effects. This conclusion is applicable specifically to electrochemical processes, but also may be relevant to all process constrained by nanoscale mixing of diffusion limited structures such as thermal catalysts, separation membranes, microbial growth and human cellular functions.

Acknowledgements

This work was financially supported by NASA-URC Center for Advanced Nanoscale Materials at the University of Puerto Rico Río Piedras Campus under Grant No. NNX10AQ17A. Funds were also provided by NASA Office of Education and Secor Strategies. E. Nicolau greatly appreciates NASA Graduate Student Researchers Program (GSRP) under Grant No. NNX08AV42H (2008–2011), and NASA Jenkins Pre-Doctoral Fellowship for financial support (2011–2012). C. Poventud acknowledges NASA Jenkins Pre-Doctoral Fellowship for financial support. The authors also acknowledge Irma Candelaria from the UPR Machine Shop for technical help and Bio-Logic USA for kindly lending an SP-50 potentiostat to use during flight. E. Nicolau and C. Poventud contributed equally to this work.

References

- [1] M. Mognato, L. Celotti, Mutation Research 578 (2005) 417.
- [2] B. Lorber, R. Giege, Journal of Crystal Growth 231 (2001) 252.
- [3] A.T. Borchers, C.L. Keen, M.E. Gershwin, Nutrition 18 (2002) 889.
- [4] E. Hartmann, P. Marquardt, H. Ditterich, H. Steinberger, Advances in Colloid and Interface Science 46 (1993) 221.
- [5] K. Nishikawa, Y. Fukunaka, E. Chassaing, M. Rosso, Journal of Physics: Conference Series 327 (2011) 012045.
- [6] B.K. Boggs, G.G. Botte, Journal of Power Sources 192 (2009) 573.
- [7] R.I. Masel, J.C. Gangley, E.G. Seebauer, Journal of Power Sources 137 (2004) 53.
- [8] M. Cooper, G.G. Botte, Journal of Electrochemical Society 153 (2006) A1894.
- [9] J. Solla-Gullon, F.J. Vidal-Iglesias, V. Montiel, J.M. Feliu, A. Aldaz, Journal of Power Sources 171 (2007) 448.
- [10] Y.F. Cheng, L. Zhou, M. Amrein, Journal of Power Sources 177 (2008) 50.
- [11] F. Vitse, M. Cooper, G.G. Botte, Journal of Power Sources 142 (2005) 18.
- [12] E.P. Bonnin, E.J. Biddinger, G.G. Botte, Journal of Power Sources 182 (2008) 284.
- [13] G.G. Botte, F. Vitse, M. Cooper, Journal of Power Sources 142 (2005) 18.
- [14] R. Lan, S. Tao, Electrochemical and Solid State Letters 13 (2010) B83.
- [15] H. Matsushima, T. Nishida, Y. Konishi, Y. Fukunaka, Y. Ito, K. Kuribashayi, Electrochimica Acta 48 (2003) 4119.
- [16] H. Matsushima, B. Kiuchi, Y. Fukunaka, K. Kuribayashi, Electrochemistry Communications 11 (2009) 1721.
- [17] H. Kaneko, K. Tanaka, A. Iwasaki, Y. Abe, A. Negishi, M. Kamimoto, Electrochimica Acta 38 (1993) 729.
- [18] H. Guo, J.F. Zhao, F. Ye, F. Wu, C.P. Lv, C.F. Ma, Microgravity Science and Technology 20 (2008) 265.
- [19] D. Kiuchi, H. Matsushima, Y. Fukunaka, K. Kuribayashi, Journal of Electrochemical Society 153 (2006) E138.
- [20] A. Iwasaki, H. Kaneko, Y. Abe, M. Kamimoto, Electrochimica Acta 43 (1998) 509.
- [21] H. Gerisher, A. Mauerer, Journal of Electroanalytical Chemistry 25 (1970) 421.
- [22] F. Vidal-Iglesias, J. Solla-Gullon, J.M. Perez, A. Aldaz, Electrochemistry Communications 8 (2006) 102.
- [23] T. Miura, Y. Katayama, K. Endo, Electrochimica Acta 50 (2005) 2181.

- [24] N.J. Bunce, D. Bejan, Electrochimica Acta 56 (2011) 8085.
- [25] T.S. Ahmadi, Z.L. Wang, A. Henglein, M.A. El-Sayed, Chemistry of Materials 8 (1996) 1161.
- [26] A.C.A. de Vooys, M.T.M. Koper, R.A. van Santen, J.A.R. van Veen, Journal of Electroanalytical Chemistry 506 (2001) 127.
- [27] S. Wasmus, E.J. Vasini, M. Krausa, H.T. Mishima, W. Vielstich, Electrochimica Acta 39 (1994) 23.
- [28] F.J. Vidal-Iglesias, N. García-Aráez, V. Montiel, J.M. Feliu, A. Aldaz, Electrochem-
- [20] r.J. VIUAI-Iglesias, N. Garcia-Araez, V. Montiel, J.M. Feliu, A. Aldaz, Electrochemistry Communications 5 (2003) 22.
 [29] F.J. Vidal-Iglesias, J. Solla-Gullon, V. Montiel, J.M. Feliu, A. Aldaz, Journal of Physical Chemistry B 109 (2005) 12914.
 [30] F.J. Vidal-Iglesias, J. Solla-Gullon, P. Rodriguez, E. Herrero, V. Montiel, J.M. Feliu, A. Aldaz, Electrochemistry Communications 6 (2004) 1080.