Chronoamperometric Study of Ammonia Oxidation in a Direct Ammonia Alkaline Fuel Cell under the Influence of Microgravity

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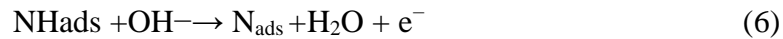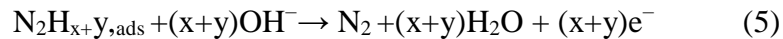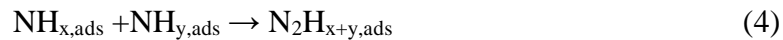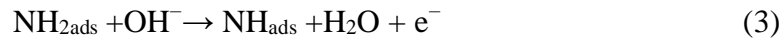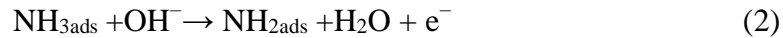
Abstract

This is a study of the chronoamperometry performance of the electrochemical oxidation of ammonia in an alkaline fuel cell for space applications. Under microgravity the performance of a fuel cell is diminished by the absence of buoyancy since nitrogen gas is produced. The following catalysts were studied: platinum nanocubes of ca. 10nm, platinum nanocubes on a Vulcan carbon support and platinum on carbon nanoonion support of ca. 10nm. These nanomaterials were studied in order to search for catalysts that may reduce or counter the loss of ammonia oxidation current densities performance under microgravity conditions. Chronoamperometries at potential values ranging from 0.2 V to 1.2V vs. cathode potential (Breathing Air/300ml/min/12psi) in 1.0M NH_4OH (30ml/min in anode) were done during over 30 parabolas. The current densities at 15s in the chronomaperometry experiments showed diminishing current Pt mass densities under microgravity and in some cases to showed improvement of up to 92%, for Pt-carbon nanoonions, and over 70% for the three catalysts versus ground at potentials ranging from 0.2 to 0.4V after 5 minutes of chronoamperometry conditions. At higher potentials, 1.0V or higher, Pt nanocubes and Pt-carbon nanoonions showed enhancements of up to 32% and 24%, respectively. We attribute this behavior to the sizes of the catalyst materials and the time needed for the N2 bubble detachment from the Pt surface under microgravity.

Introduction

Fuel cells have been researched for various applications: proton electrode membrane fuel cells[3], microbial fuel cells[4], and alkaline fuel cells[5] and have been used successfully in space applications since the Apollo missions.[6] Hydrogen and methanol are commonly used in fuel cells.

Ammonia for fuel cells is cheap, produces water and nitrogen (clean fuel) and it is manufactured and stored on an industrial scale.[3,7,8] Ammonia fuel cells have been proposed in a two-step process where the ammonia first is cracked into hydrogen and then used in a fuel cell.[9] However, ammonia can be used as a fuel in a Direct Ammonia Alkaline Fuel Cells, without the cracking step. The most accepted mechanism for the oxidation of ammonia was presented by Gerischer and Mauerer:[10]

$$NH_{3(aq)} \rightarrow NH_{3ads} \qquad (1)$$

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

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

$$NH_{x,ads} + NH_{y,ads} \rightarrow N_2H_{x+y,ads} \qquad (4)$$

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

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

As it can be seen in the mechanism, the electrochemical oxidation of ammonia produces nitrogen gas. On the ground, nitrogen gas floats away because of the buoyancy of the gas leaving a clean platinum catalyst surface making of the platinum surface available to oxidize more ammonia. In the case for the electrochemical oxidation of ammonia under the influence of microgravity, the nitrogen gas produced near the surface of the catalyst stays in the vicinity due to the lack of buoyancy. This was demonstrated by cyclic voltammetry under microgravity conditions by E. Nicolau et al.[11], showing a decrease in the ammonia oxidation peak current. Experiments in microgravity have studied the formation of bubbles. Thompson et al. studied it the formation or nitrogen bubbles in a microgravity drop tower observing that in the absence of gravity surface tension is a driving force for the bubble detachment.[12] Kaneko et al. showed a decrease of current density with the formation of bubbles in microgravity.[13] Herman et al. studied the effects of an electrical field on the formation of bubbles on microgravity, showing

that at higher electrical fields better detachment of the bubbles is obtained.[14] Carrera et al. studied the detachment of bubbles from a plate orifice and a tube orifice, showing that the plate orifice, having more area, the bubbles anchors to the surrounding surface making the detachment more difficult.[15] Buyevich and Webbon did a theoretical study on bubble formation under microgravity finding that differences in the injector geometry could increase the bubble detachment volume due to conditions of incomplete wetting because of broadening of the bubble base.[16,17] Balasubramaniam observed that the migration of a bubble under microgravity is due to a thermal gradient on the system.[18]

The formation of H_2 and N_2 formation of bubbles in ground forces has been studied at Pt ultramicro- and nano-electrodes.[19, 20,21,22] They studied the formation of electrochemically generated H_2 and N_2 bubbles and subsequent detachment. The bubble detachment from the Pt electrode surface takes ca. 1-2s. Here we found that changes in ammonia oxidation currents changed after 5 minutes under most of the Pt catalyst materials studies under micrgravity.

Experimental

Catalysts

The catalysts were synthesized on the laboratory, the Platinum nanocubes were synthesized by the method presented by R. Martínez et al.[1, 23] (see Figure 1a). Briefly, 11 g of Brij30 and 2.1 mL of Chloroplatinic Acid were added to 38.29 g of n-heptane in a container, the mixture was well mixed. This was followed by the addition of 0.079g of Sodium Borohydride to reduce the platinum molecular precursor. The reaction took place for 20 minutes. Acetone was added to induce the precipitation of the Pt nanocubes. After the particles were precipitated they were rinsed with acetone, methanol and nanopure water.

Platinum on carbon nano-onions were synthesized by the Rotating Disk Slurry Electrode (RoDSE) method presented by D. Santiago et al.[2] (see Figure 1b). Briefly, 50 mg of carbon nanoonions, produced from nanodiamond powder, was dissolved in 50 mL of sulphuric acid 0.1M and placed in the RoDSE electrochemical cell. A voltage of -
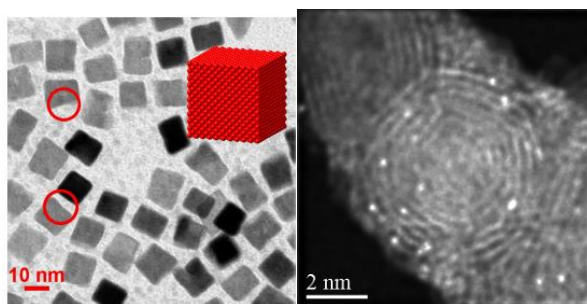

Figure 1. Transmission electron microscopy of (a) Pt nanocubes[1] and (b) Pt-CNO[2]. Published with permission.

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0.2V vs. Ag/AgCl was applied to the glassy carbon rotating disk electrode while placed in the slurry solution. The rotating speed used was 900 rpm. While the potential was applied for 16 hours, 2 mL of 5mM potassium hexachloroplatinate was added every two hours to the electrochemical RDE cell containing the carbon nanoonions slurry solution. The produced platinum-carbon nanoonions catalyst slurry solution was vacuum filtered and dried in an oven at 60°C for 12 hours.

Catalysts ink preparation

The following quantities were used for each catalyst ink preparation:

a. Pt Nanocubes- 5 mg of Platinum Nanocubes, 59 µL of FAA-3 liquid ionomer , 250 µL of Dimethylformamide

b. Pt Nanocubes- Carbon Vulcan- 25 mg, 59 µL of FAA-3 liquid ionomer, 750 µL of Dimethylformamide

c. Pt Carbon Nanoonions- 25 mg, 59 µL of FAA-3 liquid ionomer, 750 µL of Dimethylformamide

d. Pt black- 5 mg, 59 µL of FAA-3 liquid ionomer, 250 µL of Dimethylformamide

To prepare the ink for each catalyst, 59 µL of FAA-3 liquid ionomer and 250 µL of dimethylformamide were dispensed into each vial containing the synthesized catalyst powders. The ink was homogenized in a sonic bath for 2 hours. The catalyst ink was painted over the gass diffusion layer (GDL) on a hot plate at 60°C.

Fuel Cell Assembly (exploded view)
Alkaline Membrane (Fumion)
Anode- Pt black/Pt Nanocubes   Cathode- Pt black/Pt-Rh

Steel plate
Copper plate
Diffusion Layer
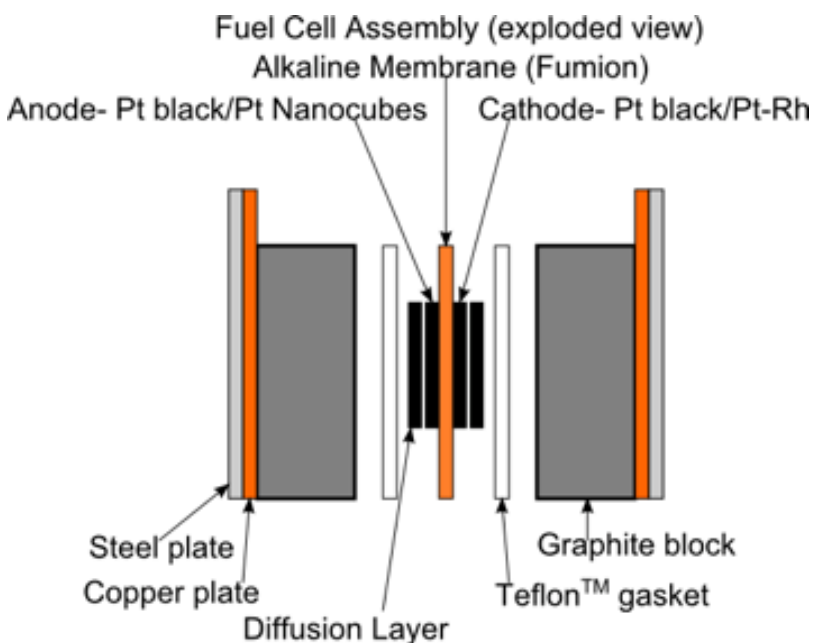Graphite block
Teflon™ gasket

4

Figure 1. Exploded view of the Direct Ammonia Alkaline Fuel Cell

Membrane Electrode Assembly (MEA)

The Membrane Electrode Assembly is the part of the fuel cell that allows the transfer of OH$^-$ ions from the cathode side to react with the ammonia on the anode side. It consists of a Fumion FAA-3 PK-130 anion exchange membrane (Fumatech); on each side of the membrane there is a catalyst adhered to the membrane and an ELAT LT1400W gas diffusion layer (Nuvant) over the catalyst. On the cathode side all MEAs had 1 mg/cm^2 of platinum black. The anode side carried three different catalysts: Platinum nanocubes, Platinum nanocubes on vulcan support and platinum on carbon nano-onions support. The MEA is constructed by assembling one Catalysts containing GDL against each side of the membrane. Care is taken to identify the anode side from the cathode side.

Fuel Cell

The experiment consists of a fuel cell with a 5 cm^2 active area. The fuel cell anode was fed with an ammonium hydroxide solution (1.0M or 0.1M) on a closed loop connected to a peristaltic pump at 30ml/min. The cathode side was connected to a breathing air tank on the inlet and the outlet was connected to the exhaust system of the plane at 300mL/min at 12psi.

Experiment box

The experiment box was a modification of the box used by Nicolau et al.[11] The experiment box is a triple containment system made of Makrolon® designed and constructed for closed loop, selfcontained experiments, it was modified to adapt a hose from an external air tank and for the experiment exhaust to connect to plane exhaust system. The box is bolted to the airplane floor.

Electronics rack

The fuel cell is connected to a Biologic SP-50 potentiostat and a computer in an 80/20 frames rack system near the experiment box. The reference and counter electrode connections are on the cathode side of the fuel cell, the working electrode is connected to the anode side of the fuel cell.

b)
Air
Regulator

a) Air Tank

c)
Pressure
Relief Valve

To airplane
exhaust

i)

h)

f)

e)

d)

g)

a) Air tank
b) Air regulator
c) Pressure relief valve
d) Metering valve
e) Humidifier
f) Fuel cell
g) Peristaltic pump (closed loop)
h) Peristaltic pump (closed loop)
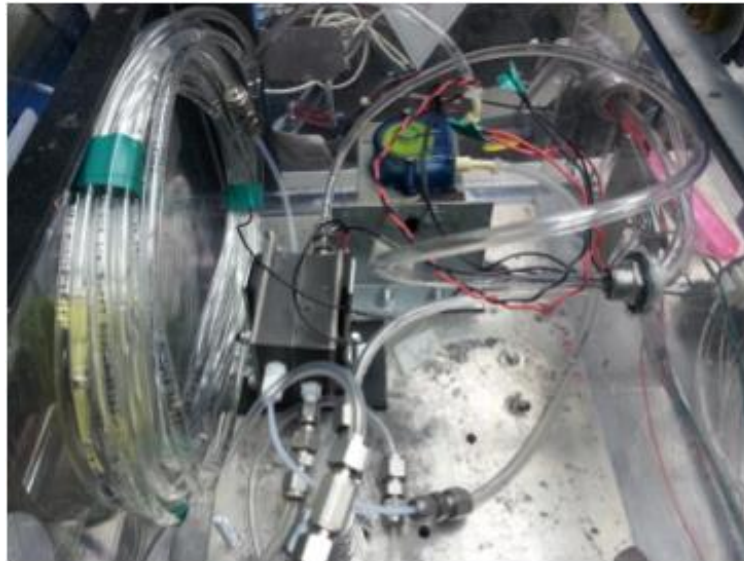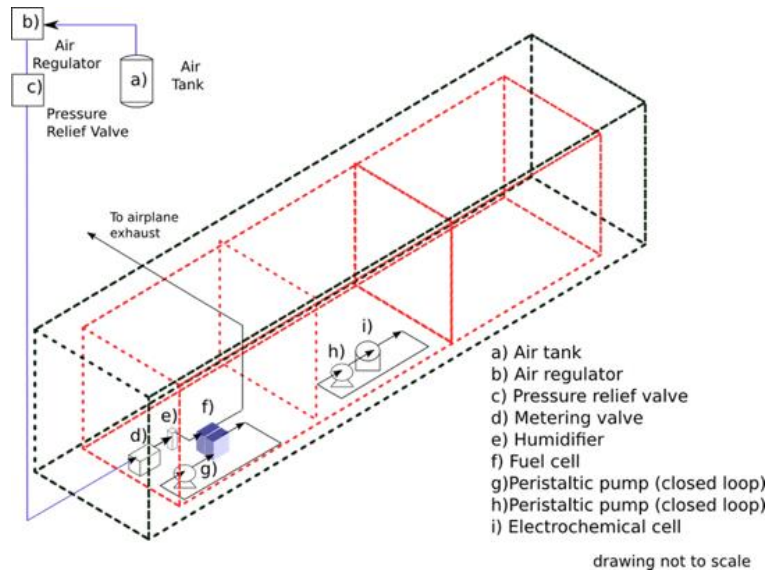i) Electrochemical cell

drawing not to scale

Figure 3. Containment box and microgravity experiment set up.

1. Results and discussion

Figure 4 is a transient representation of the current versus time for a fuel cell under an applied voltage of 0.45 V. The current was recorded for 10 parabolas during the microgravity and hypergravity period. It can be observed a decrease in current when the plane changes from hypergravity (410 µA at 1.7g) to microgravity (370 µA at 0.02 g). This data validates the observations made in electrochemical half cells by Nicolau et al.[11]; that there is an impairment of performance probably caused by the stagnant nitrogen gas, product of the oxidation of ammonia. On each cycle gravity changes from microgravity to normal gravity and then to hypergravity again. The current decrease phenomena is reversed when the plane returns to hypergravity, regaining the current production when the Nitrogen gas floats away from the surface of the catalysts.
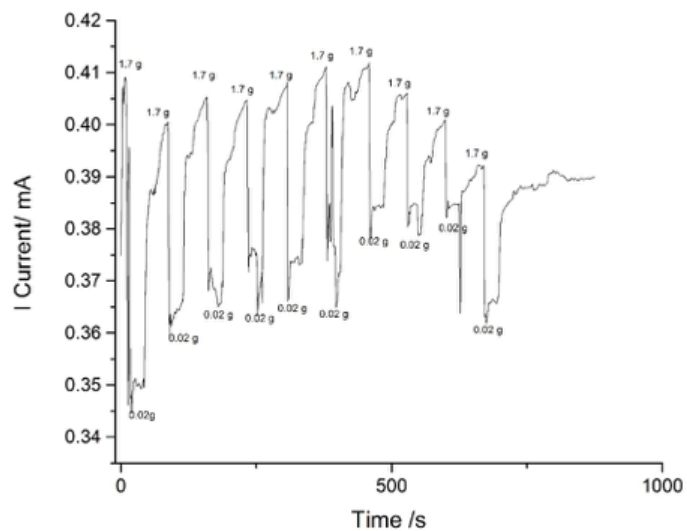
Figure 4 is a transient representation of the current versus time for a fuel cell under an applied voltage of 0.45 V.

Figure 4. Chronoamperometry of a direct ammonia alkaline fuel cell @ 0.45V vs. cathode (Breathing Air/300ml/min/12psi) in 1.0M NH_4OH (30ml/min in anode) during 10 parabolas. Anode (5mg of Pt black): NH_4OH 30ml/min, Cathode (5mg of Pt black): Air 150 mL/min.

Platinum Nanocubes

For the Platinum Nanocubes catalyst of 10nm in diameter, Figures 5 show chronoamperometric tests measuring current produced by the fuel cell at different applied voltages (0.2 V, 0.4V, 0.6 V, 0.8V, 1.0V, 1.2V vs. cathode). The anode had ammonia 0.1M at 30mL/min and on the cathode air at 300 mL/min. At 0.2 V and 0.6V, the current produced in microgravity is less than the performance on ground. The chronoamperometry at 0.4V shows at slight improvement of performance for the microgravity compared to the ground experiment up to a point where it stabilizes over time giving the same performance as the ground case, this equalization occurs in the region where the oxidation of the ammonia in proximity to the electrode surface is depleted and now the ammonia from the bulk solution diffuses toward the electrode. At 0.8V and 1.0V the performance at microgravity is better than the performance on the ground. At 1.2V the performance on microgravity is better during the period where the ammonia near the electrode is depleted once it enters the zone controlled by diffusion the performance decays and is lower than the ground counterpart. At 1.2V N_{ads} is forming which adsorbs to the Platinum active areas thus inactivating part of the Platinum and reducing the catalyst activity in addition to the effect caused by the loss of buoyancy.
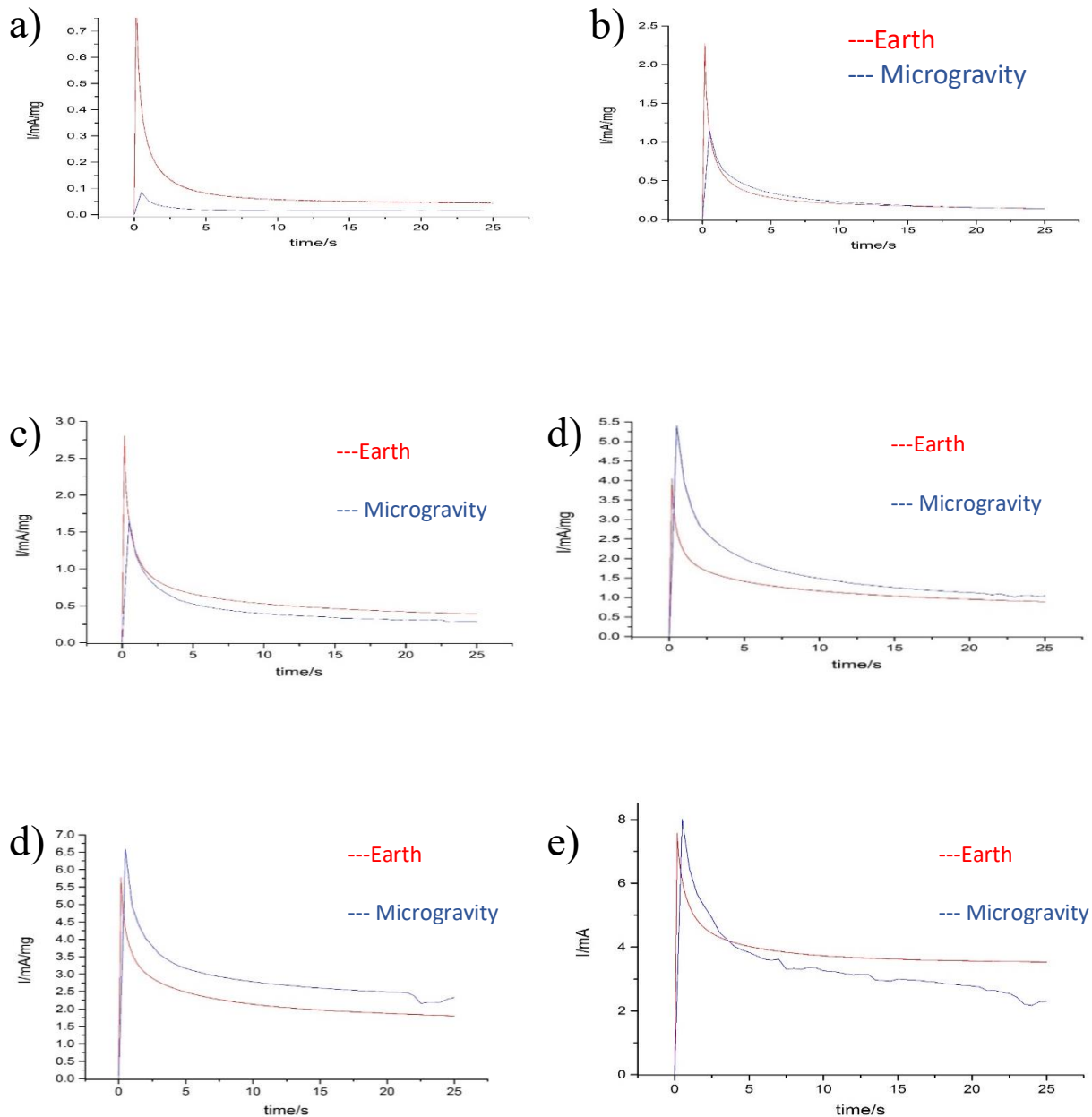
Chronoamperometry Platinum Nanocubes

Figure 5 . Chronoamperommetry of ammonia oxidation at applied potentials of 0.2, 0.4, 0.6, 0.8, 1.0 and

1.2V vs. cathode (Breathing Air/300ml/min/12psi) in 0.1M NH$_4$OH (30ml/min in anode). Anode- 5.2mg

of Pt Nanocubes and Cathode-5mg Pt Black.

Platinum Nanocubes on Carbon Vulcan Support

Figures 6 show chronoamperometric tests measuring current produced by the fuel cell at different applied voltages (0.2 V, 0.4V, 0.6 V, 0.8V, 1.0V, 1.2V). The Anode has Ammonia 0.1M at 30mL/min and on the cathode air at 300 mL/min. At 0.2 V and 0.4V, the current produced in microgravity is significantly less than the performance on ground. At 0.6 V and 0.8V, the current produced in microgravity and on the ground are the same until 9 seconds of microgravity have elapsed. After 9 seconds the microgravity current is slightly bigger. For 1.0 V after 9 seconds the microgravity current is slightly lower than on the ground. At 1.2V the microgravity current is lower than the current on the ground. Again at 9 seconds is when the ammonia near the electrode is depleted and the current is diffusion controlled. The performance of the microgravity improves with higher values of applied voltage until it reaches 1.0 V where the microgravity current equates the current on ground at 1.2V then microgravity performance decrease compared to the ground.
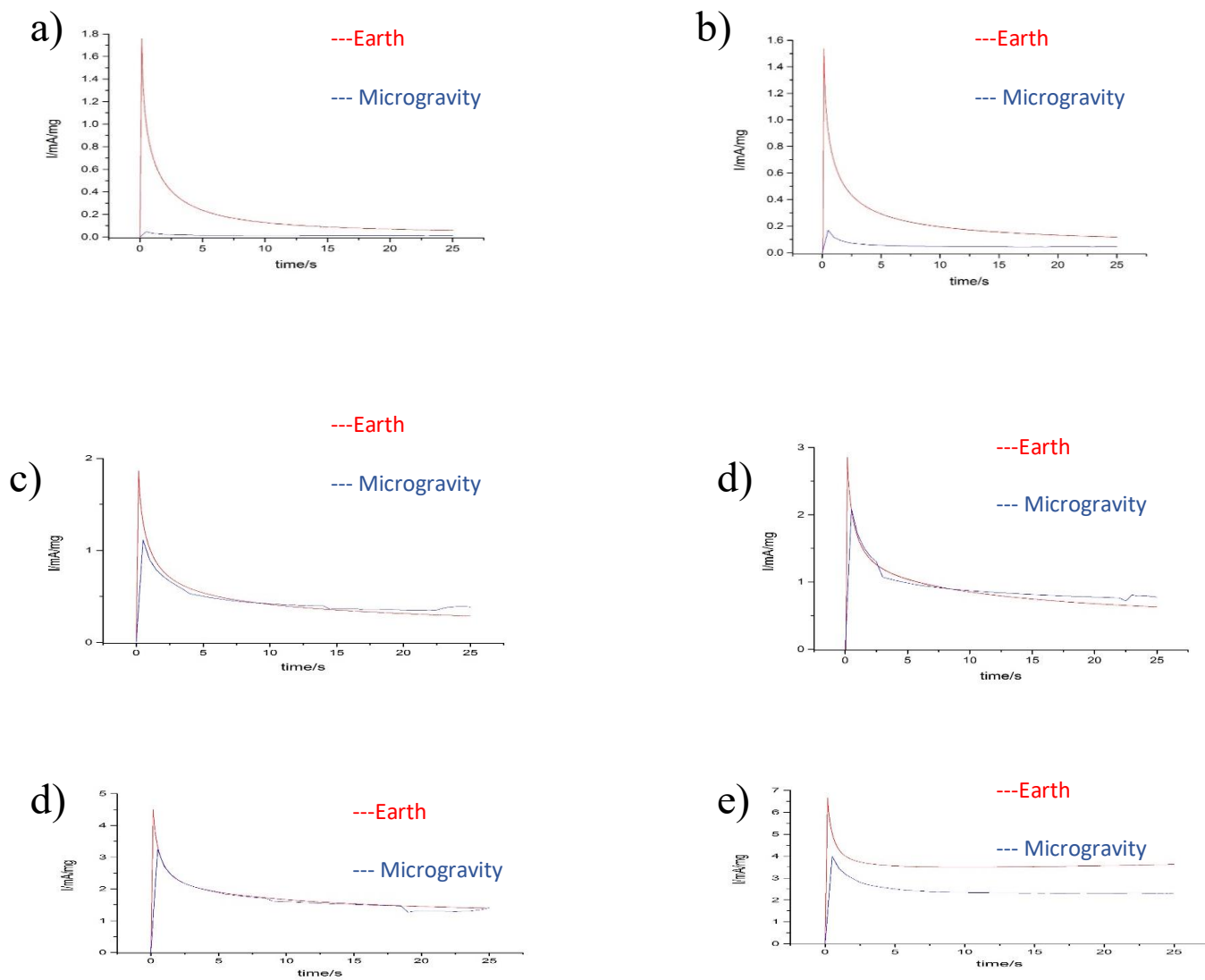
Chronoamperometry Platinum Nanocubes Vulcan

Figure 6. Chronoamperommetry of ammonia oxidation at applied potentials of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2V vs. cathode (Breathing Air/300ml/min/12psi) at in 0.1M NH_4OH (30ml/min in anode). Anode- 5.3mg of Pt nanocubes in carbonVulcan (ca. 20% loading) and Cathode-5mg Pt Black.

Chronoamperometry Platinum on Carbon Nanoonions

Figure 7 show chronoamperometric tests measuring current produced by the direct ammonia alkaline fuel cell at different applied voltages (0.2 V, 0.4V, 0.6 V, 0.8V, 1.0V, 1.2V vs. cathode). The anode had a flux of ammonia 1M at 30mL/min and on the cathode air at 300 mL/min. For the applied voltages of 0.2V, 0.6V and 0.8V the performance of the catalysts was reduced in microgravity. At 0.4V, 1.0V and 1.2V the performance in microgravity decreased until between 5 to 6 seconds, then the microgravity performance was better in the diffusion controlled region.
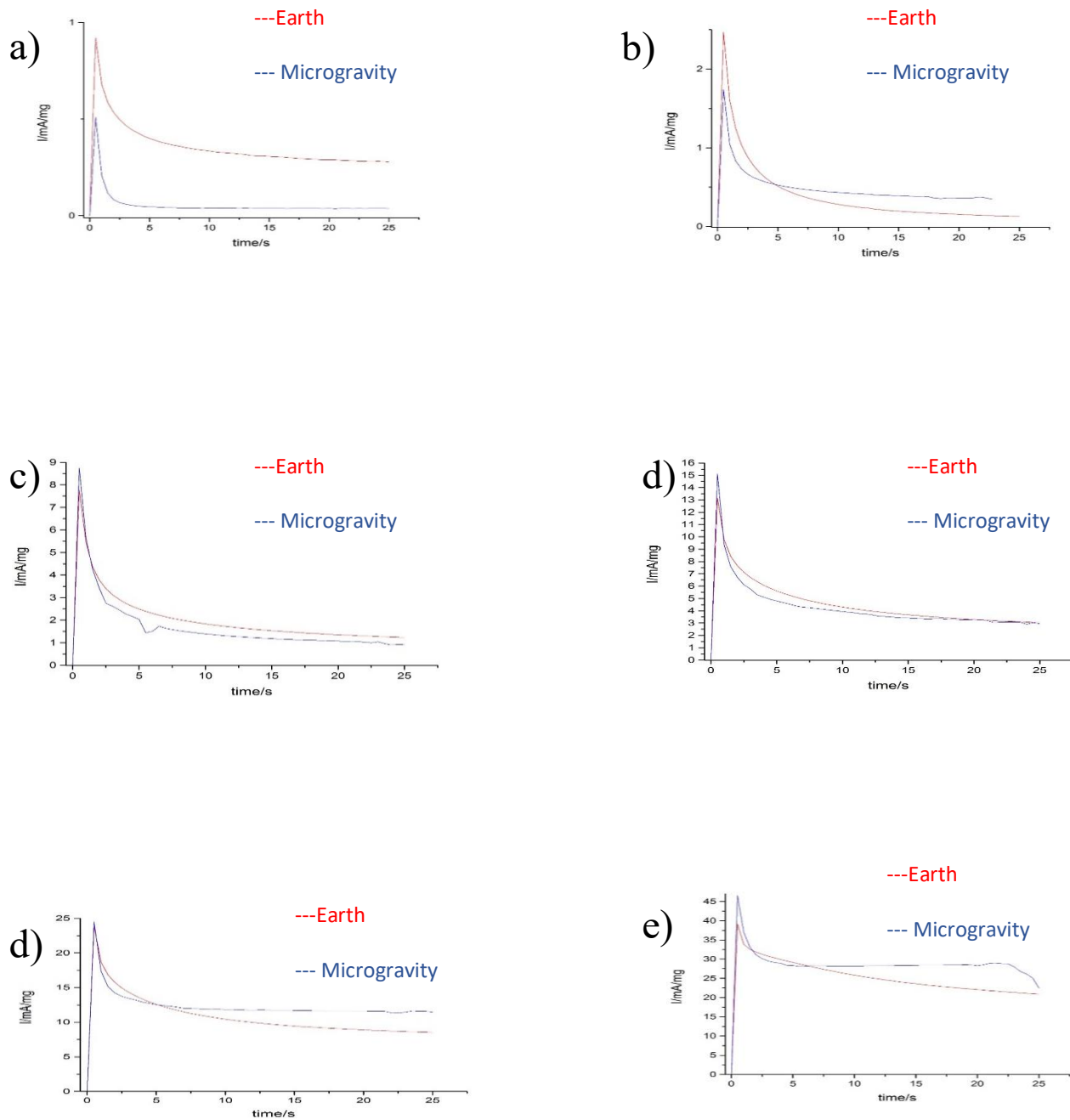
Platinum Nanoonions

Figure 7. Chronoamperommetry of ammonia oxidation at applied potentials of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2V vs. cathode (Breathing Air/300ml/min/12psi) in 1.0M NH_4OH (30ml/min in anode). Anode- 3.2mg of Pt in carbon nanoonions (ca. 13% loading) and Cathode-5mg Pt.

In order to determine if there was a shift in the potential of the cathode electrode that was used as a reference electrode, currents at 15min of from the chronoamperometery were taken for each potential. A plot of the current at 15min vs. the applied potential is shown in Figure 8.
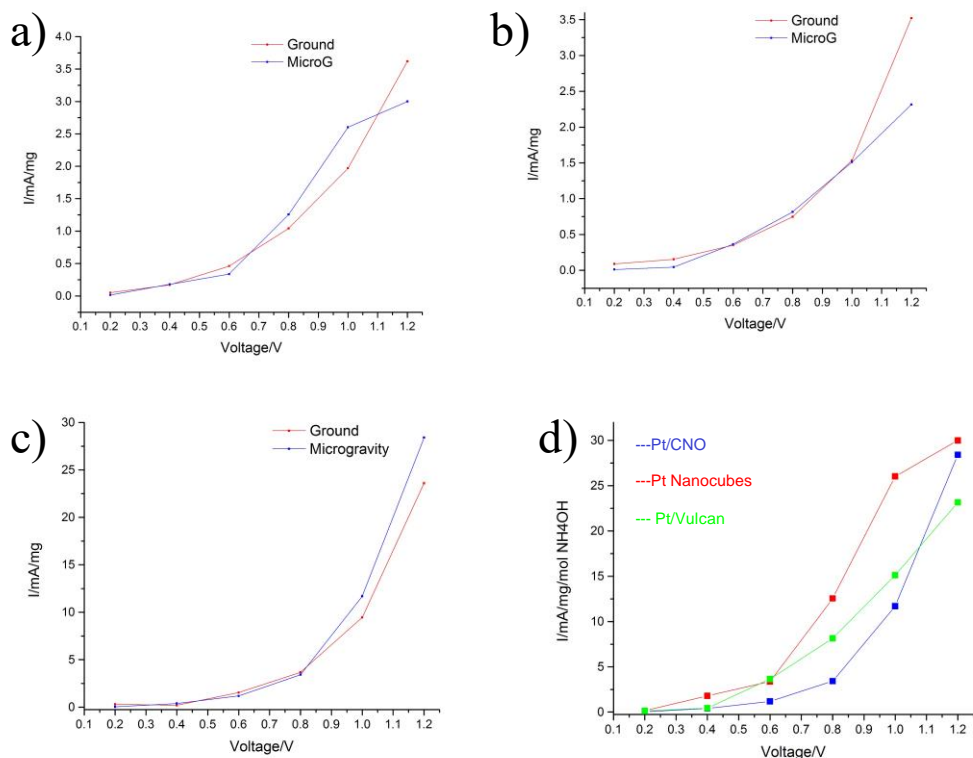

Figure 8. Current values at 15 seconds from the chronoamperometries from 0.2V to 1.2 V shown in Figures 5, 6, and 7. a) Pt Nanocubes b) Pt Nanocubes in Vulcan c) Pt in carbon Nanoonions d) Pt Nano-onions vs. Pt Nanocubes vs. Pt Nanocubes Carbon Vulcan, Normalized by Pt mass and molarity of NH4OH under microgravity conditions.

Conclusions

This research has shown a difference between the performance of the current Pt mass densities produced by a direct ammonia fuel cell under microgravity and ground experimental conditions. For the case of a fuel cell with Platinum black as a catalyst on the anode there is a

reduction in produced current Pt mass densities of 7.5% between the hypergravity and microgravity experimental episodes. The decrease in current Pt mass densities was shown that is reversed when the gravity is applied to the fuel cell, there is a direct influence from microgravity on the electrochemical oxidation of ammonia.

For the platinum nanocubes the decrease in current production in microgravity was shown except for the applied voltages of 0.4V (5%), 0.8 V (21%) and 1.0V (32%) where the current produced in microgravity was higher than in the ground. Nanocubes are 10nm crystalline Pt (100) planes, which are preferential for the ammonia oxidation.

For the Platinum Nanocubes in Carbon Vulcan support the optimum operation voltages were 0.6V (3% current increase vs ground) and 0.8V (9% current increase vs ground) when the oxidation is occurring in the zone of diffusion controlled electrochemical oxidation reaction.

The platinum in carbon nanoonions support had optimum operation voltages of 0.4V (99% current increase vs. ground), 1.0V (24% current increase vs. ground) and 1.2V (22% current increase vs. ground) where the current produced under microgravity conditions was better than the current produced in ground.

Of all three catalysts, the platinum on carbon nanoonions showed the best performance increase microgravity versus ground at 0.4V (99%). The high surface area and spherical morphology of the carbon nanoonions may be taking part on improving the release of the stagnant nitrogen gas that interferes with the oxidation of the ammonia. The higher surface area of the carbon nanoonions (>942 m^2/g vs. 262 m^2/g for carbon Vulcan) provides more nucleation sites where the nitrogen gas can grow and be released.[24] The improved current in the Platinum carbon nanoonions catalyst can be related to a better release of the nitrogen bubbles that hinder ammonia oxidation. The curved surface of the 5 nm nanoonion particles works in an analogous way to the tube orifice in Carrera's[15] paper, in the sense that curvature offers less surrounding surface where the bubble can anchor.

The mechanism of bubble formation has been studied at Pt ultamicroelectrodes and nanoelectrodes showing the formation of electrochemically generated H_2 and N_2 bubbles and subsequent detachment.[19, 20,21,22] The bubble detachment from the Pt electrode surface takes ca. 1-2s. This has been seen for hydrogen and nitrogen bubble formation at Pt ultramicro- and nano-electrodes. In our case, we find that the detachment of N_2 from the platinum nanoparticles may

be ocrrurign at ca. 5-10 second since at the tiem scale the current increases. This may be explained by the protective shielding the N_2 bubble has on the Pt surface to avoid its passivation that occurs in ground. Under microgravity the lack of buoyancy in this nanomaterials has a positive effect on its catalytic performance at time longer that 5-10 seconds. This happens mainly at potentials higher than 0.8V vs. cathode. Below you may find a scheme of this proposed mechanism.

Table 1. Comparative performance of catalyst in microgravity versus ground (positive values are an increase of performance) at 15 minutes of the chronoamperometry data.

Applied Voltage vs. Cathode (Breathing Air/300ml/min/12psi) at in 0.1M NH₄OH (30ml/min in anode)	Pt Nanocubes (100% metal loading)	Pt-Nanocubes Carbon Vulcan (20% metal loading)	Pt-Nano-onions (13% metal loading)
0.2 V	-73%	-86%	-88%
0.4 V	5%	-71%	99%
0.6 V	-27%	3%	-23%
0.8 V	21%	9%	-7%
1.0 V	32%	-1%	24%
1.2 V	-17%	-34%	20%

2. Acknowledgements

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