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"JÚLIO DE MESQUITA FILHO"

INSTITUTO DE QUÍMICA

**MUHAMMAD SUFAID KHAN**

Estudos da atividade para redução de oxigênio e da  
estabilidade de nanopartículas de PdNi e PdCu de diferentes  
composições suportadas em carbono

Studies of oxygen reduction activity and stability of carbon-  
supported PdNi and PdCu nanoparticles of different  
compositions

Araraquara

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Tese apresentada ao Instituto  
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dos requisitos para obtenção  
do título de Doutor em  
Química.

**Orientadora:** Prof<sup>ª</sup>. Dr<sup>ª</sup>. Hebe de las Mercedes Villullas

**Araraquara**

**2018**

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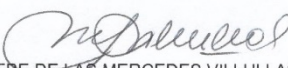
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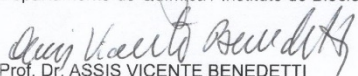
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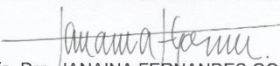
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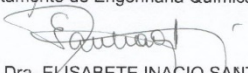
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## List of Publications

1. **Muhammad Sufaid Khan.**, et al. Removal of basic dye from aqueous solution by nanoscale zerovalent iron (NZVI) as adsorbent. Journal of Chemical Society of Pakistan, v. 35, n. 3, p. 745-748, 2013.
2. Jan Nisar; **Muhammad Sufaid Khan**; Mudassir Iqbal and Muhammad Anas Khan. Catalytic Thermal Decomposition of Polyethylene Determined by Thermogravimetric Treatment. Journal of Chemical Society of Pakistan, v. 36, n. 5, p. 829-836, 2014.

3. Jan Nisar; **Muhammad Sufaid Khan**; Munawar Iqbal; Afzal Shah; Ghulam Ali; Murtaza Sayed; Rafaqat Ali Khan; Faheem Shah; Tariq Mahmood. Thermal decomposition study of polyvinyl chloride in the presence of commercially available oxides catalysts. *Advances in Polymer Technology*, v. -, p. 1-8, 2017.
4. Abdur Rashid; Abida Farooqi; Sardar Khan; Salman Zahir; Shah Jehan; Seema Khattak; **Muhammad Sufaid Khan**; Raees Khan. Fluoride prevalence in groundwater around fluorite mining area in the flood plain of river Swat, Pakistan. *Science of the Total Environment*, 2018. Ms. Ref. No.: STOTEN-D-17-08735 (Submitted after minor corrections).

### Participation in events / conferences

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2. **KHAN, M. S.**; MILIAN, R. P.; GALLO, I. B. C.; VILLULLAS, H. M. Carbon-supported PdCu nanoparticles: activity for oxygen reduction in alkaline solutions and stability studies. XVI Brazilian MRS Meeting, Gramado (RS), 10<sup>th</sup> to 14<sup>th</sup> of September 2017.
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4. **KHAN, M. S.**; MILIAN, R. P. ; GALLO, I. B. C.; VILLULLAS, H. M. Carbon-supported PdCu and PdNi nanoparticles for oxygen reduction electrocatalysis. 26<sup>th</sup> National and 14<sup>th</sup> International Chemistry Conference Chemical Society of Pakistan (CSP) 5<sup>th</sup> to 8<sup>th</sup> of October 2015.

## DEDICATION

I dedicate this thesis  
to my late parents.

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## ABSTRACT

The slow kinetics of the oxygen reduction reaction is the main cause of the severe performance losses of fuel cell cathode. Pt is the most active pure metal to catalyze this reaction. However, because of their limited availability and high price, the use of cheaper metals to act as catalysts in fuel cell electrodes is highly desirable. In this context, Pd-based catalysts are getting increasing attention. Thus, the main objective of this work was to study the oxygen reduction reaction on carbon-supported PdM (M = Ni, Cu) catalysts with different atomic ratios (Ni and Cu 10-50% in atoms), in acidic and alkaline solutions. The modified polyol method was used for the preparation of PdM nanoparticles that were then supported on carbon powder. The catalysts were characterized by X-ray diffraction (XRD) to investigate the crystalline structure and by X-ray absorption spectroscopy (XAS) to examine the electronic properties. The electrochemical behavior was studied by cyclic voltammetry. The PdNi/C and PdCu/C catalyst and a Pd/C reference sample were evaluated as electrocatalysts for the oxygen reduction reaction in acidic and alkaline solutions using the rotating ring disk electrode technique. Results showed formation of PdM alloys and an increase in the electronic occupation of the Pd 4d band. In both media, all PdM/C samples were more active for oxygen reduction than Pd/C, with activity increasing as the percentage of Ni or Cu increased. The production of hydrogen peroxide was small indicating that the reduction of oxygen proceeds mainly via the four-electron path. PdCu/C catalysts were more active than PdNi/C materials in acidic medium, but PdNi/C samples had better performance in alkaline solution. In addition, stability tests revealed that the presence of Ni and Cu considerably decreases the dissolution of Pd in acidic medium, although the stability of the materials was lower in alkaline than in acidic medium.

**Keywords:** Oxygen reduction reaction, Pd-based catalysts, PdM nanoparticles, electrocatalysis, Fuel cell cathode.

## RESUMO

A cinética lenta da reação de redução de oxigênio é a principal causa das severas perdas de desempenho dos catodos de células a combustível. A Pt é metal puro mais ativo para catalisar esta reação. Entretanto, devido sua baixa abundância e alto custo, o uso de metais mais baratos para atuar como catalisadores nos eletrodos de células a combustível é muito desejável. Neste contexto, catalisadores baseados em Pd têm atraído cada vez mais atenção. Assim, o principal objetivo deste trabalho é estudar a reação de redução de oxigênio em catalisadores PdM (M = Ni, Cu) com diferentes composições (Ni e Cu 10-50% em átomos), em soluções ácidas e alcalinas. O método do poliol modificado foi utilizado para preparar as nanopartículas PdM, que foram posteriormente suportadas em pó de carbono. Os catalisadores foram caracterizados por difração de raios X para investigar a estrutura cristalina e por espectroscopia de absorção de raios X para determinar as propriedades eletrônicas. O comportamento eletroquímico foi examinado por voltametria cíclica. Os materiais PdNi/C e PdCu/C, assim como uma amostra de Pd/C usada como material de referência, foram testados como eletrocatalisadores para a reação de redução de oxigênio em meio ácido e alcalino utilizando a técnica do eletrodo de disco-anel rotatório. Os resultados mostraram formação de ligas PdM e um aumento na ocupação eletrônica da banda 4d do Pd. Em ambos os meios, os materiais PdM/C se mostraram mais ativos para a redução de oxigênio que o Pd/C, com atividades que aumentam à medida que cresce a percentagem de Ni ou Cu. A produção de peróxido de hidrogênio foi baixa, indicando que a redução de oxigênio ocorre principalmente via 4 elétrons. Os catalisadores PdCu/C se mostraram mais ativos que os de PdNi/C em meio ácido, mas as amostras de PdNi/C foram mais ativas em meio alcalino. Além disso, testes de estabilidade revelaram que a presença de Ni ou Cu diminuiu consideravelmente a dissolução de Pd em meio ácido, mas a estabilidade destes materiais em meio básico é menor que em ácido.

**Palavras-chave:** Redução de oxigênio, catalisadores baseados em Pd, nanopartículas PdM, eletrocatálise. cátodo

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## LIST OF ABBREVIATIONS

|       |                                          |
|-------|------------------------------------------|
| AFC   | Alkaline Fuel Cell                       |
| AST   | Accelerated Stability Test               |
| CV    | Cyclic Voltammetry                       |
| DAFC  | Direct Alcohol Fuel Cell                 |
| DMFC  | Direct Methanol Fuel Cell                |
| ECSA  | Electrochemical Active Surface Area      |
| EXAFS | Extended X-Ray Absorption Fine Structure |
| MA    | Mass activity                            |
| ORR   | Oxygen Reduction Reaction                |
| PEMFC | Proton Exchange Membrane Fuel Cell       |
| RHE   | Reversible Hydrogen Electrode            |
| RRDE  | Rotating Ring Disk Electrode             |
| SA    | Specific activity                        |
| XAS   | X-Ray Absorption Spectroscopy            |
| XANES | X-Ray Absorption Near Edge Structure     |
| XRD   | X-Ray Diffraction                        |

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## **1. INTRODUCTION**

Alternative ways for energy production as well as renewable energy sources have become increasingly relevant over the last years. The production of energy from fossil fuels causes environmental pollution, which has a considerable impact on climate and public health. To avoid and/or reduce the impact of fossil fuels burning on human health and environment, it becomes of paramount importance to develop greener and cost-effective sustainable energy systems. Among other possibilities, the use of electrochemical devices to convert chemical energy into electricity is presently considered a viable approach to clean energy generation. In particular, the development of fuel cell technology [1,2] is considered as one of the most promising ways of obtaining clean energy [3].

### **1.1. Fuel cells**

Fuel cells are electrochemical devices where the oxidation of the fuel at the anode and the reduction of oxygen at the cathode side occur in such a way that allows the production of electricity. Electricity is produced from the charge-transfer processes occurring at the electrodes (anode and cathode), where a catalyst is often used to accelerate the electrochemical reactions [1,2].

Sir William Robert Grove was the first to demonstrate, in 1839, a fuel cell [4]. The concept of fuel cell started from a succession of experiments on water electrolysis in a setup for which the proposed name was gas voltaic battery. That gas voltaic battery was composed of two platinum electrodes immersed in a dilute sulfuric acidic electrolyte. He observed that during electrolysis the passage of current through the cell led to the breaking up of water molecules into hydrogen and oxygen. Furthermore, Grove realized that when the power supply was taken out, a small current circulated through the cell due to the opposite reaction.

Although the concept of the alkaline fuel cell was known from the beginning of the 20<sup>th</sup> century, the viability of alkaline fuel cells was demonstrated in 1959 by Frances Thomas Bacon, at Cambridge University, by developing an alkaline fuel cell known as Bacon cell. That Bacon cell had power capacity of 5 to 6 kW. However, a high gas pressure (20 to 40 bar) was required during operation, which made the Bacon cell heavy [2].

Moreover, in 1960, Pratt and Whitney used the licensed patent of Bacon and constructed an engine. The main focus of this modification to engine was to minimize the gas pressure by using a strong basic solution. The Pratt and Whitney manufactured engine was used in the Apollo spacecraft. Research on fuel cells continued and in 1960s Thomas Grubb and Leonard Niedrach also developed a fuel cell which was used for power generation in the Gemini spacecraft [2]. History of fuel cell development is found in literature [5].

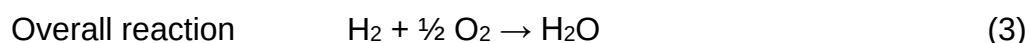
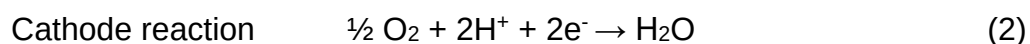
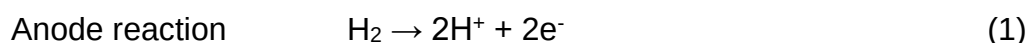
Generally, a fuel cell is composed of two electrodes immersed in an electrolyte, in which the electrochemical oxidation of the fuel at the anode and a reduction reaction at the cathode allow converting chemical energy in to electricity. An electric current is produced as the electrons released in the oxidation reaction circulate through the external circuit towards the cathode and an electrolyte present between the anode and cathode conducts the ionic charges between the two electrodes. At the current stage, there are several different types of fuel cells [1,2]. The main types in different stages of development to be marketable are classified on the bases of the type of electrolyte and are summarized in Table 1.

**Table 1** – Classification of fuel cells based on types of electrolytes. Adapted from reference [6].

| Type                                           | Electrolyte                                                                                      | Operating temperature | Fuel                                    |
|------------------------------------------------|--------------------------------------------------------------------------------------------------|-----------------------|-----------------------------------------|
| Alkaline fuel cell (AFC)                       | 35-45 % KOH                                                                                      | 60-90 °C              | Pure hydrogen                           |
| Polymer electrolyte membrane fuel cell (PEMFC) | Proton exchange membrane and anion exchange membrane                                             | 60-90 °C              | Pure hydrogen, methanol, ethanol        |
| Phosphoric acidic fuel cell (PAFC)             | 100% H <sub>3</sub> PO <sub>4</sub>                                                              | 180-220 °C            | Hydrogen                                |
| Molten carbonate fuel cell (MCFC)              | Molten carbonates (62 % LiO <sub>2</sub> CO <sub>3</sub> , 38 % K <sub>2</sub> CO <sub>3</sub> ) | 550-650 °C            | Hydrogen, hydrocarbons, carbon monoxide |
| Solid oxide fuel cell (SOFC)                   | Stabilized zirconia and yttria                                                                   | 800-1000 °C           | Hydrogen, hydrocarbons, carbon monoxide |

### 1.1.1. Proton Exchange Membrane Fuel Cell (PEM)

Proton Exchange Membrane (PEM) fuel cells are also known as Polymer Electrolyte Fuel Cells (PEFCs). A PEM fuel cell possesses higher power capacity and smaller volume and are lighter compared to the other types of fuel cells. When the PEMFC is fed with hydrogen fuel, the oxidation of hydrogen and the reduction of oxygen produce electricity, water and heat [7]. Hence, the operational process of this type of fuel cell is environmentally friendly. The reactions that occur in the H<sub>2</sub>/O<sub>2</sub> PEMFC are:

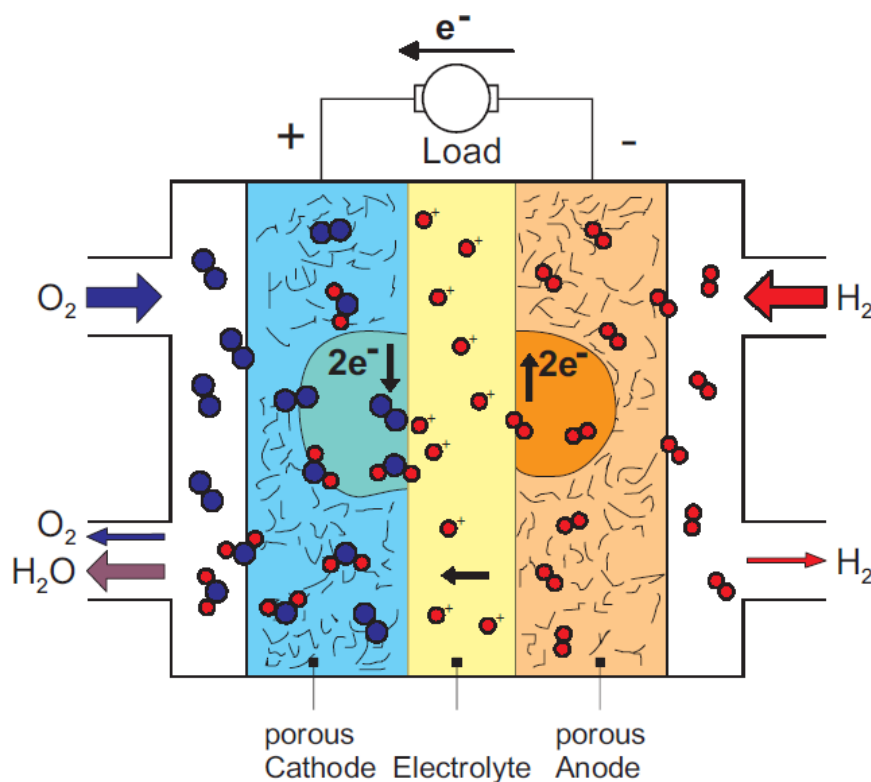


On the anode catalyst, the hydrogen molecules are oxidized to H<sup>+</sup> liberating electrons that are transported through the external circuit. On the cathode catalyst, oxygen molecules are reduced. The transport of H<sup>+</sup> from anode to cathode occurs through the electrolyte. Both electrochemical reactions occur on the surface of a catalyst. In cells that operate at low temperature the catalyst is usually Pt and the electrolyte is a proton-exchange membrane. During power production, losses related to the reaction kinetics (activation loss), resistance (ohmic loss) and concentration depletion (mass-transport loss) reduce the power efficiency.

Inside the PEM fuel cell, the porous carbon electrodes have catalysts that usually consist of Pt or Pt-based alloys materials in the form of nanoparticles. The solid polymer membrane that acts as electrolyte is usually Nafion<sup>®</sup>. A scheme of a PEMFC is shown in Figure 1.

The PEMFCs is a low temperature fuel cell and its temperature rises up to 80 -100 °C in operation. Low temperature operation and low warm-up time of components are advantages of the PEMFC. The general applications of the PEMFCs are vehicles, portable electronic devices and back-up, among others.

**Figure 1** - Schematic diagram of a  $\text{H}_2/\text{O}_2$  PEM fuel cell. Reproduced from reference [7].



Generally, this type of fuel cell gives a potential of 0.7 V at full load. To obtain higher voltages several fuel cells can be connected in series (stacks). Stacks of different fuel cell types are made on the bases of production capacity from several kilowatts to tens of megawatts.

Although the use of hydrogen as fuel in PEMFC produces higher current densities, production of pure hydrogen, storage and delivery from one station to another involve technical challenges. Hence, utilization of alternative fuels without those requirements is desirable for the future energy need. The use of liquid fuels (such as methanol, ethanol, etc.) in Direct Alcohol Fuel Cells (DAFCs), which are PEMFCs fed with alcohol, seems to have several advantages regarding storage and distribution. From a thermodynamic point of view, the alcohol oxidation efficiency is about 97 %, which is higher than that of hydrogen oxidation (83 %). The hydrogen volume energy capacity is 2.6 kWh/L, which is lower than that of ethanol (6.3 kWh/L) and methanol (4.8 kWh/L), respectively. Therefore, alcohols are considered viable fuels to replace hydrogen to satisfy future energy demand [8,9].

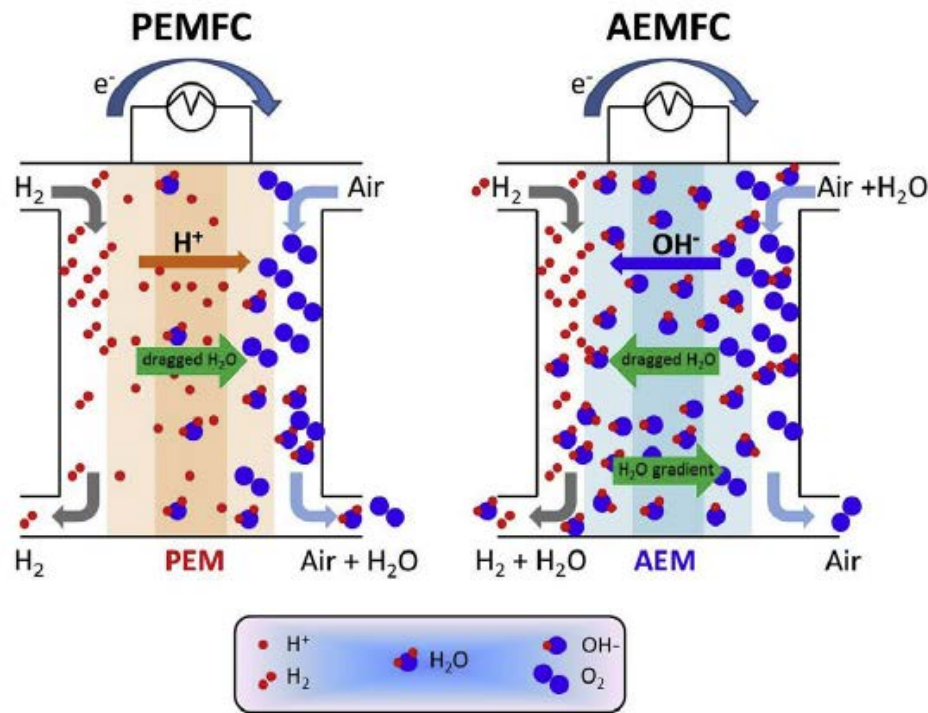
### 1.1.2. Alkaline fuel cells

The Alkaline Fuel Cell (AFC) is considered a very important type of cell and it was used in space technology. The AFC is operated at low temperature, about 100 °C. The electrolyte used in AFCs is an aqueous solution of KOH. The electrolyte concentration is 85 wt.% and 35 to 50 wt.% KOH for AFCs operated at high and low temperature, respectively. The KOH electrolyte is embedded in a solid matrix (usually asbestos). Different types of non-precious elements are used as electrocatalysts for cathode and anode. Despite the many advantages of AFCs, there are also some drawbacks, like poisoning by carbon dioxide. Even a small amount of CO<sub>2</sub> can badly affect the stability and efficiency of AFCs due to formation of carbonate [5]. Therefore, in the last few years great attention was given to develop alkaline exchange membrane fuel cell (AEMFC), because they have some advantages over PEMFCs [10].

The use of anion exchange membranes in alkaline fuel cells has many advantages, such as enhanced ORR kinetics in the alkaline environment and the possibility of using cheaper metals as electrocatalysts or Pt-free materials that are more stable in alkaline than in acidic media [11]. In addition, there are more options for fuels to be used in alkaline medium as substitute of hydrogen [12]. Over the last years, a large amount of reports began to focus on AEMFCs as the availability of appropriate AEMs was growing [13]. However, the amount of data on activity and stability of catalysts in alkaline media available in the literature is much lesser than for acidic environments.

Generally, the PEM and AEM fuel cells are similar. The principal difference is that the solid membrane is acidic (proton exchange) in the PEMFCs and alkaline (anion exchange) in AEMFCs. The differences between a PEMFC and an AEMFC are illustrated in Figure 2. In the AEMFC, the hydroxide ions move from the cathode to the anode, while in the PEMFC the hydrogen ion move from the anode to the cathode of the fuel cell.

**Figure 2** - Schematic diagrams of the PEMFC and AEMFC. Reproduced from reference [10]. Permission to reproduce this figure is not required.



It should be kept in mind that during the electrochemical process in the AEMFC, the hydroxide ions and water are not moving as in the same direction as protons are transported in the PEM fuel cells. The reduction of oxygen at the cathode and the oxidation of hydrogen occurring at the anode of the AEMFC are given by the following reactions:



As shown in reaction (5), water is formed as a product like in a PEMFC, but in the AEMFCs water is produced at the anode and at the same time water reacts at the cathode. This unique water movement situation together with the high pH medium show the distinctive nature of the AEM fuel cells [10].

Over the last two decades, several different aspects of fuel cell technology have been widely investigated [14]. Overall, PEMFCs and AEMFCs are presently

regarded as adequate systems for energy generation [15,16]. While research on this area has led to significant progress, the cell performance is still affected by the sluggish kinetics of oxygen reduction, which produces considerable losses of cell potential [1,2].

## 1.2. The oxygen reduction reaction

The oxygen reduction reaction (ORR) plays a crucial role in biological process needed to sustain life, such as respiration, in corrosion, in many industrial reactions and in electrochemical energy conversion systems.

The ORR plays a significant role in electrochemistry. In particular, ORR electrocatalysis [17,18,19,20,21] is one of the most important research areas related to the development of fuel cell catalysts.

The ORR is a multi-step process. It is known that in an acidic medium it occurs by two distinct routes: the direct reduction to water, which involves the transfer of 4 electrons, and the reduction via hydrogen peroxide, which involves the transfer of 2 electrons [18,22,23]:

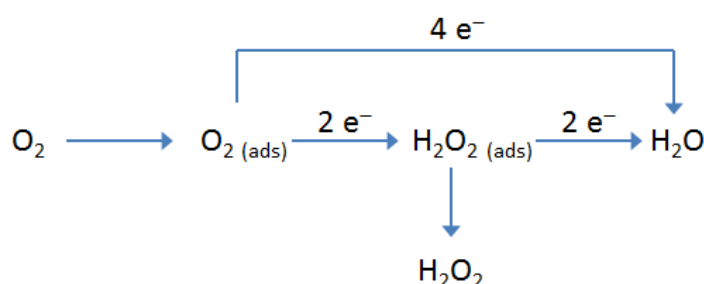


The hydrogen peroxide formed in the two-electron route can diffuse to solution or be reduced to water [23]:



These routes are shown in the simplified reaction scheme of Figure 3.

**Figure 3** - Simplified ORR mechanism in acidic medium, adapted from reference [23].



Similarly, the electrochemical reactions in alkaline medium, in which ORR proceeds either by a two-electron or through four-electron pathways, are [18,22,23]:



Besides reactions (6) to (11) that take place in aqueous media, in non-aqueous aprotic solvents the ORR can also involve one-electron path, in which  $\text{O}_2$  is converted into superoxide ( $\text{O}_2^{2-}$ ) [18].

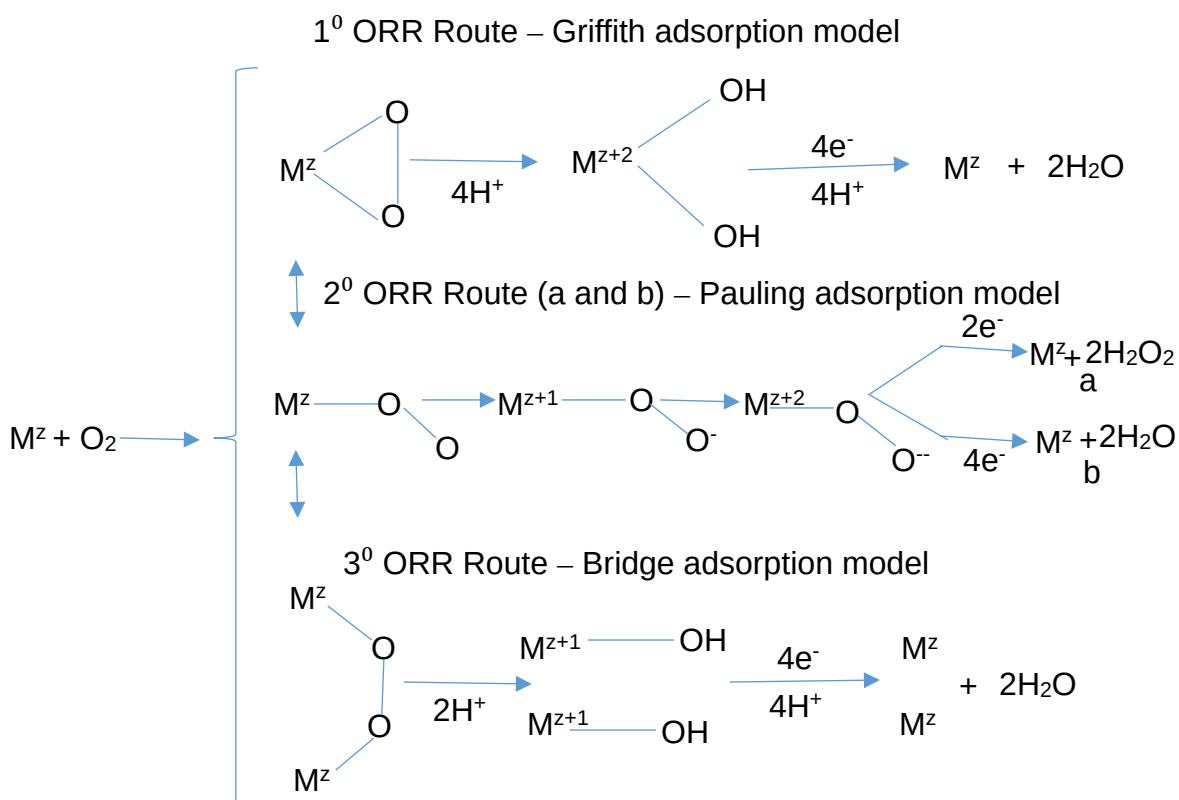
The thermodynamic electrode potentials at standard conditions for  $\text{O}_2$  reduction reactions are presented in Table 2. The actual mechanism through which the ORR occurs might be much more difficult and include different intermediates, which initially depended on the electrode nature, electrocatalyst and medium.

**Table 2** – Thermodynamic electrode potentials of electrochemical  $\text{O}_2$  reduction, adapted from reference [21].

| Electrolyte                  | ORR reactions                                                                           | Thermodynamic electrode potential at standard conditions, V |
|------------------------------|-----------------------------------------------------------------------------------------|-------------------------------------------------------------|
| Acidic aqueous solution      | $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$                | 1.229                                                       |
|                              | $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$               | 0.70                                                        |
|                              | $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$      | 1.76                                                        |
| Alkaline aqueous solution    | $\text{O}_2 + \text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$                | 0.401                                                       |
|                              | $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{OH}_2^- + \text{OH}^-$ | -0.065                                                      |
|                              | $\text{OH}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$             | 0.865                                                       |
| Non-aqueous aprotic solvents | $\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^-$                                      | Value strongly dependent on solvent used                    |
|                              | $\text{O}_2^- + \text{e}^- \rightarrow \text{O}_2^{2-}$                                 |                                                             |

The oxygen molecule adsorbs in different ways on the surface of a catalyst and that influences the reduction mechanism [18,23], as shown in Figure 4. For instance, the adsorption of oxygen following the model of Griffith occurs only in metals that have at least two unpaired electrons in valence orbitals. On the other hand, the adsorption of oxygen as in the bridge model occurs in metals with at least one unpaired electron. Adsorption according to the model proposed by Pauling takes place when the distance between the catalytic sites is much larger than the oxygen-oxygen bond length or when there are steric impediments that hinder the adsorption of the two atoms of the oxygen molecule. On Pauling's model, the oxygen molecule adsorbs on a single catalytic site, as can be observed in the scheme of Figure 4.

**Figure 4** - Models for O<sub>2</sub> adsorption and reduction mechanism. Adapted from reference [23].



### 1.3. Catalysts for oxygen reduction

Generally, the 4-electron  $O_2$  reduction is extremely non-reversible. In this regard, one of the challenges is to get experimental potentials closer to the thermodynamic reversible potential of this process at room temperature. For example, if Pt electrodes are utilized in acidic or basic media under ambient conditions, the deviation from thermodynamic electrode potential (1.23 V vs RHE) is quite large and the experimental potential value is hardly around 1 V. At room temperature, the exchange current density of ORR on Pt, which is the most active metal in acidic solutions, lays between  $10^{-7}$  and  $10^{-10}$  A cm<sup>-2</sup> [21].

Therefore, to overcome the limitation imposed by the ORR slow kinetics it is necessary to increase the activity of the catalysts. So far, the approach to this problem consisting in alloying Pt with first-row transition metals has been relatively successful. Pt-based binary systems such as PtFe [24-30], PtCo [27, 30-32], PtNi [27,30,32], PtCu [27,33], etc., have shown enhanced catalytic activities. The additional advantage of this approach is the partial substitution of Pt by other less expensive metals. Most significant results were discussed in review articles [34-36].

Pt is still the most commonly used metal in carbon-supported catalyst materials for fuel cells reactions in acidic or alkaline media [37], but it is an expensive and rare metal. To overcome the drawbacks of high costs, the development of new and cheaper electrocatalysts is needed. Viable catalysts to substitute expensive Pt-based materials must have the ability of selectively catalyzing the four-electron reduction of oxygen to produce water at low overpotentials, with low  $H_2O_2$  production. Another issue is the catalyst stability because good durability is needed for fuel cell technology commercialization.

#### 1.3.1. Palladium and palladium-alloy catalysts

In the search for catalysts less expensive than Pt and Pt-based materials, new materials for ORR electrocatalysis have been suggested as an alternative to Pt, such as Pd and Pd-based alloys [38-40]. This is a promising approach because the cost of Pd is much lower than the cost of Pt [41] and it is more abundant in the earth crust. Besides that, Pd and Pt belong to same group of the periodic table and have several similar properties. Consequently, the catalytic

behavior of Pd should be expected to be close to that of Pt for some processes. However, several research works showed that in acidic solution the ORR catalytic activity of Pd is considerably lower than that of Pt [39,42]. Moreover, Pd catalysts have lower durability in acidic medium [43-45]. Despite the lower activity, in acidic environments Pd-based catalysis are alcohol tolerant and that is advantageous for PEMFCs fed with methanol and ethanol [40].

Several studies of the ORR were done for Pd-based catalyst in acidic solutions, such as PdNi [44-47], PdCo [47,48], PdAg [47] and PdCu [47,49], reporting activities for the ORR better than for Pd.

Generally, it is considered that Pd alloys with metals with smaller atomic size than Pd enhance the ORR catalytic performance [39]. Ni is one of the best options for alloying with Pd to improve the catalytic performance for the ORR. Literature results show improved catalytic activity for a PdNi thin film prepared by sputtering [50] compared with Pd, but lower than the activity of Pt. Another group synthesized a PdNi alloy through metallic reductive precipitation, but its catalytic performance was poorer than for the PdNi thin film alloy prepared by sputtering [51]. Data for carbon-supported PdNi, PdFe and PdCo [44] evidenced that the second metal increases the stability, but dissolution still occurs.

In acidic medium, Pd and Pd-based catalysts have low stability against Pd dissolution [43-45]. Pd is much more stable in  $\text{OH}^-$  solutions and, hence, great attention was given to catalysts for ORR in alkaline medium. Jiang et al. found that Pd/C showed higher activity than Pt/C for the ORR at room temperature and up to 60°C [52]. In other studies, the ORR activity and stability of Pd nanocubes in alkaline medium was found to be similar or better than Pt [53]. Generally, Pd-based materials show better catalytic performance in alkaline solutions than in acidic [54].

Ni is one of the non-noble metals showing attractive performance as electrode material in combination with Pd. PdNi/C electrocatalysts are considered to be economically feasible, while they are also more efficient catalysts compared to Pd/C and Pt/C in alkaline solution [55]. Pd-based alloys with nonprecious metals also show enhanced activity and stability in alkaline medium [40,55-57]

Considering that Cu helps to improve the ORR catalytic performance of Pt and Pd have similar electronic shells, it is reasonable to expect that PdCu alloys might have enhanced catalytic performance. Theoretical calculations predicted

that PdCu in 50:50 atomic composition should show high catalytic activity for ORR [58] and literature results showed improved performances for PdCu materials [59-64].

Generally, comparison of published results for PdNi and PdCu materials is very difficult because materials properties and the experimental conditions of ORR measurements differ. Some results about the catalytic activities for ORR of PdCu and PdNi materials in acidic and alkaline solutions are summarized in Table 3 to illustrate the divergences among them. Results for ORR on Pd and Pd-based catalysts were discussed in review articles [20,39,54,65].

**Table 3** – Summary of some results for PdCu and PdNi electrocatalysts reported in the literature.

| Preparation method                                 | Nominal composition                                                           | XRD size               | EDX composition                             | Mass activity                                                                | Specific activity                                                  | Particle size (nm)            | Medium                                | Ref. |
|----------------------------------------------------|-------------------------------------------------------------------------------|------------------------|---------------------------------------------|------------------------------------------------------------------------------|--------------------------------------------------------------------|-------------------------------|---------------------------------------|------|
| Simple Galvanic Replacement                        | Mesoporous PdCu                                                               | —                      | Pd:Cu 85:15 EDS                             | —                                                                            | 0.6 mA/cm <sup>2</sup><br>Half wave 0.84 V                         | 3                             | 0.1 M HClO <sub>4</sub>               | [64] |
| Copper metal organic framework                     | PdCu 1 (2 wt.% Cu and 13.6 wt % Pd)<br>PdCu 2 (0.25 wt.% Cu and 16.2 wt.% Pd) | 0.3869 nm<br>0.3907 nm | —                                           | Pt>PdCu in HClO <sub>4</sub> at half wave 0.85 V<br>PdCu 1>Pd>PdCu 2 in NaOH | Pt>PdCu in HClO <sub>4</sub><br>Half wave PdCu1>Pd > PdCu2 in NaOH | 4 ± 1.1<br>4 ± 1.5<br>4 ± 1.5 | 0.1 M HClO <sub>4</sub><br>0.1 M NaOH | [66] |
| Dealloying                                         | PdCu 50:50                                                                    | —                      | —                                           | 0.15 A/mg <sub>Pd</sub>                                                      | 0.22 mA/cm <sup>2</sup><br>at 0.9 V                                | Around 7                      | 0.1 M HClO <sub>4</sub>               | [61] |
| Co-impregnated, HT                                 | PdCu 1:1<br>PdCu 1:3                                                          | ~0.388 nm<br>~0.384 nm | 49.1:50.9<br>24.8:75.2 ICP-AES<br>47.5:10.7 | At 0.85 V, at 600 °C<br>95 and 135 mA/mg <sub>Pd</sub>                       | —                                                                  | 21 ± 5.1<br>23.3 ± 8.3        | 0.6 M HClO <sub>4</sub>               | [67] |
| Colloidal synthesis and HT                         | PdCu 1:1                                                                      | —                      | —                                           | 23 mA/mg <sub>Pd</sub> at 0.9V<br>and 500 °C                                 | 33 µA/cm <sup>2</sup> <sub>Pd</sub> at 0.9V<br>and 500 °C          | 10 ± 2.5<br>at 500 °C         | 0.1 M HClO <sub>4</sub>               | [62] |
| Modified polyol method and HT                      | PdNi 80:20                                                                    |                        | 83.7:16.3<br>83.4:16.6 at 500°C             | At 0.7 V and 500 °C<br>100 mA/mg <sub>Pd</sub> at                            | At 500 °C 4<br>mA/µc at 0.7 V                                      | 5.6-6.7                       | 0.5 M H <sub>2</sub> SO <sub>4</sub>  | [51] |
| Modified Galvanic Replacement                      | PdNi 1:1                                                                      | 0.3798 nm              | —                                           | ~600mA/g <sub>Pd</sub>                                                       | ~1440 µA/m <sup>2</sup>                                            | 30 and shell<br>thickness 5   | 0.1 M KOH                             | [55] |
| Electrochemical dealloying in acidic solution      | PdNi 20:80                                                                    | 0.3820 nm              | 91:9<br>dealloying<br>EDS                   | 1.1 mA/µg at 0.80 V<br>0.4 mA/µg at 0.85 V                                   | —                                                                  | ~ 10 pore<br>size             | 0.1 M HClO <sub>4</sub>               | [68] |
| One-step mild dealloying of PdNiAl precursor alloy | Nanoporous PdNi Alloy                                                         | —                      | 75:25 EDS                                   | 0.18 A/mg at 0.9 V                                                           | 0.21 mA/cm <sup>2</sup><br><sub>Pd</sub> at 0.9V                   | ~ 5                           | 0.1 M HClO <sub>4</sub>               | [69] |

Mass activity: current/mass; Specific Activity: current/area; HT: Heat Treatment

### 1.3.2. Stability challenges

Besides the required higher catalytic activities, the catalyst stability is also an important challenge for commercialization of the fuel cell system. For practical applications of fuel cells, lifetime is a very important factor. There are different lifetime required, which depend upon the application of the fuel cells. For example, The American Department of Energy proposed lifetime of 20,000 hours for buses, 3,000 to 5,000 hours for cars and 40,000 for stationary uses. It is noticed that the lifetime of fuel cell for stationary applications is higher than automotive use. The difference is basically due to the energetic working conditions and differences in the voltage due to on/off. The pre-commercial PEM fuel cell stack still does not fulfill these requirements. There are many factors that affect the lifetime of the PEMFC [70,71], which include degradation of the catalyst layer, the gas diffusion layer and the membrane.

So far, carbon-supported Pt or Pt-based catalysts have higher durability than other materials in the acidic environment of PEMFCs [37,72]. Nevertheless, their durability is still insufficient [72,73]. The factors that affect the durability of the catalyst layer are agglomeration, sintering, leaching and contamination by impurities [72,74,75,76]. Generally, literature reports show that nanoparticles supported on carbon have stability to some extent [34,77]. The corrosion of carbon causes degradation of the catalyst layer and different carbon forms [78,79,80] and other alternatives as mixed carbon-oxide supports are investigated [26,81,82].

In last decade, many studies reported addition of non-precious elements to Pd electrocatalysts that lead to ORR performance analogous to that of Pt. However, in acidic media those materials do not have the stability needed for practical application. That is another reason for the interest in AEMFCs, because non-precious metals and alloys shows much higher stability in alkaline solution than in acidic medium [11,40,83,84].

## 5. CONCLUSIONS

In the present study, carbon-supported PdNi and PdCu nanoparticles have been prepared successfully by a modified polyol method. Based on the results obtained, we can conclude that:

- ✓ Alloys were formed leading to decrease in lattice parameter (for both systems);

- ✓ The addition of second metal (Ni or Cu) lead to an increase in the occupation of the 4d band of Pd. Distinct behavior was observed for PdCu/C 50:50;

- ✓ Addition of Ni or Cu lead to better ORR activity for oxygen reduction in dilute  $\text{H}_2\text{SO}_4$  and NaOH solutions, compared with Pd/C.

- ✓ For all bimetallic materials, ORR activity improves as the percentage of second metal (Ni or Cu) increases. Samples of 50:50 composition are the most active.

- ✓ Activity for ORR of all studied materials is higher in alkaline solution than in acidic solution, as expected.

- ✓ In acidic medium, PdCu/C catalysts are more active than PdNi/C materials of similar nominal percentage of second metal. PdCu/C 50:50 has the best performance and stability;

- ✓ In alkaline medium, PdNi/C catalysts have higher ORR activity than PdCu/C, but all PdNi/C and PdCu/C samples degrade (extent depending of composition),

- ✓ Generally, the kinetic current density increases as the 4d band of Pd is more filled and as the Pd-Pd distance decreases. So, it is likely that both properties play a role.

✓ The amount of hydrogen peroxide produced is small on the studied materials. So, in all cases the oxygen reduction reaction proceeded via 4-electrons mechanism (acidic and basic media).

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