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**Oxygen reduction reaction studies on Pd
coatings prepared by galvanic exchange of
silver, nickel and copper**

Bachelor's Thesis (12 ECTS)

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Oxygen reduction reaction studies on Pd coatings prepared by galvanic exchange of silver, nickel and copper

Abstract:

Biggest challenge for fuel cells is the necessity for efficient, platinum-free catalysts for oxygen reduction reactions. Using pure metals is not a viable option due to the problems with efficiency, stability or cost of the catalyst. Thus, using cheaper metals such as silver, copper and nickel in combination with palladium using the galvanic exchange can produce bimetallics which could be a viable alternative to currently used platinum-based catalysts. Using rotating disc electrode studies and cyclic voltammetry it was possible to measure and determine the improvement in electrocatalytic activity compared with pure metals.

Keywords: Oxygen reduction reaction, galvanic exchange, rotating disc electrode, electrocatalytic activity

CERCS: P401 Electrochemistry

Hapniku redutseerumisreaktsioon hõbeda, nikli ja vase galvaanilisel vahetusel saadud Pd katetel

Lühikokkuvõte:

Kütuseelementide suurim takistus on vajadus efektiivse plaatinaava katalüsaatori järgi hapniku elektrokeemiliseks redutseerumiseks. Puhaste väärismetallide kasutamine ei ole jätkusuutlik valik, kuna need ajavad hinna kõrgeks ja sageli pole nad ka piisavalt efektiivsed ja stabiilsed. Seega odavamate metallide, nagu näiteks hõbe, vask ja nikkel, dekoreerimine galvaanilise vahetusega kõrge aktiivsusega metalliga, nagu näiteks pallaadium, võimaldab valmistada bimetaalseid katalüsaatoreid, kus kallimat komponenti on väga väikestes kogustes, kuid elektrokeemiline aktiivsus on kõrge. Tsüklilist voltamperomeetriat ja pöörleva ketaselektroodi meetodit kasutades näidati, et puhaste vähemaktiivsete metallide aktiivsus kasvab, kui neid dekoreerida aktiivse metalliga.

Võtmesõnad:

Hapniku redutseerumisreaktsioon, galvaaniline vahetus, pöörleva ketaselektroodi meetod, elektrokatalüütiline aktiivsus

CERCS: P401 elektrokeemia

TABLE OF CONTENTS

INTRODUCTION	4
1 LITERATURE REVIEW	5
1.1 Oxygen reduction reaction	5
1.2 Oxygen reduction reactions on Pd	6
1.3 Oxygen reduction reactions on Ag.....	7
1.4 Oxygen reduction reaction on Ni	8
1.5 Oxygen reduction reaction on Cu	8
1.6 Oxygen reduction reaction on Pd alloys with Cu, Ni, Ag.....	9
1.7 Galvanic exchange of metals	10
1.8 Rotating disk electrode studies.....	10
1.9 Koutecky-Levich theory.....	11
2 THE AIMS OF THE THESIS	13
3 EXPERIMENTAL PART.....	14
3.1 Materials and equipment	14
3.1.1 Preparation for measurements	14
3.1.2 Cyclic voltammetry.....	15
3.1.3 Galvanic exchange	15
3.1.4 ORR measurements using rotating disc electrodes	15
3.1.5 Data collection	16
3.2 RESULTS AND DISCUSSION	17
3.2.1 Cyclic voltammetry measurements.....	17
3.2.2 Oxygen reduction reaction results	19
3.2.3 Conclusions.....	28
SUMMARY.....	29
REFERENCES	30

INTRODUCTION

Fossil fuels are one of the leading factors of increasing greenhouse gas emissions and affecting the climate, in 2019 approximately 74% of greenhouse gas emissions were directly related to fossil fuels [1]. The automotive industry is responsible for more than a half of the used fossil fuels thus by implementing fuel cell electric vehicles we could drastically reduce fossil fuel usage and the impact it has on the climate [2]. Unfortunately, the overall process of oxygen reduction reaction (ORR) which occurs at the cathode of the fuel cells is sluggish in its kinetics, thus it requires a catalyst to improve its efficiency [3]. The catalyst in this case has to be efficient as well as stable, to continuously run without having the need to be replaced and the most widely used catalyst for improving the kinetics of the ORR is platinum. However, at the time of writing this thesis the price of Pt is 29.34 euros per gram, because it is a rare and an expensive metal it is difficult to use it at large scale [4]. It is the main reason for my work where I perform galvanic exchange on relatively cheap copper, nickel and silver with palladium that is more abundant on Earth than platinum and by using cyclic voltammetry (CV) I am able to determine their ORR activity. By using galvanic exchange, it is possible to deposit a very thin layer of coating of the expensive metal while keeping its electrocatalytic properties thus we could drastically reduce the cost of fuel cells. Many ORR studies have been conducted on single crystal noble metal electrodes, but as their surfaces are perfect the obtained data cannot be directly compared with real life conditions [5, 6]. For this reason, I am using for my studies bulk electrodes, which consist of a metal disc surrounded by Teflon. This method allows me to obtain a more realistic perspective on how the ORR occurs on the metal and how it is impacted by small quantities of precious metal deposited by galvanic exchange. This method provides challenges with establishing a standardized base because it is difficult to obtain a well-polished surface which is required to minimize the differences in electrode surface between all of the experiments. It is important to research this because the automotive industries has pledged to reduce internal combustion engine production by 2035, which means that there will be a huge increase in the demand for fuel cell electrical vehicles and thus using Pt-based cathodes in proton exchange membrane fuel cells is not a viable option [7]. Creating bimetallic cathodes which could compete in kinetic performance with platinum ones but also being a fraction of its price is a viable solution to this problem. I have decided to use palladium instead of Pt because Pd is more abundant in the Earth's crust [8], while the activity towards ORR is similar and as I am using galvanic exchange to produce my bimetallic electrodes I am using a very small amount of this metal thus it eliminates the problem of palladium's high price.

1 LITERATURE REVIEW

1.1 Oxygen reduction reaction

The oxygen reduction reaction is well known to be sluggish but it is a fundamental process in biological respiration and energy production in systems such as fuel cells [9]. It is a multielectron process, which involves multiple elementary steps and a number of reaction intermediates which contributes to major voltage losses. For the past decade's scientists have been working hard on speeding up the kinetics of the ORR [9]. There are two main pathways for ORR: four-electron direct pathway in acidic aqueous solution with water as the final product: [10]



Or with formation of hydrogen peroxide through two-electron pathway and further reducing peroxide to water:



If the reactions take place in aqueous alkaline solutions:



E^0 refers to standard electrode potential at 25 °C. Depending on the application both of these pathways have unique significance, for example, the 4-electron reduction pathway is more preferred in fuel cell processes and the two electron reduction of O_2 should be avoided. The incomplete oxygen reduction leads to low energy conversion efficiency and formation of free radicals and intermediates, that can also cause damage to the fuel cell. The two electron pathway sees its use in the industry for the production of H_2O_2 [11].

Figure 1 shows a general scheme for oxygen reduction in alkaline solution [12].

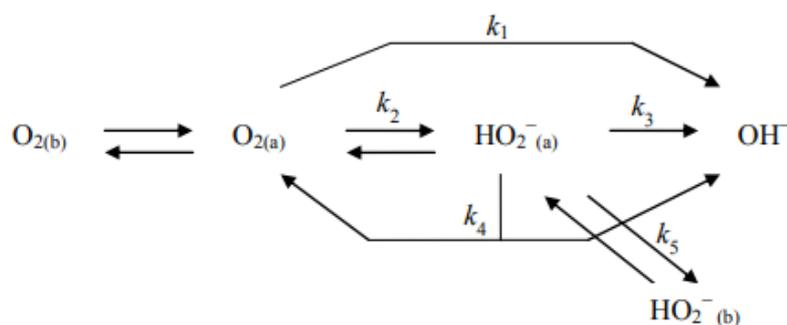


Figure 1. General scheme of the ORR on alkaline solution. (a) means adsorbed species and (b) stands for in bulk solution, k_i are heterogeneous rate constants for respective reactions.

1.2 Oxygen reduction reactions on Pd

Palladium belongs to the same metal group in the periodic table as platinum and it has similar characteristics such as crystal structure as well as atomic size and the oxygen reduction reaction proceeds with the same four-electron transfer pathway [13]. Even though the cost of palladium per gram is almost two times higher as compared to Pt it is still considered as a viable option for replacing platinum catalysts, but more focus is put on alkaline media, because the ORR activity of Pd in acidic media is generally lower than that of platinum [14]. By looking at the ORR activity in alkaline media, palladium performs almost the same as platinum and this can be accounted to the fact that only OH^- anions are present in the solution which leads to a lower inhibition effect caused by the anion adsorption. Furthermore it is also possible to increase the ORR activity by adding a different metal, which often leads to an increase in the activity which surpasses the activity of platinum [8]. Palladium electroactivity is strongly influenced by the oxidation of its surface thus it relies on potential cyclic conditions, which results in lower currents for cathodic sweeps than anodic [15]. Additionally, it has been studied that if the palladium surface has PdO oxides it leads to a partial decrease in the activity and production of the peroxide intermediates [16]. From previous experiment analysis of the ORR results it has been shown to produce two distinct Tafel slope regions, that represented a slope value at high current densities to be at ~ 120 mV and a slope value of ~ 60 mV at low current densities [15, 17]. For both regions the rate-determining step was the first electron transfer to the O_2 molecule and the differences in the slope values arises from the adsorption of oxygen-containing species. Another important factor to consider is the stability of palladium and palladium-based catalysts [14]. It has been proven that the overall stability of the palladium catalysts is significantly lower than platinum-based catalyst [18]. The conditions in the fuel cells currently used in the

automotive industry are very harsh having high temperatures, high potentials, low pH and repeated acceleration and deceleration can cause severe degradation [19, 20].

1.3 Oxygen reduction reactions on Ag

Due to the scarcity and price of platinum which is the metal of choice to be used for fuel cells a lot of work has gone into measuring and looking for alternative metals. One such metal could be Ag, however, the main criteria for choosing a metal is whether the ORR pathway is direct $4e^-$ pathway or does it create an intermediate hydrogen peroxide, which result in lower reduction currents and a possibility of poisoning or destroying the fuel cell [21]. The oxygen reduction activity of silver in alkaline conditions (room temperature, ~1 M KOH) is slightly lower than the ORR activity of platinum. But often this lower activity gets accepted because it has been proven that silver is generally more stable in long-term operations than platinum, and more importantly it is also cheaper [22]. However, Ag electrodes are only considered for alkaline media because its activity in acidic media is drastically lower (Figure 2) unlike platinum group metals that are good ORR electrocatalysts in both alkaline and acidic media [23]. Initially silver proved to be challenging for proving kinetics and mechanisms of its oxygen reduction reaction, because there was no standardization between the research groups. But more recent works have proven that Ag in alkaline media shows a lot of similarities with platinum, for example, the ORR proceeds mostly through a 4-electron pathway. It has also been found that Ag does not show pH dependence, unless in very alkaline media some increase in activity can be noticed [24]. Thus, concluding from the pH-independence at low overpotential, Ag cathodes experience a chemical step that follows the first electron transfer and that there is a negligible effect of adsorbate interaction.

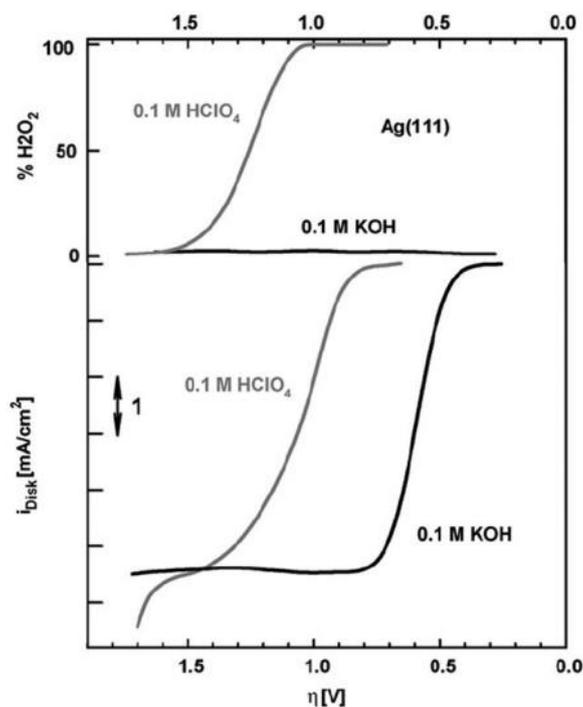


Figure 2. Ag(111) electrode O_2 electro-reduction currents (bottom part) in 0.1 M KOH and 0.1 M $HClO_4$ with corresponding H_2O_2 production (top part) [25] .

1.4 Oxygen reduction reaction on Ni

Nickel is in the same metal group in the periodic table as platinum, but it is a lot more abundant on Earth compared to platinum [26]. Even though nickel is a good heat conductor, versatile and widely used there have not been any review articles on the ORR activity on Ni based electrodes. There have been a lot of studies on using nickel in a bimetallic structure most often together with platinum because of nickel's properties to combine with other metals. In these studies, an improvement would be observed when comparing bare Pt with bulk alloy electrodes consisting of 75% platinum and 25% nickel [27]. Scientists concluded that there was an increase in the ORR activity and stability of long-term measurements. However, due to presumably low ORR activity in alkaline media there have not been that many studies focusing on using bulk nickel electrodes [28, 29].

1.5 Oxygen reduction reaction on Cu

Copper usage has been steadily increasing over the past years, yet it's price compared to nickel, silver and palladium is drastically lower, thus there have been studies to determine the kinetics of the ORR on copper as a pure metal as well as in bimetallic structures [30]. Several of the studies done have been using the rotating ring-disc electrode (RRDE) method, which is slightly different from the method I am using which is rotating disc electrode

method, main difference is that the RRDE method has an addition of a ring electrode around the central disc [31]. These studies concluded that a four-electron ORR pathway occurs on Cu electrodes, however, the reaction mechanism was strongly dependent on the nature of adsorbates. For example, in 0.1 M HClO₄ solution using Cu (111) the adsorption of oxygenated species induced a two-electron pathway, which had a low overpotential however at negative potential the current plateau suggested the direct 4e⁻ oxygen reduction mechanism. However using Cu(100) showed that at the whole potential range the process occurred through a 4-electron pathway [32]. Very important factor for copper is also its surface structure because scientists from Morocco determined that a less catalytic surface was when using Cu⁰ and that a surface consisting of Cu and Cu¹⁺ had a more catalytic surface which lead them to conclude that a formation of a catalytic film increased the rate of oxygen reduction [33]. Another major advantage for copper-based electrodes reported for containing sodium chloride solution, because it was observed that the copper derivatives such as Cu₂O and CuCl₂⁻ catalysed the decomposition of hydrogen peroxide, which prevented a build-up of the intermediate product during the ORR process which is also beneficial for fuel cells [30, 33]. Because of these reasons it is important to consider surface conditions, temperature, electrolyte conditions and characteristics of the substrate when working with copper [32, 33].

1.6 Oxygen reduction reaction on Pd alloys with Cu, Ni, Ag

Studies on ORR activity of palladium alloys with nickel, copper and silver date back as far as 1970, but there has been an increase in the studies in the last decade due to the increasing demand for fuel cells [34]. Because nickel is abundant and relatively cheap it seems as a viable option, and recent studies have shown that nickel and palladium alloys have unique electronic and surface characteristics, which are quite different from mono-metal electrodes [35]. It has been reported that Ni nanoparticles exhibit a high susceptibility in regards to surface absorption of O₂ molecules. which facilitates ORR [26]. Copper by itself is a metal which is electroactive thus combining it with palladium seems as a clear choice. For example in acidic conditions Pd/Cu alloys have been shown to be moderately active [14]. But experiments conducted with thin-film Pd/Cu electrodes in alkaline solution showed great electroactivity, which was similar to pure palladium and scientists resulted it to the porous surface of Pd and the residual Cu which was trapped in the nanostructures thus modifying the structure and improving the electroactivity [36]. Silver, in regards to the ORR activity, counts as an active element because it catalyses the direct 4-electron pathway, however its

activity is lower than that of pure palladium, but because it is cheaper and more abundant it is a viable option for the Pd/Ag alloy [37]. The experiments using these alloys have shown that even a minor alloying of palladium with silver increases its electroactivity in regards to pure electrodes, and particularly in the case of 10%Ag/90%Pd alloy it outperformed both of the mono metal electrodes by 20 to 55 mV.

1.7 Galvanic exchange of metals

Galvanic exchange or galvanic replacement is a reaction that happens spontaneously and replaces a surface layer of a metal (further represented as M) by a more noble metal (further represented as M_{noble}) and this reaction occurs according to the general principle $nM + mM_{\text{noble}} \rightarrow nM^{m+} + mM_{\text{noble}}$ [38]. Galvanic replacement occurs due to the difference in the equilibrium potential of the two used metals or metal ion redox couples [39]. For this process the oxygen levels and the pH must be precisely set to ensure no parasitic cathodic processes, for example, oxide formation or in rarer cases oxygen reduction or even hydrogen evolution do not happen [40]. The result from this process will most probably be a bimetallic material having a M_{noble} -rich shell with a M-rich core which leads to a decrease in the noble metal loading and a change in the metal M properties as well as minor changes in the properties of M_{noble} metal [41]. To perform galvanic replacement a metal such as, Cu, Fe, Co, Ni, must be placed in a solution containing ions of more noble metals, for example, Pt, Au, Pd, Ag. The amount of the M_{noble} that is replacing the metal M depends on the time the metal is submerged in the solution, however the metals do not replace each other at a perfect rate which is explained by the Kirkendall effect [39]. Main idea of it is that an atom can move into a vacant site, effectively causing the atom and the vacant spot change places. If a large-scale diffusion happens it is possible to observe a flux of atoms in one direction and a flux of vacancies on the other.

1.8 Rotating disk electrode studies

Rotating disc electrode (RDE) is one of the most common methods implemented in electrochemistry, especially for the understanding of the electrochemical catalytic reaction mechanisms, for example electrocatalytic oxygen reduction reaction. One of the most crucial aspects of the fuel cell and other oxygen reduction reaction related technologies is the mechanisms and kinetics of the ORR catalysed by non-noble or noble metal-based electrocatalysts or metal-free catalysts. Rotating disc electrode studies are useful for

measuring the reactant concentrations, reaction electron transfers numbers, diffusion coefficients, reaction intermediates and reaction rate constants, which all helps us to evaluate the activity of the catalysts and their catalysed oxygen reduction reaction mechanisms [42].

The overall construct of this electrode is relatively simple, a disk of electrode material is implanted in a shaft of an insulating material. One of the most common ways is to use a platinum wire which gets sealed in a glass tube which then gets grounded smooth and made sure to be perpendicular to the shaft's axis [43]. Another common way, which is also what was used in my experiments, is that the metal gets implanted in Teflon, epoxy resin, or other plastic types. It is important to have an exact alignment of the disk otherwise when used at high rotation rates there is a risk of breaking of the electrode. It is also vitally important that the imbedded metal creates a perfect seal with the plastic because if there are any gaps contamination or incorrect measurements might occur. The electrode gets attached to the motor directly and then it gets rotated at certain frequencies [44].

1.9 Koutecky-Levich theory

Most often used theory for data analysis which is collected by rotating disk electrode studies for catalysed oxygen reduction reaction is called Koutecky-Levich theory, which provides the relationship between the ORR transferred number of electrons, oxygen concentration, oxygen diffusion coefficient, rotation rate of the electrode and the viscosity of the electrolyte solution [45]. From this analysis we can estimate the ORR mechanism and kinetics, and thus it provides us with data about the activity of electrocatalysts which then helps us to design future catalyst. For the use of Koutecky-Levich theory most frequently used parameters are: oxygen concentration (solubility), O₂ diffusion coefficient and the viscosity of used electrolyte solution.

The Levich equation expresses a sigmoidal voltammograms with a steady-state limiting current I_{lim} [12]:

$$I_{lim} = 0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2} \quad (7)$$

Where rotation speed is represented with ω (rad s⁻¹), kinematic viscosity of the electrode is ν (m² s⁻¹), diffusion coefficient is D (m² s⁻¹) for the electroactive species, electrode area is represented with A (m²), Faraday constant is F (96,485.34 C mol⁻¹) and n represents the overall number of transferred electrons per each reacting species.

Electrochemical rate constant represented by k in electrochemically irreversible reactions is usually given as:

$$k = k^* \exp\left(-\frac{(n+a)FE}{RT}\right) \quad (8)$$

In this equation R represents the universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), T stands for temperature given in K, a stands for the transfer coefficient and standard electrochemical rate constant is given as k^* ($\text{m} \cdot \text{s}^{-1}$), n^* represents the total number of transferred electrons before rate-determining step. When using a uniformly accessible rotating disc electrode, Levich and Koutecky put forward a procedure where variable rotation speeds were used for the analysis of the voltammetric data [45]. Another form of the Koutecky-Levich equation is:

$$\frac{1}{j} = \frac{1}{kc_\infty} + \frac{1}{DC_\infty/X_D} \quad (9)$$

which is used when reactions are controlled by both kinetics and diffusion for RDE, total flux is represented with j and the reacting electroactive species is associated with the electrode rotation speed represented in the equation with w , C_∞ is bulk concentration of the species which react in the solution, potential dependent rate constant is represented with k , and the thickness of the diffusion layer is represented as χ_D : [45]

$$\chi_D = 1.61w^{-1/2}\nu^{1/2}D^{1/3} \quad (10)$$

But more often this equation is represented in the long form which is the combined form of previously mentioned equation parts:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = -\frac{1}{nFkC_{O_2}^b} - \frac{1}{0.62nFD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}^bw^{1/2}} \quad (11)$$

2 THE AIMS OF THE THESIS

The aim of my thesis is to prepare palladium coatings onto silver, nickel and copper electrodes using galvanic exchange and characterise those electrochemically by measuring their oxygen reduction reaction activity. The necessary subgoals to achieve are:

1. Prepare the copper, silver and nickel electrodes so their surface would be perfect or as close to perfect as possible by mechanical polishing.
2. Decide from literature articles and prepare the required concentration of tetrachloropalladate solution required for galvanic exchange.
3. Perform initial cyclic voltammetry measurements to determine the surface quality and perform the initial rotating disc electrode voltammetry measurements to determine the oxygen reduction reaction activity.
4. Carry out the galvanic exchange for a set amount of time.
5. Do cyclic voltammetry measurements to determine the surface characteristics of the bimetallic electrode as well as perform the rotating disc electrode measurements to obtain data about the oxygen reduction reaction activity.
6. Repeat the galvanic exchange with different time lengths and the measurements of the electrodes.
7. Graph and analyse the acquired data to determine the surface characteristics and oxygen reduction reaction activity.

3 EXPERIMENTAL PART

3.1 Materials and equipment

Materials required – potassium hydroxide (Sigma-Aldrich, *pro analysi*), silver, nickel and copper electrodes encapsulated in Teflon, tetrachloropalladate solution (Sigma), alumina powder (Buehler) and emerypaper (Buehler), chemical etching solution (33% of volume CH_3COOH (Sigma), 33% of volume $(\text{CH}_3\text{CO})_2\text{O}$ (Sigma), 33% of volume HNO_3 (Sigma) and 1% of volume HCl (Sigma) [46]).

Equipment required – 2 glass cells in 3-electrode configuration for electrochemistry measurements, 2 Luggin capillaries, 2 auxiliary electrode compartments, 2 gas bubblers, 2 gas inlets, reference electrode (reversible hydrogen electrode, RHE), auxiliary electrode (platinum wire), corks, potentiostat (Autolab PGSTAT30), rotator (EDI101, Radiometer) with corresponding speed control unit (CTV101, Radiometer), argon (Linde, purity of 99.999%), oxygen (Linde, purity of 99.999%) and hydrogen (Linde, purity of 99.999%), additional cell for galvanic exchange, Milli-Q water system (Merck Millipore).

All of the materials and equipment used was from Institute of Chemistry electrocatalysis laboratory led by Prof. Kaido Tammeveski and all of the experiments were conducted at a room temperature of 23 ± 1 °C.

3.1.1 Preparation for measurements

Preparation started with performing acid washing of my glassware. The glassware was placed in a large beaker, first poured certain amount of hydrogen peroxide onto those and then added concentrated sulphuric acid, approximately 3 L to create the solution called piranha solution. I boiled this solution for approximately 6 h till the hydrogen peroxide had reacted and residual water boiled off. After the solution had cooled down, I washed my glassware with large amounts of Milli-Q water, which is created by purifying water using ion exchange cartridges. This process was performed to ensure that the used glassware had no contaminations. The process of acid washing was performed at least once a month, for daily work before and after the experiments all of the components were washed with extensive amounts of Milli-Q water. The preparation of metal electrodes consisted of initial polishing on emerypaper using grits of 600, 1200 and 4000 followed by polishing on paper using 1 and 0.3 micrometre size alumina powder (Buehler) in the figure eight pattern to ensure equal polishing in all directions. Furthermore, for the Ni and Cu electrodes chemical etching was performed for 2 min, to maximize the possibility of having a clean and uniform

surface. After this the electrodes were sonicated in ethanol and Milli-Q water to remove any polishing residues. For the preparation of electrolyte solution, I used KOH pellets which were dissolved in Milli-Q water to obtain the electrolyte solution of 0.1 M KOH, fresh solution was prepared before every experiment. Additionally, I prepared the galvanic exchange solution by mixing PdCl₂ powder with HCl acid and Milli-Q water to obtain a 1 mM solution of tetrachloropalladate. The galvanic exchange solution and one of the electrochemical cells with the alkaline solution were saturated with Ar gas, and the other cell with the KOH solution was saturated with O₂ gas.

3.1.2 Cyclic voltammetry

After all of the preparation work was done and the electrochemical cells were set up for working 3 types of measurements were conducted in the Ar saturated cell. Firstly, I performed the “short range” cyclic voltammetry measurement where the current range was from 0.1 to 1 V with potential scan rate of 50 mV s⁻¹, this measurement lasted 10 cycles and its main purpose was to condition the electrode and make sure it is uniform for further work by getting rid of any oxides that might have formed. Secondly, I performed the “long range” cyclic voltammetry measurement where the higher vertex potential was limited to 1.4 V and the main purpose of this measurement was to determine the surface characteristics of the electrode, this measurement consisted of 2 potential cycles. Lastly, I performed the background current measurements, which were needed for data analysis. These measurements were repeated for all of the electrodes used including after each galvanic exchange.

3.1.3 Galvanic exchange

Galvanic exchange was performed for all of the electrodes by submerging the electrode in the tetrachloropalladate solution which was saturated with argon to avoid any parasitic cathodic processes and the overall time would be 1, 5, 30 and 60 min and afterwards they were rinsed with Milli-Q water to remove any excess material and placed back into electrochemical cell for cyclic voltammetry measurements.

3.1.4 ORR measurements using rotating disc electrodes

To measure oxygen reduction reaction activity, I used the rotating disc electrode method, where my electrode was connected to a rotator inside the electrochemical cell with 0.1 M KOH solution that has been saturated with oxygen and was rotated at 360, 610, 960, 1900,

3100, 4600 rpm. The rotation of the electrode creates a flux of analyte to the working electrode. Measuring range was from 0.1 to 1 V with the potential scan rate of 10 mV s^{-1} .

3.1.5 Data collection

Experimental data was collected using General Purpose Electrochemical System (GPES) software, which is also responsible for controlling the conditions for the experiments and the acquired data was analysed using MS Excel as well as OriginPro which was used for creating the graphs.

3.2 RESULTS AND DISCUSSION

3.2.1 Cyclic voltammetry measurements

After running the previously mentioned “short range” cyclic voltammetry measurements, which conditioned and cleaned the electrodes, the “long range” cyclic voltammetry was conducted and the CV results are plotted in Figure 3. From the graph it is possible to determine the surface characteristics of the metal and bimetallic electrodes, which was produced by the galvanic exchange and it is possible to observe how the typical surface characteristics of Pd increase as the time increases for the galvanic exchange. As this process has two parts the oxidation when scanning in the positive direction and reduction part when scanning in the negative direction it is possible to observe the changes in the surface characteristic on both parts. Initially, clean Ag does not show any peaks below 0.95 V, the surface oxidation of Ag starts at approximately 1.1 V and one can observe 3 peaks that correspond to the formation of different Ag oxides [47]. When Pd is deposited already, then the surface oxidation starts at lower potentials, which is the expected behaviour for Pd [48].

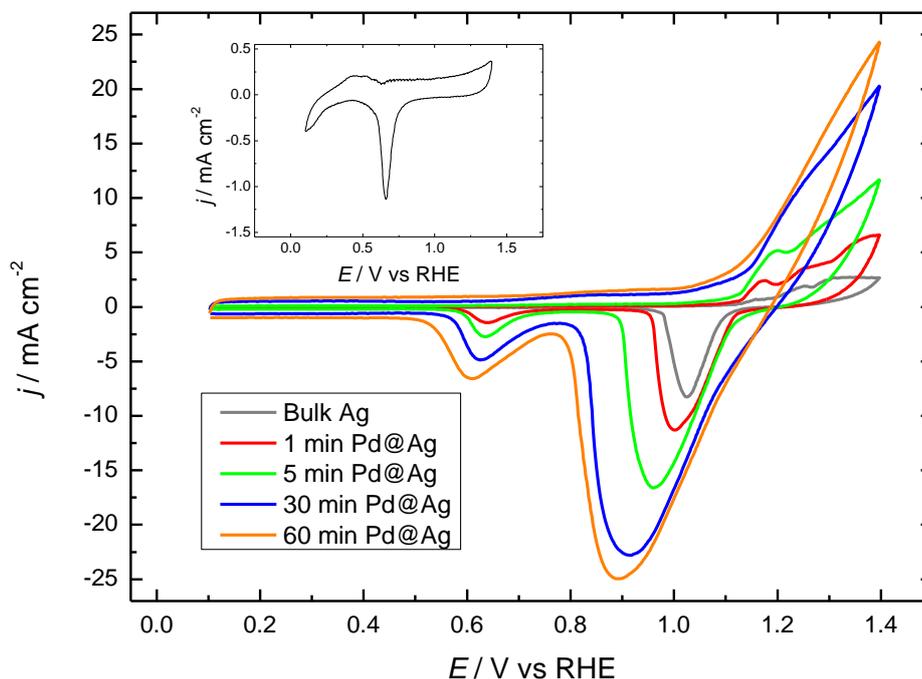


Figure 3. Cyclic voltammograms of Ag coated with Pd with different time lengths in 0.1 M KOH solution saturated with Ar. Inset shows the cyclic voltammogram of bulk Pd. Scan rate: 50 mV s^{-1} .

While initially pure Ag has only one cathodic peak at ca 1.05 V, which corresponds to the reduction of Ag surface oxides, then after already 1 min of galvanic exchange another peak appears at ca 0.6 V. This peak corresponds to the reduction of Pd oxides. Also, from these results I calculated the electroactive surface area of Pd from the oxide reduction peak, which is located at approximately 0.6 V and this value was collected into Table 1. The charge under the reduction peak located at ca 0.6 V was calculated and a value of $424 \mu\text{C cm}^{-2}$ was used as it is the charge density for a monolayer of PdO reduction [48].

Further, looking at the electrochemical behaviour of bulk copper electrodes. After the cleaning and the conditioning steps the surface characteristics were determined by the “long range” cyclic voltammetry measurements in the 0.1 M KOH solution saturated with Ar. It is possible to observe the characteristics of pure Cu as well as the bimetallic characteristics of Cu@Pd in Figure 4. For the initial pure Cu electrode, the measurement range was increased to be from -0.1 V to 1.4 V due to the characteristics of this metal. Similarly, to Ag different oxides are formed and reduced on Cu. Clear Pd peaks are not appearing even after 60 min of galvanic exchange and thus the electroactive surface areas could not be estimated.

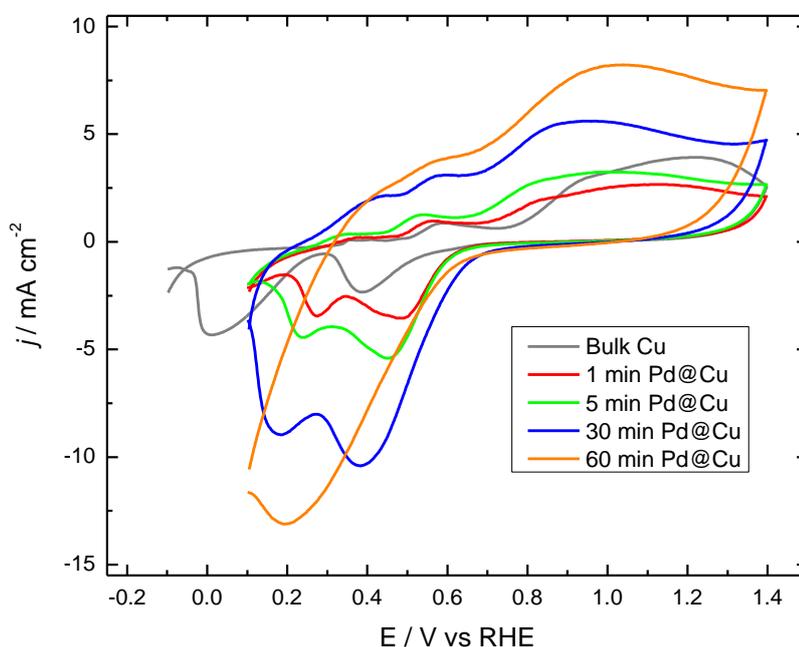


Figure 4. Cyclic voltammograms of Cu coated with Pd at different time periods in 0.1 M KOH solution saturated with Ar. Scan rate: 50 mV s^{-1} .

Similar characterisation was carried out using Ni electrode and electrochemical response was compared to those obtained after performing the galvanic exchange of the metal. The CV results are presented in Figure 5. As expected with increasing the Pd deposition time the amount of Pd increases was the case when bulk Ag electrode was used. With Ni one can also see so-called hydrogen region forming as there is current increase observable in the potential range from 0.1 to 0.4 V.

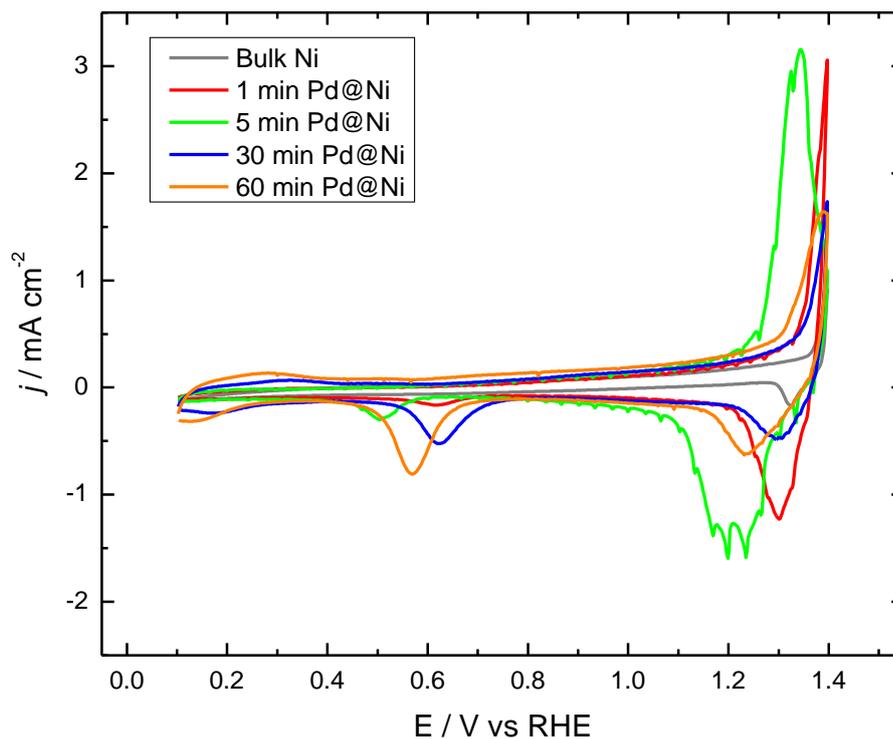


Figure 5. Cyclic voltammograms of Ni coated with Pd at different time periods in 0.1 M KOH solution saturated with Ar. Scan rate: 50 mV s^{-1} .

3.2.2 Oxygen reduction reaction results

Further looking at Ag bulk electrodes. Following the cyclic voltammetry measurements, the electroactive characteristics of pure Ag and the bimetallic Ag@Pd were measured in 0.1 M KOH solution saturated with oxygen using the rotating disc electrode method. Figure 6 shows a typical set of RDE polarisation curves obtained with bulk Ag electrode that had

been in 1 mM H_2PdCl_4 solution for 5 min. A similar set of RDE polarisation curves were obtained with all Pd@Ag electrodes.

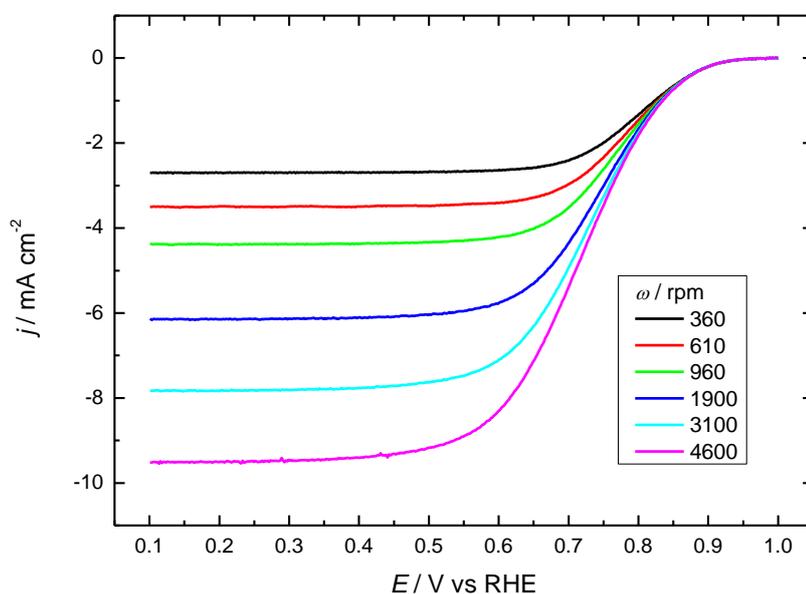


Figure 6. RDE polarisation curves for oxygen reduction at different electrode rotation rates with 5 min Pd@Ag in O_2 -saturated 0.1 M KOH with scan rate of 10 mV s^{-1} .

As expected the measured current-density increases with increasing the electrode rotation rate. This is the expected behaviour as according to the RDE theory the flux of oxygen increases with higher electrode rotation rate. These data were used to construct the Koutecky-Levich plots from which the number of electrons transferred per O_2 molecule was determined (Figure 7). The n value was 4 already with bulk Ag and it did not change when Pd was deposited onto the electrode via galvanic exchange.

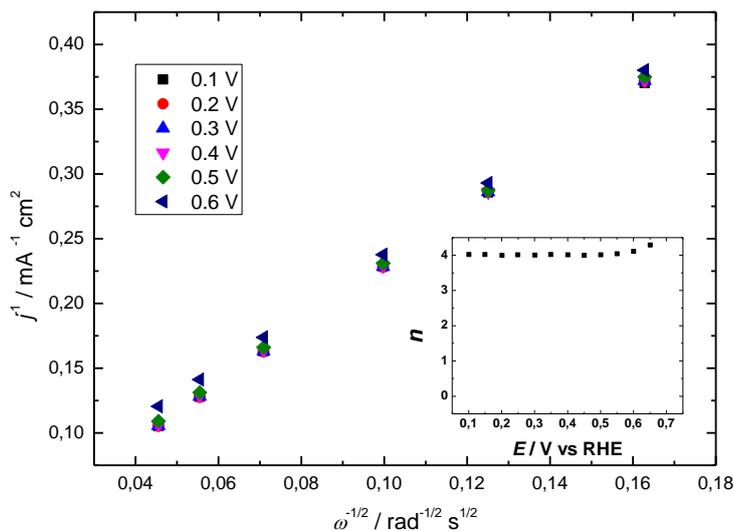


Figure 7. Koutecky-Levich plot derived from RDE polarisation data presented in Figure 6 and inset displays the number of electrons transferred per O_2 molecule as a function of potential.

Figure 8 represents the obtained RDE data at 1900 rpm. All Pd@Ag electrodes have a single-wave polarisation curve that reaches current plateau. The plateau current is somewhat lower with bulk Ag, but with all Pd@Ag electrodes it reaches the theoretical value. As the theoretical limiting current plateau is reached then one can expect that the number of electrons transferred per O_2 molecule is 4 or close to it which was confirmed by the Koutecky-Levich analysis.

When comparing the progression of Pd deposition via galvanic exchange then one can observe the half-wave potential ($E_{1/2}$) shifting. This is due to the increase in electroactivity as the length of galvanic exchange increases and more Pd is deposited and Ag is dissolved.

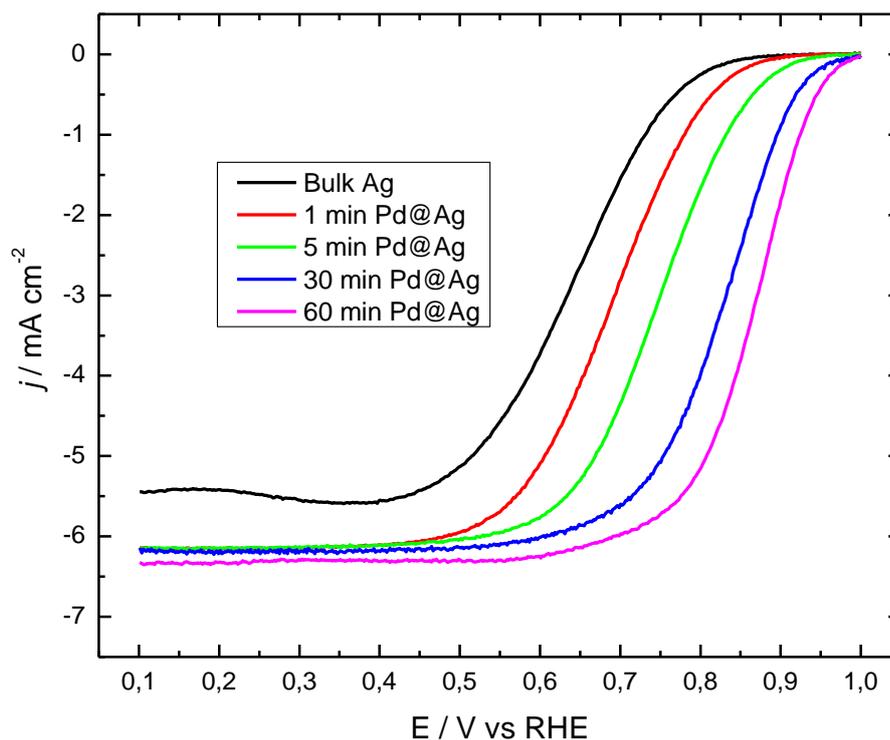


Figure 8. Comparison of RDE results for ORR at 1900 rpm in 0.1 M KOH solution saturated with O_2 of Ag electrodes coated with Pd at different time periods. Scan rate 10 mV s^{-1} .

Looking at experiments conducted with bulk Cu electrodes. After electrochemical characterisation of Pd@Cu by the CV measurements, the RDE measurement of ORR was performed in the 0.1 M KOH solution which was saturated with O_2 and the results of the electroactivity at 1900 rpm was graphed. From Figure 9 it can be seen that bulk copper has a maximum in the polarisation curve at about 0.5 V. The Koutecky-Levich analysis showed also that number of transferred electrons depend on the potential as one can assume from the polarisation curve. Already 1 min of Pd deposition is enough to suppress the minimum at 0.4 V but despite background current correction the diffusion limited current plateau is not perfect. However, one can see clear improvement in half-wave potential with increasing Pd deposition time. Also, number of electrons transferred per O_2 molecule increase to 4, thus resulting in production of water, in the whole range of potentials studied which corresponds to the results obtained in [49] as well as the observed results on thin Pd films [50].

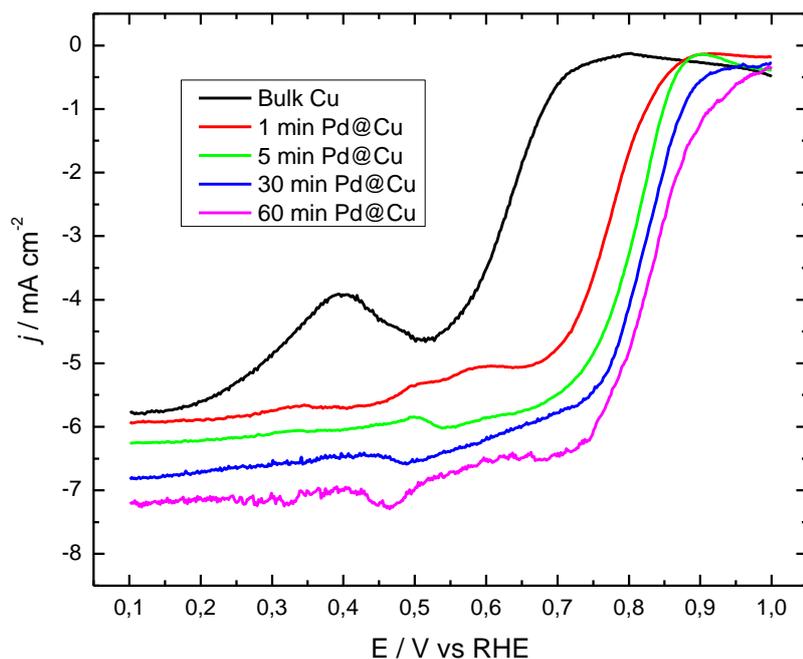


Figure 9. Comparison of RDE results for ORR at 1900 rpm in 0.1 M KOH solution saturated with O_2 of Cu electrodes coated with Pd at different time periods.

Results obtained with Ni electrode are visible in Figure 10, and from these it is possible to observe how Ni by itself does not possess any electroactivity towards oxygen reduction reaction, but as more palladium gets deposited the electroactivity of the bimetallic electrode increases. The Koutecky-Levich analysis revealed that after 1 min of Pd deposition the number of electrons transferred per O_2 molecule was reaching 3 but it can be assumed that the amount of Pd was simply not enough to yield proper reduction current. After 5 min of deposition the n value increased, but it was still not enough for complete oxygen reduction. After 30 min the number of electrons transferred had improved further as it was close to 4 indicating that water was the main product of the ORR process. One can also see that while initial improvement of the $E_{1/2}$ value was significant, then only small improvements are visible from 30 to 60 min of galvanic exchange. This suggests that the maximum ORR activity of Pd@Ni is achieved after 1 h of galvanic exchange.

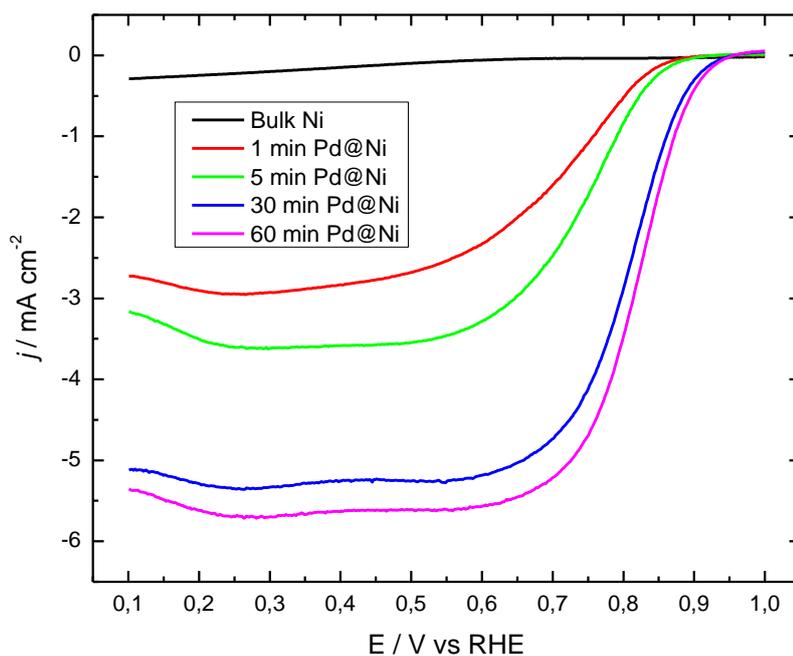


Figure 10. Comparison of RDE results for ORR at 1900 rpm in 0.1M KOH solution saturated with O_2 of Cu electrodes coated with Pd at different time periods.

Furthermore, by looking at Figure 11 we can see how the oxygen reduction reaction activity is compared with bulk palladium, 60 min galvanic exchange Pd@Ni, 60 min galvanic exchange Pd@Cu and 60 min galvanic exchange Pd@Ag, from this we can conclude that the cheaper metal electrodes after the 60 min galvanic exchange are capable of performing similarly or even better in the case of Ag electrode against the bulk palladium electrode.

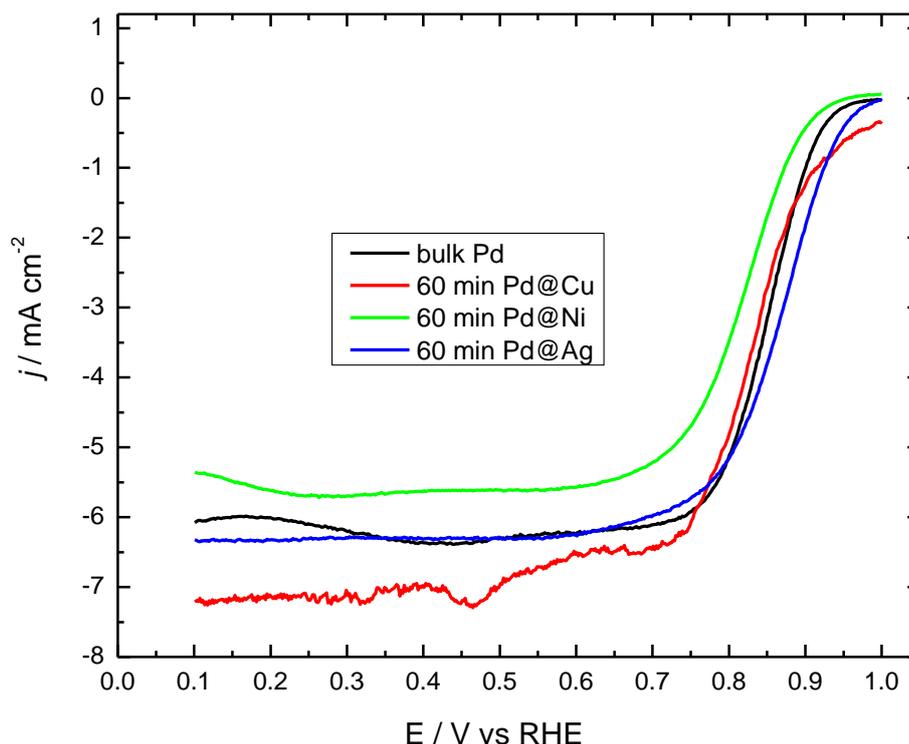


Figure 11. Comparison of the ORR on bulk Pd, 60 min galvanic exchange Pd@Ni, 60 min galvanic exchange Pd@Cu and 60 min galvanic exchange Pd@Ag at 1900 rpm in 0.1M KOH solution saturated with O₂.

From the RDE results it is possible to create the Tafel plots for ORR visible in Figure 10. Tafel plots present how efficient an electrode is at producing kinetic current in response to potential changes [51]. By looking at our results we can conclude that by increasing the duration of the galvanic exchange we are able to improve the efficiency of the cheaper metals which also corresponds to the results obtained in the RDE experiments. The Tafel slope values are listed in Table 1 from which we can see that the slope values with palladium on Cu and Ni are rather similar to that of bulk Pd and is close to -60 mV. This suggests that the ORR on Pd@Cu and Pd@Ni follow the same pathway as on bulk Pd and the rate limiting step is the slow transfer of the first electron to the O₂ molecule [49, 52-54]. With Ag as support the Tafel slopes are somewhat higher, but similar to the findings previously reported with silver [55]. This is somewhat expected as the Ag oxide reduction peak (Figure 3) also increased significantly during the galvanic exchange.

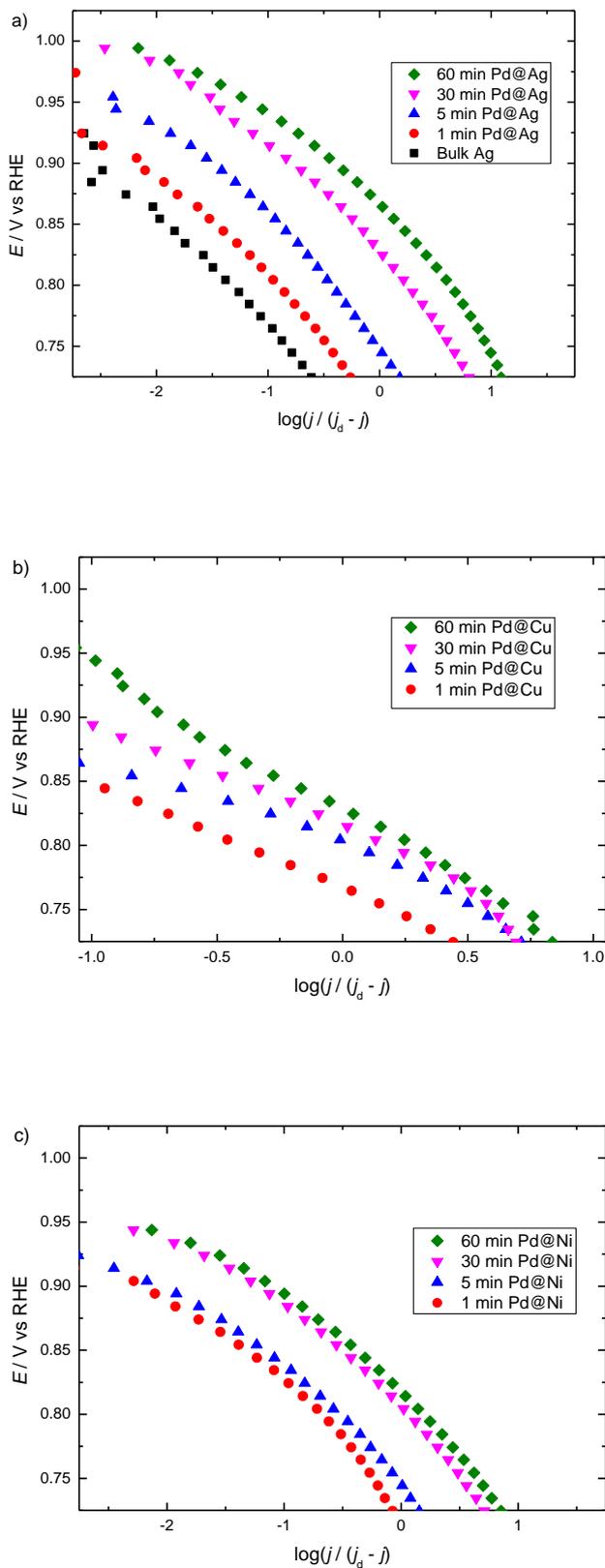


Figure 12. Tafel plots for ORR at a) Pd@Ag, b) Pd@Cu and c) Pd@Ni catalysts derived from Figures 8, 9 and 10, respectively.

The obtained data from our experiments has been collected in the Table 1, which lists the electrochemical surface area of Pd half-wave potential, Tafel slope value and kinetic current at 0.9 V of all the metals and bimetals studied. As electroactive surface area could not be determined with all electrodes then kinetic current-densities were compared (that is kinetic current per geometric area of electrode) which was highest for 60 min Pd@Ag followed by 60 min Pd@Cu and bulk Pd.

Table 1. Kinetic parameters for all measured electrodes.

Used metal and time of galvanic exchange	Electrochemical surface area (cm²)	Half-wave potential (V)	Tafel slope (mV)	Kinetic current-density (mA cm⁻²)
Bulk Pd	0.499	0.85	-69	-1,2
Bulk Ag	NA	0.64	-101	-0,024
1 min Pd@Ag	0.49	0.69	-70	-0,039
5 min Pd@Ag	0.91	0.74	-83	-0,19
30 min Pd@Ag	1.78	0.83	-86	-1.02
60 min Pd@Ag	2.73	0.86	-89	-2.52
Bulk Cu	NA	0.42	NA	NA
1 min Pd@Cu	NA	0.76	-82	-0.14
5 min Pd@Cu	NA	0.80	-53	-0.14
30 min Pd@Cu	NA	0.82	-77	-0.59
60 min Pd@Cu	NA	0.82	-112	-1.46
Bulk Ni	NA	0.41	NA	NA
1 min Pd@Ni	0.045	0.71	-55	-0.018
5 min Pd@Ni	0.082	0.74	-57	-0.032
30 min Pd@Ni	0.20	0.81	-70	-0.32
60 min Pd@Ni	0.31	0.82	-70	-0.46

3.2.3 Conclusions

In conclusion, from the obtained cyclic voltammetry results it is possible to determine that the surface characteristics of the cheaper metals (Ag, Ni, Cu) change and present more characteristics of palladium metal. From the ORR experiments it is possible to conclude that the overall electrocatalytic activity for all of the cheaper metals improve and by the 60-minute mark of galvanic exchange it is reasonable to assume that the ORR activity is similar to that of bare palladium. From the Tafel plots I concluded that the rate-limiting step is the transfer of the first electron to the oxygen molecule. By using the Koutecky-Levich equation it is possible to calculate that all of the cheap metal electrodes at the 60-minute mark of galvanic exchange reached the four-electron oxygen reduction reaction pathway. Thus, the obtained results prove that galvanic exchange is a good method to prepare bimetallic catalysts for oxygen electroreduction and silver is very good metal to be used as a core to prepare core-shell nanoparticles.

SUMMARY

Copper, silver and nickel electrodes were prepared using galvanic exchange with palladium with different time periods of 1, 5, 30, 60 min in 1 mM H_2PdCl_4 . Surface characteristics of the used metals and created bimetals were measured using cyclic voltammetry in various ranges depending on the properties of the specific metals in 0.1 M KOH. Rotating disc electrode studies of the oxygen reduction reaction were conducted at different electrode rotation speeds and the obtained results were used in the creation of Tafel plots and for the Koutecky-Levich analysis. From the results obtained it was possible to determine that with increasing time of the galvanic exchange the surface characteristics of the metals changed and it was possible to observe the influence of palladium characteristics. Additionally, the electrocatalytic activity of the bimetal catalyst increased with increasing the duration of the galvanic exchange and all of the bimetal catalyst activity at 60-min mark was similar to that of bare bulk Pd electrode as well as the number of transferred electrons was close to 4 indicating the direct four-electron pathway without the formation of intermediate peroxide.

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