Journal of New Materials for Electrochemical Systems 17, 055-065 (2014)
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Oxygen Reduction Reaction (ORR) on a Mixed Titanium and Tantalum Oxy-nitride Catalyst Prepared by the Urea-based Sol-gel Method

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Received: February 11, 2014, Accepted: April 05, 2014, Available online: May 09, 2014

Abstract: *The electrochemical stability and activity of different compositions of titanium and tantalum oxy-nitride nano-catalysts were investigated for the oxygen reduction reaction (ORR). A new sol-gel method was used to produce a nano-powder mixture of Ti and Ta oxy-nitride from their alkoxides using urea as a nitrogen source. The precursors prepared by the sol-gel method were annealed in a* N_2 + 3% H_2 *atmosphere at determined temperatures (500, 700 and 900 °C) inside a silica tube furnace. X-ray diffraction results proved that by using this method a considerable amount of nitrogen was inserted into the catalyst structure at a relatively low temperature. Energy dispersive spectroscopy showed that the prepared catalyst should be oxidized carbonitride of titanium and/or tantalum. Heat treatment had a major effect on the onset potential by changing the crystallinity of the catalyst, so that the onset potential of titanium oxynitride increased from ca. 0.05 V to 0.65 V vs. NHE by increasing the temperature from 500 to 700 °C. Increasing the Ta concentration also led to a higher onset potential but lower ORR current. For instance, the onset potential for the ORR for tantalum oxynitride heat treated at 700 °C was ca. 0.85 V vs. NHE while this value was ca. 0.65 V vs. NHE for titanium oxynitride. However, the ORR current was 100 times smaller in tantalum oxynitride, most likely because of a low electrochemically active surface area. Electrochemical measurements suggested that an appropriate composition of titanium and tantalum was required to have both a good onset potential and ORR current by improving the catalytic activity and increasing the active surface area and electrical conductivity.*

Keywords: titanium and tantalum oxy-nitride, urea-based sol-gel, oxygen reduction reaction (ORR)

1. INTRODUCTION

Fuel cells are one of the most probable interesting alternative energy devices which exhibited high efficiency and environmentally friendly properties. Among them, due to their high energy density, Polymer Electrolyte Membrane Fuel Cells (PEMFC) are the most promising type for commercial fuel cell vehicles applications because they can operate at low temperatures ranging from room temperature to 80 °C [1].

The platinum nano-particle supported on carbon (Pt/C) is the state-of-the art commercial electro-catalyst used in PEMFCs due to its high specific surface area and high electrocatalytic performances for the Hydrogen Oxidation Reaction (HOR) and the Oxygen Reduction Reaction (ORR) [2, 3]. However, the electrocatalytic activity for the ORR is insufficient to obtain the appropriate power with low electro-catalyst loading even with platinum [4]. The limited abundance of Pt natural resources and its high cost are significant obstacles in the future commercialization of PEMFCs [4-9]. On the other hand, the dissolution and deposition of extremely dispersed Pt particles in the electrolyte and oxidation of the carbon support during long-term operation decreases the cell performance. This makes impossible the drastic reduction of Pt usage [8, 10]. Thus, the commercial viability of PEMFCs requires the development of better electro-catalysts to improve the fuel-cell performance.

Some researchers [11-15] have revealed that Pt-based alloys with transition metals exhibited much higher ORR activity than pure Pt as they believed that the presence of the metal species changes the electronic structure of Pt, leading to a weaker interaction between the Pt surface and the unwanted Pt-OH intermediate. In this regard, Pt-M (M= Pd, Co, Ni, Cr, Mn, and Fe) alloys have

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become attractive to ameliorate the catalytic activity and reduce the cost [16-20]. However, poor long-term stability due to the dissolution of these transition metals in acidic conditions hinders the practical application [21]. Additionally, the leaching out of metal ions would contaminate the membrane and limit the fuel cell performances. Therefore, the development of non-noble electro-catalysts with high activity and durability in acidic conditions becomes one of the most important topics in PEM fuel cell research.

Transition metal nitrides, which are well known as valve metals, are used as anticorrosion and coating materials, and groups 4 and 5 metal oxides, like Ti, V, Nb and Ta oxides, have high chemical stability in acids [21-25]. Therefore, group 4 and 5 metal nitrides, oxides and oxy-nitrides are expected to be stable under an acidic and oxidative atmosphere. In addition, it has been reported that these compounds have some electro-catalytic activity for the ORR [24-28].

Transition metal carbonitrides have been studied [22-25]. They started with transition metal carbides because of their electrical conductivities. Although, for example, tungsten carbide has electronic properties, like platinum, it has a very low corrosion resistance under acidic and oxidative conditions. They found that in addition to the enhancement of electrocatalytic activity, the chemical stability of the tungsten carbide was significantly increased by the addition of Ta to the pure WC catalyst [29]. This enhancement was most probably because of the passive oxide film formation on the catalyst surface. Therefore, other studies were carried out on the transition and non-transition metal oxides like, like zirconium oxide [30, 31], titanium oxide [32], cobalt oxide, tin oxide and niobium oxide [33]. In particular, because titanium oxide is an abundant natural resource and supports some electrochemical reactions, it is worth being studied. It has been found that the electrocatalytic activity of titanium oxide for the ORR might be affected by a surface state change, such as the crystalline structure and work function [32]. It was shown that the onset potential for the ORR was increased up to 0.65 V for the electro-catalysts heat-treated at 900 °C. The heat-treated electro-catalysts were chemically and electrochemically stable in acid solution, so that the average Ti concentration of the electro-catalysts after 24 days at 50 °C in 0.1 $mol.dm^{-3}$ sulphuric acid under atmospheric conditions was about 3.5×10^{-7} $mol.dm^{-3}$ [32]. This amount was smaller than the solubility of the platinum black powder under the same electrolyte at a lower temperature (20 °C) after 25 h (5.6×10^{-7} $mol.dm^{-3}$) [34].

In spite of the high stability in acidic conditions of the metal oxides of groups 4 and 5 transition metals, these oxides were almost insulators, and it is clear that the electro-catalysts must have some electrical conductivity. For instance, the ORR hardly proceeds on the tantalum oxide due to the big gap between the upper energy level of the valence band and the Fermi level of tantalum oxide [35]. The most effective means to narrow this wide band-gap of the oxides was to insert N and/or C. In addition, transition metal nitrides and/or carbides have high electrical conductivity (e.g. TaC 4×10^{4} $S.cm^{-2}$; TaN $4-7\times10^{3}$ $S.cm^{-2}$ [10]). In this regard, Azuma and co-workers studied the electrochemical properties of ZrN, NbN, CoN, TiN and VN prepared by reactive RF sputtering. Ishihara and co-workers also studied chromium carbonitride and tantalum carbonitride prepared by the reactive sputtering [36, 37]. However, as a consequence of a large decrease in the Gibbs energy, transition metal oxides are thermodynamically more stable than their carbonitride and nitride and thus, these nitrides and carbonitrides are essentially unstable under the ORR conditions [38, 39]. Also, it was seen that the pure nitride of transition metals, such as Ta_3N_5, show poor catalytic activity for the ORR and the onset potential was below 0.4V vs. RHE. On the other hand, tantalum oxynitrides or partially oxidized tantalum carbonitrides had both chemical and electrochemical stability and definite catalytic activity for the ORR [4, 24, 26, 40-42]. Ishihara and co-workers believe that an oxygen molecule hardly adsorbs on the surface of perfect oxides, such as Ta_2O_5 and/or TiO_2, and that it is essential to form some defects as the oxygen adsorption sites on a surface while the metal is basically kept at the highest oxidation state [22, 33]. These surface defects, which lead to lower ionization potential, work function and, consequently, a higher density of the state of electrons, are mostly made by changing the crystallinity with a heat treatment process [24, 26]. Zirconium oxy-nitride [25, 27, 43] and partially oxidized niobium carbonitride [28] also were studied as a non-platinum cathode catalyst for the ORR. So far, the obtained current and onset potential for the ORR were much smaller than those for the platinum based electro-catalyst. It is then necessary to continue the investigation of transition metal oxides and/or oxynitrides to improve the electrocatalytic properties.

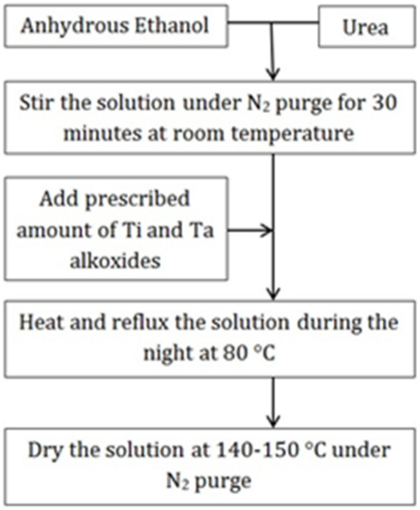

Figure 1. Schematic flowchart of the preparation of Ti-Ta-ON precursor using urea-based sol-gel method.

In previous studies, transition metal nitride and/or carbonitride were normally used as the starting materials to produce partially oxidized metal carbonitride. These nitrides and/or carbonitrides were prepared mostly at high temperatures up to 1600 °C over 8 hours. In this study, a new urea-based sol-gel method is used to prepare a mixture of titanium and tantalum oxynitride at a much lower temperature and duration. The maximum heat treatment temperature in this work is 900 °C. As a result of this sol-gel method there are both metal carbide and nitride besides metal oxide in the catalyst structure. The stability and electrochemical activity of these electro-catalysts were also evaluated in order to use them as a non-platinum electro-catalyst for the ORR. In previous studies, other researchers took electrochemical measurements of the pre-

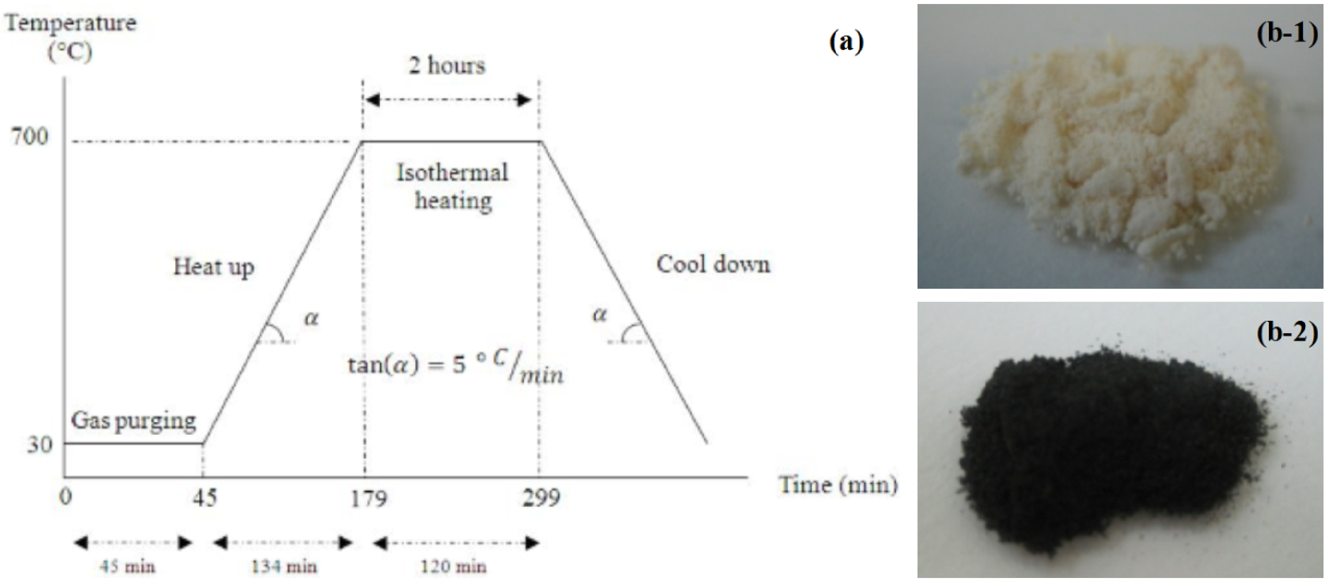

Figure 2. (a) Heating step of the calcination process, (b-1) light yellow powder before calcination, (b-2) fine shiny black powder after 700 °C heat treatment for 2 hours

pared electro-catalysts supported by carbon black. It was noted that the mixture of the carbon black as a current collector was required to obtain sufficient electrical conductivity. Using carbon black increased the ORR current as much as 60 times, however, there was no enhancement in onset potential for the ORR which, of course is not affected by the carbon surface area. In fact, carbon black increased the surface area, which acted on the active sites of the electro-catalysts and had sufficient electrical conductivity. In this study the prepared electro-catalysts are characterized without carbon black and, therefore, the ORR current might be much lower compared with those of the other oxides electro-catalyst in the literature which are supported on carbon black. The aim of our work is to evaluate the ORR intrinsic electrocatalytic parameters of the oxy-nitrides electro-catalysts without any carbon support. The electro-catalysts will be also characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Titanium (IV) isopropoxide [$Ti(O^{i}C_3H_7)_4$] (97%) and tantalum (V) ethoxide [$Ta(OC_2H_5)_5$] (99.8%) were purchased from Sigma-Aldrich and used without further purification. Urea (reagent ACS 99%) was obtained from Fischer Scientific and anhydrous ethanol was used as the mutual solvent.

2.2. Sol-Gel Procedure

The flowchart in Figure 1 describes the experimental procedure to prepare a mixture of titanium and tantalum oxy-nitride precursor. First, an appropriate amount of urea was dissolved in 42 mL of absolute ethanol under a nitrogen atmosphere at room temperature. After 30 minutes, the determined amount of titanium (IV) isopropoxide and tantalum (V) ethoxide (as the starting materials) was added drop by drop to the solution with continuous stirring to achieve a molar ratio of metal source to urea and solvent of 1:2:45. This reaction was very slow, and it was allowed to continue through the night at 80°C under reflux conditions in order to ensure completion of the reaction. Then, the resulting homogeneous light yellow solution was dried at 140-150 °C while the color of the remnant slowly changed into yellowish red. The yellowish red precipitates were cooled to room temperature and ground into fine powder. All steps of this procedure were carried out under nitrogen to decrease the probability of oxygen and moisture existence as low as possible.

2.3. Heat treatment

The obtained precursors were subjected to a specified nitridizing gas (N_2 + 3% H_2) with ca. 180 mL/min flow rate at 500, 700 and 900 °C. This process was done inside a silica tube furnace (Model: 55031-A, 800 Watts, 115 Volts, by LINDBERG/HEVI-DUTY). The precursors were converted to titanium and tantalum oxy-nitride at high temperature, and crystallinity, particle size and specific surface area changed to modify the property of the catalyst. A heating schedule shown in Figure 2 (a) was adopted in this study. After 45 minutes of gas purging, approximately 2 g of the precursor, which had been placed in a crucible, were heated up to the desired temperature at a heating rate of 5 °C/min. The isothermal heat treatment time was 2 hours. The sample was then furnace cooled at a cooling rate identical to the heating rate. Figure 2 (b) shows the precursor before and after heat treatment at 700 °C.

2.4. Physicochemical Characterization

In order to characterize the crystalline structure and phase identification, powder X-ray diffraction (XRD) data were collected using a Philips X'Pert diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å) (at 50 kV and 40 mA) in a scan range (2θ) from 10° to

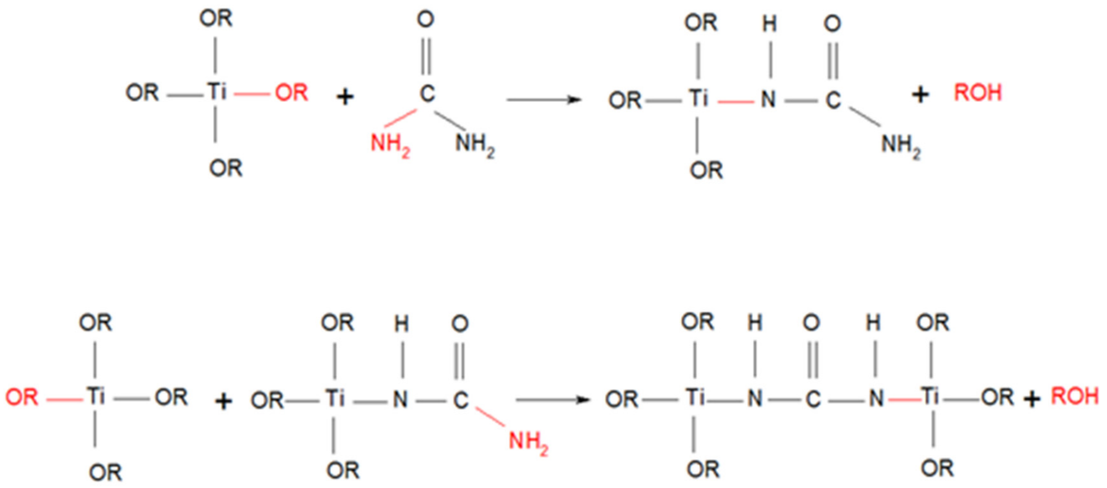

Figure 3. Proposed mechanism of the reactions involved between titanium isopropoxide and urea during the sol-gel process

85° at a speed of 2° min^{-1}. The surface morphologies were examined through a scanning electron microscope (SEM, JEOL JSM-840) equipped with an Energy Dispersive X-Ray Spectroscopy (EDS) to analyse the Ti, Ta, O, N and C contents of different samples.

2.5. Electrochemical Measurements

All electrochemical experiments were conducted through a conventional 3-electrode cell containing 0.5 M sulphuric acid (0.5 mol.dm^{-3} H_2SO_4) saturated with N_2 or O_2 at atmospheric pressure and room temperature. The silver-silver chloride electrode (Ag/AgCl sat. KCl) and the platinum (Pt) mesh were used as the reference and counter electrodes, respectively. To prepare the working electrode, 10 mg of the catalyst without any addition of carbon black was added to a mixture of 480µL absolute ethanol and 20µL Nafion 5 % wt by 10 minutes ultrasonic treatment. Then, ca. 20µL of this ink was placed slowly and layer by layer on a glassy carbon rod (CH Instruments Inc. CHI 104, diameter = 3 mm). Before adding the next layer, the previous one should be completely dried to obtain a uniform and fully covered surface. This step is very important to avoid the oxidation and reduction peaks related to the glassy carbon rod during the measurements. The catalyst loading was ca. 10 mg per geometric cm^2. All electrode potentials referred to the Normal Hydrogen Electrode (NHE) scale.

Cyclic voltammetry (CV) in the range of 0.0 to 1.2 V (versus NHE) was performed to evaluate the electrochemical stability of the prepared catalysts. The scan rate was adjusted to 100 mV.s^{-1} and N_2 gas was bubbled into the 0.5 M H_2SO_4 solution at 30 °C. After the cyclic voltammetry had reached a steady state, slow scan voltammetry (SSV) was performed at 5 mV.s^{-1} scan rate in both N_2 and O_2 atmosphere to evaluate catalytic activity for the ORR. Because the particle sizes of the specimens are different, the real surface area is hardly estimated. Therefore, the current reflects the ORR activity for a determined amount of the powder. So, in this study the current density is expressed based on the geometric surface area (standardized current) of the working electrode.

3. RESULTS AND DISCUSSION

3.1. Possible mechanism of the titanium oxynitride elctrocatalyst formation

The reaction is between the Ti/Ta alkoxide and urea. When we compare this reaction with the reaction of Ti or Ta alkoxide with water, this reaction is very slow and we cannot see any obvious change in the system. While in reaction with water a white precipitate of Ti/Ta hydroxide (which turns to Ti/Ta oxide at higher temperature) appears immediately. In this regard we let the Ti/Ta alkoxide to be exposed to urea for a longer time (during the night) and also higher temperature. The solvent which was used is ethanol and to avoid evaporation we followed the reaction under reflux condition, to bring the alcohol back to the system.

But, what is the exact mechanism between the Ti/Ta alkoxide and urea is not completely clear from this work. However we suggest the following general steps of a possible reactions involved during the sol-gel process of the titanium oxynitride formation (Figure 3).

This reaction can be continued to make a big network, which under heat treatment condition breaks to titanium nitride, titanium oxide or a mixture of them: titanium oxy-nitride. The same reaction might happen for the tantalum alkoxide, so that even having a big network of a mixture of titanium and tantalum is possible.

Titanium isopropoxide and tantalum ethoxide boiling points are 232 and 155 °C, respectively. Therefore, we do not have any decomposition of the chemicals and the forming electrodes in our working conditions of 80 °C at atmospheric pressure during the night and under reflux condition. The XRD and EDS results support this possible reaction in the sol-gel process; otherwise we cannot have a more TiN in the electro-catalyst structure. This is not the case of the previous sol-gel methods. Our experimental results showed that when urea is added during the heat treatment of the samples, no TiN is observed in the structure. In contrary the TiN amount in the sample increases significantly when urea is added to the mixture of the electrocatalyst preparation during the sol-gel

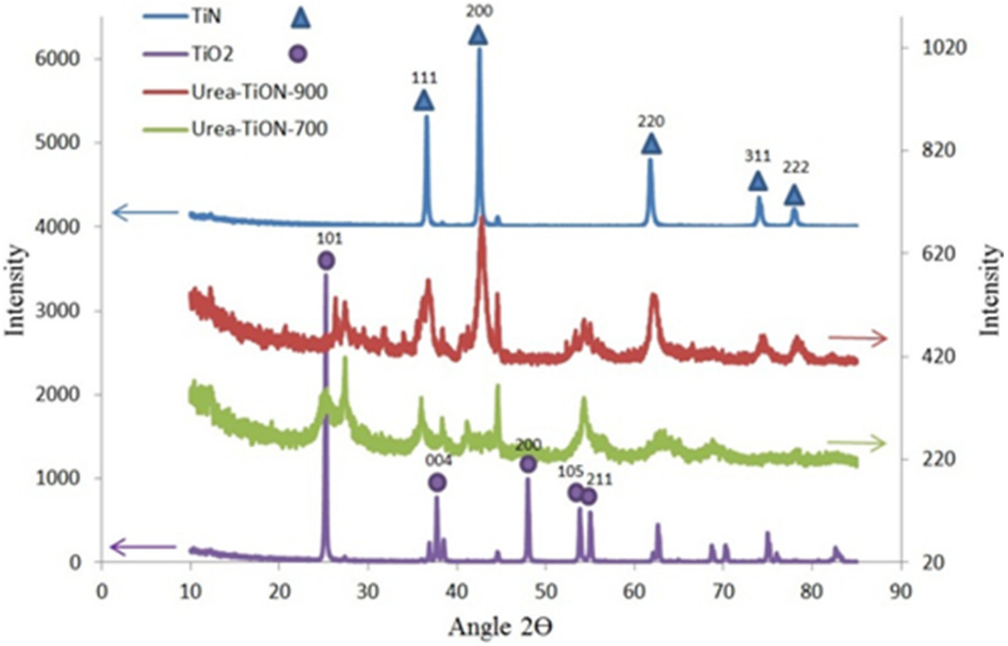

Figure 4. XRD patterns of titanium oxy-nitride powder annealed at 700 °C (Urea-TiON-700) and 900 °C (Urea-TiON-900) for 2 hours; TiN and TiO_2 reference materials were purchased from Sigma-Aldrich and Fisher Scientific, respectively.

process. Therefore, urea and titanium isopropoxide cannot be remained unchanged at the end of sol-gel process.

3.2. Physicochemical characterization

Figure 4 shows the XRD patterns of the TiO_xN_y catalysts obtained from the urea-based sol-gel method after calcination at 700 °C and 900 °C for 2 hours. Pure anatase TiO_2 and TiN purchased from Fisher Scientific and Sigma-Aldrich, respectively, were used as references. The five diffraction peaks at 2θ of 36.56°, 42.54°, 61.71°, 73.99° and 77.89° can be indexed as the cubic Fm3m unit cell of TiN [(111), (200), (220), (311) and (222)] with a=4.2417 Å and α=90° cell parameters. These peaks are identified with a small blue triangle on top of them. As well, strong diffraction peaks at 25.25°, 37.75°, 47.95°, 53.79° and 55.05° are respectively assigned to (101), (004), (200), (105) and (211) facets of the anatase structure of titanium dioxide micro powder. All peaks are in good agreement with the standard spectrum (JCPDS No. 38-1420 for TiN and No. 21-1272 for TiO_2).

From these patterns it is obvious that the (101) anatase TiO_2 peak at 25.25° in both samples vanished and changed to a (110) rutile structure at 27.8°. Also, by increasing the temperature from 700 to 900 °C the intensity of this peak was reduced. As well, the intensity of (200), (105) and (211) TiO_2 anatase peaks is reduced by increasing the temperature. Meanwhile, the growth of the (111), (200), (220), (311) and (222) peaks related to the TiN is obvious in the sample heat treated at 900 °C. These results prove the nitrogen is embedded into the lattice using this method. From the XRD patterns we conclude that the nitrogen content ratio relative to the oxygen content in the prepared samples is considerable. In addition, diffraction intensity increases with increasing particle size. These results suggested that the nano-sized powders were obtained by the sol-gel method and heat treatment, because of their relatively low intensity compared to the TiO_2 and TiN micro powders. However, increasing the temperature made the peaks much sharper, which indicates the growth of the crystallite structures.

Figure 5 shows the Scanning Electron Microscopy images (SEM) and the Energy Dispersive Spectra (EDS) of the TiO_xN_y electro-catalyst heat treated at 900 °C. Figures a-1 and a-2 show respectively the SEM images and the EDS of the electro-catalyst prepared by the urea-based sol-gel method. Figures 5 (b-1) and 5 (b-2) are the respective SEM images and EDS for the sample prepared by the regular oxide-based sol-gel method without the addition of urea. Comparing the EDS results shows that the electro-catalyst prepared using the urea-based method contains more nitrogen and carbon than the regular oxide based sol-gel method. The particle size of the sample prepared from the oxide-based method (spheres in Figure 5 (b-1)) is much smaller than those of the sample prepared using urea. These results show that inserting nitrogen (which comes from urea) inside the catalyst structures leads to sintering and bigger particles size. It seems that using the oxide-based sol-gel method of preparation leads to a sample which is similar to an oxide based electro-catalyst without defects in the electro-catalyst. Conversely using the urea-based sol-gel method of preparation leads a nitrogen-doped sample which contains more defects in the structure. These defects might contribute in the improvement of the ORR by easing the oxygen adsorption.

3.3. Electrochemical stability

Figure 6 shows the cyclic voltammogram (CV) in a nitrogen atmosphere of the samples containing 25 % Ta and 75 % Ti, which were heat treated at 500 and 900°C. The shape of the CV for the sample heat treated at 500°C is significantly different from those of

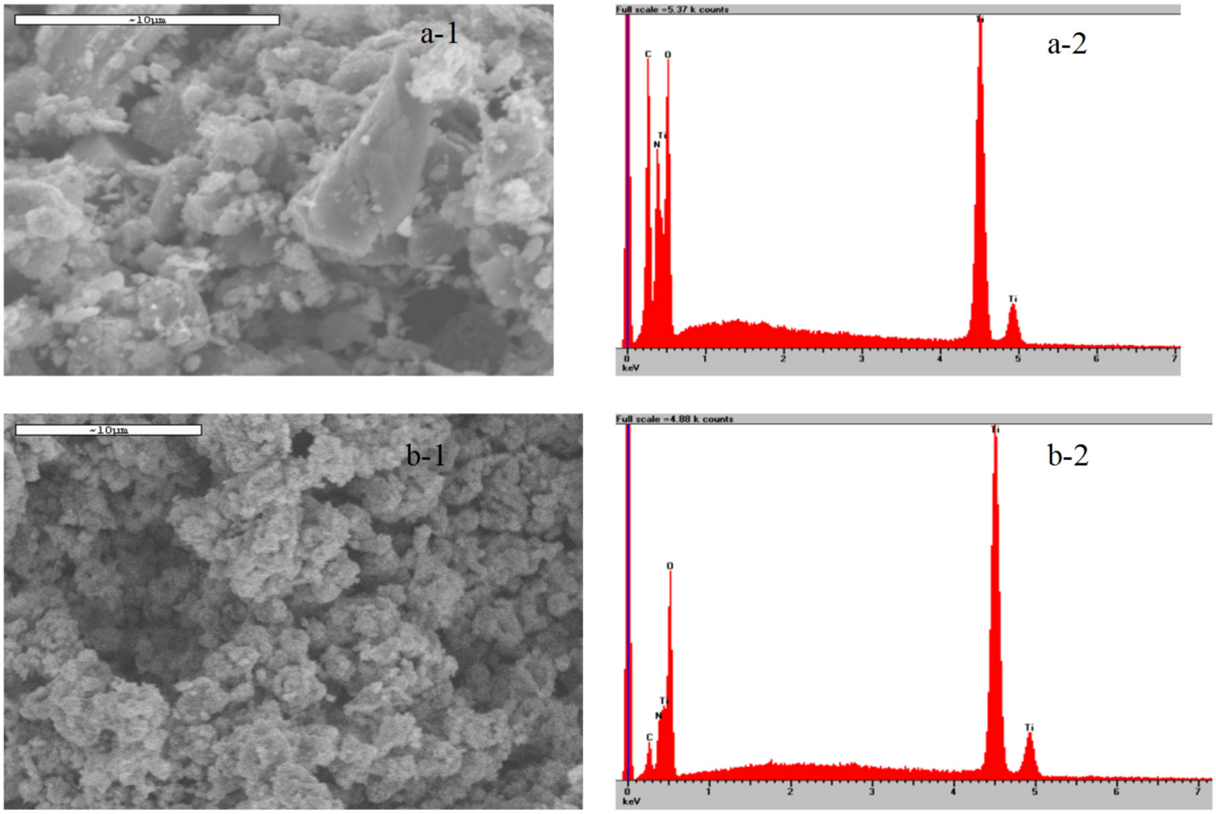

Figure 5. (a) SEM images and EDS of the TiO_xN_y prepared from urea-based sol-gel method and (b) TiO_xN_y prepared from regular oxide-based sol-gel method without the addition of urea.

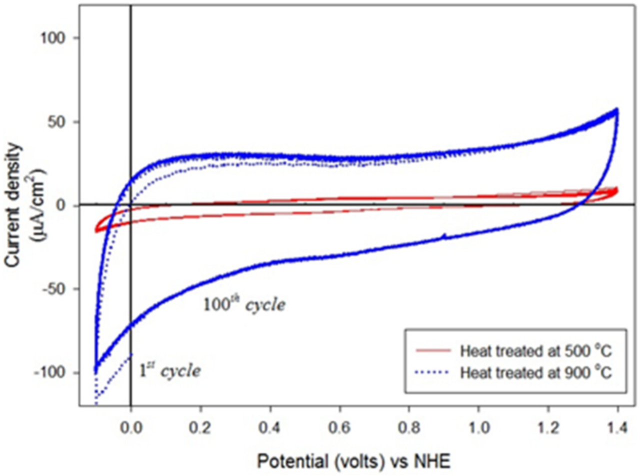

Figure 6. Cyclic voltammetry (under nitrogen and with 100 mV/s scan rate) of the samples containing 25 % Ta and 75 % Ti heat treated at 500 °C (red line) and 900 °C (blue dot).

the sample annealed at 900°C. But in both cases after several potential cycles (100 cycles at the rate of 100 mV/s scan rate) the first scan and the last one were almost the same. The CVs of the specimens with different Ta amounts and heat-treated at 500, 700 and 900 °C also reached a similar steady state. These results revealed that the heat treated mixture of Ti and Ta oxy-nitrides had high electrochemical stability in an acidic solution. Furthermore, there was no specific anodic peak because of catalyst oxidation and dissolution. The current density at any potential of the sample annealed at 500°C is smaller than those of the sample heated at 900°C. This might be related to the increase of the elctrochemical active surface area with the sample heating temperature. The calculated cathodic and anodic electric charge densities at steady state were almost the same, which confirms the surface stability of the specimens. These electric charges in the CV were calculated using the following equation:

$$Q = \int i.dt = \int i\frac{dE}{v} = \frac{1}{v}\int i.dE$$

Where *Q, I, t, v* and *E* are respectively the electric charge (C), current density (Amp/cm^2), time (second), scan rate (mV/second), and electrode potential (Volt).

Comparing the CVs of the samples heat treated at 500 and 900 °C, in figure 6, shows that the amount of the electric charge density increases with the isothermal heat treatment temperature. This behaviour might be owing to the increased active surface area as a result of the rising temperature. The calculated amount of these charges for different samples is depicted in Figure 7. There is a linear relationship between the anodic and cathodic electric charge density values that agree well with each other. This is mostly due to

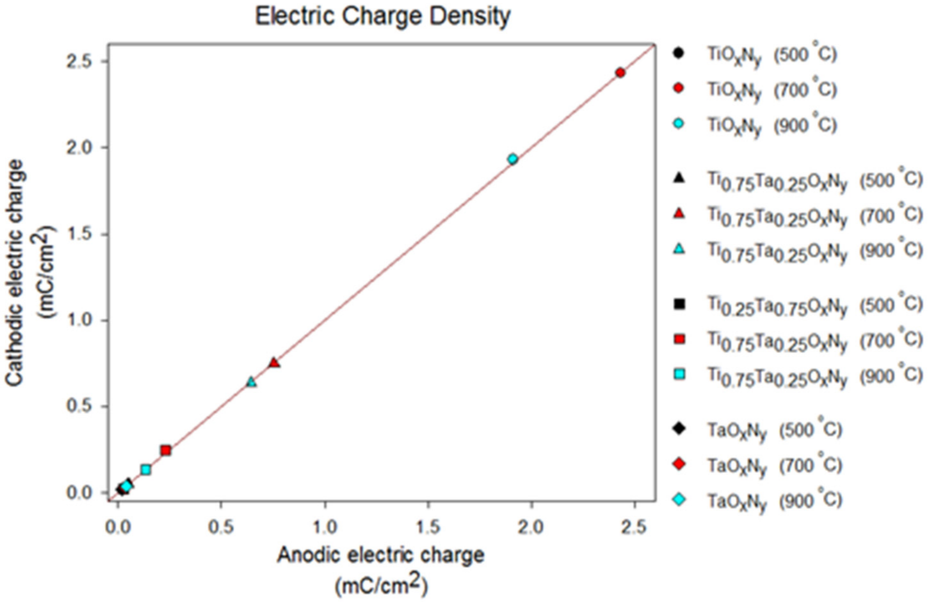

Figure 7. Comparison of the anodic and cathodic charges calculated from the cyclic voltammogram

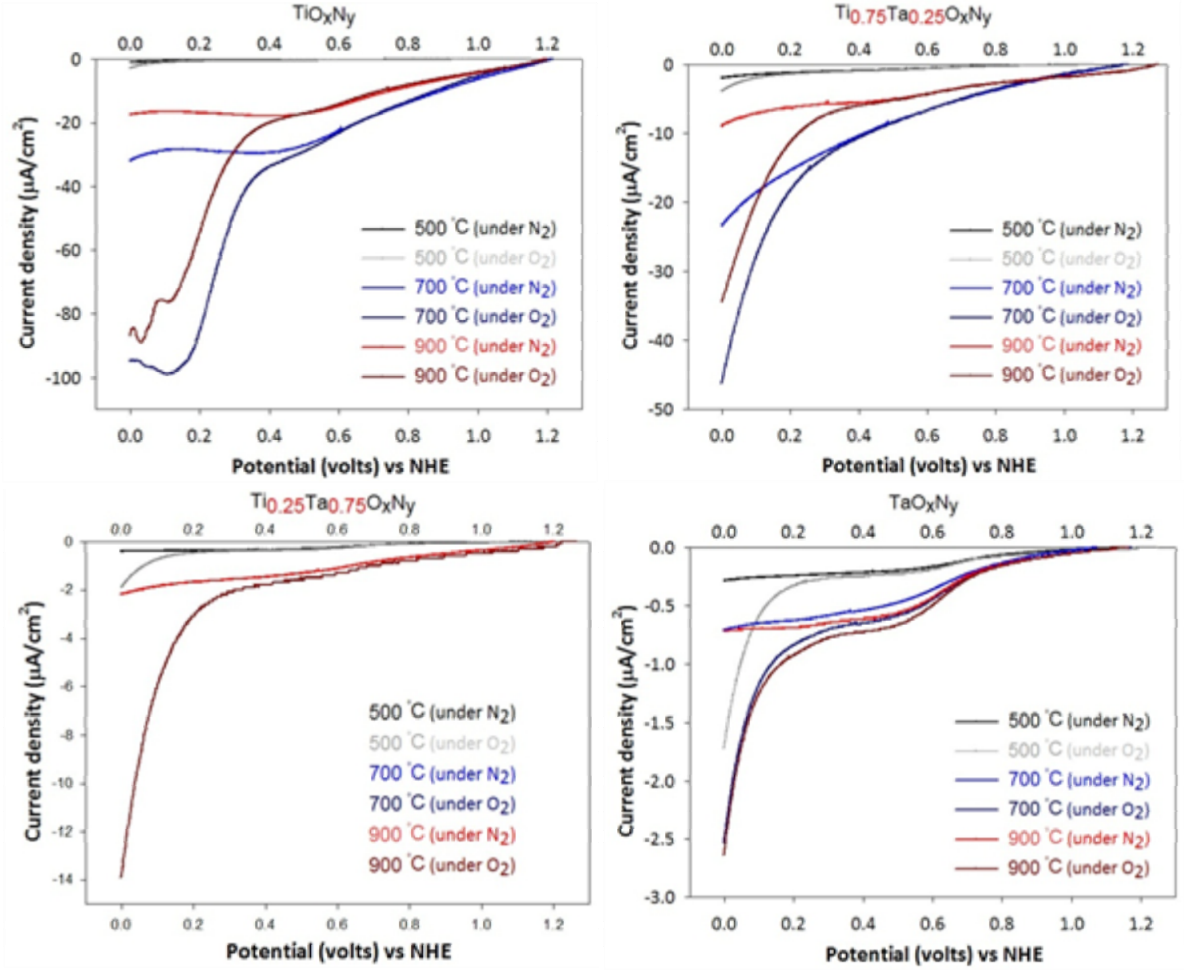

Figure 8. Comparison of the SSV (scan rate: 5 mV/s) results of different specimens with various Ta percentages heat-treated at 500, 700 and 900 °C.

the same charge and discharge of the electric double layer, indicating that no one-direction oxidation or reduction reaction of the catalyst occurred. As shown in this figure in all cases the charge increased with the heat-treatment temperature up to 700 °C, and then decreased. As well, this value decreased by increasing the Ta amount. Assuming that the real surface area is proportional to the charge of the electric double layer, the specimens heat-treated at 700 °C had the highest real surface area. This charge value for tantalum oxy-nitride is in good agreement with the literature [4, 10, 24, 41]. However, a comparison between titanium oxide and our prepared titanium oxy-nitride proves there is much more surface area in titanium oxy-nitride. This is supported by the work of Kim et al. [3 who reported that titanium oxide exhibited less than 100 μC.cm^{-2} charges ; while this amount is around 2000 μC.cm^{-2} for titanium oxy-nitride heat treated at 700 °C.

3.5. Eelectrocatalytic activity for the ORR

After the CVs reached steady state, slow scan voltammetry (SSV) (scan rate: 5 mV.s^{-1}, 1.2 V to 0 V vs. NHE) was performed in a nitrogen and oxygen atmosphere. However, the potential–current curves in the slow scan voltammetry immediately reached

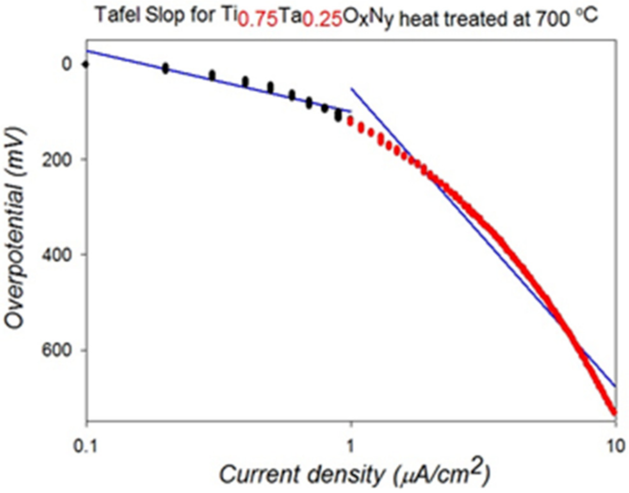

Figure 9. The Tafel plot of the ORR for the sample containing 25 % Ta and heat treated at 700 °C for 2 hours

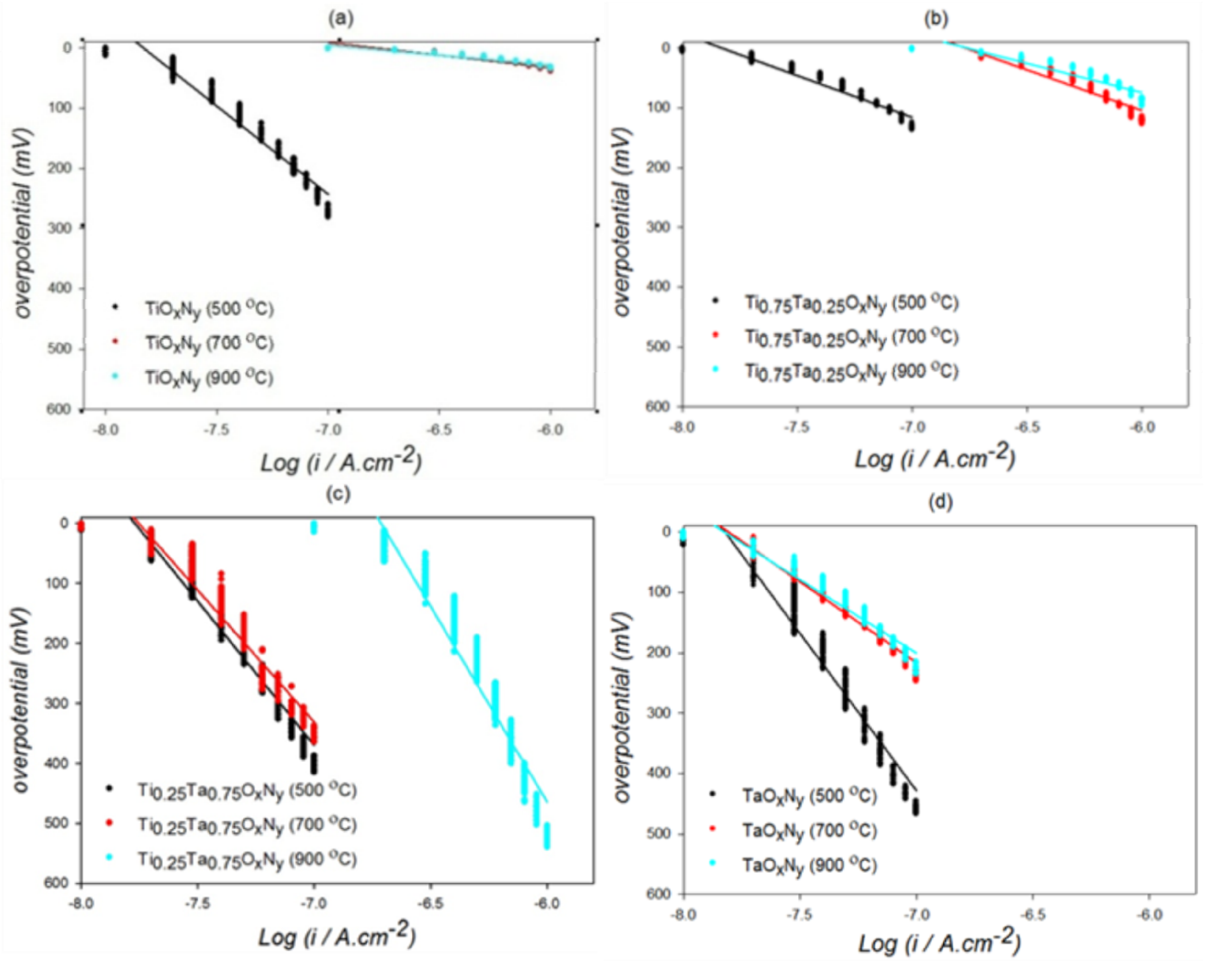

Figure 10. Tafel plots of different samples heat treated at 500, 700 and 900 °C under N_2 for 2 hours: a)TiO_xN_y electro-catalysts; b) $Ti_{0.75}Ta_{0.25}O_xN_y$ electro-catalysts; c) $Ti_{0.25}Ta_{0.75}O_xN_y$ electro-catalysts; d)TaO_xN_y electro-catalysts

steady state, the curve at the 3^{rd} cycle with the cathodic scan was used to avoid the effect of the initial state. The cathodic current obtained under O_2 atmosphere increased when the potential was decreasing, however such an increase in the obtained cathodic current under N_2 was not observed. The obtained current under N_2 atmosphere is the charge current of the double layer capacitance. The difference between the current under O_2 atmosphere (i_{O2}) and that under N_2 atmosphere (i_{N2}) corresponded to the oxygen reduction current (i_{ORR}), that is, i_{ORR}. This current density is evaluated on the basis of the geometric surface area of the working electrode. The onset potential for the ORR, E_{ORR}, was defined as the electrode potential at the $i_{\mathrm{ORR}} = -0.2$ μA.cm^{-2} and it is utilized to evaluate the electrocatalytic activity for the ORR.

Figure 8 shows the SSV of all samples heat treated at 500, 700 and 900 °C for 2 hours under $N_2 + 3\%\ H_2$ atmosphere. According to these curves, it is revealed that by increasing the heat treatment temperature from 500 to 700 or 900 °C, the i_{ORR} and E_{ORR} increased significantly, however the specimen heat treated at 700 °C had the highest electric charge density. These results indicate that the electrocatalytic activity for the ORR significantly depends on the heat-treatment temperature, so that the onset potential of titanium oxy-nitride increased from ca. 0.05 V to 0.65 V vs. NHE by increasing the temperature from 500 to 700 °C. This is an indication that the electrocatalytic activity of the ORR increases when the temperature of the heat treatment increases. In addition, by increasing the Ta content in the mixture, the defined onset potential increased; the electric charge, however, drastically decreased. It might be related to the poor electrical conductivity of the electro-catalysts. Therefore, the increase of the onset potential with the content of the embedding Ta in the electro-catalyst improved its electrocatalytic activity for the ORR. On the other hand, because of the big particle size and small surface area of the electro-catalysts containing Ta, the obtained current density was small compared to that of the titanium oxy-nitride. For instance, onset potential for the ORR for pure tantalum oxy-nitride heat treated at 700 °C was ca. 0.85 V vs. NHE while this value was ca. 0.65 V vs. NHE for pure titanium oxy-nitride. However, the ORR current was 100 times smaller for tantalum oxy-nitride based electro-catalyst, when compared to those of titanium oxy-nitride based electro-catalyst. In this study, we did not mix the prepared electro-catalysts with carbon black to increase the active surface area for the ORR and, hence, the obtained current was small in comparison with the literature. So, it is assumed that finding the optimum amount of Ta to insert inside the Ti-based electro-catalyst is critical to have both good activity and a highly active surface area. This optimization is still under development.

The Tafel plot of the ORR for the sample containing 25 % Ta and heat treated at 700 °C for 2 hours is shown in Figure 9. In the low current density regions the Tafel slope of about 128 mV/decade ± 10 mV/decade was observed, indicating the high reaction rate in comparison to the high Tafel slope obtained for the other annealing temperature. However, in the most high current density regions, this amount increased significantly. As it is accepted classically, the change of the Tafel slope appears to be related to the change in the nature of the adsorbed oxygen-containing species with potential, a transition that strongly affects the ORR. The Tafel plots of all other electro-catalysts are represented in various curves of Figure 10. The changes in the Tafel

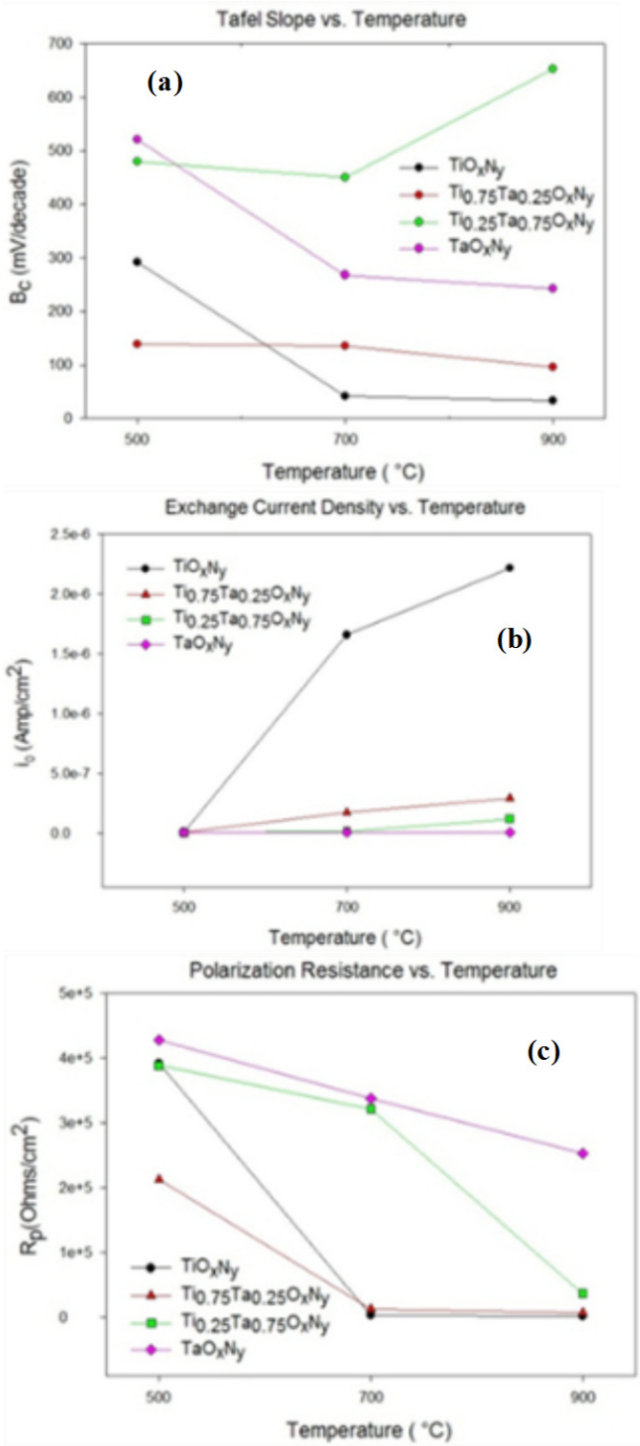

Figure 11. Effect of the annealing temperature on the basic electro-catalytic parameters: (a) Variation of the Tafel slope vs annealing temperature; (b) Variation of the exchange current density vs annealing temperature; and (c) variation of the polarization resistance vs temperature for different samples.

slope can be observed from these curves and the calculated exchange current density and polarization resistance are presented in the various curves of figures 10.

Figure 11(a) shows that when the sample is annealed at 500°C, the lowest Tafef Slope (about 120 mV/decade) is obtained for $Ti_{0.75}Ta_{0.25}O_xN_y$ electro-catalyst and it does not change when the annealing temperature increases. The highest Tafel slope is obtained with TaO_xN_y electro-catalyst and it decreases when the annealing temperature increases. But at 900°C its Tafel slope is still higher (~250 mV/decade) than those of $Ti_{0.75}Ta_{0.25}O_xN_y$ (~120 mV/decade). The TiO_xN_y electro-catalyst exhibited a Tafel slope of about 300 mV/decade when annealed at 500°C but decreases to less than 60 mV/decade when annealed at 900°C. On the other hand its exchange current density (Figure 11(b)) increases from $2x10^{-9}$ A/cm^2 to $2x10^{-6}$ A/cm^{-2} when its annealing temperature increases from 500°C to 900°C. The other electro-catalysts exhibit exchange current densities for sample annealed at 500°C which are lower than the TiO_xN_y electro-catalyst annealed at the same temperature. The exchange current densities of these other samples (Figure 11(b)) do not increase significantly (less than $2x10^{-7}$ A/cm^{-2}) with the annealing temperature, up to 900°C. Figure 11(c) shows a decrease of the polarization resistance with the annealing temperature and the lowest resistance polarization is respectively obtained for $Ti_{0.75}Ta_{0.25}O_xN_y$ and TiO_xN_y based electro-catalysts annealed at 900°C. Based on these various basic parameters, the performance for the ORR of these electrodes increases in the following orders: TaO_xN_y < $Ti_{0.25}Ta_{0.75}O_xN_y$ < $Ti_{0.75}Ta_{0.25}O_xN_y$ < TiO_xN_y. Also, inserting a small amount of Ta could improve the onset potential for the ORR besides having an acceptable Tafel slope and exchange current density. The best electro-catalyst for the ORR is obtained with TiO_xN_y based electro-catalyst.

4. CONCLUSION

Using a new urea-based sol-gel method in this study led to the preparation of a mixture of titanium and tantalum oxy-nitride nano-powder at a relatively low temperature as a non-Pt cathode catalyst for the ORR. XRD and EDS results revealed that a considerable amount of nitrogen and carbon was inserted into the metal oxide structure to enhance the catalytic activity most likely by improving the electrical properties and also introducing the defects in the surface. Compared to the other method explained in the literature, this investigation shows that preparing the TiO_xN_y and/or TaO_xN_y is possible at 900 °C instead of 1600 °C. Electrochemical stability determined by CV curves shows that the TaO_xN_y, $Ti_{0.25}Ta_{0.75}O_xN_y$, $Ti_{0.75}Ta_{0.25}O_xN_y$ and TiO_xN_y are significantly stable after 100 scans between -0.2 and 1.4 Volts. Heat treatment had a major effect on the onset potential by changing the crystallinity of the catalyst, so that the onset potential of titanium oxynitride increased from ca. 0.05 V to 0.65 V vs. NHE by increasing the heat treatment temperature of the sample from 500 to 700 °C. Increasing the Ta concentration also led to have a higher onset potential but lower ORR current. As an example, the onset potential for the ORR for pure tantalum oxy-nitride heat treated at 700 °C was ca. 0.85 V vs. NHE while this value was ca. 0.65 V vs. NHE for pure titanium oxy-nitride. However, the ORR current was 100 times smaller in tantalum oxy-nitride than in titanium oxynitride, probably because of the low electrochemical active surface area. Electrochemical measurements suggested that an appropriate composition of titanium and tantalum was required to have both a good onset potential and ORR current by improving the catalytic activity and increasing the active surface area and the electrical conductivity. In particular based on these various results, it can be concluded that the performance for the ORR of these electrodes increases in the following orders:

TaO_xN_y < $Ti_{0.25}Ta_{0.75}O_xN_y$ < $Ti_{0.75}Ta_{0.25}O_xN_y$ < TiO_xN_y.

5. ACKNOWLEDGEMENTS

The author wishes to acknowledge the help of Jeff Lullo in commenting on an early draft of this article.

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