



Effect of catalyst on electrolysis of ammonia effluents

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ABSTRACT

The electrolysis of ammonia (NH_3) was studied as a remediation process for the removal of ammonia from wastewater, with the advantage of producing hydrogen while returning clean water to the environment. An electro-catalyst able to support the electro-oxidation of ammonia at low concentrations was designed. Two substrates were tested, Raney nickel and carbon fiber. Carbon fiber was found to be a better substrate for the electrolysis of ammonia at low concentrations. The performance of noble metals such as Rh, Pt and Ir, electroplated on the carbon fiber substrate was also evaluated. Rh–Pt–Ir and Pt–Ir on carbon fiber substrate were found to be the most promising electrodes for the electrolysis of ammonia at low concentrations. The maximum ammonia conversion was $91.49 \pm 0.01\%$ for a typical concentration of ammonia found in sewage water and the Faradaic efficiency was $91.81 \pm 0.13\%$ on the selected anode.

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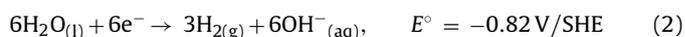
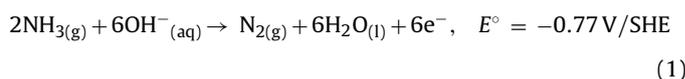
1. Introduction

There are negative effects on the environment that are the result of poorly applied technological procedures. Ammonia emissions are an example of these inadequate processes. Ammonia is related to eutrophication and particulate matter, therefore the removal of ammonia from wastes is imperative [1,2]. The presence of ammonia is widely known in sources such as industrial wastewater in both gaseous and aqueous forms. This contaminant could also be found in agricultural runoff from fertilizers in the form of NH_4^+ . Typical ammonia concentrations in municipal wastewater effluents are in the range of 0.5–2 mM (8.5–34 ppm) with pH values between 5 and 8 [3,4], and 0.6–6 mM (10–102 ppm) with pH values of 10.8–11.5 [5].

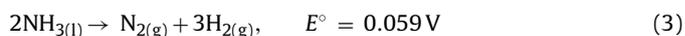
Marincic and Leitz [3] studied the electro-oxidation of ammonia at low concentrations to evaluate the possibility of ammonia removal from wastewater. Catalysts of different compositions such as platinized platinum, graphite, titanium, and tantalum, as well as, titanium coated with platinum black were tested for reactivity and economic feasibility of the electro-oxidation at room temperature. The authors tested the effect of: different catalyst loadings ($0.5\text{--}20\text{ mg cm}^{-2}$), pH (5.55–12.8), concentrations of ammonia (0.12–10 mM or 2–170 ppm), electrolytes (such as NaCl, K_2SO_4 , phosphate buffer and K_2HPO_4), and current density on the electro-oxidation of ammonia. It was found that only platinum elec-

trodes were able to support the electro-oxidation of ammonia at a reasonable rate. However, the cost of the materials was very high due to the electrode area required for the reaction. The maximum current densities reported by the authors were 11.2 mA cm^{-2} in dynamic conditions, and 2.20 mA cm^{-2} in static conditions.

Recently, Botte [6] and Vitse et al. [7] proposed a new technology for the production of hydrogen on demand based on the electrolysis of ammonia, since ammonia can be used as a hydrogen carrier. According to the authors the reactions involved are:



where reactions (1) (ammonia oxidation), and (2) (water reduction), take place at the anode and cathode of the ammonia electrolytic cell, respectively; yielding the following overall reaction:



The electrolysis of ammonia has several advantages: low operating temperature, hydrogen is produced on demand without the need for storage, the technology can use sustainable renewable energy sources, and the process can be extended as a wastewater treatment technique [8].

Botte et al. [7] have suggested that the technology can be used as a remediation process with hydrogen co-generation. However, the authors worked at high concentrations of ammonia. For the

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technology to be extended as a water remediation process, an electro-catalyst should be developed which can oxidize ammonia at the concentrations found in the effluents with significantly high current densities when compared to Marincic and Leitz [3] results. The proposed technology [7] can be used as an application for purification of ammonia effluents with hydrogen cogeneration. This paper presents results based on the catalyst testing in the presence of low concentrations of ammonia, at the characteristic effluent concentrations.

Within this context, the objectives of this paper are:

- (1) Design an electro-catalyst to electrolyze ammonia at low concentrations. The new catalyst should have a high surface area with low loadings of noble metals. In this sense, two different substrates were tested, Raney nickel, as suggested by Cooper and Botte [9], as well as carbon fibers [6,7,10]. Therefore, the first part of this paper deals with the identification of the best substrate for the electro-catalyst.
- (2) Evaluate the performance of different noble metals electroplated on the surface of the selected substrates mentioned in objective 1. Previous studies have suggested that the presence of noble metals enhance the electrolysis of ammonia [7,8]. According to Cooper and Botte [9], Rh enhances the activity towards the OH^- adsorption, which seems to be a limitation for the reaction due to the competition between the adsorption of ammonia and OH^- on platinum electrodes, causing a blocking effect on its active zones [11]. The authors also found that Rh effectively fills the empty active sites on the Pt surface for the ammonia oxidation reaction. Sathe and Botte [10] mentioned that Rh is characteristic for its electronic conductivity on carbon fibers, improving the adherence and deposition. Giner and Moser [12] reported that catalyst materials from the platinum group such as Pt and Ir, enhanced the kinetics for the electro-oxidation of ammonia. McKee et al. [13] also proposed the usage of Pt–Ir as a catalyst material for the dissociation of ammonia for ammonia fuel cells. Based on this background information, different metals such as Rh, Pt, and Ir at different loadings and combinations were tested to determine their effect on the electrolysis of ammonia at low concentrations.
- (3) Determine the conversion and Faradaic efficiency of the reaction as well as the effect of ammonia and hydroxyl ion concentrations on ammonia electrolysis using the best catalyst determined from previous objective.

2. Experimental

2.1. Electro-catalyst preparation

Two catalyst materials were used, Raney nickel and carbon fiber substrate, plated with noble metals. The substrates presented a geometric area of 6 cm^2 for Raney nickel, and 4 cm^2 for carbon fiber, formed by wrapping the fibers on a titanium gauze (titanium gauze 18 mesh woven with 0.28 mm diameter wire) as described by Sathe

and Botte [10]. The titanium gauze was attached to an annealed (as described by manufacturer), 99.7% pure titanium wire (0.81 mm diameter, and 20 cm long), both titanium gauze and wire were purchased from Alfa Aesar. Raney nickel substrate was deposited on the titanium gauze using the procedure described by Cooper and Botte [14].

The carbon fiber substrates were prepared by wrapping $7 \mu\text{m}$ diameter polyacrylonitrile (PAN) carbon fibers (Celion G30–500) from BASF on the titanium gauze as described in the literature [6,7,10]. Each bundle of the fiber consisted of 6000 filaments with an average length of 35 cm. Titanium gauze was chosen as the support for the carbon fibers so as to increase the electronic conductivity of the substrate. Furthermore, electrodeposition of noble metals on titanium does not take place unless the surface is properly treated (chemically or mechanically) [15,16], this guaranteed that the noble metals would deposit on the fibers preferentially. The carbon fiber substrates were cleaned with acetone, and air dried before the electrodeposition. Each electrodes weight was recorded before and after the deposition of noble metals.

All the plating salts for the electrodeposition were 99.9% pure obtained from Alfa Aesar. Dihydrogen hexachloroplatinate (IV) acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) with 38% Pt content, rhodium (III) chloride trihydrate ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) with 38.5% of Rh content, and iridium (III) chloride trihydrate ($\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$) with 55% of Ir content were used to perform the electrodeposition of Pt, Rh, and Ir, respectively.

One of the objectives of the paper was to select the best substrate for the anode electrode in ammonia electrolysis. In order to do this two substrates were chosen, both electroplated with Pt–Ir based on the findings from Vitse et al. [8] The authors observed that this combination of noble metals as electro-catalyst provided the lowest voltage for ammonia electrolysis and the highest efficiency on comparison with Pt foil. Both substrates, Raney nickel and carbon fiber, were electrodeposited galvanostatically with the combination of noble metals in a glass cell using platinum foil as the counter electrode. The platinum counter electrode had 20 cm^2 of geometric area, 0.1 mm of thickness, 99.95% of purity, and it was purchased from ESPI metals. In this sense, the counter electrode was three times larger than the geometric area of the Raney nickel working electrode, and five times larger than the carbon fiber working electrode.

The electrodeposition of Pt–Ir on the Raney nickel substrate was performed simultaneously. The plating conditions are summarized in Table 1. The plating bath for Pt–Ir was prepared by dissolving the corresponding quantities of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ salts (keeping a weight ratio of 1:5 Pt to Ir), in order to achieve a concentration of 0.1 mg ml^{-1} in a total volume of 250 ml of solution, containing 95 ml of 32% (w/v) NaOH and 155 ml of HPLC grade water. At room temperature, the electroplating process involved increasing the current systematically in a step form under constant solution stirring condition. The current was changed from 1.5 to 30 mA with increments of 6 mA every 10 min. The apparatus used for electroplating was a ARBIN cycler BT2000, which was

Table 1
Experimental conditions used for electroplating Pt–Ir on the Raney nickel substrates

Parameters	Pt–Ir
Salts	$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (38% Pt) + $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (55% Ir)
Chemicals	NaOH 32% (w/v) and high performance liquid chromatography (HPLC) water
Concentration of salt (mg ml^{-1})	0.1
Temperature of plating bath ($^\circ\text{C}$)	25
Loading (mg cm^{-2} of Substrate)	8
Steps of current (mA)	1.5–30
Increment of current (mA)	6
Steps time (min)	10
Voltage range (V)	–0.015 to –1.2

used to maintain the voltage in the range of -1.2 V so as to avoid the hydrogen evolution region that tends to form Pt black. The total experimental time depends on the desired amount of noble metals to be deposited over the substrate. After every step of current, the Raney nickel electrode was weighed to assure the desired loading of 8 mg cm^{-2} was achieved.

Carbon fiber electrodes were electroplated with different noble metals and its combinations (Rh, Pt, Pt–Rh, Pt–Ir, and Rh–Pt–Ir). The total loading for noble metals was kept at about 5 mg cm^{-1} of carbon fiber bundle, namely Electrode 1 (Rh: 5 mg cm^{-1}), Electrode 2 (Pt: 5.3 mg cm^{-1}), Electrode 3 (Pt–Rh: 5.2 mg cm^{-1}), Electrode 4 (Pt–Ir–Rh: 5.1 mg cm^{-1}), and Electrode 5 (Pt–Ir: 4.6 mg cm^{-1}), such that the effect of the different materials tested could be determined. Rhodium was deposited as a first layer in all the electrodes that contained this metal in order to (a) increase the electronic conductivity of the fibers [10], (b) increase the adherence of the other noble metals [10], (c) minimize OH^- surface blocking effect [9], and (d) provide complete coverage of the fibers [9], while the second layer was formed by either deposition of Pt or Pt–Ir alloy. The procedure described by Sathe and Botte [10] was used for the electrodeposition of different metals over the carbon fibers (see Table 4 of the reference for a summary on plating conditions). The plating procedure for Pt–Ir on carbon fiber substrates is described as an example. The plating bath was prepared by dissolving the required quantities of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ salts (in order to achieve a concentration of 0.4 and 1.04 mg ml^{-1} of Pt and Ir, respectively) in 250 ml of 1 M HCl solution. The solution was heated to 80°C and mixed with a stirring bar. The plating was performed galvanostatically at a current of 250 mA in intervals of 20–30 min using a ARBIN cyler BT2000. The voltage was kept below -1.3 V to avoid the formation of Pt black. After every time interval, the weight of the electrode was measured to assure the loading was 5 mg cm^{-1} of carbon fiber bundle.

2.2. Polarization techniques

The electrochemical performance of the electrodes was determined by using cyclic voltammetry and galvanostatic polarization techniques. A ARBIN cyler BT2000 instrument was used to perform the experiments in an all glass, three electrode, 1-l closed cell. The polarization potentials during the experiments were measured with a Hg/HgO reference electrode. A Luggin-Haber capillary, located 3 mm away from the working electrode, filled with a solution of 20 vol.% KOH was used. A sweep rate of 10 mV s^{-1} was maintained and the working electrode was scanned from -0.8 to 0.1 V for 20 cycles during the cyclic voltammetry experiment. The counter electrode for these experiments was a 20% Rh, 80% Pt–Ir on carbon fiber counter electrode. The same electrode was used as cathode for the galvanostatic experiments so as to decrease the over-potential of the cathodic reaction (see Eq. (2)). The counter electrode had a loading of 7.6 mg cm^{-1} of carbon fiber bundle with a geometric area of 4 cm^2 , and it was prepared using the procedure described before.

During the galvanostatic testing of the electrodes different constant currents were set and the stable potential response of the system was recorded. The experiment began with 1-min resting period followed by current variation in a staircase form, which consisted current steps of 10 mA and each step lasted for 30 min till final current of 150 mA. The cell voltage was limited to 1 V so as to protect the catalyst materials, as well as to guarantee that the potential response was under the water electrolysis standard potential of 1.23 V [17]. At all times the solution was mixed with a stir bar.

The electrochemical measurements were performed with different concentrations of ammonia (0.001–1 M) and potassium

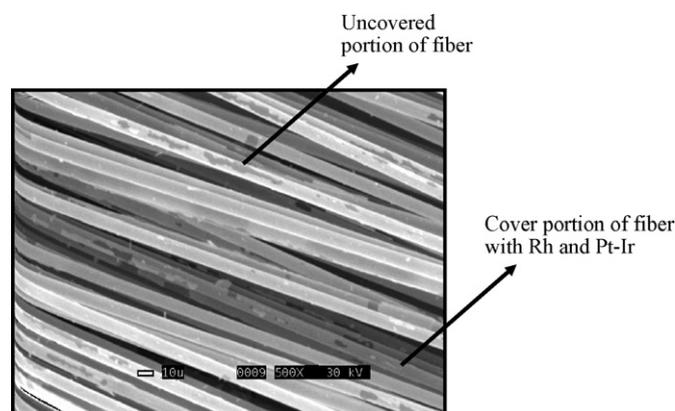


Fig. 1. Typical morphology for carbon fiber catalyst with 20% Rh and 80% Pt–Ir (loading: 7.6 mg cm^{-1} of carbon fiber bundle). Magnification at $500\times$. The morphology is characterized by a uniform coverage layer of Pt–Ir–Rh on the carbon fiber substrate.

hydroxide (0.2–1 M). The chemicals used were 99.9% pure provided by Fischer Scientific. The volume of the solution used in the electrochemical cell was 800 ml and all the experiments were performed at room temperature. The conductivity and pH of the solution was measured by a multi-sense conductivity/pH Cell, Mettler Toledo, MC 226.

2.3. Catalyst characterization

The morphology of the electrodes was determined using a scanning electron microscope (JEOL JSM-5300), operating at 30 kV and 80 mA. The electrodes were observed after the electrodeposition of noble metals in order to analyze the deposition coverage along with the uniformity and adherence of the deposited layers. Typical morphology of the electrodes reported in this publication are similar to the ones shown and described by Sathe and Botte [10]. As an example, a typical morphology for the Pt–Ir–Rh counter carbon fiber electrode (loading: 7.6 mg cm^{-1} of carbon fiber bundle) used in the polarization techniques is shown in Fig. 1. The photo-micrography at $10\text{ }\mu\text{m}$ of scale and magnification of $500\times$ shows the characteristic morphology for a Pt–Ir–Rh/carbon fiber electrode, which shows a uniform coverage of noble metals on the carbon fiber substrate. The deposition of the noble metal alloy (Pt–Ir) on the Raney nickel electrode displayed their deposition only on pre-selected areas, showing a non-uniform coverage. This is in agreement with the results reported by Cooper and Botte [9], even though the authors reported results were for Pt–Rh alloy.

2.4. Conversion and Faradaic efficiency

The ammonia concentration was measured with an ion selective electrode apparatus [18] from Thermo Electron Corporation, Model Orion 710A+. The concentrations were tested before and after the experiments in order to calculate the ammonia conversion and the Faradaic efficiency for the process. The experimental time tested was compared to the theoretical time calculated based on Faraday's Law. All the values reported in the article have considered instrumental errors.

3. Results and discussion

3.1. Performance of different substrates

Fig. 2 presents the sustained periodic response of Pt–Ir Raney nickel and carbon fiber electrodes during cyclic voltammetry at a scan rate of 10 mV s^{-1} . The reported current was normalized by geo-

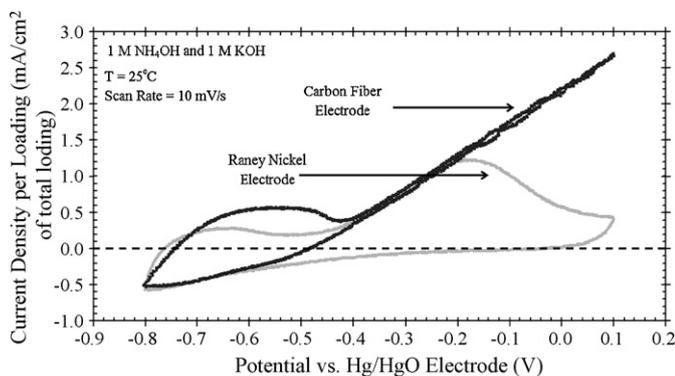


Fig. 2. Cyclic voltammograms for Pt–Ir on Raney nickel and carbon fiber substrates at 1 M NH_4OH , 1 M KOH, 25 °C, and 10 mV s^{-1} . The carbon fiber electrode showed better performance towards the electro-oxidation of ammonia since surface blockage effect is not observed.

metric area and total loading of noble metals in order to correct for the differences between the two substrates evaluated. The experiments were performed at 25 °C using a solution of 1 M NH_4OH and 1 M KOH. A high concentration of ammonia was chosen to avoid diffusion limitations that may be present at low concentrations of ammonia. The oxidation currents reported were above -0.5 V vs. Hg/HgO reference electrode, which was due to the electro-oxidation of ammonia as reported in literature [8,9]. The slopes of the curves for both electrodes seems to be similar, which indicates that the rate of ammonia electro-oxidation (per geometric area and total noble metal loading) was about the same; however, the reaction on the Raney nickel electrode was not continuous (observed peak at -0.2 V vs. Hg/HgO reference electrode). The current decrease observed with the Raney nickel electrode at the polarization potential may be caused by the blockage of active sites on the catalyst due to adsorbed OH^- ions as explained by Botte. This drop in current cannot be associated with diffusion limitations because of high ammonia concentration in the electrolyte [11]. The surface blockage in the Raney nickel may be due to a non-uniform coverage of the substrate, which also causes a lower active (noble metal) surface area for the reaction when compared to carbon fiber electrode. Carbon fiber electrodes may present a higher surface area than Raney nickel electrodes that possibly is contributing with the reactive capacity. Cooper and Botte reported the presence of exposed Raney nickel zones after the electrodeposition of noble metals, which indicated a non adherent deposition of the catalysts [9].

Based on the discussion supported by Cooper and Botte [9] related to the non-uniform coverage of noble metals on the Raney

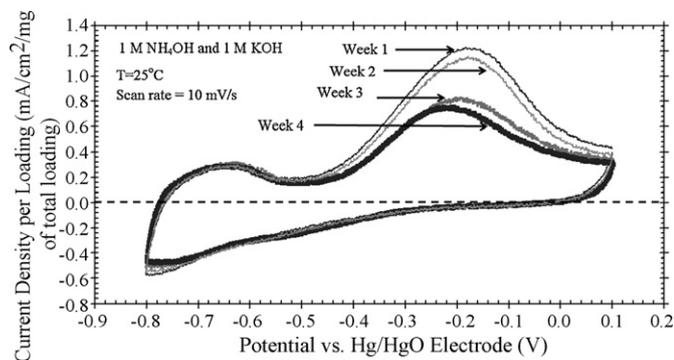


Fig. 3. Cyclic voltammograms performance of the Pt–Ir Raney nickel electrode with time at 1 M NH_4OH , 1 M KOH, 25 °C, and 10 mV s^{-1} . A decrease in reactivity over time was observed. From week 1 to week 4, the current decreased 200 mA.

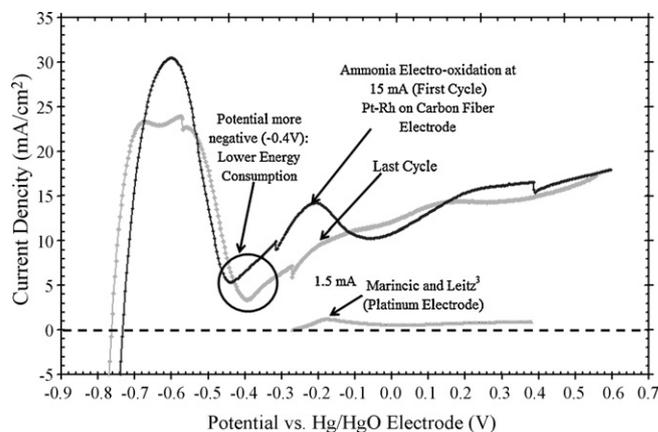


Fig. 4. Comparison of the electrochemical performance of the Pt–Rh carbon fiber electrode with Marincic and Leitz [3] electrode (platinized Pt on Pt foil) at 1.03 mM NH_4OH and 0.1 M KOH. The currents were normalized by geometric area. The peak of current density is observed in the literature at 1.5 mA cm^{-2} approximately, whereas with the carbon fiber substrate, the peak current density is observed at 15 mA cm^{-2} . Carbon fiber substrates showed 10 times higher currents than platinized Pt catalysts.

nickel substrate, one of the consequences may be the degradation of the material with time. To evaluate the stability of the Raney nickel electrode with time, the electrode was exposed to air after each experiment, and the same electrode was tested weekly for a month at the conditions used in Fig. 2. The results on time related evaluation of the electrodes are shown in Fig. 3, in which the uniform and sustained periodic state of the Pt–Ir Raney nickel electrode reported a significant decrease in the current with time. A decrease in approximately 200 mA of current is an indication of reactivity lost for the catalyst. The requirement is a reactive catalyst that perform electro-oxidation at similar current conditions for a specific voltage range (-0.8 to $+0.1$ V) with time. Raney nickel catalyst did not show the desired behavior towards the ammonia electro-oxidation reaction.

Another important comparison between the substrates is the electrode weight. The total weight of the Raney nickel substrate (excluding catalyst loading) was 1170.0 mg, which is considerably heavier than the weight for carbon fiber electrode (886.2 mg). Based on the results shown in Figs. 2 and 3, and the weight of the electrodes, carbon fiber was selected as the best substrate for the electro-oxidation of ammonia. Its advantages over Raney nickel include: (1) uniform coverage of noble metals, (2) minimization of surface blockage effect, and (3) light weight.

3.2. Performance of carbon fiber substrate electrodes at low concentrations of ammonia

The previous section experiments were performed at high concentrations of ammonia; however, the electrochemical performance of the electrodes needs to be tested at the concentrations of ammonia found in wastewater. Fig. 4 presents a comparison of Pt–Rh carbon fiber electrode (Electrode 3) with a 0.13 cm^2 platinized Pt electrode developed by Marincic and Leitz [3]. The reason to select a Pt–Rh carbon fiber electrode for comparison instead of a platinized Pt electrode was based on the electronic conductivity and adherence properties that Rh had displayed in its previous applications [10]. It was also a purpose of the investigation to determine the improvement on Rh over Pt, as well as the different substrates. The experiment was performed at the conditions described by Marincic and Leitz [3]: 1.03 mM NH_3 and 0.1 M KOH (equivalent to 12.8 pH), at 25 °C. The apparatus used to test the Pt–Rh carbon fiber electrode was a Solartron 1287 Electrochemical

Interface. The data from Marincic and Leitz was digitalized using the software Get Data Version 2.17 [19], their potential was measured vs. a SHE and it was corrected to Hg/HgO reference electrode by adding -0.092 V . The sweep rate used was 3.33 mV s^{-1} at static conditions. In the first cycle two peaks were observed; the first peak occurs at -0.60 V vs. Hg/HgO, which is associated with the electro-adsorption of OH^- as reported in the literature [9,11]. The second peak occurs at -0.20 V vs. Hg/HgO and it is related to the electro-oxidation of ammonia. The decrease in the current density with increase in potential is associated with diffusion limitations as the ammonia concentration in the electrolyte is low. The electro-oxidation of ammonia using the Pt–Rh electrode took place at a lower potential than the platinized Pt electrode developed by Marincic and Leitz [3], which might be due to the difference in the electrode composition. The fact that ammonia oxidation takes place at lower potential represents an improvement for the electrolysis of ammonia at low concentrations as the energy consumed by the process will be lowered. Furthermore, the current density observed for the oxidation peak with the carbon fiber electrode is 10 times higher than the one reported by Marincic and Leitz [3], which could be caused by an increase in the surface area. After 10 cycles, the ammonia in solution was depleted as no ammonia oxidation peak was observed in the last cycle. Fig. 4 was plotted based on current density per geometric area of electrode without including the total catalyst loading since Marincic and Leitz [3] did not specify the loading for the platinized platinum micro-electrode used in their experiment.

3.3. Effect of different noble metals on the electro-oxidation of ammonia at low concentrations

The different electrode materials were tested for the electro-oxidation of ammonia at low concentrations. The experiments were performed in $20\text{ mM NH}_4\text{OH}$ and 0.2 M KOH solution. Fig. 5 shows the cyclic voltammetry for different electrodes with a scan rate of 10 mV s^{-1} at 25°C . The reported current was normalized with respect to total catalyst loading for the electrode so as to account for any differences. Electrodes 3 and 4 showed the same current density value of approximately $0.44\text{ mA cm}^{-2}\text{ mg}^{-1}$ for ammonia

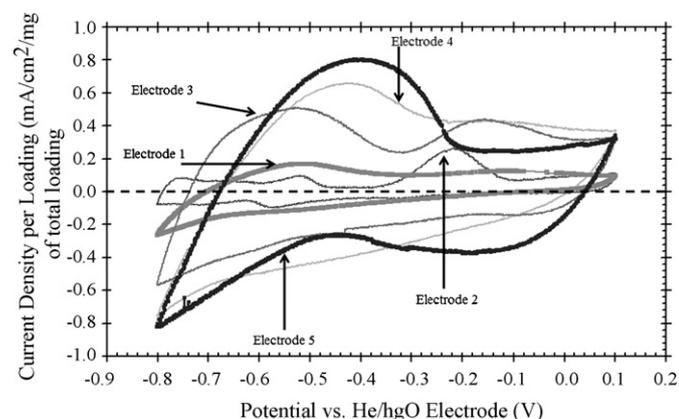


Fig. 5. Cyclic voltammetry curves for carbon fiber electrodes with different noble metals materials at $20\text{ mM NH}_4\text{OH}$, 0.2 M KOH , and 25°C . The currents are normalized per noble metal loading to correct for any difference. Electrodes 3 (Pt–Rh: 5.2 mg cm^{-1}), and 4 (Pt–Ir–Rh: 5.1 mg cm^{-1}), seemed to have the same current response ($0.5\text{ mA cm}^{-2}\text{ mg}^{-1}$ of total loading). Electrode 2 (Pt: 5.3 mg cm^{-1}) showed some reactivity by having a current peak response of $0.3\text{ mA cm}^{-2}\text{ mg}^{-1}$ of total loading, while Electrode 5 (Pt–Ir: 4.6 mg cm^{-1}) showed a high current peak that seems to be a combination of the electro-oxidation of ammonia and electro-adsorption of OH^- . The electro-oxidation of ammonia is not observed on Electrode 1 (Rh: 5.0 mg cm^{-1}).

oxidation peak. Electro-oxidation of ammonia reaction kinetics for each electrode was slightly different, which can be related to the composition of noble metals present in the electrodes. It can be noticed that for the Rh Electrode 1, the electro-oxidation of ammonia was not observed, which indicates the capacity of the Rh to improve the OH^- adsorption, but the inefficiency to enhance the ammonia electro-oxidation is probably due to a weak ammonia adsorption than OH^- adsorption. Electrode 2 showed an ammonia oxidation peak with current density approximately $0.3\text{ mA cm}^{-2}\text{ mg}^{-1}$ of total loading, but this value was not as high as the ones observed with electrodes 3 and 4 ($\sim 0.5\text{ mA cm}^{-2}\text{ mg}^{-1}$ of total loading). On the other hand, Electrode 5 shows an interesting behavior, since the peaks for the electro-adsorption of OH^- and electro-oxidation of ammonia seem to be merged (this electrode was further tested under galvanostatic conditions to elucidate this matter, see Fig. 6). In order to determine which electrodes displayed the best performance, further analysis should be carried out to compare the capacity of developing higher currents at lower potentials. Electrodes 2–5 exhibited a good performance in cyclic voltammetry experiments. Reaction kinetics observed with Pt–Rh electrode was significantly improved than either Rh or Pt electrodes (1 and 2), probably due to the synergistic effect of the Rh (adherence, electrical conductivity) [10], and Pt (activity towards ammonia electro-oxidation) [12,13]. The presence of Pt–Ir also enhances the oxidation of ammonia at low concentrations. Furthermore, the presence of Rh–Pt–Ir may be the perfect combination for the best catalyst at the conditions tested, by combining all the characteristics provided by each one of the catalyst materials used.

3.4. Galvanostatic performance of the electrodes

The most promising electrodes selected based on the results shown in Fig. 5 (electrodes 2, 4, and 5) were tested galvanostatically. As mentioned in the experimental description, a Pt–Ir–Rh electrode was used as counter electrode to minimize the cell voltage (decrease cathodic over-potentials). The intention of this test was to determine the electrode that achieves the highest current at the lowest cell voltage for electro-oxidation of ammonia. Fig. 6 shows the comparison of the performance of different electrodes in $20\text{ mM NH}_4\text{OH}$, 0.2 M KOH solution, which was constantly stirred, at 25°C . The current was increased from 10 mA to the maximum achievable current for each electrode in increments of 10 mA . Each current step was sustained for 30 min . Electrode 4 (Pt–Ir–Rh electrode deposited) showed the best behavior with the highest cur-

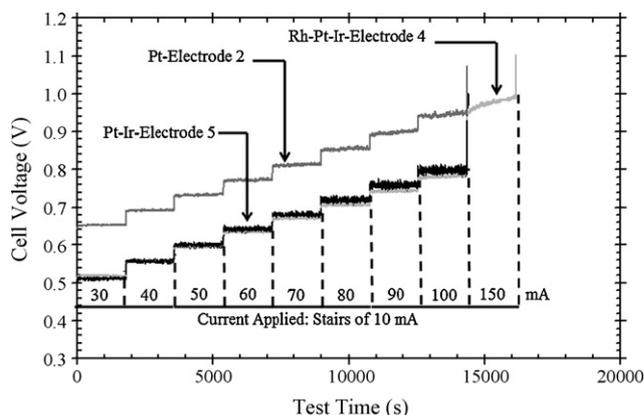


Fig. 6. Galvanostatic performance of the most promising electrodes for the electrolysis of ammonia (Electrodes 2, 4, and 5), based on the results of Fig. 5. The experiments were performed at $20\text{ mM NH}_4\text{OH}$, 0.2 M KOH , and 25°C . Pt–Ir–Rh was used as the cathode. Electrode 4 (Pt–Ir–Rh) showed the highest current and the lowest voltage for all the currents tested.

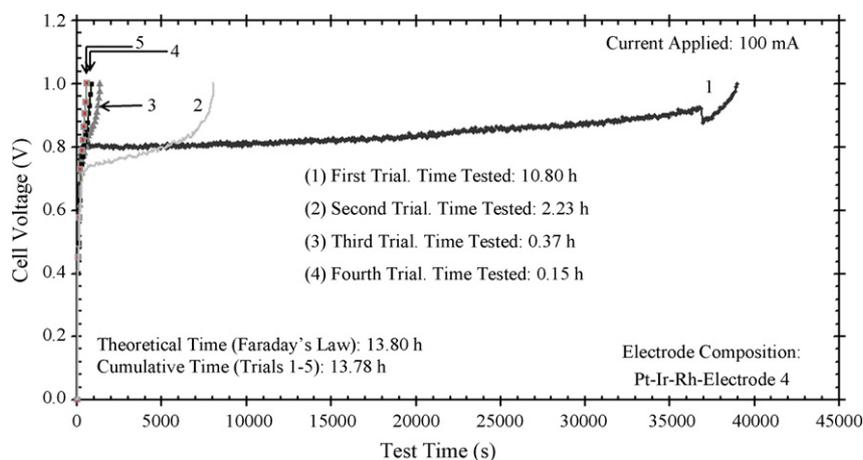


Fig. 7. Galvanostatic performance of Pt–Ir–Rh electrode at 100 mA. Initial concentration of 21.50 mM NH_4OH , 0.2 M KOH, and room temperature. The experimental elapsed time was the same as the theoretical time calculated by Faraday's Law for a total of 13.78 h. The final NH_3 concentration was 1.83 mM, with a process conversion of $91.49 \pm 0.01\%$ and Faradaic efficiency of $91.81 \pm 0.13\%$.

rent response of 150 mA. Electrode 4 also reported a difference in potential of approximately 100 mV with respect to Electrode 2. Cell voltages for Electrodes 4 and 5 were similar for all the applied currents except for 150 mA. Based on the results shown, it appears that at low ammonia concentrations the synergistic effect of Rh–Pt–Ir is a perfect complement to enhance the ammonia electrolysis (lowest cell voltage at the highest current). The combination of Pt–Ir loading over carbon fiber electrode was also promising. However, the Pt–Ir electrode reached 1 V immediately after setting the applied current to 150 mA, while the Rh–Pt–Ir electrode did reach the limiting voltage of 1 V progressively with time. This is an indication that the Rh–Pt–Ir electrode can reach higher current than the Pt–Ir electrode at the same conditions. Therefore, the Rh–Pt–Ir electrode was chosen for further testing and development.

3.5. Efficiency and conversion

The Faradaic efficiency and the conversion for the electro-oxidation of ammonia were determined on the best electrodes chosen from Fig. 6. Pt–Ir–Rh Electrode 4 was selected for the test as it performed similar to Electrode 5 according to Fig. 6. The current was maintained at 100 mA, and the experiment was performed until the cell voltage of the system reached the maximum voltage of 1 V. Higher voltages were not attempted to avoid the electrolysis of water. The experiment was performed in five steps. Fig. 7 shows the results of the electrochemical test. During the first trial, it took 10.80 h for the electrolytic cell to reach 1 V. The reasons for the increase in the voltage could be: (1) ammonia was completely depleted from the bulk, and (2) concentration overpotential (depletion of ammonia concentration at the surface of the electrode). To determine the cause, the system was allowed to rest for 15 min and then it was polarized again at the same current (trial 2). The fact that the system was stable for a longer period of time indicated the effect of concentration overpotential on the electrolysis. The same procedure was continued until the cell voltage rose immediately (at short elapsing time) to 1 V during trial 5. After trial 5, the concentration of ammonia in the solution was too low for the cell to operate at 100 mA. Finally, the time was accounted for a total of five trials and the total time was compared with the theoretical time calculated according to Faraday's law. The ammonia concentration was measured at the beginning and end of the test in order to determine the percentage of ammonia conversion, as well as the Faradaic efficiency of the process. The initial concentration was 21.50 mM ammonia, and the final concentration was

1.83 mM, yielding a percentage of $91.49 \pm 0.01\%$ for ammonia conversion. The Faradaic efficiency was $91.81 \pm 0.13\%$. These percentage values are considered high but still they could be improved by using a combination of cells in cascade operating conditions at different currents, and taking into consideration the power consumption as well as the conversion and efficiency of the process. Future research will focus on experiments using cascade conditions for improving ammonia conversion efficiency. The final ammonia concentration obtained was still considerably high to be released into the environment without any pollution consequences, the acceptable value should be in the order of 0.08 mM according to EPA [20]. Minimization of the final concentration of ammonia after the electrolysis to comply with EPA is a topic of future work. Preliminary results in our laboratory indicate that a combination of ammonia electrolytic cells arranged as a cascade process would achieve the required EPA threshold for an ammonia effluent.

4. Conclusions

Two different substrates were evaluated for the electro-oxidation of ammonia at low concentrations. Electrodes prepared on a Raney Nickel substrate presented lower reactivity for the electro-oxidation of ammonia at low concentrations when compared to the carbon fiber substrate. In summary, carbon fiber is a better substrate than Raney nickel for the electro-oxidation of ammonia at low concentrations based on: (1) uniform coverage by noble metals; (2) no surface blockage effect; (3) light weight.

The carbon fiber electrodes developed performed ten times better than the electrodes reported in the literature [3]. The electrochemical performance of different noble metals deposited on carbon fibers was evaluated. Electrodes containing Pt–Ir–Rh and Pt–Ir seemed to be the most promising candidates for the electrolysis of ammonia at low concentrations based on the cyclic voltammetry and galvanostatic results. The process demonstrated a $91.49 \pm 0.01\%$ conversion of ammonia and a Faradaic efficiency (at a current density of 25 mA cm^{-2} and 25°C) of $91.81 \pm 0.13\%$ by using Pt–Ir–Rh catalyst on carbon fiber substrate with a loading of 5 mg cm^{-1} of carbon fiber bundle. This implies that the electro-oxidation of ammonia at low concentrations and at a current density of 25 mA cm^{-2} follows Faraday's law closely, which indicates ammonia conversion to hydrogen and nitrogen.

Future experimental studies will find a strategy to decrease the concentration of NH_3 and KOH for ammonia electrolysis. EPA standard regulations for ammonia emissions in water sources should

be accomplished [20]. In a future publication, adjustments to the current density will be performed to decrease the concentration of ammonia in the solution and improve the efficiency and the conversion of the reaction.

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References

- [1] S.W. Gay, K.F. Knowlton, Ammonia emissions and animal agriculture, Virginia Cooperative Extension, Biological Systems Engineering, Publ. no. 442-110. Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 2005.
- [2] U.S. EPA, Final Rule to Add PM_{2.5} Precursors to the Transportation Conformity Rule, EPA 420-F-05-005, 2005.
- [3] L. Marincic, F.B. Leitz, J. Appl. Electrochem. 8 (1978) 333–345.
- [4] S.-q. Xia, T.-y. Gao, Z.-y. Zhou, J. Environ. Sci. 14 (2002) 541–546.
- [5] U.S. EPA, Wastewater Technology Fact Sheet Ammonia Stripping, EPA 832-F-00-019, Washington, D.C., 2000.
- [6] G.G. Botte, Pending Patent, 2005.
- [7] G.G. Botte, F. Vitse, M. Cooper, Pending Patent, 2004.
- [8] F. Vitse, M. Cooper, G.G. Botte, J. Power Sources 142 (2005) 18–26.
- [9] M. Cooper, G.G. Botte, J. Electrochem. Soc. 153 (2006) A1894–A1901.
- [10] N. Sathe, G.G. Botte, J. Power Sources 161 (2006) 513–523.
- [11] G.G. Botte, Electrode Processes VII, in: V.I. Birss, D. Evans, M. Josowicz, M. Osawa (Eds.), PV 2004-18, The Electrochemical Society Proceedings Series, Pennington, NJ, 2005, p. 203.
- [12] J.D. Giner, J.R. Moser, US Patent 3,650,838 (1972).
- [13] D.W. McKee, B. Hills, A.J. Scarpellino, Jr., US Patent 3,730,774 (1973).
- [14] M. Cooper, G.G. Botte, J. Mater. Sci. 41 (2006) 5608–5612.
- [15] J.-P. Guenau De Mussy, J.V. Macpherson, J.-L. Delplancke, Electrochim. Acta 48 (2003) 1131–1141.
- [16] E. Mahé, D. Devilliers, Electrochim. Acta 46 (2000) 629–636.
- [17] J. Larminie, A. Dicks, Fuel Cell Systems Explained, 2nd ed., John Wiley & Sons Ltd., 2003, pp. 25–33.
- [18] E. Cellar, Procedures for Using the Ammonia Ion Selective Electrode. Operation Manual, Ohio University, Athens, OH, 2005.
- [19] Software Get Data[®] <http://www.getdata.com.ru>.
- [20] EPA, Water Quality Standards, OAC Chapter 3745-1, Columbus, OH.